Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

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IDL 9.4 Broad exploitation strategy and risk benefit appraisal

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Summary

This report seeks to develop an understanding of the "value proposition" for iron nanoparticles/ nanoscale zero valent iron (nZVI) in remediation in terms of a risk benefit appraisal of its use given the current state of knowledge. Scenario analysis is used to explore likely market potential and the factors affecting this over the short, medium and longer term. An analysis of strengths, weaknesses, opportunities and threats (SWOT) and how these might change over time has been used to draw some conclusions about the broad actions that might support better exploitation of nanoremediation.

This report focusses on nZVI, as the most frequently used nanoparticle type. Future NanoRem work will involve undertaking similar analyses for other nanoparticles being developed by NanoRem. This report provides a brief overview and status quo of nZVI and an outline risk benefit appraisal for the technology. It describes a scenario approach to understanding possible nanoremediation market trends. The process and findings of an expert consultation workshop conducted by NanoRem are discussed. A SWOT analysis is provided utilising collected information to establish the strengths, weaknesses, opportunities and threats of/to the nanoremediation market. Next steps are suggested.

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1 Introduction

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) is a research project, funded through the European Commission's Seventh Framework Programme. NanoRem focuses on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This is being undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), market demand, overall sustainability, and stakeholder perceptions.

In situ remediation techniques (exploiting biological, chemical, physical stabilisation and/or thermal processes within the subsurface) are being increasingly used to avoid excavation of materials or surface treatment of groundwater from "pump and treat" projects. The use of nanoparticles potentially extends the range of available *in situ* remediation technologies, and it may offer particular benefits in some applications (Bardos *et al.* 2014, O'Carroll *et al*. 2013, Bardos *et al*. 2011).

This report forms NanoRem Internal Deliverable 9.4 (IDL 9.4), which fulfils part of Task 9.3.1 and builds on the results of Task 9.2.1, the "Sustainability and Markets" workshop in Oslo, December 2014 (Tomkiv *et al.,* 2015). The objective of Task 9.3.1 is to develop an understanding of the "value proposition" (the overall promise of value to be delivered) for nanoremediation approaches developed by NanoRem in the short, medium and longer term in order to develop a preliminary broad exploitation strategy.

This report focuses on nano-scale zero valent iron (nZVI) as the best known and most frequently encountered NP, although the information provided may also be indicative for other nanoparticle types used in remediation. An overview will be provided of nZVI as a remediation technology and its market *status quo*. Key elements of a risk-benefit appraisal are provided to highlight the short term potential of nZVI. Additionally, the preliminary results are presented for a scenario approach used to help determine the factors likely to be responsible for nZVI market development. By determining factors affecting markets, the medium to longer term potential for exploitation, including possible challenges, can be established. The report concludes with a Strengths, Weaknesses, Opportunities and Threats (SWOT) analysis.

2 Brief Technology Description

Micro-scale zero valent iron (granular ZVI) has been used as a treatment reagent for *in situ* groundwater remediation for many years, in particular within permeable reactive barriers (NATO, 1998). Nano-scale zero valent iron (nZVI) is a type of iron NP that has been injected *in situ* as a groundwater and aquifer treatment.

NPs are typically defined as particles with one or more dimension of less than 100nm (Rauscher *et al.* 2014). As a result of their size, nanoparticles can have markedly different physical and chemical properties to their bulk counterparts, enabling them to be utilised for novel purposes, including the potential for use in remediation. To date the most widely used NP in remediation has been nZVI. Whilst the possibility of unique characteristics gives nZVI promise for beneficial applications, it is simultaneously a cause of concern, as there is a degree of uncertainty with regards to particle behaviour, fate and toxicity. As produced, most nZVI tested falls into the 10-100 nm size range (O'Carroll *et*

al. 2013, Müller & Nowack 2010, Karn *et al.* 2009, Nurmi *et al.* 2005), although it tends to agglomerate to form larger particles.

The first documented field trial of nZVI, in 2000, involved treatment of trichloroethylene in groundwater at a manufacturing site in Trenton, New Jersey, USA. It was anticipated by several commentators that nZVI technology would take off rapidly because of its perceived benefits such as rapid and complete contaminant degradation. However, subsequent uptake of the technology has been relatively slow. Bardos *et al.* (2014) identified around 70 projects documented worldwide at pilot or full scale. Most such deployments of nZVI have focussed on the degradation of chlorinated solvents for plume (i.e. pathway) management although pilot studies have also demonstrated successful treatment of BTEX, perchlorates, hexavalent chromium, diesel fuel, PCBs and pesticides. O'Carroll *et al*. (2013) detail the chemical processes involved in the treatment of chlorinated solvents and various metals by nZVI. Several approaches can be taken to NP deployment for contaminant remediation, including direct injection. Direct injection may be directed towards a contaminant 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. Direct injection may be under gravity-fed conditions or accomplished under pressure via an engineered fracture in the subsurface.

Although the establishment of the nanoremediation market has been slow there are a number of initiatives and development opportunities to expand its uptake, including the NanoRem project. NanoRem aims to aid upscaling of nanoremediation technologies, which could potentially deliver cost reductions associated with economies of scale. Additionally, NanoRem will investigate the fate, transport and toxicity of nanoparticles in the environment to address public and regulatory concerns related to the current uncertainties associated with nanoremediation.

3 Status Quo

In 2007, a European report forecast that the 2010 world market for environmental nanotechnologies would be around $6 billion (Rickerby & Morrison 2007). In practice, this market has not been achieved. To date, the use of nZVI 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 reduction and granular ZVI (e.g. permeable reactive barriers) (see Appendix 1: Chapter 2). Lee *et al.* (2014) have reviewed 60 field applications worldwide. Bardos *et al*. (2011) identified just 58 examples of field scale applications of nZVI, which was expanded to 70 examples by Bardos *et al.* (2014). Of the identified examples, only 17 were in Europe (Czech Republic, Germany and Italy). The limited adoption of nZVI is linked to uncertainty over the balance of benefits versus risks from NP use in remediation. An additional factor that is likely to have affected the development of the nanoremediation market is that nanoremediation costs are thought to be high relative to other technologies (see Section 4.2)

Dread[1] describes a situation of significant uneasiness about a technology, for example, nuclear or genetic modification technologies. This is not necessarily related to specific concerns. Technologies

[1] To dread is to anticipate with great apprehension or fear.

that evoke dread can acquire a stigma, which is often perpetuated by the media and those who oppose the technology (Marchant *et al.* 2008; Gilligan, 2006). This has been a particular impediment to the adoption of nZVI compared with other technologies as it appears to lead to a heightened perception of risk of nanotechnology's use amongst the public and other stakeholder groups, including landowners (Tomkiv *et al.* 2015). More specific regulatory concerns exist about nZVI use in remediation, including its potential human health implications and its possible ecotoxicological effects. As the potential risks of NP deployment for *in situ* remediation are considered to be poorly understood, precautionary and conservative regulatory positions have been taken in a number of countries. For example, there has been a voluntary moratorium on the release of engineered NPs in the UK, in response to a Royal Society/Royal Academy of Engineering report (Anon. 2012, RS/RAE 2004).

Process based remediation techniques seen as "new" within a particular jurisdiction 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 and landowners 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 nZVI 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 nZVI based *in situ* remediation techniques, compared with other *in situ* remediation techniques.

4 Risk Benefit Appraisal

This risk-benefit appraisal has been summarised from Bardos *et al.* (2014), the full report of which forms Appendix 1 of this report.

4.1 Potential Benefits of Using nZVI in Remediation

The principal potential benefits of nZVI use that have led to its development, particularly in comparison to the use of conventional zero-valent iron are the extent and speed of contaminant degradation possible from nZVI. These result from the greater surface area (and therefore increased reactivity) of nZVI. Furthermore, there may be a potential extension of the range of treatable contaminants to include types traditionally seen as recalcitrant. This may include destruction of organic contaminants and the transformation and/or precipitation of inorganic contaminants (Huang *et al.* 2013, Liu *et al.* 2005, Song and Carraway 2005, Zhang 2003). Several studies have suggested that nZVI may have advantages over granular ZVI for *in situ* stabilisation (and reduction) for a range of potentially toxic elements (Li *et al.* 2006a and 2006b). However, there is some uncertainty regarding whether or not nZVI will extend the range of treatable contaminants in the field compared to granular ZVI, although it is projected that at least a comparable treatment capability will be achieved.

When compared to bioremediation, nZVI usage also offers a probable reduction in the formation of toxic intermediate products for the degradation of some chlorinated solvents (e.g. the chloroethenes). Bench scale studies of nZVI use indicate that in the presence of nZVI, perchloroethene is degraded fully to ethane, ethene, or other light non-chlorinated hydrocarbons, without the build-up of toxic intermediates that are part of the metabolic sequence followed in bioremediation (Taghavy *et al.* 2010, Wang *et al.* 2010, Henn and Waddill 2006, Gavaskar *et al.* 2005). Moreover, the overall evidence supports a view that nZVI has little, if any, deleterious effect on (and may possibly even

stimulate) dehalorespiration, a key process in biological remediation (Comba *et al.* 2011, Kirschling *et al.* 2010, Xiu *et al.* 2010). nZVI therefore has the potential for synergistic application with bioremediation techniques.

As the active lifespan of nZVI is likely to be limited (owing to passivation and agglomeration), the impacts on the receiving environment and ecology are likely to be reduced compared to other *in situ* remediation options.

4.2 Implementation Issues for Using nZVI in Remediation

The high chemical reactivity of nZVI particles means that their specific activity and ability to move through the subsurface is limited by a number of processes within the sub-surface, namely:

- Agglomeration - where NPs adhere together in clusters,
- Passivation - where nanoparticle surfaces are chemically inactivated (although activity may remain within particles)
- Sorption onto or entrapment within aquifer material.

To help overcome these problems, and thus increase the usefulness of nZVI in remediation, a number of modifications to the nanoparticles have been developed, including: stabilisation, emulsification, and anchoring the particles to a supporting matrix. In addition, bimetallic nanoparticles have been developed. These are also nZVI variants typically containing a small amount of a noble metal, such as palladium (typically less than 1%) which acts as a catalyst, increasing both reaction rates and the range of treatable contaminants. These are particularly useful in transforming more recalcitrant contaminant classes such as the aryl halides (Zhu *et al.* 2008, Zhu & Lim 2007).

The processes limiting activity and mobility, combined with their typically high reactivity, means that the handling of nZVI products requires quite a lot of care. Handling needs to prevent the oxidation (and indeed for some products combustion) of nZVI on exposure to air. The design of both injection processes and an overall injection grid needs to take account of the relatively low mobility of nZVI in the subsurface and the high density of nZVI suspensions which affects how they are handled and pumped.

Treatment costs are contentious. Overall, cost-effectiveness for nZVI, as is also the case for other *in situ* processes, is likely to be specific to site circumstances and characterisation (Cook 2009). The available evidence suggests that currently costs for nZVI are likely to be higher than granular ZVI on a weight for weight basis. At present, nZVI costs in the USA are typically in the order of $30-40/lb while granular ZVI is around $1-5/lb and millimetre-scale iron is generally in the range of $0.25-0.75/lb (D.W. Elliott 2011 Pers. Comm.) However, as nZVI has the potential to be more reactive, nZVI may be comparable to granular ZVI cost-wise in terms of actual remediation outcome, as theoretically less would be required for the same treatment impact. It should also be noted that material cost of the reactive media (e.g. nZVI) may only be a small proportion of an overall site remediation budget; Lacinová *et al.* (2013) showed that implementation costs associated with nZVI use (e.g. management, operational costs) were collectively higher than nZVI material cost. In addition, over the medium to longer term, economies of scale in production should reduce nZVI production, transport, handling

and application costs.

4.3 Potential Deployment Risks from nZVI Use in Remediation

For the purposes of clarity this report refers to risks from the use of introduced nZVI as "deployment risks" to distinguish these risks from the risks from contamination being managed as a remediation process. Perceived deployment risks from nZVI use, as a part of general concerns over the environmental release of nanoparticles, have led to a precautionary regulatory approach in many countries, in some cases leading to a voluntary moratorium on the release of engineered NPs (e.g. in the UK, see Section 3). Such a stringent regulatory position is not well supported by the available documented evidence.

As with many substances deployed by different *in situ* remediation techniques, the use of nZVI may pose risks to human health and the environment. The level of risk depends on the likely fate, transport and toxicity to receptors of the substance added and the likely exposure of those receptors to the substances.

In the case of nZVI research based on laboratory studies and the fate of naturally occurring iron NPs indicates that the long term fate of manufactured nZVI in an aquifer will be conversion into larger particles of iron (II) and (III) oxides/hydroxides, similar to naturally occurring minerals (Reinsch *et al.* 2010, Sohn *et al.* 2006, Johnson *et al*. 2013). Transport of nZVI will be limited by processes of agglomeration and sorption (Tratnyek and Johnson 2006; Phenrat *et al.* 2007), as well as its density. The transport of readily reactive nZVI will diminish rapidly as a result of processes of passivation. In broad terms there is an inverse relationship between reactivity and mobility; the most reactive particles agglomerate and sorb to surfaces more readily, reducing distance transported. If nZVI has been modified to increase mobility, it is likely to have lost a significant degree of reactivity to achieve this, meaning the particles which pose the greatest hazard in terms of reactivity are also the most easily contained.

The direct effects of nZVI on human health are poorly understood. Concerns regarding the toxicity of nZVI can be broadly split into those related to dose-response relationship of the iron and of the particles' nano-scale size. With regards to iron toxicity, it should be noted that iron is an essential element for growth in nearly all species, including humans. Although as for any element, Fe can be toxic at high enough concentrations. It has been suggested that for toxicity associated with NP size, unique behaviours are only observed in NPs smaller than 30nm and that larger particles can be considered analogous to bulk materials (Auffan *et al.* 2009). nZVI used in remediation is typically in the 10-100nm size range as produced, but tends to agglomerate to larger particles.

Laboratory studies have reported contradictory results with regards to the toxicity of nZVI. For example, nZVI has been found to cause toxic effects in bacterial cells *in vitro* over and above toxicity levels caused by granular ZVI (Lee *et al*. 2008). However, nZVI toxicity was attributed to the prevailing deoxygenated conditions. Other studies have reported no or mixed impacts of nZVI on soil and groundwater micro-organisms (Fajardo *et al.* 2013*,* Wang *et al.* 2012). For non-microbial soil and water organisms, such as *collembola, ostracods* and earthworms, some degree of toxic response to nZVI has been shown in laboratory experiments (El-Temsah & Joner 2013*,* El-Temsah & Joner 2012). However, toxicity was largely observed to reduce in magnitude over time, which was attributed to oxidation. Overall, the toxicity of nZVI appears largely attributable to changes in pH and deoxygena-

tion of water.

The principal receptors of concern are likely to be groundwater and surface water, and their ecologies, away from the area impacted by the pollutants being remediated. Assuming that nZVI is deployed in the subsurface, where it remains, human health exposure pathways are likely to be limited to those possible from occupational exposure. Occupational exposure during nZVI deployment can occur through dermal contact, inhalation, and ingestion. Appropriate measures should be in place relating to the manufacture and transport of nZVI, for example as defined in Material Safety Data Sheets, so occupational exposure scenarios are regarded as routinely managed and therefore unlikely.

Deployment risks from the use of nZVI are likely to be manageable. The available evidence, which is typically based on laboratory based data and/or modelling, indicate that their environmental persistence is relatively short (<1 year (Phenrat *et al.* 2009, Liu & Lowry 2006), typically days or weeks) and its ability to travel is extremely limited (<1m to, exceptionally, 100 m for modified nZVI). Indeed, it has been speculated that even modified nZVI is not likely to travel much farther than 100 m from an injection location and much shorter distances when site conditions limit mobility. Most reports of field scale deployments of nZVI report that nZVI travels only a few metres from the injection point. However, it is generally felt that there are insufficient well validated field studies of nZVI to draw firm conclusions about its mobility under field conditions. This evidence gap is a major research priority for the NanoRem project over the next few years (to 2016).

4.4 Sustainability Considerations for Using nZVI in Remediation

Until recently, little work had been undertaken on assessing the sustainability of nZVI use in remediation, although some NGOs have raised questions about the sustainability of nano-material production, particularly the use of rare metals for doping, as well as its energy budget. nZVI offers certain aspects which could bring about sustainability gains over other remediation options. For example, nZVI may have a potentially lower impact on soil functionality compared with competing technologies (e.g. *in situ* heating or chemical oxidation). Nonetheless, certain elements also threaten to undermine opinions about the sustainability of the technology. These include concerns about the life cycle impacts of nZVI production and use and the intertwined issues of heightened risk perceptions and fear of nanotechnology, which potentially compromise social acceptance of nZVI use. It should be noted, however, that evidence for actual risks relating to nZVI is scant. Overall, whether or not nZVI demonstrates a sustainable *in situ* remediation option is likely to be largely based on site context and the suitability of the technology to the site in question. NanoRem has recently held an international workshop considering sustainability of nanoremediation, which will be published later in 2015 (Tomkiv *et al.* 2015). In addition, the NanoRem project will be carrying out site specific sustainability assessments of nanoremediation (WP8.3).

4.5 General Risk – Benefit Appraisal for nZVI Deployment

nZVI is anticipated as having two major benefits for process based remediation, at least in theory: possible extension of the range of treatable contaminant types, and increasing the efficacy of treatment (speed and degree of completion), and several additional or consequent benefits. To date, the use of nZVI in remediation in practice has largely been for chlorinated solvents in aquifers, competing with more established techniques such as *in situ* bioremediation, chemical reduction and granular

ZVI (e.g. permeable reactive barriers). The majority of nZVI 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, Germany and Italy).

At present nano-remediation may offer advantages in some applications, compared with other *in situ* remediation tools, but this will be highly dependent on site specific circumstances. In the medium to longer term nanoremediation could substantially expand the range of treatable land contamination problems.

The available evidence supports, but does not irrevocably confirm, a view that the risks of nZVI deployment should be considered in the same way as other potentially hazardous treatment reagents (such as persulphates) (commonly used *in situ* remediation reagents (Nathanail *et al.* 2007, US EPA 2006) which are potentially harmful to the biological functioning of soil and can be transported over significant distances in groundwater plumes).

A substantial impediment to the use of nZVI in remediation is the uncertain basis for understanding the risks of its deployment to the wider environment, in particular to groundwater and surface water receptors. Although most laboratory studies and subjective practitioner experience would suggest that adverse effects would be minor, localised and short-lived, there is a lack of effective particle monitoring technologies and peer reviewed and validated data from applications in the field that corroborates this view. This presents a significant challenge to regulatory acceptance which the NanoRem project seeks to address.

5 Market Development in the Medium to Longer Term

In order to develop an exploitation strategy that considers the medium to longer term potential market development for nZVI, any analysis has to deal with an uncertain future. The factors (i.e. drivers and uncertainties related to driver development) that foster or inhibit the evolution of the market need to be better understood. It is unclear how the factors likely to influence the nanoremediation market development are linked, and how they are likely to develop in the future. It is challenging, therefore, to make any straightforward predictions regarding the emerging nanoremediation market. As a result, traditional supply and demand modelling is unsuitable. A scenario approach will therefore be used to help forecast potential market developments. The outcomes of this work could be used to inform an exploitation strategy for nanoremediation. By using a scenario-based approach, a more robust understanding of the factors determining the market system can be developed. The outcomes are utilisable for: “real-world” business development, deducing strategies for market activities; informing policy development, identifying governance options for market expansion; and/or informing regulatory authorities, highlighting the potential for nanoremediation.

5.1 The Scenario Approach

Scenarios can be defined as “internally consistent stories about ways that a specific system might evolve in the future” (March *et al.* 2012). In essence, a scenario-based approach to understanding possible market trends uses available evidence and stakeholder participation to develop a number of narratives describing the potential evolutionary outcomes of a specific market system. Hence, this approach has been applied in order to help determine:

(i) What the factors (drivers and uncertainties) are in the nanoremediation market-system.

(ii) What the extent of the factors' impact is.

(iii) How the factors interdepend.

The analysis of scenario storylines and factors supports the identification of alternative development trajectories, and finally enables the production of planning-oriented, responsive or proactive exploitation strategies.

Scenario design and analysis differ, but usually a stepwise approach is taken. In NanoRem, the following procedure was selected:

1) Conducting a present situation analysis to establish the baseline and framework for scenario development
2) Filtering and systematising factors that drive or inhibit market development. Key determinants are established.
3) Projection of key factors' developments and producing consistent stories about ways the system might evolve in the future. Multiple alternative development trajectories can be identified.
4) Deciding on planning-oriented exploitation strategies, which may be responsive or proactive. Development of governance recommendations.

Figure 1 below, gives an overview of the the work conducted so far as part of a scenario approach, and ongoing work. The steps are discussed further in the following sections. The approach is discussed in more detail in NanoRem IDL 9.3 (Tomkiv *et al.* 2015).

