Nanoremediation for Soil and Groundwater Clean-up - Possibilities and Future Trends

NanoRem Final Conference

### Frankfurt am Main, Germany, 21st November 2016

The final conference of the EU project NanoRem („Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment", www.nanorem.eu) will take place on 21st November 2016, as a pre-conference to the DECHEMA Symposium.

The conference titled „Nanoremediation for Soil and Groundwater Cleanup – Possibilities and Future Trends" presents the most recent developments and opportunities for soil and groundwater remediation by use of different nano particles. Project partners expect an intensive exchange of ideas with remediation practitioners.

NanoRem is a four year project with 29 partners from 13 countries, coordinated by the University of Stuttgart. It has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 309517.
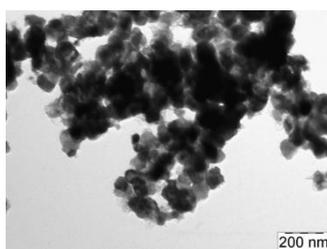
Date: 21st November 2016

Venue: DECHEMA, Haus Frankfurt,
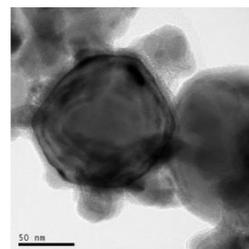Theodor-Heuss-Allee 25,
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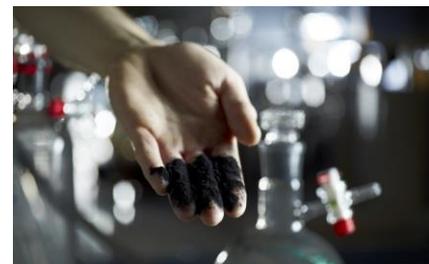
Carbo-Iron®, © A. Künzelmann, UFZ
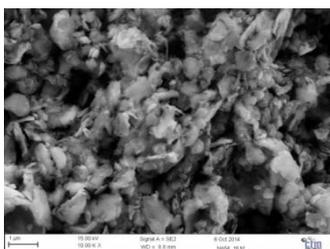
Abrasive Milling nZVI particles, © CTM   *nZVI particles, © UPOL*   *nZVI particles, © UPOL*   *Milled nZVI particles, © UVR-FIA*

Agenda

| 9:30-10:30	Registration
10:30	**Welcome** - *Thomas Track, DECHEMA*
	What´s behind nanoremediation - technique, particles, … *Chair: Rolf Gerhardt, Project Advisory Group (PAG), DB AG, Germany*
10:45	**NanoRem in a nutshell** *Hans-Peter Koschitzky, VEGAS University of Stuttgart, Germany*
11:10	**nZVI: design, performance and application possibilities** *Miroslav Cernik, Technical University of Liberec, Czech Republic*
11:35	**non ZVI: design, performance and application possibilities** *Katrin Mackenzie, Helmholtz Centre for Environmental Research UFZ Leipzig, Germany*
12:00	**Subsurface nanoparticle transport** *Thilo Hofmann, University of Vienna, Austria*
12:25	**Lunch**
	Field application of nanoremediation tools and lessons learned from NanoRem *Chair: Paul Bardos, R3 Ltd, Great Britain*
13:30	**Large scale experiments: performance, upscaling and lessons learned for application in the field** *Kumiko Miyajima, VEGAS University of Stuttgart, Germany*
13:55	**Nanoremediation - a consultant's perspective** *Petr Kvapil, Aquatest, Czech Republic*
14:20	**Nanoremediation - a site owner's perspective** *Pierre Matz, Solvay Belgium*
14:45	**Where will our nanoparticles go? Numerical modeling of nanoparticles transport** *Pauline van Gaans, Deltares, The Netherlands and Tiziana Tosco, Polito, Italy*
15:00	**Where are our nanoparticles? At site and in-situ monitoring** *Deborah Oughton, Norwegian University of Life Sciences, Norway*
15:15	**Coffee break**
	Continued on next page

	Operating windows and recommendations from NanoRem
	Chair: Hans-Peter Koschitzky, VEGAS University of Stuttgart, Germany
15:45	**Generalized guideline for nanoremediation application**
	Jürgen Braun, VEGAS University of Stuttgart, Germany
16:15	**Safe application of nanoremediation - Renegade nanoparticles quo vaditis? Risk assessment = regulatory reassurance**
	Paul Nathanail, Land Quality Management Ltd, Great Britain
16:35	**Panel discussion: Possibilities and future trends of nanoremediation**
	Chair: Paul Nathanail, LQM, Great Britain
	Participants:
	• *Paul Bardos (R3 Environmental Technology Ltd, Great Britain)*
	• *Harald Burmeier (ITVA, Ingenieurtechnischer Verband für Altlastenmanagement e.V., Germany)*
	• *Rolf Gerhardt (Deutsche Bahn AG, Germany)*
	• *Thomas Held (ARCADIS GmbH, Germany)*
	• *Dietmar Müller-Grabherr (EEA, Environment Agency Austria and COMMON FORUM, EU)*
17:15	**Closing remarks**
	Hans-Peter Koschitzky, VEGAS University of Stuttgart, Germany
17:20 – 20:00	**Poster session and NanoRem final reception**

Experimental setup for reactivity studies in columns © VEGAS/USTUTT

Preparation of suspension for the injection into the Large Scale Flume © VEGAS/USTUTT
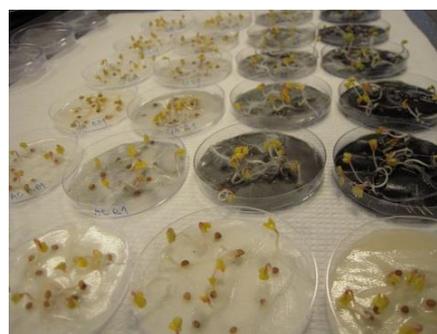
Nanoparticles were tested for their potential effects on plant root elongation © Claire Coutris, NIBIO, Norway

NanoRem in a nutshell

Hans-Peter Koschitzky, Joachim Roos, Alexandra Gens

VEGAS, University of Stuttgart, Germany

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

The NanoRem consortium is multidisciplinary, cross-sectoral and transnational. It consists of 29 partners from 13 countries organised in 11 work packages. The consortium includes 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 is co-ordinated by the VEGAS team (Research Facility for Subsurface Remediation) from the University of Stuttgart in Germany.

For the structure of the project please see the figure on the back of this brochure.

The *Design and Production Group* comprises 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* is 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).

NanoRem project goals and main results

The overall aim of the NanoRem project was to demonstrate that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater. NanoRem provided a direct link between SME (small and medium sized enterprises) on the production side and SME on the application side of groundwater remediation using NPs. Six project goals were identified at the project outset. These are listed below along with brief text describing how these goals were met.

Detailed information will be available latest from January 2017 onwards at www.nanorem.eu. Amongst others, twelve NanoRem-Bulletins will be offered for download.

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 Table 1 along with the main study results regarding reactivity, stability, mobility, delivery, fate and ecotoxicity. More information can be found within the Bulletin No 4 "A Guide to Nanoparticles for the Remediation of Contaminated Sites" and at www.nanorem.eu.

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.
   ✓ Nano-scale zerovalent iron particles (nZVI) have been improved via a new surface coating so that they are available as an air-stable dry powder in spite of a large specific surface. This allows for a more convenient handling (transportation to the site, storable) - see also Bulletin No 4 "A Guide to Nanoparticles for the Remediation of Contaminated Sites".

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, while results from the large scale experiments are available in the project deliverable "*Final Report on Three Large-Scale Experiments and Generalized Guideline for Application*".
   ✓ Indications regarding the usefulness of NPs are given in the Site bulletins.

✓ With regard to ecotoxicological aspects it was found that no significant toxic effects were observed on soil and water organisms when ecotoxicological tests were undertaken for a range of nanoparticles available for remediation (including with respect to the particles' interaction with contaminants and the resulting products).

✓ Furthermore, effects on selected soil and water organisms were monitored for up to nine months after NP treatments of the pilot sites. 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. However, a positive effect of NP injection on indigenous microbial communities and more specifically, the apparition of organohalide-respiring bacteria after NP injection, was observed both at the Solvay and Balassagyarmat sites. More information can be found at www.nanorem.eu.

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* (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.

✓ Numerical tools for *Forecasting NP Transport for Soil Remediation* (Bulletin No 6) include a 1D modelling tool (MNMs)[1] 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)[2] 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.

✓ 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.

✓ *Pre-Deployment risk assessment* (Tool) is used to establish whether NanoRem particles can be injected without causing pollution of groundwater or surface water.

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[1] **M**icro- and **N**ano-particles transport, filtration and clogging **M**odel **S**uite,
www.polito.it/groundwater/software
[2] **M**icro and **N**anoparticle transport **M**odel in 3D geometries
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

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.
✓ 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*).
✓ 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.

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

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

✓ 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.

Project results online – the Nanoremediation 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:

1) The bulletins include the most relevant information in a condensed and concise way.

2) More detailed information on nanoparticles and tools are located in the "Nanoparticles and Tools" shelf.

