

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

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WP9: Dissemination, Dialogue with Stakeholders and Exploitation

## DL9.2 Final Exploitation Strategy, Risk Benefit Analysis and Standardisation Status

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#### **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 Seventh Framework Programme. NanoRem focuses on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation of polluted soil and groundwater.

This report provides an overview of NanoRem WP9 outputs. The overall objective of WP9 is to facilitate dissemination, dialogue and exploitation, transmitting the results of NanoRem widely amongst user communities. The work outlined in this report had the aim of developing an understanding of the "value proposition" (the overall promise of value to be delivered) for the nanoparticles (NPs) tested by the NanoRem project for remediation in terms of a risk-benefit appraisal of its use given the current state of knowledge, and so understanding their markets and how they might best be exploited in an overarching way<sup>1</sup>. Primarily this appraisal relates to iron based NPs, for example variants of nanoscale zero valent iron (nZVI), since these are the particles that have been deployed in the field to date and have the greatest evidence base from which to draw conclusions. Hence these are the particles that are currently being exploited or are most market-ready. Other NanoRem NPs tested in the lab are mentioned but not explored in detail.

Nanoremediation may offer notable advantages in some remediation applications for example their relative speed of action and potential applicability to source term problems. These benefits are site specific and niche rather than representing some kind of over-arching step change in remediation capabilities, although this over-arching potential may remain a possibility, for example treatment of recalcitrant problem compounds such as fuel oxygenates. The principal constraints to these opportunities remain perceived treatment costs and availability of cost and performance data from "real" applications, as opposed to pilot deployments in the field. Nonetheless, NanoRem has achieved a major shift in the technical discussion of nanoremediation across many practitioners in the international contaminated land management market, in that it is now seen as a viable option, albeit it at the "early adoption" stage, rather than being seen as an emerging approach of fringe interest. There has always been a minority interest in the technology, but NanoRem has succeeded in making it worthy of consideration by the majority of contaminated land remediation service providers.

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

NanoRem has demonstrated and improved the market readiness of a number of NPs and provides a tool box containing application guidance, safety datasheets and tools for them, making available field

<sup>&</sup>lt;sup>1</sup> Specific business and exploitation plans for individual nanoremediation products are outside the scope of DL9.2



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scale deployment test outcomes in a series of independently peer reviewed technical bulletins. NanoRem also shown that nanoremediation can be deployed in a targeted way and has substantive evidence that the ecological risks of NP deployment in the subsurface have been greatly overstated. Indeed, the NanoRem project has developed a range of supporting deployment risk assessment and sustainability assessment tools to ensure that nanoremediation is safe, effective and sustainable, with a level of scrutiny that far exceeds that which has been required for many of the subsurface amendments required to initiate competitor technologies such as in situ bioremediation or in situ chemical reduction using conventional reducing agents such as micro scale iron or sodium dithionite.

Based on NanoRem's work the main selling points for nanoremediation are:

- Increasing regulatory confidence, facilitated in large part by NanoRem
- Broad source and pathway management applications
- Rapid effectiveness compared with in situ biological remediation (ISBR) and conventional approaches to in situ chemical reduction (ISCR)
- Resilient to conditions inhibitory to ISBR and can facilitate ISBR / Synergistic with ISBR and ISCR
- Portable and more rapidly deployed compared to options like pump and treat
- Reduced risk of taint of sensitive aquifers
- Ecological and aquifer impacts now relatively well understood compared to ISCR and ISBR
- Rapid initiation of treatment by nZVI can also support faster initiation of ISBR.

However, several substantial market barriers remain: productising NPs and their deployment so that it is no longer so bespoke, the perceived cost of nanoremediation and increasing the number of well documented commercial deployments of nanoremediation. These represent the major gaps remaining after the conclusion of NanoRem, which, to some extent remain a "work in progress".

Many variants of nanoremediation are viable remediation options for niche applications in many European jurisdictions. However, market inertia remains owing to a lack of cost and performance reporting or real, practical deployments of nanoremediation at scale. Market inertia also persists because of concern over costs and concern over risks of an additional higher level of regulatory scrutiny compared with more regularly used alternatives. Hence, for ongoing development the following areas of effort are suggested.

- Continuing productisation of nanoremediation technologies to make them more easily deployable and with less effort.
- Development of nanoremediation alternatives with a more competitive pricing (for example via integrated approaches such as linkage to use of micro-scale iron and/or ISBR).
- Providing information that is packaged in a way that it can readily support nanoremediation deployment, building on the information already consolidated in the NanoRem toolbox.

In the medium term there continues to be an interest in the possibility of nanoremediation addressing recalcitrant contaminants or emerging contaminants, or contaminants seen both as emerging and recalcitrant. There is a large body of research evidence related to nanoremediation for its current niche applications (chlorinated solvents and heavy metals). Future research and innovation could usefully address nanoremediation for dealing with emerging / recalcitrant contaminants.



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#### 1 Introduction

#### 1.1 Nanoremediation status at the beginning of the NanoRem project

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

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

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

The first documented field trial of nZVI, in 2000, involved treatment of trichloroethylene in ground-water at a manufacturing site in Trenton, New Jersey, USA (Elliott and Zhang, 2001). Several commentators anticipated that nZVI technology would take off rapidly because of its perceived benefits such as rapid and complete contaminant degradation. In 2007, a European report forecast that the 2010 world market for environmental nanotechnologies would be around \$6 billion (Rickerby and Morrison 2007). In practice, this market was not achieved. However, subsequent uptake of the technology has been relatively slow compared to other contemporary process based technologies. At the time of the project proposal inception Bardos *et al.* (2011) identified just 58 projects documented worldwide at pilot or full scale. The use of nZVI in remediation in practice was largely a niche application for chlorinated solvents in aquifers, competing with more established techniques such as *in situ* bioremediation, chemical reduction and granular ZVI (e.g. in permeable reactive barriers). The limited adoption of nZVI was linked in this report to uncertainty over the balance of benefits versus risks from NP use in remediation and a lack of well documented / validated field scale deployments.



Dread<sup>2</sup> 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 nanoremediation compared with other technologies. More specific regulatory concerns existed 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 were considered to be poorly understood, precautionary and conservative regulatory positions were taken in a number of countries (Read *et al.* 2015). For example, there has been a voluntary moratorium on the release of engineered NPs in the UK, in response to a Royal Society/Royal Academy of Engineering report (Anon. 2012, RS/RAE 2004).

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

#### 1.2 The NanoRem project

NanoRem was a research project, funded through the European Commission's Framework 7 research programme. The NanoRem project focused on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of NPs, market demand, overall sustainability, and stakeholder perceptions. The project was designed to unlock the potential of nanoremediation processes from laboratory scale to end user applications and to support both the appropriate use of nanotechnology in restoring land and water resources and the development of the knowledge based economy at a world leading level for the benefit of a wide range of users in the EU environmental sector (CL:AIRE 2016A).

The NanoRem consortium was multidisciplinary, cross-sectoral and transnational. It included 29 partners from 13 countries organised in 11 work packages. The consortium included 19 of the leading nanoremediation research groups in the EU, nine industry and service providers (seven of which were SMEs) and one organisation with policy and regulatory interests. The consortium was coordinated by the VEGAS team (Research Facility for Subsurface Remediation) from the University of Stuttgart in Germany.

The project comprised a number of Work Packages (WPs) organised on three broad groupings (as shown in Figure 1, below):

• The *Design and Production Group* comprised two work packages (WP2 and WP3) to facilitate the intense focus on different NPs and their corresponding production and application strengths.

<sup>&</sup>lt;sup>2</sup> To dread is to anticipate with great apprehension or fear.



- The *Performance Group* was established to bridge the gap from production to application (WP4-WP7), to work closely together to ascertain potentials and limitations of NPs, and to extend the limits of economic and ecological NP application.
- The Application and Dissemination Group was responsible for successfully transferring the technology to the end-user. This comprises the proof of concept in large scale indoor experiments (WP8) and the demonstration at a number of pilot sites (i.e. field tests, WP10), risk assessment, sustainability and lifecycle assessment considerations (WP8 and WP9).

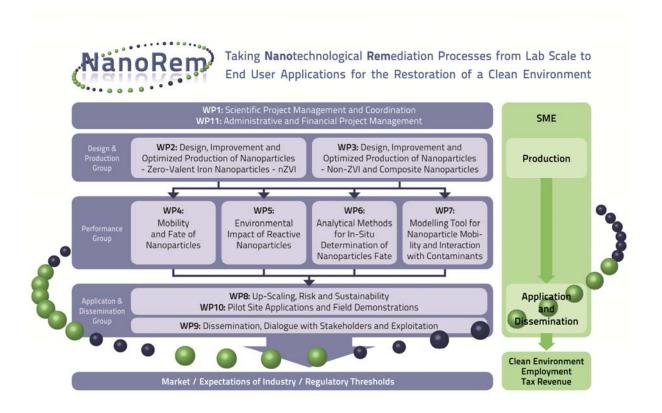


Figure 1: NanoRem Project Overview

#### 1.3 General stakeholder opinions: risks, sustainability and markets

The way in which a new technology is framed influences public perception. This is one of the factors determining why some new technologies become the focus of much public concern, while others are adopted without much attention (Read *et al.* 2015). The NanoRem project supported dialogue and engagement with various European stakeholders in order to explore consensus about appropriate uses of nanoremediation, understand its environmental risk-benefit, market demand, overall sustainability and stakeholder perceptions.

NanoRem held two elicitation workshops as a part of the stakeholder engagement and dialogue. The first workshop was held in Nottingham in July 2013 and included key international stakeholders (including experts from the technical WPs of NanoRem, members of PAG and delegates from as far afield as the USA and Australia). The workshop developed the conceptual model of NPs moving in the saturated zone and discussed likely transport, fate and toxicity characteristics of the NanoRem NPs, in order to evaluate the potential environmental risks of NP deployment. (The Nottingham



workshop is summarised in Annex 2). The second workshop was organised in Oslo in December 2014. It focused on collecting opinions from a range of stakeholders on key sustainability issues and ethical concerns as well as market development opportunities in the medium to longer term related to nanoremediation (for a summary of Oslo workshop see Annex 2 and Tomkiv *et al.* 2015). This chapter will summarise general stakeholder opinions on risk, sustainability and markets, which were gathered during these workshops.

The aims of the NanoRem project can only be achieved with a comprehensive understanding of the environmental risk-benefit balance for the use of NPs. One of the main aspects to address – according to the first workshop – is the issue of 'renegade' NPs; those, which are injected into the groundwater, but either do not reach intended treatment area or pass through it. In this context, the risk is driven by where NPs get to (transport); what happens to them (fate); and the potency of with which they can harm human health or specific environmental receptors (toxicity) or pollute control waters. These aspects were discussed in detail during the first workshop. The workshop participants agreed that NPs were unlikely to penetrate into the aquifer more than a few metres from the point of injection and were likely to interact with the aquifer matrix, groundwater and each other to rapidly lose mobility. There is a potential for the NanoRem NPs to be toxic, but they would be substantially less potent than nano-silver. A pre-deployment risk assessment protocol was developed based on developing a conceptual site model (CSM) with the NPs as the source term. This CSM for NPs is separate to the CSM used to describe the contamination problem at the site. The pre deployment risk assessment protocol has been updated taking account of the results of the NanoRem field trials and other experiments, for details see DL8.2 (Braun et al. 2016).

The outcomes of the first workshop, supported with evidence from the literature, formed the basis for a simple and conservative protocol for use during NanoRem field trials to control the risk posed by NP deployment and to reassure regulators that trials would be safe.

The discussions on sustainability, as part of the second workshop, revealed a need for a broader perspective and more attention to the relationship between environmental, social and economic factors. They also showed that there is little difference between nanoremediation and other technologies when the generic sustainability issues are considered. Uncertainties in risks and benefits related to the use of nanoremediation technology were found to be the most important factor that will influence its future development. Additional challenges include reduction of production costs for the different NPs and increasing the lifetime of the product in order to justify these costs. It is also important to enhance the transport mobility of the particles in the subsurface, identify possible synergies with other *in situ* remediation techniques, and establish appropriate methods to determine the environmental fate of particles. The findings of the workshop were used to frame retrospective sustainability assessments for NanoRem trial sites.

NanoRem has applied a "scenario" approach to give insights into the diversity of factors that potentially influence the future development of the nanoremediation market system - including its institutional setting. Dialogue with stakeholders has been a crucial step in the scenario development process. Their cross-sectorial and transdisciplinary expertise was gathered to identify and evaluate factors that are likely to drive or inhibit the development of the nanoremediation market.

The expert stakeholders discussed not only factors influencing the market development, but also the relationship between them. A factor can be active or passive depending on whether it is more likely



to influence other factors or get influences by them. According to results from Oslo workshop, the most active factors that would be expected to determine development of the nanoremediation market were science-policy-interface and availability of validated information on NP application potential. These factors were confirmed in two focus group events, which took place in Berlin in March 2015 and in London in July 2016. Both events brought together regulatory, industry and academic expert stakeholders interested in NP-enhanced remediation (more detailed explanation of the Nano-Rem market analysis can be found in Chapter 5).

## 1.4 Overall project achievements in brief (bench marked against opinions from Nottingham and Oslo)

The overall aim of the NanoRem project was to demonstrate that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater. Six project goals were identified at the project outset. These are listed below along with brief text describing how these goals were met.

## 1) Identify the most appropriate nanoremediation technological approaches to achieve a step change in remediation practice.

Model systems (NPs + conditions mimicking real environmental conditions), both existing and novel, have been used to investigate mobility, reactivity (destruction, transformation or sorption of contaminants), functional lifetime and reaction products. For NP optimisation the influence of size, surface chemistry, structure and formulations on the performance was investigated leading to enhanced NPs as well as novel NP types. The step-change focus was to extend the range of practically treatable contaminants (CL:AIRE 2016B).

#### 2) Develop lower cost production techniques and production at commercial scales of NPs.

Laboratory scale production processes were scaled up to an industrial level. The step-change focus was to produce substantially cheaper and more sustainable NPs.

- Production was scaled up successfully resulting in a commercially available and economically competitive technology.
- Nanoscale zerovalent iron particles (nZVI) have been improved via a new surface coating so that they are available as an air-stable dry powder in spite of a large specific surface. This allows for a more convenient handling, i.e. transportation to the site, storable (CL:AIRE 2016B).
- 3) Determine the mobility and migration potential of NPs in the subsurface, and relate these both to their potential usefulness and also their potential to cause harm.

Experiments for mobility and migration potential ranged from laboratory scale (columns), over large-scale contained laboratory systems to field tests. Furthermore, investigations included unintended secondary effects of NPs application on environment and ecosystems.

4) Develop a comprehensive set of tools for design, application and monitoring practical nanoremediation performance and determine the fate of NPs in the subsurface.

These are described in Section 2.4 and Annex 1.



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5) Engage in dialogue with key stakeholder and interest groups to ensure that research, development and demonstration meets their needs, is most sustainable and appropriate whilst balancing benefits against risks.

The main focus was on ensuring that research addresses real market and regulatory interests. Communicating findings regarding renegade particles and the relative sustainability of nanoremediation over the life cycle of a typical remediation project is vital. Information and knowledge is being shared widely across the Single Market so that advances in nanoremediation can be properly exploited.

6) Carry out a series of full scale applications in several European countries to provide cost estimations and performance, fate and transport findings.

NPs were applied into both large-scale contained laboratory systems and during field trials on the pilot sites, to provide on-site validation of the results on a representative scale both in terms of the effectiveness of nanoremediation as well as the environmental fate of the NPs and their associated by-products.

As described in Section 1.3, NanoRem extensively surveyed opinions from nanoremediation users and "consumers" as well as other stakeholders (i.e. site owners or managers, regulators, technology suppliers, service providers such as consultants and contractors, planning authorities and academic interests) at targeted workshops and focus groups as well as at open sessions at international conferences and via on-line surveys and outreach to key European stakeholder networks, and further afield via its Project Advisory Group.

The key needs that a remediation technology needs to be able to fulfil are that (a) it achieves the desired risk management performance, (b) its deployment is sustainable and cost effective, (c) that its performance is verifiable (d) that it complies with all necessary regulatory requirements, and (e) a number of market requirements such as service providers can use it reliably and reproducibly and that there is sufficient knowledge in the market that it can be considered during remedial option appraisal and subsequent design, build and implementation is straightforward.

The NanoRem project has demonstrated and improved the market readiness of a number of NPs and is providing a toolbox containing application guidance, links to safety datasheets and tools for them (see Annex 1), making available field scale deployment test outcomes in a series of independently peer reviewed technical bulletins<sup>3</sup>. NanoRem has also shown that nanoremediation can be deployed in a targeted way and has substantive evidence that the ecological risks of NP deployment in the subsurface have been greatly overstated. Indeed, the NanoRem project has developed a range of supporting deployment risk assessment and sustainability assessment tools to ensure that nanoremediation is safe, effective and sustainable, with a level of scrutiny that far exceeds that which has been required for many of the subsurface amendments required to initiate competitor technologies such as *in situ* bioremediation or *in situ chemical* reduction using conventional reducing agents such as micro scale iron or sodium dithionite.

<sup>&</sup>lt;sup>3</sup> Available early 2017 from <u>www.claire.co.uk/nanorem</u>



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#### 1.5 Aims of DL9.2 Report

This Deliverable focuses on the commercial or near commercial NP types considered by NanoRem, and in particular on types tested by NanoRem in the field, summarised in Table 1. Hence primarily this report relates to iron based NPs, for example variants of nZVI, since these are the particles that have been deployed in the field to date and have the greatest evidence base from which to draw conclusions. Clearly these are the particles that are currently being exploited or are most market-ready. Other NanoRem NPs tested in the lab are mentioned but not explored in similar detail, although the information about iron NPs may also be indicative for other NP types. The full range of NanoRem NPs are listed in NanoRem Bulletin #4 (CL:AIRE 2016B).

**Table 1:** NanoRem Field tested and commercially available NPs

Particle name	Type of particle	Target contami- nants	Process of contaminant removal	Manufacturer
Carbo-Iron®	Composite of nZVI and activated carbon	Halogenated or- ganics (contami- nant spectrum as for nZVI)	Adsorption + Reduction	ScIDre GmbH, Germany
FerMEG12	Mechanically ground nZVI particles	Halogenated hydrocarbons	Reduction	UVR-FIA GmbH, Germany
NANOFER 25S	Nano scale zero valent iron (nZVI)	Halogenated hydrocarbons and heavy metals	Reduction	NANO IRON s.r.o., Czech Republic
NANOFER STAR	Air stable pow- der, nZVI	Halogenated hydrocarbons and heavy metals	Reduction	NANO IRON s.r.o., Czech Republic
Nano-Goethite	Pristine iron oxides stabilised with HA	Biodegradable (preferably non- halogenated) organics, such as BTEX; heavy met- als	Oxidation (catalytic effect on bioremediation) + Adsorption of heavy metals	University of Duisburg-Essen, Germany

#### DL9.2 provides the following:

- An outline of the possible applications of nanoremediation, providing: an overview of NPs and
  deployment techniques tested (in upscaling and field tests); applications for nanoremediation, its
  risk management performance and the NanoRem toolbox which provides a framework for the
  broad range of design and implementation tools, evaluations and trials provided by NanoRem;
- An outline of risk-benefit appraisal activities is provided for the commercial and near commercial
   NanoRem NPs;
- An outlook on the sustainability of using the commercial and near commercial NanoRem NPs;
- Scenario analyses of nanoremediation markets in the medium to longer term;



 A broad exploitation strategy at a high level across nanoremediation technologies, including a SWOT analysis of the general market position of nanoremediation; suggestions for the facilitation of immediate opportunities and broadening its general appeal; as well as a short summary of specific exploitation actions which took place in NanoRem along with an assessment of the gaps and opportunities at the end of the project.

This material is supported by a series of detailed annexes. This report forms NanoRem Deliverable 9.2, providing an overview of NanoRem WP9 work up to project end and superseded NanoRem Deliverable 9.1 which reported on work to Month 24, i.e. February 2013 to January 2015 (Bardos *et al.* 2015).

## 2 Technologies and applications investigated by NanoRem

#### 2.1 Overview of NPs and deployment techniques tested at field scale

The NanoRem projected tested a number of particles, including a selection which is now field tested and commercially available (see Table 1) and a selection at a more developmental stage, see CL:AIRE 2016B. It carried out a number of field tests at Pilot sites listed in Table 2 below. The principle means of deployment used at the field sites were direct injection or emplacement via gravity feed in pre-drilled wells.

**Table 2:** Listing of NanoRem Field Trials

NanoRem Site Name	Spolchemie I	Spolchemie II	Solvay	Balassagyarmat	Neot Hovav	Nitrastur
Site Primary	AQUATEST	AQUATEST	Solvay	Golder	Ben Gurion University	Tecnalia
Investigator			•		of the Negev	
Country	Czech Republic	Czech Republic	Switzerland	Hungary	Israel	Spain
Current use	Industry	Industry	Industrial brownfield, some subletting	Brownfield	Industry	Brownfield
Specification of	dissolved plume	residual phase and	pooled phase and	dissolved plume	phase and plume in	anthropogenic backfill
contamination		dissolved plume	dissolved plume		fractures	containing heavy
(source/plume)						metals
Main contaminant(s)	chlorinated	BTEX (mainly Toluene	chlorinated	PCE, TCE, DCE	TCE, cis-DCE, toluene	As, Pb, Zn, Cu, Ba, Cd
	hydrocarbons	and xylenes), styrene	hydrocarbons			
Type of Aquifer	porous, unconfined	porous, unconfined	porous, unconfined	porous, unconfined	fractured	porous, unconfined
Hydraulic conductivity	10 <sup>-4</sup> to 10 <sup>-6</sup> m/s	10 <sup>-4</sup> to 10 <sup>-6</sup> m/s	8 10 <sup>-3</sup> to 2 10 <sup>-5</sup> m/s	5 10 <sup>-3</sup> to 2 10 <sup>-8</sup> m/s	n/a	2 10 <sup>-4</sup> to 10 <sup>-5</sup> m/s
Seepage velocity	0.2 m/d	0.9 m/d	5-20 m/d	0.3 m/d	not available	1 m/d
NP used	NANOFER 25S/	Nano-Goethite	FerMEG12	Carbo-Iron®	Carbo-Iron®	NANOFER STAR
	NANOFER STAR					
NP provided by	NANO IRON, s.r.o.	University Duisburg	UVR-FIA GmbH	ScIDre GmbH	UFZ	NANO IRON, s.r.o.
		Essen				
Mass of NP injected	200 kg / 300 kg	300 kg	500 kg	176.8 kg	5 kg	250 kg
Injection System	Direct Push	Direct Push	Wells (with packers)	Direct Push	Wells (with packers)	Wells (with packers)
Remediation outcome	see NanoRem Project Bulletins on Pilot Sites					

#### 2.2 Application and risk management performance of nanoremediation

nZVI can be produced in different ways. It can also 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). As a remediation tool, nZVI can be applied in two broad contaminant risk management configurations: elimination of source terms and/or pathway (plume) management. A range of deployment techniques may be used to achieve these.



#### 2.2.1 Types of nZVI and nZVI Production

Wiesner *et al.* (2006) and Yan *et al.* 2013 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. Top-down approaches include milling / attrition processes and condensation processes. Both NPs produced top down by attrition or bottom up from the conversion of dissolved iron are being tested by the NanoRem project (see Table 1). A novel approach also being tested within the NanoRem project is the encapsulation of nanoscale ZVI within microscale activated carbon particles, 'Carbo-Iron' (Bleyl et al. 2012).

The mode of production of the nZVI has a strong bearing on the particle size range and form. These properties in turn affect the longevity of the iron NPs in the subsurface, their effectiveness as reducing agents, and their transportation and fate in the aquifer (O'Carroll 2013). Once nZVI has been deployed in an aquifer, it is subject to three processes which reduce its effectiveness in the environment: agglomeration, passivation and immobilisation.

- **Agglomeration** particles are attracted to each other and adhere together creating larger assemblages, which reduces their effective surface area and reactivity and typically reduces their mobility in water and hence their effective surface area.
- **Passivation** results from the oxidation of surfaces by groundwater constituents such as dissolved organic matter or nitrates, or by interaction with aquifer surfaces, before it reaches the contaminants it is intended to react with.
- *Immobilisation* in the aquifer solid matrix through processes of sorption, sedimentation (Bennett et al. 2010).

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 catalysts such as palladium to improve reactivity and suspension in emulsions to better access free-phase non-aqueous phase liquids NAPL. Within the NanoRem project a range of nZVI / NZVI based particles are being tested (see Table 2) including two surface modifications:

- Pyrophoric nZVI, and
- Oxide stabilised nZVI iron NPs which is air stable and activated prior to use.

Injection in suspensions with biopolymers (carboxymethyl cellulose (CMC) or agar agar), can be used to facilitate transport (Velimirovic *et al.* 2016) to change the viscosity or bulk density of the injection suspension.

#### 2.2.2 Use of nZVI in Remediation

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 (Vegter *et al.* 2002, Nathanail and Bardos 2004). In many cases, this risk management is achieved by integrating a combination of measures:

- At the source term, e.g. contaminant mass removal (source);
- Within the pathway, e.g. plume control or monitored natural attenuation
- Via the receptor, e.g. institutional controls such as planning restrictions.



Additionally, there is developing interest worldwide in ensuring that any such risk management measure is achieved in the most sustainable way possible, known as 'sustainable remediation' (see Chapter 4).

Nanoremediation has been applied as an *in situ* remediation, i.e. to treat aquifers within the subsurface. Like all *in situ* remediation technologies, the performance of nanoremediation is fundamentally constrained by how well the treatment agent can be delivered to the contamination problem, i.e. the accessibility of the contamination to be treated. This accessibility is determined by the interaction between the treatment agent and the subsurface materials. Key subsurface properties controlling accessibility for *in situ* processes are: 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 a NAPL (Beck and Jones 1995).

There are general limitations to the effectiveness of any *in situ* approach to source removal / destruction. Complete mass removal is rarely possible for large source terms, 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). However, nZVI deployment may be effective for mopping up small source terms, for example, what are often termed "secondary sources". Secondary sources may be used to describe two different types of source: (a) free product that has migrated away from the original source term (Kueper *et al*, 2014), and (b) more colloquially, smaller sources on a contaminated site as typically site remediation activities focus on the dominant contamination problems. Dealing with small and secondary sources may be an important potential application for nZVI.

There are relatively few ways in which treatment agents can be introduced into the subsurface. They can be backfilled into an excavated zone, for example after a tank removal. They can be contained inside a well drilled into the subsurface. They can be directly injected into the subsurface e.g. via a Geoprobe. The field deployment of nZVI to date has been via some form of injection by direct push or via wells (Comba *at al.* 2011).

Conventional microscale ZVI has also been widely used in permeable reactive barriers (PRBs) for pathway management (Environment Agency 2002). Unmodified nZVI may be too reactive to have sufficient longevity in the subsurface to be useful as a PRB matrix, although a US Department of Energy Report (2009) described a pilot application of nZVI into an existing well array being used as a PRB to control chromium (VI) migration.

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).

Injection of some NP suspensions can be problematic if the injection criteria (e.g. injection pressure and flowrates were) are not optimized for a given subsurface. In such cases difficulties in injecting target amounts and "daylighting" of injected materials, i.e. the reappearance of injected materials at the surface in the vicinity of the injection point may occur. This was observed both in some Nano-



Rem field trials, and reported in various other field applications (e.g. CITYCHLOR Consortium 2013; Su et al. 2013; US EPA 2016). Besides the optimisation of injection parameters, migration of injected nZVI away from the well may also be assisted by changing the properties of nanoparticles (such as reducing sticking coefficient, Johnson et al., 2009) or changing the viscosity and bulk density of the injection fluid. NanoRem has been investigating modifying nZVI and Carbo-Iron® suspensions using thickening agents such as CMC and agar agar to improve injectability and transportability in the subsurface (Busch et al. 2015; Velimirovic et al.2016.)

NanoRem has been investigating other forms of aquifer manipulation to improve the effectiveness of introduced nZVI. NanoRem has investigated at bench scale, using column tests, whether increasing aquifer pH can improve the longevity of nZVI, testing milled iron, NANOFER 25S. These tests indicate that while increasing pH to pH 12 reduces corrosion on nZVI, it also reduces reactivity with PCE, likely as a result of increased surface passivation (Menadier Stavelot 2015).

Emerging approaches include combined treatments including nZVI with other treatments, for example, thermal destruction (Phenrat *et al.* 2015), electrokinetic treatments (Gomes *et al.* 2015a and b) and *in situ* bioremediation (Bruton *et al.* 2015). Of these combined bioremediation and chemical dechlorination *in situ* is most developed, and the synergy between nZVI addition and supporting biological processes of dehalorespiration is a significant opportunity for nZVI deployment (Kocur *et al.* 2015).

#### 2.3 NanoRem generalised guideline for the application of nanoremediation

The generalised guideline for the application of nanoremediation (CL:AIRE 2017) gives a comprehensive overview about the implementation of nanoremediation. While it is a stand-alone document it is supported by a range of publications offered in the "Nanoremediation Toolbox" described in Annex 1. Additionally, within the NanoRem project six pilot site studies have been conducted successfully. The descriptions of the sites, chosen remediation approach, monitoring and the outcomes are described in dedicated NanoRem Bulletins (<a href="https://www.claire.co.uk/nanorem">www.claire.co.uk/nanorem</a>).

The aim of this guideline is to assist practitioners and consultants in screening nanoremediation as a possible remediation option for a given site. If nanoremediation is deemed beneficial, the guideline will provide criteria for the design of a successful nanoremediation. It lists parameters to monitor to control the success of the measure. In addition the guideline will help regulators to evaluate a given nanoremediation scheme on its potential benefits or pitfalls. Prerequisites of a successful remediation such as a detailed site investigation, a conceptual site model (CSM), an overview of commercially available NPs (NP) and the corresponding operating windows (OW) are not discussed in detail, however corresponding background material is being offered in the appendix of the guideline. The key stages covered by the application guideline are as follows. These stages have been carefully designed to ensure that decisions for suitability can be made on the basis of the smallest possible investment of time and money, e.g. pre-screening before bench trials before pilot tests etc.

- Pre-screening: A simple approach to match OW to site requirements to give a quick indication of
  "favourable"/ "unfavourable" and indicates critical parameters to be investigated in more detail.
- Site and contaminant specific particle tests: bench scale testing to verify producer claims and provide assurance that the NPs being considered have the required reactivity. If reactivity test work is positive, then bench scale testing of mobility (transport) experiments need to be con-



ducted. These have the dual purpose to give an indication on a radius of NP transport and in parallel yield parameters to calibrate a numerical model to eventually assist in the design of a remediation scheme.