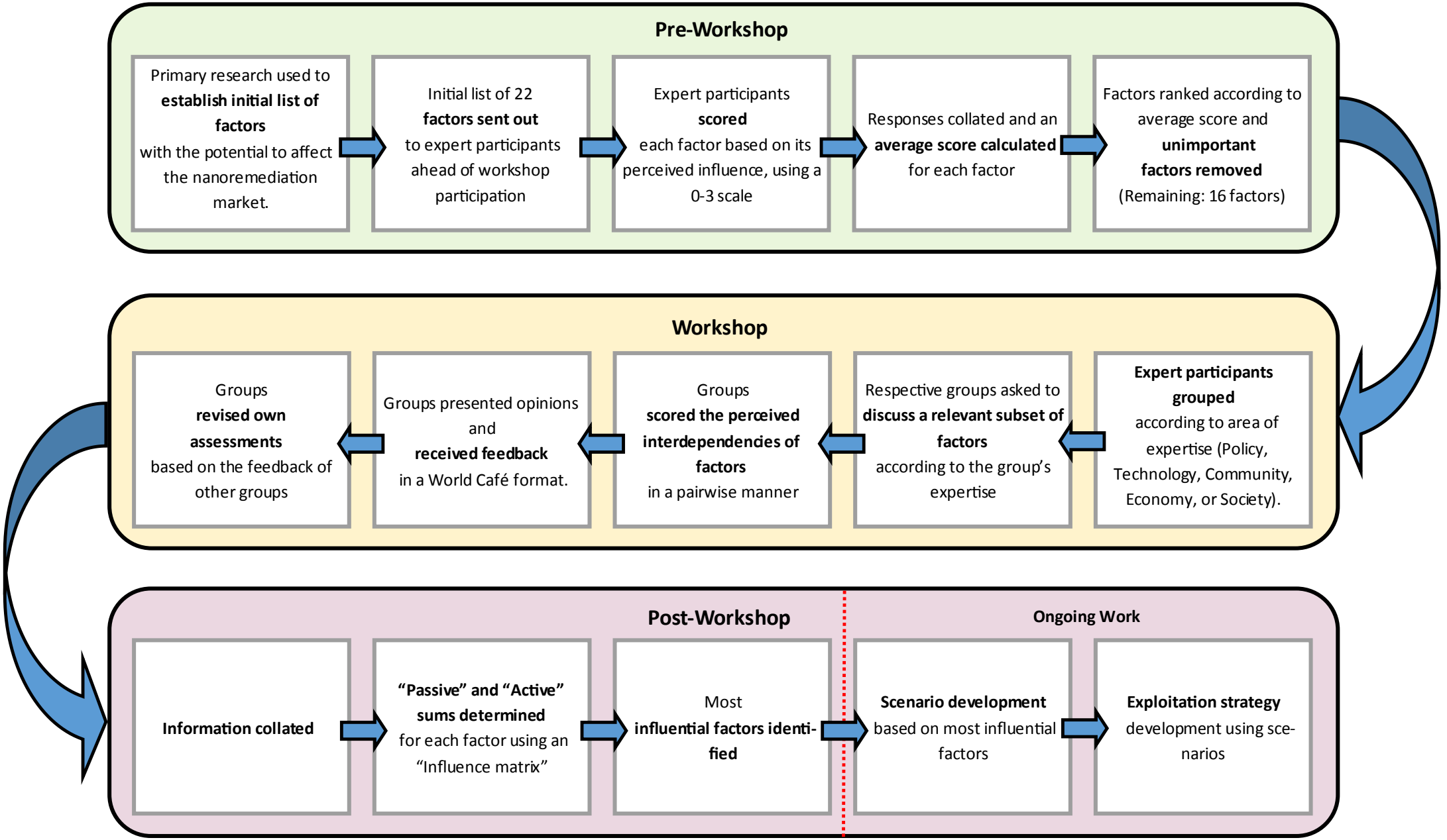
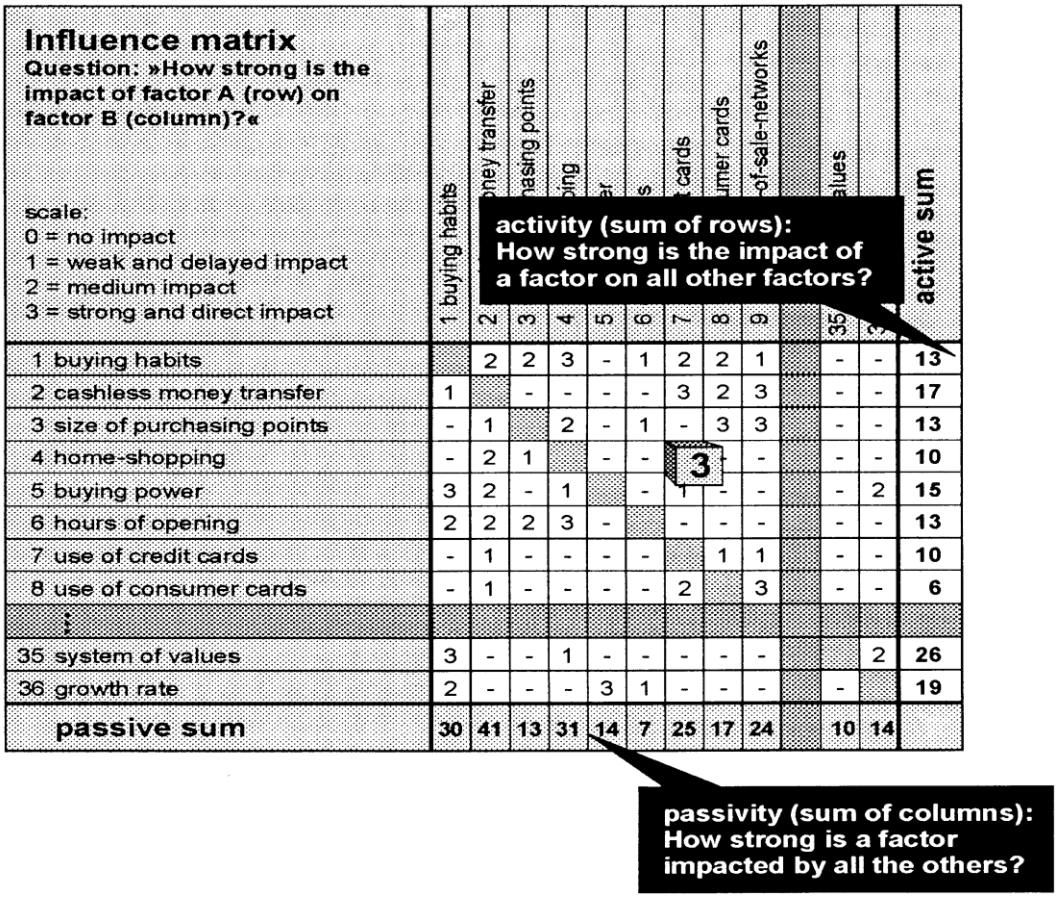


Figure 1: Overview of the scenario approach process. The "Influence matrix" can be seen in Figure 2, below.



	1 buying habits	2	3	4	5	6	7	8	9		35		active sum
1 buying habits		2	2	3	-	1	2	2	1		-	-	13
2 cashless money transfer	1		-	-	-	-	3	2	3		-	-	17
3 size of purchasing points	-	1		2	-	1	-	3	3		-	-	13
4 home-shopping	-	2	1		-	-	3		-		-	-	10
5 buying power	3	2	-	1		-	1	-	-		-	2	15
6 hours of opening	2	2	2	3	-		-	-	-		-	-	13
7 use of credit cards	-	1	-	-	-	-		1	1		-	-	10
8 use of consumer cards	-	1	-	-	-	-	2		3		-	-	6
⋮													
35 system of values	3	-	-	1	-	-	-	-	-			2	26
36 growth rate	2	-	-	-	3	1	-	-	-		-		19
passive sum	**30**	**41**	**13**	**31**	**14**	**7**	**25**	**17**	**24**		**10**	**14**	

Figure 2: Influence matrix used to calculate "passive" and "active" sums (Gausemeier et al. 1998)

5.2 Establishing the Baseline for Scenario Development

To fulfil step one of the scenario development approach, a baseline understanding of the nanoremediation market and the set of factors with the potential to influence the market for nanoremediation was established. This was achieved via key-informant interviews and literature analysis, taking into account the *status quo* and risk-benefit appraisal outlined in Sections 2 and 3 above. This preliminary research helped establish a variety of external determinants from economy, technology development, politics and society that may affect:

- The property market in general;
- The industry for contaminated land remediation broadly, and;
- The potential evolution of nanoremediation in particular.

Expert engagement (key informant interviews and expert discussion) was utilised to establish the most worthwhile timeframe for the scenario approach. A consensus was reached that evolution of the market up to 2025 was the most appropriate scope. It was felt that a very long-term assessment would be impossible due to the significance of unknown and uncertain factors. Nevertheless, any factors found to be potentially more time-sensitive will be reported and carefully considered when determining exploitation strategies.

After several iterations with expert involvement, a condensed list of 22 potentially influencing factors was established.

5.3 Systematising Market Development Factors

To aid step two of the scenario design process, a "Market Opportunities" session was included in the Sustainability and Markets workshop held by the NanoRem project in December 2014, in Oslo. The workshop involved participants selected for their cross-sectorial and transdisciplinary expertise. Participants included senior experts in relevant fields and stakeholders, such as: land managers; consultants; technology contractors; planners; and regulators. For detailed discussion of this workshop, see NanoRem IDL 9.3 (Tomkiv *et al.* 2015).

The 22 factors determined in the preliminary research stage (see Section 5.2) were grouped into different categories (policy, economy, society, communication, technology and megatrends). The use of categories helped to align the factors with appropriate expertise for later discussions. In order to further condense the list of factors and remove less important factors, the list was sent to the workshop participants in advance of the workshop. Participants were asked to provide feedback on how important they perceived each factor to be for the development of the EU nanoremediation market from present to 2025. Participants scored each factor according to the following scale:

(0) = Negligible relevance – the factor is not an important driver or inhibitor;

(1) = Minor relevance – the factor might have a limited but not so important effect;

(2) = Considerable relevance – the factor is likely to have a notable (indirect) effect;

(3) = Key relevance – this factor is most certainly among those of utmost importance to push or pull the nanoremediation market development.

The responses (20 respondents) were collated and an average score score (the arithmetic mean as the sum of the scores collected from all the respondents, divided by the number of the respondents) was calculated for each factor. The results are shown in Table 1, below, in descending order of obtained scores.

Table 1: Preliminary factors and their perceived importance with regards to influencing nanoreme-

diation market development in the EU up to 2025

Factor	*Score*	*Category*
Most important factors (≥2.00):		
Innovation on treatment of known contaminants with NP	2.48	Technology
Regulation of nanoparticles	2.45	Policy
Validated information on NP application potential	2.40	Communication
Costs of competitive technologies	2.35	Economy
Standardization for nanoparticles	2.20	Policy
Innovations along NPs production chain	2.18	Technology
Environment (especially soil) protection policies	2.10	Policy
Synergies with other technologies	2.05	Technology
Public stakeholder dialogue	2.00	Communication
Less important factors (>1.50 and <2.00)		
NP treatment of emerging contaminants	1.95	Technology
Public perception of NPs in general	1.93	Society
Science-Policy-Interface	1.93	Communication
Technology and research policies	1.75	Policy
Growing number of nanoparticles suppliers	1.73	Economy
Real estate market development	1.68	Economy
Innovation attitude	1.60	Society
Environmental awareness	1.55	Society
Minor relevant factors (≤1.50)		
EU economic development	1.50	Economy
Globalisation	1.20	Megatrend
Industrial and military land use	1.00	Society
Climate change	0.70	Megatrend
Demographic change	0.60	Megatrend

The scorings indicate that several factors influence the market's development. Some of the scorings, e.g. the ability to treat emerging contaminants with NPs, are surprising and may indicate either bias or epistemic issues in the mind of the responders. As no factor had a scoring > 2.50, it was concluded that no factor is likely to singlehandedly "push" or "pull" nanoremediation market development.

In order to create scenarios, the interdependencies of the factors determined to be important needed to be better understood. Stakeholders were provided with the factors in Table 1, including short descriptions of each factor. During the workshop, stakeholders were asked to provide opinions,

comments and suggestions about the factors and were also asked to identify and discuss the interrelations of the factors. In order to do this, stakeholders were divided into smaller groups based on their field of expertise. The groups formed were Regulators / Policy makers, Technology, Communication, Economy and Society. Participants in the respective groups were asked to discuss the influence of three or four factors of their respective expert domain on the full list of factors identified to be of importance. Next, following a "World Café ™" format, the experts were invited to discuss the results of the other groups and finally to review and revise their own assessments based on the feedback of others. These discussions are reported in detail in Tomkiv *et al.* (2015)

After the workshop, the information collected from the group sessions was analysed and the factors that are more "active" in influencing other factors were identified, as well as those that are more driven by the active ones. These relationships are expressed by the "active sum" and "passive sum" in Table 2, below. Table 2 lists the factors recorded in Table 1 in order of their activity (i.e. how influential a factor is relative to other factors). Where a factor has a high active sum, it is highly influential with regards to other factors. Factors with a high active score need only change a small amount to have a big impact on the nanoremediation market. Where a factor has a high passive sum it is highly susceptible to the influences of other factors.

The third and fourth steps of the scenario approach will be carried out over Year 3 of the project and have the objectives of deducing recommendations for the exploitation strategy based on a deeper understanding of the key factors identified as market determinants. During the third step, key factors will be filtered in order to guide the design of consistent stories about ways the market system might evolve in the future. In the fourth step, recommendations will be concluded from this exercise.

Table 2: Interrelatedness of factors determining the development of the nanoremediation market

Factor	Active sum*	Passive sum*
Science-Policy-Interface	38	26
Validated information on NP application potential	36	21
Environment (especially soil) protection policies	25	17
Public stakeholder dialogue	25	20
Synergies with technologies	24	20
Innovations along NPs production chain	24	21
Costs of competitive technologies	24	24
Growing number of nanoparticles suppliers	24	28
Regulation of nanoparticles	23	19
Technology and research policies	23	27.5
Innovations in treatment of known contaminants with NP	22	29.5
Environmental awareness	21	19
NP treatment of emerging contaminants	19	26
Innovation attitude	16,5	24
Public perception of NPs in general	14	21
Real estate market development	11,5	8

*Active and Passive sums had a maximum potential value of 48. The closer the active sum for a factor is to 48, the more influential that factor is. Conversely if the passive sum for a factor is close to 48, it is likely to be highly influenced by changes in other factors.

The factors “Science-Policy-Interface” and “Validated information on NP application potential” are by far the two most active drivers and, hence, crucial in determining the development of the nanoremediation market. The three factors being most heavily influenced in their development by the other determinants are “Innovations in treatment of known contaminants with NP”, “Growing number of nanoparticle suppliers” and “Technology and research policies”.

5.4 Projection of Factor Development and Establishing Consistent Scenarios

As part of ongoing work, a series of expert engagement activities is underway. In March 2015, NanoRem conducted a first focus group meeting and expert workshop in Berlin, Germany, in order to discuss the establishment of consistent scenarios. The participants were provided with an overview of the interim results of the scenario analysis work. They were shown that the two most “active” of the key factors were identified as: “Science-Policy-Interface” and “Validated information on NP application potential” (see Table 2: **Interrelatedness of factors determining the development of the**

nanoremediation marketand hence, these factors are likely to be crucial in determining the development of the nanoremediation market system. These two factors were suggested for the development of framing elements for a conceptual scheme for scenario states. The participants discussed the meaning of these factors and tentatively defined them as follows:

- Science-Policy-Interface is part of a broader 'Dialogue', which is the process by which stakeholder groups (in particular those from science, policy and regulation) have informal/formal discussions, consultations and other forms of engagement in order to ascertain the potential application of nanoremediation (in general or in specific cases).
- Validated information on NP application potential is an 'Information' dimension, which describes the quality of available information for decision-making. Information can range from a level of great uncertainty with regards to the potential developments of the market and the set of factors driving the market, to a situation where information about nanoremediation is readily available, well tested, and broadly accepted (i.e. "validated"). "Validated information" gives credence to a decision regarding its applicability.

These dimensions form the conceptual scheme for the scenario states of the nanoremediation market. These scenario states show four potential future states for the market, see Figure 3 below, (going clock-wise in each quadrant of the matrix):

I. Validated information is broadly available AND there is comprehensive dialogue between stakeholders, in particular those from science, policy and regulation.

II. Validated information is lacking and uncertainty is still significant BUT there is comprehensive dialogue between stakeholders, in particular those from science, policy and regulation.

III. Validated information is lacking and uncertainty is still significant AND there is no or only minimum dialogue between stakeholders, in particular those from science, policy and regulation.

IV. Validated information is broadly available BUT there is no or only minimum dialogue between stakeholders, in particular those from science, policy and regulation.

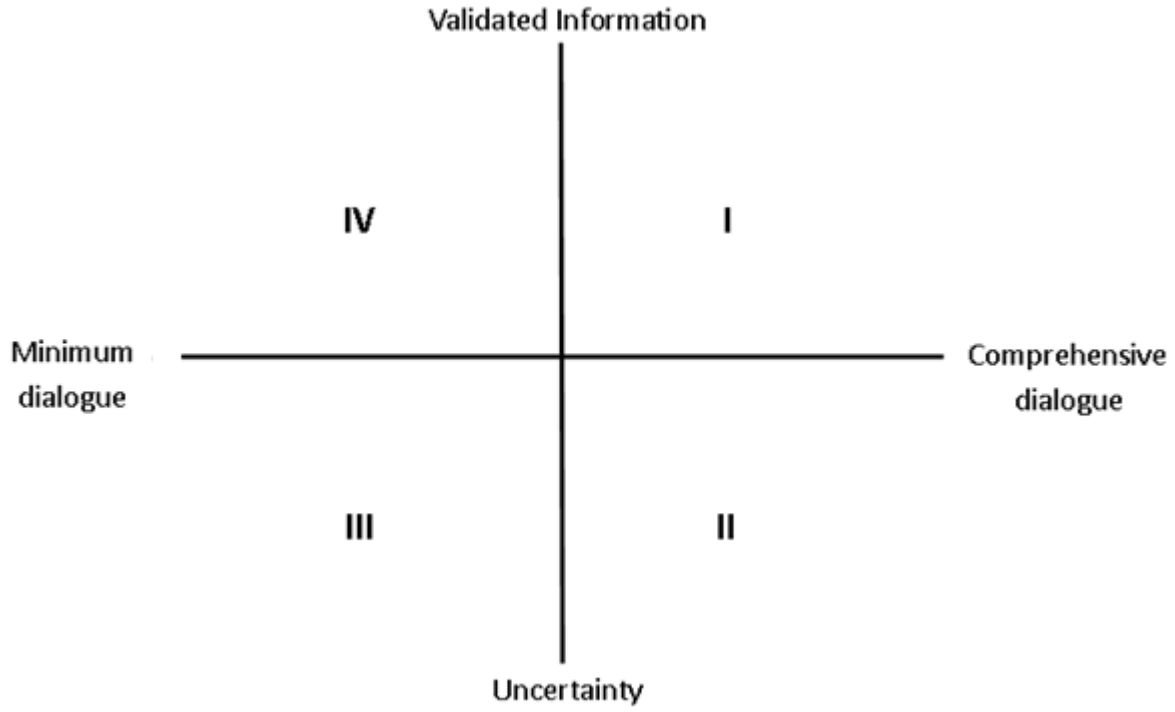


Figure 3 - Conceptual Scheme for Scenario States

The final steps of the scenario analysis will be the discussion of the key factors' developments within the different scenario states, and based on these, the deduction of scenario storylines. These discussions will finally inform the conclusion of recommendations for the exploitation strategy. The Berlin workshop was the first event in a series of further expert engagement activities foreseen in Year 3 of the NanoRem project.

6 SWOT Analysis

A SWOT (strengths, weaknesses, opportunities and threats) analysis of factors that may affect (positively or negatively) the value proposition and exploitation of the nanoremediation market has been developed (Table 3). This summarises the main findings of Appendix 1: nZVI risk-benefit appraisal. SWOT issues naturally fall into a series of broader categories. We have indicated these in Table 3 and used a colour scheme to make them more obvious. An ongoing task of Year 3 of the NanoRem project will be to link the categorisations used in the SWOT with the broader market factor categories used in Table 1 (exploitation).

Table 4 provides an initial, and tentative, view on how time sensitive the broader categories may be: if they will change over time; what we can say now about likely changes; and how certain we are about these changes.

Over the second half of the NanoRem project, this tentative and preliminary view will be integrated with the forthcoming focus group work. This assessment will also be expanded to encompass other NP types under investigation by NanoRem (potentially: air-stable powder nZVI, milled iron, biomagnetite, palladised biomagnetite, carbo-iron, Fe-zeolites, Fe-oxides, barium ferrate, nano-goethite, Al and Mg), being developed by the project over Years 3 and 4 of the project. Years 3 and 4 of the pro-

ject will also see the risk benefit appraisal broadened to these other NP types.