3) Other dissemination products and selected project deliverables can be found in the "Supporting Information" shelf.
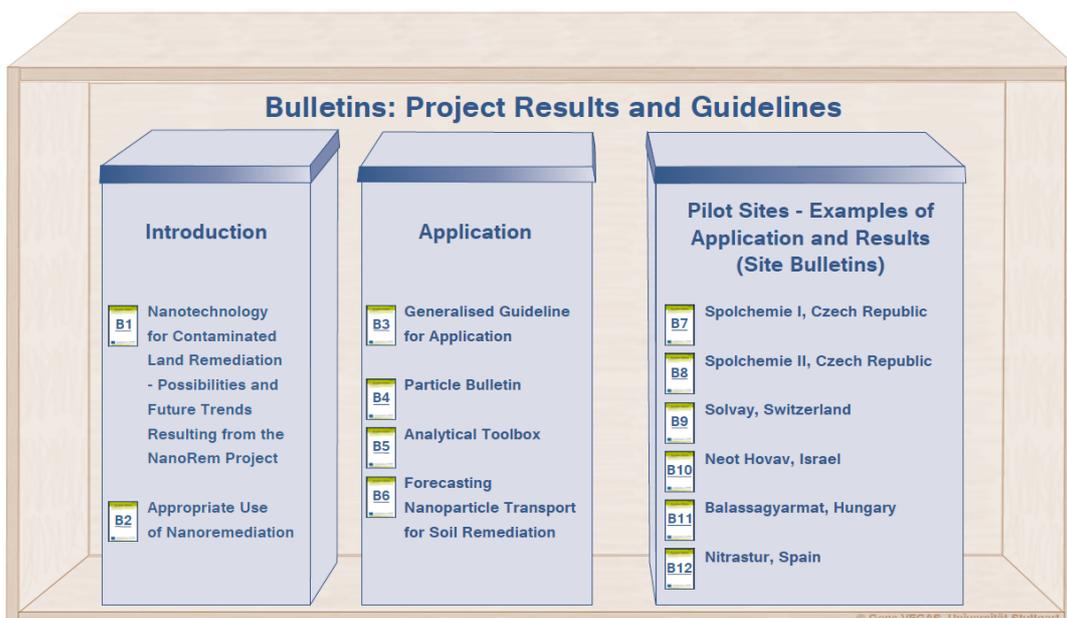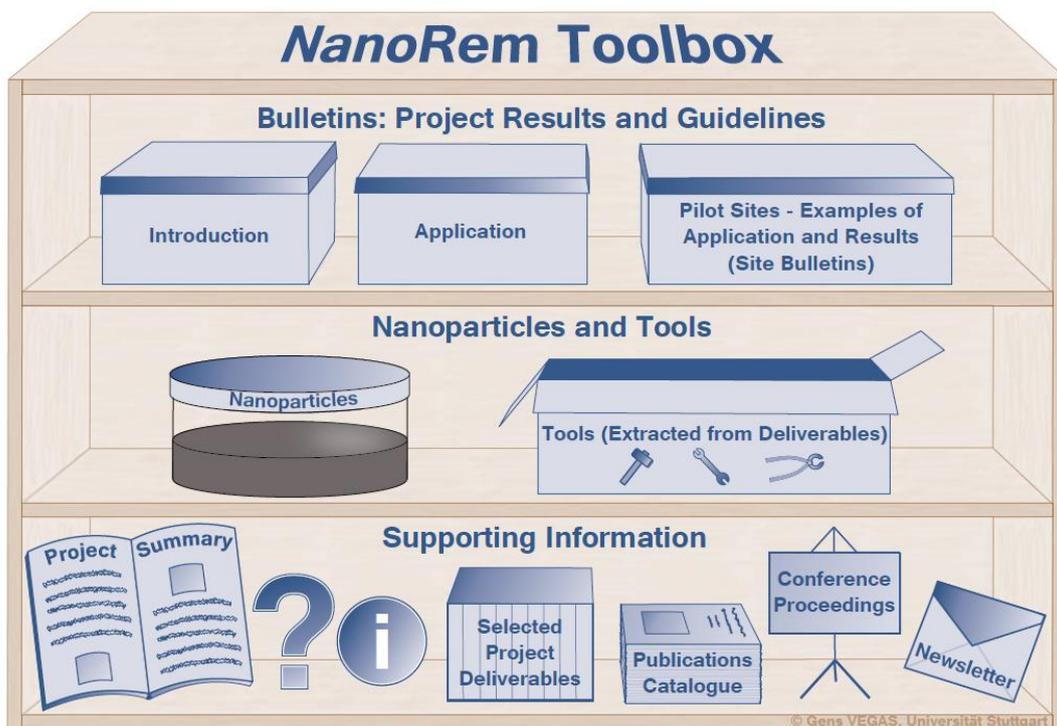
nZVI: design, performance and application possibilities – New Iron based nanoparticles for nanoremediation

Miroslav Černik[1], Kristyna Pešková[1], David Ribas[2,3], Vicenç Martí[2,3], Josep Antoni Benito[3], Jan Filip[4], Radek Zbořil[4], Melanie Auffan[5]

[1]Technical University of Liberec, Czech Republic
[2]CTM Technological Centre, Foundation Spain
[3]Technical University of Catalonia, Spain
[4]Palacký University, Czech Republic
[5]CNRS-CEREGE, France

NanoRem ("Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment") is a research project, funded through the European Commission's Seventh Framework Programme with the overall aim to support and develop the appropriate use of nanotechnology for contaminated land remediation and management in Europe. NanoRem focuses on facilitating the practical, economic and exploitable nanotechnologies for *in situ* remediation.

The objectives of the presentation is to provide an overview of the ZVI (zero-valent iron) nanoparticles developed, studied and produced during the project and their main characterization, physical and chemical properties, and application areas.

Various types of nZVI materials were available on the market prior the project start, but all had particular drawbacks. NZVI produced in water slurry is gradually oxidized due to its reaction with water, where the content of the active phase is significantly reduced in the product. Increased shipping costs (due to the presence of water in the product) and massive aggregation of nanoparticles are major problems that make the whole application significantly more expensive and less successful.

The development of an air-stable nZVI product with high nZVI content and suitable for additional post-processing surface modification was the main objective of the project in the nZVI material research part.

Types of nanoparticles

Two types of nZVI-particles were produced within the project, namely

- NANOFER STAR – Air-stable nZVI produced by solid-thermal reduction of iron oxide powder

- milled iron nanoparticles with an abrasive (alumina) – Abrasive Milling nZVI.

In the case of NANOFER STAR, the iron oxide shell stabilizes the surface of the nanoparticles and prevents their significant oxidation for a number of weeks. A combination of various parameters during synthesis (an appropriate mixture of N_2, Ar and O_2 gases, temperature and time) affects the resulting thickness of the iron oxide shell and, thus, the properties of the resulting product. The proportion of the magnetite/maghemite phase increases during the passivation process of the nZVI surface. The passivating oxide shell on the surface of the nanoparticles, studied by transmission

electron microscopy (TEM), has a thickness of ~4 nm to ~20 nm depending on the passivation conditions. The shell thickness influences the stability, reactivity, storage and also the agglomeration of the nanoparticles. A layer of 4 nm is adequate for most situations and preferred for the final product. When preparing the slurry, a selected organic surface modifier is incorporated into the solution (e.g. carboxymethylcellulose (CMC)) and the solution is dispersed in order to obtain a homogeneous suspension and break up agglomerated nanoparticles. The second step can be performed days or a week later on site. The produced suspension is then diluted to the final nZVI concentration (from 2 to 10 g/l) to be used for injection in the field for remediation.

Milled ZVI nanoparticles are produced in a two-stage top-down process. The basic raw material (Carbonyl Iron Powder, CIP-SM, BASF), a coarse, high purity granulated iron powder in the first stage is milled by a planetary ball mill (P-5, Fritsch, Germany) using hermetic steel vials. The second stage uses wet grinding with mono ethylene glycol (MEG) as the grinding liquid. MEG was chosen to prevent NP oxidation during the milling process (compared to water) and to eliminate the production of flaky-shaped nanostructures (compared to ethanol). Moreover, MEG is water miscible and it is degraded in a few weeks. The addition of alumina has a positive effect on particle milling by breaking down the iron flakes even more extensively and by this production of smaller particles. Additionally, alumina contributed to producing nanoiron particles from the abrasion of the grinding media. Finally, the fraction of particles under 1µm is almost 100%. This result was possible using a grinding media of 0.5 mm in diameter (iron balls) and an alumina concentration of 8.04g in 100ml.

The NPs were tested in the laboratory and their physical and chemical properties and reactivity were compared with commercially available NPs.

Particle characteristics

NANOFER STAR

The NANOFER STAR particles are predominantly composed of ZVI (~79%) with a minority of Wüstite (1-3%) and Magnetite (17%) compared to NANOFER 25S which has smaller amounts of oxides but surface modifier (sodium polyacrylate). The basic advantage is that NANOFER STAR particles can be stored on air in a dry form for a couple of weeks at least.

The pH was the first parameter to be analyzed, due to the fact that changes in the pH provide information about the aqueous oxidation of NP. As nZVI oxidizes to ferrous and/or ferric iron, the pH increases, hydrogen evolves, and oxidisable species are consumed (H^+). The initial pH of the prepared solutions of NANOFER STAR and standard NP supplied as a slurry (NANOFER 25S) were significantly different. While NANOFER 25S started at pH ~11, NANOFER STAR suspensions have a pH of ~8. During the seven days of the experiment, the pH values remained constant for the standard NP slurry (NANOFER 25S), while in the case of NANOFER STAR, after ~2 days it started to increase and continued up to 10. The largest pH changes for NANOFER STAR occurred during the first three days. This indicated that oxidation of NANOFER STAR took place for three days, while NANOFER 25S particles were more stable. Knowing that NANOFER STAR is designed to be more stable against oxidation, these pH data indicate that NANOFER 25S was already significantly oxidized (during storage), while NANOFER STAR NP were more metallic and sensitive to oxidation. This result also showed the fact that NANOFER STAR needed a significant time for it activation (about 2 days).

