

PROJECT FINAL REPORT

Grant Agreement number: FP7-309517

Project acronym: NANOREM

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

Funding Scheme: Collaborative Project (Large-scale integrating collaborative projects)

Period covered: from 01.02.2013 to 31.01.2017

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² The home page of the website should contain the generic European flag and the FP7 logo which are available in electronic format at the Europa website (logo of the European flag: http://europa.eu/abc/symbols/emblem/index_en.htm logo of the 7th FP: http://ec.europa.eu/research/fp7/index_en.cfm?pg=logos). The area of activity of the project should also be mentioned.

The present report is the Final Report of the NanoRem project to the EU. The only difference is that information addressing only the EU (administrative information) has been omitted in the present report.

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Executive Summary

Different nanoparticles (NPs) were developed within NanoRem. (i) nano-scale zero valent iron (nZVI) NANOFER 25S, NANOFER STAR (both thermal reduction of iron oxide) and FerMEG12 (milled), and (ii) non-zero valent iron (non ZVI) and composite NP. These include Nano-Goethite (iron oxide coated with humic substances), Carbo-Iron® (nZVI embedded in colloidal activated carbon, Trap-Ox Fe-zeolites (NPs trapping the contaminant by adsorption), Bionanomagnetite (NPs synthesized by bacteria), Barium ferrate (a ferrate(VI) salt) and NanoFerAl (alloy of iron and aluminium).

All were intensively tested and optimized with respect to mobility and reactivity in column experiments, the three nZVI particles, Carbo-Iron® and Nano-Goethite additionally in large scale experiments and at different field sites. In lab-scale studies, the migration potential of some types of NPs was optimised by using special additives. Other NPs types were shown to form stable suspensions as delivered by their producers.

A suite of standard and non-standard ecotoxicity tests, covering both terrestrial and aquatic organisms, did not lead to any hazard classification according to EU regulation for any of the tested particles. All particles, except the FerMEG12, can be considered non-toxic to organisms living in aquatic and terrestrial ecosystems. Effects on selected soil and water organisms were monitored for up to one year after NP injection at the pilot sites. In three out of four sites, no toxic effects were observed. A temporary increase in toxicity was observed right after NP injection at a one pilot site only.

Analytical methods and field measurement devices are needed to follow the fate of nanoparticles during and after injection, and to evaluate the efficiency of remediation. A variety of methods have been developed and tested at NanoRem field injection sites, ranging from *on site* sampling and measurement to *in situ* tracking using magnetic susceptibility.

Numerical tools for forecasting NP transport for groundwater remediation include a 1D modelling tool (MNM) for the assisted quantitative analysis of column tests and the preliminary design of pilot NP injections in simplified geometry (radial 1D simulations). Moreover, a full 3D transport module (MNM3D), for the simulation of particle injection in heterogeneous domains and prediction of NP fate and transport at the field scale is now available.

Large Scale Experiments (LSE) transferred the results from the lab scale (homogeneous condition) to technical scale (homogeneous or controlled heterogeneous condition). In field pilot test the LSE results were verified under 3D heterogeneous field conditions. NANOFER STAR, FerMEG12 and Carbo-Iron® led to a (partial) degradation of CHC sources. Nano-Goethite particles were shown to “polish” a remaining BTEX contamination (groundwater plume) after a primary source removal. In the field trials on the pilot sites, the results of the LSE were validated in terms of effectiveness of nanoremediation and with respect to the environmental fate of the NPs and their associated by-products. It could be shown that nanoremediation works if the appropriate particles are selected for the conditions present at the site.

Guidelines (“Guidelines for Application of Nanoremediation”) give a comprehensive overview on the implementation of nanoremediation. Their aim is to assist practitioners and consultants in considering nanoremediation as a possible remediation option for a given site and facilitate the communication between regulators and consultants. Recommendations for risk assessment of NP deployment and considerations of the sustainability and market prognoses for nanoremediation have been produced, as well as a broad exploitation strategy and risk-benefit appraisal. The project results are offered in the NanoRem Toolbox: www.nanorem.eu/toolbox.

1 Summary description of project context and objectives

Land contamination, affects large areas across the EU, potentially 2.5 million sites (EC/JRC 2014 Reference Report on the management of contaminated sites in Europe in 2011 <http://ies.jrc.ec.europa.eu/index.php>). The Roadmap to a Resource Efficient Europe (EC 2011) suggests that by 2050 there should be no net land take sealed by built development. This will only be possible with effective “recycling” of formerly used land, including contaminated land. With this in mind, a study by JRC (JRC 2007) indicates a major chance for nanotechnology in a rapidly growing worldwide remediation sector.

The use of nanoparticles (NP) for remediation soil and groundwater, called “nanoremediation” may offer a step-change in remediation capabilities based on lab scale findings, which show that the range of treatable contaminants and the speed by which they can be degraded or stabilised can be substantially increased compared to conventional *in-situ* remediation technologies for the saturated zone (aquifers).

Nanoremediation describes the *in-situ* use of NPs for treatment contaminated soil and groundwater. Depending on the use of different particles nanoremediation processes generally involve reduction, oxidation, sorption or their combination. NPs are usually defined as particles with one or more dimensions of less than 100nm. In practice, nanoremediation may apply to particles which are larger, for example composites with embedded NPs. NPs used in remediation are mostly metals or metal oxides, most frequently nanoscale zero valent 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 nanoparticles in the subsurface.

But so far, gaps in knowledge about the appropriate use of nanoparticles for the remediation of soil and/or groundwater contaminations, the limited availability (variety and amount) of different NPs for various contaminants, the perception of relatively high costs using NPs for remediation and last but not least the concerns about health and safety led to rather limited practical use of nanoremediation. This means, the “operating windows” of the technology “nanoremediation” were not clear and available. Moreover, concerns are raised by a number of national risk-benefit studies which were conducted in many countries. NanoRem has identified about 70 documented field projects worldwide.

See: <http://www.NanoRem.eu/Displaynews.aspx?ID=525>.

From the beginning all partners were convinced that practical, economic and exploitable nanotechnology for *in-situ* remediation can only be achieved in parallel with a holistic approach and a comprehensive understanding of the environmental risk-benefit balance for the use of NP market demand, overall sustainability and stakeholder perceptions. The development of this understanding was also a major part of the NanoRem project, and is fully in line with the integrated, safe and responsible approach to nanotechnology development advocated by the EU’s nanotechnology policy (EC 2009).

The aim of NanoRem was to facilitate the appropriate use of nanotechnology for contaminated land and brownfield remediation and management in Europe. The project was designed to unlock the potential of nanoremediation and so support both the appropriate use of nanotechnology in restoring land and aquifer 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. In other words, NanoRem’s aim was to demonstrate that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater. The project provided a direct link between SMEs (small and medium sized enterprises) on the production side and SMEs on the application side of groundwater remediation using NPs. Six project goals were identified at the project outset:

- (1) Identification of the most appropriate nanoremediation technological approaches to achieve a step change in practical remediation performance.
- (2) Development of lower cost production techniques and production at commercially relevant scales, also for large scale applications.
- (3) Determination of the mobility and migration potential of nanoparticles in the subsurface, and their potential to cause harm, focusing on the nanoparticle types which are most likely to be adopted into practical use in the EU.
- (4) Development of a comprehensive toolbox for field scale measurement and monitoring of nanoremediation performance and determination of the fate of nanoparticles in the subsurface, including analytical methods, field measurement devices, decision support and numerical tools.
- (5) Dissemination and dialogue with key stakeholder interests to ensure that research, development and demonstration meet end-user and regulatory requirements and information and knowledge is shared widely across the EU.
- (6) Provide applications at representative scales including field sites to validate cost, performance, and fate and transport findings.

To reach these ambition goals 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, 9 industry and service providers (7 SMEs) and one organisation with policy and regulatory interest. The consortium was co-ordinated by the VEGAS team (Research Facility for Subsurface Remediation) from the University of Stuttgart in Germany. The project was structured in three groups.

- The **Design and Production Group** comprised two work packages (WP2 & WP3) to facilitate the intense focus on different NPs and their corresponding production and application strengths.
- 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 & WP9).

2 Description of the main S&T results/foregrounds

The six project goals are listed below along with a detailed description of how these goals were met.

Goal (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 optimization 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.

✓ NPs available are listed in Table1. More information can be found within the Bulletin No 4 “A Guide to Nanoparticles for the Remediation of Contaminated Sites”.

nZVI particles:

There are generally 3 types of nZVI NP developed/optimized within the project: NANOFER 25S, NANOFER STAR, FerMEG12.

NANOFER 25S are surface modified NANOFER 25, basic nanoparticles produced by the thermal reduction of iron oxide in hydrogen atmosphere at high temperature by NANOIRON project partner. The particles consist of majority of zero-valent iron and their surface is modified by axilate to protect their rapid oxidation and aggregation. The final product is a water slurry consisting of 77% of water, 3% of axilate, 14-18% of ZVI, and 2-6% of magnetite. Mean particle size is 50-80 nm, specific surface area over 25 m².g⁻¹ and pH of the slurry above 11. The particles were intensively tested within the project in laboratory and at Spolchemie site (CZ). Availability of particles is in range of hundred kg/month.

NANOFER STAR NPs were developed and optimized within the project. NPs are also based on NANOFER 25 but their surface protection is arranged by a tiny oxide shell (about 4 nm). Basic advantages of NP are Surface stabilization, Transportability, Air-Stability and Reactivity. They consist of a slightly smaller portion of ZVI (80%) and higher of oxides (wustite, magnetite). Other characteristics are similar to NANOFER 25S. The particles are distributed as dry powder (4 times lighter compared to NANOFER 25S) and can be stored in the air for a few weeks (as minimum). In the project the NP were tested in laboratory and at Spolchemie (CZ), Barreiro (PT) and Nitrastur (ES) sites. Additional surface modification (e.g. by CMC) can be provided directly before the injection on-site. Availability of particles is in the range of hundred kg/month.

FerMEG12 (UVR-FIA GmbH) are ZVI NPs produced in a two-stage milling. The basic raw material ATOMET 57 (Rio Tinto, Quebec Metal Powders Ltd.) is in the first stage grinded dry up to a particles size of < 40 µm. The second stage uses wet grinding (< 100 nm) with mono ethylene glycol (MEG) as the grinding liquid and the addition of a surfactant. MEG (water dilutable and biodegradable polymer) was chosen to prevent NP oxidation during the milling process (compared to water) and to eliminate production of flaky-shaped nanostructures (compared to ethanol). The particles were intensively tested within the project in the laboratory and at the Solvay site (CH). Availability of particles is in the range of hundred kg/month.

Non-ZVI and composite particles:

Nano-Goethite is an iron oxide coated with humic substances, developed at the Helmholtz Zentrum München and the Universität Duisburg-Essen. Nano-Goethite is enhancing microbial iron reduction and can also be used for the adsorption of heavy metals. Nano-Goethite is supplied as an aqueous suspension which can be easily injected into aquifers, and thus can overcome the limitation of bulk iron oxides in remediation, which cannot be injected into soils. Nano-Goethite is field tested and commercially available from the University of Duisburg-Essen.

Carbo-Iron[®] is a zero-valent-iron-based composite where nanoiron structures are embedded in colloidal activated carbon (AC) (<1 µm) leading to highly mobile ZVI particles. Carbo-Iron[®] exhibits properties of AC and ZVI and thus is a reactive adsorber (trap&treat). It can reduce a broad range of halogenated hydrocarbons, metals and metalloids. The long-term support of microbial processes after its application in the field was observed. Carbo-Iron[®] has been licensed to two companies: a SME to produce the material (partner SciDre GmbH) and a SME specialized in nanoremediation (NanoRem spin-off Intrapore GmbH).

Trap-Ox Fe-zeolites offer a completely new mode of action for nanoremediation, i.e. trapping of contaminants by adsorption and catalyzed radical-driven oxidation of adsorbed contaminants by hydrogen peroxide. By this means, a unique combination of a sorption and oxidation barrier is achieved which is especially suited for efficient treatment of contaminant plumes and rebound effects. The strength of radical-driven oxidation is its wide application range with respect to treatable target contaminants. Thus, Trap-Ox Fe-zeolites substantially extend the range of practically treatable contaminants and provide the requested step-change.

