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

Paul Bardos (r3), Brian Bone (r3), Padraig Daly (r3), Dan Elliott (Geosyntec), Sarah Jones (r3), Gregory Lowry (CEINT), Corinne Merly (BRGM)

April 28, 2015

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 309517

Principal Authors:

Name, First Name	Partner Organisation
Bardos, Paul Bone, Brian Daly, Padraig Jones, Sarah	r3 Environmental Technology Ltd, UK
Elliott, Dan	Geosyntec Consultants Inc., USA
Lowry, Gregory	Centre for Environmental Implications of Nanotechnology, USA
Merly, Corinne	Bureau de Recherches Géologiques et Minières, France

Contributing Authors:

Name, First Name	Partner Organisation
Bartke, Stephan	Helmholtz Centre for Environmental Research – UFZ, Germany
Braun, Jürgen	University of Stuttgart, VEGAS, Germany
Harries, Nicola	CL:AIRE, UK
Hartog, Niels	KWR Water Research, NL (Formerly Deltares)
Hofmann, Thilo Wagner, Stephan	University of Vienna, Austria
Nathanail, Paul	Land Quality Management Ltd, UK;

Reviewed by PAG member(s):

Name, First Name	Partner Organisation
Chao, Chih	Tunghai University
Elliott, Dan	Geosyntec Consultants Inc., USA
Leaf, Catherine	Environ Ltd, UK
Lowry, Gregory	Centre for Environmental Implications of Nanotechnology, USA
Darmendrail, Dominique	COMMON FORUM on Contaminated land in the European Union, France

Acknowledgements

Authors for Acknowledgment

The authors gratefully acknowledge the following for their contribution and feedback on this risk/benefit analysis: Chih Chao, Tunghai University, Taiwan; Dominique Darmendrail, COMMON FORUM, France; Erik Joner, Bioforsk, Norway; Catherine Leaf, ENVIRON, UK; Katrin Mackenzie, Helmholtz Centre for Environmental Research – UFZ, Germany; Deborah Oughton, NMBU, Norway.

Author Explanatory Note

PAG members Dan Elliott and Gregory Lowry are cited as main authors in this report as an acknowledgment of the large input received from these members during the review process, including substantial modifications and input of original material.

NanoRem Issues Paper Acknowledgement

The NanoRem project acknowledges receipt of research funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement number (FP7-309517). This paper reflects only the authors' views and that the European Union is not liable for any use that may be made of the information contained within.

The authors would also like to acknowledge Department of Environment, Food and Rural Affairs, (Defra) England who funded the project CB0440 "Risk/benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment" (2011) [1]which this paper used as an initial starting reference and built part of its findings from.

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.

Table of Contents

List of Figures

List of Tables

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.

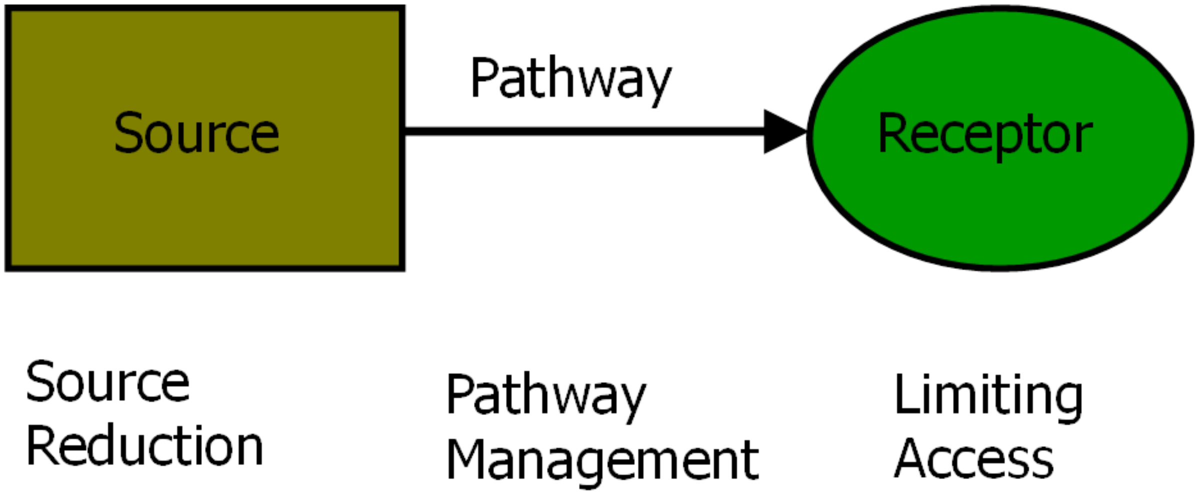

Figure 1: Remediation interventions for risk management

---

[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^{TM}, 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).

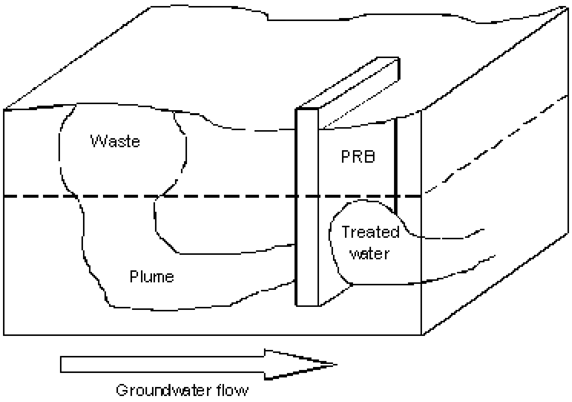

Figure 3: Typical PRB Configuration (from Nathanail *et al.* 2007)

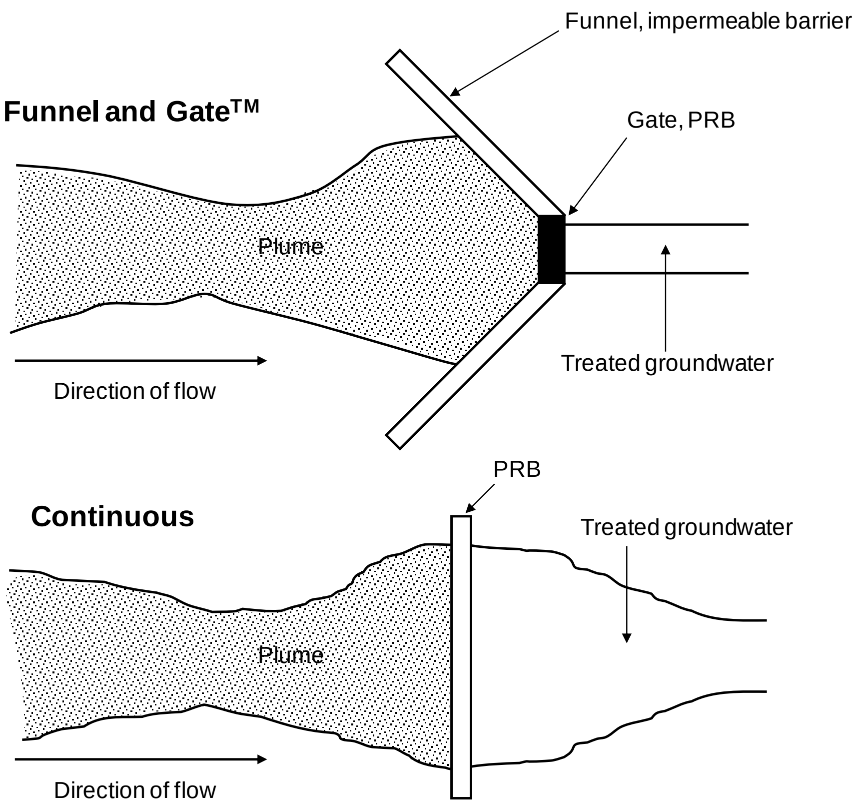

Figure 4: Funnel and Gate™ and Continuous PRB Configurations (from Nathanail *et al.* 2007)

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).

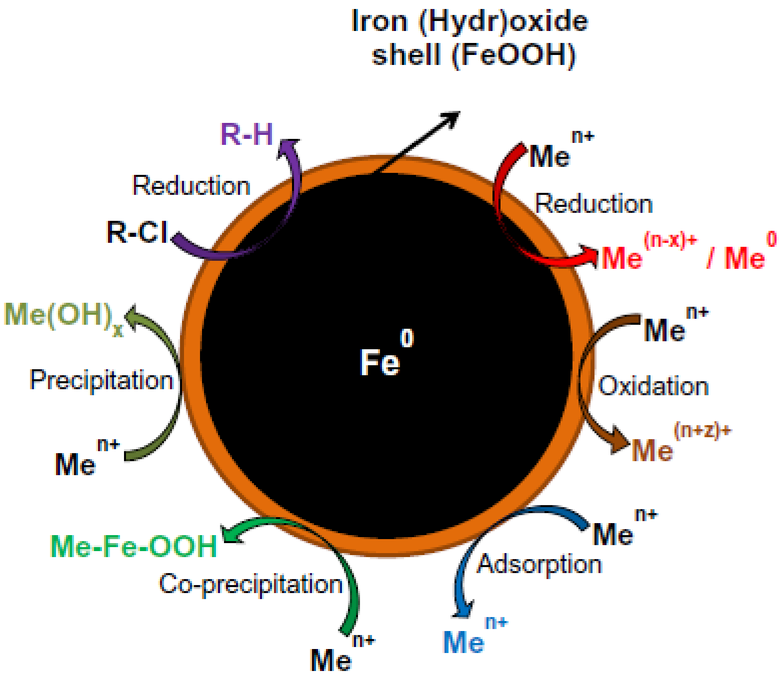

Figure 5: Core–shell structure of nZVI depicting various mechanisms for the removal of metals and chlorinated compounds (O'Carroll *et al.* 2013, adapted from Li *et al.* 2006).

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^{TM} 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.

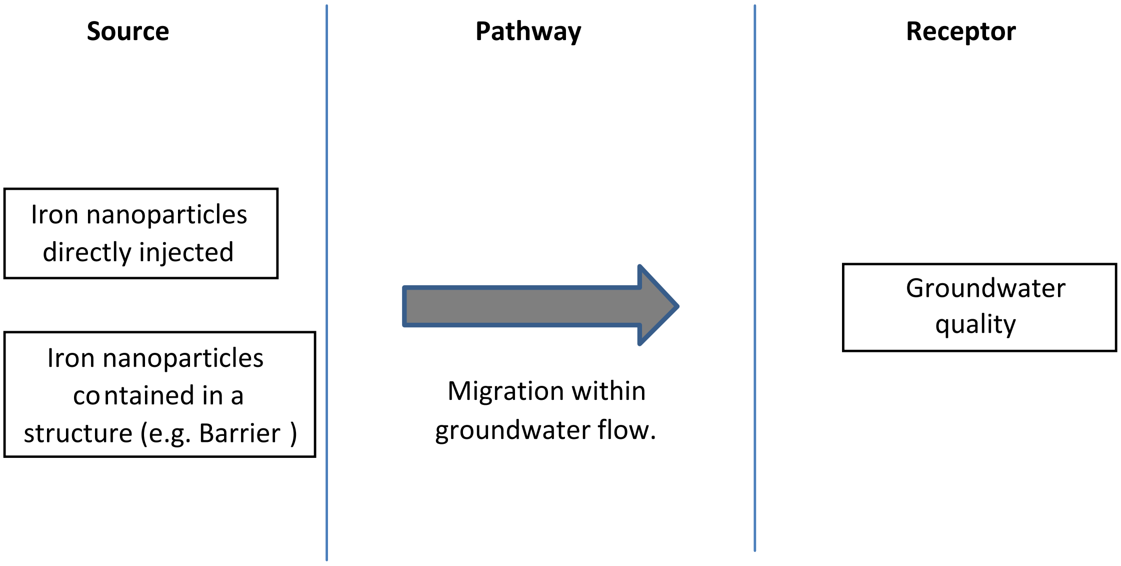

Figure 6: Conceptual model for the potential impacts of nZVI use *in situ* for remediation on surface waters

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.