Therefore, after 2 days of aging, a TEM image was taken to see surface changes. The images suggest that the oxide layer became irregular in shape, and probably led to the formation of smaller nanoparticles. Energy dispersive X-ray spectroscopy (EDX) profile measurements for NANOFER 25S confirmed the presence of oxygen all along the trajectory line after two days. This means that even the core of the particles was oxidized. In the case of NANOFER STAR, the amount of oxygen along the trajectory line remained slightly greater at the edges after two days. However, after seven days the oxide surface layer also disappeared in NANOFER STAR with the EDX profiles indicating that the oxygen is homogeneously distributed.

Basic reactivity tests were performed with chlorinated ethenes (CE) and hexa-valent chromium. Results of tests with CE showed a significant improvement of NANOFER STAR reactivity after the 2-days activation process compared to non-activated NPs.
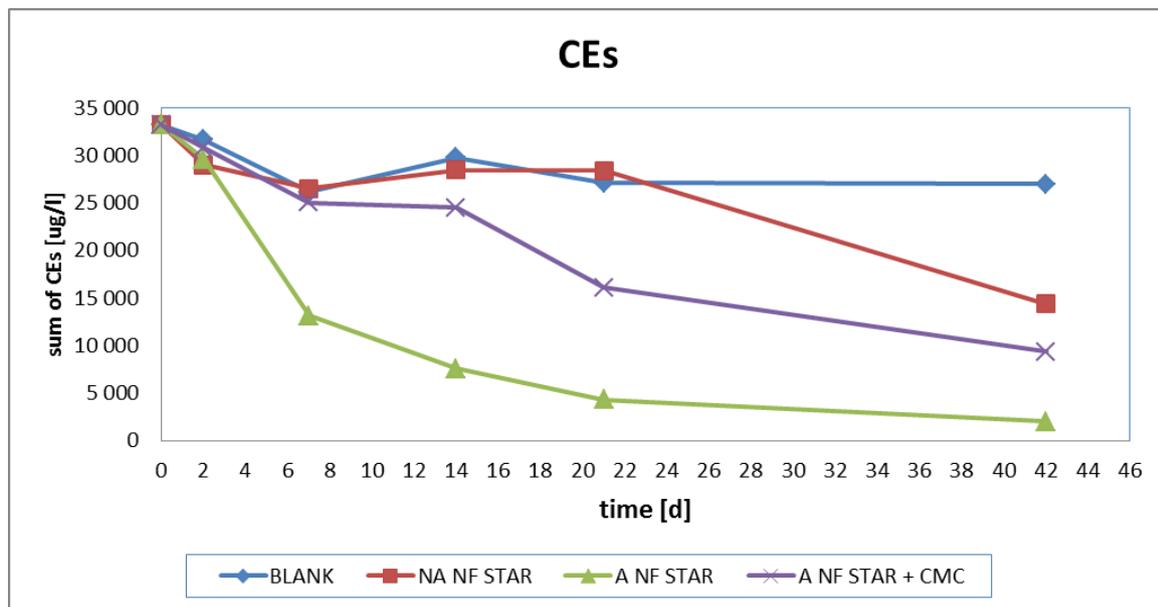

Fig 1: Comparison of the rate of CE degradation by freshly prepared NANOFER STAR (NA), activated NANOFER STAR (A) and activated NANOFER STAR additionally modified by CMC.

MILLED NANOPARTICLES

After a long period spent fine tuning the milling process, two different samples were selected for further characterization.

• NA 64, using a Ø 5mm ball composed of low carbon steel (AISI 1010) and an alumina concentration of 53.6 g/l, and

• NA 84, using a Ø 0.5mm ball composed of high carbon steel (0.80-1.20%) and an alumina concentration of 80.4 g/l.

The NPs milled with alumina were tested and their physical and chemical properties and reactivity were compared with commercially available NPs (NANOFER 25S, NANOFER STAR and milled A01).

Trichloroethylene (TCE) and Tetrachloroethylene (PCE) were selected as the representative contaminants of the CE family. Both contaminants were tested simultaneously at concentrations simulating a real site. It can be concluded that the performance of all nanoparticles is much higher

than commercially available NPs (NANOFER STAR, 25S and A01). The reactivity towards PCE is the most robust example of where nanoparticles can eliminate high concentrations of PCE with iron concentrations below 1g/l.
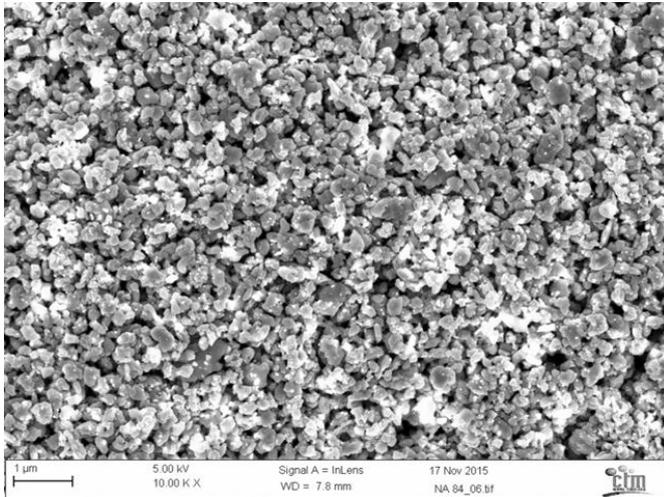
Fig 2:   Scanning electron microscope (SEM) picture of the sample NA 84.
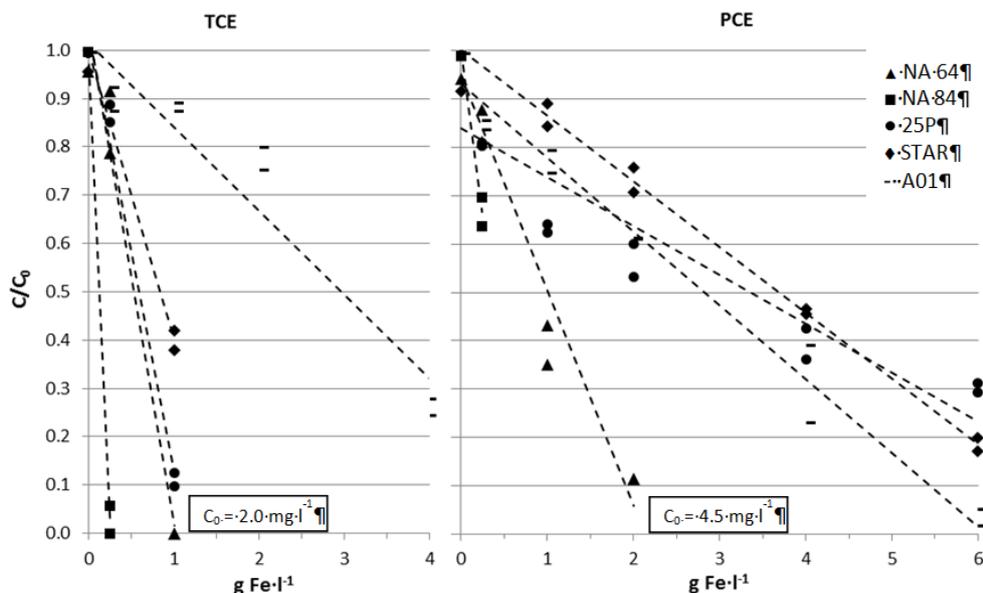
Fig 3:   Depletion curves of CEs for the produced nanoparticles NA 64, NA 84 and the commercial reference irons NANOFER 25P, NANOFER STAR and A01.

SUMMARY OF NP AVAILABLE

During the project existing types of NPs were tested, namely NANOFER 25 and 25S, which are produced as commercial products of the NANOIRON s.r.o. company and A01 as a product of the UVR-FIA GmbH. Additionally, a new type of dry nanoparticles NANOFER STAR was developed, tested and scaled up to industrial production (NANOIRON). Simultaneously, new types of milled particles based on milling with alumina were developed and tested. Both new products have better properties compared to the existing types (reactivity, stability, migration). The NP application field is for remediation of chlorinated ethenes, heavy metals and other chlorinated compounds, mainly.

non ZVI: design, performance and application possibilities

Katrin Mackenzie[1], Agnes Krok[2], Anett Georgi[1], Nimishi Joshi[3], Christine Herrmann[4],
and other WP3 participants

[1]Helmholtz Centre for Environmental Research Leipzig - UFZ, Germany, [2]University Duisburg-Essen, Germany,
[3]University of Manchester, UK, [4]VEGAS, University of Stuttgart, Germany