Table 3: nZVI Strength, Weakness, Opportunity and Threat (SWOT) for the use of nZVI in remediation

Strengths		**Weaknesses**	
>Improving the speed of contaminant destruction (Appendix 1: Chapter 3.3)	Relative effectiveness	>Field scale deployments are limited in scope of remediation problem being addressed and tend to lack verified / validated performance information (Appendix 1: Chapter 3.1)	Field scale experience
>Improving the extent of contaminant destruction (Appendix 1: Chapter 3.3)	Relative effectiveness	>Knowledge gaps regarding fate, transport, toxicity in environment (Appendix 1: Chapter 5)	Current knowledge
>Extending the treatable range of contaminants (Appendix 1: Chapter 3.2)	Relative effectiveness	>Knowledge gaps relating to toxicity to humans (Appendix 1: Chapter 5.3.5)	Current knowledge
>70 known field scale deployments (Appendix 1: Annex 1)	Field scale experience	>Handling risks may be greater than granular ZVI (Appendix 1: Chapter 4.4)	Relative risks
>Limited longevity of action may reduce environmental risks (Appendix 1: Chapter 3.5)	Relative risks	>Limited longevity due to rapid agglomeration & passivation. May require several applications (Appendix 1: Chapter 4.1)	Relative effectiveness/ Ease of use
>Compatibility with other treatments (Appendix 1: Chapter 3.6)	Synergy	>Poor mobility due to rapid agglomeration & passivation in the short term (Appendix 1: Chapter 4.3)	Relative effectiveness/ Ease of use
>Can utilise existing techniques for deployment (Appendix 1: Chapter 2.2)	Ease of use	>Potential groundwater contamination by NPs (Appendix 1: Chapter 8)	Relative risks
>As an *in situ* technique there may be reductions in site costs compared to *ex situ* remediation (e.g. reduced waste generation, reduced fuel usage) (Appendix 1: Chapter 3.5)	Relative costs	>Lack of comprehensive sustainability assessment (Appendix 1: Chapter 6)	Current knowledge
>As an *in situ* technique there may be reductions in some site risks compared to *ex situ* remediation (e.g. reduced exposure of workers to contaminants) (Appendix 1: Chapter 3.1)	Relative risks	>Cost of nZVI is currently high relative to granular ZVI (Appendix 1: Chapter 4.1)	Relative costs

Opportunities		**Threats**	
>Concentration of field scale experience in some countries, e.g. Czech Republic, creates an opportunity for cross comparison of field scale deployments in one jurisdiction (Appendix 1: Annex 1)	Field scale experience	>Unwillingness to provide regulatory or problem holder permission to use nZVI (Appendix 1: Chapter 6.2)	Field scale experience
>Cost reductions associated with economies of scale (Appendix 1: Chapter 4.1)	Relative costs	>Potentially significant public concern about nanotechnology being inherently risky (Appendix 1: Chapter 6.2)	Technology dread
>Optimisation of field trials improving nanoparticle delivery methods (Appendix 1: Chapter 4.3)	Relative effectiveness	>Numerous coatings, modifiers, catalysts which could make establishing risks complicated (Appendix 1: Chapter 5.3.3)	Relative risks
>Treatment of contaminants in the vadose zone (Appendix 1: Chapter 1)	Relative effectiveness	>Costs remaining high relative to competing technologies (Appendix 1: Chapter 4.1)	Relative costs
>Potential for treatment of source terms (Appendix 1: Chapter 3.4)	Relative effectiveness	>Source term treatment effectiveness is in general constrained by the accessibility of the source (Appendix 1: Chapter 3.4)	Relative effectiveness
>Improved understanding could lead to reduced public and regulatory fears (Appendix 1: Chapter 6.2)	Technology dread	>Difficulties in tracking nanoparticle transport (Appendix 1: Chapter 5.2)	Relative risks
>Inclusion of nanoremediation in *in situ* integrated treatment approaches (Appendix 1: Chapter 3.6)	Relative effectiveness		

Table 4: Possible future trends affecting broader SWOT categories

Item	Time sensitive?	Possible development by 2025	Certainty of development
Relative costs	Yes	Economies of scale may lead to cost reductions related to: a) production of NPs b) application of NPs Increased costs of NP material could raise costs.	Dependent on level of market uptake and the overall demand for NPs.
Field scale experience	Yes	Additional field trials including a wider range of contaminants could strengthen the evidence base for nZVI effectiveness and reduce public concerns associated with deployment safety	Highly likely. This is a key task of the NanoRem project (WP10)
Relative effectiveness	Yes	a) Research funding to address difficult contaminants and develop novel NPs b) Vadose zone treatment, if developed, could have huge benefits for difficult / untreatable problems such as highly recalcitrant contaminant classes (e.g. PCBs, dioxins, etc.) c) Development of coatings to improve persistence and mobility	a) Likely – There are a number of research projects taking place across Europe b) Currently vadose zone treatment has not been well investigated, but exploiting NPs for this use may be possible c) Relatively certain, research being carried out, including by NanoRem
Relative risks	yes	Development of coatings to improve persistence and mobility – introducing an additional element of risk	Relatively certain, research being carried out, including by NanoRem
Ease of use	Yes	Development of coatings to improve persistence and mobility	Relatively certain, research being carried out, including by NanoRem
Technology dread	Yes	Field trials and research into potential toxicological effects could help address “dread” associated with the technology	Improvement of the situation is possible. NanoRem is working towards consensus development for appropriate NP use. NICOLE and Common Forum will assist
Current knowledge	Yes	Knowledge expansion leading to reduced dread, improved certainty of effectiveness, increased uptake of the technology.	Improvement of the situation is likely. NanoRem is working towards improved knowledge and dissemination

Item	Time sensitive?	Possible development by 2025	Certainty of development
Relative costs	Yes	Economies of scale may lead to cost reductions related to: a) production of NPs b) application of NPs Increased costs of NP material could raise costs.	Dependent on level of market uptake and the overall demand for NPs.
Synergy	yes	New synergies could be discovered, incorporating previously untrialled technologies in combination with nZVI	Likely – experimental work exploring synergies of nZVI with e.g. bioremediation are already under way, including by NanoRem

7 Conclusions and Recommendations for Developing an Exploitation Strategy

Preliminary scenarios have been developed regarding the nanoremediation market in Europe in 2025. However, the final step of the scenario analysis is still in development. The preliminary scenarios will be used to derive recommendations for entrepreneurs and policymakers. Towards this objective, the next steps are to further discuss the potential future development directions of the key factors identified above (potentially meaning step 3 of the scenario design procedure introduced in Section 5.1 will be updated). This will be discussed in future stakeholder engagement activities. Focus group events will be planned, potentially including participants of the Oslo Workshop. Based on these discussions, conclusions on the medium to longer term exploitation opportunities will be established that reflect the interactions identified in the Oslo workshop and the directions of factor development and scenario storylines to be discussed in the Focus Groups events.

A SWOT analysis for nZVI use currently indicates a relatively evenly balanced perspective for the strengths, weaknesses, opportunities and threats for nanoremediation. This is consistent with its fairly low penetration into the market thus far. A number of these factors are time sensitive as shown in Table 4. Therefore encouraging the exploitation of nanoremediation in a broad way depends on achieving improvements in these factors over time. While this is only a tentative analysis, it does indicate that improvements over time will happen and NanoRem's activities are a key component in achieving this improvement.

SWOT analysis will be expanded, and ongoing work will endeavour to link SWOT categories with market factor categories (see Section 7). Discussions regarding the time sensitive aspects of the SWOT categories will be integrated into upcoming focus group work where possible.

Ongoing work in NanoRem will seek to determine a greater level of linkage and evidence for nZVI exploitation between scenario analysis and SWOT analysis. Future scenario development and SWOT work is anticipated to include other NP types.

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Appendix 1: A Risk/Benefit Appraisal for the Application of Nano-Scale Zero Valent Iron (nZVI) for the Remediation of Contaminated Sites

The complete report follows on the next page.

Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment

Project Nr.: 309517
EU, 7th FP, NMP.2012.1.2

WP9: Dissemination, Dialogue with Stakeholders and Exploitation

A Risk/Benefit Appraisal for the Application of Nano-Scale Zero Valent Iron (nZVI) for the Remediation of Contaminated Sites

Supporting MS3 - NanoRem information for decision makers – initial version

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1. Bardos, P., Bone, B., Elliott, D., Hartog, N., Henstock, J. and Nathanail, P. 2011. Risk/benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment. Defra. http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=17502

Executive Summary

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) is a research project, funded through the European Commission's Framework 7 research programme. NanoRem focuses on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This is being undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), market demand, overall sustainability, and stakeholder perceptions. Through examination of the currently available documented evidence, this paper attempts to assess the relative risks and benefits of nZVI usage for *in situ* remediation, and identify the areas where further investigation might be required. An overview of nZVI use in field, pilot and laboratory trials to date is provided. This paper supports Milestone 3 of the NanoRem project, and is intended to help stakeholders by providing a basis for evidence-based decisions.

This paper reviews the use of nZVI in remediation in the context of contaminant risk management, i.e. the breaking of linkages between source, pathway and receptor. It describes the likely benefits of nZVI deployment, and issues affecting its use. It details the existing document level on the risks of deployment of nZVI (i.e. the potential for the nZVI treatment agent itself to cause human health or environmental risks) and its sustainability as a technique. It suggests the key issues that might impact the regulation or permitting of nZVI use in remediation and provides general conclusions about risks versus benefits and continuing research needs.

Use of nZVI in Remediation

In situ remediation techniques (exploiting biological, chemical, physical stabilisation and/or thermal processes) are being increasingly used to avoid excavation of materials or surface treatment of groundwater from "pump and treat" projects. The use of nanoparticles potentially extends the range of available *in situ* remediation technologies, and may offer particular benefits in some applications.

Zero valent iron (essentially finely ground iron) has been used as a treatment reagent in *in situ* remediation for many years, in particular for permeable reactive barriers. Nano-scale zero valent iron (nZVI) is a type of iron nanoparticle that has been investigated for deployment for *in situ* remediation, i.e. within the subsurface, as a groundwater and aquifer treatment.

Nanoparticles (NPs) are typically defined as particles with one or more dimension of less than 100nm (Rauscher *et al.* 2014). As a result of their size, nanoparticles can have markedly different physical and chemical properties to their bulk counterparts, enabling them to be utilised for novel purposes, including the potential for use in remediation. However, whilst the possibility of unique characteristics gives nZVI promise for beneficial applications, it is simultaneously a cause of concern, as there is a degree of uncertainty with regards to nZVI particle behaviour, fate and toxicity.

The first documented field trial of nZVI, in 2000, involved treatment of trichloroethylene in groundwater at a manufacturing site in Trenton, New Jersey, USA. It was anticipated by several

commentators that nZVI technology would take off rapidly because of its perceived benefits such as rapid and complete contaminant degradation). However, subsequent uptake of the technology has been relatively slow. This report has identified around 70 projects documented worldwide at pilot or full scale. Additionally, Lee *et al.* (2014) have reviewed 60 field applications worldwide. Most such deployments of nZVI have focussed on the degradation of chlorinated solvents for plume (i.e. pathway) management although pilot studies have also demonstrated successful treatment of BTEX, perchlorates, hexavalent chromium, diesel fuel, PCBs and pesticides.

Potential Benefits of using nZVI in Remediation

The principal potential benefits of nZVI use that have led to its development, particularly in comparison to the use of conventional zero-valent iron are the extent and speed of contaminant degradation possible from nZVI. These result from the greater surface area (and therefore increased reactivity) of nZVI. Furthermore, there may be a potential extension of the range of treatable contaminants to include types traditionally seen as recalcitrant. However, there is some uncertainty regarding whether or not nZVI will extend the range of treatable contaminants in the field, compared to conventional ZVI, although it is projected that at least a comparable treatment capability will be achieved.

When compared to bioremediation, nZVI usage also offers a probable reduction in the formation of toxic intermediate products for the degradation of some chlorinated solvents (e.g. the chloroethenes). Moreover, the overall evidence supports a view that nZVI has little, if any, deleterious effect on (and may possibly even stimulate) dehalorespiration, a key process in biological remediation. nZVI therefore has the potential for synergistic application with bioremediation techniques.

As the active lifespan of nZVI is likely to be limited (owing to passivation and agglomeration – see below), the impacts on the receiving environment and ecology are likely to be reduced compared to other *in situ* remediation options.

Implementation issues for nZVI

The high chemical reactivity of nZVI particles means that their specific activity and ability to move through the subsurface is limited by a number of processes within the sub-surface, namely:

- Agglomeration - where NPs adhere together in assemblages,
- Passivation - where nanoparticle surfaces are chemically inactivated (although activity may remain within particles)
- Sorption onto material within the aquifer.

To help overcome these problems, and thus increase the usefulness of nZVI in remediation, a number of modifications to the nanoparticles have been developed, including: stabilisation, emulsification, and anchoring the particles to a supporting matrix. In addition, bimetallic nanoparticles have been developed. These are also nZVI variants containing a small amount of a noble metal, such as palladium (typically less than 1%) which acts as a catalyst, increasing both reaction rates and the range of treatable contaminants. These are particularly useful in transforming more recalcitrant contaminant classes such as the aryl halides (Zhu *et al.* 2008, Zhu & Lim 2007).

The processes limiting activity and mobility, combined with their typically high reactivity, means that the handling of nZVI products requires quite a lot of care. Handling needs to prevent the oxidation (and indeed for some products combustion) of nZVI on exposure to air. The design of both injection processes and an overall injection grid needs to take account of the relatively low mobility of nZVI in the subsurface and the high density of nZVI suspensions which affects how they are handled and pumped.

Treatment costs are contentious. Overall, cost-effectiveness for nZVI is likely to be specific to site circumstances and characterisation. The available evidence suggests that currently costs for nZVI are likely to be higher than microscale ZVI on a weight for weight basis. However, as nZVI has the potential to be more reactive, nZVI may be comparable to micro-ZVI in terms of cost in terms of actual remediation outcome, as less would be required for the same treatment impact. It should also be noted that material cost of the reactive media (e.g. nZVI) may only be a small proportion of an overall site remediation budget. In addition, over the medium to longer term economies of scale in production should reduce nZVI costs.

Potential Deployment Risks from nZVI Use

Perceived risks from nZVI use, as a part of general concerns over the environmental release of nanoparticles, have led to a precautionary regulatory approach in many countries, in some cases leading to a voluntary moratorium on the release of engineered NPs. Such a stringent regulatory position is not well supported by the available documented evidence.

As with many substances deployed by different *in situ* remediation techniques, the use of nZVI may pose risks to human health and the environment. This risk depends on the likely fate, transport and toxicity to receptors of the substance added.

In the case of nZVI research based on laboratory studies and the fate of naturally occurring iron NPs indicates that the fate of manufactured nZVI in an aquifer will be conversion into larger particles of iron (II) and (III) oxides/hydroxides, similar to naturally occurring minerals. Transport of nZVI will be limited by processes of agglomeration and sorption, as well as its density, and the transport of readily reactive nZVI will diminish rapidly as a result of processes of passivation. In broad terms there is an inverse relationship between reactivity and mobility; the most reactive particles agglomerate and sorb to surfaces more readily, reducing distance transported. If nZVI has been modified to increase mobility, it is likely to have lost a significant degree of reactivity to achieve this, meaning the particles which pose the greatest hazard in terms of reactivity are also the most easily contained.

Knowledge about direct effects of nZVI on human health is limited. Concerns regarding the toxicity of nZVI can be broadly split into those related to the toxicological effect of the actual iron and those related to the particles' nano-scale size. With regards to iron toxicity, it should be noted that iron is an essential element for growth in nearly all species. It has been suggested that for toxicity associated with nanoparticle size, unique behaviours are only observed in nanoparticles smaller than 30nm and that larger particles can be considered analogous to bulk materials. nZVI used in remediation is typically in the 10-100nm size range as produced, but tends to agglomerate to larger particles.

Laboratory studies have reported contradictory results with regards to the toxicity of nZVI. For example, toxicity has been found to bacterial cells *in vitro* by nZVI over and above micro-ZVI. However, this was attributed to deoxygenated conditions. Other studies have reported no or mixed impacts of nZVI on soil and groundwater micro-organisms. For non-microbial soil and water organisms, such as collembola, ostracods and earthworms, some degree of toxic response to nZVI has been shown in laboratory experiments. However, toxicity was largely observed to reduce in magnitude over time, which was attributed to oxidation.

The principal receptors of concern are likely to be groundwater and surface water, where this is in close proximity to the injection area, and their ecologies. Assuming that nZVI is deployed in the subsurface, where it remains, human health exposure pathways are likely to be limited to those possible from occupational exposure. Occupational exposure during nZVI deployment is the most likely route of exposure for humans to nZVI; exposure can occur through dermal contact, inhalation, and ingestion. Appropriate measures should be in place relating to the manufacture and transport of nZVI, for example as defined in Material Safety Data Sheets, so occupational exposure scenarios are regarded as unlikely.

Risks from the use of nZVI are likely to be manageable. The available evidence, which is typically based on laboratory based data and/or modelling, indicate that their environmental persistence is relatively short (<1 year, typically days or weeks) and their ability to travel is extremely limited (<1m to 100m). Indeed, it has been speculated that even modified nZVI is not likely to travel much farther than 100 m from an injection location and much shorter distances when site conditions limit mobility. Most reports of field scale deployments of nZVI report that nZVI travels only a few metres from the injection point. However, it is generally felt that there are insufficient well validated field studies of nZVI to draw a firm conclusions about its mobility under realistic field conditions. This evidence gap is a major research priority for the NanoRem project over the next few years (to 2016).

Sustainability Considerations

Little work to date had been undertaken on assessing the sustainability of nZVI use in remediation, although some NGOs have raised questions about the sustainability of nano-material production, particularly the use of rare metals for doping, as well as its energy budget. nZVI offers certain aspects which could bring about sustainability gains over other remediation options. For example, nZVI may have a potentially lower impact on soil functionality compared with competing technologies (e.g. *in situ* heating or chemical oxidation). Nonetheless, certain elements also threaten

to undermine opinions about the sustainability of the technology. These include concerns about the life cycle impacts of nZVI production and use and the intertwined issues of heightened risk perceptions and fear of nanotechnology, which potentially compromise social acceptance of nZVI use. It should be noted, however, that evidence for actual risks relating to nZVI is scant. Overall, whether or not nZVI demonstrates a sustainable *in situ* remediation option is likely to be largely based on site context and the suitability of the technology to the site in question. Part of the NanoRem project considers the sustainability of nanoparticle remediation (WP9).

"Deployment risks" and permitting nZVI use

A sound understanding of the fate and transport of nZVI is needed to ensure remediation objectives are achieved while negative impacts are avoided. These considerations will be site specific. The use of a conceptual site model and the source – pathway – receptor paradigm provide a framework for determining likely deployment risks and how they might be managed. For the purposes of clarity this report refers to risks from the use of introduced nZVI as "deployment risks" to distinguish these risks from the risks from contamination being managed as a remediation process. The principle deployment risks for nZVI use are related to:

1. Human health impacts and impacts from spillages during the deployment process which should be addressed by regulatory permitting related to good operating practice
2. Impacts on surface water biology which should be addressed by regulations related to the types of allowable subsurface deployments.

In addition, the direct discharge of hazardous substances is prevented under the Groundwater Daughter Directive (Directive 2006/118/EC) and this may be relevant to the use of some modified NPs.

An approximate position, not contradicted by current evidence, is as follows. Risks from nZVI, including many modified forms, are manageable, since its persistence in a reactive form in the environment appears to be relatively short (< 1-2 years), and its ability to travel from injection points is limited (from <1m to an unproven 100 m for some modified types).

While this seems a relatively positive risk output for the environmental use of nZVI, supporting evidence outside of laboratory studies is scant. For all nZVI types there seems to be insufficient field scale observational data to categorically substantiate a view of limited nZVI transport and persistence that would be seen as satisfactory by all regulatory authorities.

The current state of knowledge militates a cautious approach to deployment risks for surface water given the current uncertainties in knowledge related to persistence of reactive nZVI in the subsurface and its potential migration. Table A sets out the key issues that should be considered whilst designing and permitting nZVI deployment.

Table A Checklist of permitting issues specific to the use of nZVI

Technology related	**Site related**
* Type of nZVI, physical and hazardous properties and any amendments used (doping metals, coatings, emulsification or other agents), in particular for surface water organisms * Types of deployment approaches used * Emissions from the treatment process (to air land and water) * Likely nZVI migration * Likely nZVI persistence in a reactive form * Likely fate and toxicity of pristine and reacted nZVI and any amendments * Likely maximum dispersion of nZVI under a range of standardised aquifer and groundwater conditions	Applicant/organisation/site * Site specific application / deployment approach * Deployed mass * Deployment risks (with appropriate cross reference to health and safety regime) * Appropriate cross reference to health and safety regime * Conceptual model (including all plausible contaminant linkages related to the contaminants, products resulting from the treatment process, emissions to air, land and water, and the resultant material following remediation) * Environmental risk assessment (for all plausible contaminant linkages identified in the conceptual model) * Monitoring plan * Pollution control measures * Contingency measures (e.g. in the event of a spillage) * QA/QC plan * Qualitative risk assessment based on type, longevity and mass of NPs deployed, standardised aquifer conditions and distance to surface water/groundwater receptor or compliance point.

The assessment of deployment risks for nanoremediation has been reported in detail by NanoRem, following an expert elicitation workshop: (LQM 2014 - 2014 'NanoRem Deliverable 9.2.1 (Potential environmental risks of nanoparticle deployment)'). This report is available from www.nanorem.eu.

Risk – benefit appraisal for nZVI deployment

nZVI is anticipated as having two major benefits for process based remediation, at least in theory: possible extension of the range of treatable contaminant types, and increasing the efficacy of treatment (speed and degree of completion). To date, the use of nZVI 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 reduction and ZVI (e.g. permeable reactive barriers). The majority of nZVI 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, Germany and Italy).

At present nano-remediation may offer advantages in some applications, compared with other *in situ* remediation tools, but this will be highly dependent on site specific circumstances. In the medium to longer term nanoremediation could substantially expand the range of treatable land contamination problems.

The available evidence supports, but does not irrevocably confirm, a view that the risks of nZVI deployment should be considered in the same way as other potentially hazardous treatment reagents (such as persulphates).

A substantial impediment to the use of nZVI in remediation is the uncertain basis for understanding the risks of its deployment to the wider environment, in particular to groundwater and surface water receptors. Although most laboratory studies and subjective practitioner experience would suggest that adverse effects would be minor, localised and short-lived, there is a lack of effective particle monitoring technologies and peer reviewed and validated data from applications in the field that corroborates this view. This presents a significant challenge to regulatory acceptance which the NanoRem project seeks to address.

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1. Introduction

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) is a research project, funded through the European Commission's Framework 7 research programme. NanoRem focuses on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This is being undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), market demand, overall sustainability, and stakeholder perceptions. Through examination of the currently available documented evidence, this paper attempts to assess the relative risks and benefits of nZVI usage for *in situ* remediation, and identify the areas where further investigation might be required. An overview of nZVI use in field, pilot and laboratory trials to date is provided. This paper supports Milestone 3 of the NanoRem project, and is intended to help stakeholders by providing a basis for evidence-based decisions.

In parallel to this Risk/Benefit Appraisal, a report following a workshop and literature review on "Potential environmental risks of nanoparticle deployment" has been developed (LQM 2014). This report details the outcomes from an elicitation workshop held by the NanoRem consortium in July 2013 and in conjunction with this Risk/Benefit Appraisal provides an overview of key environmental issues associated with the deployment of nanoparticles for the remediation of contaminated sites.

Nano-scale zero valent iron (nZVI) is a type of iron nanoparticle (NP). Nanoparticles (NPs) are typically defined as particles with one or more dimension of less than 100nm (see Section 2.1 and LQM 2014) Use of nZVI for remediation is a relatively new technology and while the first field-scale application of nZVI occurred in 2000, iron particles in the micro to millimetre scale have been used in remediation for over twenty years. As produced, most nZVI tested falls into the 10-100 nm size range (O'Carroll *et al.* 2013, Müller & Nowack 2010, Karn *et al.* 2009, Nurmi *et al.* 2005), although it tends to agglomerate to form larger particles.

The properties of materials can be different at the nanoscale for two main reasons. Firstly, nanomaterials have a relatively larger surface area which can make materials more chemically reactive. Secondly, particularly at lower size ranges, quantum effects can begin to affect their physical behaviour (Roduner 2006). A range of iron NP types and process configurations for remediation technologies have been developed, at least to laboratory scale, to exploit this enhanced reactivity. However, the majority of applications in the field have been *in situ* injections of nZVI (Bardos *et al.* 2011a, Li *et al.* 2006b, Elliott and Zhang 2001). nZVI is a highly reactive reducing agent and as such degrades some organic compounds (e.g. chlorinated solvents) and changes the oxidation state of elements (e.g. chromium, uranium) (O'Carroll *et al.* 2013). This underlies its functionality in soil and groundwater remediation. However, this same high surface reactivity and the potential ability of such small particles to cross cell membranes) might also have led to concerns over possible negative health and environmental impacts (RS/RAE 2004).