References

ADELEYE, A. S., KELLER, A. A., MILLER, R. J., AND LENIHAN, H. S. 2013. 'Persistence of commercial nanoscaled zero-valent iron (nZVI) and by-products', Journal of Nanoparticle Research, 15,1, 1-18.

AHMADI, M., MASHOON, F., KAVEH, R., AND TARKIAN, F. 2011 'Use of Mechanically Prepared Iron Nano Particles for Nitrate Removal from Water', *Asian Journal of Chemistry*, **23**, 3, 1205-1208.

AL-SHAMSI, M. A., AND THOMSON, N. R. 2013 'Treatment of a Trichloroethylene Source Zone using Persulfate Activated by an Emplaced Nano-Pd–Fe0 Zone', *Water, Air, & Soil Pollution*, **224,** 11, 1-12.

ANON 2012 'Not enough evidence for nanotech clean-up', ENDS Report 446, March 2012, 24-26.

AUFFAN, M., ACHOUAK, W., ROSE, J., RONCATO, M-A., CHANÉAC, C., WAITE, D.T., MASION, A., WOICIK, J.C., WIESNER, M.R. AND BOTTERO, J-Y. 2008 'Relation between the redox state of iron-based nanoparticles and their cytotoxicity toward *Escherichia coli*', *Environmental Science and Technology*, **42**, 17, 6730-6735.

AUFFAN, M., DECOME, L., ROSE, J., ORSIER, T., DE MEO. M., BRIOIS, V., CHANEAC, C., OLIVI, L., BERGE-LEFRANC, J-L., BOTTA, A., WIESNER, M.R. AND BOTTERO, J-Y. 2006 'In vitro interactions between DMSA-coated maghemite nanoparticles and human fibroblasts: A physicochemical and cyto-genotoxical study', *Environmental Science and Technology*, **40**, 14, 4367-4373.

AUFFAN, M., ROSE, J., BOTTERO, J. Y., LOWRY, G. V., JOLIVET, J. P., AND WIESNER, M. R. 2009a. 'Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective', *Nature*, **4,** 10, 634-641.

AUFFAN, M., ROSE, J., WIESNER, M.R. AND BOTTERO, J-Y. 2009b 'Chemical stability of metallic nanoparticles: A parameter controlling their potential toxicity in vitro', *Environmental Pollution*, **157**, 4, 1127-1133.

BAER, D. R., TRATNYEK, P. G., QIANG, Y., AMONETTE, J. E., LINEHAN, J., SARATHY, V., NURMI, J. T., WANG, C-M. AND ANTONY, J. 2007 'Synthesis, Characterisation, and Properties of Zero-Valent Iron Nanoparticles'. In FRYXELL, G.E. AND CAO, G. (eds.) *Environmental Applications of Nanomaterials: Synthesis, Sorbents and Senors*, Imperial College Press, London, 49-86.

BAIGET, M., CONSTANTÍ, M., LÓPEZ, M. T., AND MEDINA, F. 2013 'Uranium removal from a contaminated effluent using a combined microbial and nanoparticle system', *New Biotechnology*, **30**, 6, 788-792.

BOPARAI, H. K., JOSEPH, M., AND O'CARROLL, D. M. 2011 'Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles', *Journal of Hazardous Materials,* **186,** 1, 458-465.

BARDOS, P., BAKKER, L., DARMENDRAIL, D., HARRIES, N., HOLLAND, K., MACKAY, S., PACHON, C., SLENDERS, H., SMITH, G., SMITH, J. AND WILTSHIRE, L. 2013 'ThS E3 Sustainable use of the subsurface sustainable and green remediation – global update' [Online] Available at: < http://www.zerobrownfields.eu/HombreMainGallery/Docs/AquaConSoil%202013_Sustainable%20and%20Green%20Remediation_Global%20Update.pdf>.

BARDOS, P., BONE, B., ELLIOTT, D., HARTOG, N., HENSTOCK, J. AND NATHANAIL, P. 2011a 'Risk/benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment' – CB0440. Report for the Department of Environment, Food and Rural Affairs. [Online] Available at: <http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=17502>

BARDOS, R. P., BONE, B. D., BOYLE, R., ELLIS, D., EVANS, F., HARRIES, N. AND SMITH, J.W.N. 2011b. 'Applying Sustainable Development Principles to Contaminated Land Management Using the SuRF-UK Framework', *Remediation Journal,* **21**, 2, 77-100.

BARNES, R.J., RIBA, O., GARDNER, M.N., SINGER, A.C., JACKMAN, S.A. AND THOMPSON, I.P. 2010 'Inhibition of biological TCE and sulphate reduction in the presence of iron nanoparticles', *Chemosphere*, **80,** 554–562.

BENNETT, P., HE, F., ZHAO, D., AIKEN, B., AND FELDMAN, L. 2010 '*In situ* testing of metallic iron nanoparticle mobility and reactivity in a shallow granular aquifer' .*Journal of Contaminant Hydrology*, **116,** 1, 35-46.

BERGE, N. D.; RAMSBURG, A. 2009 'Oil-in-water emulsions for encapsulated delivery of reactive iron particles' *Environmental Science and Technology*, **43**, 5060–5066.

BEZBARUAH, A.N., KRAJANGPAN, S., CHISHOLM, B.J., KHAN, E. AND BERMUDEZ, J.J.E. 2009a 'Entrapment of iron nanoparticles in calcium alginate beads for groundwater remediation applications', *Journal of Hazardous Materials*, **166**, 2-3, 1339-1343.

BEZBARUAH, A.N., THOMPSON, J.M. AND CHISHOLM, B.J. 2009b 'Remediation of alachlor and atrazine contaminated water with zero-valent iron nanoparticles', *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants and Agricultural Wastes*, **44**, 6, 518-524.

BISWAS, P., AND WU, C. Y. 2005 'Nanoparticles and the environment', *Journal of the Air & Waste Management Association*, **55**,6, 708-746.

BLAISE, C., GAGNE, F., FERARD, J.F. AND EULLAFFROY, P. 2008 'Ecotoxicity of selected nano-materials to aquatic organisms', *Environmental Toxicology*, **23**, 5, 591-598.

BOXALL, A.B.A., TIEDE, K. AND CHAUDHRY, Q. 2007 'Engineered nanomaterials in soils and water: How do they behave and could they pose a risk to human health?', *Nanomedicine*, **2**, 6, 919-927.

BRUNNER, T.J., WICK, P., MANSER, P., SPOHN, P., GRASS, R.N., LIMBACH, L.K., BRUININK, A. AND STARK, W. 2006 'In vitro cytotoxicity of oxide nanoparticles: Comparison to asbestos, silica, and the effect of particle solubility', *Environmental Science and Technology*, **40**, 14, 4374-4381.

BAFU (Bundesamt für Umwelt). 2010 'Noch viele Fragezeichen', *Nanotechnologie*, **3**, 21-22; 24; 26-27; 30.

BURGHARDT, D. AND KASSAHUN, A. 2005 'Development of a reactive zone technology for simultaneous *in situ* immobilisation of radium and uranium', *Environmental Geology*, **49**, 2, 314-320.

CAREY, M. A., FRETWELL, B. A., MOSLEY, N. G., AND SMITH, J. W. N. 2002. *Guidance on the use of permeable reactive barriers for remediating contaminated groundwater.* Environment Agency, National Groundwater & Contaminated Land Centre. [Online] Available at: <http://www.environment-agency.gov.uk/research/planning/40381.aspx>

CHANG, M. C., AND KANG, H. Y. 2009 'Remediation of pyrene-contaminated soil by synthesized nanoscale zero-valent iron particles', *Journal of Environmental Science and Health Part A*, **44**, 6, 576-582.

CHANG, M. C., SHU, H. Y., HSIEH, W. P., AND WANG, M. C. 2007 'Remediation of soil contaminated with pyrene using ground nanoscale zero-valent iron', *Journal of the Air & Waste Management Association*, **57,** 2, 221-227.

CHANG, M. C., SHU, H. Y., HSIEH, W. P., AND WANG, M. C. 2005 'Using nanoscale zero-valent iron for the remediation of polycyclic aromatic hydrocarbons contaminated soil', *Journal of the Air & Waste Management Association***, 55**, 8, 1200-1207.

CHENG, R., WANG, J.L. AND ZHANG, W.X. 2007 'Comparison of reductive dechlorination of p-chlorophenol using Fe-0 and nanosized Fe-0', *Journal of Hazardous Materials*, **144**, 1-2, 334-339.

CHENG, R., ZHOU, W., WANG, J., QI, D., GUO, L., ZHANG, W-X. AND QIAN, Y. 2010 'Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: Role of nano-Ni and its size effect', *Journal of Hazardous Materials*, **180**, 1-3, 79–85.

CHAUDHRY, Q. AND CASTLE, L. 2011 'Food applications of nanotechnologies: An overview of opportunities and challenges for developing countries' *Trends in Food Science and Technology*, **22,** 11, 595-603.

CHEN, Z. X., JIN, X. Y., CHEN, Z., MEGHARAJ, M., AND NAIDU, R. 2011 'Removal of methyl orange from aqueous solution using bentonite-supported nanoscale zero-valent iron' *Journal of colloid and Interface Science*, **363,** 2, 601-607.

CHEN, Q., LI, J., WU, Y., SHEN, F., AND YAO, M. 2013 'Biological Responses of Gram-positive and Gram-negative Bacteria to nZVI (Fe0), Fe2+ and Fe3+' *RSC Advances,* **3**, 33, 13835-13842.

CHEN, P. J., WU, W. L., AND WU, C. W. 2013 'The zerovalent iron nanoparticle causes higher developmental toxicity than its oxidation products in early life stages of medaka fish' *Water Research,* **47**, 11, 3899-3909.

CHOI, H., AL-ABED, S.R., AGARWAL, S. AND DIONYSIOU, D.D. 2008 'Synthesis of reactive nano-Fe/Pd bimetallic system-impregnated activated carbon for the simultaneous adsorption and dechlorination of PCBs', *Chemistry of Materials*, **20**, 11, 3649-3655.

CHOWDHURY, A. I., O'CARROLL, D. M., XU, Y., AND SLEEP, B. E. 2012 'Electrophoresis enhanced transport of nano-scale zero valent iron', *Advances in Water Resources*, **40**, 71-82.

CHRYSOCHOOU, M., MCGUIREA, M., AND DAHALB, G. 2012 'Transport Characteristics of Green-Tea Nano-scale Zero Valent Iron as a Function of Soil Mineralogy', *Chemical Engineering*, **28**, 121-126**.**

COMBA, S., DI MOLFETTA, A. AND SETHI, R. 2011 'A comparison between field applications of nano-, micro- and millimetric zero-valent iron for the remediation of contaminated aquifers', *Water, Air, and Soil Pollution,* **215**, 595–607.