The goal of NanoRem was to support the wanted "step-change" in nanoremediation by adding new particle types with new target contaminants to the nanoremediation toolbox. Therefore, beside the classical iron nanoparticles (NPs), further non-ZVI and composite particle types were developed and tested in the project. These particles provide various modes of action, including adsorption of organic and inorganic contaminants, (catalytic) reduction and oxidation as well as biostimulation. Several of these new particles have the potential to add previously non-treatable contaminants to the portfolio of nanoremediation, such as dichloroethane, fuel oxygenates or selected pharmaceuticals and pesticides. The particles are in various development states: from laboratory status to ready-for-market; two of the particles - Nano-Goethite and Carbo-Iron® – were brought to field application.
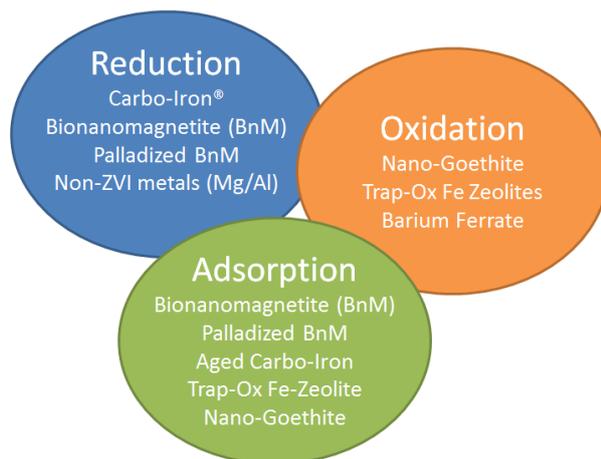

Fig 1: Overview of non-iron and composite particles allocated to three different reaction types

The main achievements for the non-ZVI and composite particles are:

— closing gaps in knowledge about these new particles
— supporting the targeted "step-change" in performance over existing solutions,
— largely to overcome the limited mobility of the NPs in use, and
— the extension of the operating windows for the nanoremediation toolbox by adding new particle types targeting new contaminants.

The practical use of nanoremediation has, up to now, been largely linked with the treatment of chlorinated solvents *in situ* and their selective transformation into less toxic, more biodegradable products. The non-ZVI and composite particles provide properties which allow new nanoremediation treatment options. The spectrum of chemically treatable groundwater pollutants are extended from the conventional nanoiron-based options to non-halogenated substances and non-reducible metal ions and covers reduction, oxidation and sorption strategies. Figure 1 assigns the developed particles to their main mode of action.

Overview of non-ZVI and composite particles, their performance and development state

NanoRem accomplished an extension of the "particle toolbox" of nanoremediation by adding reactive non-nZVI and composite particles which in turn also extend the spectrum of contaminants which can be targeted by nanoremediation. Figure 2 provides a small collection of the treatable substance classes.
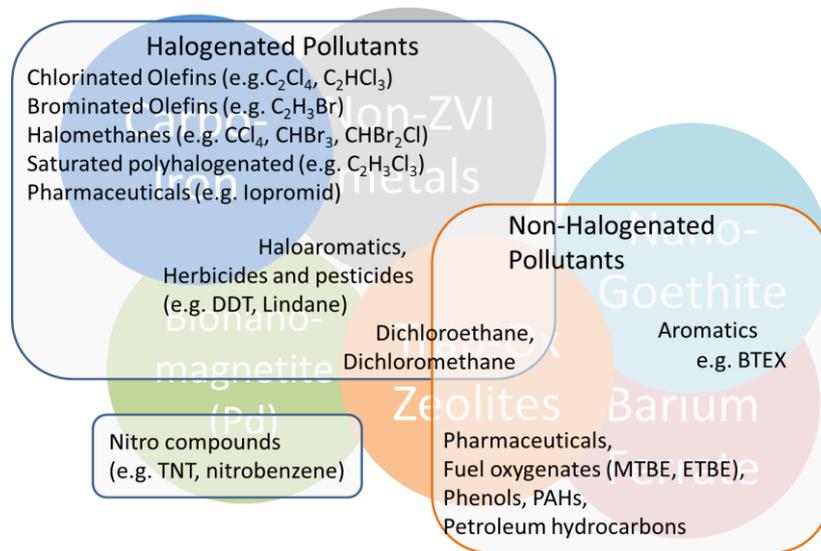
Fig 2: Selection of pollutants treatable by non-ZVI and composite particles

The following particle descriptions provide an overview of the single particles, their principle applicability and perspectives for nanoremediation approaches.

Carbo-Iron® is a composite of metallic iron embedded within colloidal activated carbon (AC) grains. As bare iron, Carbo-Iron can reduce a broad range of halogenated hydrocarbons and is able to reduce/precipitate metals and metalloids. Carbo-Iron is also an iron-based reagent, where several properties are simply the same as we know from iron. However, in the research process leading to the development of Carbo-Iron we tried to learn what would have to be changed in order to reach a better performance. Embedding the iron in the carbon framework, the carrier not only acts as spacer between the nanoiron structures helping to suppress the particle agglomeration tendency and to increase the subsurface mobility, it also transfers material properties from the AC to the composite. The close neighbourhood of the iron to AC enables the enrichment of pollutants at the iron and extends the retention time at the reaction sites. This affects a suppression of the generation of partial reduction products. Figure 2 gives an impression of the application area of Carbo-Iron (darker blue zone) with the focus on its reduction properties. The long-term support of microbial processes after its application at a PCE field site (prior to NanoRem) was observed.[1] Carbo-Iron functions after its reaction phase still as a strong adsorber for hydrophobic pollutants. Its use for the generation of sorption barriers for control of pollutants with high hydrophobicity (e.g. PCBs, PHAs…) is discussed. Carbo-Iron particles are at the development state "*tested in the field and ready-for market*".

Nano-iron oxide particles of the nano-goethite type are well-suited for stimulation of bioremediation of hydrocarbon-contaminated groundwater. By iron-reduction, oxidation of organic pollutants such as BTEX aromatics is accomplished.[2] Up to now, the UDE iron oxide nano-goethite is the only nanoparticle suspension for this application which: shows superior transport properties in the lab for a range of sediments, has been successfully injected at field sites, has shown no renegade mobility, has proven a high potential for the bioremediation of BTEX contaminations with a sustained, rebound-free reaction, is available at industrial quantities and is largely non-toxic. Additionally, Nano-iron oxide was successfully tested as adsorbent for heavy metals, in particular towards As and Cu. Nano-iron oxide particles are at the development state "*tested in the field and ready-for market*".

Bionanomagnetite and Palladized Bionanomagnetite are biogenerated magnetic nanoparticles which show enhanced reduction properties. Bionanomagnetite (Bnm) is especially suited for adsorption of metals and metalloids. In addition, it shows magnetic properties and a high resistance to inhospitable aquifer conditions (e.g. strongly alkaline pH where other methods fail).[3] Bnm is able to efficiently reduce Cr(VI). In lab-scale experiments, addition of Bnm (5 wt%) to chromite ore processing residue (COPR) from a site in Glasgow, UK, was shown to immobilize the readily leachable Cr(VI) by reducing it to Cr(III). Bnm reduced a significant fraction of mineral bound Cr(VI), forming a product that was recalcitrant to air re-oxidation. With respect to organic contaminants Bnm was shown to reduce nitroaromatics and azo dyes to the corresponding amines. Bnm also proved suitable against nuclear contaminants such as Tc(VII) and Np(V) which are reduced very efficiently to Tc(IV) and Np(IV), respectively. The reactivity of Bnm is driven by Fe^{2+} (ferrous) in the chemical structure (and reactive surface) which is subsequently oxidized to ferric (Fe^{3+}) during the reduction of contaminants. This exhausts the reduction potential of Bnm for remediation applications. With the addition of palladium to Bnm catalytically active particles were generated, which could facilitate continual reactivity and reduce substrates in the presence of external electron donors such as hydrogen and formate ions. Doping bionanomagnetite with Pd generates potent hydrogenation and hydrodehalogenation catalysts which open up an extended target pollutant spectrum, including a wide variety of halogenated organics. Biomagnetite-based nanoparticles can be produced at larger scale using naturally occurring bacteria and waste iron materials to reduce costs and environmental impact. Their development state is "*ready for field testing*".

Trap-Ox Fe-Zeolites are a particle family tailored for *in-situ trapping and catalytic oxidation* of organic contaminants. Trap-Ox Fe-Zeolites provide excellent sorption properties for small organic substances (MTBE, BTEX, DCA and others) and can be used as sorption barrier. Fe-zeolites tailored for high adsorption affinity (e.g. Fe-MFI120) beat activated carbon with respect to adsorption of small contaminant molecules such as MTBE. Fe-zeolites are a powerful tool for *in situ* chemical oxidation (ISCO) operating at near-neutral conditions and combine the high sorption ability for pollutants (trap) with their efficient oxidation (ox). Fe-zeolites catalytically generate OH-radicals from H_2O_2 for fast mineralization of recalcitrant pollutants such as fuel oxygenates (e.g. MTBE), BTEX or even reduction-resistant halogenated substances (e.g. dichloroethane).[4] For optimal suspension stability and transport within porous media, Trap-Ox Fe-zeolites form stable suspensions under slightly alkaline conditions (pH 8 to 9) even at high particle concentrations (10 g L^{-1}) in synthetic groundwater and without the need of additional stabilizers. Based on lab-scale column experiments Trap-Ox Fe-zeolites show high mobility in porous media and can be re-used after deposition on sediment for several cycles of contaminant adsorption and intermittent oxidation after adding H_2O_2. The optimal Trap-Ox Fe-zeolite for a certain contamination case is selected based on contaminant and site conditions. Trap-Ox Fe-BEA35 successfully catalysed contaminant oxidation also under adverse conditions (very hard synthetic groundwater, pH 8.5). In addition, a fluorescence labelling approach was developed for particle tracking. Trap-Ox Fe-zeolite particles are at the development state "*ready for field testing*".