The scale of contaminated land in the European Union (EU) is large, but estimates of its size are only tentative. In August 2007, the European Environment Agency (EEA) concluded that "potentially polluting activities" may have occurred at nearly three million sites across Europe. Brownfield land can encompass contaminated sites, and may be present at a million or more locations in the EU (EEA

2007, Oliver *et al.* 2005). The Roadmap to a Resource Efficient Europe (EC 2011) suggests that by 2050 there should be no net land take from soil sealing by built development (from current levels of 1000 km^2 per year across the EU). This will only be possible with effective "recycling" of formerly used land, including contaminated land. The scale of response needed is substantial. Two NGOs have recently suggested that soil deterioration (also resulting from contamination) affects all Member States and costs Europe an estimated €38 billion a year (DNR & EEB 2011).

It was forecast that nanotechnologies would offer a step-change in remediation capabilities as indicated by laboratory scale findings, which show that the range of treatable contaminants and the speed by which they can be degraded or stabilised can be substantially increased over conventional in-situ saturated zone remediation technologies (Müller and Nowack 2010). A 2007 report (JRC Ispra 2007) projected that the 2010 world market for applications of environmental nanotechnologies would be approximately $6 billion across four sectors: remediation, protection, maintenance, and enhancement. Remediation was thought to represent the fastest growing sector.

In practice this step change and the JRC predictions for nanotechnology use in remediation, made in the mid-2000s, have not been achieved. Nanotechnologies have been used for remediation, "nanoremediation", primarily for treating soils in the saturated zone and groundwater *in situ* (see Annex 1). They have not tended to be used for the treatment of unsaturated soils as the nanoparticles used to date in the field are rapidly inactivated or oxidized in the presence of air.

To date, there have been relatively few commercial deployments of nanoremediation. While some projects may have gone unreported in the technical literature, just 70 examples of field scale applications of nZVI have been identified from a wide range of information sources, these are included in Annex 1 to this report. Only 17 of these were in Europe (Czech Republic and Germany), although bench-scale nanoremediation research is widespread across the EU. The majority of applications in the field were *in situ* injections of nZVI. Annex 1 also indicates that practical use of nanoremediation is largely confined to the treatment of chlorinated solvents *in situ*, with a few examples of treatment of other contaminants such as chromium VI, pesticides, polychlorinated biphenyls and nitrates. This market niche already has well established techniques e.g. *in situ* bioremediation, *in situ* chemical reduction and permeable reactive barriers. An ITRC report (2011a) gives an overview of the relative advantages of currently available remediation technologies (including briefly nZVI) for the treatment of DNAPL and suggests that a combination of techniques may be most effective in reducing chlorinated solvent contamination.

The reasons for the failure in market development of nZVI are linked to uncertainty over the balance of benefits versus risks from NP use in remediation, in the contexts of sustainable risk management. A number of national risk-benefit studies have taken place in, for instance in Austria, Belgium, Canada, Switzerland, UK and USA (Gouvernement du Québec 2006, Karn *et al.* 2009, OVAM 2006a & b, Bardos *et al.* 2011a, Bundesamt für Umwelt 2010, Grieger *et al.* 2010). Nanoremediation costs are thought to be high compared with other technologies. In a number of countries, the potential risks of the deployment of NPs for *in situ* remediation are considered to be poorly understood, leading to precautionary and conservative regulatory positions. For example, there has been a voluntary moratorium on the release of engineered NPs in the UK in response to the Royal Society/Royal Academy of Engineering report (Anon 2012, RS/RAE 2004) and in Germany

(http://www.ennsatox.eu/the_science/?contentid=275&pr_id=259). In addition, in common with all remediation approaches, the sustainability of NP use will come under increasing scrutiny, as part of an emerging worldwide discussion on achieving "sustainable remediation" being advanced by: COMMON FORUM, Sustainable Remediation Forum-UK, Sustainable Remediation Forum-NL, United States Environment Protection Agency, Sustainable Remediation Forum (USA), and Network for Industrially Contaminated Land in Europe (Bardos *et al.* 2013).

This paper has been produced as part of the FP7 NanoRem project, based in part on earlier work carried out for the Department of the Environment Food and Rural Affairs (Defra) in the UK (Bardos *et al.* 2011a). The purpose of this paper is to review the current state of evidence for the assessment of benefits relative to risks of nZVI use in remediation *in situ*. This assessment is intended to help provide a basis for evidence-based policy, regulation and decision-making and to identify areas of uncertainty that require further investigation. The paper contains the following sections:

- nZVI applications in contaminated land risk management
- Likely benefits compared with the existing state of practice
- Implementation issues
- Deployment risk factors
- Sustainability considerations including risk perception issues
- Risk benefit appraisal
- Management of deployment risks
- Considerations for permitting use of nZVI
- Conclusions and recommendations.

nZVI is deployed as part of a remediation process, i.e. to manage risks from a contamination problem. However, there is scope for confusion in terminology regarding risks, as there is also concern that the NPs themselves have hazardous properties that pose risks in their own right. Therefore this paper uses the term "deployment risks" to refer specifically to risks originating from the NPs themselves, and "contaminant risks" to describe risks related to the contamination the nanoremediation seeks to manage. It should be noted that the need to manage risks from remediation agents is not unusual. Many *in situ* treatments add substances to the subsurface that are potentially hazardous, for example reagents used in *in situ* chemical oxidation, surfactants or solvents.

2. Application of nZVI in Remediation

nZVI is used in two broad contaminant risk management configurations: elimination of source terms and/or pathway (plume) management. A range of deployment techniques may be used, and the nZVI may be modified in different ways to improve its remediation effectiveness (in particular its

ability to be transported through zones of contamination, its resistance to deactivation, and its ability to bring about contaminant degradation). All of these interventions have a bearing on the relative balance of deployment risks and benefits from the nZVI use. O'Carroll *et al.* (2013) detail the chemical processes involved in the treatment of chlorinated solvents and various metals by nZVI.

2.1 Production and Types of nZVI

Wiesner *et al.* (2006) describe two general nZVI synthesis methods that 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 nZVI. Bottom-up techniques tested at least at laboratory scale include: reduction of iron salts in solution (Lien *et al.* 2006, Elliott and Zhang 2001, Wang and Zhang 1997); heating iron pentacarbonyl (Karlsson *et al.* 2005); reacting iron oxides with hydrogen (Li *et al.* 2006b); gas phase reduction of FeOOH; reduction of nano-scale ferrihydrite (Fe2O3) 0.5H2O; and a range of combined physical and chemical processes (Tiehm *et al.* 2009, Li *et al.* 2006b). The top-down approach begins with micrometre to millimetre-sized iron filings, which are ball-milled to fine, nano-sized particles. This method is employed, for example, by Golder Associates[1]. Top-down methods may also include condensation and attrition processes (Li *et al.* 2006b, Wiesner *et al.* 2006).

In practice, nZVI is subject to three processes which reduce its effectiveness in the environment: agglomeration, passivation and sorption, all being related to the high chemical reactivity of nZVI.

- ***Agglomeration*** describes how nZVI particles are attracted to each other and adhere together creating larger assemblages, which in almost all cases reduces their mobility in water and hence their effective surface area.
- ***Passivation*** results from the oxidation of nZVI before it reaches the contaminants it is intended to react with (although activity may remain within the particles).
- ***Immobilisation*** in the aquifer solid matrix (e.g. through the processes of sorption, sedimentation described in LQM (2014))

These processes are described in more detail in Section 5.1.2.

A number of modifications have been developed to improve the effectiveness of nZVI by reducing the scale of agglomeration and the immediacy of passivation. Other modifications include doping with other metals to improve reactivity and suspension in emulsions to better access free-phase non-aqueous phase liquid NAPL (Parbs and Birke 2005, US EPA 2008). Modifications which have been developed include:

- Stabilisation approaches using a range of coatings, including biopolymers such as starch, chitosan and carboxymethyl cellulose (Bezbaruah *et al.* 2009a, Geng *et al.* 2009, He *et al.* 2007, He and Zhao 2005, Phenrat *et al.* 2008, Tiraferri *et al.* 2008, Saleh *et al.* 2008, Tiraferri and Sethi 2009, Xiao and Wazne 2013, Zhu *et al.* 2006); "natural" organic matter such as humic acid (Xie and

[1] http://www.clu-in.org/conf/tio/nano-iron/

Shang 2005; Zhu *et al.* 2008); polyelectrolytes (Saleh *et al.* 2005, Saleh *et al.* 2007, Saleh *et al.* 2008, Schrick *et al.* 2004, Kanel and Choi 2007, Zhao *et al.* 2008, Sirk *et al.* 2009, Wang *et al.* 2010); and amphiphiles including various surfactants (Hydutsky *et al.* 2007, Kanel *et al.* 2007, Zhu *et al.* 2008)

- Bimetallic nanoparticles (BNP) e.g. in Schrick *et al.* (2002), Kim *et al.* (2008), Quinn *et al.* (2009), Hosseini *et al.* (2011) which typically utilize small quantities (i.e. <1% by weight) of other metals (e.g. Nickel, palladium, platinum, etc.) to serve as catalysts to increase reaction rates and the types of compounds that are amenable to reduction by the iron. It has been suggested, however, that bimetallic particles may age more rapidly and consequently experience a faster decrease in reactivity (Yan *et al.* 2010, Shrick *et al.* 2002, Zhu *et al.* 2007, O'Carroll *et al.* 2013).

- Emulsified nZVI (eZVI), where aqueous nZVI is surrounded by an oil-liquid membrane (Quinn *et al.* 2005, O'Hara *et al.* 2006, Berge and Ramsburg 2009)

- Anchored nZVI, i.e. supporting nZVI and BNP on carbon, cellulose acetate, polymeric resin or silica to prevent agglomeration and aid dispersion of the nZVI (Mackenzie *et al.* 2008, Ponder *et al.* 2001, Sunkara *et al.* 2010). Jia and Wang (2013) demonstrate high stability in nZVI supported on montmorillonite. Further, there have been several demonstrations of nZVI supported on bentonite or organobentonite successfully treating a range of contaminants including Cr (VI), atrazine, chlorophenols and methyl orange (Li *et al.* 2013, 2012, Chen *et al.* 2011 Zhang *et al.* 2010, Yan *et al.* 2013, Shi *et al.* 2011). nZVI anchored to ceramic materials is also being developed at laboratory-scale, to support applications in permeable reactive barriers, described in Section 2.2.2 (Cundy *et al.* 2008).

A further overview of nanoparticle modifications can be found in LQM (2014).

Interestingly, nZVI 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 nZVI activity against organic contaminants (Kim *et al.* 2013, Lee *et al.* 2009, Zhang *et al.* 2009).

2.2 Approaches to Nanoparticle Deployment

In many cases, risk management is achieved using a combination of measures, such as contaminant mass removal (source); plume control (pathway); and institutional controls (restricting use of a resource). The purpose of remediation is to manage risks from contamination. This is achieved by breaking the connections between contaminant sources, receptors and the pathways between them as shown in Figure 1 (Vegter *et al.* 2002, Nathanail and Bardos 2004). Nano-particles can potentially be deployed:

- As a source term treatment to reduce contamination sources or
- As a pathway management treatment to prevent contaminant migration along pathways[2].

At field scale, it is the ability to deliver 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 non-aqueous phase liquid (NAPL).

This is a general limitation for *in situ* NAPL source treatment for groundwater problems which typically have a limited effectiveness (US EPA 2005, US EPA 2008). Complete mass removal is rarely possible, and because residual, sparingly soluble NAPL can lead to low concentrations in excess of groundwater threshold values, the residual source is still problematic (Gavaskar *et al.* 2005, Teutsch *et al.* 2001).

There are two broad types of intervention by which nZVI can be employed for the remediation of contaminants *in situ*: by direct injection into the aquifer, or potentially contained *in situ* treatment applications such as the matrix of an engineered permeable reactive barrier. Table 1 describes how these measures are used for different risk management applications. Annex 1 lists known field scale applications of nZVI up to 2013.

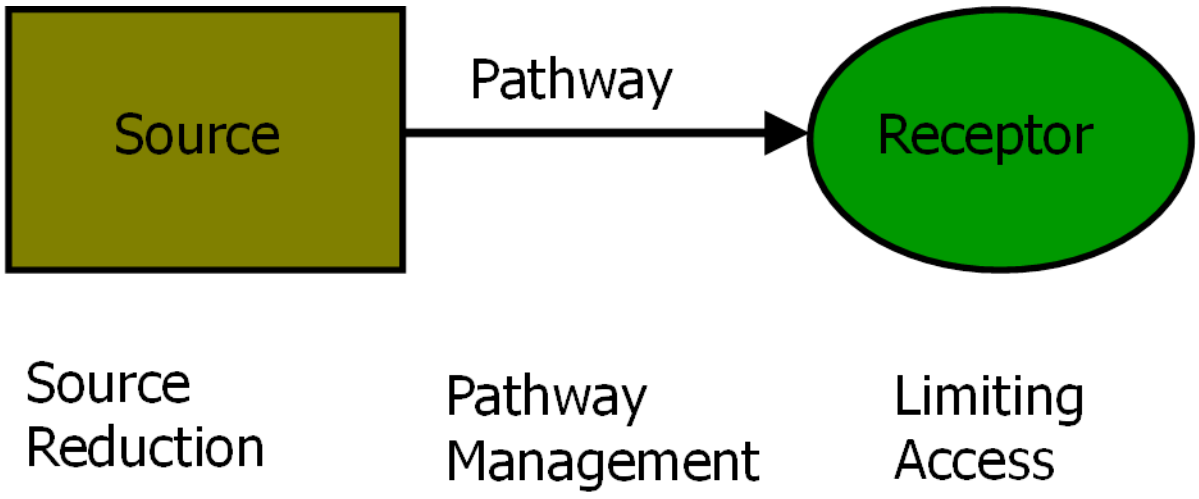

Figure 1: Remediation interventions for risk management

[2] NB In general remediation processes do not play a role in receptor management, which typically proceeds using strategic measures such as institutional controls controlling access of or re-use options for a site

Table 1: Saturated Zone Source and Pathway Management Interventions Potentially Capable of Employing nZVI

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

2.2.1 Direct Injection

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. Direct injection may be under gravity-fed conditions or accomplished under pressure via an engineered fracture in the subsurface created by an overpressure of water (hydrofracture) or air (pneumatic facture). Fracturing is seen as advantageous for the delivery of remediation treatments into low permeability soils (Schuring 2002).

The first demonstration of direct injection of iron NPs in the field was carried out using Fe/Pd BNP at a manufacturing site in Trenton, NJ, USA during the summer of 2000. This initial proof-of-concept field demonstration involved the injection well delivery of approximately 2.5 kg of BNP slurry (approximately 1 g/L by weight) in a test area of the following dimensions: 3 m by 4.5 m over a saturated thickness of 6 m (Elliott and Zhang 2001). This test area was situated within a larger dilute TCE plume in surficial groundwater with concentrations ranging from 445-800 mg/L (Elliott and Zhang 2001). The BNPs used in the 2000 proof-of-concept testing were determined to be generally in the range of 100-200 nm. A larger, 25-kg Fe NP injection, also featuring 100-200 nm iron but at a delivery loading of 5-10 g/L, was conducted in the same test area in 2003. A large-scale injection of 224 kg of polymethacrylic acid (PMA)-stabilized Fe NP slurry (20 g/L) was conducted in 2007 at one of the principal TCE source areas of the site, immediately downgradient of a former 5,000-gallon

aboveground storage tank of TCE (D. W. Elliott 2013 pers. comm). In the large-scale injection, the PMA-stabilized iron was generally in the size range of 50-100 nm, based upon particle size distribution characterization conducted at Lehigh University prior to the study (D. W. Elliott 2013 pers. comm).

The vast majority of known *in situ* applications of nZVI have used direct injection techniques (e.g. see Figure 2). A variety of direct injection approaches exist, but their basic aim is to introduce a slurry of nZVI at a specific depth and in a specific amount directly into soil and/or aquifer materials. These are supplied under either gravity-fed or pressure conditions. nZVI is typically supplied in a liquid slurry, both to ensure a stabilised and active iron NP product, and because the introduction of nZVI particles into the subsurface requires their suspension in some form of a slurry (Henn and Waddill 2006, Müller and Nowack 2010, Comba *et al.* 2011). nZVI 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 to have a known behaviour in groundwater. It may be that the desired behaviour is for the nZVI to disperse through the aquifer carried by groundwater flow, or the opposite, so that the nZVI remains close to the injection points, depending on the desired remediation application.

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

Typically, nZVI injection can be carried out using several methods (Müller and Nowack 2010, US EPA 2005:

- Direct push techniques involve a direct push rig or stationary injection point to introduce nZVI slurry into the treatment zone (D. W. Elliott 2013 pers. comm).

- Pneumatic or hydraulic fracturing uses air or water to create a fracture network of preferential flow paths around the injection point and enhance nZVI distribution.
- Pressure pulse technology uses regular pulses of pressure while injecting the nZVI slurry.
- Liquid atomization injection combines an nZVI-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).
- Injection using foam surfactant carrying nZVI for delivery of nZVI into the vadose zone (developed to lab-scale: Ding *et al.* 2013, Shen *et al.* 2011).

While conventional groundwater transport processes (advection and diffusion) account for migration of nZVI within the transport zone, transport can be enhanced using more active measures. These include the use of well infrastructure to enhance the gradient by introducing recirculation loops or pressurized injections. Recirculation may be used via upgradient injection wells and downgradient extraction wells to improve delivery of the particles. The abstracted groundwater may be mixed with additional particles and re-injected in the injection wells (US EPA 2008).

The choice of method and detailed design of the injection process (e.g. injection point spacing) is site specific. It depends on the amount (concentration and flux) and disposition of contamination within the groundwater; the chemical composition of the aquifer materials and groundwater and how these affect aggregation and sorption / desorption of both contaminants and nZVI; the hydrogeology of the site (including permeability, stratigraphy, groundwater flow etc); the type of nZVI particles 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 removal by biodegradation given the available electron acceptors). The remediation operator should be able to show that there will not be significant impacts on aquifer permeability, pH or redox that affect either the effectiveness of the remediation approach or perhaps the quality of the aquifer in the longer term.

These considerations affect the choice of nZVI 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 nZVI products will be available or offered by the service provider, so the injection approach will be designed around the offered product.

2.2.2 Permeable Reactive Barriers

A permeable reactive barrier or treatment wall treats dissolved phase contaminants in a fixed treatment zone within the groundwater flowpath. The treatment zone can be considered conceptually in three parts: an active agent, a permeable matrix that supports and anchors the agent; and an amenable containment for this matrix. There are many possible PRB configurations (Carey *et al.* 2002, Parbs and Birke 2005). These range from highly engineered approaches like the Funnel and Gate™, where sheet piling or slurry walls direct 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, see Figure 4. In this latter case the aquifer materials form the containment and the matrix.

Cundy *et al.* (2008) describe test work where iron permeable reactive barriers are placed *in situ* using electric fields generated from iron rich electrodes, although this has yet to deliberately exploit nano-scale processes. Comparably, Reddy and Karri (2007) assessed electrokinetic delivery of nZVI for *in situ* remediation of Pentachlorophenol (PCP). The results suggested nZVI was deployed at least partially successfully, although transport was limited by aggregation and settling in the anode. However, the paper notes that NPs may not have contributed to PCP degradation. Chowdhury *et al.* (2012) investigated the ability of an external electric field to enhance mobility of nZVI in porous media. Their results suggested electrokinetic delivery enhanced migration of nZVI through the media studied and that utilization of an oxygen scavenger (Na_2SO_3) decreased oxidation of nZVI. Similarly, Jones *et al.* (2011) found stabilized nZVI transport was improved through electrophoresis compared to diffusion alone. Potentially similar techniques could be used to increase the zone of influence of wells in direct injection scenarios as well.

The use of nZVI in PRBs has been suggested (e.g. Kanel *et al.* 2007). However, nZVI has a relatively short functional lifetime in the environment. Under optimal conditions, the maximum lifetime of nZVI is likely to be 1 to 2 years. Liu and Lowry (2006) determine the reactive lifetime of nZVI to be a function of pH and contaminant loading. This limited reactive lifetime would appear to militate against nZVI being used in PRBs, whereas millimetre to micrometre scale zerovalent iron (ZVI) has been widely used in PRBs. However, Olson and Lee (2006) proposed the use of nano-scale iron (II) sulphide in PRBs. Nonetheless, 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 nZVI (Yan *et al.* 2010).