Bionanomagnetite (BNM) is synthesized by Fe (III)-respiring subsurface bacteria in the presence of an electron donor such as lactate or acetate and an insoluble Fe(III) electron acceptor. BNM shows good reactivity and can remediate heavy metals e.g. Cr (VI), emerging contaminants including radionuclides and also a broad spectrum of redox active organic compounds such as perchloroethylene (PCE) and trichloroethylene (TCE). BNM is also amenable to surface modifications in order to extend its reactivity. For example, a unique nano heterocatalyst via reductive precipitation of Pd on the surface of BNM was generated.

Palladized bionanomagnetite (Pd-BNM) offers to extend the spectrum of treatable substances due to its ability to conduct catalytic hydrodechlorination. The particles can remediate a broad range of toxic contaminants also at high pH contaminated sediments and therefore extend the nanoremediation abilities. The mobility of BNM can be improved by using inexpensive and non-toxic stabilizers like guar gum and starch, while maintaining activity.

Barium ferrate (BaFeO₄) is a ferrate(VI) salt which exhibits a low solubility in water and could hence be used as a slow-release oxidant providing a depot-effect in the aquifer. However, chemical oxidation of e.g. BTEX contaminants is favoured under strong acidic conditions, which is of limited practical relevance. Therefore, recent tests have been focusing on the use of BaFeO₄ as an electron acceptor to improve the microbial degradation of 4-nitrotoluene (enhanced natural attenuation).

Magnesium (Mg⁰) and **aluminium** (Al⁰) particles show iron-like reaction potential, but have a much lower material density which is identified as one of the crucial properties for improved subsurface transport. Compared to pure Al and Mg particles pollutant degradation (tetrachloroethene) could be improved by using Al/Mg metal alloy particles as well as mechanically activated Al particles (by ball milling them together with Al₂O₃ or Si prior to use). However, particles show poor long-term reaction behaviour and are therefore not recommended for field application.

NanoFerAl (a composite of iron and aluminium) has been registered as petty patent since column tests performed under field-relevant conditions had indicated promising results with regard to the relationship between pollutant (tetrachloroethene) degradation and anaerobic corrosion.

Goal (2) Develop lower cost production techniques and production at commercial scales of nanoparticles.

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

✓ The production was upscaled successfully resulting in a commercially available and economically competitive technology.

nZVI particles:

Nano-scale zerovalent iron particles (nZVI) have been improved via an inorganic coating of Fe-oxide layer, new surface organic coating and other accompanying technologies (e.g. new type of on-site dispersion) 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 (transportation to the site, storable, lower transport cost) - see also Bulletin No 4 "A Guide to Nanoparticles for the Remediation of Contaminated Sites".

The activation process is necessary for NANO FER STAR to enable sufficient reactivity. The standard activation protocol is based on preparation of the 20% slurry which stays for about 48 hours at room temperature. During the activation process, the NANO FER STAR's surface washes and disintegrate and in this way Fe(0) is available for reaction. The NANO FER STAR surface can be modified with CMC after the activation process.

The production was upscaled successfully resulting in a commercially available and economically competitive technology. Currently, all of the products developed and tested in WP2 (nZVI particles) are available in large amounts from industrial production. The actual production capacity of air-stable powder NANO FER STAR and water slurry of NANO FER 25S of 200 kg/month can be easily increased by a multi-shift operation or by using multiple devices. Similarly, milled NP FerMEG12 (UVR-FIA GmbH) can be produced in hundred kg/monthly. Moreover, NANOIRON improved the on-site stabilization and dispersing process.

All NP were intensively studied at the laboratory, compared to each other and with other types of available NP. Significant attention was paid to NP mobility in different environments. Surface modification with organic compounds (e.g. CMC) can significantly improve their mobility especially in low permeable environment.

Non-ZVI and composite particles:

For the newly developed particles, which were chosen for up-scaled testing within NanoRem (Nano-Goethite and Carbo-Iron), the primary issue was ensuring an up-scaled production in order to allow field-scale operation. During further progress, efforts for optimization of the production in terms of sustainable and cheaper production were made. Depending on the development state of the other new particles, two further types were available at larger amounts. Based on the commercial availability of the precursor of Trap-Ox Fe-Zeolites, this particles type is available at industrial scale. For Bionanomagnetite, microbial synthesis was successfully up-scaled.

Nano-Goethite production process developed in the lab could be transferred to industrial scale. Suspensions are provided at cubic-meter containers (IBCs) with an iron concentration of 100 g/L and can be diluted on-site to a working concentration of 10 g/L. The production of Nano-Goethite is simple and fast. Due to electrosteric stabilization, the stock remains in suspension for at least 5 days, and stirring can be applied to maintain colloidal suspension stability for resuspension after storage.

Carbo-Iron[®]-production can be conducted via two different pathways. For the up-scaled industrial production the carbothermal pathway was chosen which generates an air-stable product which showed a low tendency to anaerobic corrosion in aqueous test systems. In cooperation with SciDre, the responsible project partner for the large-scale production, Carbo-Iron[®] production was brought to commercial size. The targeted particle quality with iron contents of 20...30 wt% has been achieved and production batches show reproducible quality. For the up-scaled experiments (large scale flume experiment at USTUTT and field test in Balassagyarmat, Hungary) the requested amount of Carbo-Iron has been produced. SciDre took licence for Carbo-Iron production and starts the optimization process in terms of sustainable and cheaper production.

Production of Trap-Ox Fe-zeolites is based on commercially available zeolite products from optimized large-scale industrial production which are used as raw material and modified by iron loading and stabilization steps in order to obtain catalytically active Trap-Ox Fe-zeolite particles. Suspension formulations were developed which provide suitability for low-pressure injections and optimal particle transport, at minimum consumption of additional chemicals and without stabilization agents. Large-scale production of ready-for-application Trap-Ox Fe-zeolite formulations was not conducted within NanoRem due to the fact, that the particles were not planned for field testing. Nevertheless, the convenience of developed preparation procedures and the existing collaboration between UFZ and a local zeolite producer form the basis for timely large-scale production on demand for future field testing and applications.

Biosynthesis of Bionanomagnetite (BNM) is scalable and the dimensions of the material can be fine-tuned by controlling biomass densities and other parameters during production, while the addition of dopants can be used to optimise magnetic properties, underpinning future commercial exploitation. BNM can also be synthesized from a range of synthetic Fe(III) mineral phases, including ferrihydrite and schwertmannite, while more recent NanoRem work has focused on identifying waste iron sources as suitable low cost substrates. Lifecycle assessments of this improved, sustainable process are underway. As part of this work, BNM nanoparticles from waste or environmental sources supplied by collaborating NanoRem partners.

Goal (3) Determine the mobility and migration potential of nanoparticles 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.

✓ Information on “*Stability, Mobility, Delivery and Fate of optimized NPs under Field Relevant Conditions*” can be found in the respective project deliverable.

Stability, mobility, delivery and fate under field relevant conditions was determined for

- (i) field tested and commercially available particles (NANOFER 25S, NANOFER STAR, FerMEG12, Carbo-Iron[®] and Nano-Goethite),

- (ii) premarket particles, Trap-Ox Fe-zeolites,
- (iii) “Lab to Premarket” particle Bionanomagnetite and (iv) “Lab” particles, Mg/Al particles.

Optimized mobility of **NANOFER 25S particles (NANO IRON s.r.o.)** is obtained by addition of carboxymethyl cellulose (CMC) into the particle suspension which has $c_{\text{particle}} \approx 10 \text{ g/L Fe(0)}$ and $c_{\text{CMC}} \leq 10 \text{ g/L}$ and exhibits a Newtonian fluid behaviour. Such optimized NANOFER 25S suspension is successfully delivered into VEGAS sand to ca. 0.5 m from the injection point. If NANOFER 25S particles are to be injected into a porous medium in an aqueous suspension, their subsurface mobility could be ca. 6 fold enhanced when the porous medium is precoated with 10 mg/L of Na humate (water soluble salt of humic acid derived from leonardite). Nevertheless, since such a mobility enhancement is limited to homogenous, well sorted, highly porous and permeable aquifers, hardly found at contaminated sites, the benefit is insufficient and therefore not recommended for field applications. In the contact with the groundwater from Spolchemie I field site, CZ, NANOFER 25S particles gradually oxidize to a green rust and then to ultra-small ferric oxides/oxyhydroxides. NANOFER 25S particles can partly degrade a PCE NAPL to ethene (dominating) and ethane, with 92% of the consumed Fe(0) anaerobically corroded within 56 days.

Mobility of **NANOFER STAR particles (NANO IRON s.r.o.)** in Dorsilit and VEGAS sand up to 1.3 m from the injection point is obtained by addition of 3% polyacrylic acid (PAA) into a particle suspension with $c_{\text{particle}} = 1 \text{ g/L}$. PAA provides a highly negative zeta potential of particles (ca. -60 mV) and a small particle size with $d_{50} \approx 1.6 \mu\text{m}$. While low amount of CMC (0.25%) added into the suspension (with $c_{\text{particle}} = 10 \text{ g/L}$) does not improve the mobility of NANOFER STAR particles, after adding a higher amount of CMC (10 g/L) NANOFER STAR particles can be delivered into VEGAS sand to ca. 0.6 m from the injection point. Since this distance is very similar to that for CMC-modified NANOFER 25S particle suspension, CMC-modified NANOFER STAR particle suspension is preferentially recommended for field applications, given that NANOFER STAR particles are air stable and therefore easy to handle. Though biofilm grown onto porous medium clearly interacts with NANOFER STAR particles, it does not influence their mobility. NANOFER STAR particles anaerobically degrade PCE to ethene (dominating) and ethane. After one month of the reaction with anaerobic contaminated groundwater from Spolchemie I field site, CZ, ca.12% of the initial Fe(0) within NANOFER STAR remain unconsumed, while the rest anaerobically corroded into a green rust. This result obtained in a batch reactor is in accordance with the field observation, where even more Fe(0), ca. 30%, remain unconsumed after a prolonged reaction time of 5 months.

Addition of 1 g/L agar agar into an aqueous suspension of **milled ZVI (FerMEG12, UVR-FIA GmbH)** with $c_{\text{particle}} = 1 \text{ g/L}$ increases the suspension viscosity and the negative zeta potential of particles (to ca. -33 mV) and lowers the particle sedimentation rate, without altering the average particle size ($d_{50} = 12 \mu\text{m}$). The mobility of agar agar-stabilized FerMEG12 particle suspension is significantly improved compared to that of unmodified suspension, with $L_{T 50} > 3 \text{ m}$ in Dorsilit and VEGAS sand, as well as in porous media from Spolchemie I, CZ and Solvay, CH field sites. Dehalogenation of TCE by pristine milled ZVI is somewhat faster for the Balassagyarmat, HU, compared to the Solvay, CH field site conditions, due to the higher SO_4^{2-} content for the former conditions. Major TCE degradation products (ethene and ethane) and the type of particle passivation (maghemite and magnetite) after 3.5 month of reaction appear not to be site-specific. Presence of agar agar reduces the TCE dechlorination rate by an order of magnitude compared to that of pristine particles. This is, however, not necessarily a drawback since the lower initial corrosion rate and consequent extended lifetime of agar-agar stabilized FerMEG12 particles may in some cases be regarded

as an advantage over the use of nZVI particles. The final products of the PCE DNAPL degradation with FerMEG12 particles are ethene and ethane, with the anaerobic corrosion accounting for 66% of the overall Fe(0) consumption.

CMC effectively stabilizes **Carbo-Iron[®] (SciDre GmbH, UFZ Leipzig)** (when $c_{\text{particle}} \leq 30$ g/L). Long-term suspension stability is achieved with $c_{\text{CMC}} = 0.1\text{--}0.2 \times c_{\text{particle}}$, allowing for longer particle travel distances during the injection (“plume treatment mode”, $L_{T\ 50} \approx 2$ m). When $c_{\text{CMC}} = 0.05\text{--}0.09 \times c_{\text{particle}}$ a “metastable” suspension is formed, suitable for a shorter injection time and a particle emplacement closer to the injection port (“source treatment mode”, $L_{T\ 50} < 1$ m). CMC-stabilized Carbo-Iron[®] is mobile in Dorsilit and VEGAS sand and in the porous medium from the Balassagyarmat field site, HU, with the max travel distance ($L_{T\ 99.9}$) > 4.5 m estimated for the latter. The optimal conditions for a source treatment imply a metastable Carbo-Iron[®] suspension and the 3-fold intermittent injection, as confirmed in the LSF experiment, where a near-source emplacement of the large proportion of particles mass was achieved. Carbo-Iron[®] particles combine sorption and degradation of organic contaminants. There is no significant difference between the reactivity of Carbo-Iron[®] in groundwater and synthetic water. Reaction rate constants with dissolved PCE (“plume treatment” simulation) derived from batch- and column reactors are almost identical. In a PCE “source treatment” simulation the PCE conversion amounts to ca. 72% under Fe-limited conditions within 75 days. Compared to a particle-free column, the PCE discharge from a Carbo-Iron[®]-loaded column is lower for several orders of magnitude. Transformation of Fe(0) within Carbo-Iron[®] e.g. into magnetite is comparable to that of nZVI.