COOK, S. 2009 'Assessing the use and application of zero-valent iron nanoparticle technology for remediation at contaminated sites', Prepared for the US Environmental Protection Agency. [Online] Available at: <http://www.clu-in.org/download/studentpapers/Zero-Valent-Iron-Cook.pdf>

COUTRIS, C., HERTEL-AAS, T., LAPIED, E., AND JONER, E. J., AND OUGHTON, D. H. 2012. 'Bioavailability of cobalt and silver nanoparticles to the earthworm *Eisenia fetida*', *Nanotoxicology*, **6**, 2, 186-195.

CULLEN, L. G., TILSTON, E. L., MITCHELL, G. R., COLLINS, C. D., AND SHAW, L. J. 2011 'Assessing the impact of nano-and micro-scale zerovalent iron particles on soil microbial activities: Particle reactivity interferes with assay conditions and interpretation of genuine microbial effects', *Chemosphere*, **82**, 11, 1675-1682.

CUNDY, A., HOPKINSON, L. AND WHITBY, R.L.D. 2008 'Use of iron-based technologies in contaminated land and groundwater remediation: A review', *Science of the Total Environment*, **400,** 1-3, 42-53.

DE BOER, C. V., KLAAS, N., AND BRAUN, J. 2010 'Chemical Reduction of PCE by Zero Valent Iron Colloids Comparison of Batch and Column Experiments', *Permeable Reactive Barriers & Reactive Zones*, **15**.

DE BOER C., KLAAS N., AND BRAUN J. 2009 'Anwendung nanoskaliger Eisenkolloide zur In-Situ-Sanierung anthropogener CKW-Kontaminationen im Untergrund.' Wissenschaftlicher Bericht Nr. VEG 36, 2009/05. University of Stuttgart

DEGUELDRE, C., TRIAYC, I., KIMD, J-I., VILKS, P., LAAKSOHARJUG, M. AND MIEKELEY, N. 2000 'Groundwater colloid properties: A global approach', *Applied Geochemistry*, **15**, 7, 1043-1051.

DE VELOSA, A. C., AND PUPO NOGUEIRA, R. F. 2013 '2, 4-Dichlorophenoxyacetic acid (2, 4-D) degradation promoted by nanoparticulate zerovalent iron (nZVI) in aerobic suspensions', *Journal of Environmental Management*, **121**, 72-79.

DICKINSON, M., AND SCOTT, T. B. 2010 'The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent', .*Journal of Hazardous Materials*, **178**, 1, 171-179.

DING, Y., LIU, B., SHEN, X., ZHONG, L., AND LI, X. 2013 'Foam-Assisted Delivery of Nanoscale Zero Valent Iron in Porous Media', *Journal of Environmental Engineering*, **139**, 9, 1206-1212.

DNR (German League for Nature and Environment) AND EEB (European Environmental Bureau) 2011 'Soil: worth standing your ground for. Arguments for the Soil Framework Directive'. EEB, Brussels. [Online] Available at: <www.eeb.org/EEB/?LinkServID=1D2DA6F8-B28F-78BB-6E212DDC63EE80E7>

DONG, H., AND LO, I. 2013 'Influence of calcium ions on the colloidal stability of surface-modified nano zero-valent iron in the absence or presence of humic acid', *Water Research,* **47**, 7, 2489-2496.

DOUVALIS, A. P., ZBORIL, R., BOURLINOS, A. B., TUCEK, J., SPYRIDI, S., AND BAKAS, T. 2012. 'A facile synthetic route toward air-stable magnetic nanoalloys with Fe–Ni/Fe–Co core and iron oxide shell' *Journal of Nanoparticle Research*, **14**(9), 1-16.

DROR, I., JACOV, O. M., CORTIS, A., AND BERKOWITZ, B. 2012 'Catalytic Transformation of Persistent Contaminants Using a New Composite Material Based on Nanosized Zero-Valent Iron', *ACS Applied Materials & Interfaces*, **4**, 7, 3416-3423.

DU, Q., ZHANG, S., PAN, B., LV, L., ZHANG, W., AND ZHANG, Q. 2013 'Bifunctional resin-ZVI composites for effective removal of arsenite through simultaneous adsorption and oxidation', *Water Research*, **47**, 16, 6064-6074.

DUSINSKA, L. FJELLSBØ, M. OLSEN, S., BAUN, A., DEKKERS, S., NOWACK, B., KUHLBUSCH, T. SOM, C. DE HEER, C., CASSEE, F., HANDY, R. LYNCH, I., FERNANDES, T., HAUSIADIS, K., PILOU, M., VOLKOVOVA, K., AND GROSSBERNDT, S. 2012 'D3.10 Final Report with recommendations for Impact Assessment of Engineered Nanomaterials', [Online] Available at: <http://www.nanoimpactnet.eu/uploads/Deliverables/D3.10.pdf>

ELLIOTT, D.W. 2010 *CLU-IN Webinar Presentation*. [Online] Available at: <http://www.clu-in.org/conf/tio/nano-iron/prez/1280x1024/ppframe.cfm?date=502>

ELLIOTT, D.W., LIEN, H-L. AND ZHANG, W-X. 2007 'Nanoscale Zero-Valent Iron (nZVI) for Site Remediation'. In FRYXELL, G.E. AND CAO, G. (eds.) *Environmental Applications of Nanomaterials: Synthesis, Sorbents and Senors,* Imperial College Press, London, 25-48.

ELLIOTT, D. W., LIEN, H. L., AND ZHANG, W. X. 2008 'Zerovalent iron nanoparticles for treatment of ground water contaminated by hexachlorocyclohexanes', *Journal of Environmental Quality*, **37,**6, 2192-2201.

ELLIOTT, D.W. AND ZHANG, W-X. 2001 'Field assessment of nanoscale biometallic particles for groundwater treatment', *Environmental Science and Technology*, **35**, 24, 4922-4926.

EL-TEMSAH, Y. S., AND JONER, E. J. 2013 'Effects of nano-sized zero-valent iron (nZVI) on DDT degradation in soil and its toxicity to collembola and ostracods', *Chemosphere*, **92**, 1, 131-137.

EL-TEMSAH, Y. S., AND JONER, E. J. 2012a 'Ecotoxicological effects on earthworms of fresh and aged nano-sized zero-valent iron (nZVI) in soil', *Chemosphere*, **89**, 1, 76-82.

EL-TEMSAH, Y.S. AND JONER, E.J. 2012b 'Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil', *Environmental Toxicology,* **27**, 1, 42-49.

ENVIRONMENT AGENCY 2006 'A people's inquiry on nanotechnology and the environment', Science Report SCHO0607BMUJ-E-P. Environment Agency, Bristol, UK. ISBN: 978-1-84432-782-9; [Online] Available at: <www.sciencewise-erc.org.uk/cms/assets/Uploads/Project-files/NanodialoguesA-peoples-inquiry.pdf>

EUN, C.K. AND MYUNG, H. 2007 'Cytotoxic effects of nanoparticles assessed *in vitro* and *in vivo*', *Journal of Microbiology and Biotechnology*, **17**, 9, 1573-1578.

EUROPEAN COMMISSION (EC) 2011 'Roadmap to a Resource Efficient Europe'. Brussels, 20.9.2011, COM(2011) 571 final. [Online] Available at:

<http://ec.europa.eu/environment/resource_efficiency/pdf/com2011_571.pdf.>

EUROPEAN ENVIRONMENT AGENCY (EEA) 2007 'Progress in management of contaminated

sites (CSI 015)' - Assessment published on line August 2007. [Online] Available at:

<http://themes.eea.europa.eu/IMS/IMS/ISpecs/ISpecification20041007131746/IAssessment1152619898983/view_content>

EUROPEAN ENVIRONMENT AGENCY (EEA) 2013 'Environment and human health' Joint EEA-JRC report. EUR 25933 EN. [Online] Available at: <www.eea.europa.eu/publications/late-lessons-2>

EUROPEAN ENVIRONMENT AGENCY (EEA) AND JOINT RESEARCH CENTRE (JRC) 2013a 'Late lessons from early warnings: science, precaution, innovation. EEA, Copenhagen, Denmark. [Online] Available at: <www.eea.europa.eu/publications/environment-and-human-health>

FAGERLUND, F., ILLANGASEKARE, T. H., PHENRAT, T., KIM, H. J., AND LOWRY, G. V. 2012 'PCE dissolution and simultaneous dechlorination by nanoscale zero-valent iron particles in a DNAPL source zone', Journal of Contaminant Hydrology, **131**(1), 9-28.

FAJARDO, C., ORTÍZ, L. T., RODRÍGUEZ-MEMBIBRE, M. L., NANDE, M., LOBO, M. C., AND MARTIN, M. 2012 'Assessing the impact of zero-valent iron (ZVI) nanotechnology on soil microbial structure and functionality: A molecular approach' *Chemosphere*, **86**, 8, 802-808.

FAJARDO, C., SACCÀ, M. L., MARTINEZ-GOMARIZ, M., COSTA, G., NANDE, M., AND MARTIN, M. 2013 'Transcriptional and proteomic stress responses of a soil bacterium Bacillus cereus to nanosized zero-valent iron (nZVI) particles', *Chemosphere*, **93**, 6, 1077-1083.

FAN, D., ANITORI, R. P., TEBO, B. M., TRATNYEK, P. G., LEZAMA PACHECO, J. S., KUKKADAPU, R. K., ENGELHARD, M. H., BOWDEN, M. E., KOVARIK, L. AND AREY, B. W. 2013 'Reductive Sequestration of Pertechnetate (99TcO4–) by Nano Zerovalent Iron (nZVI) Transformed by Abiotic Sulfide', *Environmental Science & Technology*, **47**, 10, 5302-5310.

FERGUSON, C., DARMENDRAIL, D., FREIER, K., JENSEN, B. K., JENSEN, J., KASAMAS, H., URZELAI, A. AND VEGTER, J. 1998. 'Risk Assessment for Contaminated Sites in Europe: Vol 1: Scientific Basis', Nottingham: LQM Press.

FRIENDS OF THE EARTH 2010 *Nanotechnology, climate and energy: overheated promises and hot air?* [Online] Available at: <http://www.foe.co.uk/resource/reports/nanotechnology_climate.pdf >

GATTI, A.M. AND RIVASI, F. 2002 'Biocompatability of micro- and nanoparticles. Part I: in liver and kidney', *Biomaterials*, **23**, 11, 2381-2387.

GAVASKAR, A., TATAR, L. AND CONDIT, W. 2005 *Cost and Performance Report Nanoscale Zero-Valent Iron Technologies for Source Remediation*, Contract Report CR-05-007-ENV. [Online] Available at: <http://www.cluin.org/download/remed/cr-05-007-env.pdf>

GEIGER, C.L., CLAUSEN, C.A., BROOKS, K., CLAUSEN, C., HUNTLEY, C., FILIPEK, L., REINHART, D.D., QUINN, J., KRUG, T., O'HARA, S. AND MAJOR, D. 2002 'Nanoscale and Microscale Iron Emulsions for Treating

DNAPL'. In HENRY, S.M. AND WARNER, S.D. (eds.) *Chlorinated Solvent and DNAPL Remediation*, Oxford University Press, North Carolina, 132-140.

GEIGER, C.L, CARVALHO-KNIGHTON, K., NOVAES-CARD, S., MALONEY, P. AND DEVOR, R. 2009 'A Review of Environmental Applications of Nanoscale and Microscale Reactive Metal Particles'. In GEIGER, C.L. AND CARVALHO-KNIGHTON, K.M. (eds.) *Environmental Applications of Nanoscale and Microscale Reactive Metal Particles*, Oxford University Press, North Carolina, 1-20.