As ***non-ZVI metals*** magnesium and aluminium particles were selected since they show iron-like reaction potential and have a much lower material density which is identified as one of the crucial properties for subsurface transport. Reactivity towards the main target contaminant PCE was investigated under flow-through conditions (column experiments). The results indicate that PCE

degradation could be improved by using mechanically activated Al particles (by ball milling them together with Al_2O_3 or Si prior to use). Al/Mg metal alloy particles also showed a higher PCE degradation compared to pure Al and Mg particles. For Al/Mg metal alloy particles only traces of TCE (equivalent to << 1% transformation of PCE to TCE) and DCE were found, but no vinyl chloride. Ethene and ethane were detected as final degradation products. Combining magnesium, aluminium or silicon with iron to *iron alloys* could possibly merge the properties of the elements and extend the range of contaminants that can be treated. Especially a combination of iron and aluminium prepared by mechanically alloying the metals showed promising results and will be further investigated. A special product named NanoFerAl has been patented (petty patent). The development state of non-ZVI metals and alloys is *"lab-scale test"*.

Barium ferrate is an example of a ferrate 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. The past decade showed a significant increase in publications about the use of ferrate(VI) for "super-iron" batteries or wastewater treatment. Studies for the best preparation procedure of $BaFeO_4$ focussed on an electrochemical synthesis route. The oxidation of BTEX contaminants has been investigated using toluene as model contaminant. However, toluene degradation is favoured under strong acidic conditions, which is considered to be of limited practical relevance. Therefore, current experiments are focusing on the use of $BaFeO_4$ for stimulating microbial degradation of 4-nitrotoluene (by providing an electron acceptor). The development state of the particles is *"lab-scale test"*.

Conclusions

The performance of the newly developed non-ZVI and composite particles shows their potential for a broader future utilization of the nanoremediation technology. Two of the particles are currently commercialized (Carbo-Iron and Nano-iron oxide); the Trap-Ox Fe-Zeolites and Bionanomagnetite particles are ready for first field tests. Even though this will not be accomplished within the project, NanoRem was the trigger for their development and concurrent testing with established particle systems showing their high potential.

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Subsurface nanoparticle transport

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Transport of nanoparticles in saturated porous media is of substantial interest for nanoremediation of groundwater. Understanding the transport of nanoparticles is essential for predicting the deliverability and fate of nanoparticles which are envisioned to be injected into contaminated aquifers.

Transport of colloids (including engineered nanoparticles) in the subsurface under saturated flow conditions and constant solution composition can be described by particle advection, hydrodynamic dispersion and deposition/filtration (Chen et al., 2001). The first step, transport of colloidal particles from the pore fluid to the vicinity of a collector grain, is typically described by three mechanisms: interception, gravitational sedimentation and Brownian diffusion (Tufenkji and Elimelech, 2004). The transport is usually quantified by the single collector contact efficiency (η_0), which reflects the frequency of particle collisions with the collector surface. The second step, attachment to the collector surface, is directly related to the interaction energy between the particle and the collector surfaces. The attachment is typically quantified by the attachment efficiency (α), which represents the fraction of the collisions that lead to successful particle attachment. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Elimelech et al., 1995), which includes the sum of the electrostatic interactions and van der Waals interactions, is commonly used to qualitatively analyze the particle-collector interaction.

Nanoparticle emplacement into contaminated aquifers is strongly influenced by the injection technique and injection velocity as well as the texture of the underlying aquifer. Important geochemical factors controlling deposition and release kinetics of nanoparticles in natural porous media (collector) are the charge of mineral surfaces within the porous media and surfaces of nanoparticles (including surface charge heterogeneity), as well as the type and concentration of solutes in groundwater. Surface charge is especially influenced by the solution pH and the presence of specifically adsorbing ions, such as Ca^{2+} and humic substances (Kretzschmar and Sticher, 1998). Other properties of nanoparticles (such as particle composition, size and shape) and the properties of the particle suspension (including particle concentration, type and concentration of particle stabilizers and rheological properties) also influence deposition and release kinetics of nanoparticles.

Within the NanoRem project, transport of nanoparticles in the subsurface was investigated at different scales; from small-scale water saturated sand-packed columns up to large-scale containers and flumes. Laboratory column tests with NANOFER 25S, NANOFER STAR, FerMEG12 (milled zero valent iron), Carbo-Iron®, Trap-Ox Fe-zeolites, Bionanomagnetite and Nano-Goethite were performed in Work Package 4 "Mobility and Fate of Nanoparticles". Tests were carried out at various chemical and physical conditions in order to account for the inherent aquifer heterogeneities. The experimental transport data were analyzed and modeled using colloid filtration theory, in order to derive parameters such as single collector efficiency and attachment efficiency (Tufenkji and Elimelech, 2004). These parameters serve as input parameters for upscaling and prediction of travel distance applying numerical modeling: one-dimensional models, for homogeneous and isotropic porous media and three-dimensional models, for heterogeneous porous media. In addition to

one-dimensional column experiments, cascades of interdependent, one-dimensional column experiments were applied to account for the radial distribution of nanoparticles in the subsurface upon the injection, as well as for the changes in injection pressure (Comba and Braun, 2012). This approach is applied to select suitable injection parameters (such as flow rate of the field pump, radius of influence and concentration of a particle stabilizer) for a given porous medium. The results served well to select the composition of nanoparticle suspension with an optimal transport for field application, to predict its radial transport distance, as well as to predict the variation of the injection pressure.

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Large scale experiments: performance, upscaling and lessons learned for application in the field

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In the frame of the NanoRem project, investigations on nano-sized particles (NPs) mobility and reactivity have been undertaken at various scales including in large scale containers with volumes of over 240 m³. Large scale upscaling investigations are indoor experiments at a field relevant scale with exactly controlled initial and boundary conditions and a highly disaggregated monitoring grid. They allow for a closed mass balance, exact and dense monitoring of contaminants and particles mobility and reactivity. The goals of the investigations were to transfer the results of small 1D or 2D lab experiments on particle performance to 3D large scale experiments (LSE) and to apply the LSE techniques and results to improve field injections. Specific goals of the large experiment were to design, set-up and test optimal injection systems for different NPs, to quantify transport distance and NP distribution in the porous media as well as contaminant treatment efficiency and longevity of NPs.

To achieve these goals, three LSEs were conducted using three different particle types:

- Large scale flume experiments, LSF 1 to test nano-ZVI (nZVI) particles (NANOFER STAR) and LSF2 to test composite nZVI particles (Carbo-Iron®) for the remediation of a chlorinated hydrocarbon (CHC) source in a saturated aquifer
- Large scale container experiment (LSC) to test application of iron-oxides Goethite particles for the removal of a BTEX plume.

1) Large scale flume experiments to remove a CHC source

Aquifer and Contaminant Source Zone: Large scale injection tests were performed in an artificial aquifer in a large flume (each L x W x H = 6 x 1 x 3 m) with a saturated thickness of 1.7 m and a corresponding unsaturated zone of 1.3 m (Figure 1). The aquifer was unconfined with a homogeneous hydraulic conductivity of $K = 4 \times 10^{-4}$ m/s. 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.

Each aquifer was contaminated with 2 kg of free phase of perchloroethene (PCE), establishing a contaminant source zone in the middle of the aquifer where PCE remained trapped as residual phase with an average PCE saturation of approx. 0.6 % (Figure 1). The cylindrical source zone has a radial extension of approximately 0.45 m and a height of 1 m, resulting in a volume of approx. 0.64 m³ with a corresponding pore volume of 0.21 m³.
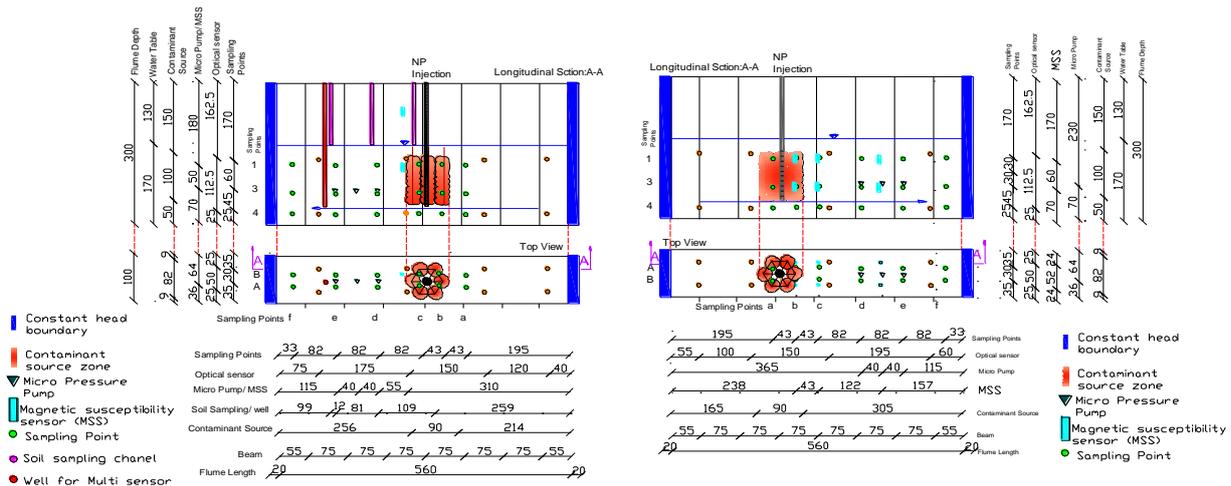
Fig 1:   Schematic image of LSFs

NP Injection was designed to achieve a radius of transport (ROT) for NP of r = 0.5 m throughout the source zone and to deposit at least m = 2.6 kg of nZVI (based on stoichiometry to degrade 2.0 kg of PCE) within the source zone. To allow for competitive reaction in the aquifer and inhomogeneous particle emplacement 10 kg of NANOFER STAR and 14 kg (around 3.5 kg nZVI content) of Carbo-Iron® were injected at the respective experiments.