Nano-Goethite (University of Duisburg-Essen) stabilized with a humic acid coating is stable in aqueous suspension. Such stabilized particles are mobile in VEGAS sand, with $L_{T\ 50}$ of ca. 1 m. Nano-Goethite can be delivered into porous medium from Spolchemie II, CZ field site to ca. 2.5 m from the injection point. Mobility of renegade particles is unlikely, since particles lose 75% of their stabilizing humic acid coating while moving through the porous medium. Nano-Goethite assists biodegradation of both benzoate and toluene, with a higher Fe(II) reduction and degradation rate for benzoate. A slow Nano-Goethite-assisted benzoate reduction is observed in flow-through column reactor, with benzoate being degraded in the presence of electron acceptors other than Nano-Goethite. Nano-Goethite does not change its elemental composition upon long-term (1 year) aging, while the size and crystallinity of the particles increases over time.

Slightly alkaline suspensions (pH 8.0–8.5) of both types of **Trap-Ox Fe-zeolites (UFZ Leipzig)**, Trap-Ox Fe-BEA35 and Trap-Ox Fe-MFI120, are stable over several hours even at high particle concentrations (10 g/L) in a very hard water (F.I.h) in the absence of stabilizers. Such suspensions of Trap-Ox Fe-zeolites are mobile in standardized Dorsilit and VEGAS sand at moderate flow velocity of 10 m/d at a high particle concentration (10 g/L). It is therefore anticipated that Trap-Ox Fe-zeolites can be injected into the subsurface by simple injection techniques such as direct push or well injection without suspension stabilizers. Trap-Ox Fe-BEA35 actively adsorbs and catalytically (with H_2O_2) oxidizes MTBE even beyond 4 adsorption/regeneration cycles and remains active for at least 2 months. Aging of Trap-Ox Fe-BEA35 in very hard water containing NOM for 38 days altered the uptake of divalent cations, but the Fe^{3+} content and specific surface area of particles remain nearly unchanged.

Bionanomagnetite (University of Manchester) is not stable in aqueous suspension. Suspension stability of bionanomagnetite is significantly improved by addition of various stabilizers, with humic acid Na salt (0.5 g/L) being the most effective one. It provides a highly negative zeta potential of particles (-35 mV) and lowers the particle size in the suspension (to $d_{50} = 2.7$ μm). Unlike pristine bionanomagnetite, the stabilized particles (with 0.5 or 1 g/L humic acid Na salt) are mobile under the injection condition in Dorsilit sand, with a $L_{T\ 50}$ of 2.4 m and a $L_{T\ 99.9} > 4$ m, indicating that this stabilizer should be considered for an eventual

field injection of bionanomagnetite. Under the groundwater flow condition no mobilization of bionanomagnetite is expected, as shown in VEGAS sand. Suspension stabilizers lessen the reactivity of bionanomagnetite with respect to Cr(VI), but the reactivity can be recovered by particles functionalization with Pd. Palladized bionanomagnetite (both in stabilized and pure aqueous suspensions) is able to rapidly remove >99% and >90% of initial Cr(VI), respectively and to completely dehalogenate PCE to ethane with a $k_{\text{obs}} = 4.4 \times 10^{-3}$ 1/h.

Mg/Al particles (VEGAS, University of Stuttgart) exhibit a poor long-term reactivity with respect to PCE, indicating that these particles are not beneficial for field application, and therefore their performance in terms of stability, mobility and deliverability was not investigated further.

✓ Results from the large scale experiments are available in the project deliverable “*Final Report on Three Large-Scale Experiments and Generalized Guideline for Application*”.

The goals of the Large Scale Experiments (LSE) were to transfer the results of the 1 and 2D lab scale tests (homogeneous condition) on particle performance to 3D large scale experiments (homogeneous or controlled heterogeneous condition) and to apply the LSE techniques and results to improve field 3D injections (heterogeneous condition). Specific goals of the LSE were to design, set-up and test optimal injection systems for different NPs, and to make a standard of NP transport/deposition of 3D injection and NP reactivity to contaminant treatment as well as longevity. To achieve these goals, three LSEs were set-up and five injections were conducted using four different particle types. All injection boundary conditions were determined based on the best results of lab scale experiments:

Large scale flume experiments to chemically reduce a CHC source:

Three dimensional large scale injection tests were performed in an artificial homogeneous sandy aquifer ($K \sim 4 \times 10^{-4}$ m/s) in a large flume ($L \times W \times H = 6 \times 1 \times 3$ m) with a saturated thickness of 1.7 m and a corresponding unsaturated zone of 1.3 m. Groundwater flow was regulated by constant head boundaries to keep a seepage velocity of $v = 2.31 \times 10^{-6}$ m/s = 0.2 m/d. The aquifer was contaminated with 2 kg of free phase of perchloroethene (PCE), establishing a contaminant source zone of approx. 0.65 m³ in the middle of the aquifer as residual phase (PCE saturation approx. 0.6 %). In the middle of the source zone, a colloidal suspension of NPs was injected to achieve 0.5 m radius of transport (ROT) over a depth of 1 m (vertical extension of PCE source). At least 2.6 kg of nZVI (stoichiometrically required to reduce the PCE source) were deposited in this zone. For all injections in the LSF tests, injection pressure was higher than applicable overburden pressure (0.5 bar) and indicated that some limited soil fracturing might have occurred.

LSF1 (nZVIs): suspensions of NANOFER 25s (1 m³ at $c_{\text{NP}}=10$ g/L) and NANOFER STAR (1 m³ at $c_{\text{NP}}=10$ g/L with stabilizer $c_{\text{CMC}} = 5$ g/L) were injected intermittently at injection rates of 0.1 m³/h and 0.5 m³/h respectively using a direct push injection rod. NANOFER 25s NP were transported only within a radius of 0.15 m around the injection point due to the low injection rate and the absence of stabilizer. Therefore, very little PCE degradation was observed. Based on the chloride (degradation product) production, the longevity of 25s particles was determined to be approx. 300 days. The total degraded mass of PCE for this period was obtained as 18 g. In contrast, NANOFER STAR was transported more than 0.4 m in all direction and thus extended over the whole contaminant source volume. After the injection a significant decrease of PCE and a high production of chloride were observed indicating a high PCE degradation; even after 100 days of the injection chloride production continues. While the degradation is still in progress, the total mass of PCE degraded during 90 days was determined to be 190 g. The particle transport and reactivity on PCE degradation was much improved for NANOFER STAR particles, due to a higher injection rate and the

usage of stabilizer. A similar improvement of particle performance with NANO FER STAR particles was also observed in the field application in Usti nad Labem, CZ.

LSF2: In the first injection a volume of 0.7 m³ of Carbo-Iron® suspension at cNP=20 g/L (cnZVI= ~5 g/L) with stabilizer cCMC = 2 g/L was injected via an injection well at a rate of 0.2 m³/h. During a second injection a volume of 0.25 m³ of suspension at cNP=8 g/L (cnZVI ~ 2 g/L) with cCMC = 0.8 g/L was injected via a direct push rod at 0.25 m³/h. For both injections, similar particle transport behavior was observed: 1) particles were transported preferentially upward and downstream, 2) transport distance of the nZVI NP was much less than that of activated carbon particles (~0.3 m and > 2 m respectively), 3) some amount of activated carbon was mobile until 60 days after the injection. This behavior resulted in a partial covering of the contaminant source zone but concurrently established a huge adsorptive zone at downstream. Particle longevity was determined around 100 days, during this time period degraded PCE and adsorbed PCE were obtained as 120 g and 200 g respectively. Due to adsorption PCE mass flux in the outlet was kept around 2.5 g/L, which corresponds to approx. 50 % of initial PCE mass flux.

Large scale container experiment to microbially degrade a BTEX plume:

A field scale 3D injection test was performed in an artificial heterogeneous sandy aquifer, which consists of randomly distributed high and low permeability zones ($K \sim 4 \times 10^{-3}$ m/s and $4 \sim \times 10^{-4}$ m/s respectively) in the large VEGAS container (9 x 6 x 4.5 m). The aquifer thickness was 3.7 m with a corresponding unsaturated zone of 0.8 m. Ground water flow was controlled by constant head boundaries resulting in an average seepage velocity of $v = 4.86 \times 10^{-6}$ m/s = 0.4 m/d. The aquifer was contaminated by a toluene plume ($c_{\text{tolu}} = 60$ mg/L) located at the center line of aquifer. The plume had a cross sectional area of 4 m² perpendicular to the direction of flow and was located just below the water table. In the middle of the plume, a colloidal suspension of Goethite NPs was injected to achieve 1.5 m ROT throughout the depth of the contaminant plume (2 m). Approx. 120 kg of NPs were thus deposited to degrade a toluene mass flux of 35 g/L. The application was conducted by gravity injection at 0.7 m³/h via an injection well (3" of ID). NPs were transported over 1.5 m with sufficient concentration to fully cover the depth of the plume (more than 2m). At lower levels no NPs were observed during the injection but after 24 h a relatively high NP concentration was observed (4.3m of maximum transport distance from the injection well). All NPs could be placed in the vicinity of the injection zone. The analytical results indicated some degradation but, unfortunately, were insufficient for a quantitative proof of biodegradation rate of toluene. The findings of the LSC led to a change of the field application in Usti nad Labem. Now the goal was no longer to attack a plume but to polish after a primary remediation and, thus, the injection concentration in the field was reduced.

Conclusion: NPs mobility and reactivity for 3D injection were well investigated. Results of the LSEs were transferred to the field sites and the outcomes there showed agreement with the large scale experiments.

- ✓ Indications regarding the usefulness of NPs are given in the Site bulletins.
- ✓ The environmental impact of the NPs used in the project was investigated.

This is important to ensure that the technology is environmentally safe and that the environmental and societal benefits of removing hazardous pollutants using nanoremediation are not outweighed by the potential hazardous effects of nanoparticles. The project deliverable “*Dose response relationships, Matrix effects on Ecotox*” compiles the results from ecotoxicity tests on a range of nanomaterials developed during the project, in order to contribute to the hazard assessment required under REACH. A suite of standard and non-standard ecotoxicity tests were carried out using aqueous suspensions of nanomaterials in the absence of

environmental matrices (i.e. soil-free, DOC-free). In the event that nanomaterials exhibited toxicity, we also determined whether the presence of organic matter affected the outcome of ecotoxicity tests (matrix effects on ecotox). The low toxicities found in the standard organisms do not lead to any hazard classification according to EU regulation for any of the tested particles and the results indicate that the particles, except the FerMEG12 particles, can be considered non-toxic. In the absence of intrinsic toxicity of most of the particles, the second part of the deliverable was limited to tests on FerMEG12 particles. The presence of humic acid did not change the outcome of the ecotox tests, contrary to what was expected.

✓ Furthermore, effects on selected soil and water organisms were monitored for up to one year after NP treatments of the pilot sites (both large-scale experiments and field sites).

Tests included time-course sampling to assess effects of ageing, and account for the (assumed) reduction in toxicity caused by nanoparticles transformation and adsorption to solid matrices. Data from ecotoxicity tests with nanoparticle-treated groundwater and soil were non-existent prior to NanoRem, and therefore represent a strong innovative aspect of the present project. The information provided in the project deliverable “*Influence of Transformation and Transport on Ecotox*” is essential to furthering a robust and empirically based understanding of the ecotox aspects of nZVI and other NPs in the environment, and how this changes over time. Despite differences amongst field sites, the sampling strategies were harmonized, both with regards to sampling locations and sampling frequency. Sampling wells were all chosen within the contaminated area, with one well located upstream from the NP injection point, and three wells downstream from the NP injection point. Regarding sampling frequency, several time points were chosen to cover the situation prior to NP injection (as a reference point with maximum toxicity expected), and after NP injection. The whole sample toxicity was measured and no fractionation was carried out, implying that the impact of groundwater quality as well as contaminant mixtures was assessed directly. This whole sample toxicity testing approach enabled identification of the most problematic samples as well as the relative development in toxicity (or reduction) over time, as a function of the remediation action initiated. In three out of four sites investigated, no toxic effects were observed at concentrations applied in the field studies. A transient increase in toxicity was observed right after NP injection at the Solvay site.