- Monitoring: As for all remediation the monitoring of a nanoremediation application may be divided in pre-, during, and post-deployment. For nanoremediation especially the deployment phase itself is critical since in this phase the distribution of the NP (which in the end controls success and efficiency of a given measure) in the subsurface is verified. The guideline describes the monitoring phases in and suggests innovative and conventional monitoring devices associated with each phase.
- Model Assisted Upscaling of NP Mobility: Optionally quantitative modelling may be used to
  translate the results from laboratory column tests to estimated performance in the field. The
  main purpose of the modelling is to predict the NP mobility at different stages of the technology
  application, both in the planning and design stages (i.e. support the design of the injection plan),
  and later to predict the long-term particle mobility after injection (i.e. support the monitoring).
- **Pilot Tests:** The main aim of pilot field tests is the definition of specific conditions for the design and implementation of operational applications of NPs at the area of interest with respect to the selection of the right nanomaterial, evaluation of its efficiency and longevity of selected particles, and thus to make a prediction of duration an technical as well as economic success of a given remediation scheme.
- *Full Scale Design:* Based on the pilot test and in conjunction with the numerical model a full scale nanoremediation can be designed. The key part of the design is to match the contaminant distribution and inventory with a targeted deployment of NPs. The main challenge of the full scale design is to balance technical and economical questions, i.e. homogeneous NP distribution vs. number of injection points.
- Site Installations and Particle Deployment: Site installations necessary for a successful NP deployment comprise both above ground and below ground installations. Below ground installations may be emplaced beforehand if wells are being used or during particle deployment if the subsurface allows for the use of direct push injection technology. Above ground installations include mobile equipment containing mixing containers, dispersers, pumps etc. Deployments need to cognoscente of Material Safety Data Sheets requirements.
- Long Term Performance: Test and confirmation of a successful nanoremediation is achieved via long term monitoring. During this phase contaminants, reaction products, metabolites and general milieu parameters of the ground water are monitored on a regular (monthly) basis, in order to verify the success of the remediation.

## 3 Risk-Benefit Appraisal for NanoRem technologies

#### 3.1 Technology benefits

This section aims to describe nanoremediation technology benefits. It is based on two types of information (1) literature data published on the use of NP for contaminated land remediation up to 2016 and (2) NanoRem Project results (including laboratory testing and field trial results). Nanore-



mediation technology share a number of generic benefits with other *in situ* remediation approaches such as minimising disruption to site operations; minimising exposure of site workers to contaminants and reagents; and reduced generation of processes waste and emissions. In common with *in situ* biological reduction (ISBR) and other forms of *in situ* chemical reduction (ISCR), nanoremediation offers the chance to avoid long term site infrastructure required for engineered processes such as pump and treat or *in situ* air sparging. However, this section focuses on how nanoremediation may also offer specific and particular benefits in some applications. These include benefits related to *the range of treatable contaminants, the speed* by which they can be treated, *the range of environmental conditions* under which nanoremediation can perform, *the potential for source term treatment*, and *potential synergies with other treatments*. This section focuses on nZVI for which the best evidence base exists; however, other NPs – especially those tested by NanoRem – are discussed wherever possible.

#### 3.1.1 Extended range of treatable contaminants

Literature data indicate that using nZVI enables a broader range of treatment capability for contaminants compared with both conventional ZVI and biodegradation. nZVI demonstrates the 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 et al. reported two studies focusing on nZVI remediation of soils impacted by PAHs, particularly pyrene, which appeared to demonstrate declining contaminant concentrations over time and as a function of nZVI dose, but which did not identify specific degradation mechanisms (Chang et al. 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). Fan et al. (2013) demonstrated the ability of sulphidated nZVI to reductively sequester pertechnetate for the remediation of technetium contaminated groundwater. Nanoscale / micro-scale metallic particles have also been shown at laboratory-scale to be a potential remediation technique for energetic (explosive) materials (Geiger et al. 2009, Naja et al. 2008). Doping nZVI with metals such as palladium further improves its reactivity and the range of treatable problems by introducing extended catalytic properties (Cook 2009, Sirk et al. 2009, Quinn et al. 2009, Kim et al. 2008, Saleh et al. 2007, Elliott and Zhang 2001). In addition, according to the Kharisov's review (Kharisov, 2012), common environmental contaminants that can be transformed by nanoscale iron particles (NZVI, supported and alloys nZVI, iron oxide and FeOOH) may include: chlorinated and brominated methanes, pesticides (DDT, lindane), organic dyes (Orange II, Chrysoidine, Tropaeolin O, Acid Orange, Acid Red), heavy metal ions (Hg2+, Ni2+, Ag+, Cd2+, Cr (VI)), dioxins, other organic contaminants (N-nitrosodimethylamine, TNT, dinitrotoluene, RDX (Hexahydro-1,3, 5- trinitro-1,3, 5- triazine) and inorganic anions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, AsO<sub>4</sub><sup>3-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>). Laboratory results offer unprecedented details about the intraparticle reaction mechanisms and demonstrate intrinsic advantages of nZVI for arsenic encapsulation, treatment, and remediation (Ling and Zhang, 2014; Yan et al. 2012)

<u>In NanoRem</u>, lab-tests were performed on nZVI (different NANOFER types, milled iron (FerMEG12, Abrasive Milling nZVI)), composite NPs (e.g. Carbo-Iron®, nano-iron oxides (Goethites)) and non nZVI particles (Trap-Ox Fe-zeolites, Biomagnetite, Mg/Al particles, Barium Ferrate, Nano-FerAl). Among all



the NPs tested, the results showed successful degradation of chlorinated olefins (TCE, PCE, DCE), brominated olefins (Tribromoethene), halomethane, saturated polyhalogenated (dichloroethane, dichloromethane, aromatics/phenols (low substitution degree), aromatics/phenols (high substitution degree, PCBs, PCP), herbicides and pesticides, BTEX and MTBE / ETBE, metals and metalloids and nitro compounds. The success of degradation for one set contaminant was highly dependent on the type of NP tested: for example, solely NANOFER or Trap-Ox Fe-zeolites were able to degrade dichloroethane or dichloromethane. Moreover, results with Carbo-Iron® indicate effectiveness for degrading chlorinated solvents, brominated solvents and Cr(VI).

A number of modifications have been developed to improve the effectiveness of NPs by reducing the scale of agglomeration and the immediacy of passivation. As an example, the carbon fraction of the carbo-iron is protective of the iron and reduces agglomeration problems as it overcomes the problem of magnetic attraction. Modification of the suspension (e.g. with CMC) can reduce agglomeration, passivation and sorption onto aquifer materials. Preparation of the suspension modification is a critical success factor (tested at lab and field scale).

Literature data show that most deployments of nZVI have focussed on the degradation of chlorinated solvents, although pilot studies have also demonstrated successful treatment of benzene, toluene, ethylbenzene and xylenes (BTEX), perchlorates, hexavalent chromium, diesel fuel, polychlorinated biphenyls (PCBs) and pesticides. O'Carroll et al. (2013) detail the chemical processes involved in the treatment of chlorinated solvents and various metals by nZVI. A review of ~100 field deployments (see Annex 3) indicates that nZVI was used to treat contaminants such as other halogenated organic compounds (Methylene chloride, 1,2-dichloropropane, 1,2-dichloretheane, Vinyl chloride, TCA, Hexachlorobutadiene), PAHs (Benzo[a]Anthracene), other inorganic compounds (Bis(2-Ethylhexyl)phthalate, perchlorate, Freon, NO<sub>3</sub>), other organic compounds (PCBs, diesel, light hydrocarbons), and other metals (Cr, Ni).

<u>In NanoRem</u>, field testing was performed at sites contaminated by "standard" contaminants such as chlorinated organic compounds (TCE, PCE, DCE, Hexachloroethane, Carbon tetrachloride), LNAP (Toluene, BTEX and TPH) and metals (Arsenic and Cd, Cu, Zn, Pb), since the main purpose of these trials were to test injection, delivery and efficiency.

#### 3.1.2 Improving the speed of contaminant destruction

<u>Literature data</u> indicate that the speed with which contaminants can be degraded or stabilised by NPs can be substantially increased over conventional *in situ* saturated zone remediation technologies because a greater amount of iron is readily available for reaction (e.g. Müller and Nowack 2010; Li *et al* 2008). This may bring wider benefits. Karn *et al.* (2009) suggest that shortened timescales (e.g. compared with pump and treat) not only reduce costs but also reduce the time that workers are exposed to a contaminated site during its treatment.

<u>NanoRem</u> laboratory and field results showed that activation process has improved speed and kinetics for air stable nZVI NANOFER STAR. In NanoRem laboratory tests were carried out to determine reaction rates for each NP with respect to one or two contaminants. The reaction rate constant depends on the concentration of NP solution, the water / field / environmental conditions and the contaminants concentrations. NanoRem reaction constant rates ranges of each NP studied were in the



following NanoRem deliverables, downloadable from <a href="www.nanorem.eu">www.nanorem.eu</a>, DL 2.2, DL 3.2, DL 4.2, and are as follows:

- NANOFER 25S:  $K_{obs}^4$  ranges from 1.7 to 2.6  $10^{-3}$ /h for PCE (for a NP concentration of 1.1g/L). As for information, Velimoric (2013) found a reaction rate of 1.4. $10^{-2}$ /h for PCE (for an NP concentration of 5g/L), which was found to be faster than other particles of ZVI used.
- Optimised NANOFER STAR: a  $K_{SA}^{5}$  of 1.73x10<sup>-5</sup> L/m2/h for PCE with water from the Spolchemie site was found.
- Milled iron: K<sub>obs</sub> ranges from 1.4.10<sup>-3</sup>/h to 2.8.10<sup>-3</sup>/h for TCE depending on the water used (site (Solvay site, Balassagyarmat site or laboratory).
- Nanogoethite: K<sub>obs</sub> of 1.9. 10<sup>-2</sup>/h (for Toluene) and 7.75. 10<sup>-2</sup>/h (for Benzoate) for a NP concentration of 1g/L were determined.
- Carbo-Iron®: K<sub>obs</sub> of 7.6. 10<sup>-3</sup>/h (for PCE) for an NP concentration of 1g/L was found.
- Trap-Ox Fe-zeolites: K<sub>obs</sub> (for MTBE) of respectively 1.3/h (for an NP concentration of 50g/L) and 1.1 h (for an NP concentration of 10g/L) were obtained.
- Biomagnetite (Bnm): K<sub>obs</sub> of 6.6. 10<sup>-2</sup>/h (for Cr) for an NP concentration of 0.75g/L was found
- Pd-Bnm: K<sub>obs</sub> of 1.5/h (for Cr and an NP concentration of 0.32g/L) and 4.4. 10<sup>-3</sup>/h for PCE were found.
- Al/Mg: Kobs of 3.1. 10-3/h (for PCE) was found.
- BaFeO4: Kobs of 7.6. 10-4/h (for Toluene) was found

#### 3.1.3 Improving the extent of contaminant destruction

A further claim made for nZVI use in remediation is that it offers the potential for rapid and complete treatment without the generation of toxic intermediate breakdown products, or that it generates more benign reaction products compared with *in situ* bioremediation (Bezbaruah 2009, Nurmi *et al.* 2005). Avoidance of toxic intermediates could be a major process benefit, if it is achievable in the field, particularly for sites where the pathway to potential receptors is relatively short.

Literature reports of bench scale studies 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 treat-

<sup>&</sup>lt;sup>5</sup> Surface area normalised reaction rate constant



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<sup>&</sup>lt;sup>4</sup> Observed reaction rate constant

ments and nZVI applications in the field, depending on site specific circumstances (and the sufficiency of added nZVI). However, it is also possible that the process intermediates observed during nZVI use in the field may be a consequence of biological processes rather than abiotic processes. Furthermore, the theoretical outcome remains one of complete contaminant destruction.

NanoRem field tests results on observation of degradation products were as follows.

- At the Spolchemie site I, results and a current redox potential of EH=-100 mV suggest that the injected NANOFER STAR is still active after 250 days (8 months 1 week) and is still reducing the contaminants to the final degradation products no significant increase of VC or cis-DCE was observed in the micro-pumps well. However, in one of the open screening well (PV112), a significant increase of DCE in groundwater was observed 150 days after the injection, breakpoint of direct reduction of PCE and TCE to ethane and ethane (Figure 14) because of an increase of ORP above 0 mV. 174 days after the injection DCE concentration peaks and 40 days later it sharply decreases again. This decrease could be induced by reactivation of injected nZVI or DCE degrades under unspecified changes in microbiology.
- At the Solvay site, the degradation products cis-DCE and trans-DCE were never detected in some monitoring wells at all. The highest concentrations were found 2 weeks after injection in B153D (270 µg/l cis-DCE and 130 µg/l trans-DCE). In general, the concentration of cis-DCE was approximately twice the concentration of trans-DCE. Three months after the injection ethane is the final degradation product and only traces of ethane are detected.
- At the Balassagyarmat site, a slight increase of TCE, cDCE and VC concentration but only traces of ethane and ethane were detected, which proofs the abiotic dehalogenation induced by Carbo-Iron® injection. The significant reduction of PCE and enhanced microbiological degradation/chemical reduction in the closest monitoring wells to the injection points can be detected, but ethene, ethane production as indicators for CAH abiotic reduction can be detected only in small concentration right after the injection. As well, a slight increase of TCE, cDCE and VC concentration were detected in trace levels. The presence of cDCE can be either attributed to intermediate formation in abiotic degradation pathway or indicates microbial activity beyond the sphere of action. Some of the immediate decrease of the PCE concentrations after the injection can be attributed to dilution due to the injected volume.

#### 3.1.4 Extended range of environmental conditions

nZVI has been shown to be effective across a broad range of soil pHs, temperatures, and nutrient levels (Kharisov, 2012). Nanoremediation would also not be subject to conditions which might be inhibitory to biological processes.

<u>NanoRem</u> laboratory-scale results showed that Biomagnetite NP had a high resistance to inhospitable aquifer conditions (e.g. pH). Biomagnetites are considered to be reactive against a wide range of environmental conditions and at a range of pH values. Very high degradation rates were observed for biomagnetite and Pd-biomagnetite ( $K_{obs}$  respectively of 6.6.10-2/h and 1.5/h) for the treatment of Cr(VI) under very basic conditions (pH=12).

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

There are limitations to the effectiveness of any *in situ* approach to source removal / destruction (see Chapter 2). However, nZVI deployment may be effective for mopping up small source terms, for ex-



ample, what are often termed as secondary sources. Secondary sources may be used to describe two types of sources: (a) free product that has migrated away from the original term source (*Kueper et al.*, 2014) and (b) more colloquially, smaller sources on a contaminated site.

<u>Literature review information</u> indicates that dealing with small and secondary sources may be an important potential application for nZVI. Summary information from the US EPA (EPA, FRTR 2006) describe a pilot application of bimetallic nano[particles (platinum doped nZVI) BNP for dispersed sources of chlorinated solvents, which achieved rapid removals of dissolved phase chlorinated solvents at some but not all well locations.

Some of <u>NanoRem</u> findings may be relevant for promoting source treatment term. They include the following: 1) Inclusion of surfactant in the NP suspension to assist accessibility to NAPL; 2) Carbo-Iron® has advantages for free phase NAPLs as the Carbo-Iron® is hydrophobic. The carbon fraction sorbs NAPL to bring in intimately to the iron. The possibility of Carbo-Iron® entering the NAPL phase has not been yet been observed for methodological reasons, but it certainly collects at the phase boundary; 3) The potential for providing source term treatment is highly dependent on the existing deployment techniques and their ability to deliver NPs in the contaminated zone. The above ground preparation of the suspension appears to be more critical to success than the actual injection approach. There is a need for good information about the permeability of the subsurface to use the right technology to inject the material, but this also applies widely across other remediation materials consider in the subsurface. Injection into low permeability layers is not feasible.

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

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

The degree of contamination treatment success of these three test sites varied depending on the site and the type of NPs injected. As an example, at the Spolchemie site, the second NANOFER STAR injection showed efficient degradation of PCE. As for the two other sites, removal of contaminants was demonstrated but contaminants concentration in groundwater remains elevated over the course of the experiments. At the Solvay site, even if the concentrations of contaminants found in the test area are very high compared to the nearest extraction well, it has been concluded that a successful treatment of the identified secondary source will only have a small impact on the concentration of contaminants in the extraction well. The working hypothesis that back diffusion of the contaminants from the clay formation is responsible for the contamination of the ground water, could not be verified as free phase was present. At the Spolchemie II site, the concentrations of contaminants are still very high on the site due to a slow bioremediation process, especially under anoxic/anaerobic conditions (iron reducing conditions).



#### 3.1.6 Synergy and enhancement effect

<u>The literature</u> describes a number of emerging approaches include combined treatments including nZVI with other treatments, for example, thermal destruction (Varanasi *et al.* 2007), electrokinetic treatments (Gomez et al. 2015a and b) and *in situ* bioremediation (Bruton *et al.* 2015). Of these combined bioremediation and chemical dechlorination *in situ* is most developed, and the synergy between nZVI addition and supporting biological processes of dehalorespiration is a significant opportunity for nZVI deployment.

Various studies have suggested than nZVI may be suitable for deployment in conjunction with other remediation technologies, with some studies even demonstrating a synergistic effect. For example, Jiamjitrpanich *et al.* (2012) examined the compatibility of nZVI with phytoremediation techniques for 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 bench-scale observations indicate that nZVI use is synergistic and stimulatory for *in situ* anaerobic biodegradation of chlorinated solvents by dehalorespiration. Laboratory studies indicate that nZVI application does not appear to be inhibitory to (and may even be stimulatory for) biological reductive dechlorination associated with water-derived cathodic H<sub>2</sub> production during its anaerobic corrosion (Comba *et al.* 2011, Kirschling *et al.* 2010, Xiu *et al.* 2010). Kuang *et al.* (2013) found corroborating results to this, demonstrating that both nZVI and Ni/Fe composite NPs increased the biodegradation of phenol by *Bacillus fusiformis* at pH 6 and 8; nZVI was also demonstrated to increase biodegradation at low pH (pH 3). These laboratory findings are consistent with observations during applications of nZVI in the field, where biological reductive dechlorination continues or is stimulated (e.g. He *et al.* 2010; Kocur *et al.* 2015). Indeed, Lacinová et al. (2013) showed that in field tests, combined nZVI and biodegradation achieved greater reduction in chlorinated solvents in a contaminated aquifer (76% compared to 48% for nZVI alone).

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

At the NanoRem Spolchemie II site, the application of Nanogoethite particles was being used as an *in situ* technology for enhancing the microbial activity with the aim to degrade the BTEX contamination at the area. The results showed that the removal of BTEX is effective, but concentration remains very high. This fact indicates there is ongoing process of microbial degradation of BTEX, occurring slowly.

#### 3.2 Risks of deployment

This section is based on work summarised by Nathanail et al. (2016). Ongoing work that is based on the field trials and other research carried out during NanoRem, has been incorporated into the Risk Screening Model (RSM) reported in DL 8.2. However this work merely confirms that the NanoRem NPs do not travel distances that are likely to lead to their escaping a polluted plume of groundwater.



What happens to NPs (NPs) that are injected into polluted groundwater but either do not reach the intended treatment area or pass through it to reach parts of the aquifer that they were not intended to reach<sup>6</sup>

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

During the early stages of the NanoRem project, a qualitative risk assessment protocol was developed for the NPNPs that were to be investigated in the laboratory and in the field. The protocol applied to renegade NPs. This protocol was based on an expert elicitation workshop hosted by Land Quality Management Ltd (LQM) in Nottingham and an extensive review of the literature. It found that the NPs being investigated by NanoRem are likely to have low toxicity and ecotoxicity; are likely to interact with aquifer matrix, each other and groundwater to, often rapidly, cease to be mobile NPs and; are likely to be difficult to penetrate into the aquifer more than a few metres from the point of injection. While there were considerable uncertainties particularly with regards to the transport of NanoRem NPs the ability of NPs to penetrate far into the formation was likely to be very limited.

NanoRem laboratory and field work has helped refine our understanding of the transport of NPs. Most of the upscaling (large containers and field sites) was for porous materials. The results from the large containers and field trials showed maximum travel distances of 2.5m and 5m respectively. WP4 (Mobility and Fate of NPs) reported  $L_{T99.9\%}$  values which are predicted maximum travel distances calculated using the results of the column experiments. Early experiments show predicted transport distances to just over 20m (21.8m). Column experiments on optimised particles in field relevant conditions had predicted distances ( $L_{T99.9\%}$ ) of just over 30m (32.2m).

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

WP5 (Environmental Impact of Reactive NPs) reported results of toxicity testing of NanoRem NPs and generally found that toxicity was low; typically the limiting concentration was 100 mg/l.

A more detailed Risk Screening Model (RSM) for application of NanoRem NPs to groundwater remediation has been developed. The RSM includes conceptual exposure scenarios, consideration of fate, transport and toxicity and a spreadsheet based model to estimate transport distances. The RSM has been developed with only the NanoRem NPs in mind but may inform risk assessment for other NPs as well.

The risk model for NP applications considers the macro-scale transport of NPs within saturated media and is based on a modified advection-dispersion equation as described within NanoRem DL7.1 (eq. 10a and 10b, Tosco et al., 2016) and the MNMs user manual (Eq 5-1, Bianco et al., 2015), i.e.

<sup>&</sup>lt;sup>6</sup> NanoRem calls such NPs 'renegade' particles.



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from DL7.1. The Environment Agency Remedial Targets Methodology, RTM (Environment Agency, 2006) has been used as the basis for deriving the transport element of the risk model that estimates a screening level NP concentration versus distance from the NP source (injection) zone. The RTM is accompanied by a MicrosoftTM Excel spreadsheet tool for four Levels of assessment. The RTM spreadsheet model has been modified at the Level 3 stage (i.e. saturated zone transport) by incorporating some of the key NP parameters into one of the analytical solutions (currently the Ogata Banks equation) used to describe the advection-dispersion including degradation and retardation of solutes downstream of the source term. The model has been compared against the numerical solution currently included within the MNMs 2015 (v 1.012) model (Bianco et al., 2015). The methodology depends on calculating values of attachment (k<sub>att</sub>) and detachment (k<sub>det</sub>) using the MNMs model (microand NP transport, filtration and clogging model suite) developed by WP7 (Modelling Tool for NP Mobility and Interaction with Contaminants).

For the continuous injection scenario the modified RTM model can be used to estimate the time at which 'breakthrough' (very low but non-zero concentration) occurs at a distance 100m downstream (23 years), with the NP concentration distance profiles at specific times (1-50 years) also shown. Clearly, a continuous injection for the lengths of time assumed is unrealistic but even for such a cautious assumption the travel time is predicted to be relatively high and travel distance limited. The density of NPs per litre can also be modelled for various distances downstream of the injection point. After one year very low concentrations are estimated only 20m downstream from the injection point. These findings compare well against evidence from the NanoRem field trials, notably at the Hungary field pilot site (Balassagyramat).

The comparison of the modified RTM model (analytical solution) output with that provided by the MNM's (numerical solution) output provides an indication that the simplified models can provide similar outputs for the same inputs. A number of key limitations and assumptions have been identified but it is considered that our approach provides a useful basis for a suitably cautious risk assessment methodology. The final version of this model is available via DL8.2 (Braun et al. 2016).

Nano particles below a certain size begin to behave in ways that seem to be different to their micro equivalents. Irrespective of that, the increasing surface area to mass ratio means that particles below 100nm can improve currently deployed *in situ* groundwater remediation technologies and have the potential to deal with presently recalcitrant substances. The UK government supported a joint Royal Society/ Royal Academy of Engineering recommendation that the use of novel manufactured NPs be prohibited for use in environmental remediation while uncertainties about the risks such particles posed were being addressed. NanoRem has included work on the risks posed by NPs injected into polluted groundwater for remediation purposes. This work has drawn on published literature as well as field trials and laboratory studies by NanoRem partners to inform a qualitative and semi quantitative risk assessment protocol on the magnitude of risks posed by NPs that escape the zone of polluted groundwater they were intended to remediate. Such renegade particles have been found not to migrate distances significant enough to pose a credible risk to unpolluted groundwater, surface waters or ecosystems.

NanoRem's experimental work has helped inform our understanding of the levels of risk that could be posed by deploying NPs for remediation: WP5 results suggest that the toxicity of NanoRem NPs is low; WP4 predictions of maximum transport distances (up to 30m) are greater than the results of the



field trials reports by WP8 (Up-Scaling, Risk and Sustainability) and WP10 (Pilot Site Applications and Field Demonstrations) (up to 5m); i.e. NP migration distance is low.

While there are considerable uncertainties particularly with regards to the transport of NanoRem NPs the ability of NPs to penetrate far into the formation is likely to be very limited. Their ability to escape dissolved phase plumes is likely to be even more limited. Research goes on for ways to increase the migration distance and a simplified quantitative approach to estimating transport distances has been developed.

This reinforces the view that it seems reasonable to conclude that overall risks of deployment are low.

#### 3.3 Risks, benefits and technology cross-comparisons

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

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

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

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

NPs are *able to migrate* below ground to some extent compared with microscale ZVI which is essentially immobile (Mueller, 2012, Lefèvre, 2016).

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



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

Aggregation, agglomeration and corrosion (and associated volumetric corrosion products) are passivation mechanisms which are predominant for nZVI and affect their reactivity (Noubaptec, 2012, Hosseini, 2015). According to Velimovic experiments (2014), microscale ZVI has approximately a 10-30 times lower corrosion ratio than nZVI. As less reactive particles will sustain reducing conditions for longer times and give better performance, microscale ZVI is known to have *a longer longevity* than nZVI (Comba, 2011). *Lower persistence of nZVI* might be attributed to their high reactivity and their lack of selectivity. Moreover, field efficiency decrease with the size of the Fe0 particle (mmZVI having better efficiency than μmZVI than nZVI, Noubactep, 2012).

#### 3.3.2 Cross comparison with principal remediation alternatives

This section is more of a generic benchmarking, written very much with a practitioner in mind, and so has some overlap with Section 3.4.1.

To date land contamination problems addressed by nanoremediation relate to source control and/or pathway management for nonaqueous phase liquids (NAPLs), such as chlorinated solvents, and hazardous elements such as dissolved As or Cr(VI) species, although a range of other problems are also treatable (O'Carroll *et al.* 2013). These contaminants are highly prevalent problems, according to the 2014 JRC report, see Figure 2, accounting for perhaps more than 50% of contamination problems.

in soil in groundwater Others Others 10 % Cyanides 1 % Phenois Mineral oil Mineral oil 1 % Cyanides 1 % PAH PAH Phenols 11 %

Most frequently applied occurring contaminants

Figure 2: Most frequently occurring contaminants (From JRC 2014)

The main competing *in situ* remediation alternatives to nanoremediation for these contaminants are ISBR and conventional forms of ISCR using reducing agents such as micro-ZVI sodium dithionite or calcium polysulphide<sup>7</sup> (Nathanail, *et al.* 2007).

Use of nZVI can also be stimulatory for ISBR, and support completion past known potential stall points for ISBR (Kocur *et al.* 2015). Similar synergies are exploited in commercial reagents for ISCR using microscale ZVI<sup>8</sup>, but NPs are more rapidly effective.

https://clu-in.org/techfocus/default.focus/sec/In\_Situ\_Chemical\_Reduction/cat/Overview/



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Conventionally, ISCR and ISBR are primarily pathway (plume) management intervention with limited scope to address source terms; they have limited effectiveness against several important contamination issues such as fuel oxygenates, fluoridated organics and various other recalcitrants; they may be associated with modifications to aquifer properties that render them unacceptable in some circumstances; and ISBR may be subject to process stall.

The NanoRem project has developed a range of supporting deployment risk assessment and sustainability assessment tools (see Annex 1, toolbox) to ensure that nanoremediation is safe, effective and sustainable, with a level of scrutiny that far exceeds that which has been required for many of the subsurface amendments required to initiate ISBR or ISCO/R. NanoRem has also clarified the benefits of nanoremediation, and provided a strong scientific evidence base addressing concerns such as potential ecological and water environment impacts. Table 3 provides a comparative benchmarking across risks and benefits for nanoremediation and its two main competitor approaches ISBR and ISCR. Cost indications in Table 4 are based on a Czech case study (Kvapil *et al.* 2016). Table 4 provides a more complete comparison of the relative costs used for nanoremediation to bioremediation (using lactate injection) and ISCR using microscale ZVI alone. The comparison is based on a Czech example and a Czech cost base. It is only illustrative, and there are generally few hard and fast rules for cost estimation for *in situ* remediation technologies. The modelled application is for a pathway management of a chlorinated solvent plume, and is benchmarked against nanoremediation in % terms. It is based on treatment to Czech regulatory thresholds within three years. In this example, ISBR is substantially cheaper than nanoremediation.

Table 3: Benchmarking costs, risks and benefits of nanoremediation against ISBR and ISCR

		Nanoremediation	Conventional ISCR	ISBR
Risks	Human health	Some NPs are hazard- ous, some are air stable and safer to handle. No exposure once suc- cessfully deployed.	Some reagents, such as dithionate, are potentially hazardous.  No exposure once successfully deployed.	Materials are safe to handle.  No exposure once successfully deployed.
	Aquifer ecology	Injections are typically in highly disturbed environments. No NP specific ecotoxicity found by NanoRem. Ultimate fate is as iron oxides which are plentiful in soils.	Injections are typically in highly disturbed environments. Ecological impacts unstudied, but assumed minimal.	ctions are typically ghly disturbed envinents. Ecological acts unstudied, but Injections are typically in highly disturbed environments. Ecological impacts unstudied, but
	Water	Injected materials have limited lifetimes and limited travel distance, and are not associated with taint of the subsurface	Lifetimes and travel distance of injected dithionite has not been widely studied, may be extensive. The travel distance of mZVI is essentially zero.  High levels of sulphate and low pH remaining	Injected substrates to stimulate bioremediation are soluble or release soluble substrates possibly causing taint for water supplies <sup>10</sup> .

<sup>&</sup>lt;sup>8</sup> E.g. <u>www.peroxychem.com/markets/environment/soil-and-groundwater/products/ehc-iscr-reagent</u>

<sup>&</sup>lt;sup>10</sup> This concern has led regulators in some regions to prevent ISBR deployment in some cases, e.g. at the Písečná site, CZ



<sup>&</sup>lt;sup>9</sup> Note ISBR is mediated by deliberate modification of aquifer ecology to stimulate dehalorespiration.