GENG, B., JIN, Z., LI, T. AND QI, X. 2009 'Kinetics of hexavalent chromium removal from water by chitosan-Fe^0 nanoparticles', *Chemosphere*, **75**, 825-830.

GILBERT, B., LU, G. AND KIM, C.S. 2007 'Stable cluster formation in aqueous suspensions of iron oxyhydroxide nanoparticles', Journal of Colloid and Interface Science, **313**, 1, 152-159.

GILLIGAN, J. M. 2006. Flexibility, Clarity, and Legitimacy: Considerations for Managing Nanotechnology Risks. *Environmental Law Reporter News and Analysis*, **36** (12), 10924.

GOLDER ASSOCIATES, 2009. 'Nano-Scale Zero-Valent Iron State of the Technology: Lessons Learned from R&D, Production and Global Field Implementations'. [Online] Available at: <http://www.oecd.org/dataoecd/23/1/44027622.pdf>

GOUVERNEMENT DU QUEBEC 2006 *'Ethics and Nanotechnology: A Basis for Action'*. Position Statement at Commission de L'éthique de la Science et de la Technologie, National Library of Canada, Québec.

GRIEGER, K. D., FJORDBØGE, A., HARTMANN, N. B., ERIKSSON, E., BJERG, P. L., AND BAUN, A. 2010 'Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for *in situ* remediation: Risk mitigation or trade-off?', .*Journal of Contaminant Hydrology*, **118**(3), 165-183.

HANDY, R.D., VON DER KAMMER, F., LEAD, J.R., HASSELLÖV, M., OWEN, R. AND CRANE, M. 2008. 'The ecotoxicology and chemistry of manufactured nanoparticles', *Ecotoxicology*, **17**, 4, 287-314.

HE, F. AND ZHAO, D. 2005 'Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water', *Environmental Science and Technology*, **39**, 9, 3314-3320.

HE, F., ZHAO, D., LIU, J. AND ROBERTS, C.B. 2007 'Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater', *Industrial and Engineering Chemistry Research*, **46**, 1, 29-34.

HE, F. AND ZHAO, D.Y. AND PAUL, C. 2010 'Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for *in situ* destruction of chlorinated solvents in source zones', *Water Research*, **44**, 7, 2360 – 2370.

HENDERSON, A.D. AND DEMOND, A.H. 2007. 'Long-term performance of zero-valent iron permeable reactive barriers: a critical review', *Environmental Engineering Science* **24,** 4, 401-423.

HENN, K.W. AND WADDILL, D.W. 2006 'Utilization of nanoscale zero-valent iron for source remediation — A case study', *Remediation Journal*, **16**, 2, 57-77.

HILDEBRAND, H., KÜHNEL, D., POTTHOFF, A., MACKENZIE, K., SPRINGER, A. AND SCHIRMER, K. 2010 'Evaluating the cytotoxicity of palladium/magnetite nano-catalysts intended for wastewater treatment', *Environmental Pollution*, **158**, 1, 65-73.

HM GOVERNMENT 2010. 'UK Nanotechnologies Strategy- Small Technologies, Great Opportunities'. First published March 2010 © Crown Copyright URN 10/825

HOCHELLA, M.F., MOORE, J.N., PUTNIS, C.V., PUTNIS, A., KASAMA, T. AND EBERL, D.D. 2005 'Direct observation of heavy metal-mineral association from the Clark Fork River Superfund Complex: implications for metal transport and bioavailability', *Geochimica et Cosmochimica Acta,* **69,** 7, 1651-1663.

HORZUM, N., DEMIR, M. M., NAIRAT, M., AND SHAHWAN, T. 2013 'Chitosan fiber-supported zero-valent iron nanoparticles as a novel sorbent for sequestration of inorganic arsenic', *RSC Advances*, **3**, 1, 7828-7837.

HOSSEINI, S. M., ATAIE-ASHTIANI, B., AND KHOLGHI, M. 2011) 'Nitrate reduction by nano-Fe/Cu particles in packed column', *Desalination*, **276**, 1, 214-221.

HUANG, Q., SHI, X., PINTO, R.A., PETERSEN, E.J. AND WEBER JR, W.J. 2008 'Tunable synthesis and immobilization of zero-valent iron nanoparticles for environmental applications', *Environmental Science and Technology*, **42**, 23, 8884-8889.

HUANG, P., YE, Z., XIE, W., CHEN, Q., LI, J., XU, Z., AND YAO, M. 2013 'Rapid Magnetic Removal of Aqueous Heavy Metals and their Relevant Mechanisms Using Nanoscale Zero Valent Iron (nZVI) Particles' *Water research,* **47**, 12, 4050-4058.

HYDUTSKY, B.W., MACK, E.J., BECKERMAN, B.B., SKLUZACEK, J.M. AND MALLOUK, T.E. 2007 'Optimization of nano- and microiron transport through sand columns using polyelectrolyte mixtures', *Environmental Science and Technology*, **41**, 18, 6418-6424.

IAHS (INTERNATIONAL ASSOCIATION OF HYDROLOGICAL SCIENCES) 2002. *Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution*, Proceedings of Groundwater Quality 2001 Conference. Sheffield, UK, June.

IBRAHEM, A. K., ABDEL MOGHNY, T., MUSTAFA, Y. M., MAYSOUR, N. E., EL DARS, M. S. E. D., AND FAROUK HASSAN, R. 2012 'Degradation of Trichloroethylene Contaminated Soil by Zero-Valent Iron Nanoparticles' *ISRN Soil Science*, doi:10.5402/2012/270830.

IRGC (International Risk Governance Council) White Paper N° 2, "Nanotechnology Risk Governance", IRGC, Geneva 2006. <http://www.irgc.org/IMG/pdf/IRGC_white_paper_2_PDF_final_version-2.pdf>. Accessed 1 October 2011

ITRC (INTERSTATE TECHNOLOGY AND REGULATORY COUNCIL) 2011a 'Integrated DNAPL site strategy' Technical/Regulatory Guidance. [Online] Available at: <http://www.itrcweb.org/Guidance/GetDocument?documentID=35>

ITRC (INTERSTATE TECHNOLOGY AND REGULATORY COUNCIL) 2011b 'Permeable Reactive Barrier: Technology update' Technical/Regulatory Guidance. [Online] Available at: <http://www.itrcweb.org/GuidanceDocuments/PRB-5-1.pdf>

ITRC (INTERSTATE TECHNOLOGY AND REGULATORY COUNCIL) 2008 'In Situ Bioremediation of Chlorinated Ethene: DNAPL Source Zones', Interstate Technology and Regulatory Council, Washington DC. [Online] Available at: <http://www.itrcweb.org/Documents/bioDNPL_Docs/BioDNAPL3.pdf>

ITRC (INTERSTATE TECHNOLOGY AND REGULATORY COUNCIL) 2001 'Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater', Interstate Technology and Regulatory Cooperation Work Group *In Situ* Chemical Oxidation Work Team. [Online] Available at: <http://international.vrom.nl/Docs/internationaal/ENGELSE%20versie%20circulaire%20B odemsanering%202009.pdf>

JIA, H., AND WANG, C. 2013 'Comparative studies on montmorillonite-supported zero-valent iron nanoparticles produced by different methods: reactivity and stability', *Environmental Technology,* **34**,1, 25-33.

JIAMJITRPANICH, W., PARKPIAN, P., POLPRASERT, C., AND KOSANLAVIT, R. 2012 'Enhanced Phytoremediation Efficiency of TNT-Contaminated Soil by Nanoscale Zero Valent Iron' *International Proceedings of Chemical, Biological & Environmental Engineering: Environment and Industrial Innovation*, **35**, 82-86.

JOHNSON, R. L., NURMI, J. T., O'BRIEN JOHNSON, G. S., FAN, D., O'BRIEN JOHNSON, R. L., SHI, Z., SALTER-BLANC, A. J., TRATNYEK, P. G., AND LOWRY, G. V. 2013 'Field-scale transport and transformation of carboxymethylcellulose-stabilized nano zero-valent iron', *Environmental Science & Technology*, **47**, 3, 1573-1580.

JOHNSON, R.L., O'BRIEN JOHNSON, G., NURMI, J.T. AND TRATNYEK, P.G. 2009. 'Natural organic matter enhanced mobility of nano zerovalent iron', *Environmental Science and Technology*, **43**, 14, 5455–5460.

JONES, E. H., REYNOLDS, D. A., WOOD, A. L., AND THOMAS, D. G. 2011 'Use of Electrophoresis for Transporting Nano-Iron in Porous Media', *Ground Water*, **49**, 2, 172-183.

KANEL, S.R AND CHOI, H. 2007 'Transport characteristics of surface-modified nanoscale zero-valent iron in porous media', *Water Science and Technology*, **55**, 1-2, 157-162.

KANEL, S.R., GRENACHE, J.M. AND CHOI, H. 2007 'Arsenic (V) removal from groundwater using nano scale zero-valent iron as a colloidal reactive barrier material', *Environmental Science and Technology*, **40**, 6, 2045-2050.

KARLSSON, M. N. A., DEPPERT, K., WACASER, B. A., KARLSSON, L. S., AND MALM, J. O. 2005 'Size-controlled nanoparticles by thermal cracking of iron pentacarbonyl', *Applied Physics A*, **80**,7, 1579-1583.

KARN, B., KUIKEN, T. AND OTTO, M. 2009 'Nanotechnology and *in situ* remediation: A review of the benefits and potential risks', *Environmental Health Perspectives*, **117**, 12, 1823-1831.

KEANE, E. 2009 ‘Fate, Transport, and Toxicity of Nanoscale Zero-Valent Iron (nZVI) Used During Superfund Remediation’, United States Environmental Protection Agency Report. [Online] Available at: <http://83.cebed1.client.atlantech.net/download/studentpapers/Zero-Valen-Iron-Keane.pdf >

KEENAN, C.R., GOTH-GOLDSTEIN, R., LUCAS, D. AND SEDLAK, D.L. 2009 ‘Oxidative stress induced by zero-valent iron nanoparticles and Fe(II) in human bronchial epithelial cells’, *Environmental Science and Technology*, **43**, 12, 4555-4560.

KELLER, A. A., GARNER, K., MILLER, R. J., AND LENIHAN, H. S. 2012 ‘Toxicity of nano-zero valent iron to freshwater and marine organisms’, *PloS one*, **7**,8, e43983.

KERSTING, A.B., EFURD, D.W., FINNEGAN, D,L,, ROKOP, D.J., SMITH, D.K. AND THOMPSON, J.L. 1999 ‘Migration of plutonium in groundwater at the Nevada Test Site’, *Nature*, **397**, 56–59.

KAHRU, A. AND DUBOURGUIER, H.C. 2010 ‘From ecotoxicology to nanoecotoxicology’ *Toxicology,* **269,** 2, 105-119

KIM, D. G., HWANG, Y. H., SHIN, H. S., AND KO, S. O. 2013 ‘Deactivation of nanoscale zero-valent iron by humic acid and by retention in water’ *Environmental Technology*, **34**, 12, 1625-1635.

KIM, K. R., LEE, B. T., AND KIM, K. W. 2012b ‘Arsenic stabilization in mine tailings using nano-sized magnetite and zero valent iron with the enhancement of mobility by surface coating’, *Journal of Geochemical Exploration*, **113**, 124-129.