As bacteria are likely to be among the few organisms that will ever come into contact with reactive nanoparticles used for remediation, nanoparticle-microbial interactions during and after remediation were also studied. The composition of microbial communities in soils and aquifers was characterized, prior to, during and after NP application. In addition, metabolic capacities and rates were monitored to assess to what extent and with what delay microbial functions were affected and restored, if negatively impacted. More specifically, the presence of dehalogenation genes, organohalide-respiring bacteria, and enzymes involved in the degradation of organic contaminants (organochlorides TCE, PCE and cDCE) was monitored.

- *Spolchemie I* – The composition of microbial communities appeared to be minimally affected by the addition of NP. The injection of NANO FER STAR caused a transient negative effect on selected organohalide respiring bacteria and dehalogenation genes, but the groundwater was colonized again with monitored bacteria within approximately one month.
- *Spolchemie II* – Most wells experienced more significant shifts in microbial community composition following NP addition, for example the increase in the proportion of bacteria able to oxidize toluene and ethylbenzene. After inducing a transient decrease in the proportion of bacteria respiring organohalide or involved in BTEX degradation pathways,

Nano-Goethite injection led to the increase in bacteria possessing enzymes involved in the aerobic and anaerobic degradation of BTEX.

- *Solvay* – The injection of FerMEG12 had a positive effect on indigenous microbial communities, especially on organohalide-respiring bacteria.
- *Balassagyarmat* – The injection of Carbo-Iron[®] resulted in the increase in vinyl chloride reductase genes and organohalide-respiring bacteria. In addition, the total bacterial biomass increased in most of the monitored wells after NP injection, indicating that other bacterial groups (such as sulfate or nitrate-reducers) were supported by the newly established conditions.

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

The bulletins and tools described below can be downloaded from www.nanorem.eu.

- ✓ *Appropriate Use of Nanoremediation* (Bulletin No 2). The aim of this short position paper is 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.
- ✓ The *Generalised Guideline for Application of Nanoremediation* (Bulletin No 3 and Tool) gives a comprehensive overview on the implementation of nanoremediation. The aim of this guideline is to assist practitioners and consultants in screening nanoremediation as a possible remediation option for a given site and facilitate the communication between regulators and consultants.

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.

The included pre-screening tool matches commercially available nanoparticles (NP) and their operating windows (OW) with the requirements of a site as delineated in the conceptual site model (CSM) to propose one type of commercially available NP to remediate a given contaminant type at a given site. Prior to decide on a NP it is strongly recommended to site specific verify the claims of the producer experimentally. Once a reactivity test of the suspension for a given contaminant proved successful mobility (transport) experiments need to be conducted. 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.

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.

The implementation of a NP-based remediation technology at a contaminated site usually requires the support of some form of quantitative modelling, to translate the results from

laboratory column tests to estimated performance in the field. The guideline describes “MNM” (Micro- and Nano-particles transport, filtration and clogging Model Suite) for the evaluation of laboratory experiments and “MNM3D” (Micro- and Nano-particles transport Model in 3D geometries) for a full 3D transport simulation of particle injection in heterogeneous domains, and for the prediction of NP fate and transport at the field scale.

Pilot field tests are designed to define specific conditions for the design and implementation of operational applications of nanoparticles 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.

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 nanoparticles. 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 necessary for a successful NP deployment comprise both above ground and below ground installations. For the design of the above ground installations and especially during operation worker’s health and safety issues (Material Safety Data Sheets!) need to have top priority next to technical and economical questions.

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. The criteria for the decision on the success of a nanoremediation have to be defined beforehand and a monitoring program chosen accordingly. The monitoring results will be compared to the status defined during the pre-injection phase.

In order to implement nanoremediation at different locations within the EU (and beyond) local regulatory requirements have to be fulfilled. Frequently or likely asked questions posed by regulators are listed to facilitate communication between consultant and regulator.

As for the application of any other remediation technology, there is no “generic” cost calculation for nanoremediation, rather the total cost will be a function of many parameters. The main cost drivers are listed in the guideline.

✓ Numerical tools for *Forecasting NP Transport for Soil Remediation* (Bulletin No 6) include a 1D modelling tool (MNM)³ for the assisted quantitative analysis of laboratory-scale column tests and the preliminary design of pilot NP injections in simplified geometry (radial 1D simulations), and a full 3D transport module (MNM3D)^{4,5} for the simulation of particle injection (in one or more injection points) in heterogeneous domains and prediction of NP fate and transport at the field scale. The Bulletin gives details on how the tools can support the various stages of the design, implementation and evaluation of a nanoremediation.

Nanoparticles (NPs) used in groundwater remediation are typically delivered to the contaminated area dispersed in water-based slurries, and injected through wells, trenches or using appropriate tools such as direct push equipment. The design of such a field-scale

³ Micro- and Nano-particles transport, filtration and clogging Model Suite, www.polito.it/groundwater/software

⁴ Micro and Nanoparticle transport Model in 3D geometries

⁵ Bianco, C., Tosco, T., Sethi, R. (2016) A 3-dimensional micro- and nanoparticle transport and filtration model (MNM3D) applied to the migration of carbon-based nanomaterials in porous media. *Journal of Contaminant Hydrology*, 193, pp. 10-20. DOI: 10.1016/j.jconhyd.2016.08.006

injection of engineered NP suspensions for the remediation of a polluted site requires a reliable estimation of the particle distribution after injection. In addition, regulators will require information on the long-term mobility of the injected particles that may remain in the subsurface after reaction with the contaminant. Numerical models can help to answer the many questions that arise when designing a nanoremediation. Numerical models to simulate the transport of dissolved contaminants in aquifer systems are widely available. However, well established field-scale NP transport models are still lacking, and the definition of proper approaches and numerical tools is a current research topic.

We developed modelling tools that are intended to be used in the design of a nanoremediation and in the interpretation of the outcomes. This applies to both preliminary laboratory tests as to field-scale deployment, with the specific aims of (i) aiding in the design and interpretation of laboratory tests, and (ii) enabling prediction of NP fate and transport and effectiveness at the field scale. The main advantages of using modelling in nanoremediation design lay in complementing and thereby reducing otherwise too extensive laboratory testing, in the ability to explore in advance different options for field application, in guiding the design and execution of the required monitoring, and in testing assumptions.

Research focussed on the one hand at pore scale models to increase our understanding of fundamental NP behaviour; on the other hand we developed macro-scale tools which can be used to forecast NP behaviour during and after the injection (Figure 1).

The pore scale modelling built on previous research by Raoof et al⁶ and Seetha et al⁷. Results from model simulations at the scale of a single pore⁷ were implemented in the pore network model NanoPNM that was based on the pore network developed by Raoof⁶.

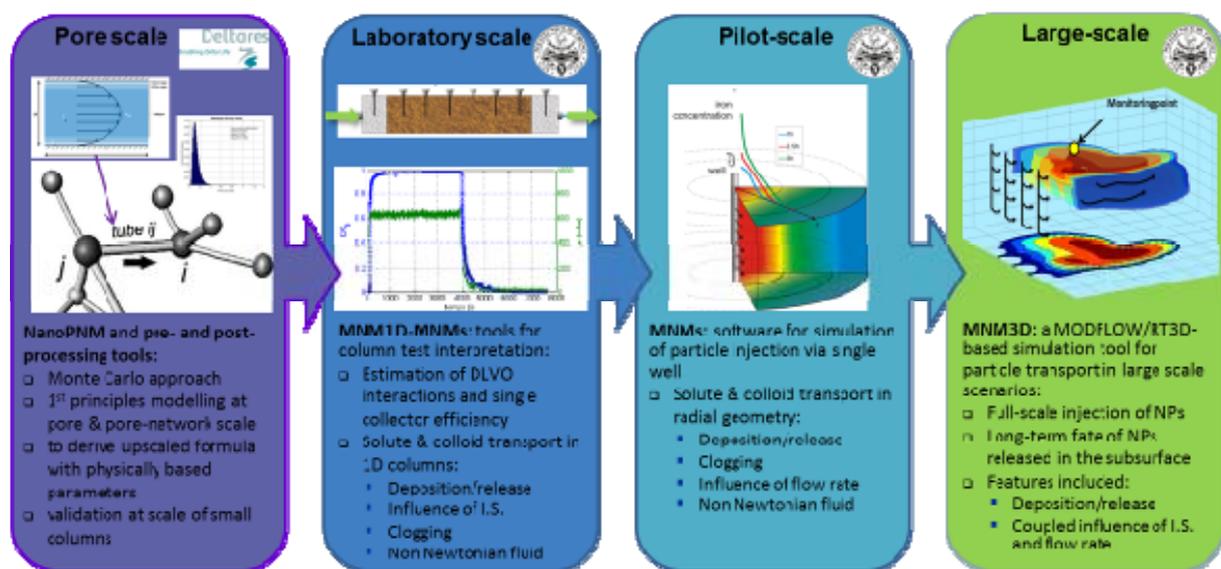


Figure 1: Numerical tools available at the moment in NanoRem for simulation of nanoparticles transport at different scales (Source: Stichting Deltares / Politecnico di Torino)

⁶ Raoof, A. and S.M. Hassanizadeh (2010). A new method for generating pore-network models of porous media. *Transport in porous media* **81**(3): 391-407; Raoof, A., H.M. Nick, S.M. Hassanizadeh and C.J. Spiers (2013). PoreFlow: A complex pore-network model for simulation of reactive transport in variably saturated porous media. *Computers & Geosciences* **61**: 160-174.

⁷ Seetha, N., Kumar, M.M., Hassanizadeh, S.M. and Raoof, A. (2014). Virus-sized colloid transport in a single pore: Model development and sensitivity analysis. *Journal of contaminant hydrology* **164**: 163-180; Seetha, N., Hassanizadeh, S.M., Kumar, M.M. and Raoof, A. (2015). Correlation equations for average deposition rate coefficients of nanoparticles in a cylindrical pore. *Water Resources Research* **51**(10): 8034-8059.

A first conclusion from the pore scale modelling is that porosity and grain size alone will always be incomplete predictors for hydraulic conductivity and dispersivity, as the grain packing plays an independent role. This also implies that hydraulic conductivity and dispersivity from packed columns may differ between different columns as well as from the actual field values. Ideally, laboratory tests should be performed on undisturbed columns, but at least a NP breakthrough test should always be combined with a tracer test for the exact same column. Representativeness of laboratory columns for the field situation needs to be taken into account when upscaling to the field scale.

A second conclusion is that relationships used for pore-scale attachment and detachment - as functions of pH, Ionic Strength, NP and porous medium zeta potentials, NP and pore sizes, and flow velocity -, obtained by solving particle transport equations in a cylindrical pore with smooth surfaces and uniform surface properties, predict less attachment at the macro scale than observed in laboratory experiments. Hence, these commonly used variables are not enough to effectively predict colloid retention under environmental conditions. Other possible factors including NP interaction, grain surface roughness and surface chemical heterogeneity can contribute to the enhanced NP adsorption. The evaluation of these factors should be explored using microscopic and columns scale experiments under controlled conditions.

NP transport in porous media (PM) at the macro scale (i.e. the scale of interest for field applications of NP-based remediation) is usually described by a modified advection-dispersion equation that takes into account the mass exchanges between liquid and solid phase, due to physical and physico-chemical interactions. Attachment/detachment are strongly influenced by both operative and natural conditions, e.g. flow velocity, NP and PM size distributions and surface properties, chemical properties of the fluid, such as ionic strength (IS) and pH, and viscosity of the injected suspension. A NP transport simulation tool effective in assisting the design of a field-scale NP application has to take into account these effects in a quantitative and coupled way⁸.

MNMs³ has been developed to assist the analysis of laboratory scale column transport tests (1D) and for a preliminary design of field-scale injection (in a simplified radial symmetric geometry). MNMs is a complete tool for the simulation of particle transport in 1D saturated porous media and for the interpretation of laboratory column transport tests. MNMs provides tools to simulate 1) interaction energy profiles following the DLVO (Derjaguin and Landau, Verwey and Overbeek) and Extended-DLVO approach; 2) single collector attachment efficiency η_0 ; 3) transport of dissolved species under equilibrium sorption and first order degradation; 4) NP transport under transient IS and in the presence of Non-Newtonian carrier fluids and clogging phenomena; and 5) NP pilot-scale injection through a single well (radial simulation tool) for non-Newtonian NP slurries, with estimate of the eventual clogging.