		Nanoremediation	Conventional ISCR	ISBR
			after dithionate or poly- sulphide reduction	
	Supporting measures	Pre-deployment risk assessment available and published.	No pre-deployment risk assessment tool.	No pre-deployment risk assessment tool.
Benefits	Breadth of solutions	Wide range of treatable contaminants.  Source term and pathway management applications.  Suitable for situations inhibitory to microbial dehalorespiration processes.	Wide range of treatable contaminants. Tendency to pathway management applications. Suitable for situations inhibitory to microbial dehalorespiration processes	More restricted range of treatable contaminants. Potential for stall (e.g. TCE> DCE) Tendency to pathway management applications. May be prevented by toxic or other inhibitory conditions
	Speed and completeness of action and synergies	Rapid treatment effects owing to nanoscale processes.  Moderate migration in the subsurface.  Tendency to complete degradation of contaminants.  Synergistic with ISBR and ISCR.	Slower treatment effects.  Microscale ZVI does not readily move in the subsurface.  Tendency to complete degradation of contaminants.  Synergistic with ISBR and nanoremediation	Slower treatment effects.  Soluble substrates migrate rapidly in the subsurface  Tendency to stall for some problems <sup>11</sup> .  Synergistic with nanoremediation and ISCR.
	Ease of de- ployment	Portable systems (not requiring fixed infrastructure).  Some systems require specialised deployment interventions.  NanoRem is addressing the issue that deployment knowhow is not widespread <sup>12</sup> .	Portable systems (not requiring fixed infrastructure). Widespread know-how and systems.	Portable systems (not requiring fixed infrastructure). Widespread know-how and systems.
	Track record	Limited track record, relatively few suppliers.	Well established tech- nology, many vendors, moderate track record.	Well established tech- nology, many vendors, substantial track record.
Costs	Cost estimat- ing	Bespoke costings needed for each deployment option appraisal.	Many consultants have a good knowledge of relative treatment costs.	Many consultants have a good knowledge of relative treatment costs.
	Cost levels	100%	70-90%	60%

<sup>&</sup>lt;sup>11</sup> E.g. stall at DCE, which may then require additional intervention such as bioaugmentation with *Dehalococcoides*. <sup>12</sup> Inappropriate deployment can be associated with failure to reach target volumes and even daylighting to the surface



15/12/2016

**Table 4:** Cost Benchmarking of remediation options for an example contaminant plume (Kvapil *et al.* 2016)

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

#### 3.4 Appropriate use of nanoremediation

#### 3.4.1 Regulatory Position

Nanoremediation must comply with the same regulatory requirements applying to any other substance being injected into the subsurface as part of a remediation process; and the same health and safety requirements for materials handling and use:

- 1. Materials and substances used in remediation must fully comply with prevailing health and safety legislation, and public domain material safety sheets are a prerequisite.
- 2. Adequate demonstration that the remediation being deployed will achieve the necessary risk management goals for the purpose it is being used for. As for all contaminated land management activities, effective use of conceptual site models underpins reliable and robust decision making.
- 3. Risk management of any substance release, unreacted fractions and potential by-products in the ground (including delivery, transport and change over time) with respect to human health, ecological and environmental risks/toxicity.
- 4. Compliance with REACH regulation with respect to production and marketing of (new) substances. Note: Under REACH, the different forms (solids, powders, nanomaterials, etc.) of the same substance can be considered within a single registration of a substance. However, the registrant must ensure the safety of all included forms and provide adequate information to address the different forms in the registration, including the chemical safety assessment and its conclusions, e.g. through different classifications where appropriate (EC 2016).

At a European level nanoremediation is not seen as being a special case from a regulatory stand-point. However, given that there can be general public concerns over nanotechnologies, NanoRem has carried out comprehensive ecological testing of a range of NPs, sustainability assessments and risk-benefit analyses. Additionally, NanoRem has developed a protocol for risk assessment of NP deployment *in situ* for its own work (Nathanail *et al.* 2016). Other key outputs include in depth reporting of field studies (described below) and field based monitoring protocols. All of these outputs are or will be included in the nanoremediation toolbox (see Section 2.4).

There are no specific generic sustainability advantages or disadvantages to the use of nanoremediation. As for all *in situ* remediation work, sustainability is highly dependent on site specific factors,



and all technologies should be considered on their particular merits for any particular site. With regard to eco-toxicological aspects it was found that no significant toxicological NP related effects were observed on soil and water organisms when ecotoxicological test were undertaken using the Nano-Rem NPs (including with respect to the particles' interaction with contaminants and the resulting products)<sup>13</sup>. However, toxicity was detected from a process additive for one of the milled nZVI products, but this may have been an anomaly. Field scale observations detected transient perturbations in aquifers, attributed to (intentional) pH and redox shifts resulting from NP introduction. Of course, NP injections were taking place into already highly disturbed subsurface environments.

#### 3.4.2 Appropriate Use

There are a number of nanoremediation variants. To date, nanoremediation has mostly been deployed as an *in situ* chemical reduction or oxidation technology (ISCR/ISCO). However, it can also act as an *in situ* stabilisation technology, and there is also good evidence that some approaches can act to enhance processes of *in situ* anaerobic bioremediation. The type of effect depends on the type of NP deployed.

Although the first deployment of nanoremediation in the field took place as early as 2000, its rate of adoption has been slow compared for example with other ISCO/ISCR technologies over the past 15 years. While more than 100 field deployments have taken place worldwide, the majority of these have been field tests rather than practical commercial technology deployments. It is therefore fair to describe nanoremediation as an *emerging* technology, with a number of variants entering regular commercial use in some countries; and other variants more or less at a pre-commercial stage, and some still the subject of research.

The status of a number of nanoremediation applications is *pre or early stage commercial*, i.e. *ready for adoption* for a range of applications. As for any ISCO/ISCR technology, the *appropriate* use of nanoremediation requires:

- Sound technical evidence for effectiveness of the nanoremediation solution being offered for the particular problems being considered,
- A sound rationale for the specific risk management functionality required, linked to a robust site conceptual model and suitable verification procedures,
- A clear option appraisal case, including consideration of sustainability aspects, for example as described by ISO (ISO 2015) and
- That all materials used must fully comply with all relevant safety health and environmental information requirements and must be suitably documented as doing so.

#### 3.4.3 Applications

As described in Chapter 2 and Annex 1, nanoremediation technologies have predominantly been applied to remediate chlorinated solvents, but have also been applied in the mitigation of heavy metals and BTEX. Most field applications so far have focused on plume (groundwater) management. There have been few applications for treatment of contaminant source terms. There is potentially a good opportunity for source management using nanoremediation in dealing with secondary or dif-

<sup>13</sup> http://www.nanorem.eu/Displaynews.aspx?ID=824



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fuse sources, for example, smaller spills or residual sources remaining after an extraction treatment. In addition, there is growing evidence that nanoremediation works well in tandem with biological treatments, facilitating a more rapid change in subsurface redox conditions and hydrogen availability facilitating microbial processes such as dehalorespiration.

### 4 Nanoremediation and sustainability

Sustainability considerations are increasingly being used in decision-making processes for soil and groundwater remediation, requiring an evaluation of environmental, economic and societal aspects. A number of global initiatives have been set up to provide guidance and tools for sustainability assessment of remediation (<a href="http://www.claire.co.uk/projects-and-initiatives/surf-international">http://www.claire.co.uk/projects-and-initiatives/surf-international</a>), and NICOLE and Common Forum published a position statement on "Risk-informed and sustainable remediation" (<a href="http://www.nicole.org/uploadedfiles/2013%20NICOLE-Common-Forum-Joint-Position-Sustainable-Remediation.pdf">http://www.nicole.org/uploadedfiles/2013%20NICOLE-Common-Forum-Joint-Position-Sustainable-Remediation.pdf</a>) that indicates both regulatory and industry support for integrating sustainability assessment with risk-based management of land contamination.

Nanoremediation is an emerging remediation technology, and the NanoRem project provided a unique opportunity to assess sustainability characteristics of nanoremediation against established remediation technologies. As part of the NanoRem project, the sustainability of nanoremediation was debated with a cross-sectoral stakeholder group at a "Sustainability and Markets" workshop and two sites were subject to qualitative sustainability assessment.

#### 4.1 "Sustainability and Markets" workshop

The "Sustainability and Markets" workshop was held in Oslo on 3-4 December 2014. It involved 36 participants (20 external to the NanoRem project) from nine different countries, including land managers, consultants, technology contractors, planners, regulators and other experts, with various background and interests.

Interactive brainstorming discussions in The World Café<sup>TM</sup> style were held to investigate the range of generic "nanoremediation" sustainability issues that either related directly to the technology, or to the perceived risks and benefits. The overall consensus was that it was legitimate to explore the sustainability of nanoremediation, but with a clear understanding of the technology, its advantages and limitations. Some concerns were expressed including the current cost of production of NPs, public perception of risks and knowledge gaps (uncertainty). The fact that no substantive "new" issues were identified was a positive outcome, indicating that the boundaries of the NanoRem project had been well defined.

A case study was presented based on information from one of the pilot sites (pre-site trial) to take the generic thinking developed during The World Café<sup>TM</sup> session and to consider sustainability assessment in the context of a specific site. The delegates were split into groups and asked to carry out a qualitative assessment of pre-selected remediation options to treat a contaminated groundwater plume, and to identify criteria that are likely to be important and that differentiate between management options within the site context. It was concluded that there is little to differentiate between nanoremediation and the other *in situ* technology assessed (enhanced bioremediation) apart from



uncertainty and evidence. This conclusion would be tested for one NanoRem pilot site with the benefit of information from the site trial being available.

### 4.2 Sustainability assessments

The NanoRem project has carried out qualitative sustainability assessments for the use of nanore-mediation at two sites:

- 1. A retrospective assessment for an existing nanoremediation deployment at the Spolchemie I pilot site in the Czech Republic
- 2. A forward looking assessment for a potential nanoremediation deployment in the UK.

Assessments were carried out by a small group of remediation professionals from AQUATEST, CL:AIRE, r3 and, for the UK site, Vertase FLI Ltd. This provided a blend of practical experience of remediation, sustainability assessment and knowledge of the site and stakeholders' views. The assessors used a workbook prepared for NanoRem (available from <a href="http://www.nanorem.eu/displayfaq.aspx?id=12">http://www.nanorem.eu/displayfaq.aspx?id=12</a>) that is based on recognised good practice from European and UK networks. An example radar plot showing the ranking of each technology against environmental indicators is shown in Figure 3. Further information is available in NanoRem DL8.2 (Braun et al. 2016).

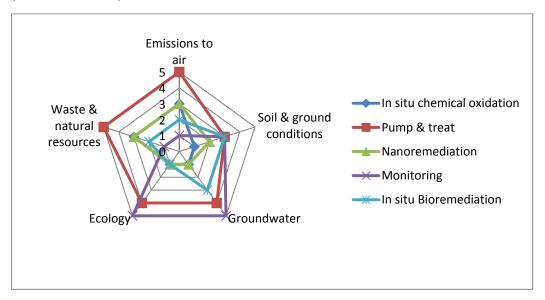


Figure 3: Radar plot for Spolchemie 1: Environmental indicators

The findings from both sustainability assessments indicate that nanoremediation compares favourably with other *in situ* options. This is an encouraging outcome, despite widely reported concerns over the release of NPs and emerging status of the technology. Further differentiation of the *in situ* options may be refined by progressing to a more quantitative tier of assessment and/or engaging the opinions of wider stakeholders. Both assessments were contractor-led and are therefore preliminary and, in practice, would be used to support further stakeholder engagement. This has not taken place (yet) at either site owing to site sensitivities and timing, but a further stage of engagement with wider stakeholders would be standard practice. Wider stakeholder engagement may lead to some change to the outcomes, but nanoremediation is still likely to compare favourably with other *in situ* options, particularly when supported by field test data.



These assessments provide a unique resource that can benefit any technology providers, site owners, regulators and consultants who are involved in future nanoremediation projects by informing them of the potential sustainability benefits and challenges associated with the application of this technology. This NanoRem work has also provided an opportunity to apply the work produced by key networks in Europe to the sustainability assessment of such an emerging technology.

## 5 Nanoremediation markets in the medium to longer term

In order to develop an exploitation strategy that considers the medium to longer term potential market development for nano-particle enabled remediation, any analysis has to deal with an uncertain future. The factors (i.e. drivers and uncertainties related to driver development) that foster or inhibit the evolution of the market need to be better understood. It is unclear how the factors likely to influence the nanoremediation market development are linked, and how they are likely to develop in the future. It is challenging, therefore, to make any straightforward predictions regarding the emerging nanoremediation market. As a result, traditional supply and demand modelling is unsuitable. A scenario approach has therefore been used to help forecast potential market developments and identify key factors. The outcomes are utilisable for: "real-world" business development, deducing strategies for market activities; informing policy development; and/or informing regulatory authorities, highlighting the potential for nanoremediation.

### 5.1 Introduction / the Scenario Approach

Scenarios can be defined as "internally consistent stories about ways that a specific system might evolve in the future" (March *et al.* 2012, 127). In essence, a scenario-based approach to understanding possible market trends uses available evidence and stakeholder participation to develop a number of narratives describing the potential evolutionary outcomes of a specific market system. Hence, this approach has been applied in order to help determine:

- (i) The factors (drivers and uncertainties) are in the nanoremediation market-system,
- (ii) The relative impact of the factors, and
- (iii) How the factors are interdependent.

The central idea of the scenario approach as applied in NanoRem has been to use stakeholder engagement formats to gain strategic market, regulatory and academic knowledge on how the market for nanoremediation in Europe could develop until 2025 – thereby identifying different plausible future states and, more importantly, key factors determining theses future states and the decision points and disruptive elements in the development of these factors (see Figure 4).

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

- 1) Conducting a present situation analysis to establish the baseline for scenario development and a framework for factor identification.
- 2) Filtering and systematising factors that drive or inhibit market development. Establishing key determinants (driving and inhibiting factors).
- 3) Projection of how key factors' might change and producing consistent stories about ways the system might evolve in the future. Identification of multiple alternative development trajectories is possible.



### 4) Conclude on lessons for exploitation strategies.

Figure 4 below gives an overview of the scenario approach used. The steps are discussed further in the following sections. The overall approach is discussed in more detail in IDL 9.4 (Bardos *et al.* 2015) and the workshops are discussed in further detail in NanoRem IDL 9.3 (Tomkiv *et al.* 2015) and in Annex chapters 11.3 and 11.4.

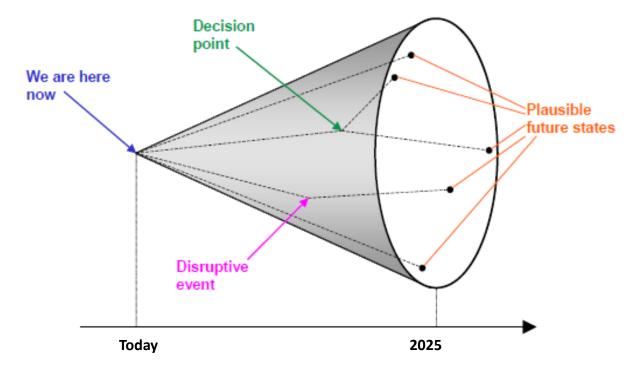


Figure 4: Conceptual Model of Scenario Approach based on Timpe and Scheepers (2003)



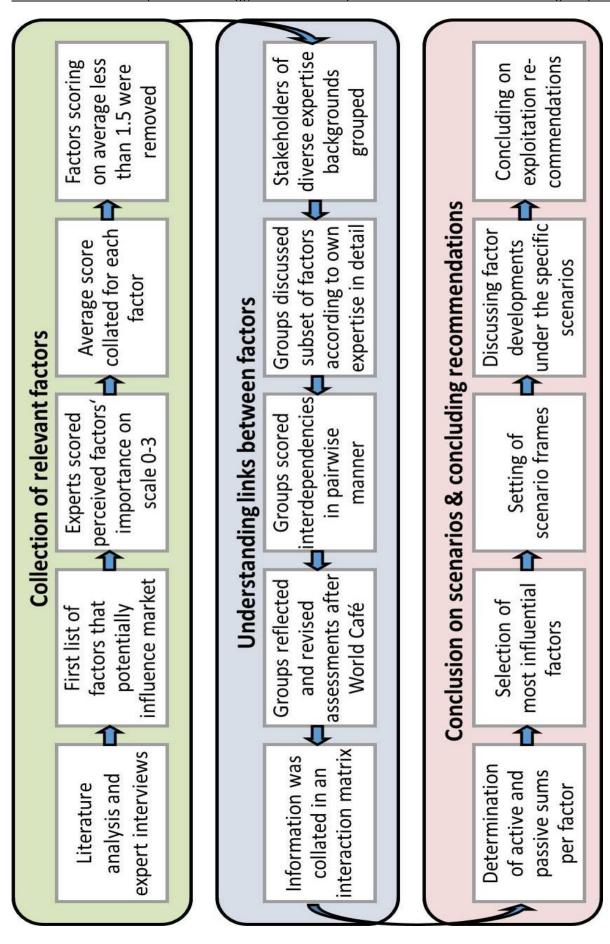


Figure 5: Scenario development process in the NanoRem project

NanoRem

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### 5.2 Establishing the Baseline for Scenario Development

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

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

Expert engagement (key informant interviews and expert discussion) was utilised to establish the most worthwhile timeframe for the scenario approach. A consensus was reached that evolution of the market up to 2025 was the most appropriate scope. It was felt that an assessment looking into the far future would be impossible due to the significance of unknown and uncertain factors. Nevertheless, any factors found to be potentially more time-sensitive will be reported and carefully considered when determining exploitation strategies. After several iterations with expert involvement, a condensed list of 22 potentially influencing factors was established.

## 5.3 Systematising Market Development Factors

To aid step two of the scenario design process, a "Market Opportunities" session was included in the Sustainability and Markets workshop (see Section 4.1).

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

- (0) = Negligible relevance the factor is not an important driver or inhibitor;
- (1) = Minor relevance the factor might have a limited but not so important effect;
- (2) = Considerable relevance the factor is likely to have a notable (indirect) effect;
- (3) = Key relevance this factor is most certainly among those of utmost importance to push or pull the nanoremediation market development.

The responses were collated and an average score (the arithmetic mean as the sum of the scores collected from all 20 respondents divided by the number of the respondents) was calculated for each factor. The results are shown in Table 5, below, in descending order of obtained scores.



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**Table 5:** Preliminary factors and their perceived importance with regards to influencing nanore-mediation market development in the EU up to 2025

Factor	Score	Category		
Most important factors (≥2.00):				
Innovation on treatment of known contaminants with NPs	2.48	Technology		
Regulation of NPs	2.45	Policy		
Validated information on NP application potential	2.40	Communication		
Costs of competing technologies	2.35	Economy		
Standardisation for NPs	2.20	Policy		
Innovations along NPs production chain	2.18	Technology		
Environment (especially soil) protection policies	2.10	Policy		
Synergies with other technologies	2.05	Technology		
Public stakeholder dialogue	2.00	Communication		
Less important factors (>1.50 and <2.00)				
NP treatment of emerging contaminants	1.95	Technology		
Public perception of NPs in general	1.93	Society		
Science-Policy-Interface	1.93	Communication		
Technology and research policies	1.75	Policy		
Growing number of NPs suppliers	1.73	Economy		
Real estate market development	1.68	Economy		
Innovation attitude	1.60	Society		
Environmental awareness	1.55	Society		
Minor factors (≤1.50)	1	<u>'</u>		
EU economic development	1.50	Economy		
Globalisation	1.20	Megatrend		
Industrial and military land use	1.00	Society		
Climate change	0.70	Megatrend		
Demographic change	0.60	Megatrend		

The scorings indicate that several factors influence the development of the market. Some of the scorings, e.g. the ability to treat emerging contaminants with nanoparticles, appear to be surprising and may indicate either bias or epistemic issues in the mind of the responders. As no factor had a scoring > 2.50, it was concluded that no factor is likely to singlehandedly "push" or "pull" nanoremediation market development. However, factors with a score of < 1.5 were omitted from further assessment.

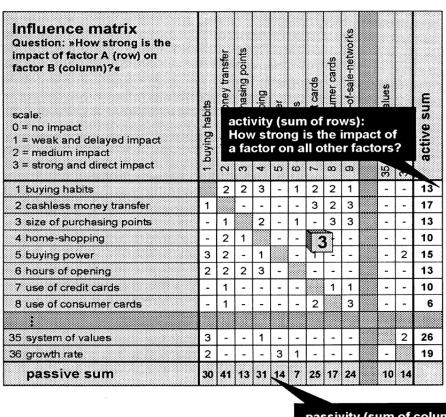


 Table 6:
 Factors likely to influence the nanoremediation market in Europe by 2025

Innovation on treatment of known contaminants with NPs (NPs)	NPs are effective in treating a range of contaminants. They may be superior to existing remediation approaches (being quicker or cheaper to apply or offering another added value) on a site specific basis.
Regulation of NPs	While moratoria against use of NPs for remediation still exist in a few instances, the emerging trend is that NPs can be deployed using existing regulatory regimes. Uncertainties are those experienced in general for the injection of "new" types of material into the subsurface.
Validated information on nano particle (NP) application potential	'Information' dimension describing the quality of available information for decision-making. Information quality can range from a level with great uncertainty with regards to the potential developments of the market and the set of factors driving the market, to a situation where information about nanoremediation is readily available, well tested, and broadly accepted (i.e. "validated").
Costs of competitive technologies	There are already competitive nanoremediation technology solutions, but their international market penetration is low and they face strong competition from more established in situ technologies. Cost effectiveness is highly site specific
Innovations along NPs production chain	The production of NPs could be boosted by improved efficiency based on increasing knowledge and economies of scale, making NPs cheaper.
Environment (especially soil and groundwater) protection policies	There is policy uncertainty at a European level for remediation drivers in general (e.g., with-drawing of Soil Framework Directive versus increasing concerns over 'emerging contaminants'). Specific to nanoremediation 'moratoria' against use exist in some countries/regions but these may be reconsidered, particularly as a result of current research work
Synergies with technologies	NPs can be applied in remediation integrated with other approaches, e.g. bioremediation.
Public stakeholder dialogue	Refers to communication with general public. Risks, uncertainties and benefits should be communicated in targeted formats with relevant public stakeholders. (Dialogue work currently being conducted in the UK may indicate increasing acceptability of nanotechnology use in remediation.)
NP treatment of emerging contaminants	NPs are may be effective in remediating various emerging contamination problems, but research and practical experience are fairly limited at present.
Public perception of NPs in general - What people think of nano	Public perception of NPs is patchy with low consumer knowledge and ambiguity in risk perception. The increasing use of 'nano-products' implies increasing levels of public acceptance for the technology in general, although concerns over some specific potential pollutants such as nano-silver remain.
Science-Policy-Interface - Communication with others	Broadly understood as 'Dialogue' process by which stakeholder groups (in particular those from science, policy and regulation) have informal/formal discussions, consultations and other forms of engagement in order to ascertain the potential application of nanoremediation (in general or in specific cases).
Technology and research policies	European and national policies fund R&D into innovative technologies, generating new knowledge, including a range of nanoremediation R&D and demonstration work (such as NanoRem).
Growing number of NPs suppliers - supplier having available more produces	More producers are entering the market. Suppliers are typically remediation service providers, such as consultancies. More suppliers are considering nanoremediation, although the number investing in expertise, capacities and credibility to provide nanoremediation remains relatively small at present
Real estate market develop- ment	The property market has begun to recover since the financial crash increasing the demand for suitable areas for development – which in turn influences the demand for the remediation of contaminated land.
Innovation attitude – People like new technology	There is an increasing openness in the remediation sector towards innovation paired with will- ingness to invest in inventions and knowledge creation along with greater readiness to apply innovative technologies.
Environmental awareness and sustainability	There is increasing support for ensuring a more sustainable approach to contaminated land management, and this will increasingly affect remediation decision-making. This is a highly site specific consideration.



In order to create scenarios, the interdependencies of the factors determined to be important needed to be better understood. Stakeholders were provided with the factors in Table 5, including short descriptions of each factor. During the workshop, stakeholders were asked to provide opinions, comments and suggestions about the factors and there feedback resulted in more précised descriptions of the factors as given in Table 6. Having reached a joint understanding of the factors, they were also asked to identify and discuss the interrelations of the factors. In order to do this, stakeholders were divided into smaller groups based on their field of expertise. The groups formed were Regulators / Policy makers, Technology, Communication, Economy and Society. Participants in the respective groups were asked to discuss the influence of three or four factors of their respective expert domain on the full list of factors identified to be of importance. For each group a poster with an empty influence matrix was provided showing a short list of factors from the respective field of a group's expertise in the rows on the vertical axis and the full list of factors in the columns on the horizontal axis. Figure 6 illustrates the influence matrix's outline.



passivity (sum of columns): How strong is a factor impacted by all the others?

Figure 6: Interaction matrix illustration (Gausemeier et al., 1998, p. 119)

In a first phase the participants were asked to review and provide opinions, comments and suggestions about the collected factors in the rows. Next, participants were asked to identify and discuss the interrelations of the development of each of their, i.e. to discuss pairwise the influence of development of a factor from the vertical axis on the development of a factor from the horizontal axis. For the assessment, again used a scoring was requested (Figure 6): Considering the European Union in



2025, the impact of the development of the factor in the row on the development of the factor in each column was gauged using the scale:

- (0) = No impact;
- (1) = Weak / delayed impact;
- (2) = Medium impact;
- (3) = Strong / direct impact.

At the end of this phase, each group had filled in their part of the influence matrix. Next, following a "World Café <sup>TM</sup>" format, the experts were invited to discuss the results of the other groups and finally to review and revise their own assessments based on the feedback of others. Facilitators guided these discussions from the identification to the review of the linkages of factors. At the end of the phase, the participant returned to their "home table" and revisited their assessments based on the feedbacks collected from the other groups. At the end of the Session, the annotated posters and notes of facilitators were collected and interpreted. These discussions are reported in detail in Nano-Rem IDL 9.3 (Tomkiv *et al.* 2015) and summarised in Annex Section 11.2.

After the workshop, the information collected from the group sessions was analysed and the factors that are more "active" in influencing other factors were identified, as well as those that are more driven by the these active factors (passive). These relationships are expressed by the "active sum" and "passive sum" as indicated in Figure 6 above and in Table 7, below. Table 7 lists the factors recorded in Table 6 in order of their activity (i.e. how influential a factor is relative to other factors).

**Table 7:** Interrelatedness of factors determining the development of the nanoremediation market

Factor	Active sum*	Passive sum <sup>*</sup>
Science-Policy-Interface	38	26
Validated information on NP application potential	36	21
Environment (especially soil) protection policies	25	17
Public stakeholder dialogue	25	20
Synergies with technologies	24	20
Innovations along NPs production chain	24	21
Costs of competitive technologies	24	24
Growing number of NPs suppliers	24	28
Regulation of NPs	23	19
Technology and research policies	23	27.5
Innovations in treatment of known contaminants with NP	22	29.5
Environmental awareness	21	19
NP treatment of emerging contaminants	19	26
Innovation attitude	16.5	24
Public perception of NPs in general	14	21
Real estate market development	11.5	8

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



### 5.4 Projection of Factor Development and Establishing Consistent Scenarios

As part of the work in the final phase of the scenario development, a series of expert engagement activities has been undertaken. In March 2015, NanoRem conducted a first focus group meeting and expert workshop in Berlin, Germany, in order to discuss the establishment of consistent scenarios. Further special sessions at AquaConSoil conference 2015 and RemTech 2016 as well as a second focus group meeting and expert workshop in London, UK, complemented the process.

In each event, the participants were provided with an overview of the interim results of the scenario analysis work. They were shown that the two most "active" of the key factors were identified as: "Science-Policy-Interface" and "Validated information on NP application potential" (see Table 7) and hence, these factors are likely to be crucial in determining the development of the nanoremediation market system. These two factors were suggested to develop framing elements for a conceptual scheme for scenario states. The participants discussed the meaning of these factors in the Berlin event and tentatively defined them as follows:

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

These dimensions form the conceptual scheme for the scenario states of the nanoremediation market – and were confirmed in all expert engagement events. These scenario states show four potential future states for the market, see Figure 7 below, (going clock-wise in each quadrant of the matrix):

- I. Scenario I "Knowledge exchange": Validated information is broadly available AND there is comprehensive dialogue between stakeholders, in particular those from science, policy and regulation.
- II. Scenario II "Dialogue under uncertainty": Validated information is lacking and uncertainty is still significant BUT there is comprehensive dialogue between stakeholders, in particular those from science, policy and regulation.
- III. Scenario III "Isolation in uncertainty": Validated information is lacking and uncertainty is still significant AND there is no or only minimum dialogue between stakeholders, in particular those from science, policy and regulation.
- IV. Scenario IV "Isolated knowledge": Validated information is broadly available BUT there is no or only minimum dialogue between stakeholders, in particular those from science, policy and regulation.



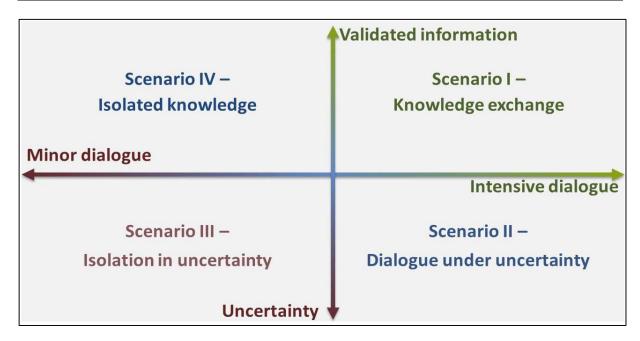


Figure 7: Conceptual scheme for scenario states

These initial findings were presented to and discussed at additional engagement activities, in particular in the two focus group events in Germany and the UK. The focus group format is commonly used to complement other methods of information collation (Morgan 1996, Rizzo et al. 2015). Whereas interviews and questionnaires were used beforehand to collect information on market driving or inhibiting factors, the focus group format was chosen to elucidate the potential development of the different drivers under different scenarios in order to conclude on recommendations for exploitation of the technology. As Rizzo and colleagues (2015) describe, focus groups are a special type of stakeholder engagement used to collect information from a limited number of members. Participants are guided by a facilitator through a discussion focussing on several related topics in order to collate opinions and expertise of group members in a comfortable environment (Rennekamp & Nall 2003, Wilcher et al. 2000). Such settings enable participants to define and frame their individual points of view by comparing them to others' perspectives (Rizzo et al. 2015).