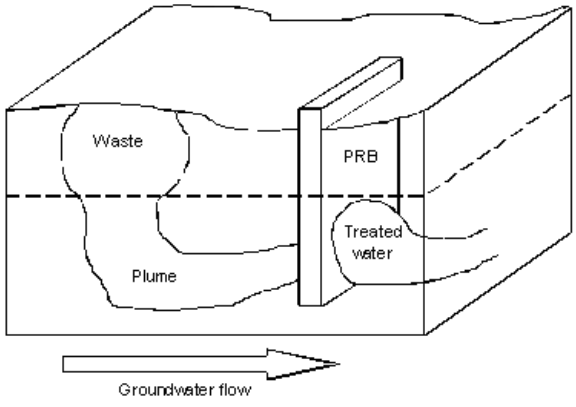

Figure 3: Typical PRB Configuration (from Nathanail *et al.* 2007)

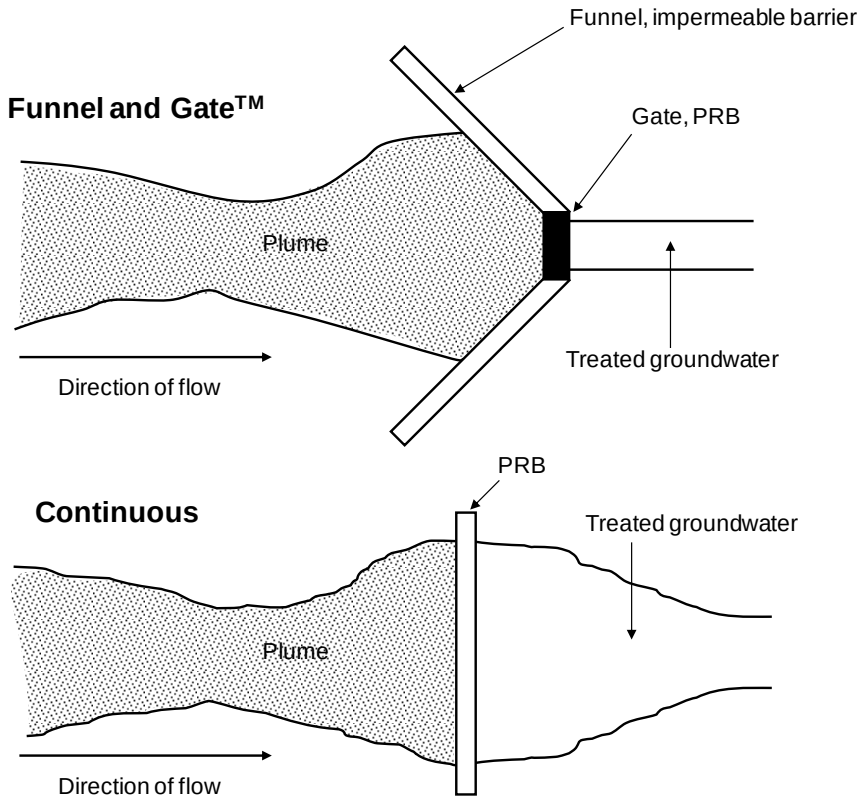

Figure 4: Funnel and Gate™ and Continuous PRB Configurations (from Nathanail *et al.* 2007)

3. Benefits of Using Nanoparticles in Remediation

Over the last 30 years, approximately 80,000 sites have been remediated in European countries [European Commission, 2014[3]]. Early efforts were largely based on containment, "pump and treat" and/or removal to landfill. However, treatment based approaches began to become widely available from the late-1980s [NATO / CCMS, 2002[4]]. Process-based, *in situ* technologies (exploiting biological, chemical, physical solidification / stabilisation and thermal processes) are now a major remediation market segment (Nathanail *et al.* 2013), although they are still only employed on a minority of projects. The use of nanoparticles potentially extends the range of available *in situ* remediation technologies, and may offer particular benefits in some applications. Zero valent iron (essentially finely ground iron) has been used as a treatment reagent in *in situ* remediation for many years, in particular for permeable reactive barriers. Nano-scale zero valent iron (nZVI) is a type of iron nanoparticle that has been investigated for deployment for *in situ* remediation, i.e. within the subsurface, as a groundwater and aquifer treatment.

Some proponents of the use of nZVI 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 (Elliott and Zhang 2001, Müller and Nowack 2010, Rickerby and Morrison 2007, Tratnyek and Johnson 2006). However, like

[3] European Commission – Life and Soil Protection, 2014 - ISBN 978-92-79-34664-4.
[4] NATO / Committee on the Challenges of Modern Society – 2002 overview report NATO/CCMS pilot study. www.cluin.org/download/partner/phase_iii_overview.pdf

many remediation techniques, the transfer of use of nZVI from laboratory scale experiments to practical remediation applications has seen this potential constrained.

The broad potential benefits seen for using nZVI fall into a number of categories: extending the treatable range of contaminants and improving the effectiveness of contaminant destruction; improving the extent and rate of contaminant destruction; providing source term treatment capability; limited longevity of action; and compatibility with other treatments. Each of these categories is described in more detail in the sections following.

3.1 General Benefits of *In Situ* Remediation Approaches

In situ treatments have several advantages over *ex-situ* treatments or removal to landfill. They generally involve less physical disruption to an operational site, process and waste generation emissions.

In the majority of remediation projects the contaminated materials (solid or liquid) are removed to the surface prior to treatment (*ex situ*). This has the advantage that the treatment process can be easily monitored and controlled, samples can be easily collected, and that the overall process can be more easily validated. However, in many cases the excavation of contaminated material may be neither desirable, nor even feasible; e.g. the material may be extremely odorous; the contamination may be at significant depth; or the contamination may be below significant plant infrastructure or building footprints.

In such cases the contamination can be addressed using *in situ* remediation technologies. An *in situ* approach enables remediation to be undertaken with minimal disruption to site operations and with minimal exposure of site workers and others to the contaminants (e.g. in dust, gas or vapours). The "footprint" of an *in situ* remediation project tends to be much smaller than for an *ex situ* scheme, meaning that treatment can usually be carried out where access and available space are restricted. Excavation of soil and pumping of water are reduced or even not needed, resulting in savings in cost and fuel and reducing the volume of waste generated.

3.2 Extending the Range of Treatable Contaminants

As a result of its smaller particle size, nZVI is able to deliver a very high specific surface area for chemical reactions per unit mass of iron added, making it more reactive than its micro-scale equivalents. The nano-scale effects may also extend the range of treatable contaminants leading to the destruction of organic contaminants and the transformation and/or precipitation of inorganic contaminants (Huang *et al.* 2013, Liu *et al.* 2005, Song and Carraway 2005, Zhang 2003).

Several studies have suggested that nZVI[5] may have advantages over conventional ZVI for *in situ* stabilisation (and reduction) for a range of potentially toxic elements (Li *et al.* 2006a and 2006b).

[5] Whilst out of scope of this paper, 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 purposes (Han 2009; Ramos *et al.* 2009; Shipley *et al.* 2010). Further, nano-scale iron phosphate has been tested at laboratory-scale for the immobilisation of copper (II) and lead (Liu and Zhao 2007a and 2007b).

Several laboratory studies have demonstrated the ability nZVI to treat hexavalent chromium (Cr(VI)). For example, Liu *et al.* (2012) demonstrated a greater reduction in Cr (VI) in contaminated groundwater when nZVI-chitosan beads were applied compared to conventionalsized ZVI; Singh *et al.* (2012) showed successful treatment of Cr (VI) contaminated soil in both laboratory and windrow experiments with nZVI treatment; Seo *et al.* (2013) showed successful treatment of Cr (VI) using a combination of metal reducing bacteria and modified nZVI (bio-FeS/siderite). Further, Saeedi *et al.* (2013) demonstrated that nZVI coupled with EDTA and acetic acid showed improved Cr (VI) removal in an nZVI PRB, compared to EDTA and acetic acid alone.

Laboratory studies using nZVI 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 (Cheng *et al.* 2010, Chang *et al.* 2009, 2007, 2005, Zhu and Lim 2007, Lowry and Johnson 2004, Xu and Zhang 2000). Chang and co-authors reported two studies focusing on the nZVI-mediated remediation of soils impacted by PAHs, particularly pyrene, which appeared to demonstrate declining contaminant concentrations over time and as a function of nZVI dose but which did not identify specific degradation mechanisms or pathways (Chang *et al.* 2009, 2007, 2005). nZVI has also been considered as a treatment for radionuclides such as radium and uranium (Burghardt and Kassahun 2005), with several laboratory studies suggesting this to be feasible (Scott *et al.* 2011, Dickinson and Scott 2010). Indeed, Fan *et al.* (2013) demonstrate the ability of sulfidated nZVI to reductively sequester pertechnetate for the remediation of technetium contaminated groundwater.

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). Doping nZVI with metals such as palladium further improves its reactivity and the range of treatable problems by introducing extended catalytic properties (see Section 2.1). (Kim *et al.* 2008, Quinn *et al.* 2009, Cook 2009, Sirk *et al.* 2009, Saleh *et al.* 2007, Elliott and Zhang 2001). Annex 2 gives an overview of the known treatability of contaminant categories by nZVI based on bench scale work. However, this extended range of treatable contaminants is not as well documented in the field. Field scale test-work and practical applications of nZVI have focussed on chlorinated solvent problems (see Annex 1). Overall, there is uncertainty regarding whether or not nZVI specifically will extend the range of treatable contaminants in the field compared to conventional ZVI, although it is projected that at least a comparable treatment capability will be achieved, with some possible advantages for certain contaminants, such as PCBs.

3.3 Extent and Speed of Contaminant Destruction

Owing to its smaller particle size and hence greater surface area per unit volume, nZVI can increase reaction rates and potentially allow greater penetration through the subsurface in comparison to micro-scale or granular ZVI equivalents. The use of nZVI 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). Karn *et al.* (2009) suggest that shortened timescales (e.g. compared with pump and treat) not only reduce

costs but also reduces the time that workers are exposed to a contaminated site during its treatment. The certainty of the claim of increased reaction speed, taking into account field conditions, is questionable owing to the heterogeneous nature of *in situ* conditions. However, in idealised conditions, this statement may be realisable owing to enhanced reaction rates of nZVI.

A further claim made for nZVI use in remediation is that it offers rapid and complete treatment without the generation of toxic intermediate breakdown products, or generates more benign reaction products (Bezbaruah 2009b, Nurmi *et al.* 2005). 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 nZVI is for degrading chlorinated solvents such as perchloroethene (PCE), trichloroethene (TCE), and other chlorinated aliphatic hydrocarbons. Bench scale studies of nZVI use indicate that in the presence of nZVI, PCE is degraded fully to ethane, ethene, or other light non-chlorinated hydrocarbons, without the build-up of toxic intermediates (Taghavy *et al.* 2010, Wang *et al.* 2010, Henn and Waddill 2006, Gavaskar *et al.* 2005) 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 lesser chlorinated daughter products including the dichloroethenes (cis-DCE, trans-DCE) and/or vinyl chloride (VC) (ITRC 2008). However, this claim must be treated with care. For example, *in situ* bioremediation in practice can proceed to closure without stalling at the DCE stage. 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). Overall, there are few reports of intermediate product accumulation during nZVI treatment of chlorinated solvents, although de Boer *et al.* (2010) reported that there may be some, short lived production of toxic intermediates such as VC. Available evidence therefore supports a view that process intermediates may accumulate for both *in situ* biodegradation treatments and nZVI applications in the field, depending on site specific circumstances (and the sufficiency of added nZVI). However, it is also possible that the process intermediates observed during nZVI use in the field may be a consequence of biological processes rather than abiotic processes. Furthermore the theoretical outcome remains one of complete contaminant destruction.

3.4 Providing Source Term Treatment Capability

Generally nZVI is 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[6]. The high reactivity of nZVI has led to suggestions that it could be injected as an *in situ* source management application in saturated zones, capable of destroying NAPL (Geiger *et al.* 2002, Quinn *et al.* 2005). In practice, the ability of nZVI to reduce the amount of contamination as a source is limited by the accessibility and availability of the source contamination to the nZVI being supplied to treat it, and the physical amount of iron that is needed to treat the source term. Al-Shamsi *et al.* (2013) found

[6] Emulsified nanoscale zero valent iron, see Section 2.1

treatment of NAPL using bimetallic Pd-Fe was constrained by a lack of effective injection technique. Likewise, Fagerlund *et al.* (2012) found that nZVI applied directly in the vicinity of a PCE NAPL source did not enhance NAPL dissolution and increase the speed for remediation. Moreover, the reaction rate was controlled by the dissolution rate of the NAPL. Similar results were found by Phenrat *et al.* (2011), who found poor treatment of high saturation pools of DNAPL. There are fundamental constraints to source term removal using *in situ* techniques (see section 2.2).

3.5 Limited Longevity of Action

nZVI has limited persistence in the environment as an active particle (<1-2 years maximum), even when stabilised(see Section 5). This can be a benefit or a drawback of nZVI depending on the context of the remediation site. This is *useful* for some remediation interventions where the treatment agent does not persist or where limited mobility is desired (i.e. source depletion).

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 modifications will be subject to degradation. However, it is an important feature of some technologies, for example, emulsified nZVI where the added lipids also stimulate anaerobic microbial processes (Su *et al.* 2012).

3.6 Compatibility with Other Treatments

Various studies have suggested than nZVI may be suitable for deployment alongside other remediation technologies, with some studies even demonstrating a synergistic effect. For example, Jiamjitrpanich *et al.* (2012) examined the compatibility of nZVI with phytoremediation techniques for the removal of 2,4,6-trinitrotoluene (TNT) from soil, where TNT contaminated soil was treated with hyperaccumulator plants and nZVI applications, as both single and combined treatments. Results suggested TNT removal was highest where soils were treated with a combination of nZVI and hyperaccumulator plants. Similarly, Baiget *et al.* (2013) found nZVI used in combination with a microbial bioremediator, *Shewanella putrefaciens,* produced synergistic effects for the removal of uranium from contaminated effluent.

Interestingly, field and laboratory scale observations indicate that nZVI use is synergistic and stimulatory for *in situ* biodegradation of chlorinated solvents by dehalorespiration. Laboratory studies indicate that application of nZVI does not appear to be inhibitory to (and may even be stimulatory for) biological reductive dechlorination associated with water-derived cathodic H_2 (the universal electron donor for anaerobic microbial processes) production during its anaerobic corrosion (Comba *et al.* 2011, Kirschling *et al.* 2010, Xiu *et al.* 2010), and also where the nZVI has biodegradable coatings. Kuang *et al.* (2013) found corroborating results to this, demonstrating that both nZVI and Ni/Fe composite nanoparticles increased the biodegradation of phenol by *Bacillus fusiformis* at pH 6 and 8; nZVI was also demonstrated to increase biodegradation at pH 3. These laboratory findings are consistent with observations during applications of nZVI in the field, where biological reductive dechlorination continues or is stimulated (e.g. He *et al.* 2010). Indeed, Lacinová *et al.* (2013) showed that in field tests, combined nZVI and biodegradation achieved the greatest reduction in chlorinated solvents in a contaminated aquifer (76% compared 48% for nZVI alone).

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 nZVI.

3.7 General Appraisal of Benefits

Section 3.1 describes the general benefits that may be achieved by *in situ* remediation techniques, which have led to their increasing use over recent years. This section summarises the particular additional benefits from using nZVI.

The small particle size and high reactivity of nZVI may offer remediation benefits (Tratnyek and Johnson 2006, Zhang 2003, Elliott and Zhang 2001). nZVI deployment in the field, in particular for the remediation of chlorinated solvent plumes, has now taken place at a substantial number of sites. Laboratory and theoretical studies indicate that nanoremediation also has promise for offering treatment of a wide range or persistent contaminants such as PAHs, PCPs, PCBs and trace elements such as Cr (VI). nZVI may also offer the potential for faster and more complete remediation treatments. Indeed it appears that the reactivity of nZVI may be proportional to size; Petersen *et al.* (2012) found smaller particles had increased dechlorination rates when investigating the impacts of size on polymer stabilized nZVI treatment of PCBs and TCE.

nZVI appears to be cost effective in several pathway management applications in a number of countries (see Chapter 4.1), and eZVI[7] formulations may offer a novel source management technique for non-aqueous phase liquid (NAPL) contamination problems.

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 often 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.

The potential advantages of using nZVI based on projections from laboratory-scale test-work greatly exceed those that have been demonstrated in the field. This is principally due to the heterogeneous nature of ambient conditions effecting even, adequate dispersion in the subsurface, contact with contaminants and sufficient reactive lifetime, but also due to insufficient field demonstrations which have collected the data necessary to adequately document performance, and with significant open learning legacy. The gap between field potential and field demonstration is exemplified by the field potential of nZVI in treating contaminating anions and cations (such as nitrate, arsenic and chromium) which is yet to be rigorously demonstrated in the field. Nonetheless, there have been several promising lab-scale demonstrations of nZVI treating such contaminants, including various papers on the removal of hexavalent chromium using nZVI (See section 3.1)

[7] Emulsified nanoscale zero valent iron, see Section 2.1

There is some evidence to suggest that nZVI 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.

4. Implementation Issues for Using Nanoparticles in Remediation

4.1 Cost Effectiveness of Treatment

An important factor associated with the potential application of nZVI in an environmental remediation context is the cost relative to field benefits. The cost of the nZVI is obviously a key consideration and, at present, nZVI costs in the USA are typically in the order of $30-40/lb while micro-scale ZVI is around $1-5/lb and millimetre-scale iron is generally in the range of $0.25-0.75/lb (D.W. Elliott 2011 Pers. Comm.) nZVI does tend to be expensive compared to its 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.

Cost effectiveness of nZVI compared with other remedial alternatives appears to be highly dependent on a site's specific circumstances (Cook 2009). Laboratory studies suggest that for a given contaminant, nZVI is more reactive than conventional ZVI, and therefore may be a more effective remediation agent. However, the reactivity of the nZVI only represents part of the overall cost-effectiveness. Based on laboratory investigations, compared with micro/milli-scale ZVI, smaller amounts of the more reactive, more selective (and expensive) nZVI would theoretically be needed but it is difficult to quantify the magnitude in field applications. Similarly, the more reactive nZVI can reasonably be expected to exhibit a faster utilization rate in the field which could mean that multiple injections of nZVI may be required. Other factors affecting cost effectiveness include the longevity of nZVI, bulk groundwater chemistry (passivation) and heterogeneity of receiving media (accessibility). However, assessment of nZVI cost effectiveness is problematic, as there is much uncertainty over the longevity of nZVI.

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 nZVI are best suited for use. However, there is very little information in the peer-reviewed literature with respect to cost analyses for nZVI remediation projects. Due to this paucity of information, and the possibility that nZVI effectiveness may be site-specific, it is difficult to extrapolate field-scale remediation costs from bench-scale testing data. However, anecdotal data suggest that the cost of the nZVI is likely not the driver for the overall remediation cost. Indeed, it should be noted that materials (i.e. nZVI) are typically a relatively small part of the total cost of a remediation project. However, although nZVI may be used in DNAPL source areas or within the plume (the pathway), the cost-effectiveness is likely to be related to contaminant concentrations and the degree of passivation caused by reaction with groundwater. In practice nZVI may be most effectively deployed in locations proximal to the contaminant source where contaminant concentrations are relatively high.

The overall remediation cost depends also on the extent of infrastructure (i.e. wells, pumps, recirculation loops, etc.) needed to deliver the nZVI and the number of rounds of treatment required (D.W. Elliott 2010 Pers. Comm.) Lacinová *et al.* (2013) showed that implementation costs were collectively higher than nZVI material cost. Other significant components in the cost equation include the required analytical testing, consultant / contractor labour and reporting. Consequently, there is a requirement for adequate design tools to improve the cost efficiency of nanoremediation. Costs are harder to estimate for more recalcitrant contaminants like the chlorinated benzenes as effective treatment may require multiple applications of nZVI. All other factors notwithstanding, cost effectiveness (and overall remediation effectiveness) of the nZVI approaches will decline in low permeability formations as well as 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.

One of the biggest attractions to site owners of *in situ* remediation technologies is that they can be applied to operational sites. Where contaminated material is encountered below the footprint of buildings, or under significant plant infrastructure, remediation using tradition *ex situ* technologies, would entail significant disruption to site operations. This could even include partial, or complete, demolition of the complex, (and the associated rebuilding), or extensive re-routing of the infrastructure. Both of these are can be extremely expensive and time-consuming operations requiring extensive forward planning and lead in times. In contrast, the appropriate application of *in situ* technologies (including nano remediation) can allow the remediation to be undertaken with minimal disruption to site operations which can continue whilst the remediation is being undertaken. Even if not below plant or buildings, extensive *ex situ* works can cause significant (and costly) disruption to site operations.

The most critical elements to field successes with nZVI are the development of a robust conceptual site model based on well-characterized site conditions (e.g. contaminant distribution, geochemistry, and hydrogeology) and sufficiently permeable hydrogeological conditions (e.g. hydraulic conductivity of 10^{-5} m/s or higher). It is also important for the field crew to be experienced in nZVI deployment and *in situ* remediation generally.

4.2 Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) is an important consideration for nZVI manufacture and deployment. The handling, environmental stability and contamination issues (e.g. retention in pore spaces) managed for bulk products are of considerably more important for nanoparticles (Baer *et al.* 2007). This stems from the fact that nZVI is intrinsically reactive, with properties that are not static but change over time. There is therefore little latitude for error in quality control during production, storage and handling. Because of this, nZVI manufactured considerably in advance of field use may experience a significant loss of reactivity, depending on the intrinsic stability of the product being deployed and how well it is stored. Other potential concerns could include the presence of toxic metals or other trace constituents in the source material for the nZVI, or residual solvents used during manufacture.

Remediation practitioners should be knowledgeable of the intrinsic properties/characteristics of the nZVI being used in the remediation project and be satisfied that the material batches used in treatability trials and field deployment conform to a specification. In addition, a client or regulator needs to be satisfied that the candidate materials are suitable for use at the proposed site, can be handled and deployed safely by experienced personnel to meet stated remediation objectives. A QA/QC plan will usually be required by the client/regulator to ensure that sufficient steps are in place to manage the treatment process safely and effectively.

The key elements of a QA/QC plan for field deployment fall under the following broad categories:

- Project details: to ensure that the quality objectives are clear
- Project management: to ensure that roles and responsibilities are clear and that competencies are appropriate to the work being carried out
- The products (reagents) to be used: to check that product characteristics meet the design specification)
- The treatment process: to check that products are applied in accordance with the remediation strategy, and that emissions from the process are within compliance limits
- The media being treated: to check that the remediation quality objectives are met.

The QA/QC process starts at the early planning stage, in parallel with development of the conceptual site model, remediation strategy and method statements, and continues to manage the entire collection of information that will be assessed to determine whether remediation quality objectives have been met. Further details that may apply to the deployment of nZVI (including modified varieties) are listed in Table 2.

Table 2: Parameters for consideration in the deployment of nZVI

Project details
Project Summary of Activities Remediation Objectives (lines of evidence to demonstrate risk reduction targets are achieved) Permit Compliance Limits (emissions from the treatment process)
Project Management
Environmental Management System Roles and Responsibilities (incl. Health and Safety) Qualification and Experience Accreditation Key contacts (consultees, regulators) Communication Strategy
The products (reagents) to be used

Material Safety Data Sheet (MSDS) containing information on: Product and Producer Details Composition (incl. coatings, fluids if supplied in a slurry) Hazards First Aid Measures Fire Fighting Measures Accidental Release Measures Handling and Storage Exposure Control/Personal Protection Physical and Chemical Properties Stability and Reactivity Toxicological Information Ecological Information Disposal Considerations Transport Information Regulatory information Other Information Material Batch Number(s) Conformance Test Results e.g.: Particle Size Specific Surface Area Specific Gravity Chemical Composition pH
Treatment process
Plant and Equipment used for Data Collection Maintenance/Calibration Schedules Accurate Measurement System (e.g. for routine measure of injection rate/quantity of reagent, depth of injection, pH, etc.) Environmental Monitoring of Process Emissions (emissions to air, land or water e.g. dust, noise)(Standard Operating Procedures) Sampling Remediation Products (e.g. nZVI, slurry) Laboratory Testing and Analysis Inspection/Audit and Reporting
The media being treated

Project Management (if different from above) Environmental Management System Roles and Responsibilities (incl. Health and Safety) Qualification and Experience Accreditation Key contacts (consultees, regulators) Plant and Equipment used for Data Collection Maintenance/Calibration Schedules Standard Operating Procedures (incorporating health & safety requirements) Groundwater Sampling Procedure Soil Sampling Procedure Dust Monitoring Procedure Noise Monitoring Procedure Storage, Transport and Handling of Samples Laboratory Testing and Analysis Data Analysis, Interpretation and Reporting

4.3 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 benefit of nZVI is 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. However, there is the potential for a trade-off between reactivity and mobility in the subsurface to occur, so the more mobile formulations may be less reactive (see section 5.1.2).