MNM3D⁴ has been developed for a 3D simulation of particle injection, transport and fate at the field scale in heterogeneous domains. MNM3D was developed coupling the transport solver RT3D with MNMs5 thus obtaining a modelling tool for NP transport in 3D. MNM3D solves the NP transport equations accounting for dependency of the attachment and detachment kinetics on the groundwater Ionic Strength and velocity.

MNMs is freely available for download on Polito's website³. MNM3D can be easily implemented in many open-source and commercial graphical interfaces which already support RT3D. At the moment, the implementation in Visual Modflow (Waterloo Hydrogeologic) is under evaluation with the developers of the software. Figure 2 shows an example of

⁸ Tosco, T., Gastone, F. and Sethi, R. (2014) Guar gum solutions for improved delivery of iron particles in porous media (Part 2): Iron transport tests and modeling in radial geometry. *Journal of Contaminant Hydrology* 166(0), 34-51.

application of MNM3D to the simulation of the injection of Carbo-Iron® (SciDre GmbH, UFZ Leipzig) in a flume experiment performed at VEGAS.

NanoRem DL7.2 provides more detailed examples of applications of the two models to the design of a nanoremediation.

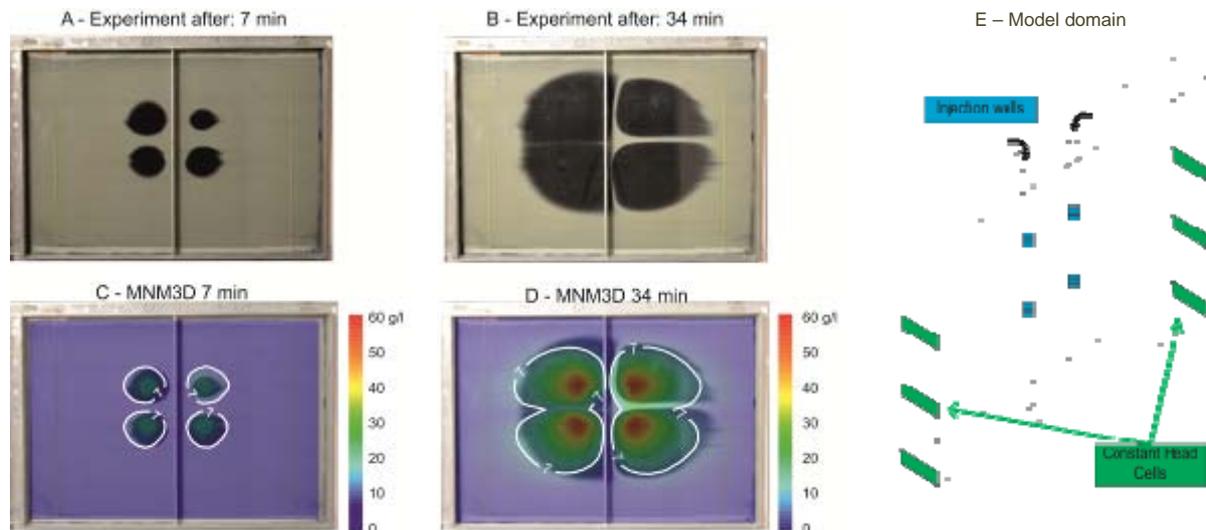


Figure 2: Carbo-Iron® injection (front view) after 7 (A) and 34 (B) mins from the beginning of NP injection: visual comparison of experimental (black) and simulated (colored plume) results of nanoparticle transport (C-D) and model domain (E).

- ✓ Analytical methods, field measurement devices (Bulletin No 5 “Monitoring Methods”) are needed to follow the fate of nanoparticles during and after injection, and to evaluate the efficiency of remediation. A variety of methods have been developed and tested at NanoRem field injections, ranging from *on site* sampling and measurement to *in situ* tracking using magnetic susceptibility.

Monitoring the behaviour of engineered NPs requires their detection in environmental media, and isolation from natural background colloidal material. This represents a potential challenge for Fe-based NPs in remediation, because of relatively high levels of naturally occurring iron and colloids. Although a good deal of experience on monitoring is available from laboratory studies, these tend to use rather high concentrations of NP, in simple media, and can rely on relatively straightforward methods for NP measurement and characterisation. Measurement during field applications is more challenging, primarily due to more complex and heterogeneous media. Extensive field studies during NanoRem have enabled the development, testing and evaluation of different methods for Fe-based NPs, and provided insight into challenges, advantages and factors influencing detection limits for field measurements.

The methods tested and developed during NanoRem range from measurement of simple chemical parameters to high-end sophisticated techniques, and cover applications in large-scale tank experiments and field applications (Table 1). Analytical development work was organised around the following areas:

1. **Development and optimisation of monitoring and tracing tools.** Techniques based on the measurement of the ferro-magnetic properties (susceptibility) of Fe for monitoring Fe NPs in the field were optimised and new methods were developed for detection of Carbo-Iron® and Fe-zeolites. In addition, the feasibility and applicability of isotope and trace

metal (rare earth element - REE) techniques for laboratory and field detection of Fe-based NPs were determined.

2. **Laboratory and field tests of the methods.** A series of tests were conducted on a number of different techniques for field monitoring, including routine methods of NP characterisation as well as the magnetic susceptibility and REE methods developed specifically for Fe-based NPs during NanoRem. Work included evaluation of the methods' applicability for Fe-based NPs and *in situ* application, assessment of detection limits and potential for routine application. The results have been consolidated into the NanoRem monitoring toolbox.
3. **Development of protocols.** Protocols were produced for on-site measurements and *in situ* characterisation of natural and engineered NPs. These include application of modern high performance analytics for samples collected in the field and analysed in the laboratory.

The applicability of the various methods depends on the phase of remediation and the question to be addressed, since the different phases have different analytical requirements and issues. The most successful methods are summarised briefly below.

Monitoring of NP dispersion during injection phase

Results from NanoRem field measurements during the injection of nZVI (NANOFER 25S, NANOFER STAR), Nano-Goethite and milled Fe (FerMEG12) show that the detection of NP suspension loads is relatively straightforward, and can be easily carried out at the site. The methods include a combination of on-site sampling and analysis of suspensions (turbidity, conductivity, redox, temperature and Fe content), or *in situ* methods such as magnetic susceptibility, redox (ORP) and H₂ measurements. The detection limits range from sub mg/L for total Fe to ca 500 mg/L for magnetic susceptibility, and are sufficient to follow the dispersion of injection liquids and NPs during injection. Given the relatively low toxicity of Fe-based NPs to organisms, these detection limits should be sufficient to assess potential ecological impacts, both within and outside the injection area. Of the various methods tested, magnetic susceptibility, turbidity and total Fe measurements are most appropriate for monitoring during injection. Both turbidity and total Fe rely on at site sampling followed by measurement, but portable detectors are available to allow rapid on site analysis.

Table 1: Overview of At Site and *In Situ* Monitoring Methods tested in NanoRem.

Type of Method	Examples	Applications	Comments
<i>In situ</i> measurement and characterisation	Ferro-magnetic methods; redox measurement; H ₂ production	Particle concentration, particle reactivity	High data resolution over time and space is possible
On site applications: sampling combined with on site or laboratory measurement techniques	Turbidity, Fe spectrometry, ultrafiltration; stable isotope and REE ratios; Mössbauer, Temperature programmed oxidation (TPO)	Particle size and concentration, Fe concentration	Turbidity, spectrometry and ultrafiltration can be carried out on site. Mossbauer, TPO, Isotope and REE ratios are laboratory measurements that can provide more detailed information on field behaviour, and/or particle reactivity

Magnetic Susceptibility is one of the very few *in situ* methods that can be used to detect Fe NPs, and has the advantage of allowing for continuous monitoring. It can be combined with other sampling and monitoring arrays. During NanoRem field tests, several susceptibility

sensors were installed in arrays in the subsurface at the Spolchemie I site, Czech Republic (nZVI – NANOFEER 24S and NANOFEER STAR) and the Solvay site, Switzerland (using milled nZVI NPs called FerMEG12) field sites, together with a temperature sensor and sampling ports. The arrays were successful in detecting the Fe NPs during injection at both sites. Despite the fact that detection limits are slightly higher (ca 500 mg/L for field studies) and instrumentation costs for the magnetic array sensors are greater than those for on-site sampling and measurement, (ca. 1000 EURO per array and 1000 EURO for the electronics), it is one of the truly *in situ* methods and has the advantage of giving continuous logging data.

Post-injection monitoring

Monitoring during the post-injection phase needs to provide information on not only the concentrations of Fe, but also its speciation in order to understand the fate and reactivity of the injected NPs. For total Fe concentration, measurements on suspensions/liquids and soils/sediments can be carried out directly after acid digestion and measurement using standard chemical analysis (e.g., ICP-OES, or spectrophotometry). Alternatively, for low particle densities, pre-concentration by centrifugation or filtration can be applied to improve detection limits. Field applications have demonstrated that Mössbauer (for nZVI) can give useful additional information on the time dependent changes in particle state and reactivity, in both water and solid phases.

Monitoring for transport of NPs out of the treatment area

Total Fe content and other chemical parameters are sufficient to follow the behaviour of injected suspensions in the application area, but more sensitive methods are needed to control for the possible transport of NPs outside the treatment area, often termed “renegade” NPs. NanoRem development has shown that ICP-MS analysis of lanthanides, rare earth elements, and other trace elements in particles and background groundwater site samples can be used “fingerprint” the injected NPs. By applying Multivariate Statistics tools such as Principal Components Analysis, it is possible to discriminate injected NPs from the background with a much greater degree of sensitivity than by measuring Fe concentrations alone. Detection limits for these methods are extremely low (ng/L levels) in clean media (as tested in laboratory column experiments); but, as for all methods, the performance and applicability in the field is highly dependent on site-specific parameters. Field tests carried out at various NanoRem field injections (nZVI, Nano-Goethite and milled Fe) show good separation of NPs from background components at most sites and detection limits of sub mg/L at most sites. Total analytical costs are higher than for total Fe measurement (ca. 1000-3000 EUR per remediation site), but by targeting selected monitoring wells, measurements can be carried out over a lower spatial and temporal frequency.

Other Particles

Methods for tracing Carbo-Iron® and Trap-Ox Fe-zeolites are still at the laboratory development phase, although preliminary results are promising. A combination of Temperature-programmed oxidation (TPO) with parallel CO₂-analysis seems to be the best approach to distinguish Carbo-Iron® from other carbon containing sediments with detection limits of 0.1-5% wt, and fluorescence labelling has proved to be successful for quantitative analysis of Trap-Ox Fe-zeolites concentration in water samples, with detection limits of about 1 mg/L.

✓ A *Pre-Deployment Risk Assessment* (PDRA, Tool) is used to establish whether NanoRem particles can be injected without causing pollution of groundwater or surface water.

Early in the NanoRem project, a qualitative risk assessment protocol was developed for the NPs that were to be investigated in the laboratory and in the field. (LQM, 2014) Later in the project the protocol was modified (Nathanail et al., 2016).

For each site where NPs are to be injected into polluted groundwater plumes the steps required are: (1) State the legislative context. The relevant legislation and thus the endpoint of exposure could be different from one country to another. Some countries consider the limit of the property, others the exposure endpoint; others would consider the exposure endpoint to be the location of the receptor e.g. the River. (2) Characterise the site sufficiently to indicate the physical and chemical properties of the aquifer that are most likely to be important design considerations, define the range of input values to account for heterogeneity (e.g. anion background concentrations, hydraulic gradients, degree of fracturing, etc). (3) Create a site specific CSM for the potential risk of renegade nanoparticles, including defining critical aquifer and site-specific properties. (4) Define the critical controlling properties of your NPs being deployed (based on the fate and transport information provided by NanoRem or within completed MSDS). (5) Quantify where possible the range of the NP parameter values (defined in 4 above) being deployed to account for NP uncertainty. (6) Consider whether critical receptors are present (human health, groundwater, surface water, eco-receptors) and where the regulatory compliance point is located (part of the CSM). (7) Consider the toxicity of the NP, stabilisers and carrier fluids (based on the information provided by NanoRem or within completed MSDS). (8) Consider the potential pathways to the critical receptor(s) (part of the CSM) – see also point 9. (9) Utilise a screening model, such as the Risk Screening Model (see below), to estimate suitably cautious transport distances and concentrations for the NP injection to evaluate your CSM and critical receptor(s).