The German focus group in March 2015 was a meeting of practitioners, regulators and academics dealing with nanoparticles and/or remediation. Most participants greatly appreciated the meeting and exchange about nanoremediation with other stakeholders whom they had usually not met before. The meeting confirmed the importance of the key factors "availability of valid information" and "dialogue between stakeholders" as meaningful framing variables of plausible future states of the market. The group strived for a joint understanding and a substantiation of these two factors which were hence used and confirmed in the following engagement activities. Moreover, the groups draw some key conclusions on the potential market development for nanoremediation. Consultant, market and industry representatives emphasised the need for more documented applications and success stories of the technology's application. The role of trustworthy communicators and knowledge arenas (such as DECHEMA or Battelle) was highlighted. The necessary recognition of the site specificity was pointed out in this respect, too. Research funding could support closing the knowledge gap, in particular related to risk understanding with public research and for elucidating the innovative potential with research driven by market interested industry and consultants. Overall, a concentrated



dialogue of problem owners, consultants, researchers and regulators was stressed to be essential. For details see Annex Section 11.4.1.

The UK focus group in July 2016 also confirmed the key market determinants being available validated information and dialogue of stakeholders. There is a need to demonstrate in the UK in UK conditions its applicability to understand the performance envelope of the technology. A specific need has been stated to clearly understand the human health risks. Also a better understanding and documentation of the fate and transport of NPs is vital for market development. In the specific context of the UK, the voluntary moratorium on environmental release of NPs was a main topic of the focus group. It is understood to be a significant market determinant in the country. Some UK workshop participants expressed hope that Defra will review this in the light of emerging validated information availability (e.g. NanoRem outcomes). However, it was emphasised that the moratorium does not prevent the regulator agreeing to pilot deployments of nanoremediation in the field, which would support the creation of further validated information and exchange of actors, and could ultimately support a case for the moratorium's removal. Last not least as summary, opportunities are seen in the UK for nanoremediation. For details of the discussions see Annex Section 11.4.2.

The expert engagement in meetings was complemented by an online consultation – see Section 5.6 below concluding into the identification of strengths, weaknesses, opportunities and threats of nanoremediation technology regarding its marketability and exploitability (see Section 6.1).

### 5.5 CEN standardisation initiatives affecting nanoremediation

NanoRem applied for a project liaison with CEN Technical Committee 352 (Nanotechnologies) in early 2013. It took, however, until December 2015 to finalize this liaison. This agreement was intended to ensure direct access to the standardisation activities in CEN, in order to include standards in the NanoRem work, but also to integrate the outcome of NanoRem in new standards and offer the expertise of the researchers in NanoRem to the respective CEN committee.

After the agreement had been finalised two meetings of the CEN TC 352 have been held. The first one in April 2016, which was on too short notice for the representative of NanoRem to attend. During the second meeting in October 2016, NanoRem as a consortium and a project was presented to the members of TC 352. The feedback from the chairman was somewhat reluctant, because he saw no real basis for standardisation in this special application of nanoparticles in remediation applications. Nonetheless, project partners producing NPs have been made aware of the CEN Guidance (draft) for the responsible development of nanotechnologies<sup>14</sup>.

### 5.6 Interim exploitation strategy web consultation outcomes

The expert engagement in meetings was complemented by an online consultation, following NanoRem's initial findings reported in the interim "Risk Benefit and Markets Appraisal Initial Exploitation Strategy" report. This consultation was made available between April and July 2015 (see Annex 3 – DL9.1 Consultation Summary for details.) Participants were asked to rate the importance of

<sup>&</sup>lt;sup>14</sup> FINAL DRAFT FprCEN/TS 16937 November 2015



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certain factors changing over the next 10 years to drive the market development for nanoremediation. They were asked to score from "3 = very important" to "0 = unimportant". The factors included:

- Costs (comparing to competing technologies)
- Field Scale Experience
- Relative Effectiveness
- Relative Risks
- Technology Dread
- Current knowledge
- Synergy (combining with other technologies)
- Sustainability

In general, the feedback is found to be in line with the discussions at the expert engagement events. Experts expect improvements of nanoremediation competiveness as **costs** are likely to remain the same or improve against other competing technologies. The majority of experts (74%) also identified that by 2025 relative **effectiveness of nanoremediation** would stay the same or improve. The assessment of the potential for **synergies with other technologies** was not harmonious.

Regarding the key drivers identified in the scenario process, the consultation results indicate the following: Related to "dialogue", experts stated that there was a low level of dialogue between most, including the scientific community, industry, and regulators. Stakeholders provided suggestions how to improve dialogue by "Independent scientists – consultant who has no conflict of interest should be approached for an opinion – in order to have a better understanding of all pros and against" and "there is nothing comparable to true success stories written in an understandable manner".

These success stories also link to the availability of "information". Indeed, field scale experience was identified as important or very important by all experts. Related to this, the majority of stakeholders identified that the risk perception and technology dread were important factors related to available information. Both are assumed to being likely to rather improve over the next ten years, stating "at the moment, there is more risks assumed and feared than really shown to exist. This will change with better knowledge basis." All stakeholders identified that current knowledge improvements are important or very important if nanotechnology was to improve its use in the next ten years. The majority expects that knowledge will improve in the next ten years whereby some explained their reasoning as "more complex information will be available".

## 5.7 General market scenario findings

In summary, the existence of validated data on case studies is critical for market development – in particular if this information can be told as success stories. In addition, dialogue between the stakeholders (science – industry – policy – general public) is crucial. An open debate is the question: Who is best to initiate the communication: Does the science bring information to the consultants and then to the regulators? – The assessment left open an answer, but their seems agreement to state that those interested in the promotion should invest, i.e. politics should found research in innovative NP to tackle emerging contaminants and prevent risks to society; researchers should communicate their results in a way that is understood by the market and regulators; consultants should dare the venture and gain from early mover advantages and so forth.



The majority of involved experts expect that knowledge will improve in the next ten and "once seen as tried and tested practitioners will be more likely to apply it". If it will be documented in a plausible way and involved actors will speak about the outcomes, it will be far more likely to foster nanoremediation and exploit the market for it. Stakeholders provided suggestions how to improve dialogue by "Independent scientists - consultant who have no conflict of interest should be approached for an opinion - in order to have a better understanding of all pros and against" and "there is nothing comparable to true success stories written in an understandable manner".

Any new technology has to prove that it is complementing or improving existing technologies at an appropriate economic cost and acceptable risks. There are no absolute blocks to an uptake of nanoremediation in the markets, but documented, validated case studies and understanding the "operational window" of nanoremediation are found to be extremely significant. Research is seen by experts as an element which could substantially change opinions as results can help to deliver the required validated information – however, academics must communicate these in an appropriate way to business and regulation.

The scenario assessment approach has yielded a wealth of insights into the diversity of factors influencing the potential market emergence of nanoremediation. In particular, it helped to conclude on the strengths, weaknesses, opportunities and threats of nanoremediation technologies general market value proposition and exploitability (see Section 6.1).

## 6 Exploitation strategy

## 6.1 A SWOT analysis of the general market position of nanoremediation

A value proposition is "a business or marketing statement that a company uses to summarise why a consumer should buy a product or use a service. This statement convinces a potential consumer that one particular product or service will add more value or better solve a problem than other similar offerings"<sup>15</sup>. A SWOT analysis was used to explore the value proposition for nZVI in Year 2 of the project (Bardos *et al.* 2015). SWOT Analysis is a useful technique for understanding Strengths and Weaknesses of a product or service, and for identifying both the Opportunities open for and the Threats it might face<sup>16</sup>. This provides an analysis of factors that may affect (positively or negatively) the value proposition and exploitation of nanoremediation in contaminated land management markets. These SWOT issues naturally fell into a series of broader categories and the Year 2 work made a tentative assessment of how the situation for each of the broad categories might change by 2025. Both the 2015 SWOT analysis and the related broader category appraisal are reproduced at the end of Annex 2 of this deliverable. Based on the forgoing chapters the SWOT analysis was updated to take into account both new information and a slightly wider range of NPs, see Table 8. However, as the dominant NP in use, the SWOT analysis is still very much dominated by nZVI variants. Similarly, the broad category analysis has been updated, see Table 99. This provides an initial - and tentative -

https://www.mindtools.com/pages/article/newTMC 05.htm Accessed November 2016



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<sup>15 &</sup>lt;u>www.investopedia.com/terms/v/valueproposition.asp</u> Accessed November 2016

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

 Table 8:
 nZVI Strength, Weakness, Opportunity and Threat (SWOT) for the use of nanoremediation

Strengths		Weaknesses	
Rapid contaminant treatment where nano-activity is taking place	Relative effectiveness		
Laboratory investigations indicate for many contaminants there is a complete destruction effect for chlorinated solvents	Relative effectiveness	Process intermediates have been found in some field deployments, although whether these are biological in origin is not clear	Relative effective- ness
Laboratory investigations indicate a wider treatable range of contaminants	Relative effectiveness	Field scale deployments remain more limited in the number of contaminant types targeted	Relative effective- ness
Nanoremediation may be more tolerant of <i>in situ</i> conditions than <i>in situ</i> bioremediation	Relative effectiveness	Repeat applications may be needed more frequently than for micro-scale iron	Relative effective- ness
Nanoremediation deployments tends to facilitate <i>in situ</i> dehalorespiration (bioremediation)	Relative effectiveness		
Material safety data sheets available for all NPs listed in Section 1.5	Current knowledge	Public domain publications of field scale deployments remain relatively scarce	Current knowledge
A comprehensive set of deployment tools and guidance are available for NanoRem, often exceeding requirements for competing technologies (e.g. related to deployment risks)	Current knowledge	Lack of examples of field de- ployments with comprehensive sustainability assessment (but expected to be a highly site spe- cific consideration)	Current knowledge
NanoRem studies indicate that ecotoxicological impacts of NPs listed in Section 1.5 would be limited in scale and duration	Relative risks		
Avoidance of long term impacts on aquifer levels of sulphate	Relative risks		
As an <i>in situ</i> technique there may be reductions in some site risks compared to <i>ex situ</i> remediation (e.g. reduced exposure of workers to contaminants)	Relative risks		
A number of air stable forms are available (e.g. NANOFER STAR, Carbo-Iron®) tested by NanoRem are now commercially available with robust delivery systems	Relative risks	Handling risks for earlier nZVI variants may be greater than granular ZVI	Relative risks



Availability of field based tests to monitor migration of NPs from NanoRem (Oughton et al. 2015).	Relative risks	Limited availability of know-how for field based NP monitoring techniques	Relative risks
Limited longevity of action may reduce environmental risks and allow more targeted applications	Relative risks / Ease of use		
Increasing availability of deployment know-how and services	Ease of use	Limited migration in the subsur- face may require additional in- jection points / wells	Ease of use
Nanoremediation is easier to deploy and requires less infrastructure and maintenance than pump and treat, and other remedial techniques depending on the mode of deployment, and can exploit existing wells	Ease of use	Deployment retains a need for fairly specialised experience and know-how	Ease of use
100 known field deployments in the field (see Section 6.2), includ- ing a number of deployments by NanoRem with measurements of NP performance and transport	Field scale deployments	Knowledge gaps remain in cost performance information. Public domain and validated reports of commercial deployments are lacking.	Field scale de- ployments
As an <i>in situ</i> technique there may be reductions in site costs compared to <i>ex situ</i> remediation (e.g. reduced waste generation, reduced fuel usage)	Relative costs	NP costs are relatively high, and there is relatively little experi- ence of overall nanoremediation project tests	Relative costs
Opportunities		Threats	
Increasing range of treatable prob- lems (contaminant types and sub- surface conditions)	Relative effectiveness	Numerous coatings, modifiers, catalysts which could make establishing risks complicated	Relative risks
Treatment of contaminants in the vadose zone	Relative effectiveness		
Potential for treatment of source terms	Relative effectiveness	Source term treatment effectiveness is in general constrained by the accessibility of the source	Relative effective- ness
Integrated approaches (e.g. combining nano and micro scale ZVI) may improve effectiveness and reduce costs (also opportunities with electro-remediation and bioremediation approaches)	Relative effectiveness		



Inclusion of nanoremediation in <i>in situ</i> integrated treatment approaches <sup>17</sup>	Relative effectiveness		
Development of more convenient deployment systems and information extending the range of potential service providers able to deploy nanoremediation	Ease of use		
Early adoption experience creates an opportunity to extend a business lead in know-how and case study experience	Field scale deployments	Unwillingness to provide regulatory or problem holder permission to use nZVI (may be addressed by NanoRem information.)	Field scale de- ployments
Improved understanding could lead to reduced public and regulatory fears, facilitated by NanoRem outputs	Technology dread	Potentially significant public concern about nanotechnology being inherently risky (appears to be declining)	Technology dread
Cost reductions associated with economies of scale or integrated treatment approaches	Relative costs	Perceived costs of nanoremedia- tion remain high relative to com- peting technologies	Relative costs

**Table 9:** Possible future trends affecting broader SWOT categories

Item	Time sen- sitive?	Possible development by 2025	Certainty of development
Relative costs	Yes	Economies of scale lead to cost reductions related to: a) production of NPs b) application of NPs Combined / integrated approaches bring costs down to competing options such as in situ bioremediation	Highly likely, scaled up production (early adoption) already occurring - see Section 6.4 - and field deployments of engineered combined approaches already taking place 18.
Field scale experience	Yes	Additional field trials including a wider range of contaminants could strengthen the evidence base for nanoremediation effectiveness and reduce public concerns associated with deployment safety	Highly likely. This has been a key task of the NanoRem project
Relative effectiveness	Yes	a) Research funding to address difficult contaminants and develop novel NPs b) Vadose zone treatment, if developed, could have huge benefits for difficult / untreatable problems such as highly recalcitrant	a) Highly likely – There are a number of research projects taking place across Europe b) Likely - Currently vadose zone treatment has not been

<sup>&</sup>lt;sup>17</sup> An interesting comment from one of the site owners engaged with NanoRem made during the final conference is that they are not afraid of complexity if it leads to a more robust, effective and lower cost remedial design. (Pierre Metz, Solvay, Pers Comm November 2016.

<sup>&</sup>lt;sup>18</sup> Cernik et al. Electric-field enhanced migration and reactivity of nZVI: implications for groundwater treatment technologies (submitted). & Cernik et al. Case study on application of nZVI supported by electrokinetics (submitted)



Item	Time sen- sitive?	Possible development by 2025	Certainty of development
		contaminant classes (e.g. PCBs, dioxins, etc.) c) Development of coatings to improve persistence and mobility	well investigated, but exploit- ing NPs for this use may be possible
			c) Highly likely - Relatively certain, research being carried out, including by NanoRem
Relative risks	Yes	Development of coatings to improve persistence and mobility – introducing an additional element of risk	Highly likely, e.g. research being carried out by Nano- Rem
Ease of use	Yes	Improvement and productising <sup>19</sup> of nanore-mediation deployment	Highly likely, research being carried out, including by NanoRem and proposed follow up projects
Technology dread	Yes	Gradually diminishing as an issue as research outcomes and information become more widely available.	Likely, for example as a result of NanoRem outputs. Additionally surveys of public attitudes indicate decreasing dread of nanotechnology, moving to more conventional concerns about chemical hazards (e.g. Beddoes <i>et al.</i> 2016).
Current knowledge	Yes	Knowledge expansion leading, improved certainty of effectiveness, increased uptake of the technology, and more straightforward deployment and permitting.	Highly likely, the NanoRem toolbox is intended as a major contribution towards this development However, a key to success will be ensuring widespread availability of this information.

## 6.2 Facilitating immediate opportunities

In 2011, Bardos *et al.* identified 58 deployments of nZVI in the field from pilot tests to commercial applications. As of November 2016 WP9 has extended this listing to over 100 field scale deployments. These are listed in Annex 3. The vast majority of these are pilot scale deployments tackling plumes in groundwater. However, there have been an increasing number of large scale deployments over the last five to ten years. The most recent deployments use more advanced NP products produced in Europe (and tested by NanoRem) as US and Japanese production and supply has diminished, as a result of low levels of use. Most applications have been for plume control (i.e. pathway management in groundwater), but a number of citations for source control measures have been included in Annex 3 and a number of examples specifically cite treatment of aquifer matrix materials,

<sup>&</sup>lt;sup>19</sup> I.e.: To take a new service, product or feature that a company has provided to a single customer or a few customers on a custom basis, and turn it into a standard, fully tested, packaged, supported and marketed product, <a href="https://www.investopedia.com/terms/p/productize.asp">www.investopedia.com/terms/p/productize.asp</a>



which implies residual source treatment. The most frequently occurring treatment problems remain (as for Bardos *et al.* 2011) chlorinated solvent and metals (such as Cr (VI) problems). However, deployments for other problems such as "pesticides" have also taken place.

In Section 6.1 several trends were identified as affecting the SWOT analysis for nanoremediation. Table 10 suggests a series of measures, that are readily achievable that could impact these trends to benefit strengths and opportunities for nanoremediation, whilst mitigating for weaknesses and threats. These suggestions are based on the focus group and stakeholder discussions reviewed in Chapter 5, as well as taking into account the existing pattern of deployment summarised in Annex 3 and the cross-benchmarking with *in situ* bioremediation and conventional approaches to *in situ* chemical reduction suggested in Section 3.4. The table also highlights where interventions are related to specific exploitation activities being undertaken by NanoRem partners (see Section 6.4).

Table 10: Readily achievable interventions to enhance nanoremediation deployment

Item	Possible trends to 2025	Interventions
	Economies of scale lead to cost reductions related to: a) production of NPs	Transfer of more readily usable nanoreme- diation systems to commercial scale manu- facture of NPs and productising deployment applications and guidance.
Relative costs  b) application of NPs  Combined / integrated approaches bring costs down to competing options such as in situ bioremediation		Effectively validated field scale deployments of combined / integrated approaches with release of reliable cost and performance data.  Specific NanoRem exploitation activity.
Field scale experience	Additional field trials including a wider range of contaminants could strengthen the evidence base for nanoremediation effectiveness and reduce public concerns associated with deployment safety	Replication of nanoremediation application via early adopters who might gain market edge in know-how / service delivery is facilitated by NanoRem outputs and guidance.  Specific NanoRem exploitation activity.
Relative effectiveness	a) Research funding to address difficult contaminants and develop novel NPs b) Vadose zone treatment, if developed, could have huge benefits for difficult / untreatable problems such as highly recalcitrant contaminant classes (e.g. PCBs, dioxins, etc.) c) Development of coatings to improve persistence and mobility	A range of related research projects are underway or at the proposal stage by NanoRem partners and evidently as the number of publications grows right across the academic community.  Specific NanoRem exploitation activity.
Relative risks	Development of coatings to improve persistence and mobility – introducing an additional element of risk	A range of related research projects are underway or at the proposal stage by NanoRem partners and across the academic community.  Specific NanoRem exploitation activity.
Ease of use	Improvement and productising of nanoremediation deployment	Include productisation as a key feature of activities in field scale deployment projects for nanoremediation and integrated approaches, using the NanoRem toolbox as a platform for further development.



Item	Possible trends to 2025	Interventions
		Specific NanoRem exploitation activity.
Technology dread	Gradually diminishing as an issue as research outcomes and information become more widely available.	Improvement of overall information availability and simple information relating to appropriate use (see Section 6.3).  Specific NanoRem exploitation activity.
Current knowledge	Knowledge expansion leading, improved certainty of effectiveness, increased uptake of the technology, and more straightforward deployment and permitting.	Improvement of overall information availability based on the NanoRem toolbox, and ensuring its availability from multiple platforms, to achieve a scenario where there is extensive exchange of well validated information (see Figure 7).  Specific NanoRem exploitation activity

# 6.3 Broadening the appeal of nanoremediation

NanoRem has undertaken a number of actions intended to broaden the appeal of nanoremediation in order to improve the extent and quality of available validated information and to improve the dialogue between various stakeholders The NanoRem actions include practical measures, engagement measures and informational measures. The practical measures include:

- Technology optimisations (for example related to NP stability and deployment modes), from lab through scale up to pilot deployments in the field
- An improved understanding of fate and transport, including the development of transport models, and, in particular, the development and testing of field based monitoring tools able to track nano-iron deployments in situ
- A comprehensive assessment of ecotoxicological impacts of NP deployment (for the types listed in Section 1.5)
- A series of field based applications with independent performance assessments.

The enabling impact of these measures for contaminated land management markets has been described throughout this report, and Section 6.2 describes how ongoing measures will enhance these benefits even further.

Engagement measures have included a range of stakeholder engagement activities described in Chapter 1, and scenario forecasting activities in particular described in Chapter 5. In addition, Nano-Rem has been represented at many conferences and provided a wide range of technical publications (listed in the Publications Catalogue, see Annex 1), and has also successfully engaged with a cross-sectoral international panel of practitioners and researchers (the Project Advisory Group). As a result of this engagement work a large number of practitioners over a number of countries have had direct (face to face) contact and discussion with one another and with NanoRem partners, including via presentations and posters at many venues.

An ongoing engagement effort has been an attempt to draft an agreed "Position Paper" on the appropriate use of nanoremediation reflecting a shared opinion with the two major European contami-



nated land management stakeholder networks: NICOLE and Common Forum<sup>20</sup>, and engaging with a NICOLE Working Group on Operating Windows, which took nanoremediation as an example of an emerging technology. While this engagement has been partially successful in raising the profile of nanoremediation with these stakeholder networks, as of November 2016, a shared or endorsed position paper was not possible. This is because of the networks already existing workload, and partly because of the difficulty of agreeing a script that relates to regulatory matters and therefore could pose a direct reputational challenge to either network. The level of ambition has been moderated to that of providing a NanoRem Bulletin on appropriate use, that provides simple "entry level" information similar to the US EPA "Citizen Guide to In Situ Chemical Reduction<sup>21</sup>" The key features of this Bulletin are summarised in Section 3.5, which will feature a *foreword* from one of the networks.

The informational measures have been collated as a NanoRem toolbox, which will be available for public access from early 2017 (see Chapter 2 and Annex 1). Key features of the tool box include:

- A series of externally reviewed bulletins describing the key outcomes of the project (including reviews of all of the field deployments)
- A generalised application guideline for nanoremediation
- A range of supporting information.
- A publications catalogue.

Section 6.4 describes how these informational measures will be continued in the period immediately after the project to maximise the impact of the project on broad awareness of nanoremediation.

### 6.4 Available cost information nanoremediation

Reliable cost and performance information for remediation technologies is a big demand from potential clients, but rarely available in a reliable way in the public domain. Where it is available, the evidence base for pricing levels is not terribly transparent, and rarely technique specific (English Partnerships 2008, HCA 2015), and so the reliability of this information is open to question. Providing information available about nanoremediation costs was not a specific part of NanoRem's field trials. However, one of the trials (in Switzerland) is close to a conventional client based feasibility study. Financial information about this trial reported at the NanoRem final conference (Matz 2016) compared costs with a typical range for pump and treat, estimated as €50 to 500 to treat 1 kg of chlorinated compounds, with treatment duration of decades. The client side (site owner) estimate of treatment costs at this site using nanoremediation was €300 to treat 1kg of chlorinated compounds, which is a comparable cost. However, the treatment time is "years" as opposed to decades. A cross comparison of pump and treat with nZVI "PRB" treatments for the Basque Region in Spain by another of the NanoRem partners estimated that nZVI based "PRBs" would be only 20% of the cost of pump and treat<sup>22</sup>. There are some historic nZVI suspension costs reported in US EPA 2016 which have a very high range, with a 2005 estimate of US\$200 and a 2009 estimate of US\$6,000 per m<sup>3</sup> of suspension. However, as the formulation is not obvious it is not possible to relate these to original NP materials costs. More recently, and in an EU context, Citychlor (2013) report the price of nZVI particles varied between €25 and €325 /kg Fe(0). This variation in price can be put down to the manufacture

Tecnalia Market opportunities in Basque country (Spain) for permeable reactive barriers (Pers Comm)



www.nicole.org and www.commonforum.eu

https://www.epa.gov/remedytech/citizens-guide-situ-chemical-reduction

and also the type of nZVI (stabilised products, modified products, conservation). However, Citychlor found that the cost of particles represented less than 5% of the cost of their pilot test at Herk-de-Stad

Over the course of the project there has been significant discussion about nanoremediation costs, seen by the Project Advisory Group and the participants in the WP9 engagement work as a major hurdle to market acceptance, both in terms of absolute pricing level, and the relatively poor availability of pricing information. A webinar discussion of costs and benefits involving NP producers, service providers and other NanoRem partners took place in November 2015, followed by an e-mail survey of NanoRem NP producers and service providers of cost drivers. Both groups were reluctant to disclose specific project pricing levels, and concerned that generic pricing data might not be very reliable, which reflects limitations on remediation technology general cost information found by previous EU studies<sup>23</sup>.

NanoRem NP producers reported the following. The producers of FerMEG12 (a milled iron NP) believe that the pricing level for market acceptability of their product will be in the region of €50 per kg nZVI. They anticipate scaling up production to achieve this pricing level in the "mid-term". NanoIron (producers of the NANOFER NPs) already supply full scale remediation projects. (Pricing of this nZVI is believed to be broadly around €100 / kg). NanoIron believe that production scale up might reduce their product costs by up to 30%, but that order of magnitude reductions are not likely. On the other hand that NP costs are only a proportion of a remediation implementation's costs, and materials costs are not an absolute prediction of competiveness. A good example of this is the success of the Regenesis²⁴ ORC® product, which compared with *in situ* air sparging could be seen as an expensive means of oxygen delivery to the subsurface on a per kg O₂ supplied basis. However, the product was commercially highly successful and led to a range of other remediation product offerings, and the commercial success of the ORC® was related to how the market perceived is effectiveness in closing projects and an overall life time project cost, which clearly was seen by many clients as price competitive with *n situ* air sparging.

### 6.5 Specific ongoing exploitation actions in NanoRem

A number of specific exploitation actions have taken place in or around the NanoRem project. Several NP types which were pre-commercial at the start of the project began commercial production or reached agreements with producers and distributors.

- Carbo-Iron® has now shifted to commercial production, following an agreement reached between UFZ and ScIDre GmbH. Agreement has been reached with a distributor.
- FerMEG12 was improved by alloying the iron with aluminium during the milling process to a very promising product and will be refined and optimized with respect to properties (reactivity and transport behaviour) and large scale production. For the new material a petty patent has been filed under the name "NanoFerAl".
- The air stable NANOFER STAR has now emerged as fully commercial product which has been deployed at a number of sites, two of which are listed in Annex 3.

<sup>&</sup>lt;sup>24</sup> www.regesis.com



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<sup>&</sup>lt;sup>23</sup> See http://www.eugris.info/displayresource.aspx?r=6508

Nanogoethite has also been productised and is being manufactured now. Particles and applications are available via Prof. Rainer Meckenstock at University of Duisburg-Essen, Germany. The Nanogoethite is also being deployed in a spin out EU project (see below) where improved particles have been developed and are currently tested in the field.

Spin out projects or proposals have been initiated including various members of the NanoRem consortium:

- The Reground project is a H2020 project (<a href="http://reground-project.eu">http://reground-project.eu</a>) including several field applications of nanogoethite, addressing mainly trace element contamination of groundwater (arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, zinc...). The project provides field demonstrations of injection of nanogoethite to produce in situ adsorption barriers for heavy metals. The nanogoethite particles have been further developed with superior stability and injection properties. They migrate over several meters distance during the injection, then precipitate building a conductive barrier where they quantitatively remove the contaminants from the groundwater flow.
- Several members have made a proposal to replicate an integrated nanoremediation (NR) and DC electrokinetic (EK) process using a combination of nano and micro scale zero valent iron, called INR-DC. This extends the range and effectiveness of nanoremediation and makes it price competitive with the current market preference, in situ bioremediation, against which INR-DC also has a very favourable performance. The proposal made under the Fast Track to Innovation scheme is currently under evaluation (November 2016).

Several spin-ot start-up companies have emerged from Nanorem Consortium members, including:, Intrapore UG, Essen, Germany and Photon Water Technology s.r.o, Czech Republic.

Owing to the ongoing interests of the consortium a number of "Year 5" actions will be supported by NanoRem partners, in particular the WP leaders in the project management group (PMG), but open to any NanoRem partner to ensure the continuing availability of NanoRem information, and collaboration to boost the impact of the NanoRem project outcomes. This is not a formal project, but rather a loose informal association of partners seeking to maximise the success of NanoRem. This 2017 dissemination business plan has six components:

- 1) Consolidating conference presentation effort number of NanoRem partners have submitted platform presentation abstracts to AquaConSoil 2017 (<a href="http://www.aquaconsoil.org">http://www.aquaconsoil.org</a>)
- 2) Partners are considering transfer of some key applications guidance information into a series of papers in a special issue of a leading practitioner journal.
- 3) Availability of NanoRem Bulletins and other toolbox components will be provided via several platforms including <a href="www.claire.co.uk/nanorem">www.claire.co.uk/nanorem</a>. <a href="www.nanorem.eu">www.nanorem.eu</a> will be maintained over 2017.
- 4) Initial discussions have taken place about combining key research outcomes as a series of papers in a special issue of a high impact journal. This may have linkage to the AquaConSoil 2017 event where selected papers are published in *Science of the Total Environment*. However a "nanoremediation" special issue of a journal is another possibility. As of November 2016 discussions are still only at a tentative stage.



- The PMG has an ambition to draft a short opinion piece for a major journal about nanoremediation such as Nature or Environmental Science and Technology to influence scientific opinion more generally, and promote interest in the project outputs. Again, as of November 2016 this is still at a tentative stage of discussions.
- 6) Some "Sub-Groups" are writing new research, development and demonstration proposals. A couple of examples are given above.

### 6.6 Gaps and opportunities at the end of the project

As set out in Section 1.4, the NanoRem project has demonstrated and improved the market readiness of a number of NPs and is providing a toolbox containing application guidance, safety datasheets and tools for them, making available field scale deployment test outcomes in a series of independently peer reviewed technical bulletins. NanoRem has also shown that nanoremediation can be deployed in a targeted way and has substantive evidence that the ecological risks of NP deployment in the subsurface have been greatly overstated. Indeed, the NanoRem project has developed a range of supporting deployment risk assessment and sustainability assessment tools to ensure that nanoremediation is safe, effective and sustainable, with a level of scrutiny that far exceeds that which has been required for many of the subsurface amendments required to initiate competitor technologies such as in situ bioremediation or in situ chemical reduction using conventional reducing agents such as micro scale iron or sodium dithionite.

Based on NanoRem's work the main selling points for nanoremediation are:

- Increasing regulatory confidence, facilitated in large part by NanoRem
- Broad source and pathway management applications
- · Rapid effectiveness compared with ISBR and ISCR
- Resilient to conditions inhibitory to ISBR and can facilitate ISBR / Synergistic with ISBR and ISCR
- Portable and more rapidly deployed compared to options like pump and treat
- Reduced risk of taint of sensitive aquifers
- Ecological and aquifer impacts now relatively well understood compared to ISCR and ISBR
- Rapid initiation of treatment by nZVI can also support faster initiation of ISBR.