KIM, H. J., PHENRAT, T., TILTON, R. D., AND LOWRY, G. V. 2012a ‘Effect of kaolinite, silica fines and pH on transport of polymer-modified zero valent iron nano-particles in heterogeneous porous media’ *Journal of Colloid and Interface Science,* **370**, 1, 1-10.

KIM, J-H., TRATNYEK, P.G., AND CHANG, Y-S. 2008. ‘Rapid dechlorination of polychlorinated dibenzo-p-dioxins by bimetallic and nanosized zerovalent iron’. *Environmental Science & Technology*, **42**, 11, 4106-4112.

KIRSCHLING, T.L., GREGORY, K.B., MINKLEY, E.G., LOWRY, G.V. AND TILTON, R.G. 2010. ‘Impact of nanoscale zero valent iron on geochemistry and microbial populations in trichloroethylene contaminated aquifer materials’, *Environmental Science and Technology*, **44**, 9, 3474–3480.

KLIMKOVA, S., CERNIK, M., LACINOVA, L., FILIP, J., JANCIK, D., AND ZBORIL, R. 2011 ‘Zero-valent iron nanoparticles in treatment of acid mine water from *in situ* uranium leaching’, *Chemosphere*, **82,** 8, 1178-1184.

KUANG, Y., ZHOU, Y., CHEN, Z., MEGHARAJ, M., AND NAIDU, R. 2013 ‘Impact of Fe and Ni/Fe nanoparticles on biodegradation of phenol by the strainBacillus fusiformis (BFN) at various pH values’, *Bioresource Technology,* **136**, 588–594.

KUSTOV, L. M., FINASHINA, E. D., SHUVALOVA, E. V., TKACHENKO, O. P., AND KIRICHENKO, O. A. 2011 ‘Pd–Fe nanoparticles stabilized by chitosan derivatives for perchloroethene dechlorination’ *Environment International*, **37,** 6, 1044-1052.

LACINOVÁ, L., ČERNÍKOVÁ, M., HRABAL AND J., ČERNÍK, M. 2013 ‘In-Situ Combination of Bio and Abio Remediation of Chlorinated Ethenes’ *Ecological Chemistry and Engineering*, **20**, 463–473.

LAND QUALITY MANAGEMENT LTD (LQM) 2014 ‘NanoRem Deliverable 9.2.1 (Potential environmental risks of nanoparticle deployment)’ http://www.nanorem.eu/

LAUMANN, S., MICIĆ, V., LOWRY, G. V., AND HOFMANN, T. 2013 ‘Carbonate minerals in porous media decrease mobility of polyacrylic acid modified zero-valent iron nanoparticles used for groundwater remediation’ *Environmental Pollution*, **179**, 53-60.

LEE, C., KIM, J.Y., LEE, W.I., NELSON, K.L., YOON, J. AND SEDLAK, D.L. 2008 ‘Bactericidal effect of zero-valent iron nanoparticles on Escherichia coli’, *Environmental Science and Technology,* **42**, 13, 4927-4933.

LEE, Y., KIM, C., LEE, J., SHIN, H. AND YANG, J. 2009 ‘Characterization of nanoscale zero valent iron modified by nonionic surfactant for trichloroethylene removal in the presence of humic acid: A research note’, *Desalination and Water Treatment*, **10**, 1-3 33–38.

LEE, C.-C., LIEN, H.-L., WU, S.-C., DOONG, R.-A. AND CHAO, C.-C. 2014 Reduction of Priority Pollutants by Nanoscale Zerovalent Iron in Subsurface Environments pp 63-96 in Aquananotechnology: Global Prospects (Eds. David E. Reisner, T. Pradeep), CRC Press. ISBN 9781466512245. For info: http://www.crcpress.com/product/isbn/9781466512245

LEWINSKI, N., COLVIN, V. AND DREZEK, R. 2008 ‘Cytotoxicity of nanoparticles’, *Small*, **4**, 1, 26-49.

LI, L., FAN, M., BROWN, R.C., VAN LEEUWEN, H.J., WANG, J., WANG, W., SONG, Y. AND ZHANG, P. 2006b 'Synthesis, properties, and environmental applications of nanoscale iron-based materials: A review', *Critical Reviews in Environmental Science and Technology*, **36**, 5, 405-431.

LI, Y., LI, J., AND ZHANG, Y. 2012. 'Mechanism insights into enhanced Cr (VI) removal using nanoscale zerovalent iron supported on the pillared bentonite by macroscopic and spectroscopic studies' *Journal of Hazardous Materials*, **227**, 211-218.

LI, Y., ZHANG, Y., LI, J., SHENG, G., AND ZHENG, X. 2013 'Enhanced reduction of chlorophenols by nanoscale zerovalent iron supported on organobentonite' *Chemosphere,* **92,** 4, 368-374.

LI, X., CAO, J. AND ZHANG, W. 2008 'Stoichiometry of Cr(VI) immobilization using nanoscale zerovalent iron (nZVI): A study with high-resolution x-ray photoelectron spectroscopy (HR-XPS)', *Industrial and Engineering Chemistry Research*, **47**, 7, 2131-2139.

LI, X., ELLIOTT, D.W. AND ZHANG, W. 2006a 'Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects', *Critical Reviews in Solid State and Materials Sciences*, **31**, 4, 111-122.

LI, Z., GREDEN, K., ALVAREZ, P.J.J., GREGORY, K.B. AND LOWRY, G.V. 2010 'Adsorbed polymer and NOM limits adhesion and toxicity of nano scale zerovalent iron to *E. coli*', *Environmental Science and Technology*, **44**, 9, 3462-3467.

LIEN, H., ELLIOTT, D.W., SUN, Y. AND ZHANG, W. 2006 'Recent progress in zero-valent iron nanoparticles for groundwater remediation', *Journal of Environmental Engineering and Management*, **16**, 6, 371-380.

LIEN, H.L., AND ZHANG, W-X. 1999 'Transformation of chlorinated methanes by nanoscale iron particles', *Journal of Environmental Engineering*, **125**, 11, 1042-1047.

LIM, T. T., FENG, J., AND ZHU, B. W. 2007 'Kinetic and mechanistic examinations of reductive transformation pathways of brominated methanes with nano-scale Fe and Ni/Fe particles', *Water Research,* **41**, 4, 875-883.

LIMBACH, L.K., WICK, P., MANSER, P., GRASS, R.N., BRUININK, A. AND STARK, W.J. 2007 'Exposure of engineered nanoparticles to human lung epithelial cells: Influence of chemical composition and catalytic activity on oxidative stress', *Environmental Science and Technology*, **41**, 11, 4158-4163.

LIU, H., CHEN, T., ZOU, X., XIE, Q., QING, C., CHEN, D., AND FROST, R. L. 2013 'Removal of phosphorus using NZVI derived from reducing natural goethite' *Chemical Engineering Journal*, **234**, 80-87.

LIU, Y., PHENRAT, T. AND LOWRY, G.V. 2005 'Effect of TCE concentration and dissolved groundwater solutes on nZVI-promoted TCE dechlorination and H_2 evolution', *Environmental Science and Technology*, **41**, 22, 7881-7887.

LIU, R. AND ZHAO, D. 2007 '*In situ* immobilization of Cu(II) in soils using a new class of iron phosphate nanoparticles', *Chemosphere*, **68**, 10, 1867–1876.

LIU, T. Y., ZHAO, L., AND WANG, Z. L. 2012 'Removal of hexavalent chromium from wastewater by Fe 0-nanoparticles-chitosan composite beads: characterization, kinetics and thermodynamics' *Water Science & Technology*, **66**, 5, 1044-1051.

LIU, Y.Q. AND LOWRY, G.V. 2006 'Effect of particle age (Fe-o content) and solution pH on NZVI reactivity: H-2 evolution and TCE dechlorination'. *Environmental Science and Technology*, **40**, 19, 6085-6090.

LOWRY, G.V. AND JOHNSON, K.M. 2004 'Congener-specific dechlorination of dissolved PCBs by microscale and nanoscale zerovalent iron in a water/methanol solution' *Environmental Science and Technology*, **38**, 19, 5208-5216.

LURIA, P., PERKINS, C., AND LYONS, M. 2009. 'Health Risk Perception And Environmental Problems'. [Online] Available at: <http://www.cph.org.uk/wp-content/uploads/2012/08/health-risk-perception-and-environmental-problems--summary-report.pdf.>

MA, X., GURUNG, A., AND DENG, Y. 2013 'Phytotoxicity and uptake of nanoscale zero-valent iron (nZVI) by two plant species' *Science of the Total Environment*, **443**, 844-849.

MACÉ, C., DESROCHER, S., GHEORGHIU, F., KANE, A., PUPEZA, M., CERNIK, M., KVAPIL, P., VENKATAKRISHNAN, R. AND ZHANG, W-X. 2006 'Nanotechnology and groundwater remediation: A step forward in technology and understanding', *Remediation Journal,* **16**, 2, 23-33.

MACKENZIE, K., SCHIERZ, A., GEORGI, A. AND KOPINKE, F-D. 2008 'Colloidal activated carbon and carbo-iron – novel materials for in-situ groundwater treatment', *Global NEST Journal*, **10**, 1, 54-61.

MACHADO, S., STAWIŃSKI, W., SLONINA, P., PINTO, A. R., GROSSO, J. P., NOUWS, H. P. A., ALBERGARIA, J. T. AND DELERUE-MATOS, C. 2013 'Application of green zero-valent iron nanoparticles to the remediation of soils contaminated with ibuprofen' *Science of the Total Environment*, **461**, 323-329.

MARCHANT, G. E., SYLVESTER, D. J., & ABBOTT, K. W. (2008). Risk management principles for nanotechnology. *Nanoethics*, **2** (1), 43-60.

MIEHR, R., TRATNYEK, P.G., BANDSTRA, J.Z., SCHERER, M.M., ALOWITZ, M.J., AND BYLASKA, E.J. 2004 'Diversity of contaminant reduction reactions by zerovalent iron: role of the reductate'. *Environmental Science and Technology,* **38**,139-147.

MOORE, M.N. 2006 'Do nanoparticles present ecotoxicological risks for the health of the aquatic environment?', *Environment International*, **32**, 8, 967-976.

MÜLLER, N.C. AND NOWACK, B. 2010 *Nano Zero Valent Iron – THE Solution for Water and Soil Remediation?*, ObservatoryNANO Focus Report. [Online] Available at: <http://www.observatorynano.eu/project/filesystem/files/nZVI_final_vsObservatory.pdf>

NAJA, G., HALASZ, A., THIBOUTOT, S., AMPLEMAN, G. AND HAWARI, J. 2008 'Degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using zerovalent iron nanoparticles', *Environmental Science and Technology*, **42**, 12, 4364–4370.

NATHANAIL, C. P. BARDOS, R. P., GILLETT, A., MCCAFFREY, C., OGDEN, R., SCOTT, D., NATHANAIL, J. 2013. "SP1004 International Processes for Identification and Remediation of Contaminated Land" [Online] Available at: <http://randd.defra.gov.uk/Default.aspx?Menu=Menu&Module=More&Location=None&Completed=0&ProjectID=16289#Description>

NATHANAIL, J., BARDOS, P. AND NATHANAIL, P. 2007 *Contaminated Land Management Ready Reference,* EPP Publications/ Land Quality Press, Nottingham.

NATHANAIL, C.P. R.P. AND BARDOS, R.P. 2004 *Reclamation of Contaminated Land*, Wiley and Sons

NOVIKOV, A.P., KALMYKOV, S.N., UTSUNOMIYA, S., EWING, R.C., HORREARD, F., MERKULOV, A., CLARK, S.B., TKACHEV, V.V. AND MYASOEDOV, B.F. 2006 'Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia', *Science,* **27**, 314, 638–641.