✓ A *Risk Screening Model* (RSM, Tool) is used to estimate the macro-scale transport of NPs within saturated media.

A Risk Screening Model (RSM) for application of NanoRem nanoparticles to groundwater remediation has been developed, to estimate the macro-scale transport of NPs within saturated media based on NanoRem DL7.1 (Bianco et al., 2015; Tosco et al., 2016). It is also derived from the Microsoft™ Excel spreadsheet tool Environment Agency Remedial Targets Methodology, RTM (Environment Agency, 2006). The RSM approach (detailed as part of the NanoRem DL8.2 reporting) also 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 RSM methodology depends on calculating values of attachment (k_{att}) and detachment (k_{det}) using the MNMs model (Bianco et al., 2015), with $k_{att}:k_{det}$ ratio used to estimate retardation of NPs. Outputs from the RSM spreadsheet model have been compared against a numerical solution currently included within MNMs and indicates the simplified models can provide similar outputs for the same inputs.

For a continuous injection scenario (i.e. a cautious assumption), using field study site inputs (Hungary), the RSM was used to estimate the time at which ‘breakthrough’ (very low but non-zero concentration) occurred at a distance 100m downstream (23 years), with the NP concentration distance profiles output at specific times (between 1-50 years). The travel times were predicted to be relatively high and travel distance limited.

For a continuous 1-year injection scenario (i.e. a cautious assumption) at a relatively high field injection concentration of an iron based NP an attachment to detachment coefficient ratio ($k_{att}:k_{det}$) of 10 or greater was predicted to be sufficient to significantly retard the movement of NPs downstream. Following 25 years of continuous injection a value of $k_{att}:k_{det}$ of 100-200+ is predicted to have the same impact. Hence $k_{att}:k_{det}$ ratios of between 10 and 100 may reasonably be expected to significantly reduce NP transport within the downstream aquifer.

Although, a number of key limitations and assumptions have been identified it is considered that the RSM approach provides a useful basis for a cautious risk assessment methodology.

Goal (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.

The information described below can be downloaded from www.nanorem.eu.

- ✓ NanoRem's *Exploitation Strategy, Risk-Benefit Analysis and Standardisation Status* summarises NanoRem's findings regarding dissemination and exploitation. Additionally, the chapter "potential impacts" provides an overview of these.
- ✓ NanoRem applied an internationally recommended approach to *Life Cycle Assessment (LCA)* on the production process of three nanoparticles (see project deliverable *Final Report on Three Large-Scale Experiments and Generalized Guideline for Application*).

Key stakeholder and interest groups want to know about the environmental impacts of nanoparticle products being used in the environment. Therefore, Life Cycle Assessment (LCA) approaches can bring some responses to these questions. LCA is a method for assessing the "environmental performance" of a product or a process throughout its life cycle, by looking into all the production processes and associated services being delivered. LCA requires that Life Cycle Inventory (LCI) data sets are produced through an inventory analysis. These inventories refer to all emissions and resources that are associated with the life cycle of the process or product.

Once developed and carried out, LCI and subsequent impact assessments can then help producers have an understanding of the environmental impact and resource uses from the product they develop. It can help them improve the process within an ecodesign approach and possibly reduce its impact and associated costs. By working towards reducing environmental impacts, they can contribute for example towards a lower-carbon resource and more efficient green economy.

Under NanoRem, LCI and impact assessments were applied to the production process of three nanoparticles of zero valent iron being used in the pilot sites. Carrying out LCI for nanoparticles production is an important step as there is indeed no or very little data available on life cycle inventories focusing on nanoparticle production (datasets on nanoparticles production are not common). Therefore, LCI were developed for each of the three selected nanoparticles considering the production of 1kg of a particle type. Results from the impact assessment show the steps in the process that have major environmental impacts, for example energy consumption during the production. This information can be taken into account as an incentive to reduce the costs of production and render it more environmentally friendly.

However, the boundary of the study has not gone beyond the production premises. Environmental performance of using nanoparticles of zero valent iron for groundwater remediation was not taken into account in the study. Therefore, the LCA of "nanoremediation by zero valent iron" has not been fully carried out. In future, further work could be carried out to establish the full life cycle of zero valent iron nanoparticles being used for the remediation of groundwater., In particular it could allow for the assessment of the potential environmental

performance of nanoparticles in delivering remediation against the environmental impact observed during the production process. Such work could also be used to compare environmental performance with other remediation approaches.

✓ Furthermore, the *NanoRem Case Study Sustainability Assessment Background and Workbook* has two broad purposes: to provide a background and NanoRem context for sustainable remediation and to provide a procedure to carry out a qualitative sustainability assessment of the nanoremediation technologies to be used at the field test sites.

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

Site 1: A retrospective assessment for an existing nanoremediation deployment at the Spolchemie I pilot site in the Czech Republic

Site 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 <http://www.nanorem.eu/displayfaq.aspx?id=12>) 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).

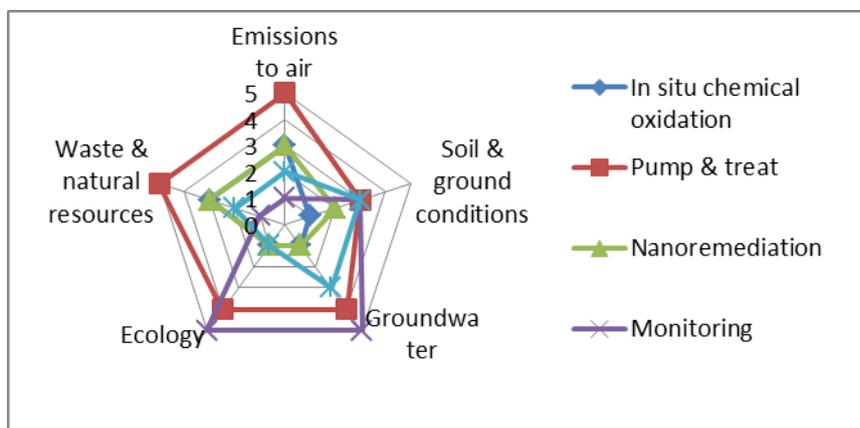


Figure 3: Radar plot for Spolchemie 1: Environmental indicators

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.

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.

✓ A description of the applications and results can be found in the Site Bulletins on www.nanorem.eu. All field trials within the project were carried out within a risk management regime for nanoparticle release that gained the required regulator approvals including where necessary using a pre-deployment risk assessment protocol. Qualitative sustainability assessments have been conducted in a retrospective sense for one of the Czech pilot sites and as part of remediation options appraisal for a separate UK based case study.

In the pilot sites it could be shown that nanoremediation works if remediation specialists select appropriate particles for a given site with a given contaminant mass and distribution, located in a given hydro-geo-chemical environment and if these remediation specialists follow the rules set down in the Guidelines for Application proposed by the NanoRem project. The field sites and the corresponding conditions are listed in Table 3 and the respective outcomes are described in detail in the site bulletins. These publications are concentrating on technical issues, which is only one (important) part of a successful implementation of a technology. This report thus refrains from repeating these issues but focuses on equally (and sometimes) important issues pertaining to successful implementation of a technology.

Regulators: The predominant question to be addressed with regulators is risk and potential benefit. Risk to human health and risk to the environment. The main issues here are ecotoxicity and longevity of nanoparticles and components of the suspension to be injected. Safety precautions (catchment wells) are to be planned if mobile additions to the suspension or very mobile particles are to be used and “renegades” are to be expected. If injection requests are well founded injection permits were given within 6 to 24 months. Regulators expect state of the art work, thus workers’ safety is not a big issue when applying for a permit.

Problem owners: While some problem owners are technology interested and supportive of new/immerring technologies, the predominant question is “(How fast) does it work? How much would I have to pay?” Main obstacle for problem owners is an insufficiently documented proof of efficiency of the technology, thus, for problem owners the best selling point is a demonstration where they can see that it works, how long remediation may take (faster than other technologies) and if it works economically. **Other stakeholders:** In none of the NanoRem site public perception was an issue as none of the sites was located in the proximity of a water extraction. Nevertheless, it is emphasized that in case of implementing nanoremediation easily understandable information material, especially with respect to possible risk of exposure should be readily available.

Killing criteria for NP application: The most important killing criteria for NP remediation is inappropriate communication, especially concerning risk, badly educated regulators (who want to cover their backs) and alarmism due to bad communication to regulators and the public.

Benefits to the NanoRem partners: The European remediation market is very competitive and cost driven. For all partners nanoremediation was not a new area of interest, however, most applications prior to NanoRem could have been described with “learning by doing”. Participation in NanoRem provided them on the one hand with a sound understanding of the hydraulic and chemical processes governing a nanoremediation and on the other hand with the

much necessary pilot sites and corresponding PR material (bulletins) to positively prove that the technology works. The project showed and clearly documented that a successful application of nanoremediation is not trivial. The guideline derived in NanoRem provides an outline and gives a handout, however it is very clear that specific expertise and experience are necessary to successfully implement a nanoremediation. In collaboration between the different WP the site partners could obtain this knowledge, thus giving them now a unique selling point and a more competitive edge on the remediation market. In addition to the partners initially involved on the sites two spin-offs (PHOTON WATER TECHNOLOGY s.r.o., CZ and *intrapore*, D) developed and are now also trying to market nanoremediation throughout Europe.

Table 2: Overview of particles available from the NanoRem project

Particle name	Type of particle	Manufacturer	Website	Process of contaminant removal	Target contaminants	Development status as of January 2017
Carbo-Iron® (industry)	Composite of Fe(0) and activated carbon	SciDre GmbH, Germany	http://www.carboiron.de	Adsorption + Reduction	Halogenated organics (contaminant spectrum as for nZVI)	Field tested and commercially available
FerMEG12	Mechanically ground nZVI particles	UVR-FIA GmbH, Germany	http://www.uvr-fia.de	Reduction	Halogenated hydrocarbons	Field tested and commercially available
NANO FER 25S	Nano scale zero valent iron (nZVI)	NANO IRON s.r.o., Czech Republic	http://www.nanoiron.cz/en/nanofer-25s	Reduction	Halogenated hydrocarbons and heavy metals	Field tested and commercially available
NANO FER STAR	Air stable powder, nZVI	NANO IRON s.r.o., Czech Republic	http://www.nanoiron.cz/en/nanofer-star	Reduction	Halogenated hydrocarbons and heavy metals	Field tested and commercially available
Nano-Goethite	Pristine iron oxides stabilized with HA	University of Duisburg-Essen, Germany	http://www.uni-due.de/biofilm-centre	Oxidation (catalytic effect on bioremediation) + Adsorption of heavy metals	Biodegradable (preferably non-halogenated) organics, such as BTEX; heavy metals	Field tested and commercially available
Trap-Ox Fe-zeolites	Nanoporous aluminosilicate loaded with Fe(III)	UFZ Leipzig, Germany	http://www.ufz.de/index.php?en=2529	Adsorbent + Oxidation (catalyst)	Small molecules (depending on pore size of zeolite) - e.g. BTEX, MTBE, dichloroethane, chloroform, dichloromethane	Premarket
Bionanomagnetite	Produced from nano-Fe(III) minerals	University of Manchester, UK	http://www.geomicrobiology.co.uk/	Reducing agent and adsorption of heavy metals	Heavy metals, e.g. Cr(VI)	Lab to premarket
Palladized bionanomagnetite	Biomagnetite doped with palladium	University of Manchester, UK	http://www.geomicrobiology.co.uk	Reduction (catalyst)	E.g. Halogenated substances (contaminant spectrum broader than for nZVI)	Lab and premarket
Abrasive Milling nZVI	Milled iron	Centre Tecnològic de Manresa, Spain	http://www.ctm.com.es/en/index.php	Reduction	Halogenated alifatics and Cr(VI)	Lab
Barium Ferrate	Fe(VI)	VEGAS, University of Stuttgart, Germany	http://www.vegas.uni-stuttgart.de	Oxidation	BTEX?, nitroaromatic compounds? (under investigation)	Lab
Mg/Al particles	Zero valent metals	Adaption of commercially available particles by VEGAS, University of Stuttgart, Germany	http://www.vegas.uni-stuttgart.de	Reduction (reagent)	Halogenated hydrocarbons	Lab
Nano-FerAl	Composite of Fe and Al	UVR-FIA GmbH / VEGAS, University of Stuttgart, Germany	http://www.vegas.uni-stuttgart.de	Reduction (reagent)	Halogenated hydrocarbons	Lab