However, a few substantial market barriers remain: productising NPs and their deployment so that is no longer so bespoke, the perceived cost of nanoremediation and increasing the number of well documented commercial deployments of nanoremediation. These represent the major gaps remaining after the conclusion of NanoRem, which, to some extent remain a "work in progress".

In addition it has not proved possible to conclude an agreed "position paper" with both European contaminated land stakeholder networks on appropriate use of nanoremediation. This gap is related in part to the still limited number of commercial deployments, and the timeline of NanoRem outcomes which mean that its most persuasive outcomes, published in peer reviewed journals, have only just started to emerge, and will continue to be supplemented into 2017 and beyond. Regards the special case of the UK moratorium on the use of nanoremediation, this remains in place, but a NanoRem meeting in the UK in July 2016 has indicated a willingness of UK regulators to consider



NanoRem evidence (preferably as journal papers), but also to support *demonstration* projects of nanoremediation in the UK.

Overall, NanoRem has significantly increased the availability of evidence for the applicability of nanoparticle enhanced remediation techniques. How these will be taken up in the market depends to a significant degree on a continued and ongoing dialogue between stakeholders (e.g. academics, regulation and business).

## 7 Concluding remarks

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

The perception of risk-benefit balance has also shifted. Niche benefits are now more strongly recognised, and some (if not most) of the concerns, for example relating to environmental risks of nanoremediation deployment, prevalent when the project was proposed and initiated, have been addressed. These now appear overstated. However, it appears to remain the case that in some jurisdictions (e.g. the UK) the use of NPs remains less attractive owing to regulatory concerns, and in others (e.g. in Italy) impeded by a lack of awareness, meaning that regulators may demand additional verification measures compared with technologies with which they have a greater level of comfort (see Annex 2). In both cases a higher level of regulatory scrutiny imposes additional project costs and complexities which make nanoremediation less appealing as a practical and cost effective remediation option.

### 8 Recommendations

Many variants of nanoremediation are viable remediation options for niche applications in many European jurisdictions. However, market inertia remains owing to a lack of cost and performance reporting or real, practical deployments of nanoremediation at scale. Market inertia also persists because of concern over costs and concern over risks of an additional higher level of regulatory scrutiny compared with more regularly used alternatives. Hence, for ongoing development the following areas of effort are suggested.

• Continuing productisation of nanoremediation technologies to make them more easily deployable and with less effort.



- Development of nanoremediation alternatives with a more competitive pricing (for example via integrated approaches such a linkage to micro-scale iron, bioremediation and/or bioremediation).
- Providing information that is packaged in a way that is easily understood by various stakeholder groups so that it can readily support nanoremediation deployment, building on the information already consolidated in the NanoRem toolbox.

In the medium term there continues to be an interest in the possibility of nanoremediation addressing recalcitrant contaminants or emerging contaminants, or contaminants seen both as emerging and recalcitrant. There is a large body of research evidence related to nanoremediation for its current niche applications (chlorinated solvents and heavy metals). So perhaps it makes sense for future research and innovation to target nanoremediation for dealing with emerging / recalcitrant contaminants.

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# 10 Annex 1 Dissemination activities

# 10.1 Overview of WP9 Outputs

Table 11 provides a list of NanoRem WP9 outputs up to project Month 24 (January 2015), including a brief description of the content of the output. These form the base material on which this report has been developed.

**Table 11**: Summary of NanoRem outputs

Output	Overview
IDL 9.1 – NanoRem Pro- ject Website	A website for the NanoRem project was developed. The website encompasses an Intranet and an Extranet. Access to the Intranet is limited to members of the NanoRem consortium. The Extranet serves for communication with stakeholders and provides Information for Decision Makers (see Milestone 3, below). Annex 1 and Annex 2 provide further information on the project website and the Information for Decision Makers.  www.nanorem.eu
Milestone 3 - Webpage operating as information / support tool for negotiations with owners / regulators	MS3 initially comprised a set of Frequently Asked Question (FAQ) pages to provide Information for Decision Makers on the NanoRem website. The focus of these pages is on nZVI. Subsequently this information was supplemented with a series of subject orientated Thematic Pages. This will be gradually expanded over time, for example to include other types of NP, leading towards MS8 (Month 36). <a href="http://www.nanorem.eu/Informationfordecisionmakers.aspx">http://www.nanorem.eu/Informationfordecisionmakers.aspx</a>
IDL 9.2 – Workshop report on "risks" including the Interim Position State- ment for field trials and research requirements	A pre-deployment "risks" workshop was held in Nottingham, UK in July 2013.  This was developed into a report (IDL 9.2). The key outcomes of this work are discussed in Section 4 and Annex 1.  The full IDL9.2 report is restricted to the NanoRem consortium. Summarised information is available at: <a href="http://www.nanorem.eu/displayfaq.aspx?id=15">http://www.nanorem.eu/displayfaq.aspx?id=15</a>
IDL 9.3 - Workshop report on "sustainability and markets"	A second workshop was held in Oslo, Norway in December 2014. This workshop focussed on understanding factors affecting available markets and key sustainability concerns across a range of professional and expert stakeholder opinions. A workshop report will be made available by Summer 2015 from:  (Tomkiv et al. 2015) <a href="http://www.nanorem.eu/displayfaq.aspx?id=12">http://www.nanorem.eu/displayfaq.aspx?id=12</a>
IDL 9.4 - Broad exploitation strategy and riskbenefit analysis (Bardos <i>et al.</i> 2015) (initial versions)	This report looked to develop an understanding of "value proposition" (Defined as: the overall promise of value to be delivered) for nZVI use in remediation in terms of a risk-benefit appraisal of its use given the current state of knowledge. It provides an overview of the interim results of scenario analysis conducted to explore factors affecting the development of the market for nanoremediation in the EU by 2025. A SWOT (Strengths, Weaknesses, Opportunities and Threats) analysis was used to draw some broad conclusions about actions that might support better exploitation of nanoremediation.  http://nanorem.eu/news.aspx



Task 9.3.2 - Risk-benefit	Discussions are ongoing with Common Forum and NICOLE networks with the
appraisal and developing	purpose of developing a link for potential future engagement work.
a market consensus	A Risk-Benefit Appraisal for the Use of nZVI report was released in June 2014
	(Bardos et al. 2014). Available at:
	http://www.nanorem.eu/Displaynews.aspx?ID=525. This was used to inform
	Milestone 3 and IDL 9.4.
	This paper is being revised and extended to a wider range of NanoRem NPs as a
	journal paper submission for 2017
MS8 - Full blown web-	Milestone delivery report completed on time, see Section 10.2 for a description
based info-tool available	of the publications catalogue, 10.3 for the WP9 segment on information pages
based upon outcome of	and 10.4 for the NanoRem Toolbox (2017)
laboratory and field stud-	
ies. Numerical Module	
available and tested.	
IDL 9.5 Broad exploitation	Incorporated as Chapters 3, 5 and 6 in DL9.2
strategy and risk-benefit	
analysis (final versions)	
IDL 9.6 Project web site	This will be completed at the end of the project as many elements such as the
and full PDF archive	NanoRem Toolbox and Bulletins will not be available until 2017.

## 10.2 Overview of the Publications Catalogue

The publications catalogue is a listing of the NanoRem output; it can be accessed via <a href="http://nanorem.eu/publications-catalogue.aspx">http://nanorem.eu/publications-catalogue.aspx</a>, illustrated in Figure 8.





Figure 8: Image of the Publications Catalogue

Either all entries can be displayed or the following subsets: Journal Papers, Dissemination Activities and Other NanoRem Output. The publications catalogue is sorted by the authors. Web links are provided for each entry.

NanoRem

As of November 2016, there were 245 entries in total including 21 journal papers, 120 presentations, 44 posters at conferences and 31 workshops.

### 10.3 Information area on web site

In broad terms there are two structural elements: an intranet web page for the project consortium, advisory group and Project Officer and an Extranet which is open access. This approach has been set out in the project communication strategy, which was most recently reviewed over year 3. The communication strategy document is available on the Intranet (NanoRem Communication Strategy and Plan Rev. 3, July 2015). The Intranet has been operational for a long period and its structure and workings are summarised in an internal working document (Project Handbook).

The extranet has the following broad functions (see Figure 9):

- Home page
- Information for decision makers (developed from Milestone 3 status)
- Project information (aims description and partners most recently updated in Year 3)
- News and downloads
- A simple search tool
- Disclaimers (terms and conditions, privacy policy)
- Contact point
- Quick links for rapid access to priority information identified by NanoRem.

These represent the final structural elements of NanoRem. The majority of these are maintained by back-office functions available from the Intranet by various members of the NanoRem consortium according to a series of editing permissions.

The remainder of this section describes the "Information for decision makers", which has been comprehensively upgraded to support the main informational elements from NanoRem's outputs. The original FAQs and thematic pages described in the Milestone 3 report have been supplemented as follows:

- 1. Overview information (thematic pages and FAQs) basically following the existing structures described in the MS3 report (see Figure 10)
- 2. A public publications catalogue which identifies all of the published outputs from the project this is a subset of a wider internal catalogue accessed from the Intranet which collates all available project outputs (see Figure 11).
- 3. Publically available safety data sheet contact information from producers of particles developed by NanoRem which are commercially available. It is not appropriate for NanoRem to host these sheets itself (See Figure 12). Note safety data sheets used for any field test will be included / reported in the relevant NanoRem Deliverable, describing the test whether the NPs are commercially available or in development.
- 4. A number of bulletins which will note high level information across a series of topics which will be drafted over Year 4. Initially this hosts a brochure produced in Year 3, so as not to show an empty page (see Figure 13).
- 5. Listing of newsletters (see Figure 14).



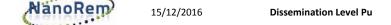
- 6. Mid-term project outcomes (from NanoRem's contributions to AquaConSoil 2015). The information collated provides a comprehensive overview of the mid-term information available from NanoRem, and a valuable informational resource ahead of its final publications (see Figure 15).
- 7. Listing of public domain deliverables (see Figure 16).



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Figure 9: NanoRem Extranet Components





Home	Information	Project Aims	Project Description	Project Partners	News	Search Intra	net
Overview Information a	and FAQ New	sletters Bulletins	Safety Data Sheets	Publications Catalogue	Midterm	Project Outputs	Deliverables
Over Intro In site proble reme is not althor nZVI reme has part trace	erview Info duction to Frequence were remediation tec- lems in several co- didiation benefits conoscale zero va- ugh it may also of has been deploy didiation of chloring promise for offerir	prmation and uently Asked Question hnologies are now in untries. The small parompared with existin lent iron (nZVI). The flen be indicative for ed in the field at a su ated solvent plumes. ng treatment of a wid	FAQs  Ins (FAQs) and Thematic  I use for managing risks  I tricle size and high react  I in situ techniques. The  Information for decision other nanoparticle types  Ibstantial number of sites  Laboratory and theoretic  I range of persistent cor	Pages from a range of soil and wate ivity of nanoparticles may of best known and most frequ- makers provided here focus	er contamir fer particul ently enco es on nZVI icular for th remediatio CPs, PCBs	nation ar untered , ne n also s and	Source
Since been list of detail the p additi Public An in make Thes also t	e the inception of raised about it the firequently aske led technical inforroject, both to up ional information, cations Catalogumportant objectiveers and to allow the FAQs are interto begin this procet progresses.	nat decision makers in ad questions" (FAQs; mation organised in idate their technical c in particular the outple. e for NanoRem is to p hem to provide feedb ided to provide initial	may need to consider. In ) to provide brief summa thematic topics. These p ontent and to extend the just of the NanoRem pro- promote exchange between lack both on the project information to support na	ten years ago, a number of c this NanoRem information a ry information, supported by lages are in constant review ir scope. Each page provide ject as they become available een nanoremediation practitio activities and nanoremediatio anoremediation project decis change area will be further de	rea we pro pages of n over the lif s signposti e in the Na oners and con more ger ion-makers	vide a nore feitime of ing to noRem  decision nerally. s, and	
7.0.0							
:	FAQ: What are r FAQ: Are there a sites? FAQ: What are t technologies? FAQ: Where hav	any risks from nZVI na the potential benefits we iron nanoparticles (	d how does nanoremedia anoparticles associated w	ith the use of nanoremediation and its likely advantages over diation?			
	EMATIC PA			and the fall and t			
The t	inematic pages a	re under developmer	nt but will provide informa	ation on the following topics:			
:	Thematic Page : Deployments	3: Implementation Iss 4: Factors Affecting P 5: Risk Perception Issi 6: Sustainability Cons 7: Risk Benefit Appral 8: Managing Deploym 9: Summary of the Re	Janoparticles in Remediat ues for Using Nanopartic otential Deployment Risk ues iderations isal ent Risks enegade Nanoparticle Ris	ion les in Remediation s from nZVI Release into the sk Assessment Protocol for Na ir Nanoremediation Deployme	anoRem Fi	eld	

**Figure 10**: Overview Information Starting Page







Figure 11: Publications Catalogue Starting Point (as of January 2016)







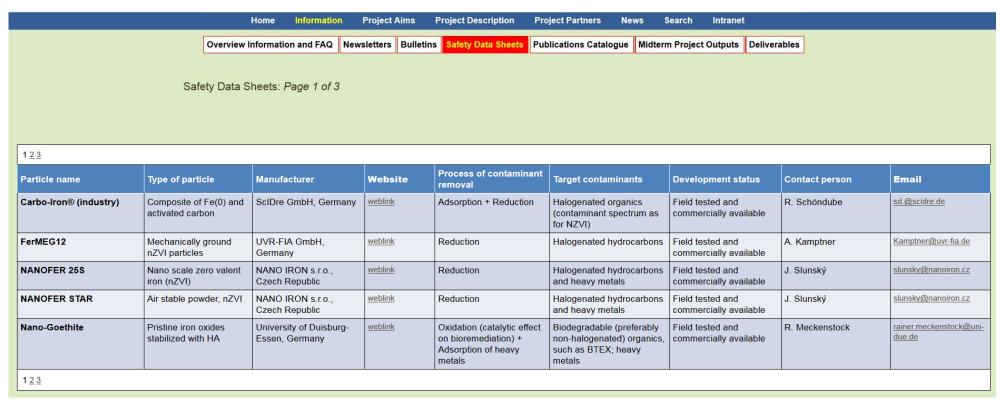


Figure 12: Safety Data Sheet Start Page as of November 2016

15/12/2016



Dissemination Level Pu DL\_9\_2\_final.docx



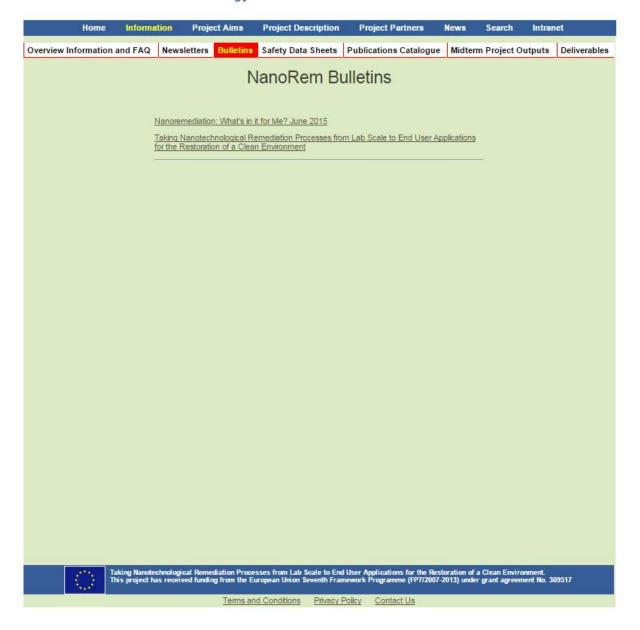


Figure 13: Bulletins Page as of January 2016





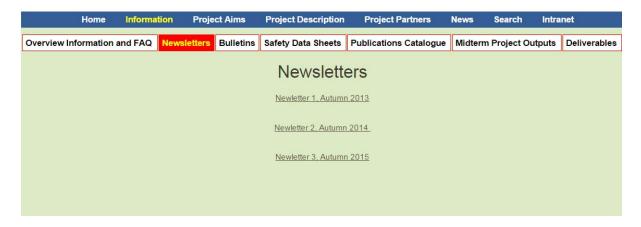


Figure 14: Newsletter listing



#### Nanotechnology for contaminated land Remediation

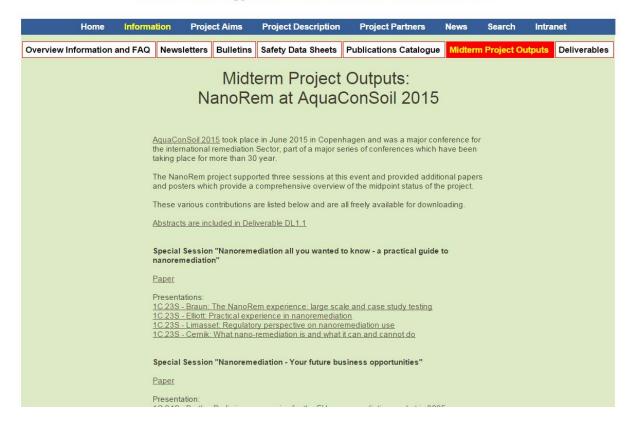


Figure 15: Sample from Midterm Outputs Page





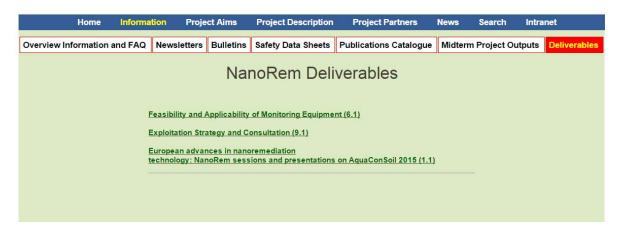


Figure 16: Deliverables Listing as of January 2016

#### 10.4 Nanoremediation Toolbox

The NanoRem Toolbox, available on <a href="www.nanorem.eu">www.nanorem.eu</a> in full from February 2017, focuses on the needs of decision makers, consultants and site owners. It provides the respective output of NanoRem in three levels, organised as a book case and divided as shelves for each level as shown in Figure 17 below:

- 1. An entry level showing the project bulletins and high level information in a condensed and concise way,
- 2. More detailed information on NPs and tools described as "NPs and Tools",
- 3. Other dissemination products and selected project deliverables as "Supporting Information".

Each of the images on these shelves provides a click through to deeper layers where specific information downloads can be found.

The NanoRem Toolbox will is the primary gateway to the NanoRem Project's results. Users can click on the images (anywhere on one of the shelfs) and will be led to a page with more details for each shelf, e.g. the "Bulletins" (see Figure 18). This deeper layer provides click through links to the various bulletins.

In the third level or "shelf" (Figure 19) there will be links to comprehensive supporting information, tailored for different levels of expertise or need for information:

- Thematic Pages and FAQs for basic entry level information
- External publications listings (conference proceedings, publications catalogue)
- Specific project outputs (selected project deliverables, project summary, newsletters, science report etc.).



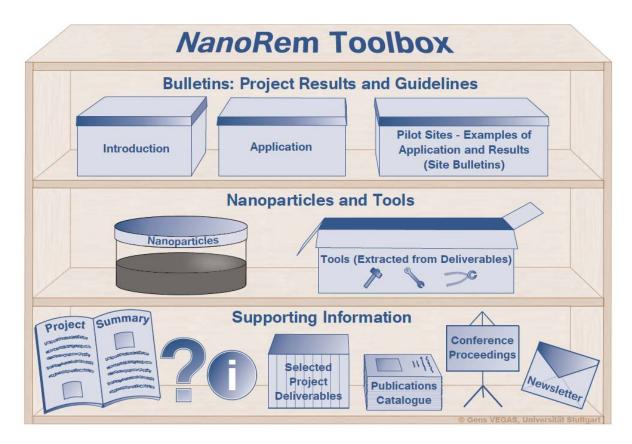


Figure 17: NanoRem Toolbox as gate to the NanoRem results

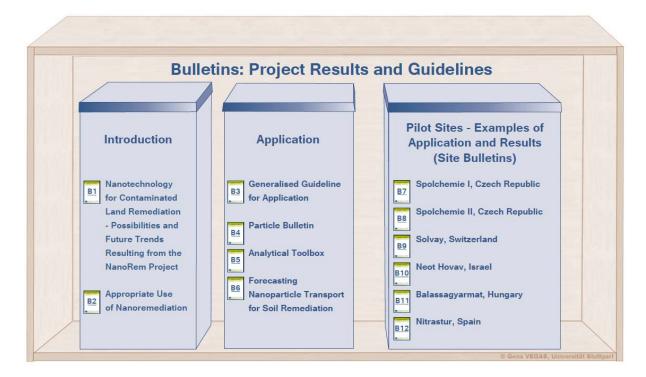
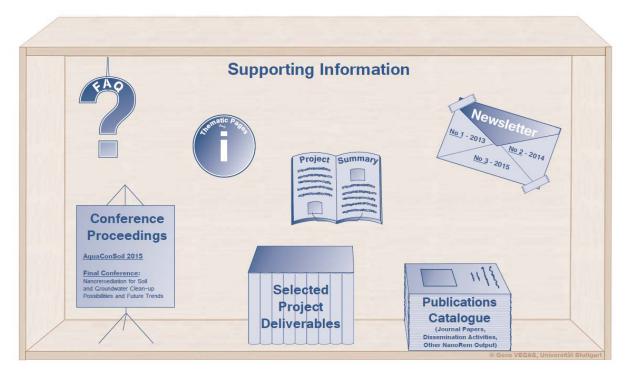


Figure 18: First level in the NanoRem Toolbox: the Bulletins





**Figure 19:** Third level in the NanoRem Toolbox: supporting information

## 11 Annex 2 Engagement / exploitation activities

#### 11.1 Nottingham stakeholder workshop summary

The overarching aim of NanoRem is to support and develop the appropriate use of nanotechnology for contaminated land and brownfield remediation and management in Europe. NanoRem focuses on facilitating the practical, economic and exploitable nanotechnology for in-situ remediation. This can only be achieved in parallel with a comprehensive understanding of the environmental risk-benefit balance for the use of NPs (NPs).

The premise for the Nanoremediation Deployment Risk Assessment Workshop was as follows:

NanoRem's focus is on remediation in the saturated zone. As such NPs (NPs) are envisaged to be introduced into groundwater either where treatment is needed or upgradient of where treatment is needed and to then travel to where the contaminants are or where contaminants will naturally be transported to, and thereby be treated. Standard health and safety precautions are assumed to have already been put in place to protect workers and the environment above ground during the manufacturing, transport, deployment and injection processes.

However regulatory, public, client and general stakeholder acceptance of the use of new technologies including nanoremediation requires the risk of a technology to be understood and mitigated before permission is given to deploy to the field. Hence, a pre-deployment risk assessment of NP introduced into the sub surface requires an adequate understanding of the fate, transport and toxicity of NP in various ground conditions.

The purpose of the Nanoremediation Deployment Risk Assessment Workshop (see Figure 20) was to draw out the current state of knowledge about the processes and parameters that will influence deployment risk assessments and to cross check this against LQM's review of the literature. That is to



say the assessment of risks posed by renegade NPs (NP) – those NP that do not reach or escape from the intended treatment zone and hence have the potential to harm human health or the wider environment. By involving experts from outside the NanoRem team drawn from around Europe and beyond a broad expertise in a range of disciplines was available to inform the research on predeployment risk assessment. Themes explored over the two day workshop held at Nottingham (16-17<sup>th</sup> July 2013) included: Transport properties (both iron and non-iron); Fate properties (both iron and non-iron); Ecotoxicology of NP; Toxicology of NP; Fate of coated NPs (both iron and non-iron); Fate of uncoated NPs (both iron and non-iron); Detection/ tracing techniques (both iron and non-iron); Injection of NP - permeation, pressure, fracking; Regulation of NP deployment; Other aspects raised by attendees.

The workshop brought together a variety of expert and professional stakeholders from research, regulation and industry. In total, 21 participants from eight countries (Australia, the Czech Republic, Germany, the Netherlands, Portugal, Slovakia, the United Kingdom and the United States of America) attended the event. Experts were drawn from a range of disciplines including nanotoxicology, human health and groundwater risk assessment, nanotechnology, environmental & colloid chemistry and environmental geology.

The workshop comprised of a combination of plenary lectures and small working group sessions. The working groups were tasked with answering a number of questions, including:

- 1. How far can NPs (and the NanoRem NP specifically) travel in the subsurface? (Within NP colloidal systems how do the dispersed phase (i.e. NP's) and dispersing medium (i.e. liquid) interact? How does this interaction vary between different particles?)
- 2. How does groundwater (the dispersing medium) movement affect NP distribution?
- 3. What controls the aggregation of NPs (and the NanoRem NP specifically)? (Aggregation impacts the transport characteristics and reactivity of engineered and natural NPs)
- 4. How should we sample groundwater to ensure the samples are representative with respect to NP?
- 5. How toxic to human health, relevant sub surface ecosystems and relevant surface ecosystems are the NanoRem NPs?
- 6. What are the major research priorities and how could these be addressed?

Session 1 involved scene setting for the workshop and an outline of the NanoRem project, through a series of slide and discussion sessions. Subsequent sessions involved two separate smaller groups discussing the same series of questions and topics. Each session had a LQM representative as a rapporteur who summarised the salient points of discussion during wrap-up sessions and subsequently expanded this as part of the written workshop record.

Session 2 considered Conceptual Site Models of NP deployment, investigating what could happen, worst and likely outcomes following injection of NPs. NP transport was considered to probably be limited and you need to work really hard to keep the nano particles suspended, so migration through aquifer and to surface water was not particularly likely. Facilitated transport of NPs (or Geo contaminants via NPs) was considered a possibility, but there was no real knowledge about the likelihood of facilitated transport. Potentially important NP, aquifer groundwater and geology parameters that were likely to be required to be known to inform risk assessments were outlined.



Session 3 considered the Transport Properties of NPs and broke this down into NP, aquifer and groundwater properties. Discussions included the potential influence of geochemical and microbiological factors on transport and current methods on how to track NPs (i.e. Magnetic susceptibility; Total Fe – ICP-AES; DNA NP tracking; Stable isotope labelling).

Session 4 considered the Fate of injected NPs with particle size and dispersant/additive types being of critical importance. Unwanted impacts (such as competitive sorption of non-target contaminants, metal mobilisation) were considered. In particular, use of impacted groundwater for spay irrigation was a potential concern.

Session 5 considered the Toxicity of NPs with respect to human and ecotox receptors. There was knowledge for some NPs (e.g. TiO<sub>2</sub> and Ag) within the group but limited knowledge about the Nano-Rem particles, though (non-nano) ZVI toxicity was considered to not have significant human toxicity. However, the group agreed that, based on current knowledge, silver NPs probably represent a worst case with respect to NP toxicity. The list of species included within the NanoRem description of works were considered by the group to include all of the relevant species that would be expected to have been studied for the NPs being investigated/based on the groups experience.



**Figure 20:** LQM Facilitating the Expert Elicitation Workshop, hosted at LQM's base in Nottingham

The workshop outcomes supported with evidence from the literature formed the basis for a simple protocol for field trial sites to use to evaluate the risk posed by their NP deployment prior to regulatory approval. This included developing a site conceptual model, with NP as the source term, to address the possible risk from renegade NPs, particularly whether there are potential pathways for NPs to relevant receptors. An example cross section of a CSM is at Figure 21.



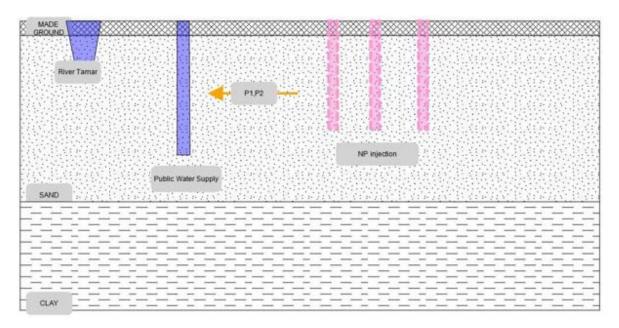


Figure 21: Cross section from CSM (This site is an example only and does not represent any of the pilot sites) (© Land Quality Management 2014)

The overall findings of the report were:

- There was limited information on NP toxicity but it was reasonable to assume that it is less potent than nano-silver; and
- NPs are likely to interact with the aquifer matrix, each other and groundwater to rapidly cease to be mobile NPs.
- Therefore, it was concluded that they were unlikely to penetrate into the aquifer more than a
  few metres from the point of injection. The protocol took a precautionary approach in recommending distances from identified receptors, and, as the majority of evidence related to porous
  aquifers, included more conservative distances for fractured or hybrid aquifers.

The workshop record was been provided as an Annex within an extensive report delivered by LQM which informed the Outline Risk Assessment Protocol for the NanoRem field study site deployments.

A paper based on the protocol developed after the workshop was published in 2016:

 Nathanail, C. P., Gillett, A., McCaffrey, C., Nathanail, J. and Ogden, R. (2016), A Preliminary Risk Assessment Protocol for Renegade NPs Deployed During Nanoremediation. *Remediation*, 26: 95–108. doi:10.1002/rem.21471

#### 11.2 Oslo stakeholder workshop summary

Nanoremediation is an emerging remediation technology, with unique characteristics that can offer a number of benefits and improvements on existing process-based remediation.

The sustainability of environmental remediation is an important concern, and one that should be included in the decision-making process. Any remediation process should consider which of the possible remediation techniques provides the best net environmental, economic and social impact in dealing with the remediation problem. The NanoRem project supports dialogue and engagement with various European stakeholders in order to explore consensus about appropriate uses of nanoremediation, understand its environmental risk-benefit, market demand, overall sustainability and stakeholder perceptions.



As part of this dialogue, a workshop on Sustainability and Markets took place in Oslo on 3<sup>rd</sup>-4<sup>th</sup> December 2014. The aim of the workshop was to collect opinions from a range of stakeholders on key sustainability issues and ethical concerns as well as market development opportunities in the medium to longer term related to nanoremediation. The focus was on developing a realistic understanding of the stakeholders' opinions on: (1) the sustainability of nanoremediation and issues influencing perceptions of its sustainability; (2) sustainability of nanoremediation compared to other remediation technologies; and (3) factors that might influence the market development for the nanoremediation technology.

The workshop gathered a variety of expert and professional stakeholders from research, regulation and industry. In total, 36 participants from nine different countries (Austria, Belgium, the Czech Republic, France, Germany, the Netherlands, Norway, Poland and the United Kingdom) attended the event. Discussions were divided into three sessions. The first session explored generic issues associated with the sustainability of nanoremediation as a technology. The second session performed a mock sustainability assessment using a hypothetical site. The last session assessed as part of a scenario development approach factors that influence medium to long-term market development of nanoremediation technology.