In practice, migration from injection points has proved hard to deliver in some projects and mobility of the nZVI has often been limited to several metres or significantly less from injection points (Uyttebroek *et al.* 2010). Breakthrough of injected materials to the surface can take place as the dispersal around the well is relatively limited (Su *et al.* 2013*)*. Furthermore, many iron NPs are highly reactive; indeed if present as dry solids, they may be spontaneously combustible in air (e.g. if dry nZVI with no surface charge), 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 nZVI before it reaches its target as it will readily sorb to and react with surfaces (Baer *et al.* 2007).

4.4 Hazards from nZVI Handling in Remediation

Once manufactured, the most significant health and safety risks for people working with nZVI 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. Renn and Rocco (2006) state that "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.

Until recently field-scale remediation applications of nZVI used heterogeneous slurries: either nZVI in water or in an aqueous mixture with other materials (e.g. surfactants, alcohols, etc.) – see Annex 1. However, more recently, air stable powder formulations have been developed. For example, Siskova *et al.* (2012) have demonstrated an air-stable nZVI formation coated with an inner shell of amorphous ferric oxide/hydroxide and an outer shell of glutamic acid. Despite the double coating, Siskova and colleagues still found the nZVI to be highly reactive.

Risks from handling are typically countered through pre-existing precautionary regulations which are well understood. As with health and safety regulations for other potential hazardous remedial agents (e.g. chemical oxidants), appropriate guidance for nZVI handling should follow procedures outlined in Material Safety Data Sheets (MSDS)[8] 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. For modified nZVI, MSDS should also contain information related to coatings.

Nanomaterials are covered by the definition of a "substance" in REACH (EU Regulation on the Registration, Evaluation, Authorisation and Restriction of Chemicals), although there is no explicit reference to nanomaterials. The general obligations in REACH, such as registration of substances manufactured at 1 tonne or more and providing information in the supply chain apply as for any other substance. The Commission Communication on the Second Regulatory Review on Nanomaterials[9] (October 2012) as well as the REACH Review[10] (February 2013) concluded that REACH and CLP[11] (Classification, labelling and packaging regulation) offered the best possible framework for the risk management of nanomaterials when they occur as substances or in mixtures. However, within this framework more specific requirements for nanomaterials have proven necessary. Therefore the Commission is considering modifying some of the technical provisions in

[8] Example MSDS for nZVI : http://www.nanoamor.com/i/u/300402/h/MSDS/MSDS_Fe_8001NJ.pdf; http://www.hepure.com/msds/msds-hc15.pdf

[9] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:52012DC0572:EN:NOT

[10] http://ec.europa.eu/environment/chemicals/reach/review_2012_en.htm

[11] http://ec.europa.eu/environment/chemicals/ghs/index_en.htm

the REACH Annexes, and has launched a public consultation[12] to this effect which was open for input from 21 June 2013 until 13 September 2013. The Commission will make an impact assessment of relevant regulatory options, in particular possible amendments of REACH Annexes, to ensure further clarity on how nanomaterials are addressed and safety demonstrated in registration dossiers.

Nanomaterials that fulfill the criteria for classification as hazardous under Regulation 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures must be classified and labelled. This applies to nanomaterials as substances in their own right, or nanomaterials as special forms of a substance. Many of the related provisions, including safety data sheets and classification and labelling apply already, independently of the tonnage in which the substances are manufactured or imported. Substances, including nanomaterials, meeting the classification criteria as hazardous should have been notified to ECHA by 3 January 2011. Any further update to the classification must also be notified. Based on the information received under REACH registrations and CLP notifications, ECHA published a classification and labelling inventory[13].

Examples such as that provided by QuantumSphere, Inc[14] show information on all of the above listed properties, including toxicological data on nZVI. Practitioners should ensure that information provided relates to the particular nZVI being utilised and the carrier matrix 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 nZVI 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 nZVI marketplace. Generally speaking, over the past several years, MSDS supplied with nZVI purchases tended to provide relatively generic data as very little toxicological, emergency response, and clean-up information was available. However, regulatory scrutiny and a recent research focus on the implications of nanotechnology use will likely change this trend.

5. Factors Affecting Potential Deployment Risks from nZVI Release into the Environment

It has been suggested that the complete life cycle of nanoproducts should be taken into consideration when assessing their risks, i.e. production, use, disposal and recycling (Dusinska *et al.* 2012). However, in the context of the deployment of engineered nanomaterials specifically as an environmental technology it makes sense to consider production and application risks separately, as they are separately regulated. Furthermore, when nano-particles are used for *in situ* remediation there is no recycling and the "disposal" of the nZVI is its fate in the subsurface. Hence, this paper considers application and deployment risks (encompassing disposal) in Chapter 5. It also takes a broader view of sustainability impacts across the nZVI lifecycle in Chapter 6.

[12] http://ec.europa.eu/environment/consultations/nanomaterials_2013_en.htm
[13] http://echa.europa.eu/web/guest/regulations/clp/cl-inventory
[14] http://www.qsinano.com/pdf/MSDS_QSI_Nano_Iron_Iron_Oxide_24_May%20_07.pdf

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

- Fate – will the substance survive in the environment?
- Transport – will the substance reach receptors?
- Toxicity – how will the substance harm the receptor?

Fate, transport and toxicity of nZVI will depend on the composition of the particles, including any coatings, the particle size and the target organism.

5.1 Fate of nZVI in the Environment

5.1.1 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. Wigginton *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. nZVI within the aqueous environment is 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 nZVI.

Nevertheless, nZVI represents a new technology, and nZVI may behave differently to its macro-scale counterparts, given its higher reactivity. Therefore a *de novo* examination of the fate and toxicity of nZVI is necessary. While the abundance of iron in the natural environment, both as introduced (reduced) and naturally occurring (usually oxidised) forms of iron NPs carries an implication of low level of risk, this cannot be simply taken for granted. This same abundance also complicates determination of NP fate. 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). This task forms a major research area for the NanoRem project.

5.1.2 Key Characteristics Related to the Fate of nZVI

Laboratory studies indicate that the *long term* fate of nZVI is ultimately to be converted into larger particles of iron (II) and (III) oxides (Reinsch *et al.* 2010, Sohn *et al.* 2006, Johnson *et al.* 2013). Key characteristics determining the fate of nZVI over time relate to its ‘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. nZVI modified for improved mobility usually has somewhat lower reactivity in order to provide this mobility.

nZVI particles, and especially unmodified nZVI, tend to agglomerate and produce potentially stable micrometre-sized particles (Tratnyek and Johnson 2006, Phenrat *et al.* 2007). If this occurs, nZVI 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, unless modified, truly 'nano-scale' iron particles do not persist for long before creating larger particles (Elliott 2010). Studies have shown that nZVI may not achieve widespread distribution in the subsurface, due to this agglomeration prior to complete dispersion within the soil or groundwater matrix, thereby limiting the radius of influence of an injection point. Agglomeration may also reduce the exposed reactive surface area of the particles. The amount of active nZVI may also be reduced through sorption to materials in the aquifer.

A number of natural processes also lead to "passivation" of nZVI. Passivation may occur through:

- The reaction of iron with non-target contaminants, groundwater constituents such as nitrate and dissolved organic matter (Reinsch *et al.* 2010, Liu *et al.* 2007).
- The reaction of iron with the subsurface matrix i.e. groundwater itself (dissolved oxygen in groundwater very rapidly oxidises nZVI to various iron oxides (Reinsch *et al.* 2010).
- Agglomeration of nZVI.

The longevity of nZVI is very highly specific to geological conditions (Xie and Cwiertny 2012). O'Carroll *et al.* (2013) state that all nZVI particles form an outer (hydr)oxide layer in aqueous solutions as a result of reactions with water. Iron carbonates and sulphates may also be formed, depending on the general groundwater redox conditions being either oxic or anoxic The nano-ironhydroxide or iron carbonate particles typically formed by nZVI in the subsurface 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. The precipitation of these mineral phases is likely under the vast majority of natural aquifer conditions with a pH of greater than 7. This passivation effect has also been found to be inhibitory to nZVI treatment of TCE (Liu *et al.* 2007). However, nZVI with an iron hydroxide shell may retain the capacity for contaminant reduction (see Figure 5) as the iron hydroxide layer may still allow electron transfer from the inner metal core, through defects in the shell surface or via the oxide conduction band. Alternately, electron transfer may occur via Fe^{2+} sorbed on the particle's surface and the hydroxide shell may act as a contaminant adsorbent in its own right (O'Carroll 2013).

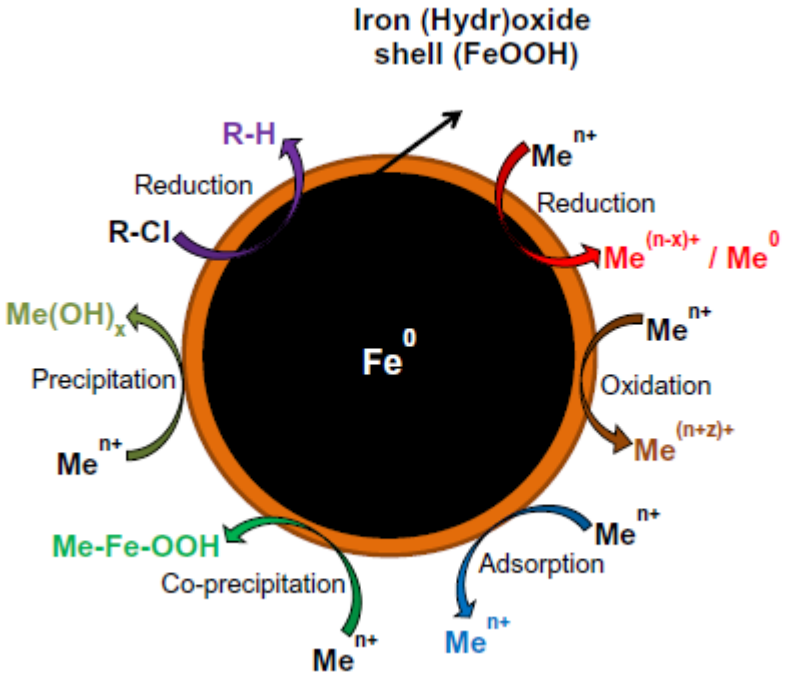

Figure 5: Core–shell structure of nZVI depicting various mechanisms for the removal of metals and chlorinated compounds (O'Carroll *et al.* 2013, adapted from Li *et al.* 2006).

Passivated nZVI 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. However, Liu & Lowry (2006) found that core reactivity can remain for a period of several months or longer.

5.2 Transport of nZVI in the Environment

Until recently, a lack of effective monitoring techniques capable of tracking injected nZVI meant field evidence reporting distance travelled by particles in the environment was poorly represented within literature studies. Early estimates suggested that nZVI could remain reactive in groundwater systems for in the order of 4-8 weeks and can flow with the groundwater for > 20 m (Zhang 2003, Elliott and Zhang 2001). Lowry and his colleagues later superseded this, with work indicating that nZVI could remain active for longer periods, in the order of 1-2 years, potentially increasing the distance attainable by nZVI (Phenrat *et al.* 2009a, Liu & Lowry 2006). In more recent years, however, available information on the transport of nZVI in the subsurface has increased and there have been a substantial number of transport studies at lab-scale, with some attempting field- scale approaches. For example, total Fe has been used multiple times as an indicator of nZVI transport in column experiments (Kim *et al.* 2012a, Raychoudhury *et al.* 2012, 2010, Tosco and Sethi 2010). Phenrat *et al.* (2010) had success using a two dimensional flow cell with a combination of total Fe measurement and using a coloured tracer to assess flow path. Recently, Johnson *et al.* (2013) demonstrated the use of multiple methods at field-scale, using a model aquifer to characterise stabilized nZVI transport, including indirect measurements such as pH and ORP as well as measuring specific

conductance as a conservative tracer. Nonetheless, whilst these studies have demonstrated improved techniques for measuring nZVI transport processes, no studies have been presented definitively determining the mobility of nZVI in the field (O'Carroll *et al.* 2013).

It has been suggested that the geochemical parameters of the receiving media have a significant effect on transport of nZVI. For example, Chrysochoou *et al.* (2012) showed in column experiments that organically coated nZVI had a higher rate of deposition in uncoated silica sand compared to Al hydroxide coated sand. This was attributed to a difference in electrostatic charges between the coated and uncoated sand. However, agglomeration was found to be greater in the coated sand. Overall, nZVI does not appear to achieve widespread distribution in the subsurface due to agglomeration limiting the radius of influence of any treatment well. Even with surface modifications that increase mobility and decrease the zeta potential, Saleh *et al.* (2008) speculate that nZVI is not likely to travel much farther than 100 m from an injection location and much shorter distances when site conditions limit mobility. Whilst extensive further research is required to definitively establish the proportion of nZVI liable to reach different migration distances, existing practical determinations in the field imply that transport of nZVI is largely limited to just a few metres from the injection point, both for unamended nZVI and emulsified nZVI (Su *et al.* 2013, Uyttebroek *et al.*2010 Tratnyek and Johnson 2006). de Boer *et al.* (2010, 2009) reported column experiments in which they observed a 2 m radius of symmetrical injection of nZVI. Keller *et al.* (2012) describe how uncoated nZVI quickly aggregated, substantially reducing transport capabilities. Ca ions particularly increased aggregation and the authors suggest injection of Ca as a barrier to transport. Dong and Lo (2013) also found Ca^{2+} to significantly increase aggregation and sedimentation for starch-modified nZVI, again reducing transportable distance.

However, depending on the composition of groundwater and the hydrologic conditions, certain nano-scale colloids may have the ability to travel unexpectedly large distances in the environment (Novikov *et al.* 2006, Kersting *et al.* 1999,Vilks *et al.* 1997). Naturally occurring nano-scale iron oxide particles with metals (such as copper (Sposito, 1989)) bound to their surface have been found in surface water systems many kilometres downstream from mining sites (Hochella *et al.* 2005). This could have implications for the injection of NPs if colloidal transport is used as an analogue for the transport of NPs in groundwater. Nonetheless, it should be noted that the relevance of this transport process to nZVI use in practical remediation appears to be unknown. Indeed, if transportation of this type were possible for nZVI, it is likely that it would only occur after passivation of the NPs by typical groundwater constituents on nZVI (See Chapter 5.1.2). Large tank experiments at field scale and most applications to date, suggest that long range transport will not likely be a concern. Yin *et al.* (2012) suggest that mobility of nZVI in subsurface applications is likely to be limited as their experiment showed that after mixing with water, nZVI was deposited within minutes, as a result of aggregation. In a study by Laumann *et al.* (2013), polyacrylic acid modified nZVI did not reach travel distances of greater than 1.6m in quartz sand (99.9% removal prior to this). Further, with even a small proportion of carbonate material (10%) travel distances were reduced to 0.8m. Johnson *et al.* (2013) found a smaller radius of influence, with less than 2% of injected nZVI reaching 1m, the maximum distance observed in the experiment. Phenrat *et al.* (2010) found comparable results, with higher Fe^0 content resulting in decreased transport as a result of agglomeration. An overview of distances reached by various nanoparticles can be found in LQM

(2014); overall, the workshop suggested the maximum distance reached by nZVI was likely to be in the region of 3-4m in sand and gravel aquifers.

5.3 Toxicity of nZVI

5.3.1 Toxicity

Many of the concerns regarding nZVI applications in remediation are related to whether or not it is toxic and likely to negatively affect ecosystem and human health. Concerns regarding the toxicity of nZVI can be broadly split into those related to the toxicological effect of the actual iron and those related to the particles' nano-scale size. With regards to iron toxicity, it should be noted that iron is an essential element for growth in nearly all species, with deficiency leading to various conditions including low red blood cell counts. Nevertheless, iron can be toxic in excess, with high exposure potentially leading to liver damage in humans (Valko *et al.* 2005).

In terms of toxicity related to the nanoscale size of nZVI, it is notable that naturally occurring iron nanoparticles are ubiquitous in the environment (Keane 2009). However, several papers have suggested that nanoparticles below 30nm in size may behave differently to naturally occurring forms and may be cytotoxic (Handy *et al.* 2008, Wiesner *et al.* 2006). Indeed, Auffan *et al.* (2009a) state that nanoparticles smaller than 30 nm *"(can) have a size-dependent crystallinity that gives them properties drastically different from the bulk material"*. Auffan and colleages proposed a sub division of NPs into those smaller and those larger than 30 nm. They found that the larger NPs essentially behaved (and therefore should be regulated) as their bulk counterparts. As most nZVI applications are in the 10-100 nm size range (see Section 1) it is arguable that they do not pose toxicity issues over and above conventional ZVI applications. A European Commission report[15] discusses size related toxicity aspects and highlights that information on the response of living systems to nanoparticles of "varying size, shape, surface and bulk composition" is required to categorize the mechanisms of nanoparticle toxicity, alongside information on fate and transport of particles. Pathways within cells are also of relevance. The report also states that there is very limited information on these aspects and toxicokinetic data for nanoparticles is urgently needed.

Nonetheless, nZVI has been found to be toxic to bacterial cells *in vitro* (Li *et al.* 2010, Auffan *et al.* 2006, Macé *et al.* 2006). Indeed, nZVI has been found to have bactericidal effects against *Escherichia coli* exceeding conventional iron *in vitro* toxicity, although bactericidal properties were significantly greater under de-aerated conditions, suggesting toxicity was as a result of lack of oxygen (Lee *et al.* 2008). In terms of toxicity mechanisms of nZVI, Chen *et al.* (2013) found Fe^{2+} and Fe^{3+} to have a stronger inactivation effect on both Gram-negative and Gram-positive bacteria strains than nZVI, indicating that toxicity arising from nZVI may be as a result of ionic Fe present on the particle surface.

Kahru and Dubourguier (2010) classify NPs with LD 50 of between 10 and 100 mg as "harmful" as opposed to "toxic" (LD50 1-10 mg/l) or "very toxic " (LD50 0.1-1 mg/l). Some laboratory based studies have indicated that at higher than prevalent background concentrations, nZVI may be toxic

[15] http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_003b.pdf

to particular soil and groundwater organisms. Barnes *et al.* (2010) report cytotoxicity of 100 mg/l nZVI to bacterial cells in river water microcosm experiments. Although nZVI is injected at concentrations typically around 5-20 g/l, it is arguable that 100mg/l nZVI is not an environmentally relevant concentration, after dilution and reaction, outside the treatment zone, let alone in surface water receptors. Although the concentration of escaped (renegade) nanoparticles have not been measured, they are unlikely to reach the concentrations in surface water or groundwater abstraction boreholes that are reported in a large proportion of the studies that cite the toxicity of nanoparticles. This is a key point to take into consideration when evaluating the toxicity of nZVI to organisms.

Further, other studies have shown no or mixed impacts for nZVI on soil and groundwater microorganisms. For example, Wang *et al.* (2012) found nZVI to show no significant effects on growth of three bacteria including *E.coli.* Saccá *et al.* (2013a) found a lack of bactericidal effect for nZVI in *Klebsiella oxytoca,* however, further investigation using a proteomic approach showed evidence of oxidative stress responses. Comparably, Fajardo *et al.* (2013) using a proteomic approach found overexpression of proteins associated with oxidative stress in *Bacillus cereus*, suggesting a negative impact of nZVI on bacteria but also rapid adaption of soil microbes. Fajardo *et al.* (2012) found no toxicity towards Gram negative *Klebsiella planticola* at concentrations below 10 mg kg^{-1}, although they found Gram positive *Bacillus nealsonii* to be negatively affected by similar concentrations.,

The effect of nZVI on bacterial community structure and function appears to be minimal; it has already been mentioned that aquifer microbial processes related to dehalogenation of solvents can continue and even be enhanced in the presence of nZVI (Comba *et al.* 2011, Kirschling *et al.* 2010, Xiu *et al.* 2010). Additionally, Kirschling *et al.* (2010) found that nZVI additions to microcosms of aquifer material had no deleterious effect on total bacterial abundance. Barnes *et al.* (2010) found that addition of nZVI did not influence bacterial community structure, although they did find short term perturbations, based on microcosm studies of river water microbial community in the presence of nZVI. Cullen *et al.* (2011) examined the effect of nano and micro-scale ZVI on microbially mediated soil processes (including ammonia oxidation potential, dehydrogenase and hydrolase activity) and found no evidence to suggest overall negative effects on the processes studied for either ZVI or nZVI. Conversely, Tilston *et al.* (2012) found nZVI addition to both uncontaminated and Arochlor contaminated soil caused disturbances to the composition of the soil bacterial community and inhibited chloroaromatic biodegradation activity, potentially suggesting nZVI may inhibit certain biodegradation processes, although this is contrary to the previously mentioned studies which suggest biodegradation is not likely to be disrupted by nZVI additions. Fajardo *et al.* (2012) argue that nZVI toxicity is highly species dependent, whilst Pawlett *et al.* (2013) state that nZVI impacts on soil microbial communities is context dependent and toxicity evaluations should consider soil texture and organic matter content.

There is some suggestion of toxicity in non-microbial soil and water organisms. El-Temsah and Joner (2013) found that nZVI applied for degradation of DDT had an initial significant impact on collembola and ostracods with 100% mortality and no production of juveniles after 7 d incubation at application rates of 1g and 10g nZVI kg $soil^{-1}$. After 30 d incubation of soil, however, there was a reduction in toxicity of nZVI to the organisms tested. This was associated with oxidation of the nZVI particles.