In order to test the performance of nZVI particles (NANOFER STAR produced by NANOIRON) and of composite nZVI particles (Carbo-Iron® produced by UFZ) colloidal suspension containing these particles and stabilizers were injected in the middle of the contaminant source zone. A total of 1 m³ of suspensions for nZVI particles and 0.7 m³ for composite nZVI particles were injected using a dispersion-circulation-injection system to keep the suspension dispersed before and during the injection. The injection conditions applied for the different particles are summarized in Table 1.

Tab 1:   NP injection conditions for two LSF experiments

	LSF 1	LSF 2	LSC
	nZVI (NANOFER STAR)	Composite nZVI (Carbo-Iron®)	Fe-oxides NP (Goethite)
Injection Method	Sequential injection at 5 different depths	Intermittent injections at one injection depth	One injection with gravity injection in injection well
Injection Rod	Direct push rod with 1" ID with 4 small injection nozzles	Injection well with $1\frac{1}{4}$" ID and 1m filter screen	Injection well with 4" ID and 2.2 m filter screen
Injection position	In the middle of the source zone	In the middle of the source zone	In expected pathway of the plume
Injection Depth	5 depths (from 1.7 to 2.3 bgl at 0.15 m interval)	As source zone (from 1.5 to 2.5 bgl)	As expected plume height (from 0.8 to 3.0 m bgl)
Vol.$_{Injection}$	(5 x 0.2 m³) total 1 m³	(2 x 0.35 m³) total 0.7 m³	6 m³
Mass$_{NP}$	10 kg	14 kg (Fe mass ~ 3.5 kg)	120 kg
C$_{NP}$	10 g/L	20 g/L	20 g/L
Stabiliser	5 g/L of CMC	1 and 2 g/L of CMC	Humic substances
Q$_{injection}$	0.5 m³/h	0.22 and 0.15 m³/h	0.7 m³/h
Max. P$_{injection}$	2.9 bar	0.7 and 1.7 bar	Water table rise 0.75 m

NP Mobility Result: During the injection of NANOFER STAR particle transport was monitored by 12 magnetic susceptibility sensors (MSS). Based on the monitoring result, most of the particles were transported almost uniformly more than 0.38 m, a small amount of particles traveled further to reach 1.44 m. As a result, a reactive zone was established with a distribution of particles extending over the whole contaminant source zone.

After the Carbo-Iron® injection, particle concentration distribution in the aquifer was monitored at all sampling ports by measuring concentration of solid mass in the sample solutions (c_{solid}) (Figure 2). From the monitoring result, most of the particles were transported to the downstream and upper sampling level. In the upper sampling plane c_{solid} were at about 1.5 times the concentrations of the lower sampling planes. Thus, Carbo-Iron® particles were transported more than 0.5 m. However, the distribution was not uniform: the upper reaches of the aquifer received higher Carbo-Iron® masses.
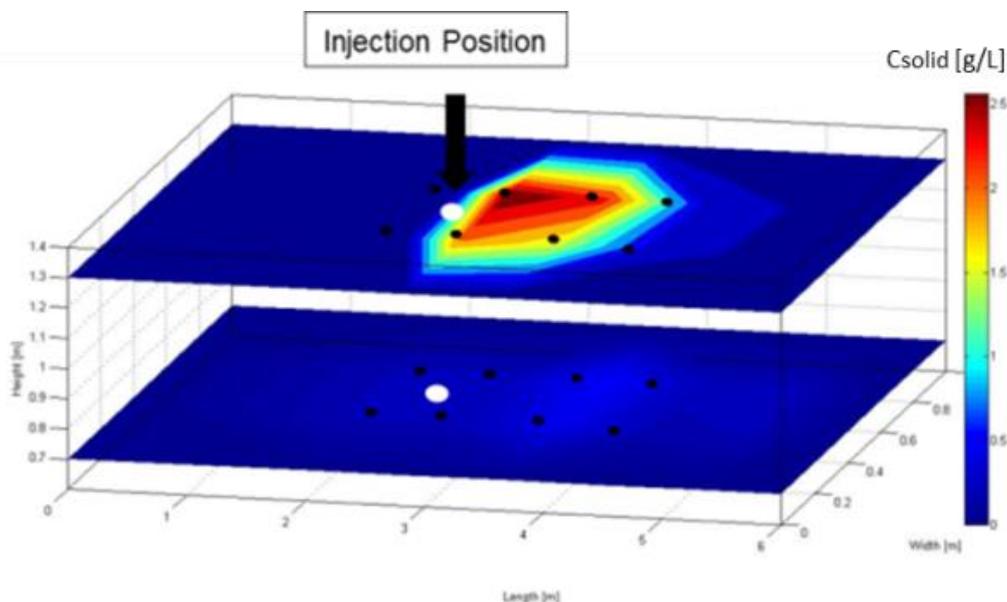
Fig 2: Carbo-Iron® distribution after the injection in the aquifer

NP Reactivity Result: The total NP performance on contaminant treatments in the aquifers were evaluated by the mass flux of contaminant (dissolved PCE) and chloride (Cl⁻) in the outlet (Figure 3). In both flumes a reduction of PCE to about half of the initial mass flux was observed immediately after the particle injection. Production of degradation products Cl⁻, ethene and ethane were also observed immediately after the injection. In the LSF of the carbo-Iron®, after 100 days the concentrations of all degradation products had reached almost 0, in other words the active nZVI particles were depleted after 100 days. However, this did not yield an increase of PCE mass flux due to the adsorption of PCE on the activated carbon. In the LSF for NANOFER STAR particles, the PCE degradation is still in progress. Therefore, Figure 3 shows preliminary result only.

Based on the produced mass of Cl⁻, the NANOFER STAR particles had degraded m = 190.3 g of PCE after 90 days, Carbo-Iron® particles had degraded m = 122.2 g of PCE after 120 days.

NANOFER STAR
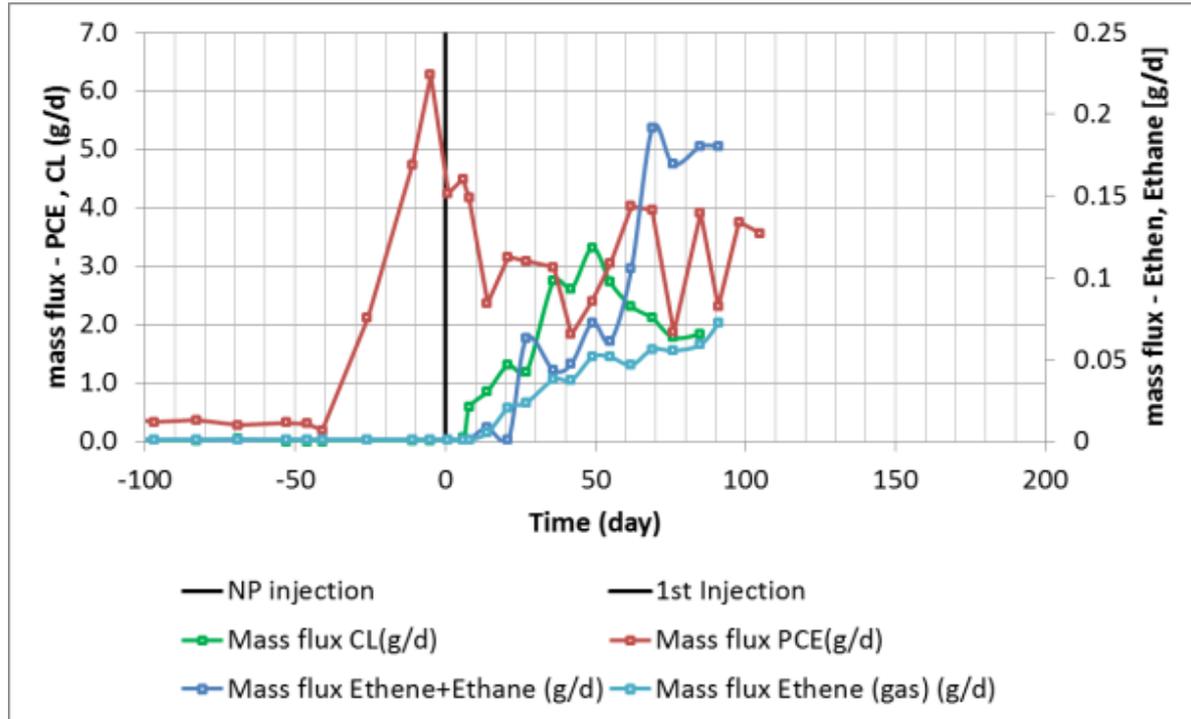
Carbo-Iron®

Fig 3:   Mass flux of contaminant and degradation products at the outflow boundary of LSFs