NOWACK, B. 2008 'Pollution prevention and treatment using nanotechnology', *Nanotechnology*, **2**, 1-15.

NOWACK, B. AND BUCHELI, T.D. 2007 'Occurrence, behavior and effects of nanoparticles in the environment', Environmental Pollution, **150**, 1, 5-22.

NURMI, J.T., TRATNYEK, P.G., SARATHY, V., BAER, D.R. AND AMONETTE, J.E. 2005 'Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics', *Environmental Science and Technology*, **39**, 5, 1221-1230.

O'CARROLL, D., SLEEP, B., KROL, M., BOPARAI, H., AND KOCUR, C. 2013 'Nanoscale zero valent iron and bimetallic particles for contaminated site remediation' *Advances in Water Resources*, **51**, 104-122.

O'HARA, S., KRUG, T., QUINN, J. AND CLAUSEN, C. 2006 'Field and laboratory evaluation of the treatment of DNAPL source zones using emulsified zero-valent iron', Remediation, **16**, 2, 35-56.

OBERDÖRSTER, E., ZHU, Z., BLICKLEY, T.M., MCCLELLAN-GREEN, P. AND HAASCH, M.L. 2006 'Ecotoxicology of carbon-based engineered nanoparticles: Effects of fullerene (C-60) on aquatic organisms', *Carbon*, **44**, 6, 1112-1120.

OLIVER, L., FERBER, U., GRIMSKI, D., MILLAR, K. AND GRIMSKI, D. 2005 'The Scale and Nature of European Brownfields'. CABERNET Project paper [Online] Available at: <www.cabernet.org.uk/resourcefs/417.pdf>

OLSON, T. M. AND LEE, J.H. 2006 'Optimization of *in situ* emplacement of nano-sized FeS for permeable reactive barrier construction', *WIT Transactions on Ecology and the Environment*, **92**, 387-392.

OSTIGUY, C., SOUCY, B., LAPOINTE, G., WOODS, C., MENARD, L. AND TROTTIER, M. 2008. Health effects of nanoparticles. Second edition. IRSST Studies and Research Projects Report R-589. [Online] Available at: <http://www.irsst.qc.ca/files/documents/pubirsst/r-469.pdf>

OTTO, M., FLOYD, M. AND BAJPAI, S. 2008 'Nanotechnology for site remediation', *Remediation*, **19**, 1, 99-108.

OVAM 2006a *Injectie van (bi)metallisch nanoschaal ijzerpartikels in met chloorkoolwaterstoffen verontreinigde aquifers. Fase 1:Literatuurstudie stand van de techniek*. [Online] Available at: <http://www.ovam.be/jahia/Jahia/pid/5>

OVAM 2006b Injectie *van (bi)metallisch nanoschaal ijzerpartikels in met chloorkoolwaterstoffen verontreinigde aquifers. Fase 2:Labotesten*. [Online] Available at: <http://www.ovam.be/jahia/Jahia/pid/5>

PARBS, A. AND BIRKE, V. 2005 *State-of-the-art Report and Inventory on Already Demonstrated Innovative Remediation Technologies*, EuroDemo Report D6-2. [Online] Available at: <http://www.eurodemo.info/project-information-2/>

PAWLETT, M., RITZ, K., DOREY, R. A., ROCKS, S., RAMSDEN, J., AND HARRIS, J. A. 2013 'The impact of zero-valent iron nanoparticles upon soil microbial communities is context dependent' *Environmental Science and Pollution Research*, **20**, 2, 1041-1049.

PETERSEN, E. J., PINTO, R. A., SHI, X., AND HUANG, Q. 2012. 'Impact of size and sorption on degradation of trichloroethylene and polychlorinated biphenyls by nano-scale zerovalent iron'. *Journal of Hazardous Materials*, **243,** 73-79.

PHENRAT, T., CIHAN, A., KIM, H. J., MITAL, M., ILLANGASEKARE, T., AND LOWRY, G. V. 2010 'Transport and deposition of polymer-modified Fe^0 nanoparticles in 2-D heterogeneous porous media: Effects of particle concentration, Fe^0 content, and coatings' *Environmental Science & Technology*, **44**, 23, 9086-9093.

PHENRAT, T., FAGERLUND, F., ILLANGASEKARE, T., LOWRY, G. V., AND TILTON, R. D. 2011 'Polymer-modified Fe0 nanoparticles target entrapped NAPL in two dimensional porous media: effect of particle concentration, NAPL saturation, and injection strategy' *Environmental Science & Technology*, **45**, 14, 6102-6109.

PHENRAT, T., LIU, Y., TILTON, R.D. AND LOWRY, G.V. 2009a 'Adsorbed polyelectrolyte coatings decrease Fe^0 nanoparticle reactivity with TCE in water: conceptual model and mechanisms', *Environmental Science and Technology*, **43**, 5, 1507-1514.

PHENRAT, T., LONG, T.C. LOWRY, G.V. AND VERONESI, B. 2009b 'Partial oxidation ("aging") and surface modification decrease the toxicity of nanosized zerovalent iron', *Environmental Science and Technology*, **43**, 1, 195-200.

PHENRAT, T., SALEH, N., SIRK, K., KIM, H-J., TILTON, R.D. AND LOWRY, G.V. 2008 'Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation', *Journal of Nanoparticle Research*, **10**, 5, 795-814.

PHENRAT, T., SALEH, N., SIRK, K., TILTON, R.D. AND LOWRY, G.V. 2007 'Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions', *Environmental Science and Technology*, **41**, 1, 284-290.

PHILLIPS, D.H., VAN NOOTON, T., BASTIAENS, L., RUSSELL, M.I., DICKSON, K., PLANT, S., AHAD, J.M.E., NEWTON, T., ELLIOT, T. AND KALIN, R.M. 2010. 'Ten year performance of an zero-valent iron permeable reactive barrier installed to remediate trichloroethene' *Environmental Science and Technology*, **44,** 10, 3861-3869.

PHILLIPS, D. H., WATSON, D. B., ROH, Y., AND GU, B. 2003 Mineralogical characteristics and transformations during long-term operation of a zerovalent iron reactive barrier. *Journal of Environmental Quality*, **32,** 6, 2033-2045.

PONDER, S., DARAB, J.G., BUCHER, J., CAULDER, D., CRAIG, I., DAVIS, L., EDELSTEIN, N., LUKENS, W., NITSCHE, H., RAO, L., SHUH, D.K. AND MALLOUK, T.E. 2001 'Surface chemistry and electrochemistry of supported zerovalent iron nanoparticles in the remediation of aqueous metal contaminants', *Chemistry of Materials*, **13**, 2, 479-486.

PRAKASH, A., MCCORMICK, A.V. AND ZACHARIAH, M.R. 2005 'Tuning the reactivity of energetic nanoparticles by creation of a core− shell nanostructure', *Nano Letters*, **5**, 7, 1357-1360.

QUINN, J., ELLIOTT, D., O'HARA, S. AND BILLOW, A. 2009 'Use of Nanoscale Iron and Bimetallic Particles for Environmental Remediation: A Review of Field-Scale Applications'. In GEIGER, C.L. AND CARVALHO-KNIGHTON, K.M. (eds.) *Environmental Applications of Nanoscale and Microscale Reactive Metal Particles*, Oxford University Press, North Carolina, 263-283.

QUINN, J., GEIGER, C., CLAUSEN, C., BROOKS, K., COON, C., O'HARA, S., KRUG, T., MAJOR, D., YOON, W-S., GAVASKAR, A. AND HOLDSWORTH, T. 2005 'Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron', *Environmental Science and Technology*, **39**, 5, 1309-1318.

RAHMANI, A., GHAFFARI, H., AND SAMADI, M. 2011 'A Comparative study on arsenic (III) removal from aqueous solution using nano and micro sized zero-valent iron' *Iranian Journal of Environmental Health Science & Engineering*, **8**, 2.

RAUSCHER, H., ROEBBEN, G., AMENTA, V., SANFELIU, A. B. CALZOLAI, L. EMONS, H. GAILLARD, C., GIBSON, N., LINSINGER, T., MECH, A., PESUDO, L. Q., RASMUSSEN, K., SINTES, J. R., SOKULL-KLÜTTG, B. AND STAMM, H. 2014. 'Towards a review of the EC Recommendation for a definition of the term "nanomaterial". JRC scientific and policy reports. IN PRESS.

RAYCHOUDHURY, T., NAJA, G., AND GHOSHAL, S. 2010. 'Assessment of transport of two polyelectrolyte-stabilized zero-valent iron nanoparticles in porous media', *Journal of contaminant hydrology*, **118**,3, 143-151.

RAYCHOUDHURY, T., TUFENKJI, N., AND GHOSHAL, S. 2012. 'Aggregation and deposition kinetics of carboxymethyl cellulose-modified zero-valent iron nanoparticles in porous media'. *Water research*, **46**,6,, 1735-1744.

REDDY, K. R., AND KARRI, M. R. 2007. 'Electrokinetic delivery of nanoscale iron particles for in-situ remediation of pentachlorophenol-contaminated soils', In *Proceedings of the International 18 Symposium on Geo-Environmental Engineering for Sustainable Development*. October 2007.

REINSCH, B.C., FORSBERG, B., PENN, R.L., KIM, K.S. AND LOWRY, G.V. 2010 'Chemical transformations during aging of zerovalent iron nanoparticles in the presence of common groundwater dissolved constituents', *Environmental Science and Technology*, **44**, 9, 3455–3461.

RENN, O. AND ROCCO, M. 2006 *Nanotechnology Risk Governance, White Paper No. 2*. [Online] Available at: <http://www.irgc.org/IMG/pdf/IRGC_white_paper_2_PDF_final_version-2.pdf>

RICKERBY, D.G. AND MORRISON, M. 2007 *Report from the Workshop on Nanotechnologies for Environmental remediation*. Joint Research Centre, Ispra, Italy, 16-17 April 2007. [Online] Available at: <http://www.nanowerk.com/nanotechnology/reports/reportpdf/report101.pdf>

RODUNER, E. 2006 'Size Matters: Why Nanomaterials are Different', *Chemical Society Reviews,* **35**, 583-59.

ROYAL COMMISSION ON ENVIRONMENTAL POLLUTION (RCEP) 2008 'Novel Materials in the Environment: The Case of Nanotechnology' London: Royal Commission on Environmental Pollution. [Online] Available at: <http://www.officialdocuments.gov.uk/document/cm74/7468/7468.pdf [accessed November 2010]>

ROYAL SOCIETY AND ROYAL ACADEMY OF ENGINEERING (RS/RAE) 2004 'Nanoscience and nanotechnologies:opportunities and uncertainties' [Online] Available at: <https://www.raeng.org.uk/news/publications/list/reports/Nanoscience_nanotechnologies.pdf.>

SAAD, R., THIBOUTOT, S., AMPLEMAN, G., DASHAN, W., AND HAWARI, J. 2010 'Degradation of trinitroglycerin (TNG) using zero-valent iron nanoparticles/nanosilica SBA-15 composite (ZVINs/SBA-15)', *Chemosphere*, **81,** 7, 853-858.

SACCÀ, M. L., FAJARDO, C., NANDE, M., AND MARTÍN, M. 2013a 'Effects of Nano Zero-Valent Iron on Klebsiella oxytoca and Stress Response', *Microbial Ecology*, **66**, 4, 806-812.