During the first session, participants discussed how nanoremediation scores across the three pillars of sustainability (environmental, economic and social). The discussions identified both the beneficial and potentially disadvantageous characteristics of nanoremediation. Important environmental benefits include that nanoremediation may be less invasive and can have a lower impact compared to some alternatives. Environmental concerns were largely related to the perceived potential intrinsic hazards of NPs themselves. From an economic point of view, nanoremediation could be faster and cheaper compared to some alternatives. However, some concerns were raised about the current high production costs for NPs. Participants noted that nanoremediation technology has the potential to create new job opportunities and enable a greater number of contaminated sites to be remediated. Concerns related to social aspects included the public perception of NPs and existing knowledge gaps and uncertainties related to nanoremediation.

In the second session of the workshop, participants were asked to assess the sustainability of nanoremediation in comparison with other risk management options for a hypothetical case study. When compared to the alternative technologies, there was little to differentiate nanoremediation from in situ bioremediation apart from uncertainty and evidence. However, many aspects differentiated nanoremediation from pump and treat technology, the most important being the use of natural resources and waste generation.

During the last session of the workshop, participants first discussed and more precisely defined and then scored a series of factors – drivers and inhibitors – determining the evolution of the market for nanoremediation in Europe according to their importance and their interlinks. These results were the bases for further elaboration of scenarios of potential market development and to derive recommendations for use in an exploitation strategy for nanoremediation.

The general conclusion of the workshop was that addressing sustainability, as part of the evaluation of remediation technologies, demands a broad perspective, including intergenerational aspects and a better understanding of the relationships between environmental, social and economic factors. Discussions about the sustainability of nanoremediation need to be site specific and have to include



comparisons to other *in situ* technologies. For these technologies a clear technical understanding of what the advantages and limitations are (operating windows) should be available and evaluated. While many of the generic issues regarding the sustainability of nanoremediation are similar to those for other remediation technologies, uncertainties in risks and benefits related to use of nanoremediation technology were deemed to be one of the most important factors impacting on its future development.

In addition to the issue of uncertainties, the workshop identified the following challenges for improving the sustainability of nanoremediation:

- (1) Reduction of production costs for the different NPs,
- (2) Enhancing the transport mobility of the particles in the subsurface (or strictly speaking in the aquifer),
- (3) Increasing the lifetime of the product in order to justify the production cost,
- (4) Identification of possible synergies with other in situ remediation techniques, and
- (5) Establishment of appropriate methods to determine the environmental fate of particles.

These challenges, as well as many other issues raised during discussions, have been serving to further validate the NanoRem research agenda.

The full workshop report is available as: TOMKIV, Y., BARDOS, P, BARTKE, S., BONE, B. AND OUGHTON, D. (2015). The NanoRem Sustainability and Markets Workshop, Oslo, Norway, December 2014. NanoRem Report IDL9.3. Available from <a href="http://www.nanorem.eu/Displaynews.aspx?ID=797">http://www.nanorem.eu/Displaynews.aspx?ID=797</a>

#### 11.3 Conference workshop session summaries / details

# 11.3.1 SustRem 2014 – NanoRem special session report: Nanoremediation: hopes or fears from the sustainability perspective

Human industrial activities have resulted in a great number of contaminated land areas in Europe and the rest of the world. Management of those areas has to prevent any unexpected risk to humans or environment. In order to ensure sustainable development of contaminated areas, there is need for innovative solutions to prevent and mitigate unacceptable risks to human health or the environment; particularly where problems seem intractable or the impacts of current treatments seem severe.

The use of NPs in remediation is seen by a number of people as offering a step change in remediation technology performance and in extending the range of treatable problems. Could nanoremediation be the answer? How sustainable is nanoremediation? What are the most important factors contributing to the overall sustainability of a nanoremediation project?

This special session explored these questions. It was organised by the EU FP7 NanoRem project (<a href="www.nanorem.eu">www.nanorem.eu</a>). The session's broad aim of it was to explore the pros and cons of "nanoremediation" as a sustainable remediation technique. The total number of people who participated in the session was 23 including four facilitators representing NanoRem project.

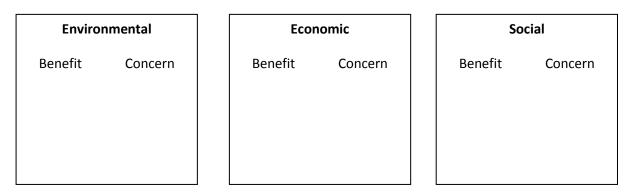
#### **APPROACH**



The session started with a brief introduction to the topic. Two short presentations were given: (1) remediation, risk assessment, land management, nanoremediation and other technologies; and (2) the concept of sustainable remediation being applied in NanoRem, in order to acquaint everybody with the discussion topic. The session then continued with three parallel discussion groups of 7-8 people using The World Café<sup>TM</sup> format. Participants were asked to answer the following questions:

- 1. What do you understand by sustainability and why is it important to you?
- 2. How sustainable do you think nanoremediation is and why? Consider environmental, economic and social aspects.
- 3. What did you learn from this discussion? Did something surprise you? Challenged you?

For the second question the participants were asked to write their ideas for sustainability concerns and benefits of nanoremediation on *Post-It* notes on their own, which were then stuck to message boards, representing the three elements of sustainable development (economy, society and environment), as shown in Figure 22. This "raw data" then served as the basis for discussions within each of the small groups. Each group considered all three elements of sustainability (Figure 23). When the participants were not sure if the issue being considered is a benefit or a concern, the post-it was put in the middle.



**Figure 22:** Message boards representing three aspects of sustainability, where participants could their Post-it notes.

#### **OUTCOMES**

Question 1: What do you understand by sustainability and why is it important to you?

Participants agreed with the broad description of sustainable remediation offered by the NanoRem presentation: that it is remediation that achieves a net benefit across environmental, social and economic aspects. However, some delegates felt that it would have been easier to have considered sustainability issues on a more site specific basis in comparison with other remediation alternatives. There was a general desire for more detailed information about nanoremediation techniques, and a perception on the part of many delegates that for this technology in particular a lack of high quality information about performance in the field was harming its future prospects as a practical remediation tool. A concern was that negative perceptions were determining decision making in many cases. High quality case studies would be most useful to demonstrate the benefits of using nanotechnology in the remediation.





**Figure 23:** Participants during the discussion on the benefits and concerns of nanoremediation across three aspects of sustainability

**Question 2:** How sustainable do you think nanoremediation is and why? Consider environmental, economic and social aspects.

Assessment of sustainability of any remediation technology involves evaluation of this technology across a range of issues, which can be grouped in three categories (Figure 24).

Environment	Social	Economic
Emissions to Air	Human health & safety	Direct economic costs & benefits
Soil and ground conditions	Ethics & equity	Indirect economic costs & benefits
Groundwater & surface water	Neighbourhoods & locality	Employment & employment capital
Ecology	Communities & community involvement	Induced economic costs & benefits
Natural resources & waste	Uncertainty & evidence	Project lifespan & flexibility

Figure 24: Overarching SuRF-UK Sustainable Remediation Considerations (CL:AIRE 2010)

The session attempted to identify "drivers" or influences on sustainability that might be generic for nanoremediation as a technology. In the course of the discussion, the following factors were recognised as important influences on how sustainable nanoremediation is perceived to be.

**Environmental aspect:** There are great <u>potential</u> benefits in nanoremediation: they could extend the range of treatable contaminants, address deep/constrained contamination, be more environmentally friendly compared to other remediation technologies, provide a better source term control measures and does not produce extra waste. However, there is a great deal of uncertainty concerning the transfer and fate of the particles in the environment, interactions of NPs with other chemicals and



media, their long-term effect on the organisms and ecosystem compartments, possible residual pollution after the remediation is complete. There is a need for thorough, long-term ecological assessment of the nanoremediation impacts. The environmental costs of NP production are also uncertain.

**Economic aspect:** Uncertainties remain in the cost-effectiveness of the nanoremediation technology compared with the other techniques. There is a clear potential of nanoremediation technology to stimulate industry and trigger development of new economies. At the same time, possible needs for importing the technology from abroad and the impact it will have on the job opportunities for the local workers should be considered too. Limited number of companies who own the technology of NP production for the use in the remediation and the scales at which they can produce those NPs will have an impact on the availability of nanoremediation technology.

**Social aspect:** There is a general concern that public perception and fear of NP release into the environment will influence the social acceptability of nanoremediation technology. However, levels of concern appear to vary from country to country. This concern is exacerbated because there appears as yet to be no substantial <u>proven</u> benefits for nanoremediation compared with alternative approaches, which undermines societal interest / regulatory interest in investing time and effort to support its implementation. Uncertainty regarding the possible health effects of NPs both if it ends up in the environmental compartment and as an occupational exposure hazard is also raising public's concern.

There is a potential to substantively change these attitudes with examples of successful remediation projects.

Question 3: What did you learn from this discussion? Did something surprise you? Challenged you?

The group discussions have shown that in general, uncertainties and lack of information are amongst the most important issues which influencing perceptions of the sustainability of nanoremediation compared to other technologies. Reducing the uncertainty, filling of the knowledge gaps as well as more active promotion of the use of nanotechnology in the remediation would be helpful in showing the benefit in using nanotechnology for the remediation of the contaminated land.

The key uncertainties identified by the discussion relating to performance, especially in the field and fate and transport of introduced NPs strongly validate the research agenda of the NanoRem project, and we had not expected this to be such a strong outcome of the session.

Many issues raised during the discussion are common for new technologies. If NanoRem can demonstrate that nanoremediation technology can treat contaminants in a better way than other technologies available; or that it can be used to treat contaminants which other technologies are unsuccessful to - this would both add to sustainability benefits and provide a stronger market impetus.

# 11.3.2 AquaConSoil 2015, Denmark, Copenhagen, Special Session 1C.24S June 2015 Report: Nanoremediation - your future business opportunities (strategic and market intelligence)

AquaConSoil has a focus on sustainable use and management of soil, sediment and water resources. The Special Session on "Nanoremediation - your future business opportunities" was co-organised by Paul Bardos (r3 environmental technology ltd, GB), Stephan Bartke (Helmholtz Centre for Environmental Research - UFZ, DE), Nicola Harries (CL:AIRE, GB) and Hans-Peter Koschitzky (University of Stuttgart, DE). The objective of the session was to provide business and strategic intelligence for del-



egates with interests in using nanoremediation at their sites or developing nanoremediation activities at their organisations.

The session was organised as part of the EU FP7 co-funded project NanoRem (<a href="www.nanorem.eu">www.nanorem.eu</a>), which has been carried out an intensive development and optimisation programme for different NPs (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact. Practical grounding in nanoremediation theory and practice, introducing also the spectrum of actions of NanoRem as a major initiative, which supports the effective deployment of nanoremediation technologies in Europe, was presented at AquaConSoil in a preceding Special Session on "all you wanted to know (a practical guide to nanoremediation)".

That Session included presentations on "What nano-remediation is and what it can and cannot do" by Miroslav Černík (Technical University Liberec, CZ), "Practical experience in nanoremediation" by Dan Elliott (Geosyntec Consultants, US), "Regulatory perspective on nanoremediation use" by Elsa Limasset (BRGM, FR) and "The NanoRem experience: large scale and case study testing" by Jürgen Braun (University Stuttgart, DE). This session was well attended by likely more than 100 conference participants. Also a question and answer section was part of that preceding session.

The Special Session on "Nanoremediation - your future business opportunities" was intended to provide conference delegates with a deeper insight on business and strategic intelligence for developing nanoremediation activities at their organisations or sites. The set-up of the Session was to allow for open, interactive exchange on the topic based on a presentation of "Preliminary scenarios for the EU nanoremediation market in 2025 – assessment of market drivers (opportunities and challenges) affecting the take-up of nanoremediation" by Stephan Bartke (UFZ, DE). Facilitated by Paul Bardos (r3, GB) and Nicola Harries (CL:AIRE, GB), the remainder main part of the session was foreseen for discussion in groups about market prospects and drivers. A plenary reporting back of discussions from the groups was to conclude the session.

Only about twelve participants – half of them from the NanoRem project half external experts from science, regulation, consultancy and problem owners, participated in the Special Session. Asked for their motivation, they indicated different objectives ranging from specific interest in applicability and market potential by a consultant, via a general interest of the potential of the technology by a problem owner to regulatory questions by a municipality delegate or questions of dealing with perceived uncertainties regarding the application of NPs in the environment by a scientist.

The introductory presentation on "What will drive the EU nanoremediation market till 2025?" introduced the participants to the scenario-approach applied in NanoRem in order to assess factors determining opportunities and challenges for the take-up of nanoremediation. Table 6 gives an overview about the factors. Detailed information on the approach used to identify the factors can be found in Bardos et al. 2015 [D9.1] or the conference paper to this Session.

Nicola Harries (CL:AIRE, GB) introduced to the participants the interactive part of the Session. This was a splitting-up of the delegates in two groups. Both groups were rather heterogeneously formed with participants from inside and outside the NanoRem project. Both groups had discussions next to a flipchart, where discussion points of attention and conclusions were kept. The discussions focused on three questions related to expected market changes, critical information needs and factors influencing in particular the delegates/their organisations. Despite or even as a consequence of the small



number of participants, the discussions in the two groups were very intense. They indicated a considerable interest in the potentials and limitations of nanotechnology for remediation. Table 12 summarizes the discussions to each of the questions:

**Table 12:** Results from group discussions at AquaConSoil on determinants of the development of the nanoremediation market in Europe by 2025

Group I	Group II	1) How is the nanoremediation market changing / likely to change by 2025?
		Lack of case studies / success stories
.,		Lack of proven results
X	X	Public acceptance – public could be scared but with time and more case
		studies more acceptance will arise
		→ Success stories needed to convince customers, regulators, public
		Need to change people's minds / perception
.,		<ul> <li>Usually this technology is seen for polishing (plume) rather than healing the</li> </ul>
X	X	source
		→ Need to convince that nanoremediation could become a main technique
		<ul> <li>Injection technology improving larger volumes + longer lifetimes</li> <li>NanoRem improving to optimize. Injection still key</li> </ul>
		Service providers need to be convinced that it is a good solution.
X		This will support convincing the industry for going for nanoremediation as
		"their clients"
		<ul> <li>Contractors interested in investing in nanoremediation</li> </ul>
		Convince the authorities for remediation targets
X		Regulatory hurdles
		Occupational
		o REACH
X		Investment needed for demonstration     In particular from ELI// if a little in the particular from ELI// if a lit
X		<ul> <li>In particular from EU/Life+</li> <li>We don't know how the future will change, but we do now that it has potentials</li> </ul>
		• We don't know now the luture will change, but we do now that it has potentials
	Х	Cost burden: likely to change
Group I	Group II	2) What is the most critical information needed to achieve a positive shift
Group I	Group II	in the uptake of nanoremediation?
Group I	Group II	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of</li> </ul>
		<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field</li> </ul>
		<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field</li> <li>o In particular important for service provider</li> </ul>
X	X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field</li> <li>o In particular important for service provider</li> <li>What set of guarantee?</li> </ul>
		<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> </ul> </li> </ul>
X	X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field</li> <li>o In particular important for service provider</li> <li>What set of guarantee?</li> </ul>
X	X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> </ul> </li> </ul>
X	X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>→ Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> </ul>
X	X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> </ul>
X	X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>→ Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work         <ul> <li>Transparency</li> <li>Ethics framework</li> </ul> </li> </ul>
X	X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>→ Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work         <ul> <li>Transparency</li> </ul> </li> <li>Ethics framework</li> <li>good procurement</li> </ul>
X	X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> </ul>
X	X X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> <li>Economics / Cost efficiency</li> </ul>
X	X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> <li>Economics / Cost efficiency</li> <li>Costs for customers</li> </ul>
X	X X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> <li>Economics / Cost efficiency</li> </ul>
X	X X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work         <ul> <li>Transparency</li> </ul> </li> <li>Ethics framework         <ul> <li>good procurement</li> <li>Education what works</li> </ul> </li> <li>Economics / Cost efficiency</li> <li>Costs for customers         <ul> <li>All cost drivers in particular</li> </ul> </li> </ul>
X X X	X X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> <li>Economics / Cost efficiency</li> <li>Costs for customers</li> <li>All cost drivers in particular</li> <li>Insurance costs</li> <li>Stop loss / cost cap insurance</li> </ul>
X	X X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> <li>Economics / Cost efficiency</li> <li>Costs for customers</li> <li>All cost drivers in particular</li> <li>Insurance costs</li> <li>Stop loss / cost cap insurance</li> </ul>
X X X	X X X	<ul> <li>in the uptake of nanoremediation?</li> <li>Critical shift is enabled by guaranteed results (← Case studies) + solid base of knowing how nanoremediation works in lab and field         <ul> <li>In particular important for service provider</li> </ul> </li> <li>What set of guarantee?         <ul> <li>E.g. remedial level/goal * ppm guaranteed?</li> <li>Decision criteria – boundaries / parameters</li> <li>Decision support tool / check list</li> <li>Operating window: High level of certainty for known conditions</li> </ul> </li> <li>For public perception and buy-in, know what does and doesn't work</li> <li>Transparency</li> <li>Ethics framework</li> <li>good procurement</li> <li>Education what works</li> <li>Economics / Cost efficiency</li> <li>Costs for customers</li> <ul> <li>All cost drivers in particular</li> <li>Insurance costs</li> </ul> <li>Stop loss / cost cap insurance</li> <li>Nanoremediation should cover more pollutants</li> </ul>



Group I	Group II	3) How are the factors identified likely to influence you or your organisation?
		What gives confidence on performance?
Х	X	Guarantee or confidence needed?
		Public perception
		UK - moratorium
Х	Х	More into practical factors
^	^	Application: Nanoremediation can be a tool in the toolbox as injection technol-
		ogy improves
X		Be on the safe side for new technologies
		→ Early failures are particularly damaging
Х		Implementation of the technology
		→ Testing large scale lab → in situ   field deployment
	X	<ul> <li>Ease of use → extra training, Health and Safety → costs for companies</li> </ul>
	Х	Science / Policy - Research funds
	Х	New technologies / emerging contaminants
	Х	Environmental awareness and sustainability
		Role of environment (especially soil) policies

As a summary, the existence of validated data on case studies is critical for market development – in particular if this information can be told as success stories. In addition, dialogue between the stakeholders (science – industry – policy – general public) is crucial. An open debate is the question: Who is best to initiate the communication: Does the science bring information to the consultants and then to the regulators? – The session left open an answer, but their seems agreement to state that those interested in the promotion should invest, i.e. politics should found research in innovative NP to tackle emerging contaminants; researchers to communicate their results in a way that is understood by the market, consultants to dare the venture and gain from early mover and so forth.

# 11.3.3 REMTECH 2016, Italy, September 2016 Report of Session on: What will drive the EU nanoremediation market till 2025 – opportunities and challenges for the utilisation of nanoremediation.

Nanotechnologies could offer a step-change in remediation capabilities: treating persistent contaminants which have limited remediation alternatives, avoiding degradation-related intermediates and increasing the speed at which degradation or stabilisation can take place. However, adoption of nanoremediation has been slower, with fewer than 100 field scale applications, since the first field application in 2000. However, the recent emergence of nanoremediation as a commercially-deployed remediation technology in several EU countries, notably the Czech Republic and Germany indicates that it is now time to look at nanoremediation as a technology in the European market-place.

Since early 2013, the EU FP7 NanoRem project (<a href="www.nanorem.eu">www.nanorem.eu</a>) has been carrying out an intensive development and optimisation programme for different NPs (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact. Nano-Rem is a €14 million international collaborative project with 29 Partners from 13 EU countries, and an international Project Advisory Group (PAG) providing linkages to the USA and Asia. It is a major initiative, which will support the effective deployment of nanoremediation technologies in Europe.



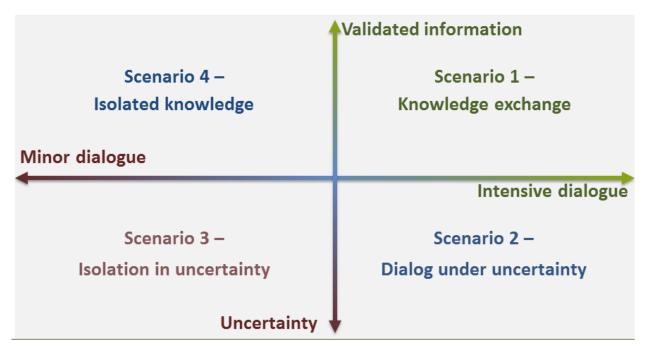
At RemTech 2016 NanoRem offered two sessions on September 21<sup>st</sup> 2016 to provide delegates with the practical, implementation, technical and market information to understand how nanoremediation might address contaminated sites and how they might deploy nanoremediation within their own organisations, whether they are a site manager, a service provider or a regulator.

The <u>first</u> session focused on providing a practical grounding in nanoremediation theory and practice with particular reference to applied examples in the field. The <u>second</u> session focused on discussing business and strategic intelligence for delegates with interests in using nanoremediation at their sites or developing nanoremediation activities at their organisations. This short paper reports the key findings of the <u>second</u> session.

Eight participants took part (two linked to NanoRem from Politecnico di Torino):

- Allessandro Mattiello, University of Udine, Italy
- Donata Visconti, University of Naples
- Federico Fuin, ARPAV Environmental Protection Agency of Venice
- Various, Politecnico di Torino
- Pietro Vaccari, Nanoverse consultancy
- Isabella Buttino, ISPRA (regulatory agency)

Overall the discussion endorsed the existing scenario analysis model summarised in the Conceptual scheme for scenario states repeated below.



The following key points emerged from an open discussion.

 Communication to the public and business is vital because many individuals fear nanotechnology, and they may have decision making influence. Additionally public confidence is very important for remediation markets in Italy because much of the investment comes from public agencies. While polluter pays principle exists in Italy, the remediation of orphan sites is paid for by public funds.



- 2. Understanding costs is vitally important, and ideally cost should be in the framing diagram as a "third dimension" in this plot because of its dominant effect on use. Costs relate to whole system costs, not just the nanomaterial cost element of a project. While there is great interest in nanoremediation, costs are perceived to be high and uncertain.
- 3. A comment from one participant was the "I came here today perceiving that nanoremediation was very expensive and very experimental. The presentations this morning [in the training session] were very convincing and show that the technology is actually more established than I thought.". This comment came from someone at a public agency who further commented that agency professionals have very little time to go out and seek information. Therefore if service providers want to succeed with a nanoremediation proposal, they need to bring high quality and validated information to the regulator to support their submission. Even information from other countries will, in principle. Promote the use of nanoremediation.
- 4. Uncertainty in whether or not a technology will meet its remediation targets is likely to prevent its use when there are other options where outcomes are more certain.
- 5. In Italy even *in situ* bioremediation is rare for chlorinated solvent problems. This is due to a reluctance of public authorities to permit in situ bioremediation. However, this reluctance is not related to any specific point of law. It arises from a lack of knowledge of the technology which is a consequence of a general lack of dialogue in Italy between the research community and public authorities. This is a long standing problem resulting from institutional; / structural reasons. Anecdotally, in one region of Italy there is a major service provider dominant in the local market who chooses not to deploy *in situ* bioremediation. Part of the reason for this is that for more "uncertain" technologies the regulator may impose more stringent (and so costly) verification requirements in order to guard against uncertainty / lack of knowledge. Companies therefore prefer to apply remediation techniques which do not carry these additional commercial risks.
- 6. These barriers for *in situ* bioremediation use certainly carry a message for attempts to introduce nanoremediation in Italy. It was commented that this could be an issue of timeline, for example twenty years ago regulators were similarly hesitant about *in situ* bioremediation in the UK, and had a similar response to impose more stringent verification needs. So perhaps a key question is how to shorten this timeline.
- 7. These barriers to the use of *in situ* bioremediation exist, even although in many cases it is one of the cheaper remedial options to deploy.
- 8. Another institutional barrier suggested was that for some service providers proposing a long term expensive and infrastructure based approach such as pump and treat may be a preferable commercial outcome.
- 9. A concern raised was that the disconnect between science and business in Italy is particularly great because there is little business investment in research projects at Italian universities. This is a systemic problem in Italy, but one consequence is that the lack of research partnership and shared endeavour between universities and business is a barrier to the developing a shared knowledge of bioremediation.
- 10. Moving forwards NanoRem's information will make a difference, as long as there is a way to connect this information to businesses and regulators. However, validated cost and performance



data would make a yet bigger difference. The importance of providing guidelines for nanoremediation deployment was emphasised as a way of bridging this communication "gap". The production of pan-European guidance by NanoRem might be very persuasive. It was also noted that in general improving Italy-EU dialogues would be beneficial.

- 11. Italian language guidance would be helpful, although not necessarily decisive.
- 12. It was suggested that gaining the influence of an influence decision maker such as politician would be a good means of market influence in Italy.
- 13. Regarding the framing diagram, several of the delegates felt that the scenario in Italy at present is one where there is a lot of information available, but not very much dialogue. The information available is also of insufficient quality as it is not somehow validated.
- 14. Also of great influence on market sentiment would be a first trial at a major industrial client in Italy, and presented at RemTech to provide a national reference point.
- 15. There are developing information networks in Italy, one of which is called Reconnet which is also linked to the RemTech conference series,

#### 11.4 Focus group meeting summaries / details

#### 11.4.1 Report on German NanoRem Focus Group Meeting

A full-day workshop of scientists and practitioners was organised as part of the EU FP7 co-funded project NanoRem (www.nanorem.eu), which has carried out an intensive development and optimisation programme for different NPs (NPs), along with analysis and testing methods, investigations of fate and transport of the NPs and their environmental impact.

The objective of the workshop "NP-based remediation technologies – Which factors drive the market development in Europe by 2025? What recommendations for business, research and regulation do we conclude today?" was to gain business, regulatory and strategic intelligence from key German stakeholders being linked to nanoremediation on the potential market development for this technology. The event was hosted in the Berlin office of the Helmholtz Gemeinschaft on 11<sup>th</sup> March 2015.

The workshop has been part of a series of activities in NanoRem to support the development of a better understanding of the value proposition of nanoremediation in Europe by 2025. It was set up in a focus group format, where participants are guided by a facilitator through a discussion in order to collate opinions and expertise of group members in a comfortable environment. The setting is designed to enable participants to define and frame their individual points of view by comparing them to others' perspectives.

The Berlin focus group brought together twelve German stakeholders having a direct link to NP application in the environment. Table 13 gives an overview of the participants:



**Table 13:** Characterisation of Berlin focus group participants

No	Background	Group
1	Consultant – affiliated with a global company	Market
2	Consultant – affiliated with a European company	Market
3	Consultant – independent expert	Market
4	Insurer – affiliated with an international insurance company	Market
5	*Producer of a nano particles	Market
6	Regulator / User from a state agency for regeneration of contaminated land	Regulator
7	Expert on environmental regulation – involved in the NanoCommission advising	Regulator
	the Federal Government	
8	Regulator of a state authority for mining and geology	Regulator
9	Toxicologist of Federal Institute for Occupational Safety and Health	Regulator
10	Toxicologist / Representative of public interests of UFZ – involved in a public de-	Science
	bate platform on nano products	
11	*Researcher and theoretical developer of a nano particle from UFZ	Science
12	*Researcher of University of Stuttgart – NanoRem coordination, Lead of applica-	Science
	tion activities in NanoRem	
-	*Facilitator of Helmholtz Centre for Environmental Research - UFZ	Facilitator

<sup>\* =</sup> NanoRem project affiliated

The meeting started with a soft opening of a rather informal get together setting allowing participants to informally introduce themselves to one another. Next, Stephan Bartke as UFZ host and facilitator opened the workshop with an introduction about the aim of the meeting. A NanoRem partner from University of Stuttgart provided the participants with an overview of the NanoRem project and the host of the workshop gave background on the exploitation strategy development for NPs in NanoRem. The format of the meeting was explained to facilitate expert input in semi-structured, open debate for robust discussion. After these introductions to the project and setting, the participants were asked to introduce themselves, their backgrounds and their expectations from the workshop. Next, NanoRem partners from Stuttgart and UFZ as well as a consultant introduced three different nanoparticles

The host of the workshop gave background information about the scenario approach and preliminary findings regarding identified market factors. He presented the conceptual scheme of four scenario states determined by the scenario framing factors "Validated information on nanoparticle (NP) application potential" and "Dialogue: Science-Policy-Interface - Communication with others". The participants critically discussed the specific meaning of the framing factors and reached a shared understanding of their meaning.

Participants were then asked to considering the EU in 2025 and answer to the question on how the factors perceived as most important will evolve under the different scenario states. In this way, the participants engaged in a discussion on the developments of the potential drivers and inhibitors of the market for nanoremediation under the scenarios.



	Validated information
Minimum dialogue	
	Intensive dialogue
Uncertainty	

In a final task, participants were asked to support the deriving of conclusions for an exploitation strategy. The participants were grouped into three groups – the composition of the groups reflected the background of the participants as either being linked to the market (consultants, industry), scientists or regulators. The groups were asked to discuss in their respective groups on the take home messages for peers providing exploitation related recommendations: Guiding questions for the discussions were:

- What are key developments and determining factors?
- Are there windows of opportunity and signals to monitor?
- What immediate requirements can be identified?
- What research gaps exist?
- What can be learned from the evaluation?
- What pitfalls can be identified?

After the collation of recommendations within each group, the other groups had the chance to ask for clarification or comment to the recommendations.

The following is summarizing the results. Different groups are indicated in different colours:

Recommendations by Market stakeholders commented by Science / Regulation

- There is a need for more well documented applications
  - Not only in English but also in national language → Research funders need to provide budgets for translations ✓
  - Source should be trusted (communication) partners
    - → renowned experts, appraisers, consultants ← which are informed by "Innovation industry / R&D"
    - $\rightarrow$  Is there a list of recommended/accepted partners no.
    - → Who shall science communicate to? Soft skill use platforms, in particular in Germany Dechema and internationally Battelle
  - Data (comprehensible, plausible) ✓
- Documentation of the variety of site conditions must be reflected
  - Significant parameters must be defined: aquifer, pollutant, nano-particle
  - Matrix: Pollutants biotechnological factors suitable nano particles
- Funding for research to provide information (R & D needed till level of readiness for marketability is achieved incl. pilot tests, field tests)
  - First-user-principle (EPA): technical feasibility (1<sup>st</sup> user) vs economic feasibility without co-funding (2<sup>nd</sup> user) → 3<sup>rd</sup> user is the first real adopter → problem: nobody wants to by the 2<sup>nd</sup> user ← depends on the costs of the material. This information can be derived from / calculated based on technical field tests. (Doubt regarding the 2<sup>nd</sup> user hypothesis.)