2) Large scale container experiment to remove a BTEX plume

Aquifer and Contaminant Plume: A field scale injection test was performed in an artificial aquifer 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. The aquifer is an unconfined heterogeneous sandy aquifer consisting of randomly distributed high and low permeability zones (K = 4 x 10^{-3} and K = 4 x 10^{-4} m/s respectively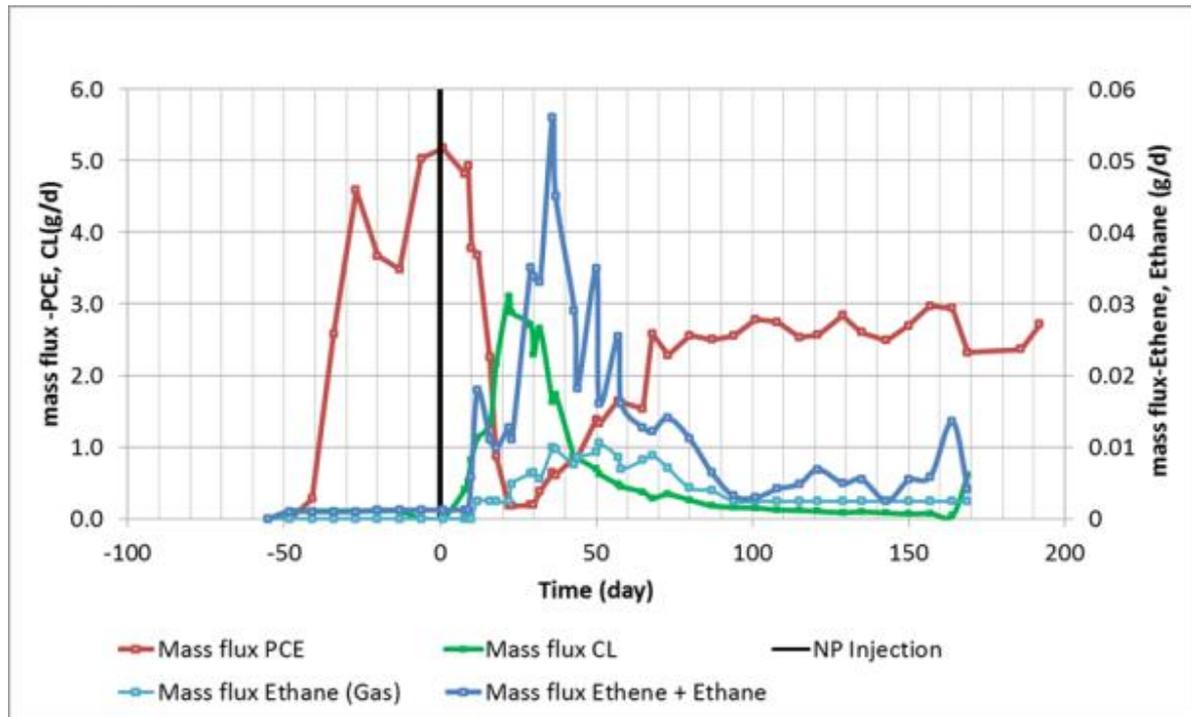) (Figure 4). Ground water flow is controlled by constant head boundaries resulting in an average seepage velocity of v = 4.86 x 10^{-6} m/s = 0.4 m/d. The aquifer was contaminated by a toluene plume (c_{tolu} = 60 mg/L) injected with the base flow. At the inflow plane the plume had an area of 2 x 2 m (4 m²) perpendicular to the direction of flow. The upper boundary of the plume was identical with the groundwater level and the plume extended over 2 layers of heterogeneous "aquifer blocks". To achieve these conditions, a high concentration toluene solution (c_{tolu} ~400 mg/L) was injected into the 4 inflow wells positioned at the center of 12 wells with mass flux of 1.60 g/h continuously then mixed with water inside of these wells to make a c_{tolu} ~ 60 mg/L solution which was transported by base flow along the whole aquifer length.

The Goethite NP Injection was designed to achieve the following criteria: a) Radius of transport (ROT) of NP was to be 1.5 m along the whole 2 m screened well section to establish a cylindrical reactive zone of V ~ 15 m³ with a corresponding pore volume of PV ~ 6m³ to intercept the whole cross-section area of the plume, b): Injected NP mass was to last for six months: For the given boundary conditions the mass flux of toluene was approx. 33.6 g/d = 6.15 kg for 182 days. Thus m = 120 kg Goethite NP were injected (see Table 1 for details) in 6 m³ of suspension.

NP Mobility result: After recovery of the water table, the final distribution of the particles was confirmed by sampling at all sampling ports. These samples were analysed by optical observation (intensity of colour) in the liquid samples. The range of the colour was ranked from 0 to 4 (4 being the darkest and corresponding to highest particle concentration) and plotted. As the plot shows, in the upper reaches of the aquifer (level 2, 3 and 4) sufficient concentration of NP was observed at a distance of 1.5 m from the injection well. At lower levels (5 and 6), very little NP were observed during the injection. However, 24 h after the injection had stopped a relatively high NP concentration was observed indicating some mobility. The maximum transport distance at level 6 was confirmed at 4.3 m from the injection well. No particles were detected in the outflow of the tank, thus confirming that all NP could be placed within and in the vicinity of the injection zone (Figure 5).

NP Reactivity Result: The evaluation of NP reactivity cannot be concluded yet, because the measurements of the reaction by NPs are still in progress.
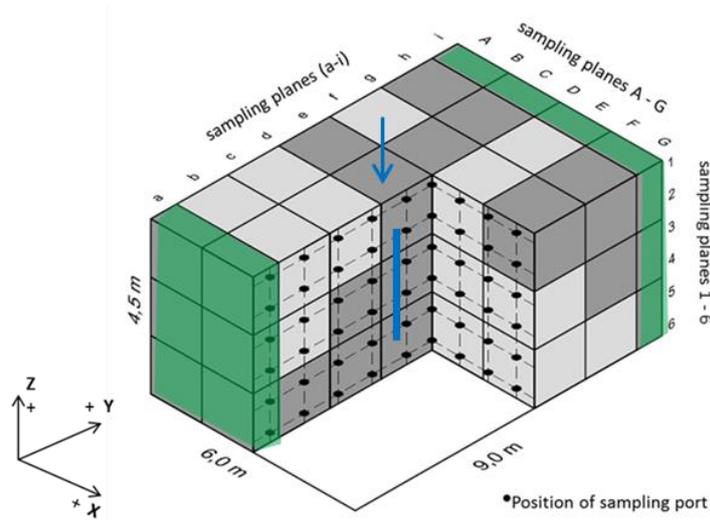
Fig 4: Schematic image of soil layers and sampling ports distribution in the LSC (light grey is high permeability, dark grey is low permeability zone, green coloured zones are constant head boundaries), blue thick line indicates the position of the injection well
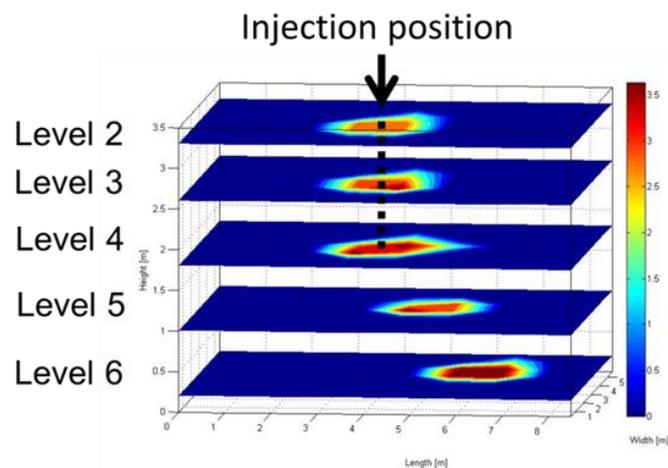
Fig 5: Goethite particle distribution

Conclusion

Different injection techniques, as shown in table 1, have to be used and optimized for different NP suspensions. Three large scale investigations showed that, given the right injection technology and the proper use of stabilizers, transport goals for all particles could be achieved. Uncontrolled movement of NPs (renegades) was not detected.

A detailed study of particle transport behavior of 3D large scale injections was realized and insight of contaminant degradation due to NPs in aquifer were revealed by the large scale experiments, which will be discussed in the presentation.

Nanoremediation - a consultant's perspective

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The synthesis and use of zero-valent iron nanoparticles (hereinafter also referred to as NPs) for contaminated groundwater remediation was studied within the project NanoRem. This technology is now considered as a promising innovative method for in-situ removal or stabilization of chlorinated hydrocarbons, selected inorganic anions, heavy metals and others. The effectiveness of this method depends on the geological and hydrogeological conditions, which affect both the reactivity of the nanoparticles with the contaminants and their migration in groundwater. In the case of low permeability, the migration of nanoparticles is very limited and the efficiency of the method may therefore be reduced.

The main competing in situ remediation alternatives to nanoremediation for these contaminants are *in situ* biological reduction (ISBR) and conventional forms of *in situ* chemical reduction (ISCR) using reducing agents such as micro zero valent iron (μZVI) or sodium dithionite. Nanoremediation does not achieve the same levels of uptake as these remediation methods. This is as probably related to five broad barriers, two of which are inter-related, i.e. (1) a prevailing public unease about the environmental release of NPs and (2) regulatory concerns that engineered particles released as an environmental technology may have unforeseen impacts on water and the environment. (3) In addition, effective deployment of the technology proved to be more complex and was perceived to be associated with (4) higher input costs. (5) The fifth barrier is a lack of well-regarded demosite reports.