Table 3: Listing of NanoRem field sites

NanoRem Site Name	Spolchemie I	Spolchemie II	Solvay	Balassagyarmat	Neot Hovav	Nitrastur
Site Primary Investigator	AQUATEST	AQUATEST	Solvay	Golder	Ben Gurion University of the Negev	Tecnalia
Country	Czech Republic	Czech Republic	Switzerland	Hungary	Israel	Spain
Current use	Industry	Industry	Industrial brownfield, some subletting	Brownfield	Industry	Brownfield
Specification of contamination (source/plume)	dissolved plume	residual phase and dissolved plume	pooled phase and dissolved plume	dissolved plume	phase and plume in fractures	anthropogenic backfill containing heavy metals
Main contaminant(s)	chlorinated hydrocarbons	BTEX (mainly Toluene and xylenes), styrene	PCE, TCE	PCE, TCE, DCE	TCE, cis-DCE, toluene	As, Pb, Zn, Cu, Ba, Cd
Type of Aquifer	porous, unconfined	porous, unconfined	porous, unconfined	porous, unconfined	fractured	porous, unconfined
Hydraulic conductivity	10^{-4} to 10^{-6} m/s	10^{-4} to 10^{-6} m/s	$8 \cdot 10^{-3}$ to $2 \cdot 10^{-5}$ m/s	$5 \cdot 10^{-3}$ to $2 \cdot 10^{-8}$ m/s	n/a	$2 \cdot 10^{-4}$ to 10^{-5} m/s
Seepage velocity	0,2 m/d	0,9 m/d		0,3 m/d	not known	
NP used	NANOFER 25S/ NANOFER STAR	Nano-Goethite	FerMEG12	Carbo-Iron®	Carbo-Iron®	NANOFER STAR
NP provided by	Nano Iron, s.r.o.	University Duisburg Essen	UVR-FIA GmbH	SciDre GmbH	UFZ	Nano Iron, s.r.o.
Mass of NP injected	200 kg / 300 kg	300 kg	500 kg	176,8 kg	5 kg	250 kg
Injection System	Direct Push	Direct Push	Wells (with packers)	Direct Push	Wells (with packers)	Wells (with packers)
Remediation outcome	See NanoRem Project Bulletins on Pilot Sites No 7	See NanoRem Project Bulletins on Pilot Sites No 8	See NanoRem Project Bulletins on Pilot Sites No 9	See NanoRem Project Bulletins on Pilot Sites No 11	See NanoRem Project Bulletins on Pilot Sites No 10	See NanoRem Project Bulletins on Pilot Sites No 12

Project results online – the NanoRem Toolbox

The nanoremediation toolbox, available on www.nanorem.eu, focuses on the needs of decision makers, consultants and site owners. It provides the respective output of NanoRem in three levels:

- (I) The bulletins include the most relevant information in a condensed and concise way.
- (II) More detailed information on nanoparticles and tools are located in the “Nanoparticles and Tools” shelf.
- (III) Other dissemination products and selected project deliverables can be found in the “Supporting Information” shelf.

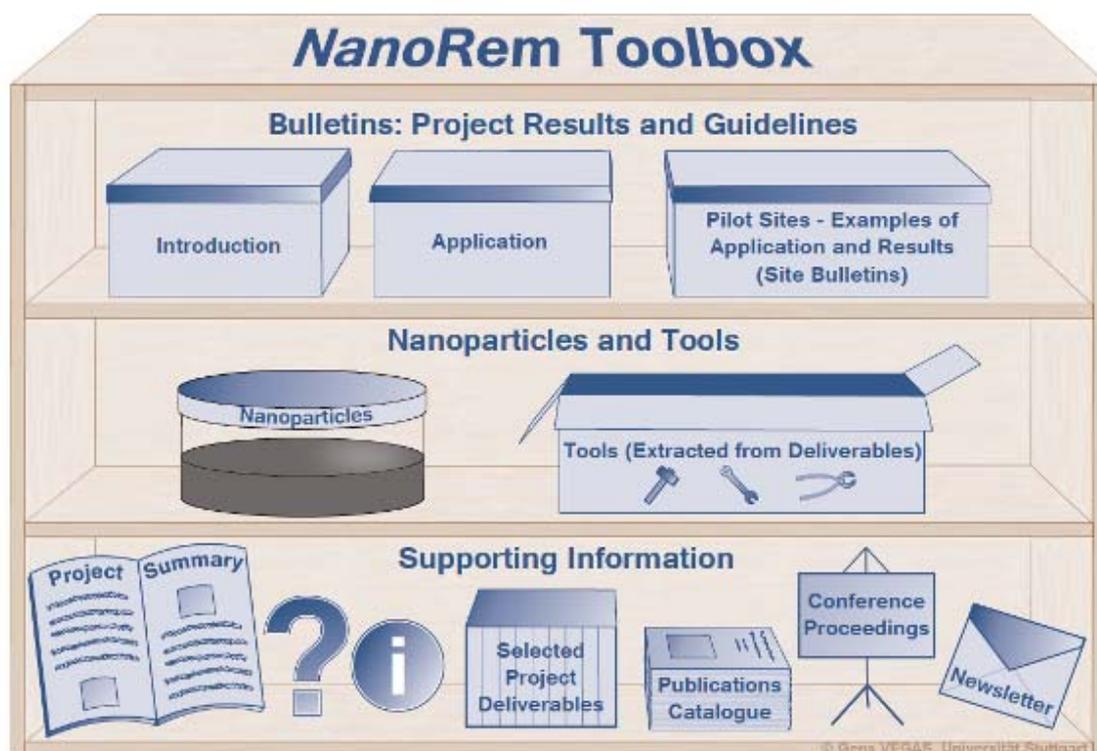


Figure 4: NanoRem Toolbox

List of bulletins

- (1) Nanotechnology for Contaminated Land Remediation - Possibilities and Future Trends Resulting from the NanoRem Project
- (2) Appropriate Use of Nanoremediation
- (3) Generalised Guideline for Application of Nanoremediation
- (4) A Guide to Nanoparticles for the Remediation of Contaminated Sites
- (5) Development and Application of Methods for Monitoring Nanoparticles in Remediation
- (6) Forecasting Nanoparticle Transport for Soil Remediation
- (7)-(12) NanoRem Pilot Site-Bulletins

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3 Potential impacts

Socio-economic impact and the wider societal implications of the project

The transfer of technology information from academia to business and vice versa, or from business to business, is vital to innovation and competitiveness in the environmental restoration industry. A good example of the importance of this transfer process can be seen in the market for nanoremediation in Europe. Laboratory scale work implies nanotechnologies could offer a step-change in remediation capabilities: treating persistent contaminants, avoiding process intermediates and increasing the speed at which degradation or stabilisation can take place (Müller and Nowack 2010). The benefits of this for Society would be not only be economic expansion, and its consequent job creation, but also a more extensive range of solutions to apply to pressing environmental problems of land contamination to extend the range of treatable solutions, and provide more effective and environmentally benign treatments. In 2007 in Europe it was forecast that the 2010 world market for environmental nanotechnologies would be around \$6 billion (JRC Ispra 2007). 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 (to be included in the reference list), see Figure 5 Figure 5, accounting for perhaps more than 50% of contamination problems.

Most frequently applied occurring contaminants

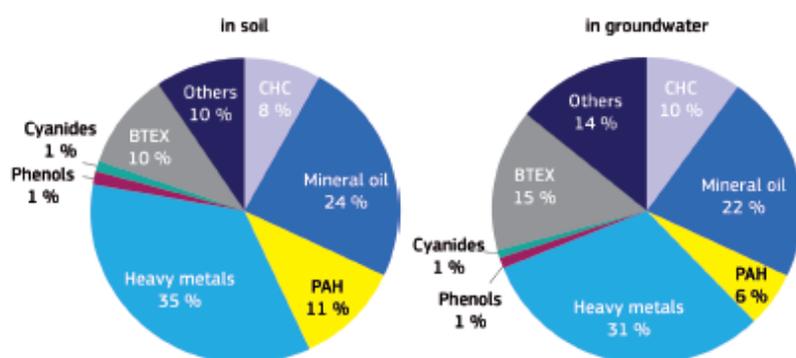


Figure 5: Most frequently occurring contaminants (From JRC 2014)

However, in practice, adoption of nanoremediation was slow. Bardos *et al.* (2011) identified just 58 examples of field scale applications of nanoremediation (using nZVI). As of November 2016 NanoRem had identified more than 100 (DL9.2).

Reasons for the limited adoption of nanoremediation may relate to concerns about their relative cost, efficacy, and long-term effectiveness in contaminated environmental media (e.g. groundwater, sediments, etc.). Few organisations like to be the “first” to take on a technical risk. There are also some regulatory concerns regarding the implications of their deployment in the field, namely on potential human health and ecotoxicological effects resulting from exposure to these nanomaterials. The potential risks of the deployment of NPs for *in situ* remediation are poorly understood, leading to precautionary and conservative regulatory positions. For example, there has been a moratorium on the use of nanoremediation in the UK in response to the Royal Society/Royal Academy of Engineering report (Anon 2012, RS & RAE 2004). A number of national risk-benefit studies have taken place, for instance in

Austria, Belgium, Switzerland, UK and USA (Karn *et al.* 2009, OVAM 2006; Bardos *et al.* 2011, Bundesamt für Umwelt 2010 Switzerland, Grieger *et al.* 2010).

In principle there were two substantive failures in technology transfer from academic laboratory scale studies to practical deployment in environmental restoration markets for nanoremediation: (1) limited penetration of technical opportunities to create substantial benefits over existing remedial alternatives in practice; (2) failure to convince sceptical regulatory and user stakeholders that NP deployment risks are acceptable and manageable.

This situation has substantively shifted as a result of the NanoRem project, through its work from bench to field scale deployments (see Figure 6). Nanoremediation has been offering 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. For example, new materials were developed, with which we can state the following success: (a) The range of non-ZVI and composite particles extends the nanoremediation application area from reduction to adsorption and oxidation (scientific, technical, environmental). (b) A broader contaminant spectrum can be treated. Beside the typical types of contaminants treatable by nZVI (such as halogenated hydrocarbons, metals/metalloids), also substances not treatable by nZVI (fuel oxygenates such as MTBE, ETBE, non-halogenated substances such as BTEX, PAHs and persistent substances, such as CH₂Cl₂, C₂H₄Cl₂ and pharmaceuticals) can now be added to the target contaminants (scientific, technical, environmental). (c) Two particles use the strategy of trap&treat, where contaminants are first enriched at the particles which also allows efficiency for low-concentration targets (environmental). 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.



Figure 6: Preparation of the monitoring equipment at the Spolchemie site 1 © VEGAS, University of Stuttgart, Germany

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, in particular concerns over ecological risks⁹. 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 provided a tool box 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 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.

Main dissemination activities

The NanoRem project established a communication plan at an early stage of this project and has undertaken a wide range of dissemination activities. These include:

- NanoRem has had a major science and technical publication output. Comprehensive publications in journals and at conferences are listed in a project Publications Catalogue. This is available in a public format for all dissemination outputs in the public domain via www.nanorem.eu.
- The project web site maintains a comprehensive information area and announcements area. Over the lifetime of the project the public area of the web site attracted around 1,500

⁹ <http://www.nanorem.eu/Displaynews.aspx?ID=824>

discrete visits per week. The information facilities on the web site were supplemented at the start of 2017 with a fully featured “Toolbox”¹⁰ (see Figure 4) providing an overarching library of the project outputs.