SACCÀ, M. L., FAJARDO, C., COSTA, G., LOBO, C., NANDE, M., AND MARTIN, M. 2013b 'Integrating classical and molecular approaches to evaluate the impact of nanosized zero-valent iron (nZVI) on soil organisms', *Chemosphere,* In Press.

SAEEDI, M., LI, L.Y, AND GHAREHTAPEH, M. A. 2013 'Effect of Alternative Electrolytes on Enhanced Electrokinetic Remediation of Hexavalent Chromium in Clayey Soil', *International Journal of Environmental Research*, **7**, 1, 39-50.

SALEH, N., PHENRAT, T., SIRK, K., DUFOUR, B., OK, J., SARBU, T., MATYJASZEWSKI, K., TILTON, R.D. AND LOWRY, G.V. 2005 'Adsorbed triblock copolymers deliver reactive iron nanoparticles to the oil/water interface', *Nano Letters*, **5**, 12, 2489-2494.

SALEH, N., SIRK, K., LIU, Y, PHENRAT, T., DUFOUR, B., MATYJASZEWSKI, K., TILTON, R.D. AND LOWRY, G.V. 2007 'Surface modifications enhance nanoiron transport and NAPL targeting in saturated porous media', *Environmental Engineering Science*, **24**, 1, 45-57.

SALEH, N., KIM, H-J., PHENRAT, T., MATYJASZEWSKI, K., TILTON, R.D. AND LOWRY, G.V. 2008 'Ionic strength and composition affect the mobility of surface-modified Fe^0 nanoparticles in water -saturated sand columns', *Environmental Science & Technology*, **42**,9, 3349-3355

SATAPANAJARU, T., ANURAKPONGSATORN, P., PENGTHAMKEERATI, P., AND BOPARAI, H. 2008 'Remediation of atrazine-contaminated soil and water by nano zerovalent iron', *Water, Air, and Soil Pollution*, **192**,1-4, 349-359.

SCHRICK, B., BLOUGH, J. L., JONES, A. D., AND MALLOUK, T. E. 2002 ‘Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoparticles’. *Chemistry of Materials*, **14**,12, 5140-5147.

SCHRICK, B., HYDUTSKY, B. W., BLOUGH, J. L., AND MALLOUK, T. E. 2004 ‘Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater’. *Chemistry of Materials*, **16**, 11, 2187-2193.

SCHURING, J.R. 2002 ‘Fracturing Technologies to Enhance Remediation’, Technology Evaluation Report TE-02-02. GWRTAC Ground-Water Remediation Technologies Analysis Center, Pittsburg PA.

SCIENCEWISE 2013 ‘Public views on advanced materials: nanomaterials and grapheme’ Version 1.3 March 2013 [Online] Available at: <http://www.sciencewise-erc.org.uk/cms/public-views-on-advanced-materials-nanomaterials-and-graphene/>

SCOTT, T. B., POPESCU, I. C., CRANE, R. A., AND NOUBACTEP, C. 2011 ‘Nano-scale metallic iron for the treatment of solutions containing multiple inorganic contaminants’, *Journal of Hazardous Materials*, **186**, 1, 280-287.

SEO, H., SUN, E., AND ROH, Y. 2013 ‘Remediation of Chromium-Contaminated Water Using Biogenic Nano-Sized Materials and Metal-Reducing Bacteria’, *Journal of Nanoscience and Nanotechnology*, **13**,6, 4405-4408.

SHEN, X., ZHAO, L., DING, Y., LIU, B., ZENG, H., ZHONG, L., AND LI, X. 2011 ‘Foam, a promising vehicle to deliver nanoparticles for vadose zone remediation’, *Journal of Hazardous Materials* **186**, 2, 1773-1780.

SHI, L. N., LIN, Y. M., ZHANG, X., AND CHEN, Z. L. 2011 ‘Synthesis, characterization and kinetics of bentonite supported nZVI for the removal of Cr (VI) from aqueous solution’, *Chemical Engineering Journal*, **171,** 2, 612-617.

SHI, J., YI, S., HE, H., LONG, C., AND LI, A. 2013 ‘Preparation of nanoscale zero-valent iron supported on chelating resin with nitrogen donor atoms for simultaneous reduction of Pb^{2+} and Pb^{3+}’, *Chemical Engineering Journal*, **230,** 166-171.

SHIH, Y., CHEN, Y., CHEN, M., TAI Y. AND TSO, C. 2009 ‘Dechlorination of hexachlorobenzene by using nanoscale Fe and nanoscale Pd/Fe bimetallic particles’, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **332**, 2-3, 84–89.

SINGH, S. P., BOSE, P., GUHA, S., GURJAR, S. K., AND BHALEKAR, S. 2013 ‘Impact of addition of amendments on the degradation of DDT and its residues partitioned on soil’, *Chemosphere*, **92**, 7, 811-820.

SINGH, S. P., RAHMAN, M. F., MURTY, U. S. N., MAHBOOB, M., AND GROVER, P. 2012 ‘Comparative study of genotoxicity and tissue distribution of nano and micron sized iron oxide in rats after acute oral treatment’, *Toxicology and Applied Pharmacology*, **266**, 1, 56-66.

SINGH, R., SINGH, A., MISRA, V., AND SINGH, R. P. 2011 ‘Degradation of Lindane contaminated soil using zero-valent iron nanoparticles’, *Journal of Biomedical Nanotechnology* **7**, 1, 175-176.

SIRK, K.M., SALEH, N.B., PHENRAT, T., KIM, H-J., DUFOUR, B., OK, J., GOLAS, P.L., MATYJASZEWSKI, K., LOWRY, G.V. AND TILTON, R.D. 2009 ‘Effect of adsorbed polyelectrolytes on nanoscale zero valent iron particle attachment to soil surface models’, *Environmental Science and Technology*, **43**, 10, 3803-3808.

SISKOVA, K., TUCEK, J., MACHALA, L., OTYEPKOVA, E., FILIP, J., SAFAROVA, K., PECHOUSEK, J. AND ZBORIL, R. 2012 ‘Air-stable nZVI formation mediated by glutamic acid: solid-state storable material exhibiting 2D chain morphology and high reactivity in aqueous environment’, *Journal of Nanoparticle Research*, **14**,4, 1-13.

SLOVIC, P. 1987. ‘Perception of risk’ *Science*, **236**, 280-285.

SOHN, K., KANG, S.W., AHN, S., WOO, M. AND YANG, S. 2006 ‘Fe(0) nanoparticles for nitrate reduction: Stability, reactivity, and transformation’, *Environmental Science and Technology*, **40**, 17, 5514-5519.

SONG, H. AND CARRAWAY, E.R. 2005 ‘Reduction of chlorinated ethanes by nanosized zero-valent iron: Kinetics, pathways, and effects of reaction conditions’, *Environmental Science and Technology*, **39**, 16, 6237-6245.

SPOSITO, G. 1989 *The Chemistry of Soils*. Oxford University Press, New York, 277.

SU, C. PULS, R. W., KRUG, T. A., WATLING, M. T., O’HARA, S. K., QUINN, J.W. AND RUIZ, N.E. 2012 ‘A two and half-year-performance evaluation of a field test on treatment of source zone tetrachloroethene and its chlorinated daughter products using emulsified zero valent iron nanoparticles’, *Water Research*, **46**, 5071-5084.

SU, C., PULS, R. W., KRUG, T. A., WATLING, M. T., O'HARA, S. K., QUINN, J. W., AND RUIZ, N. E. 2013 'Travel Distance and Transformation of Injected Emulsified Zerovalent Iron Nanoparticles in the Subsurface During Two and Half Years' *Water Research*, **47**, 4095-4106.

SUNKARA, B., ZHAN, J., HE, J., MCPHERSON, G. L., PIRINGER, G., AND JOHN, V. T. 2010 'Nanoscale zerovalent iron supported on uniform carbon microspheres for the *in situ* remediation of chlorinated hydrocarbons' *ACS Applied Materials & Interfaces*, **2,** 10, 2854-2862.

TAGHAVY, A., COSTANZA, J., PENNELL, K. D., AND ABRIOLA, L. M. 2010 'Effectiveness of nanoscale zero-valent iron for treatment of a PCE–DNAPL source zone', *Journal of Contaminant Hydrology***, 118**, 3, 128-142.

TANBOONCHUY, V., HSU, J. C., GRISDANURAK, N., AND LIAO, C. H. 2011 'Impact of selected solution factors on arsenate and arsenite removal by nanoiron particles', *Environmental Science and Pollution Research*, **18**, 6, 857-864.

TANDON, P. K., SHUKLA, R. C., AND SINGH, S. B. 2013 'Removal of Arsenic (III) from Water with Clay-Supported Zerovalent Iron Nanoparticles Synthesized with the Help of Tea Liquor', *Industrial & Engineering Chemistry Research*, **52**, 30, 10052-10058.

TEUTSCH, G., RÜGNER, H., ZAMFIRESCU, D., FINKEL, M., AND BITTENS, M. 2001 'Source remediation vs. plume management: critical factors affecting cost-efficiency', *Land Contamination and Reclamation*, **9**, 1, 129-140.

THOMPSON, J. M., CHISHOLM, B. J., AND BEZBARUAH, A. N. 2010 'Reductive dechlorination of chloroacetanilide herbicide (alachlor) using zero-valent iron nanoparticles', *Environmental Engineering Science*, **27,** 3, 227-232.

TIEHM, A., KRAßNITZER, S., KOLTYPIN, Y. AND GEDANKEN, A. 2009 'Chloroethene dehalogenation with ultrasonically produced air-stable nano iron', *Ultrasonics Sonochemistry*, **16**, 5, 617–621.

TILSTON, E. L., COLLINS, C. D., MITCHELL, G. R., PRINCIVALLE, J., AND SHAW, L. J. 2013 'Nanoscale zerovalent iron alters soil bacterial community structure and inhibits chloroaromatic biodegradation potential in Aroclor 1242-contaminated soil', *Environmental Pollution*, **173**, 38-46.

TIRAFERRI, A., CHEN, K.L., SETHI, R. AND ELIMELECH, M. 2008 'Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum', *Journal of Colloid and Interface Science*, **324**, 1-2, 71-79.

TIRAFERRI, A. AND SETHI, R. 2009 'Enhanced transport of zerovalent iron nanoparticles in saturated porous media by guar gum', *Journal of Nanoparticle Research*, **11**, 3, 635-645.

TOSCO, T., AND SETHI, R. 2010. 'Transport of non-Newtonian suspensions of highly concentrated micro-and nanoscale iron particles in porous media: a modeling approach', *Environmental Science & Technology,* **44**, 23, 9062-9068.

TRATNYEK, P.G. AND JOHNSON, R.L. 2006 'Nanotechnologies for environmental cleanup', *Nano Today*, **1**, 2, 44-48.