Similarly, El-Temsah and Joner (2012a) examined the effects of nZVI on ecotoxicity of nZVI to earthworms. At application rates of >500 mg nZVI kg soil^{-1} significant effects were observed for the parameters of avoidance, mortality and weight. At rates as low as 100 mg kg^{-1}, reproduction was observed to be affected. However, effects reduced in magnitude over time, which was again attributed to oxidation of nZVI. Saccá *et al.* (2013b) found that when comparing nZVI toxicity assessment methods, in vitro assays recorded no significant level of toxicity to the nematode *Caenorhabditis elegans,* whereas a molecular assessment approach suggested nZVI created significant changes in the expression of biomarkers in soil microorganisms. Overall, Saccá and colleagues conclude that it is not possible to thoroughly evaluate the toxicity of nZVI in soil based on currently available evidence.

For non-soil organisms, Chen *et al.* (2013) found carboxymethyl cellulose stabilised nZVI to be toxic to early stage development of the fish *Oryzias latipes*, with 50% fatality to embryos at concentrations of 200 mg/l. They also found significantly increased incidences of developmental defects, including delayed hatching and abnormal eye and circulation development at concentrations of 100-200ppm.

El-Temsah and Joner (2012b) used seed germination to test the bioavailable nZVI toxicity in aqueous solution and in two different soil types. Although inhibitory effects of the nZVI were observed above 250mg L^{-1} the study concluded that nZVI at low concentrations can be used "without detrimental effects on plants and thus be suitable for combined remediation where plants are involved". This reiterates the previously mentioned idea that nZVI is likely to be compatible with other remediation treatments. Similarly, Ma *et al.* (2013) found nZVI to be toxic to *Typha latifolia* and a *Populous* hybrid at concentrations of > 200 mg nZVI L^{-1}, but observed enhanced growth in the *Typha* plants at lower concentrations (25 and 50 mg nZVI L^{-1}).

An important consideration for toxicity in the environment is the rapid transformation of the nZVI to Fe-oxide, usually magnetite if oxidation occurs in water with limited oxygen (Reinsch *et al.*2010). Most sensitive receptor organisms will not be exposed to nZVI which is highly redox active. Rather, they will be exposed to the oxidized form of the material, namely magnetite. This is because receptors will generally be far downgradient from the injection site, and sufficient time will have passed before exposure to allow the nZVI to become oxidized. Phenrat *et al.* (2009b) demonstrated that the oxidized form of one type of nZVI was far less toxic than the fresh nZVI with Fe^0 in its core. Additionally, Auffan *et al.* 2009b showed that the toxicity of the Fe series decreased as the materials became more oxidized. Other aging mechanisms can also possibly affect reactivity, but the oxidation of the nZVI will likely have the most significant effect on toxicity.

Not surprisingly, passivation appears to reduce toxicity of nZVI; reacted or passivated nZVI appears relatively benign. Auffan *et al.* (2008, 2009b) found that chemically stable metallic NPs have no significant toxicity to *E. coli*. Phenrat *et al.* (2009a) found that partial or complete oxidation of nZVI reduced its toxicity to mammalian cell lines. Li *et al.* (2010) found that nZVI bactericidal properties against *E. coli* were mitigated if the nZVI was oxidised or sorbed to polymers or natural organic matter. In theory microbiologically mediated redox rections could also lead to passivation of nZVI (Wiesner *et al.* 2006). Auffan *et al.* (2009b) 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".

In terms of human exposure to nZVI, exposure and uptake of some forms of NP do occur, however the severity and undesirability of the consequences of such uptake are poorly understood (Moore 2006). The uncertainty of the dose-response relationship between human health and nZVI has been acknowledged (IAHS 2002) and no subsequent evidence has suggested that anything other than a precautionary approach to any studies would be sensible.

Boxall *et al.* (2007) summarise nZVI toxicity risks with a 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. Moore (2006) grouped iron with other widely recognised contaminants: *"toxic metals such as iron, copper, mercury, lead, silver, chromium and nickel"* without acknowledging that iron is an essential component of red blood cells and that it is inherently much less hazardous than the other substances listed.

In vitro tests have identified that nZVI and iron oxide NPs can be toxic to a number of human and other animal cell lines, likely via the production of reactive oxygen species (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 nZVI is unclear. For example, dose-response relationships may be uncertain (Limbach *et al.* 2007). Wiesner *et al.* (2006) present a transmission electron micrograph of a microglia cell in which black areas are interpreted as assimilated nZVI. Although they do not list any iron containing substances among the studied cytotoxic nanomaterials, they do suggest they may put cells under oxidative stress.

Conversely, absence of nZVI cellular toxicity is reported for some *in vitro* studies (Hildebrand *et al.* 2010). On the basis of limited testing across DNA from two species, Oberdörster *et al.* (2006) reported no significant toxicity issues for nZVI. Iron oxide NPs also have *in vivo* medical applications and food sector applications although there may be uncertainties about the safety of their use in these applications (Lewinski *et al.* 2008, Chaudry and Castle 2011).

5.3.2 Persistence, Bioaccumulation and Biomagnification

It has been suggested that NPs could associate with suspended solids or sediment, where they could be taken up by small organisms, bioaccumulate, enter the food chain and biomagnify. . These fate processes depend on both the characteristics of the particle and the characteristics of the environmental system (Boxall *et al.* 2007). Few data have been published on the persistence and accumulation of nZVI in organisms or biomagnification in food chains. It has been suggested that nanoscale oxide end products from nZVI use may persist in biological systems as a result of its low solubility, and that little is known of the chronic effects of this, such as mutagenicity (Auffan *et al.* 2006).

Karn *et al.* (2009) suggest that 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 US EPA has raised the possibility of biomagnification of nanoparticles; however, few data currently exist proving or disproving this hypothesis (Biswas and Wu 2005, US EPA 2007).

Coutris *et al.* (2012) demonstrated that Ag NPs did not bioaccumulate in the earthworm *Eisenia fetida,* therefore making bioaccumulation improbable for particular NPs. However, Coutris *et al.* (2012) also found that Co NPs did bioaccumulate in *E. fetida*, although at a lower rate than ionic Co. Bioaccumulation of Co is likely to have occurred as it is a constituent of blood. As Fe is also a constituent of blood, bioaccumulation of nZVI is possible. Indeed, Chen *et al.* (2013) found evidence to suggest bioaccumulation of nZVI in embryonic medaka fish, with oxidized nZVI bioaccumulating at a higher rate than the unoxidized counterpart.

It has been suggested that overall bioaccumulation and biomagnification of nanoparticles are unlikely to occur due to rapid passivation limiting the bulk of added nZVI to the injection zone, with few nZVI particles being transported to areas where exposure of external organisms to nZVI could take place. It is therefore probable that exposure is likely to be restricted to microorganisms in the treatment zone (Keane 2009).

5.3.3 Impact from Other Nanoparticle Constituents

Other constituents such as doped metals like palladium, or the use of coatings may be incorporated in iron NP products to enhance their remediation performance as discussed in Section 2. Two broad impacts on nZVI toxicity may occur as a result of this:

- nZVI coatings can also affect toxicity, with some studies showing mitigation of effects (Auffan *et al.* 2009b, Keller *et al.* 2012) and others exhibiting enhancement (Wiesner *et al.* 2006), although, in general, the dataset is rather sparse.
- nZVI components (for example doping metals) and coatings (see Chapter 2) may be toxic in their own right. However, coatings including NOM can also decrease toxicity (Phenrat *et al.* 2009b, Li *et al.* 2010).

Toxicity considerations for nZVI preparations should also include the toxicity of any non-iron trace metal catalysts used in some types of nanoparticle. 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.

Any assessment of the risks of these doped metals needs to be proportionate, as the percentage of these catalysts is small, e.g. typically less than 1%, hence only a very small mass is introduced into the subsurface. Where risk based limit values for these metals exist, with BNP concentrations used for injection in the region of several kg/m^3, and noble metal contents 0.1% of this, exceedance is unlikely to occur.

Coatings may also be added to nZVI to improve its 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 US with various polymeric and surfactant architectures to lessen agglomeration and enhance stability.

5.3.4 Indirect Impacts

A range of indirect impacts may arise from NP release into the environment, such as:

- toxicity associated with induced pH or redox conditions
- the formation of toxic intermediates during treatment of chlorinated solvents
- reduced hydraulic conductivity in the treatment zone.

These indirect impacts may also arise from other *in situ* remediation technologies, such as biostimulation or redox manipulation, and their significance in terms of remedial performance should be addressed during remediation design.

5.3.5 Human Exposure to nZVI

Exposure to nZVI may take place through dermal contact, ingestion or inhalation. Occupational exposure is the most likely route of exposure for humans to nZVI; conceptual exposure scenarios for human exposure can be found in Section 8.4 and in LQM (2014). Gatti and Rivasi (2002) 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"*. However, they 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. Once particulate iron is ingested and migrates to the low pH stomach environment, it will end up in an ionic form. Ionic iron, at low levels, can then be metabolised as an essential nutrient. Singh *et al.* (2012) found iron oxide at <30nm was capable of entering the organs of rats and that nano-iron oxide accumulated in rat tissues at a higher rate compared to bulk iron oxide. However, they found no evidence of genotoxicity at rates of up to <2000mg/kg and iron oxide was well tolerated by rats.

Inhalation is a potentially more significant exposure route for nano rather than larger sized particles, with potentially increasing pulmonary toxicity as particle size decreases (Karn *et al.* 2009). Inhalation is not a relevant exposure route for nZVI delivered to site in the form of a slurry. It is more relevant when nZVI is 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. However, it should be noted that application of nZVI is messy and residual particles may be coating equipment after its use.

Once dry, these fine powders could be a source of exposure. These particles are largely Fe-oxide aggregates at this point due to oxidation in air and are no longer likely to pose a significant threat as a redox-active material.

The potential for exposure at the various stages of using nZVI for remediation is summarised in Table 3, and is potentially significant in the absence of suitable protection measures. No information on anticipated exposure levels has been found in the literature. At the very least a basic dose-response relationship for nZVI (and the resulting Fe-oxide aggregates) for an occupational exposure level is required.

Table 3: 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	Moderate	Low
Spill	Low	High	High
Decommissioning	Low	Moderate	Low

6 Sustainability Considerations Including Risk Perception Issues

6.1 Sustainable Remediation

Section 3.1 describes the general benefits that may be achieved by *in situ* remediation techniques, which have led to their increasing use over recent years. This section summarises the particular additional sustainability considerations from using nZVI.

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.* 2013, Bardos *et al.* 2011b). Sustainability encompasses a range of considerations and the balance of benefits and negative 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.

Other assets for nZVI use may be a lowered impact on soil functionality compared with many more aggressive competing technologies, such as *in situ* heating, *in situ* chemical oxidation (see below) or use of surfactants. Indeed, Kirschling (2010) demonstrated that nZVI had no deleterious effect on total bacterial abundance and further, H2 created by nZVI stimulated sulphate reducer and methanogen populations. Conversely, large scale deployments may impact aquifer permeability as

iron corrosion products are insoluble and may form precipitates depending on aquifer conditions. Adeleye *et al.* (2013) suggest that the bulk of injected nZVI will end up in the sediment phase of an aquifer, potentially demonstrating an effect on aquifer permeability.

Potential sustainability concerns regarding nZVI might relate to the use of resources and energy for nZVI manufacture, particularly use of rare metals for doping as well as general societal reluctance to adopt new technologies. 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. The balance of benefit over negative impact for nanoremediation will be highly dependent on the context of the project, with no known assessment of nZVI applications for remediation in practice made to date (WP8 of the NanoRem project shall propose sustainable appraisal of implementation of nanoremediation).

Whilst there is a reasonably strong knowledge base on sustainability in general remediation, comparatively little is known about the relative sustainability of nZVI use in remediation. However, determining the probable sustainability of nanoparticle use for this purpose is a key goal of NanoRem. For a remediation project to be sustainable, it must be considered acceptable and beneficial from an environmental, social and economic point of view. It is likely that the social aspect will encompass the most challenging element of developing a sustainable approach to nanoremediation, largely as a result of risk perceptions associated with the technology.

6.2 Risk Perception Issues

Perceived risks describe the subjective impression of risks that might be held by particular individuals or groups of individuals. These can have a major bearing on environmental technology and contaminated land management decision making (Luria *et al.* 2009, Ferguson *et al.* 1998, Slovic 1987). An important potential barrier to the use of nanoparticles in remediation is the perception of this being a “risky” technology. Gaps in knowledge and a perception of relatively high treatment costs have led to rather limited practical use of nanoremediation. For example the UK has a voluntary moratorium on the release of engineered NPs to the environment, following on from recommendations in a 2004 report by the Royal Society/ Royal Academy of Engineering (RS/RAE). 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.

Although there has been no *de facto* prohibition of nanoremediation in the UK, this has acted as a barrier to the implementation of field trials.

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 of nanotechnology are to be fully realised. The perceived risks from nZVI of many academic commentators and NGOs appear to revolve around a lack of research (e.g. Boxall *et al.* 2007, Nowack and Bucheli 2007, Wiesner *et al.* 2006). Laboratory based studies have started to improve this knowledge base but there is still a lack of field based data. 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 the perceived risks are higher than the real risks. There are several recommendations for additional research to confirm the suspected low toxicity of nZVI to humans. Some, such as the Royal Society, take a conservative precautionary approach. Others may delay adopting nZVI due to the potential risks, despite evidence that toxicity is likely to be low for both human and environmental. 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 its adoption.

Karn *et al.* (2009) support 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".* 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 nZVI or bimetallic particles had yet been published. Private sector corporations can also adopt a cautious policy, 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 2013 Pers. Comm.)

The Royal Commission on Environmental Pollution (2008) cited in Karn *et al.* (2009) stated that the risks from 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).

A limited public consultation exercise using a focus group in the east of London (UK) identified three broad themes (Environment Agency 2006):

- Scientific uncertainties about the fate and transport of NPs once released into the natural environment and the limited availability of technical information, leading to a call for a precautionary approach;
- A call for greater openness about knowns and unknowns, and even some scepticism about true motivation behind dialogue exercises;
- The context for discussions of science, technology and risk; with questions raised about the constituencies supporting in and engaging in this debate and what their motivations might be.

More recently a synthesis of reports on public views on nanomaterials in general from the UK (Sciencewise 2013) cautioned that while there is great optimism, and that in general public opinion was supportive, there are major underlying public concerns about:

- Risk, safety and regulation linked to the level of uncertainty about toxicology, health and environmental impacts of nanomaterials.
- Applications, equity, empowerment as the public consider trade-offs between potential benefits and risks of applications: applications that were perceived to contribute to a wider social good such as healthcare or environment were considerably more supported than cosmetics or other products with less clear social benefit.
- Public engagement and transparency - more transparency about developments and more available information about products with nanomaterials are desired.

These concerns were broadly substantiated by NanoRem in a Workshop held in July 2013 (LQM 2014). The current view at a European level remains cautious about nanotechnologies. Great promise is foreseen but there is concern that there are no clear guidelines for how health, safety and environment, nor material sustainability, concerns should be integrated into product design. (EEA 2013, EEA and JRC 2013). While this gap is evident at the policy and regulatory level society's ability to foster appropriate use of nanotechnologies is hampered. It is largely in response to this that the NanoRem project is making a concerted effort to develop broad sustainability, risk and benefit appraisals for its nanoremediation applications, in consultation with leading stakeholder interests.

7 Risk Benefit Appraisal

nZVI can pose health and safety risks if improperly handled. There is evidence that it can be hazardous to human health and other organisms. The exact scale of direct and secondary risks has, as yet, not established. However, the implication is that unreacted nZVI is 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 nZVI appears to be relatively harmless in the environment, or at least of a substantially diminished potency, and may be further attenuated by agglomeration into larger particles or immobilisation within the aquifer matrix.

Any negative impact on aquifer microbiology would likely be both in the treatment zone and in a halo surrounding it, related to the ability of nZVI to migrate further. This "halo" may be relatively slight given the penetration of unamended nZVI in aquifer materials. The penetration of amended particles is less well understood.

An approximate position, not contradicted by current evidence, is as follows. Risks from nZVI, including many modified forms, are manageable, since its persistence in a reactive form in the environment appears to be relatively short (< 1-2 years), and its ability to travel from injection points is limited (from <1m to an unproven 100 m for some modified types).

While this seems a relatively positive risk output for the environmental use of nZVI, supporting evidence outside of laboratory studies is scant. For all nZVI types there seems to be insufficient field scale observational data to categorically substantiate a view of limited nZVI transport and persistence that would be seen as satisfactory by all regulatory authorities.

Dread[16] describes a situation of significant uneasiness about a technology, for example, nuclear or genetic modification technologies. This is not necessarily related to specific concerns. Technologies that evoke dread can acquire a stigma, which is often perpetuated by the media and those who oppose the technology (Marchant *et al.* 2008; Gilligan, 2006). This has been a particular impediment to the adoption of nZVI compared with other technologies as it appears to lead to a heightened perception of risk of nanotechnology's use amongst the public and other stakeholder groups, including landowners. More specific regulatory concerns exist about nZVI use in remediation, including its potential human health implications and its possible ecotoxicological effects. As the potential risks of NP deployment for *in situ* remediation are considered to be poorly understood, precautionary and conservative regulatory positions have been taken in a number of countries.

Table 4 sets out suggested research needs to substantiate a better risk benefit assessment for nZVI use.

Table 4: Research Needs (based on Otto 2010) - Areas of focus for NanoRem are underlined

Technology Implementation
• Improving the nanomaterials (stability, mobility, selectivity, reactivity, reducing toxicity by design). Specifically more information on product lifecycle analyses, manufacturing methods (& properties characterization) and storage periods (& their effects) • Optimising field applications, including development of more reliable and robust means of subsurface delivery • Introduction of more robust quality assurance and quality control guidelines for nZVI manufacturers remediation service providers leading to the production of robust MSDS
Toxicology
• Potential health and environmental effects of the spectrum of nZVI products (includes bare iron, bimetals, and surface-modified irons) • Potential effects on soil microbial populations
Fate, Transport, Transformation

[16] To dread is to anticipate with great apprehension or fear.

• Detecting nanoparticles in environmental media • Determining concentration of nanoparticles • Assessing the timeframe over which nZVI remains 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. • Measuring distance travelled in and determining proportion of nZVI particles reaching various distances in groundwater • Monitoring transformation and controls on reaction products • Determining transport distances for colloids • Determining the mobility of nZVI in real-world applications
Sustainability Assessment

Process based remediation techniques seen as "new" within a particular jurisdiction 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 and landowners 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 nZVI 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 nZVI based *in situ* remediation techniques, compared with other *in situ* remediation techniques.

What should not be overlooked is that other remediation techniques carry risks. The simplest remediation technique is excavation and removal, and this carries risks to workers (and the wider public) 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). *In situ* chemical oxidation using a Fenton's reagent was responsible for the only known fatality 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 which are potentially harmful to the biological functioning of soil, and can be transported over significant distances in groundwater plumes. Extractive technologies are also applied for NAPL treatment, for example flushing with surfactants and heating. Surfactants can damage soil structure (Nathanail *et al.* 2007). Thermal treatment may have considerable negative impacts on soil functionality. These remedial options are routinely permitted in a number of countries without the cautious positions taken in some countries to regulating the use of nZVI. It would therefore seem disproportionate to exclude nanoremediation for consideration during options appraisal where the technology is screened as being feasible having regard to site and contaminant characteristics.

As nZVI attempts to establish itself in the marketplace as a remediation option for chlorinated solvent mitigation (its current likely significant market niche), the major competing technology 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 nZVI 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. The negative impact on soil function both in the treatment zone and downgradient are not usually considered when permitting the use of established *in situ* remediation technologies.

Table 5 sets out a schematic timeframe for potential benefits from nZVI deployment, based on the broad benefits summarised in Chapter 3 and likely developments in the current direction of travel in field scale applications. The technology has significant benefits in the medium term for extending the range of treatable contamination problems in the saturated zone, and further capacity to deliver new treatment opportunities in the longer term. The realisation of these benefits is dependent on an improved understanding of the risks of nZVI deployment in the subsurface and possibly also on developing more reliable and robust means of subsurface delivery (as discussed above).

Table 5: Potential Benefits from nZVI deployment

	Realisable Now	**Medium term (circa up to 5 years) *the NanoRem ambition***	**Longer term (circa >5 years)**
Benefits	Reliable technology option for source and pathway management of NAPLs, claimed to be without release of process intermediates	Saturated zone treatment for persistent organic pollutants (POP).	Vadose zone treatment for difficult / untreatable problems such as highly recalcitrant contaminant classes (e.g. PCBs, dioxins, etc.)
Scale of benefits	Minor, there are a range of established *in situ* treatments for NAPLs, each with their relative advantages and disadvantages, Choices are often highly dependent on site specific factors. Potential wider benefits from lower negative soil impacts and fewer process intermediates.	Significant enhancement of POP reduction practices.	Potentially huge, given the large areas contaminated by recalcitrant organic compounds in Europe and further afield (e.g. Vijgen 2006)
Level of certainty	Relatively certain, based on the degree of market penetration for nZVI use in NAPL, problems worldwide,	Uncertain, as in the absence of a "critical mass" of well-studied field case studies, many stakeholders	Certainty is a function of the outcomes of the major field studies and cost-effectiveness assessments conducted

	wider benefits need to be substantiated	may be reluctant to use an approach with a limited track record and incomplete cost-benefit assessment	over the next 5 years. The nZVI technology is at a crossroads. If large, well-executed field studies demonstrate effective contaminant transformation while maintaining control of treatment area, nZVI could become a remediation staple. As it is now, it is a niche technology used primarily to support other remedial technologies
Potential development	The use of nZVI in remediation continues to be the subject of active research by multiple academic research groups in North America, Europe, and Asia-Pacific region. The development potential is strong but currently limited because of various factors cited elsewhere in this report e.g. regulatory concerns, implications-related issues (uncertain fate and transport, discharge to surface waters), and a lack of a driver from responsible parties/consultants due to cost concerns, regulatory hurdles, and uncertain cost-benefit.	Research on nZVI use in remediation is likely to continue. The outcomes of NanoRem may help reduce some of the barriers to the use of nZVI technology in remediation.	The long term development potential for nZVI is high due to steady advances in materials development, fate and transport understanding, and better experience in utilizing technology tandems with such approaches as anaerobic bioaugmentation or biostimulation. Highest development potential will be fulfilled if nZVI demonstrates cost effectiveness, comparable efficacy in field trials to laboratory results and if implications-related issues are lower than anticipated.