 Estimated number of applications in the next 3 and 10 years as stated by the two exemplary consultants in the focus group: ← Are these estimated applications a result of necessity or demand? ← likely merely "trying".

Number of nanoremediation application in Europe
3 years 10 years
1 3-5 projects | --

2-3 projects | 10 projects

2

- Innovations <u>and</u> risk research is needed ← presumably in Germany these sails have lost their wind
  - → self-interest of industry should push innovation research
  - → a societal interest needs to push risk research
- A stepwise procedure for decision making for / against application of nano-particles in remediation projects
  - The approach as such must be convincing in a cost-effectiveness-analysis and in a comparison of alternatives of established approaches
- concentrated dialogue between
  - Problem owners (who lack resources to initiate the process)
  - Consultants (who have a marketing interest) → Consultant ≠ executer of remediation how to deal with self-interest that hinders initiation of dialogue? ← it is possible if the marketability interest is stronger.
  - Researchers ← need incentives for broad dialogue beyond classic disciplines and for dissemination
  - Regulators ← Regulators must retain independence. They can and should participate in dialogue. They can actually initiate dialogue in cases of development and in advance of breakthrough (e.g. NanoDialog of German Federal Government) (← too abstract). With regard to questions of specific supervision, initialisation of dialogue by regulators is rather not conceivable.
- Carbolron® has attractive radius of impact, but durability and reactivity are still unclear
- Remediation targets in individual countries do determine the size of the market (for risk assessment it is low, for precautionary values it is high)
- The pursuit for finding and discussion a European uniform solution is excluding some national stakeholders, in particular (potential) adopters/handlers → Therefore, Germany should establish together with others a group of frontrunners to push the technology and to set benchmarks
  - positive example: Energiewende (energy transition to renewable energies) → although there was also pressure in this field
  - problem: smart-arse phenomenon The supposed wisenheimer is ignored or national animosities result in problems
  - negative point related to national solo attempts: A European solutions enables more dissemination options <-> in the case of thermic technology approaches Germany was a frontrunner on European level and these methods are increasingly adopted and accepted.

#### Recommendations by Regulators commented by Market / Science

- 1. What are the significant (determinants for) nano-remediation developments?
- Information are presented in a plausible way

→ then EU-standardisation will follow



- Benefits (only a theoretical comparison is possible) & advantages (is only possible in a project-specific way) in comparison to other methods → risk assessment should be decisive for the selection of an remediation technology/approach
- Hazard! / Danger (problem) → Effects on the environment (unintended/side effects)
  - o Hazard defence vs remediation of environmental contamination
- Hazard/Danger in particular as related to future of man ← Dangers need to be assessed and cleared (best already in lab phase)
  - o Can the danger be neglected due to the size?
    - → Are nano-particles maybe more harmful than bigger particles? ← no issue of particle size, but of type of material
    - → how can particles be retrieved later?
- 2. Are there windows of opportunity or signals?
- Publish actively in media (for discussion) → to early on prevent creation of prejudices
- Why has it to be called "Nano" at all?
- 3. Which topical demands can be identified?
- We need an assessment of the methodology (independent workshops) ← options
- Material security
- Preservation of evidence for success (monitoring)
- 4. What are research gaps?
- Effects and behaviour of particles in the soil (balance)
  - → to be derived from demands
- Eco-toxicology = the eco-toxicological methods are not the same for different particles → further investigation is needed
- 5. What can be learned from the scenario assessment?
- Communication (is the alpha and omega)
- Via dialogue → Increase and information
- 6. Which stumbling blocks are apparent?
- Uncertain statements about the advantages of the different technologies (at economic level)
- Incorrect application of particles (prevent incompetency)
- Insufficient investigation of soil/site



#### Recommendations by Science commented by Regulators / Market

• Appropriate vocabulary is needed and some generalisation must be accepted.



Appropriated communication means and technology transfer

Target at correct group

- Disseminate diversely
- What is innovative?
- For whom is this advantageous?
- → Practice orientation!
- Reduce diffuse fears of public (Engineering results assessment)
- Whereabouts and fate in environment:
   Further development of methods
   (Reach, adaptation of chemical based guidance for "nano")

What are criteria for sufficient validity (technically & economic), who formulates the requirements? 
← successful reference projects ✓

#### Participants' key conclusions in the Berlin focus group's final statements' round:

- 1. The meeting did not indicate new projects most were known before, said a consultant. Acceptance for new technology must be gained through communication and successful projects, which are a result of research and competitive costs.
- 2. Another representative of a major consultant said that the event was positive and gave helpful information for internal development of own products, e.g. for which remediation approaches nano-enabled technology might be useful and on how to optimize the distance with which NPs, in particular Carbo-Iron®, move in the soil. A personal take-home conclusion was to keep the interest for this topic and reconsider with a closer look the potentials of nanoremediation.
- 3. An advisor for the government for sustainability issues stated her surprise that apparently such a big **communication gap** remains between industry and science as well as between regulation and science. **Thinking in the scenario frames** was complex as a starting point, but turned out to be very helpful and yielding interesting insights.
- 4. A scientific partner from the NanoRem project was satisfied with how the focus group participants were gathered representing the different most relevant backgrounds. He also was pleased with the communication between the participants: Although coming from varied backgrounds it was possible to speak about the topic in a common language/jargon. The person also learned that one of the **research results** (a developed particle) although it was published several times before and assumed to be known was actually not too well known among the participants, which emphasised in turn the **need for more and better dissemination and communication of research results**.
- 5. A manufacturer of nanoparticles also underlined the **importance of communication** by stating: "It is important to do good things and to speak about them". In particular, **results of field tests** and real world applications need to be communicated and successful results need to be promoted actively. Hard results from pilot field tests are most important (not lab results).



- 6. For a regulator at German state level, nanoparticle enabled remediation was a new area of interest. Also he identified as the key determinant for further progress the current deficit in communication between the individual stakeholders (partly as represented in the focus group) and the need to find a common language/jargon between the different stakeholders. The objective must be an improved dialogue.
- 7. A consultant concluded from the meeting that potential for nanoremediation technology is acknowledged by practitioners and regulators in the focus group meeting. He was in particular satisfied to learn that participating German regulators will be willing to support use of nanoremediation technology if valid information and references are available. He assumes that the opportunity to actually use nanoremediation is easier possible in Germany than elsewhere this opportunity should be used.
- 8. A representative from the NanoRem project's core coordination team valued the groups joint assessment of the scenario frames and the discussion and validation of the respective factors. It was emphasised that the scenario framing factors need to be well defined. The communication process allowed group internal collection of view in as much as linking them. For the project a conclusion was that stakeholder discussions in their national language are important and should be encouraged also in other NanoRem countries at least those with practical applications.
- 9. Also a representative from a technical authority emphasised that **communication** is most important, particularly as it seems to be **difficult to contact regulators**. Further thinking will be needed on how to effectively address regulators on such innovative matters.
- 10. A representative of an insurance company hopes that he will get to know more **success stories** in future which report successful with nanoremediation projects, because this will make it easier to apply the technology oneself. He also agrees that communication in **national language** is more relaxed and effective.
- 11. A scientist dealing with issues of exposure risks of nano particles in the environment and related public concerns stated that she was glad to learn about an application area of nanoparticles in the environment and to have developed concrete scenarios for such a specific application field. She was surprised to realize that **communication is not optimal**.
- 12. A problem owner and state level regulator acknowledged the interesting composition of the focus group with participants from diverse areas of science, technical authorities, regulators or industry all being concerned and interested in the topic from their different perspectives. In line with lessons learned in his company in the past, he concluded: This type of getting together and discussion is a precondition for convincing authorities.

#### 11.4.2 Report on UK NanoRem Focus Group Meeting

Another full-day workshop "NP-based remediation technologies – potential market development by 2025" had the objective to gain business, regulatory and strategic intelligence from key UK stakeholders linked to nanoremediation on the potential market development for this technology to support the development of a better understanding of the value proposition of nanoremediation in Europe by 2025. This UK event was held at the Cavendish Conference Venue in London on 13<sup>th</sup> July 2016 – organised by Nicola Harries, CL:AIRE, Paul Bardos, r3, and Stephan Bartke, UFZ.

The specific format of the workshop included so-called focus group elements in order to facilitate a stakeholder engagement where through a discussion focussing on several related topics opinions and



expertise of group members are collated in a comfortable environment that enables participants to define and frame their individual points of view by comparing them to others' perspectives. The London focus group brought together twenty UK stakeholders having a direct link to NP application in the environment. Table 14 gives an overview of the participants:

Table 14: Characterisation of London focus group participants

No	Background	Group
1	Defra regulator	Regulator
2	Environment Agency	Regulator
3	Environment Agency	Regulator
4	Environment Agency	Regulator
5	Environment Agency	Regulator
6	Scottish Environment Protection Agency	Regulator
7	Natural Resources Wales	Regulator
8	Remediation contractor, environmental consultant	Practitioner
9	Consultant	Practitioner
10	Construction and demolition industry	Practitioner
11	Environmental, health and risk consultant	Practitioner
12	Engineering and consultant	Practitioner
13	Designer, planer, consultant	Practitioner
14	Remediation contractor, environmental consultant	Practitioner
15	Environmental industry	Practitioner
16	Environmental industry	Practitioner
17	*Environmental industry	Practitioner
18	Applied and environmental geochemist, environmental radioactivity	Academic
19	*Applied geoscientist, sustainable remediation	Academic
20	*Engineering geologist, risk assessment	Academic
	*Nano-particle producer and remediation contractor – Czech Republic	Practitioner
	*Researcher of University of Stuttgart – NanoRem coordination, Lead of application activities in NanoRem – Germany	Academic
	*Economist – Germany	Academic

<sup>\* =</sup> NanoRem project affiliated

The meeting started with an introduction session clarifying the background and objectives of the meeting. Beforehand, the participants had been provided with a briefing document, which has been a short paper with the aim to provide a concise and easily read overview of NanoRem's views on the appropriate use and application of nanoremediation technologies, and provide some clarity about how they are regulated in comparison with other forms of in-situ reduction and oxidation remediation technologies. This overview has been broad ranging but provided links to other NanoRem outputs where a greater depth of detail can be found. In the meeting, the objective of the workshop was emphasised, i.e. to learn about the UK specific context related to the path to an exploitation strategy for nanoremediation in the European context. Next a general overview of the NanoRem project was



provided before the participants were invited to introduce themselves with their background and interest in the event.

To further set the scene and ensure a common knowledge about the European state-of-the-art in nanoremediation technology, NanoRem partners from Germany and the Czech Republic presented "The NanoRem field testing programme for nanoremediation" and "Commercial and field scale experience of nano-iron in use in the Czech Republic and elsewhere in Europe". A general discussion was used to clarify open questions.

Next, the European context for the potential market development of NP-based remediation technologies was introduced by the German NanoRem partner from UFZ. Next to an explanation of the general scenario approach, participants were introduced to the preliminary findings regarding identified market factors found to drive European nanoremediation markets by 2025, in particular the so-called scenario framing elements which were found to be the most influential market determinants and are therefore used to frame possible future scenarios. The discussion has clearly identified the same two dominant factors that will affect the UK market as they were found in previous NanoRem workshops in Oslo and Berlin: "Validated information on nanoparticle (NP) application potential" and "Dialogue: Science-Policy-Interface - Communication with others". Combining these factors in a matrix gives four potential future scenario states.

To further learn about the opinions of participants on what they think is the potential market development of NP-based remediation technologies in the UK by 2025 under these four scenarios, a follow-up survey was introduced. The participants were invited to consider two of the possible future scenario states and to describe what it would actually look like, explaining this in terms of a broad set of market drivers. The advantage of the post-meeting survey format is that participants' views have more likely crystallised after the event when they had a chance to digest the workshop discussion on the driving or inhibiting market factors and on the likely strengths, weaknesses, opportunities and risks associated with this technology and its up-take in the UK. Some survey insights are presented in the Box below.

In a "Knowledge exchange" scenario, experts expect that case studies will be available of mitigation of highly toxic contamination and/or in difficult matrix by nanoremediation giving clear evidence of nanoremediation delivering cost-benefits over and above that of conventional remedial approaches. Valid information and dialogue will result in better identification of particular site conditions, types or combinations of contaminants and/or other site specific scenarios where nanoremediation is more (cost) effective / less disruptive than other remediation techniques. The innovation potential of nanoremediation to treat known contaminants is likely to be very important as ultimately nanoremediation is competing with a range of technologies. It is not sure it has demonstrated its niche against existing technologies so far, but by 2025 assuming the moratorium is lifted given valid information and dialogue, experts expect that "we would have completed a number of demonstrations, undertaken validation and would have a clear understanding of the potential benefits. If significant benefits are evident then this will be a clear driver for the further development and deployment of nanoremediation technologies." Increased application of NPs in common household products and advertisement of such in media acclimatises public mood and appetite for nano-enabled technologies in general. Notwithstanding, the costs of competitive technologies are likely to be very influential in a market where there is currently significant development in a range of competing technolo-



gies and costs are going down and where dialogue will also see that increasingly technologies seek to combine one or more techniques (for example ZVI and vegetable oil). By 2025 nanoremediation may have been more accepted and will also be able to be utilised in such applications, but ultimately nanoremediation has to be cost competitive in its "niche" against other technologies. If nanoremediation can also be shown to have overall lower life cycle costs for a particular project (because of greater treatment efficiency etc.) then that would also be an important positive stimulus, an expert explained. Another expert noticed that by 2025 a series of major droughts leads to severe water shortage issues precipitating drive to utilise previously marginal groundwater resources in 'difficult' matrices: This would further raise interest in NP as offering superior solution by way of treatment of difficult matrices (e.g. with secondary porosity). Regarding the regulation, an expert stated that NPs would be deployed successfully under existing regulatory regimes. With the good level of information and dialogue in this scenario it should not be a problem as the existing regulatory controls for remediation techniques fit well and could be easily adapted to incorporate the use of nanoparticles. Critical events would be lead in / development time with regulators in order for them to update (or draft new) guidance in relation to the use of nanoparticles within these existing regulatory controls (e.g. what additional controls or licence conditions specific to NPs require to be added). Training of regulatory staff in relation to review, assessment or inspection will be effective.

In a "Dialogue under uncertainty" scenario, it is expected that case studies will be available illustrating mitigation of highly toxic contamination and/or in difficult matrix by nanoremediation, but evidence of nanoremediation delivering cost-benefits over and above that of conventional remedial approaches are most likely poorly defined. The lack of validated information on safe application of nano-particles and toxicity risk, even with strong stakeholder engagement, are likely to lead to maintenance of regulatory barriers and moratoria. Good dialogue will not overcome technical uncertainty in getting a new technology approved for use by regulators. These are unable to provide direct support for any proposed lifting of a moratorium or permitting nanoremediation application, due to lack of clear evidence of 'safe' application or 'no significant effect' as identified through studies. This will be the case particularly for nanoparticles with known toxicity (Ag, CNTs), although Fe-based systems (which will have lower toxicity risk) will be less susceptible to this, an expert stated. A disruptive (positive) factor may be the successful and validated application of nanoparticle based systems in other environmental sectors (e.g. water treatment). Without validated trials and information, another expert rumoured, nanoremediation will likely remain a novel, prototype technology, higher in deployment cost and potential future liability costs than competing technologies with a higher degree of validation (e.g. ISCO). Comprehensive dialogue may mitigate this to some (likely small) extent. Notwithstanding, stakeholder dialogue on potential use of nanoremediation on emerging contaminants, which are not easily treatable by other methods, may generate funding and trial work opportunities, although validated information will be required to give confidence to move beyond prototype/small-scale trial stage. It was also stated that a lack of validation and uncertainties are unlikely to limit funding for innovative applications, particularly if stakeholder dialogue and lobbying is effective, but may in the longer term promote a shift from funding nanoremediation research to funding other nano-areas. Notwithstanding the lack of support for nanotechnology from regulators, a series of major droughts is likely to lead to severe water shortage issues precipitating the drive to utilise previously marginal groundwater resources in 'difficult' matrices, which in turn will raise the interest in nanoremediation as offering superior solutions by way of treatment. An expert believes:



"Widespread public alarm over accelerating climate change effects puts sustainability requirements at heart of decision making process, which NP remedial technology can exploit, notwithstanding limited evidence of NP".

In an "Isolation in uncertainty" scenario of lacking information and dialogue, in particular a restrictive regulation of nanoparticle use in the environment is assumed to determine the market. A likely characteristic will be a remaining of the moratorium that might also be adopted by other countries than the UK. A driver for the scepticism could likely be environment protection policies based on a precautionary principle. Another expert stated that nanoremediation would have to demonstrate technically effective and be understood before environmental awareness and sustainability became a significant and potential differentiator. Research is seen by experts as a disruptive element as results could move the market from this scenario to one where available information is pushing the development.

In an "Isolated Knowledge" scenario, the availability of validated information will reduce the likelihood of further moratoria/extension of existing moratoria. Lack of stakeholder dialogue however, particularly with regulators, poses a significant threat and could seriously undermine this. With the good level of information but poor dialogue in this scenario, nanoparticles would be unlikely to be deployed successfully under existing regulatory regimes. Regulators would be unaware or unclear as to the benefits, risks (or lack of risk) associated with nanoremediation, they would be unlikely to adapt existing guidance and licensing schemes accordingly and end users are unlikely to choose nanoremediation methods when gaining regulatory approval is likely to be time consuming. Unsuccessful field trials, which indicate residual risk to receptors from NP application, are also a significant risk, and could result in further regulatory barriers. As in the first scenario, validated trials and information will help to reduce nanoremediation costs by allowing a more targeted approach and limiting future liability risks. This is likely to make nanoremediation more cost competitive, even with limited stakeholder dialogue. However, nanoremediation might remain a market niche if only few contractors have sufficient available information on how to apply the technology efficiently. An expert also supposed that validated information may help to allay public safety fears, even without extensive stakeholder engagement. There was a risk however that without dialogue in-field applications may generate controversy and public opposition due to all nano-products being grouped together by media and pressure groups and labelled as potentially dangerous. Regarding the research area, a lack of stakeholder dialogue coupled with a feeling that nanoremediation is an established or validated technology is assumed by experts to promote a shift from nanoremediation research funding into other nano-areas which are seen as more innovative.

The meeting itself continued after lunch break with a discussion on the UK market for nanoremediation and the impacts of the voluntary moratorium, which is clearly a UK specific decisive market determinant. The session was introduced by a presentation by a regulator presenting the reasons for and background to the UK voluntary moratorium on nanoremediation followed by a NanoRem partner, academic and consultant with a presentation on what is now known on the technical state of the art.

In a final task, participants were asked to support the deriving of conclusions for an exploitation strategy and to identify "take home" messages about nanoremediation use in the UK. Participants with practitioners and regulatory backgrounds were asked to split into two groups respectively and to discuss on take home messages for their peers regarding the market potential of nanoremediation



in the UK by 2025. After the collation of recommendations within each group, the other groups had the chance to ask for clarification or comment to the recommendations.

The regulators' group remarked regarding the voluntary moratorium, that it is all about "nano" due to its physical size. Permitting requirements would need demonstration with validated information. Regulations emphasised that their job is to identify risks, others are to identify the unique benefits. There is seen a need to compare same technologies with and without nano (instead of different technologies nano with bio). It was noticed that activated carbon and iron have long track record of use in the environment. Regarding nanoparticle enabled remediation, a need is seen for a test case that is "realistic" aiming for confidence building and bringing greater certainty. Perhaps a "worst case site" vs "low hanging fruit". It was however not clear to say what will be a sufficient size for demonstration and to give confidence to the market, e.g. if it should be one or more sites or how many demonstrations would be needed. It was emphasised that reviewed, validated information is required. Site specific risk assessment is needed. If it is shown that by risk management applied NPs are contained in treatment area, it is more likely to be OK. The discussions stated that control of the treatment area could be improved by implementing an electric connective fence - to give additional benefit whilst undertaking a demonstration/trial. One regulator reminded the participants that the "Moratorium is in place due to Ministers, it is not the regulators responsibility. They have nothing to gain for this to be in place."

The regulators identified a number of potential strengths and benefits of nanoremediation technology, including the ability to treats chlorinated solvents, to **extend the list of treatable contaminants**, to facilitate bioremediation and where bioremediation could not be used that there nanoremediation was an alternative. Comparing nano ZVI with complex chemical treatments, it is assumed that the **intrinsic toxicity of iron is less than that of persulphate/permanganate**. It was noticed that **70-80 examples used worldwide are documented** so there are examples to draw on. The extent (controlled fate - electric connective fencing to stop contamination going off site) v speed of reaction (faster than bio - however there is mixed evidence to support this) have been noted next to the limited longevity. Nano remediation is seen as a first step for next technology generation with **massive potentials being possible**. Yet it is unsure if that is commercial. A sustainability assessment would be helpful – following SuRF-UK.

However, the regulators' group also identified a number of risks, including that NanoRem findings could be rather overstated. **No information proves that NPs are (non-)toxic**. The actual technology impact depends critically on application/site conditions making the technology very site specific. It is risky to determine the "right" level of coating. The "uncertainties"/"unknowns" are still prevailing as **only too few/too specific demonstrations exist**. It is unknown what the worst case can be. More general, public perception is a risk factor to be addressed with dialogue/communication. In consequence a key question is: What level of risk is acceptable – it should not be worse than any alternative technology and its performance measured against triggers based on existing knowledge.

Also **the practitioners' group** identified a number of potential strengths and benefits. General benefits are seen in the capability of nano to access the parts of contamination that other technol-



ogies cannot reach. Nano can potentially be used as source treatment compared to other technologies such as thermal. A fast remediation process is possible. Nanoremediation presents a less engineered solution, therefore it is easier to implement. Moreover, lower or no breakdown products compared to biological processes or iron products exist. Nano might potentially have a better distribution compared to other iron technologies and it is able to facilitate biodegradation. Benefits to persuade regulators and problem holders are seen in the points that nanoremediation is based on natural dietary elements and has less secondary geochemical effects and less methane – although these are not unique benefits, it indicates better effectiveness than other processes. To convince regulators and adopters, the technology needs to be cheapest and within regulatory requirements. It is uncertain if the public reaction will be there and of importance.

Risks identified by the practitioners' group are the lack of understanding what contaminants can be treated. Risks are also apparent if nanoremediation is not effective, if there was a lack of contact/delivery in sufficient time and concentration and regarding the development of sufficient skill sets of workforce. In particular **inappropriate tests** danger the market uptake as if a remediation project goes wrong all nanoremediation could be effected and reputation damaged. Therefore it must be trialled on particular contaminants to validate the process so it is not seen as a panacea for all contaminants. Using NPs can have **Health & Safety** issues – **negative publicity** if something goes wrong. Human health risks need to be better defined for public and wider community. Also uncertainty about **renegade/residual particles** and how to measure them is seen. Verification of fate of particles is critical to demonstrate what has happened to absorbed particles/where have they gone.

Uncertainties were identified by the practitioners related to different fields. In relation to benefits of coating NPs, it is not known how it actually works and more clarity of reaction to optimise the particle needs to be demonstrated. A question was also who can assess if the technology is working or appropriate. Related to verification process and particle fate, it is unclear if the technology is available to assess this and what the lines of evidence are. For the market it is open how available the products can be if there emerged a demand to apply nanoremediation widely. Related to costs, uncertainties exist on what the actual costs are, if they are competitive, and that the viability is depending on the size of the site. Regarding public perception, it is assumed that this is low but the public are becoming more informed. Moreover, a need to ensure that first trial in the UK is a success is seen, so it must be ensured that nanoremediation is used in the right controlled environment. Further uncertainties are related to the distribution of particles compared to other iron technologies and to colloids, i.e. if it is following that sort of behaviour and, therefore, how to do a proper risk assessment.

In the closing plenum, individual's conclusions were collected. The key factors driving the development identified in the UK context were the moratorium, effective communication, the Brexit, field trials, niche application/focus (to understand the operating window and technical boundary of the technology); tools/knowledge and trials; availability commercially (needs to be offered by remediation vendors); all NanoRem particles need to be in production; development of appropriate lines of evidence, protocols (verification & fate & transport) and last not least a need for clarity for which products the technology works.



Table 15 presents the <u>decision points and disruptive events</u> that were identified:

Table 15: Decision points and disruptive events identified in London focus group

Practitioner	Regulator	Decision Points/Disruptive Events
Х	Х	Results of <b>field trials</b> – are these a game changer, does it provide a benefit?
Х		Nanomaterials get a <b>bad press</b> from other particles, e.g. nanosilver
		scare, therefore need to ensure that when nanoremediation is demon-
		strated it is done well and communicated well.
Х	Χ	Permitting
		Environmental Permitting : no deterioration of soil/water quality
Х	Х	Brexit – economic problems so people unlikely to invest in demonstra-
		tions with downturn of property market.
		Brexit – could mean the relaxing of regulations Opportunity to sell UK
		expertise – therefore gain support to develop
Х		Climate change – hot summers and pressure on water in marginal are-
		as, would this create a greater driver to deal with more marginal con-
		taminated sites to release new water resources? What about public
		perception regarding drinking water?
X		Other technologies are also advancing: can nanoremediation compete
	Χ	2019 Water Framework Directive/Groundwater Directive Review:
		Soil and soil biota needs to be protected, River Basin Management:
		pressure to deliver
	Х	New EA Director feels soil is neglected
	Х	Industry needs to address all issues raised by the Moratorium in a re-
		port produced by an independent body such as Chemical Stakeholder
		Forum. Chemical Stakeholder Forum would be useful to contact as this
		is made up of NGOs & Industry and is therefore seen as independent.
	Х	REACH review – new annexes for nano
	Х	Engagement of local authorities

<u>Key conclusions</u> of the UK focus group are: First, knowledge gaps exist and need to be addressed. Second, nanoremediation is a site specific technology – there is need to demonstrate in the UK in UK conditions and understand the performance envelope of the technology. Third, a need is manifest to clearly understand the human health risks. Fourth, what the fate and transport is of NPs needs to be understood and documented. Last not least, opportunities are seen in the UK for nanoremediation.

#### 11.5 DL9.1 Consultation summary"

Following NanoRem's initial findings reported in the interim "Risk Benefit and Markets Appraisal Initial Exploitation - Strategy", NanoRem collected additional opinions from different stakeholders



about the issues raised in the report, by creating an online questionnaire and making the consultation publicly available. The aim of this questionnaire was to invite a wider selection of stakeholders that may not be as involved in nanoremediation and use their views to help strengthen the overall project findings. This consultation was made available between April – July 2015.

The consultation was advertised on a wide variety of information and news portals predominantly across Europe such as NICOLE and Common Forum and some with more global reach such as Tech Direct and EUGRIS. A total of 23 responses was received from a variety of stakeholder groups both public and private and from 12 different countries across the world including Australia, Austria, Belgium, Canada, China, Czech Republic, Germany, Netherlands, Norway, Switzerland, UK and USA. Most responses received were from the UK (22%), Czech Republic (13%) and Germany (13%).

The stakeholder groups that provided responses represented consultancy (39%), universities (17%), government agencies (13%), regulators (13%), private land owners (8%), developers (4%) and professionals (4%). Everyone was asked if they were involved or associated with the NanoRem project with the majority of respondents (91%) having no connection.

All stakeholders confirmed that they had some degree of familiarity with NP based remediation technologies with 17% confirming an emerging interest, 48% confirming some familiarity and 35% confirming that they were very familiar. However, only one respondent had used nanoremediation more than 10 times. Six respondents stated that they had used the technology more than once, three had only used it once and the remaining respondents had not used it equating to 50% of the respondents.

Stakeholders were asked to review the Strengths, Weaknesses, Opportunities and Threats (SWOT analysis) for nanoremediation use in contaminated land management that had been previously reported in DL 9.1 report (see Appendix 1). They were asked for their feedback and whether there were any factors missing from those already identified. Most stakeholders (65%) did not have any additional comments to make and felt the SWOT factors were adequate, stating "seems to capture the relevant issues", "it is one of the most comprehensive I have seen" and "pretty thorough SWOT". Only one stakeholder strongly disagreed with the SWOT factors and stated "it is incomplete - rerun". The other stakeholders identified the following factors should be considered, "lack of appropriate design tools for remediation using nZVI", "how does the huge amount of NP introduced to the underground affect the soil structure and groundwater flow (e.g. clogging)?", "poor mobility of nZVI in soil with low permeability and consumption of nZVI for reaction with other compounds than contaminants" and "contamination is mentioned instead of making a split between soil and groundwater. A weakness: remediating soil contamination. Opportunity: groundwater contamination".

Those that provided feedback on the SWOT analysis also gave further feedback stating: "most listed weaknesses are related to unsolved technical problems which make the usability of the whole technology questionable in general. The technology is not applicable/marketable so far", "we need more knowledge on the kinetics of the soil matrix - groundwater interface and the role of NP's on this", and "maybe large scale production of nZVI is difficult?".

Stakeholders were asked to rate the importance of certain factors changing over the next 10 years to drive the market development for nanoremediation. They were asked to score from "3 = very important" to "0= unimportant". The factors included:



- Costs (comparing to competing technologies)
- Field Scale Experience
- Relative Effectiveness
- Relative Risks
- Ease of Use
- Technology Dread
- Current Knowledge
- Synergy (combining with other technologies)
- Sustainability

For costs, all stakeholders felt that this was an important factor, with 30% feeling that costs would remain the same or improve against other competing technologies. These responses were caveated with statements such as "it is hard to say at this moment. We do not know about either the long-term health effects or the long term environmental effects. Also, there are many other technologies emerging all the time. Who knows what we may learn in a year from now?" and "slow development, new technologies need time to win enough recognition".

Field scale experience was identified as an important or very important factor by all stakeholders. Stakeholders explained their reasoning with statements such as "more effective case studies will help acceptability" and "think it will always be important to evaluate a technology at field scale to obtain design information - in much the same way as for other technologies".

Relative effectiveness was also considered an important (35%) or very important factor (61%) by stakeholders with only one stakeholder feeling it was not important. Stakeholders explained their high scoring for reasons such as "because of the 'negative image' of NP the proof on effectiveness is even more important than for other technologies using less criticised substances" and "the scientific evidence points to high effectiveness and as this becomes more well-known, the demand should increase". The majority of stakeholders (74%) identified that over the 10 years effectiveness of nanoremediation would stay the same or improve.