US ENIVRONMENTAL PROTECTION ACENCY 2010 'Ground Water Remedy Optimization Progress Report' [Online] Available at: <http://www.epa.gov/superfund/cleanup/postconstruction/pdfs/0809_optimization_report.pdf>

US ENVIRONMENTAL PROTECTION AGENCY (US EPA) 2009 'Nanoparticle Field Studies Supplemental Material': DOI (http://dx.doi.org/), record: 10.1289/ehp.0900793.S1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA) 2009 'Impacts of DNAPL source treatment: experimental and modelling assessment of the benefits of partial DNAPL source removal' EPA 600/R-09/096.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA) 2008 'Selected Sites Using or Testing Nanoparticles for Remediation', Office of Solid Waste and Emergency Response (OSWER Programme) Summary Sheet. [Online] Available at: < http://epa.gov/tio/download/remed/nano-site-list.pdf >

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA) 2005 'Nanotechnology for site remediation Fact Sheet'. [Online] Available at: <http://epa.gov/ncer/publications/workshop/pdf/10_20_05_nanosummary.pdf>

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA). 2003 'Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation: Volume 1 –

Performance Evaluations at Two Sites' Office of Research and Development, Cincinnati. Report EPA/600/R-03/045a.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA) 2007 'Nanotechnology White Paper' [Online] Available at: <http://www.epa.gov/osainter/pdfs/nanotech/epa-nanotechnology-whitepaper-0207.pdf.>

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (US EPA)2006 'In-Situ Chemical Oxidation' [Online] Available at: <http://www.epa.gov/ada/gw/pdfs/insituchemicaloxidation_engineering_issue.pdf>

UYTTEBROEK, M., BAILLIEUL, H., VERMEIREN, N., SCHOLIERS, R., DEVLEESCHAUWER, P., GEMOETS, J. AND BASTIAENS, L. 2010 'In Situ Remediation of a Chlorinated Ethene Contaminated Source Zone by Injection of Zero-valent Iron: From Lab to Field Scale', *Proceedings of the 4th International Symposium on Permeable Reactive Barriers & Reactive Zones*, July, 2010.

VALKO, M., MORRIS, H. AND CRONIN, M.T.D. 2005 'Metals, toxicity and oxidative stress', *Current Medicinal Chemistry*, **12**, 10, 1161-1208.

VEGTER, J., J. LOWE, AND H. KASAMAS (Eds.) 2002 'Sustainable Management of Contaminated Land: An Overview' Report Austrian Federal Environment Agency, 2002 on behalf of CLARINET, Spittelauer Lände 5, A-1090 Wien, Austria. [Online] Available at: <http://www.commonforum.eu/publications_clarinet.asp>

VIJGEN, J. 2006. 'The legacy of lindane HCH isomer production', *Main Report, IHPA*, Holte, January. [Online] Available at: <http://www.pops.int/documents/meetings/poprc/request/Comments_2006/IHPAAnnexes.pdf>

VIKESLAND, P.J., KLAUSEN, J., ZIMMERMANN, H., ROBERTS, A.L. AND BALL, W.P. 2003. 'Longevity of granular iron in groundwater treatment processes: changes in solute transport properties over time', *Journal of Contaminant Hydrology*, **64**, 1-2, 3-33.

VILKS, P., FROST, L.H. AND BACHINSKI, D.B. 1997 'Field-scale colloid migration experiments in a granite fracture', *Journal of Contaminant Hydrology*, **26**, 203–214.

WAITE, T.D., SCHAFER, A.I., FANE, A.G. AND HEUER, A. 1999 'Colloidal fouling of ultrafiltration membranes: impact of aggregate structure and size', *Journal of Colloid and Interface Science*, **212**, 264–274.

WALLACE, R. 2009. Report of the NICOLE Workshop 'Sustainable Remediation – A Solution to an Unsustainable Past?' [Online] Available at: <http://www.nicole.org/documents/DocumentList.aspx?l=1&w=n>

WAN, J., WAN, J., MA, Y., HUANG, M., WANG, Y., AND REN, R. 2013 'Reactivity characteristics of SiO2 coated Zero valent iron nanoparticles for 2, 4-dichlorophenol degradation', *Chemical Engineering Journal*, **221**, 300-307.

WANG, Q., JEONG, S. W., AND CHOI, H. 2012. 'Removal of trichloroethylene DNAPL trapped in porous media using nanoscale zerovalent iron and bimetallic nanoparticles: Direct observation and quantification', *Journal of Hazardous Materials*, **213**, 299-310.

WANG, C. B., AND ZHANG, W. X. 1997 'Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs', *Environmental Science & Technology*, **31,**7, 2154-2156.

WANG, W., ZHOU, M., JIN, Z. AND LI, T. 2010 'Reactivity characteristics of poly(methyl methacrylate) coated nanoscale iron particles for trichloroethylene remediation', *Journal of Hazardous Materials*, **173**, 1-3, 724–730.

WATLINGTON, K. 2005 'Emerging Nanotechnologies for Site Remediation and Wastewater Treatment', Report for United States Environmental Protection Agency. [Online] Available at: <http://www.clu-in.org/download/studentpapers/K_Watlington_Nanotech.pdf>)

WEI, Y. T., WU, S. C., CHOU, C. M., CHE, C. H., TSAI, S. M., AND LIEN, H. L. 2010 'Influence of nanoscale zero-valent iron on geochemical properties of groundwater and vinyl chloride degradation: A field case study' *Water Research*, **44,** 1, 131-140.

WIESNER, M.R., LOWRY, G.V., ALVAREZ, P., DIONYSIOU, D. AND BISWAS, P. 2006 'Assessing the risks of manufactured nanomaterials', *Environmental Science and Technology*, **40**, 14, 4336-4345.

WIGGINTON, N. S., HAUS, K. L. AND HOCHELLA, M. F. Jr. 2007 'Aquatic environmental nanoparticles', *Journal of Environmental Monitoring*, **9**, 12, 1306.

WU, P., LI, S., JU, L., ZHU, N., WU, J., LI, P., AND DANG, Z. 2012 'Mechanism of the reduction of hexavalent chromium by organo-montmorillonite supported iron nanoparticles' *Journal of Hazardous Materials*, **219**, 283-288.

WU, D., SHEN, Y., DING, A., QIU, M., YANG, Q., AND ZHENG, S. 2013. 'Phosphate removal from aqueous solutions by nanoscale zero-valent iron', *Environmental Technology*, **34**, 18, 2663-2669.

XIAO, R., AND WAZNE, M. 2012 'Assessment of aged biodegradable polymer-coated nano-zero-valent iron for degradation of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX)', *Journal of Chemical Technology and Biotechnology,* **88**, 4, 711-718.

XIE, Y., AND CWIERTNY, D. M. 2013 'Chlorinated solvent transformation by palladized zero-valent iron: Mechanistic insights from reductant loading studies and solvent kinetic isotope effects', *Environmental Science & Technology,* **47**, 14, 7940-7948.

XIE, Y., AND CWIERTNY, D. M. 2012 'Influence of anionic cosolutes and pH on nanoscale zerovalent iron longevity: time scales and mechanisms of reactivity loss toward 1, 1, 1, 2-tetrachloroethane and Cr (VI)', *Environmental Science & Technology*, **46,** 15, 8365-8373.

XIE, L. AND SHANG, C. 2005 'Role of humic acid and quinine model compounds in bromate reduction by zerovalent iron', *Environmental Science and Technology*, **39**, 4, 1092-1100.

XIU, Z., JIN, Z., LI, T., MAHENDRA, S., LOWRY, G.V. AND ALVAREZ, P.J.J. 2010 'Effects of nano-scale zero-valent iron particles on a mixed culture dechlorinating trichloroethylene', *Bioresource Technology*, **101**, 4, 1141–1146.

XU, J., TAN, L., BAIG, S. A., WU, D., LV, X., AND XU, X. 2013 'Dechlorination of 2, 4-dichlorophenol by nanoscale magnetic Pd/Fe particles: Effects of pH, temperature, common dissolved ions and humic acid' *Chemical Engineering Journal*, **231**, 26-35.

XU, Y. AND ZHANG, W-X. 2000 'Subcolloidal Fe/Ag particles for reductive dehalogenation of chlorinated benzenes', *Industrial and Engineering Chemistry Research*, **39**, 7, 2238-2244.

YAN, W., HERZING, A.A., LI, X., KIELY, C.J. AND ZHANG, W. 2010 'Structural evolution of Pd-doped nanoscale zero-valent iron (nZVI) in aqueous media and implications for particle aging and reactivity', *Environmental Science and Technology*, **44**, 11, 4288-4294.

YAN, M. Y., PANG, Z. H., LI, X. M., CHEN, J. Y., AND LUO, J. 2013. [Research on removal of tetrabromobisphenol A from synthetic wastewater by nanoscale zero valent iron supported on organobentonite]. *Huanjing Kexue [Environmental Science],* **34,** 6, 2249-2255.

YIN, K., LO, I., DONG, H., RAO, P., AND MAK, M. S. 2012 'Lab-scale simulation of the fate and transport of nano zero-valent iron in subsurface environments: Aggregation, sedimentation, and contaminant desorption', *Journal of Hazardous Materials*, **227**, 118-125.

ZHANG, W. 2003 'Nanoscale iron particles for environmental remediation: An overview', *Journal of Nanoparticle Research*, **5**, 323-332.

ZHANG, Z., CISSOKOA, N., WO, J. AND XU, X. 2009 'Factors influencing the dechlorination of 2,4-dichlorophenol by Ni–Fe nanoparticles in the presence of humic acid', *Journal of Hazardous Materials*, **165**, 1-3, 78–86.

ZHANG, Y., LI, Y., AND ZHENG, X. 2011 'Removal of atrazine by nanoscale zero valent iron supported on organobentonite' *Science of the Total Environment*, **409**,3, 625-630.

ZHANG, X., LIN, S., LU, X. Q., AND CHEN, Z. L. 2010 'Removal of Pb (II) from water using synthesized kaolin supported nanoscale zero-valent iron', *Chemical Engineering Journal*, **163**, 3, 243-248.

ZHANG, Z., WO, J-J., CISSOKO, N. AND XU, X-H. 2008 'Kinetics of 2,4-dichlorophenol dechlorination by Pd-Fe bimetallic nanoparticles in the presence of humic acid', *Journal of Zhejiang University Science A*, **9**, 1, 118-124.

ZHAO, Z.S., LIU, J.F., TAI, C., ZHOU, Q.F., HU, J.T. AND JIANG, G.B. 2008 'Rapid decolorization of water soluble azo-dyes by nanosized zero-valent iron immobilized on the exchange resin', *Science in China Series B: Chemistry*, **51**, 2, 186-192.

ZHOU, H., HAN, J., BAIG, S. A., AND XU, X. 2011 'Dechlorination of 2,4-dichlorophenoxyacetic acid by sodium carboxymethyl cellulose-stabilized Pd/Fe nanoparticles', *Journal of Hazardous Materials*, **198**, 7-12.

ZHU, B-W. AND LIM, T-T. 2007 'Catalytic reduction of chlorobenzenes with Pd/Fe nanoparticles: Reactive sites, catalyst stability, particle aging, and regeneration', *Environmental Science and Technology*, **41**, 21, 7523-7529.

ZHU B-W, LIM T-T, AND FENG J. 2006 ‘Reductive dechlorination of 1,2,4-trichlorobenzene with palladized nanoscale Fe^0 particles supported on chitosan and silica’, *Chemosphere*, **65**, 1137-1143.

ZHU, B-W., LIM, T-T. AND FENG, J. 2008 ‘Influences of amphiphiles on dechlorination of a trichlorobenzene by nanoscale Pd/Fe: Adsorption, reaction kinetics, and interfacial interactions’, *Environmental Science and Technology*, **42**, 12, 4513-4519.

ZHU, K., SUN, C., CHEN, H., BAIG, S. A., SHENG, T., AND XU, X. 2013 ‘Enhanced catalytic hydrodechlorination of 2, 4-dichlorophenoxyacetic acid by nanoscale zero valent iron with electrochemical technique using a palladium/nickel foam electrode’, *Chemical Engineering Journal,* **223**, 192-199

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.