8 Managing Deployment Risks

A sound understanding of the fate and transport of nZVI is needed to ensure remediation objectives are achieved while negative impacts are avoided (US EPA 2009). These considerations will be site specific. The use of a conceptual site model and the source – pathway – receptor paradigm provide a framework for determining likely deployment risks and how they might be managed. For the purposes of clarity this discussion refers to risks from the use of introduced nZVI as "deployment risks" to distinguish these risks from the risks from contamination being managed as a remediation process.

Evaluation of risk will usually be made at an agreed compliance point downgradient of the treatment zone, set to ensure protection of an identified receptor. Compliance will usually be assessed against a relevant water quality standard (such as a drinking water standard). However, there are currently no water quality standards for nZVI, nor established methods to reliably measure at a compliance point. It can be surmised that assessment of deployment risks represents a key challenge in gaining stakeholder acceptance of remediation using nZVI particles.

8.1 Considering Introduced nZVI as a Contaminant Source Term

To consider nZVI as a contaminant source term we must have an understanding of:

- The type of nZVI, mass/rate and mode of deployment
- Interaction of nZVI with aquifer materials in the treatment zone
- Interaction of nZVI with groundwater in the treatment zone
- Interaction of nZVI with target contaminants in the treatment zone

The type of the nZVI being deployed may impact on the speed of reaction, the proportion of unreacted particles that can potentially leave the treatment zone, and the release of other substances, for example metal ions from BNP or surfactant coatings.

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 treat the target contaminant/s to compensate for the interactions between the nZVI and the subsurface environment (aquifer materials and groundwater), particularly as water is a reductate for nZVI. The scale of this excess, and consequences if it is over-estimated, will be another important consideration in assessing deployment risks. A cost-effective deployment will be one where a high proportion of the nZVI can interact with target contaminants; i.e. in proximal rather than distal plume locations.

nZVI may be introduced into the subsurface in several ways:

- nZVI may be injected directly into the aquifer matrix in a range of ways from passive gravity fed systems, active pumping to introduction into engineered fracture zones;

- nZVI may be introduced in some form of contained way, for example within an engineered treatment zone, such as gate in a Funnel and Gate™ or sorbed onto some form of a matrix.

Potential reactivities and selectivities are different for different types of nZVI and also dependent on their surface modifications (Huang *et al.* 2008, Prakash *et al.* 2005). However, properties can be different even between manufacturing batches of the same nZVI type, and NP storage and handling can also affect particle reactivity. The reactivity realised in the subsurface is 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 (Liu *et al.* 2007, Miehr 2004, US EPA 2008).

A source may not need to be considered if all nZVI is consumed in the treatment zone. However, as this may be difficult to confirm, it will usually be assumed that some proportion of the particles may escape, either in pristine or reacted form.

8.2 Considering Pathways for Introduced nZVI

Currently practical nZVI applications are limited to remediation in the saturated zone. Hence *assuming* that nZVI has been properly handled and administered then pathways to human receptors via direct contact or via air borne dusts will not exist. Hence the pathway of concern will be via movement of water in the subsurface, away from the zone of nZVI introduction.

Physical characteristics of the receiving aquifer largely determine transport in the saturated zone. Important characteristics include:

- Hydraulic gradient and conductivity (permeability), as these determine the quantity of water travelling through the aquifer.
- Degree of sorting of porous media (Kim *et al.* 2012a). This strongly dictates the (non-retarding) residence time of particles being transmitted.
- Groundwater average linear velocity.
- Effective porosity of aquifer (the porosity available which is interconnected and can usefully transmit water flow).

Groundwater average linear velocity and effective porosity help estimate pathway length and amounts of dispersion and diffusion (i.e. the spread of particles). It should be noted that pathways will not be linear.

Another consideration is that nZVI will be transported as a particle rather than as a solute. Conventional solute transport models are therefore not valid to use, and risks based on nZVI migration from the treatment zone will be based on colloidal transport theory. Nanoparticles may be

transported further than expected due to facilitated transport or express a tendency to agglomerate, attach to aquifer surfaces or be removed by filtration, effectively reducing transport distance.

nZVI application may affect aquifer porosity, at least in a localised way, depending on mode of deployment. As a result of this altered porosity, the likelihood of nZVI migration to surface water receptors may also be affected. The deployment approach may deliberately extend more porous regions via introduced surfaces using hydrofracture. As water is the delivery vehicle, the nZVI will travel where the water goes, which means distribution into the more conductive regions of the porous media (Phenrat *et al.* 2011).

However, there may be negative impacts in the vicinity of injection wells in general. In practice, the migration of introduced nZVI has tended to be less than expected, or even desired (See Sections 3.3, 5.2). Clogging may result from the conversion of nZVI into mineral precipitates from iron corrosion products, as is also the case with conventional ZVI, (e.g. Phillips *et al.* 2003). Evidence of problems in field scale deployment is limited (Saleh *et al.* 2007), but perhaps can be informed by the literature on long-term performance of ZVI PRBs (e.g. Henderson and Demond 2007, Phillips *et al.* 2010, US EPA 2003). One conclusion drawn from PRB experience is that technology 'failure' is usually attributed to poor site characterisation and/or hydraulic design. The need for robust site characterisation has also been recognised by O'Carroll *et al.* (2013) and at the 1st NanoRem workshop (LQM 2014).

There is much debate, although few observational data, over whether or not nZVI 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 (US EPA 2009). Geochemical characteristics in the aquifer affect the transport and fate of nZVI along the pathway, including:

- Ionic strength which determines the potential for agglomeration (Keane 2009, Saleh *et al.* 2008 ES&T) and particularly Ca molar concentration, which often determines particle charge stabilisation
- Redox conditions which as well as affecting the performance of the nZVI determine the rate of passivation
- pH (effect on solubility, zeta potential, mineral surface charge)
- 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 nZVI) (Laumann *et al.* 2013)

Distance to the receptor clearly makes a significant difference to the likelihood of any negative outcomes of 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 passivation, agglomeration, filtration and sorption of the original form of nZVI.

8.3 Considering Receptors for Introduced nZVI

Given that the pathways of concern are via the migration of water in the subsurface, the receptors of principal concern will be 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. Groundwater itself is a receptor as well as a pathway and regulators will set or negotiate a compliance point at a site-specific distance from the treatment zone. The iron itself is unlikely to be of concern to regulators as a source of dissolved iron ions, but coatings and other modifiers may be considered as hazardous substances and their release to groundwater is prevented under the Groundwater Daughter Directive (Directive 2006/118/EC) to protect groundwater quality. Plant uptake could be a possible receptor, for example through irrigation. Potential effects on these receptors are not well understood but appear to be substantially reduced for passivated nZVI compared with reactive species.

The microbiology of groundwater could also be considered a receptor in its own right. However, all *in situ* remediation techniques impact aquifer ecology (e.g. by changing one or more of redox potential, pH, temperature, hydraulic conductivity, contaminant accessibility and availability, substrate availability). Such perturbations are usually short-lived and indeed are needed to effect treatment of the target contaminant(s). It may be viewed as disproportionate to regulate nZVI use based on its impacts on subsurface biology or pH-redox changes; a requirement not usually made of established *in situ* remediation techniques.

8.4 Developing a Conceptual Site Model

Table 6 summarises potential pollutant linkages (connected source terms, pathways and receptors) on a worst case scenario basis, i.e. that adequate measures to protect operator health and safety have not been implemented for the remediation work. In this situation 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 negative impacts on ecology in the subsurface and controlled waters should nZVI "breakout" of the treatment zone (beyond a groundwater compliance point or surface water).

Table 6: Possible pollutant linkages for nZVIs used in remediation

Source	Pathway	Receptor	Comments
nZVI: handling and transportation	Air	Human health	Potentially significant[17] - regulated under health and safety provisions
	Dermal / Ingestion	Human health	Potentially significant - regulated under health and safety provisions
nZVI powder / slurry mixing and application	Air	Human health	Potentially significant - regulated under health and safety provisions
	Dermal / Ingestion (direct)	Human health	Potentially significant - regulated under health and safety provisions
	Dermal /	Ecology	Potentially significant - control

[17] I.e. this may an issue seen as significant by a regulator, "significant" in this table is not meant to convey any kind of specific technical meaning

	Ingestion (direct)		regulated through human health and safety provisions
Injected sub-surface active nZVI	Dermal / Ingestion via aquifer – controlled waters receptor	Human health	Seen as an unlikely scenario given use at depth and dilution through an aquifer
	Dermal / Ingestion via aquifer – controlled waters receptor	Ecology and natural soil and surface water microbial processes	Limited duration and extent to an already severely impacted water body
	Aquifer	Groundwater	Potential negative impact from surface modifications (e.g. surfactants) and metal ions released from BNP. Short-term perturbation in aquifer conditions (e.g. redox, pH, microbial community)
	Soils – Plant uptake	Ecology	Seen as an unlikely scenario given use at depth in the saturated zone
	Soils – Plant uptake –dermal / ingestion	Human health	Seen as an unlikely scenario given use at depth in the saturated zone

Hence, one pollutant linkage remains where there may be a significant possibility of harm, which relates to negative impacts on surface water biology, should nZVI migrate from groundwater treatment to surface water. A conceptual site model for this pollutant linkage is illustrated in Figure 6. However, it should be noted that a conceptual site model should be developed on a project-by-project basis to take account of site and NP-specific conditions and properties. Figure 6 differentiates between nZVI directly injected into the subsurface and nZVI that might be partially constrained (e.g. within a partially contained barrier). As nZVI in the subsurface is 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 nZVI.

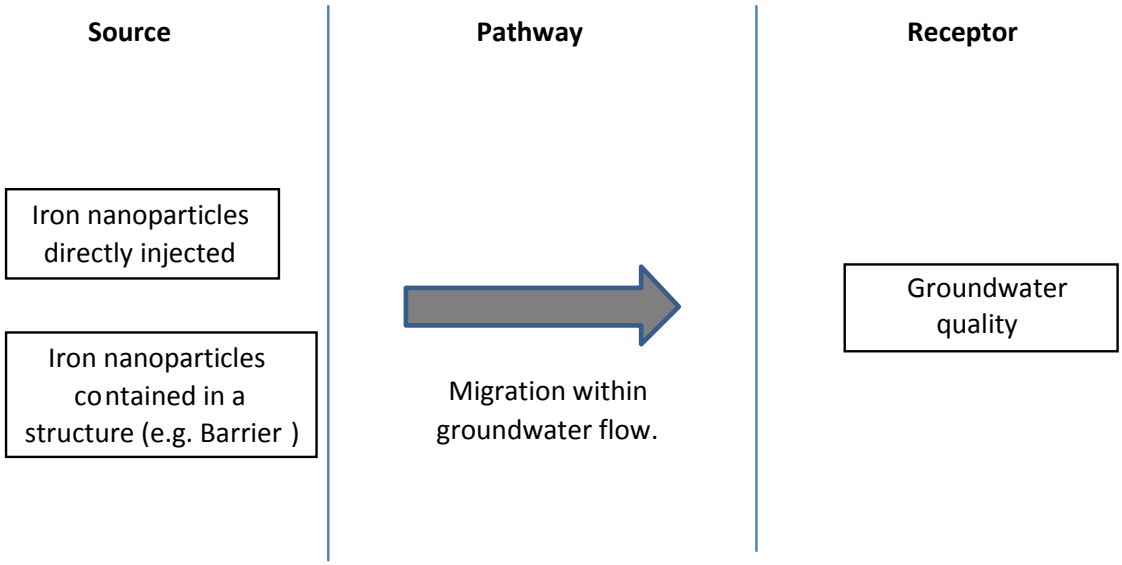

Figure 6: Conceptual model for the potential impacts of nZVI use *in situ* for remediation on surface waters

9 Considerations for Permitting Use of nZVI

The principle deployment risks for nZVI use are related to:

1. Human health impacts and impacts from spillages during the deployment process which should be addressed by regulatory permitting related to good operating practice
2. Impacts on surface water biology which should be addressed by regulations related to the types of allowable subsurface deployments
3. Impacts on groundwater quality and biology

In addition, the direct discharge of hazardous substances is prevented under the Groundwater Daughter Directive (Directive 2006/118/EC) and this may be relevant to the use of some modified NPs. The current state of knowledge militates a cautious approach to deployment risks for surface water given the current uncertainties in knowledge related to persistence of reactive nZVI in the subsurface and its potential migration. Table 7 sets out the key issues that should be considered whilst designing and permitting nZVI deployment.

Table 7: Checklist of permitting issues specific to the use of nZVI

Technology related	Site related
• Type of nZVI, physical and hazardous properties and any amendments used (doping metals, coatings, emulsification or other agents), in particular for surface water organisms	• Applicant/organisation/site • Site specific application / deployment approach • Deployed mass • Deployment risks (with appropriate cross

• Types of deployment approaches used • Emissions from the treatment process (to air land and water) • Likely nZVI migration • Likely nZVI persistence in a reactive form • Likely fate and toxicity of pristine and reacted nZVI and any amendments • Likely maximum dispersion of nZVI under a range of standardised aquifer and groundwater conditions	reference to health and safety regime) • Appropriate cross reference to health and safety regime • Conceptual model (including all plausible contaminant linkages related to the contaminants, products resulting from the treatment process, emissions to air, land and water, and the resultant material following remediation) • Environmental risk assessment (for all plausible contaminant linkages identified in the conceptual model) • Monitoring plan • Pollution control measures • Contingency measures (e.g. in the event of a spillage) • QA/QC plan • * Qualitative risk assessment based on type, longevity and mass of NPs deployed, standardised aquifer conditions and distance to surface water/groundwater receptor or compliance point.

10 Conclusions and Recommendations

nZVI is anticipated as having two major benefits for process based remediation, at least in theory: possible extension of the range of treatable contaminant types, and increasing the efficacy of treatment (speed and degree of completion). To date, the use of nZVI 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 reduction and ZVI (e.g. permeable reactive barriers). The majority of nZVI 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, Germany and Italy).

At present nano-remediation may offer advantages in some applications, compared with other *in situ* remediation tools, but this will be highly dependent on site specific circumstances. In the medium to longer term nanoremediation could substantially expand the range of treatable land contamination problems. The available evidence supports, but does not irrevocably confirm, a view that the risks of nZVI deployment should be considered in the same way as other potentially hazardous treatment reagents (such as persulphates).

A substantial impediment to the use of nZVI in remediation is the uncertain basis for understanding the risks of its deployment to the wider environment, in particular to groundwater and surface water receptors. Although most laboratory studies and subjective practitioner experience would suggest that adverse effects would be minor, localised and short-lived, there is a lack of effective particle

monitoring technologies and peer reviewed and validated data from applications in the field that corroborates this view. This presents a significant challenge to regulatory acceptance which the NanoRem project seeks to address.

In situ remediation technologies can be very advantageous in a number of circumstances and contribute to sustainable remediation approaches. The use of nZVI is potentially a useful addition to the range of available techniques, potentially allowing a more complete and rapid contaminant treatment for some problems. However, the available evidence in support of benefits is not clear cut. In the short term, providing well documented field studies, and a more detailed understanding of its fate and transport in the subsurface would also provide a clearer picture of the relative benefits of nZVI use and when its use was most appropriate.

Hence similar studies can address both uncertainties about benefits and deployment risks, in particular:

- Determination of the reaction products of iron and model reactions of mobile nano-iron particles to assess any possible unintended secondary effects on the environment and ecosystems.
- Development of analytical methods for determining the fate of nano-iron particles against the background of 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 assessment of nZVI application case studies.

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Annex 1 Overview Table of Global Iron Nanoparticle Field Applications

Annex 1 provides an overview of field and pilot scale nZVI investigations up to 2013. Further examples of nZVI field studies can be found in Lee *et al.* (2014)

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	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	Pilot	Fractured Bedrock	GW	PCB		Infiltration Wells	RNIP, Nanofer		1

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	Ref
Republic									
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
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 Infiltration	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	Carboxymethyl cellulose stabilised nZVI and bimetallic nZVI-Pd		5
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

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	Ref
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
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 encountered)	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	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

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	Ref
		unit and groundwater at 85 ft							
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 / Hydraulic Injection	nZVI	108lbs of nZVI; 1,200 lbs of emulsified oils injected into 3 points	3
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 volume 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 volume 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

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	Ref
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 bedrock	TCE	1900 µg/L	High pressure pneumatic injection	nZVI		3
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	PCBs, 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

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	Ref
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
Kaohsiung, Taiwan	Pilot	Medium - coarse sand unconfined aquifer, 4-18m bgs	Unconfined aquifer	TCA, TCE, DCA, DCE, Vinyl chloride	VC 620-4,562 µg/L, EDA 207 µg/L, DCE 1,151 µg/L, TCE 682 µg/L	Gravity feed injection	nZVI, Pd-nZVI, commercial and synthesised	40kg nZVI in 2250L dilution (commercial); 20kg in 8500L dilution (synthesised).	4,6
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,				TCE, cis-DCE, Cr(VI)			nZVI		4

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nanoparticle Type	Volume of Nanoparticle	Ref
USA									
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
Nir Galim, Israel	Pilot		Groundwater	PCE, TCE, dis-DCE		Groundwater directed through column containig nZVI composite	Diatomite supported nZVI-vitamin b_{12} composite.	50kg	7

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
5) Bennett *et al.* (2010)
6) Wei *et al.* (2010)
7) Dror *et al.* (2012)

Annex 2 Contaminant Laboratory Scale Treatability for nZVI

The range of contaminants treatable by nZVI is likely to be broadly similar to conventional ZVI, with some potential advantages for selected contaminants such as PCBs (For comparison, an overview of contaminants treatable at lab, pilot and field scale by ZVI and ZVI-carbon in PRBs can be seen in ITRC 2011b)

Contaminant	**nZVI**
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) ● Xie and Cwiertny 2013 (1,1,1,2-tetrachloroethane, Cis- dichloroethene) – Palladized nZVI. ● Kustov *et al.* 2011 demonstrated promising dechlorination of PCE with chitosan stabilized bimetallic nano-Pd-Fe. ● Petersen *et al.* 2012 found polymer stabilized nZVI degraded TCE; Ibrahem *et al.* 2012 found surfactant modified nZVI had potential for TCE degradation; Sunkara *et al.* 2010 found composite $Fe^{0/}C$ NPs showed promise as a TCE adsorbent.
Chlorinated Aromatics (Hexachlorobenzene; Pentachlorobenzene; Tetrachlorobenzene; Trichlorobenzene; Dichlorobenzene; Chlorobenzene)	● 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); Li *et al.* 2013 (Chlorophenols) Zhu & Lim 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 Johnson 2004; Choi *et al.* 2008
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 and 2,4-dichlorophenoxycetic acid dechlorination by nZVI (de Velosa and Nogueira 2013, Zhu *et al.* 2013) and Pd-Fe bimetallic nanoparticles (Zhang *et al.* 2008, Zhou *et al.* 2011, Xu *et al.* 2013) and by SiO_2 coated nZVI (Wan *et al.* 2013)
Inorganic cations (Mercury; Nickel; Cadmium; Copper; Lead; Silver; Aluminium)	● Literature search showed evidence of lead and cadmium stabilization / immobilisation proven at laboratory-scale only●Zhang *et al.* 2010 (Cadmium & Lead) ● Scott *et al.* 2011 (Cu, U^{VI})

Contaminant	**nZVI**
	● Boparai *et al.* 2011 found nZVI to be an efficient adsorbent for Cd removal from water. ● Klimkova *et al.* 2011 found nZVI (NANOFER 25S) decreased the concentration of a series of contaminants from mine leachate, including Al. ●Shi *et al.* 2013 found chlating resin supported nZVI was able to reduce Pb^{2+}
Inorganic anions (Arsenic/Arsenate/arsenite; Chromate/dichromate; Perchlorate; Uranium; Nitrates; Phosphorus; Sulphates)	Inorganic anions such as Cr(VI), As (III) & (V) and perchlorate removal by nZVI frequently evidenced at laboratory-scale. ● Elliott *et al.* 2007 (perchlorate) ●Cao *et al.* 2005, Liu *et al.* 2012, Singh *et al.* 2012, Wu *et al.* 2012 (CrVI). ● Scott *et al.* 2011 (CrVI, Cu, UVI) ● Tandon *et al.* 2013, Tanboonchuy *et al.* (As III); Du *et al.* 2013 found resin supported nZVI effectively removed As III through a combination of adsorption and oxidation. ● Rahmani *et al.* 2011 (As III) compared nano and micro scale nZVI and observed improved removal efficiency for nZVI. ● Kim *et al.* 2012b found nZVI stabilized with sodium dodecyl sulphate stabilized As in mine tailings. ● Horzum *et al.* 2013 found nZVI supported by chitosan was effective as a sorbent for inorganic As uptake. ● Ahmadi *et al.* 2011 found nZVI with an average diameter of 25nm reduced 95% of nitrate in 3h at pH 2-4. ● Shi *et al.* 2013 found chlating resin supported nZVI was able to reduce NO_3^- ●Liu *et al.* 2013 (phosphorus) ● Wu *et al.* 2013 (phosphate) ● Dickinson and Scott 2010, Baiget *et al.* 2013 (^{238}U in contaminated wastewater) ● Klimkova *et al.* 2011 found nZVI (NANOFER 25S) decreased the concentration of a series of contaminants from mine leachate, including sulphates.
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, Singh *et al.* 2013, Singh *et al.* 2011, Thompson *et al.*

Contaminant	**nZVI**
	2010
Brominated aliphatics (Bromoform; Dibromochloromethane; Dichlorobromomethane)	● Lim *et al.* 2007 (Brominated methanes),
Explosives, energetic compounds (Nitroglycerin, Trinitrotoluene, Hexahydro-1,3,5-trinitroperhydro-1,3,5-triazine)	● Jiamjitrpanich *et al.* (2012) found nZVI could be used in combination with phytoremediation for synergistic removal of TNT. ● Saad *et al.* 2010 found both nZVI and a nZVI/nano silica composite were effective at degrading nitroglycerin in contaminated water, with the stabilised particle reacting faster than the bare nZVI. ●Laboratory studies showed the degradation of RDX by nZVI in the presence carboxymethyl cellulose (CMC) stabilizer (Naja *et al.* 2008).
Isobutyl Propanoic Phenolic acid	● Machado *et al.* 2013 demonstrated that green nZVIs (produced using reducing plant extracts) effectively degraded ibuprofen in aqueous solution.