For relative risks, the majority of stakeholders felt that this was a very important factor (52%), with 17% feeling that it was not so important and only scoring with a 1. The majority of stakeholders (74%) identified that the risk perception would improve (48%) or stay the same (26%) over the next 10 years. Stakeholders provided justification for their results by stating "authorities will get more familiar with the nZVI technology" and "at the moment, there are more risks assumed and feared than really shown to exist. This will change with better knowledge basis."

The majority of stakeholders (87%) felt that the ease of use of nanoremediation was important or very important. Stakeholders gave justification for the following reasons, "efficiency affects cost" and "experience makes everything easier".

The perception of the technology was identified as important or very important by most stakeholders (78%). The majority of stakeholders felt that perception would stay the same or improve with time, however two stakeholders felt it would get worse. This they suggested was due to "nanomaterials generally are seen as more problematic".

All stakeholders identified that current knowledge improvements were important or very important if nanotechnology was to improve its use in the next 10 years. Most stakeholders (74%) identified



that knowledge would improve in the next 10 years, some explaining their reasoning by "more complex information will be available" and "once seen as tried and tested practitioners will be more likely to apply it".

The synergy with other technologies provided more varied responses from stakeholders, with 22% suggesting that it was either unimportant or less important that nanoremediation was used in combination suggesting "compatibility and cost issues" being one of the reasons. However, 78% did feel it was important stating reasons such as "probably a combination with other technologies is a more realistic option for nanoremediation than a stand-alone technology" and "multifunctional hybrid technologies will be the future".

Sustainability was considered by 96% of stakeholders as an important or very important factor when considering the effectiveness of nanoremediation and most felt that it will either stay the same or improve with time.

Stakeholders identified that there was a low level of dialogue about nanoremediation between most stakeholder groups, including the scientific community, industry, and regulators. Stakeholders provided suggestions for improving dialogue by "Independent scientists - consultants who have no conflict of interest should be approached for an opinion - in order to have a better understanding of all pros and against" and "there is nothing comparable to true success stories written in an understandable manner".

To finish, stakeholders were asked to identify any additional factors that NanoRem needed to address to improve market development. One stakeholder responded "successful demonstration of the technology to gain more trust from industrial and government sectors would be critical to the nanoremediation market development."



# Appendix 1: Consultation SWOT Analysis from DL9.1

**Table 16:** nZVI Strength, Weakness, Opportunity and Threat (SWOT) for the use of nZVI in remediation

Strengths		Weaknesses			
Improving the speed of contaminant destruction	Relative effective- ness	Field scale deployments are limited in scope of remediation problem being addressed and tend to lack verified / validated performance information	Field scale experience		
Improving the extent of contaminant destruction	Relative effective- ness	Knowledge gaps regarding fate, transport, toxicity in environment	Current knowledge		
Extending the treatable range of contaminants	Relative effective- ness	Knowledge gaps relating to toxicity to humans	Current knowledge		
70 known field scale deployments	Field scale experience	Handling risks may be greater than granular ZVI	Relative risks		
Limited longevity of action may reduce environmental risks	Relative risks	Limited longevity due to rapid ag- glomeration and passivation. May require several applications	Relative effec- tiveness/ Ease of use		
Compatibility with other treatments	Synergy	Poor mobility due to rapid agglomeration and passivation in the short term	Relative effectiveness/ Ease of use		
Can utilise existing techniques for deployment	Ease of use	Potential groundwater contamination by NPs	Relative risks		
As an <i>in situ</i> technique there may be reductions in site costs compared to <i>ex situ</i> remediation (e.g. reduced waste generation, reduced fuel usage)	Relative costs	Lack of comprehensive sustainabil- ity assessment	Current knowledge		
As an <i>in situ</i> technique there may be reductions in some site risks compared to <i>ex situ</i> remediation (e.g. reduced exposure of workers to contaminants)	Relative risks	Cost of nZVI is currently high relative to granular ZVI	Relative costs		
Opportunities		Threats			
Concentration of field scale experience in some countries, e.g. Czech Republic, creates an opportunity for cross comparison of field scale deployments in one jurisdiction	Field scale experience	Unwillingness to provide regulatory or problem holder permission to use nZVI	Field scale experience		
Cost reductions associated with economies of scale	Relative costs	Potentially significant public concern about nanotechnology being	Technology dread		



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		inherently risky	
Optimisation of field trials improving NP delivery methods	Relative effective- ness	Numerous coatings, modifiers, catalysts which could make establishing risks complicated	Relative risks
Treatment of contaminants in the vadose zone	Relative effective- ness	Costs remaining high relative to competing technologies	Relative costs
Potential for treatment of source terms	Relative effective- ness	Source term treatment effective- ness is in general constrained by the accessibility of the source	Relative effectiveness
Improved understanding could lead to reduced public and regulatory fears	Technology dread	Difficulties in tracking NP transport	Relative risks
Inclusion of nanoremediation in <i>in</i> situ integrated treatment approaches	Relative effective- ness		

NanoRem

Possible future trends affecting broader SWOT categories Table 17:

Item	Time sensitive?	Possible development by 2025	Certainty of development
Relative costs	Yes	Economies of scale may lead to cost reductions related to:  a) production of NPs b) application of NPs Increased costs of NP material could raise costs.	Dependent on level of market uptake and the overall demand for NPs.
Field scale experience	Yes	Additional field trials including a wider range of contaminants could strengthen the evidence base for nZVI effectiveness and reduce public concerns associated with deployment safety	Highly likely. This is a key task of the NanoRem project (WP10)
Relative effectiveness	Yes	a) Research funding to address difficult contaminants and develop novel NPs b) Vadose zone treatment, if developed, could have huge benefits for difficult / untreatable problems such as highly recalcitrant contaminant classes (e.g. PCBs, dioxins, etc.) c) Development of coatings to improve persistence and mobility	a) Likely – There are a number of research projects taking place across Europe b) Currently vadose zone treatment has not been well investigated, but exploiting NPs for this use may be possible c) Relatively certain, research being carried out, including by NanoRem
Relative risks	Yes	Development of coatings to improve persistence and mobility – introduc- ing an additional element of risk	Relatively certain, research being carried out, including by NanoRem



Item	Time sensitive?	Possible development by 2025	Certainty of development
Ease of use	Yes	Development of coatings to improve persistence and mobility	Relatively certain, research being carried out, including by NanoRem
Technology dread	Yes	Field trials and research into potential toxicological effects could help address "dread" associated with the technology	Improvement of the situation is possible. NanoRem is working towards consensus development for appropriate NP use. NICOLE and Common Forum will assist
Current knowledge	Yes	Knowledge expansion leading to reduced dread, improved certainty of effectiveness, increased uptake of the technology.	Improvement of the situation is likely. NanoRem is working towards improved knowledge and dissemination. For example, Nano-Rem is developing better methods of monitoring field deployments of nZVI (Oughton et al. 2015).
Synergy	Yes	New synergies could be discovered, incorporating previously un-trialled technologies in combination with nZVI	Likely – experimental work exploring synergies of nZVI with e.g. bioremediation are already under way, including by NanoRem



#### Annex 3 Overview Table of NP Field Applications Identified Worldwide, as of November 15 2016 **12**

Adapted from Bardos et al. 2011

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
Belgium Herk-de-Stad, CITYCHLOR Consortium. 2013	Pilot	Mixed permeabil- ity aquifer	GW	Chlorinated solvents (PCE and daughters)	Some free product suspected	Direct Push Injection	nZVI	
Canada, Brownfield, SK, Müller and Nowack 2010	Pilot	Unconsolidated sediments	Soil	TCE, DCE				
Canada, London, Ontario, Chowdhury <i>et al.</i> 2015	Field test	Sandy silt aquifer	GW,	TCE		nZVI was injected into an existing well	nZVI produced on site	0.14 kg
Canada, Sarnia Site, Ontario, Karn et al. 2009 Supplemental Material <sup>25</sup> , Kocur et al. 2014 and 2015	Pilot	Unconsolidated sediments	GW	PCE, TCE	TCE 86,000 μg/L	Gravity injection at four points	nZVI synthe- sised on site, stabilised with CMC	700 L of 1 g/L nZVI with 0.8 wt % CMC polymer
Canada, Valcartier Garrison Quebec***, US EPA 2016 <sup>26</sup>	Pilot	Alluvial sands and gravel, glacial sands, silts and gravels (deltaic and proglacial sands)	GW, Sands and clayey silts	TCE, DCE, VC	TCE: ~300 μg/L; DCE: ~50 μg/L	Injection Screen Wells	nZVI with a palladium cata- lyst with a soy powder surface modification	4.5 tonnes (A future full scale application is envisaged of 100 tonnes)
Czech Republic, Spol- chemie, Usti nad Labem, Site 1*, Braun <i>et al</i> . 2016	Pilot	Quaternary sand and gravel under- lain by a clay aquitard	GW	DNAPLs (chlorinated solvents)		Direct push	nZVI, NANOFER 25s and NANOFER STAR (air stable)	Injection 1: 200kg NANOFER 25s; Injection 2 ~600 kg NANOFER STAR

<sup>25</sup> See also <a href="http://www.rpic-ibic.ca/documents/RPIC">http://www.rpic-ibic.ca/documents/RPIC</a> FCS2014/Presentations/1-OCarroll <a href="http://www.rpic-ibic.ca/documents/RPIC">DMORPIC2014v2ForTranslation.pdf</a> Accessed January 2016

See also <a href="http://s3.amazonaws.com/ebcne-web-content/fileadmin/pres/4-10-2012">http://s3.amazonaws.com/ebcne-web-content/fileadmin/pres/4-10-2012</a> Nanoremediation/4-10-2012 Lilley.pdf, (2012) which also suggests Golders have deployed on 20 field sites in total



Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
Czech Republic, Spol- chemie, Usti nad Labem, Site 2*, Braun <i>et al</i> . 2016	Pilot	Quaternary sand and gravel under- lain by a clay aquitard	GW	LNAPL (BTEX, primarily toluene),		Direct push	Nano-goethite (nano-iron oxide) - used to stimulate mi- crobial activity	Test 1 60 kg Test 2 300 kg
Czech Republic, Hluk**, Müller and Nowack 2010	Pilot	Prb filter	GW	Chlorinated Ethenes	5 mg/l	Infiltration Wells	RNIP <sup>27</sup> , Nanofer <sup>28</sup>	300 kg
Czech Republic, Ho- rice**, Müller and Nowack 2010, Müller <i>et</i> <i>al.</i> 2012	Full	Low permeable aquifer	GW	PCE (TCE, DCE)	70mg/l	High pressure pneumatic injection	nZVI (RNIP and Nanofer)	2 tonne
Czech Republic, Ku- rivody**, Müller and Nowack 2010	Several Pilot/Full	Fractured bed- rock	GW, overbur- den, weathered bedrock	Chlorinated Ethenes	15 mg/l	Infiltration wells, infiltration drains	nZVI, RNIP, Nanofer**	100s kg
Czech Republic, Per- mon**, Müller and Nowack 2010	Pilot	Fractured bed- rock	GW	Cr(VI)	450 mg/l	Infiltration wells	nZVI, RNIP	150 kg
Czech Republic, Pies- tany**, Müller and Nowack 2010	Pilot	High permeable aquifer	GW	Chlorinated Ethenes	5 mg/l	Infiltration wells	nZVI synthe- sised on site	20 kg
Czech Republic, Pisec- na**, Müller and Nowack 2010, Müller et al. 2012	Full	Sandy / silt	GW	Chlorinated Ethenes chlorinated Ethanes	35 mg/l	High pressure pneumatic injection	nZVI, RNIP, Nanofer	4.5 tonnes of RNIP and Nanofer
Czech Republic, Rozmital**, Müller and Nowack 2010	Full	Fractured bed- rock	GW	РСВ	2 mg/l	Infiltration wells	nZVI, RNIP, Nanofer	1 tonne
Czech Republic, Spol- chemie**, Müller and Nowack 2010	Several Pilot/Full	Porous aquifer	GW	Chlorinated Ethenes, chlorinated Methanes	40 mg/l	Infiltration wells	nZVI, Nanofer**	Several tonnes
Czech Republic, Uhersky Brod**, Müller and	Pilot	Porous aquifer	GW	Chlorinated Ethenes		Infiltration wells	nZVI, Nanofer	150 kg

<sup>&</sup>lt;sup>27</sup> RNIP were the nZVI NPs produced by Toda Corporation in Japan (these are no longer in production)
<sup>28</sup> The producers of Nanofer state that they have additional deployments in the Czech Republic and also pilot deployments in Italy, Spain, France, Belgium, Netherlands, Canada, South Korea, and Hungary: usually 50-300kg of nZVI. However, they are not permitted to disclose further information. ###



Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
Nowack 2010								
Czech Republic, Uzin**, Müller and Nowack 2010	Pilot	Low permeable aquifer	GW	Chlorinated Ethenes	20 mg/l	Infiltration drains	nZVI, Nanofer	300 kg
Denmark, Taastrup; Danish Environmental Protection Agency-2015	Pilot	Low permeable glacial clay moraine deposits	unknown	unknown	unknown	High pressure injection	nZVI	unknown
Denmark, electrical substations at three locations, Danish Envi- ronmental Protection Agency-2015, Hindrich- sen <i>et al.</i> 2015	Pilot	The overall geology for the three sites, is clay till with various contents of sand lenses underlain by a sandy secondary aquifer	GW (sandy aquifer)	PCE and TCE)and their degradation products DCE and VC		Injection, in one location pre- injection with mo- lasses	nZVI (NANOFER 25S)	Site 195 kg; site 2, 200 kg; site 3 several tonnes in two campaigns
France, PRODEM site, Toulouse**	Pilot	Low permeable aquifer	GW	Chlorinated Ethenes, Cr(VI)	7 mg/l	Infiltration well	nZVI, Nanofer	150 kg
France, SNG site near Chalon sur Saone**	Pilot	Porous aquifer	GW	Chlorinated Ethenes, CN	30 mg/l, 20 μg/L	Infiltration well	nZVI, Nanofer	25 kg
Germany, Asperg, Müller and Nowack 2010	Pilot	Fractured rock	GW	Chlorinated Ethenes		Sleeve-pipe injec- tion	nZVI, RNIP	
Germany, Bornheim, Müller and Nowack 2010, Müller <i>et al</i> . 2012	Full (first European full scale application)	Sandy gravel		PCB, TCB, PCE, TCA, Pesticide, solvents, perchlorates		Sleeve-pipe injction	nZVI, RNIP**	1 tonne nZVI and two tonnes micro ZVI
Germany, Gaggenau, Müller and Nowack 2010	Pilot	Porous aquifer	GW	PCE		Sleeve-pipe injec- tion	nZVI, RNIP	
Germany, Hannover, Müller and Nowack 2010	Pilot	Chemicals storage facility	Soil and GW	СНС, ВТЕХ. НС		Aqueous slurry	Not specified	
Germany, Schönebeck Müller and Nowack 2010	Pilot	Porous aquifer	GW	vc		Push infiltration	nZVI, RNIP	
Germany, site Breite St. in Braunschweig, Kober et al. 2014	Pilot	Porous aquifer	GW	PCE	20 to 50mg/L	Direct push injection	Milled ZVI with a flake-like shape and thickness of <100 nm	280 kg
Germany, Thuringia, Müller and Nowack 2010	Pilot	Porous aquifer	GW	Chlorinated aliphatic hydrocarbons, Ni, Cr,	CAH: 104,000 μg/L Ni: 4,130 μg/L	Injection wells	nZVI	120 kg



15/12/2016 Dissemination Level Pu

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
				NO₃	Cr: 1,460 μg/L NO3: 70 mg/L			
Hungary, Balassagyar- mat*, Braun <i>et al.</i> 2016	Pilot (plume test no access to source)	Made ground (fill) over alluvial deposits over a bedrock aquitard	GW	Chlorinated hydrocar- bons, PCE, TCE, DCE		Direct injection	Carbo-Iron® stabilised in CMC (nZVI sorbed to acti- vated carbon)	177 kg
Hungary (industrial site, confidential), 2014 *****	Full	Unconsolidated sediments	GW	cDCE, VC		Direct injection	nZVI	5,300 kg
Hungary (industrial production site, confidential), 2015 ****	Full	Unconsolidated sediments	GW	TCE		Direct injection	nZVI	500 kg
Hungary (chemical storage facility, confidential), 2014 *****	Extended Pilot	Mixed sands	GW	Contaminant mix, volatile aromatic chlorinated hydrocarbons treated		Reactive barrier and direct injection	nZVI	700 kg
Israel Neot Hovav*, Braun <i>et al.</i> 2016	Pilot	Fractured bed- rock (Eocene chalk)	High salinity GW	Not specified		Not specified	Carbo-Iron® stabilised in CMC (nZVI sorbed to acti- vated carbon)	Not specified
Israel, Nir Galim, Jacov et al. 2012	Pilot		GW	PCE, TCE, dis-DCE		Groundwater di- rected through column containig nzvi composite	Diatomite sup- ported nZVI- vitamin B12 composite.	50kg
Italy, Biella, Müller and Nowack 2010	Pilot	Porous aquifer	GW	TCE, DCE		Gravity infiltration	nZVI	
Netherlands, Rotterdam, Citychlor Consortium 2013	Full	Not specified	GW	Chlorinated solvents (PCE and daughters)		Injection	nZVI	Not specified
Portugal, Lousal, #	Pilot	Low permeable aquifer	GW	Heavy metals		Injection wells	Nanofer 25S	500kg
Portugal, Lisbon ****	Pilot	Porous aquifer below made ground	GW	Heavy metals, (As, Pb, Zn, Cd, Cu and Ni)		Gravity injection	Nano-goethite (nano-iron oxide)	300 kg
Spain, Nitrastur*, Braun et al. 2016	Pilot	Made ground (2 to 9 m deep)	GW	Petroleum hydrocar- bons and heavy metals	Highest level of dissolved As found	Gravity feed to wells	nZVI, NANOFER STAR	250 kg



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



Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
USA, Camp Pendleton Southern California; ES EPA 2016	Pilot (possi- bly bench scale)	Not specified	GW	TCE		Ex situ treatment	nanoscale zero valent zinc	
USA, Cape Canaveral Launch Complex 15, FL, US EPA 2016	Full	Groundwater; surficial aquifer; fine/ medium sandy silts	Soil and GW	TCE	439,000 μg/L Max TCE found	Drop tip injection	Emulsified nZVI (EZVI)	Described as a full scale project
USA, Cape Canaveral, Launch Complex 34, FL, US EPA 2004; US EPA 2016	Pilot	Surficial aquifer with fine / medium grained sands	Soil and GW	TCE	1,180,000 μg/L Max TCE found	High pressure pneumatic injection and pressure pulse enhanced injection	Emulsified nZVI (EZVI)	670 US gallons of EZVI (17% iron by mass)
USA, Edison, New Jersey, US EPA 2016	Pilot and Full	Fractured bruns- wick shale bed- rock and 4-6ft of silt and clay soil	Fractured Bed- rock	TCA, TCE, DCA, DCE, cholorethane, vinyl chloride	TCA 13,000 to 1,200,000 ppb)	Injection wells	nZVI and emul- sified vegetable oil (nZVI con- tent not speci- fied)	10,000 US gallons
USA, Former Manufac- turing Site Bridgeport, Ohio, US EPA 2016	Pilot (possi- bly only bench scale)	Not applicable	GW	TCE, DCE, VC	Total to 5,800 μg/L	Ex situ treatment		
USA, Frankling Square, New York, Karn et al. 2009 Supplemental Ma- terial				PCE, TCE, 1,1,1-TCA, Cr(VI)			nZVI	
USA, Hamilton Landfill, New Jersey, Karn et al. 2009 Supplemental Ma- terial				1,1,-TCA, 1,1-DCA, 1,1- DCE, Pb, Ni			nZVI	
USA, Hamilton Township Trenton , New Jersey, US EPA 2016, Elliott and Zhang, ES&T (2001), Zhang et al (2006)	Proof of concept (2000) and field pilot3 (2003, 2007)	Middle potomac raritan magothy (mprm) aquifer. Shallow uncon- fined sandy aqui- fer (approx. 7 feet bgs to approx. 25 feet bgs).	GW	TCE, DCE, CT	400 - 3000 μg/L	2000: injection well delivery (2 phases) with recirculation 2003: direct push injection 2007: direct push injection	2000 Proof of concept – nZVI/Pd synthe- sized by Lehigh University 2003 Pilot – nZVI from PARS 2007 Pilot – nZVI from	2000: approx. 1.7 kg 2003: approx. 25 kg 2007: approx. 220 kg



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Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
							Lehigh Nano- tech LLC	
USA, Hampton, SC, Karn et al. 2009 Supplemental Material		Silty to fine sand from 25 - 45 feet bgs - then dense clay	GW	TCE, PCE	TCE 300 ppm		nZVI	
USA, Hanford Site Department of Energy, Washington State, US DOE 2009	Pilot	Sandy gravel to silty sandy gravel 3 to 9 m thick. Retrofit to an existing well based sodium dithionite prb	GW	Dissolved Cr (VI)	Circa 1000 μg/L	Injection into exist- ing well under slight pressure (1.8 m head of water).	nZVI (Toda RNIP-M2)	3710 kg
USA, Hill Air Force Base Operable Unit 2, Utah; US EPA 2016		Coarse-grained soils and overly- ing clay, silt, and fine sand	Soil and groundwater	TCE	TCE: 12 mg/kg (Max in soil); TCE: 14.3 mg/L (Max in groundwater)	Well "injection"	Stabilized Fe-Pd bimetallic NPs with CM.	5.2 kg
USA, Industrial site, Ironton, Ohio, US EPA 2016	Pilot	"Complex hydro- geology"	GW	TCE	TCE: 60 to 250 μg/L	"Injection", preferential flow along "seams" reported	Iron-Osorb <sup>TM</sup> . nZVI-silica hybrid NPs	
USA, Jacksonville, Florida, FRTR 2006; Gavaskar et al. 2005; US EPA 2016	Full	Silt / fine sands(0- 24ft) and dense clay (24-54ft). Source zone treatment	Soil and GW	TCE, TCA, DCE, vinyl chloride	Max soil concentrations: PCE: 4,360 μg/kg; TCE: 60,100 μg/kg; 1,1,1-TCA: 25,300 μg/kg. Max GW concentrations PCE: 210 μg/L; TCE: 26,000 μg/L; 1,1,1-TCA: 8,400 μg/L; cis-1,2-DCE: 6,700 μg/L	Direct push / closed loop recirculation	BNP	135 kg
USA, Kearny, New Jersey, Karn et al. 2009 Supple- mental Material				Cr(VI)			nZVI	
USA, Lakehurst, New Jersey, FRTR 2006; Ga- vaskar <i>et al</i> . 2005; US	Full	Two plumes tested: sand / gravel coastal	Soil and GW	PCE, TCE, TCA, c-DCE, vinyl chloride	900 μg/L	Direct push	BNP	1360 kg (2005) and 225 kg (2006)



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Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
EPA 2016		plain aquifer						
USA, Manufacturing Plant Middlesex County, New Jersey; US EPA 2016	Pilot	Made ground (fill) underlain by a moderately frac- tured shale bed- rock	Soil and groundwater	TCE and daughter compounds	~500 μg/L	Two separate "in- jection events"	nZVI	410 kg
USA, Mechanicsburg, PA, Karn et al. 2009 Supple- mental Material		Fractured rock	GW	TCE			nZVI with Pd	
USA, Newfields, New Jersey, Karn et al. 2009 Supplemental Material				TCE, cis-DCE, Cr(VI)			nZVI	
USA, North Slope, Pru- dhoe Bay, Alaska (aban- doned oil field) AK, US EPA 2016	Pilot	Organics over alluvial gravels	Soil	TCA, diesel fuel	Max TCA level 58,444 ug/Kg	Tested shallow physical mixing and pressurised injection at depth	BNP	
USA, Northern Alabama, (abandoned metal pro- cessing plant), US EPA 2016, Zhao and He 2007	Pilot	Heterogeneous relatively shallow semi-confined aquifer.	Soil and GW	PCE, TCE and PCB's	TCE MW-1 (1655 μg/L) MW-2 (2710 μg/L)	Gravity feed injection	CMC stabilised BNP	150 US gal- lons of 0.2 g/L Fe-Pd NP suspension
USA, Palo Alto, CA, US EPA 2016	Pilot	Ex situ testwork	GW	PCE, TCE, Freon	PCE (26,000 μg/L); TCE (70,000 μg/L);	Ex situ, field batch reactor	Starch- stabilized BNP (Fe/Pd)	
USA, Parris Island, Marine Corps Depot former dry cleaners, South Carolina, Krug et al. 2010; Su et al. 2012 & 2013; US EPA 2016	Pilot	Shallow unconfined aquifer permeable, fine to medium sand to a depth of 5.2mbg	Soil and GW	PCE, TCE, c-DCE, vinyl chloride	PCE (32,000 μg/L); TCE (10,000 μg/L); c-DCE (3,400 μg/L); Vinyl Chloride (710 μg/L) Max levels found	Direct push and pneumatic injection	Emulsified ZVI (EZVI) Emulsi- fied on site using nZVI	0.25 m3 EZVI over both injection plots (consisting of 10% nZVI, 38% corn oil, 1% surfactant and 51% tap water.
USA, Passaic, New Jersey Manufacturing Site, US EPA 2016, Zhang et al. 2006	Pilot	High permeability sands (to 21 ft bgs) with silt lens (21-26 feet bgs)	Soil and GW	TCE	Total VOC concentrations range 450 to 1,400 µg/L. Most of the contaminant mass was	The nZVI and emul- sified oil were emplaced using three injection points directly into	nZVI and emul- sified vegetable oil. ZVI com- bined with biostim	49 kg of nZVI slurry of unknown nZVI concentration and 55 kg of



Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
					bound in a low permeability silt unit.	the silt lens. Pneu- matic fracturing injections were used at two points and hydraulic injec- tion at the other		emulsified oil
USA, Patrick AFB, FL, US EPA 2016	Full	Groundwater; surficial aquifer; fine/ medium sandy silts	Soil and GW	TCE (and daughter contaminants)	150,000 μg/L (max level TCE found)	High pressure pneumatic injection	Emulsified ZVI (EZVI)	N/A
USA, Penn-Michigan, West Lafayette, Ohio, US EPA 2010; US EPA 2016	Pilot (three locations)	Sand and gravel aquifer with a high groundwater flow	GW	TCE	250 - 1,000 μg/L	Direct injection	nZVI-silica hybrid NPs (at one location with palladium) (Iron-Osorb <sup>TM</sup> )	94 kg material in total
USA, Pharmaceutical Facility, Research Trian- gle Park, NC, US EPA 2016	Pilot	Triassic basin sandstone interbedded with siltstone grading downwards into mudstones	GW in fracture bedrock	PCE, TCE, DCE, VC	The max concentration of VOCs was around 14,000 µg/L.	Injection wells	BNP	1.9 μg/L of BNP slurry The total NP mass injected was 11.2 kg.
USA, Goodyear, AZ, (Phase I) , US EPA 2016	Pilot	Alluvial deposits of western salt river valley. Impacted groundwater zone from 85-150 feet bgs. Consisting of upper alluvial unit, middle fine grained unit, lower conglomerate unit and	GW	TCE, PCE, perchlorate	Up to 39,000 μg/L total VOCs. Per- chlorate up to 150 ppb.	The field injection test consisted of the injection of 30 g/l nZVI slurry in water through one injection well.  Note the formation was "clogged" by injection <sup>29</sup>	nZVI	Approx. 10 kg

 $^{29}\ http://www.epa.gov/osp/presentations/drat/D-RAT\_Workshop\_Proceedings\_(Oct\_2-4,\_07).pdf$ 



Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
		groundwater at 85 ft						
USA, Phoenix, Goodyear, AZ, (Phase II) , US EPA 2009A, US EPA 2016	Pilot	As above	GW	TCE, PCE, perchlorate	Total contaminant concentration ranged from 3,500 to 11,000 µg/L	Injection wells	nZVI	10,400 litres of a 2.1 g/L nZVI slurry (total of 22 kg)
USA, Phoenix, Goodyear, AZ, (Phase III), Haley & Aldrich, Inc. 2011, US EPA 2016,	Pilot	As above	GW	TCE, PCE, perchlorate	Max baseline concentrations detected (μg/L): PCE: 3 TCE: 6,300 cis-1,2-DCE: 2	"Jet lance injection tool"	Stabilised nZVI (~90% nZVI; 5% polyacrylate, 5% SHMP <sup>30</sup> , 0.5% guar gum by mass)	~640 kg
USA, Picatinny Arsenal Superfund Site, New Jersey, US EPA 2009B; US EPA 2016	Pilot	"Organic rich soil"	GW	CCI4, TCE	CCl4: 250 μg/L; TCE: 87 μg/L	Injection via tempo- rary wells	nZVI (Ferragel)	~54 kg
USA, Ringwood, New Jersey, US EPA 2016	Full	N/a	GW	TCE, Bis(2- Ethylhexyl)phthalate, Benzo[a]Anthracene	TCE (1.1 μg/L); Bis (2-Ethylhexyl) phthalate (9.8 μg/L); Ben- zo[a]Anthracene (0.14 μg/L)	Push injection	Nano - Ox™	375 kg
USA, Rochester, NY (aircraft testing facili- ty)***	Pilot	Aquifer consisting of mostly sand and gravel, two plumes tested	Soil and GW	PCE, TCE, TCA, DCE, Vinyl Chloride	Maximum VOC concentration: 900 μg/L	Direct push	BNP	1.4 tonnes total
USA, Rochester, NY, (former manufacturing plant)***	Pilot	Glacial till over- burden lying above fractured sedimentary bedrock	GW in till and bedrock	TCE	Circa 1,000 μg/L	Direct push (ge- oprobe)	nZVI	10-20g/L nZVI slurry (total mass nZVI 60 kg)
USA, Rochester, NY,	Pilot	Glacial till over-	GW in bedrock	Methylene chloride,	Total contaminant	Gravity feed injec-	nZVI	10-20g/L nZVI

<sup>30</sup> Sodium hexametaphosphate



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



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



### Notes:

- \* NanoRem pilot site
- \*\* Additional information supplied by Aquatest A.S., Prague, Czech Republic
- \*\*\* Information from a web listing hosted by the University of Kentucky, USA:

www.ukrcee.org/Challenges/Documents/Groundwater/NP/Nano Projects IN PLACE.pdf, Accessed January 2016

\*\*\*\* July 2016, <a href="http://reground-project.eu">http://reground-project.eu</a>, and Rainer Meckensck personal communication (University of Essen, Reground co-ordinator)

\*\*\*\*\* Information supplied by Intrapore, Essen, Germany

# Additional information supplied by Geoplano, Portugal, November 2016

## Additional information supplied by VEGAS, Germany, November 2016

### Additional information supplied by NANO IRON, s.r.o. Czech Republic,, November 2016

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