- An important feature of the project dissemination has been to include summary information, for example about the “toolbox”, written for practitioners rather than scientists, of its key outcomes in a format accessible to a wide range of stakeholders. The “bulletins” have been produced by CL:AIRE (www.claire.co.uk) which is an experienced contaminated land information organisation. The bulletins also received independent peer review from CL:AIRE’s Technology & Research Group to ensure its usefulness and relevance to practitioners and other users. These bulletins will be made available via a range of platforms, including NanoRem and CL:AIRE web sites, as well via a press release announcement enabling their promotion by other web sites and news services (in particular EUGRIS, NICOLE and www.cluin.org). These channels are major sectoral information resources, and between them these web channels have more than 100,000 discrete visits per week from users across the world.
- NanoRem has undertaken a significant programme of stakeholder engagement including workshops of *circa* 50 delegates, and smaller focus group activities (*circa* 20 delegates), reported on in NanoRem DL9.2¹¹
 - Nottingham Nanoremediation Deployment Risk Assessment Stakeholder Workshop 16-17th July 2013
 - Oslo nanoremediation sustainability and market opportunity stakeholder workshop 3rd-4th December 2014
 - Focus group activities on nanoremediation market scenario forecasting in Berlin and London, and also at conferences listed below.
- NanoRem has promoted its outputs internationally via the activities of its Project Advisory Group, many presentations and posters on different conferences and other events (s. below).
- NanoRem has engaged directly with the two key European sectoral stakeholder networks, NICOLE (www.nicole.org) and the COMMON FORUM (www.commonforum.eu). These networks have been represented on its PAG, and have also supported the review and editing of various NanoRem outputs. NanoRem has participated in a technical working group of NICOLE focused on understanding optimal operating conditions for technologies (via the “operating windows” concept).
- NanoRem has engaged directly with a wide range of stakeholders via its Pilot site test programme: Regulators: If injection requests are well founded injection permits were given within 6 to 24 months. Regulators expect state of the art work, thus workers’ safety is not a big issue when applying for a permit. Problem owners: While some problem owners are technology interested and supportive of new/emerging technologies, the predominant question is “(How fast) does it work? How much would I have to pay?” Other stakeholders: In none of the NanoRem site public perception was an issue as none of the sites was located in the proximity of a water extraction. Nevertheless, it is emphasized that in case of implementing nanoremediation easily understandable information material, especially with respect to possible risk of exposure should be readily available.

¹⁰ <http://www.nanorem.eu/toolbox>

¹¹ <http://www.nanorem.eu/Displaynews.aspx?ID=907>

- NanoRem has leveraged dissemination special session, workshop and training opportunities with major international sectoral conference platforms including
 - AquaConSoil 9th to 12th June 2015, Denmark, Copenhagen, where NanoRem operated special technical, training and discussion sessions and provided a substantial number of platform presentations and posters. Several of these have since appeared as papers in the high impact journal *Science of the Total Environment*¹². These outputs were also collated as a midterm technical compendium of NanoRem's work and made available on its web site¹³. This collaboration also included a discussion session on nanoremediation markets which fed into the focus group activities on nanoremediation markets mentioned above.
 - SustRem 2014, Ferrara Italy. A special session on "Nanoremediation: hopes or fears from the sustainability perspective."
- NanoRem carried out several final conferencing activities
 - A main NanoRem Final Conference in association with the DECHEMA annual Symposium Strategien zur Boden- und Grundwassersanierung, A major sectoral event for more than 300 German language delegates. The final conference involved presentations by the NanoRem partners about all relevant aspects, from the particle development, over particle characterisation to their application. It also considered possible risks and included a panel discussion regarding the possibilities and future trends of nanoremediation.
 - NANOCON 2016, 8th International Conference of Nanomaterials – Research and Application, in Brno, Czech Republic on October 19th - 21st 2016. The NANOCON involved a number of different application areas of nanomaterials. Two presentations were given and a poster shown.
 - REMTECH 2016, Italy, 21st September 2016. NanoRem offered two sessions 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.

Exploitation of results

A number of specific exploitation actions have taken place in or around the NanoRem project. This segment is based on key questions asked of the project by the Commission's technical representative, a subsequent survey of its work package leaders and SMEs and the final risk benefit appraisal deliverable (DL9.2). It supplements the information already provided above about *Socio-economic impact and the wider societal implications of the project*.

NanoRem has had significant economic and commercial impacts

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® (see **Figure 8**) has now shifted to commercial production, following an agreement reached between UFZ and ScIDre GmbH. Carbo-Iron® has been licensed to

¹² <http://www.sciencedirect.com/science/journal/00489697/vsi/10WXNT6RRNZ>

¹³ <http://www.nanorem.eu/Displaynews.aspx?ID=815>

two companies – one is a SME to produce the material (partner ScIDre GmbH) and one is a SME specialized in nanoremediation (Off-spring of NanoRem Intrapore GmbH) (*commercial*)

- FerMEG12 (see **Figure 7**) 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 patent has been filed under the name “NanoFerAl” (patent reference AZ 20 2015 005 738.1).
- The air stable NANO FER 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.
- Nano-Goethite 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 Nano-Goethite 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.



Figure 8: Air-stable Carbo-Iron
© A. Kuenzelmann, UFZ, Germany



Figure 7: Milled nZVI particles
© UVR-FIA, Germany

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

- The Reground project is a H2020 project (<http://reground-project.eu>) 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).

- A module for a state-of-the-art software MODFLOW was developed.

Several spin-out start-up companies have emerged from NanoRem Consortium members, including: Intrapore UG, Essen, Germany and Photon Water Technology s.r.o, Czech Republic. NanoRem has also extended the scope of activities of some companies. These benefits are discussed in more detail below.

NanoRem has had major beneficial impacts for its participating Small and Medium Enterprises (SMEs)

Based on a survey of NanoRem SME and big company partners several benefits were identified. Highlights include the following:

- Production of Carbo-Iron[®] has been commercialized. Partner ScIDre GmbH is in close contact to users, such as the spinout SME intrapore which plans to apply Carbo-Iron[®] in the near future.
- Full scale production of a new type of NP with improved properties; additional alternatives of surface modification by organic compounds (NANO IRON s.r.o.).
- Technological development – enhanced knowledge of nanoremediation – which is leading to the creation of new project proposals and opportunities. Additionally, some SMEs have enhanced their abilities in sustainability and environmental risk assessment and risk benefit appraisal (e.g. LQM, r3, and the spin out Photon Water Technology).
- Networking / knowledge sharing – all participating SMEs have made a number of contacts, reinforced existing relationships and opened a wide range of conversations, also with academia and researchers.
- Business development: Some SMEs have initiated new business developments and relationships, for example a proposal to the FTI scheme stimulated by the spinout Photon Water Technology.
- All SME partners have succeeded in raising their publications and dissemination profile as a result of NanoRem.
- Profile and reputation: participation in NanoRem has had substantial reputational benefits for all SME partners, and has assisted in building their international profile.
- Several partners (TECNALIA, Golder, Geoplano) report enhancement of their practice for field deployment of nanoremediation (for example in terms of implementation and monitoring knowhow) enhancing their know-how offer to potential clients.
- NanoRem has provided SMEs with market knowledge for their ongoing business development, for example market entry and project replication; and has provided them with well recognized expertise to service new and existing clients.

There is an exploitation potential for several participating SMEs

SME ScIDre GmbH: The production of the high-tech material Carbo-Iron[®] requires special equipment and a complex process execution. Exploitation potentials are given by optimizing the process and market the final product with the proviso to provide better performance characteristics than competing products. Further development of the material to extend the

properties would help to market a wide range of application-optimized materials. To achieve this, scientific efforts and project further applications are on the way to develop new Carbo-Iron-like products with extended features.

Photon Water Technology has been newly established in the Czech Republic with the aim to apply new remedial technologies, where nanoremediation plays an important role. Another example is the exploitation of the AQUATEST company (formerly SME) to the Chinese market (preparation of contracts for application of NANOFER STAR in a large pilot application).

The NanoRem spinout Intrapore GmbH is in license for the use of Carbo-Iron® and will conduct also the first pilot study for Trap-ox Fe zeolites.

Furthermore, consulting SMEs (such as r3, Geoplano, LQM) are actively promoting services related to the evaluation, design, implementation and monitoring of nanoremediation. For example, Geoplano have engaged with several potential clients for nanoremediation services in Portugal and Spain, who were regularly updated by Geoplano on the evolution and advances of NanoRem. Geoplano believe this will, in the near future, be converted into effective business opportunities. LQM are partnering with a wide range of largely UK based regulatory and commercial stakeholders to lift the moratorium on nanoremediation and are working with the University of Nottingham and the British Geological Survey to develop a better understanding of nano particle behaviour in typical UK soils. R3 has taken part in the FTI proposal mentioned above and is developing strategic alliances with potential nanoremediation service providers in the UK and wider EU.

Potential users and other stakeholders (outside the consortium) have been extensively involved

NanoRem has involved a wide range of stakeholders in multiple ways in the project, including other researchers (including from domains outside NanoRem such as social science), site owners/managers, service providers (consultancies / contractors), regulators, from within and beyond the European Union. We have involved people with widely varying levels of expertise from technical people outside the remediation domain, to students, to leading scientists outside the consortium.

Dialogue has been achieved by engagement with stakeholder networks, via field test deployments and specific dialogue and focus group activities as discussed above, and additionally via the PAG, academic staff and student exchanges and also direct *pro bono* contributions, such as the assistance with a nanoremediation sustainability assessment case study provided by Vertase-FLI from the UK.

Policy-related and/or regulatory issues were properly handled

All field site applications have been through a correct permitting procedure (which went fairly quickly and lets us assume that all regulatory issues have been handled properly. Furthermore, WP9 (and the PAG) have directly engaged with the key EU stakeholder network s (COMMON FORUM and NICOLE), as described above. Additional policy and regulatory stakeholders participated in the stakeholder engagement activities described above. Bulletin 2 provides a high level introduction to the appropriate use of nanoremediation, and its drafting including inputs from external stakeholders at numerous points.

Safety issues have been properly handled

There were no problems concerning safety occurring in any of the bench of field scale experimentation or in the scale up activities. All necessary health and safety procedures were carried out. For all particles deployed in the field, Material Safety Data Sheets (MSDS) and handling instructions were developed and shared any users and applied by them, including scientists/technical staff involved in the experiments and at the field sites. Links to these safety data sheets have been provided on the NanoRem web site.

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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4 Website

The project's website is www.nanorem.eu.



5 Logo



6 List of beneficiaries

Partner No.	Organisation Legal Name	Short Name	Country	Organisation Type
1 Coordinator	University of Stuttgart (VEGAS)	USTUTT	DE	Higher Education
2	Karlsruhe Institute of Technology	KIT	DE	Research Organisation
3	Solvay (Schweiz) AG	Solvay	CH	Multinational Industry
4	Helmholtz-Zentrum für Umweltforschung GmbH	UFZ	DE	Research Organisation
5	Ben-Gurion University of the Negev	BGU	IL	Higher Education
6	Fundació CTM Centre Tecnològic	CTM	ES	Research Organisation
7	Universitaet Wien	UNIVIE	AT	Higher Education
8	University of Manchester	UMAN	UK	Higher Education
9	Fundacion Tecnalia Research & Innovation	TECNALIA	ES	Research Organisation
10	Helmholtz Zentrum München	HMGU	DE	Research Organization <i>Has left the consortium 31/03/2015</i>
11	Norwegian Institute of Bioeconomy Research	NIBIO	NO	Research Institute <i>Name change (formerly "Bioforsk")</i>
12	Technical University of Liberec	TULib	CZ	Higher Education
13	Norwegian University of Life Sciences	NMUB	NO	Higher Education <i>Name change (formerly "UMB")</i>
14	Aquatest	AQT	CZ	SME <i>Has lost status of SME, now large enterprise, effective 30/06/2015.</i>
15	Palacký University in Olomouc	UPOL	CZ	Higher Education
16	Centre National de la Recherche Scientifique	CNRS	FR	Research Organisation
17	Politecnico di Torino	POLITO	IT	Higher Education
18	Geoplano Consultores, S.A.	Geoplano	PT	SME
19	Technical University of Denmark	DTU	DK	Higher Education
20	Stichting Deltares	Deltares	NL	Research Organisation
21	r3 Environmental Technology Limited	R3	UK	SME
22	LQM, Land Quality Management Ltd.	LQM	UK	SME
23	Contaminated Land: Applications in Real Environments (CL:AIRE)	CL:AIRE	UK	Non-profit Organisation
24	Nano Iron, s.r.o.	Nanoiron	CZ	SME
25	Golder Associates GmbH	Golder	DE	SME
26	Bureau de Recherches Géologiques et Minières	BRGM	FR	Research organization

Partner No.	Organisation Legal Name	Short Name	Country	Organisation Type
27	Industrieanlagen Betriebsgesellschaft mbH	IABG	DE	<i>Has left the consortium 04/06/2013 before taking over any action</i>
28	UVR-FIA GmbH	UVR-FIA	DE	SME
29	Scientific Instruments Dresden GmbH (<i>Substitute for IABG</i>)	SciDre	DE	SME 2 nd Amendment agreed 26 March 2014 Start of work 01/01/2014
30	University Duisburg-Essen (<i>Successor of HMGU</i>)	UDE	DE	Higher Education 3 rd Amendment agreed 02 Oct. 2015 Start of work 01/04/2015