Conventionally, ISCR and ISBR (In-Situ Chemical and Biological Reduction) are primarily pathway (plume) management interventions with a limited scope for addressing source contaminants. They have a limited effectiveness against several important contaminants such as fuel oxygenates, fluoridated organics and various other recalcitrants, they may cause modifications to aquifer properties that render them unacceptable under certain circumstances, and ISBR may also be subject to process stall.

The NanoRem project clarified the benefits of nanoremediation and provided a strong scientific basis for addressing concerns such as potential ecological and aquifer impacts. The NanoRem project also facilitated the production and demonstration of the feasibility and use of several different types of nanomaterials under different legal conditions within EU and non-EU countries (e.g. Israel and Switzerland).

Based on NanoRem's work the main selling points for nZVI based nanoremediation are identified as:

- Increasing regulatory confidence, facilitated by NanoRem via the introduction of NPs in several countries
- Broad source and pathway management applications
- Rapid effectiveness compared with ISBR and ISCR, tends to complete degradation (e.g. of NAPLs)

- Resilient to conditions inhibitory to ISBR and can facilitate ISBR / Synergistic with ISBR and ISCR

- Portable and more rapidly deployed compared to options like pump and treat

- Reduced risk of taint of sensitive aquifers

- Ecological and aquifer impacts now relatively well understood compared to ISCR and ISBR

- Rapid initiation of treatment by nZVI can also support faster initiation of ISBR.

However, two substantial market barriers remain: high costs for production, and a limited range of application. From this point of view major cost drivers were identified: pre-remedial site investigation costs, material costs, operation costs and monitoring costs. Pre-remedial investigation and monitoring costs are the same for all of the discussed processes. Material and operation costs of nanoremediation may still be optimized if the process efficiency is increased (increased material longevity, lower material demand and therefore less site interventions needed).

All of these points are addressed by combined remediation approaches. These effects (reduced price and increased efficiency) are achieved if nanoremediation is combined with biological or physical and chemical processes. Two of these approaches have recently been developed and demonstrated at various sites: nZVI enhanced bioremediation and electrochemically enhanced nanoremediation.

The use of nZVI has been identified as a stimulatory for ISBR, and supports the completion of previously known potential stall points for ISBR. In the case of chlorinated ethenes, the use of nZVI may prevent the appearance of high mass of slowly degradable byproducts of degradation (like cis-DCE). In addition, this combined process may be deployed in areas with high concentrations (e.g. near source zones). The emplacement of nZVI at the right spot (identified by detailed site investigations) increases the process efficiency, shortens the remediation time, and proves to be more cost effective.

Similar synergies are exploited in commercial reagents for ISCR using microscale ZVI, but NPs are more rapidly effective. Electrochemical enhancement (DC) may be used in the case of chemical reduction processes. DC enhanced nanoremediation (INR-DC) directly addresses the cost barrier and also has a broader range of treatable issues, in particular in dealing with contaminant source management, where large volumes of contaminant may otherwise rapidly exhaust any deployed of NPs. The application of nanoparticles with the support of a DC electric field at a low intensity leads to a significant increase in the total efficiency of this remedial method. This new method was first confirmed in the laboratory (2009), and subsequently during long-term monitoring at the Horice site (Czech Republic (2010)). The first field experiments were conducted on a test polygon with three cathodes and anodes. The results of these experiments showed a significant improvement in the efficiency of this method compared with the simple use of nanoiron. The pilot system was subjsequently extended to 9 test polygons, which sufficiently covered all of the existing contamination hotspots at the site. Within 3 years of running the enhanced remediation system, the site was remedial targets were met. The method was also successfully implemented within a different environment at the Spolchemie site (Czech Republic). The method was used at this site to establish a geochemical barrier in order to limit the outflow of contaminant from the site.

Hence, the additional main selling points for combined processes (based on the NanoRem project results) are that:

- They can deliver the benefits of nanoremediation for the same price as bioremediation; by using patented electrochemical/kinetic approaches, to extend the lifetime and effectiveness of the applied NPs. They can ensure the accurate deployment of NPs by targeting their migration.

- They can provide reassurance that there is no off target migration or "renegade" iron NPs.

- They are based on the deployment of patented air-stable nZVI (NANOFER STAR). But also microscale ZVI (nanocomposites, patent pending) will be employed as it provides a more flexible deployment and shows a much longer reactivity than nZVI.

- Deployment systems make use of standard components and units (e.g. Geoprobe for direct injection.

The NanoRem project has also clarified the benefits of nanoremediation (see Table 1).

Tab 1:   Benchmarking costs, risks and benefits of nanoremediation against ISBR and ISCR3

		Nanoremediation	ISCR	ISBR
Risks	**Human health**	No exposure once successfully deployed. Some NPs are hazardous, some are air stable and safer to handle.	No exposure once successfully deployed. Some reagents, such as dithionate, are potentially hazardous.	No exposure once successfully deployed. Materials are safe to handle.
	Aquifer ecology	Injections are typically in highly disturbed environments. No NP specific ecotoxicity found by NanoRem. Ultimate fate is as iron oxides which are plentiful in soils.	Injections are typically in highly disturbed environments. Ecological impacts unstudied, but assumed minimal.	Injections are typically in highly disturbed environments. Ecological impacts unstudied, but in the long terms assumed minimal[4].
	Water	Injected materials have limited lifetimes and limited travel distance, and are not associated with taint of the subsurface	Lifetimes and travel distance of injected dithionite has not been widely studied, may be extensive. The travel distance of mZVI is essentially zero. High levels of sulphate and low pH remaining after dithionate reduction	Injected substrates to stimulate bioremediation are soluble or release soluble substrates possibly causing taint for water supplies[5].
	Supporting measures	Pre-deployment risk assessment available and published.	No pre-deployment risk assessment tool.	No pre-deployment risk assessment tool.
Benefits	**Breadth of solutions**	Wide range of treatable contaminants. Source term and pathway management applications. Suitable for situations inhibitory to microbial dehalorespiration processes.	Wide range of treatable contaminants. Tendency to pathway management applications. Suitable for situations inhibitory to microbial dehalorespiration processes	More restricted range of treatable contaminants. Potential for stall (e.g. TCE --> DCE) Tendency to pathway management applications. May be prevented by toxic or other inhibitory conditions

[3] NanoRem DL9.2 and Bardos, Nathanail, et al. (2007) (see above)
[4] Note ISBR is mediated by deliberate modification of aquifer ecology to stimulate dehalorespiration.
[5] This concern has led regulators in some regions to prevent ISBR deployment in some cases, e.g. at the Písečná site, CZ

		Nanoremediation	ISCR	ISBR
	Speed and completeness of action and synergies	Rapid treatment effects owing to nanoscale processes. Moderate migration in the subsurface. Tendency to complete degradation of contaminants. Synergistic with ISBR and ISCR.	Slower treatment effects. Microscale ZVI does not readily move in the subsurface. Tendency to complete degradation of contaminants. Synergistic with ISBR and nanoremediation	Slower treatment effects. Soluble substrates migrate rapidly in the subsurface Tendency to stall for some problems[6]. Synergistic with nanoremediation and ISCR.
	Ease of deployment	Portable systems (not requiring fixed infrastructure). Some systems require specialised deployment interventions. NanoRem is addressing the issue that deployment knowhow not widespread[7].	Portable systems (not requiring fixed infrastructure). Widespread know-how and systems.	Portable systems (not requiring fixed infrastructure). Widespread know-how and systems.
	Track record	Limited track record, relatively few suppliers.	Well established technology, many vendors, moderate track record.	Well established technology, many vendors, substantial track record.
Costs	**Cost estimating**	Bespoke costings needed for each deployment option appraisal.	Many consultants have a good knowledge of relative treatment costs.	Many consultants have a good knowledge of relative treatment costs.
	Cost levels	100%	70-90%	60%

Table 2 provides a more complete comparison of the costs of the DC enhanced nanoremediation approach (INR-DC) compared to bioremediation (using lactate injection) and ISCR using mZVI alone. This comparison is based on a Czech example and a Czech cost base. It is only illustrative, and there are generally few hard and fast rules for cost estimation for in-situ remediation technologies. The modelled application is for a pathway management of a chlorinated solvent plume, and is benchmarked against nanoremediation in % terms. It is based on treatment to Czech regulatory thresholds within three years. In this example, both INR-DC and ISBR are substantially cheaper than nanoremediation (alone), and have similar pricing levels.

Tab 2 Cost Benchmarking of remediation options for an example contaminant plume

	nZVI	ISCR (micro)	ISBR	INR-DC
Material mass (bulk) [%]	100%	500%	1000%	100%
Material costs [%]	100%	20%	10%	40%
No of injections / total time	6 injections / 2 years	6 injections / 3 years	9 injections / 3 years	3 injections and service DC / 2 years
Operation costs [%]	100%	250%	150%	110%
Monitoring costs [%]	100%	150%	150%	100%
Total costs [%]	**100%**	**90%**	**60%**	**60%**
Risk of failure	100%	130%	70%	80%

From this perspective it is expected that the nanoremediation share of the remediation market will increase as a part of the remediation train or of enhanced combined processes in the near future.

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[6] E.g. stall at DCE, which may then require additional intervention such as bioaugmentation with *Dehalococcoides*.
[7] Inappropriate deployment can be associated with failure to reach target volumes and even daylighting to the surface

Nanoremediation: a site owner's perspective

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Our experience with nanoremediation: the Solvay pilot site

At the Solvay site in Switzerland the primary source of chlorinated solvent contamination is contained by an impermeable barrier (Figure 1). This barrier together with two pumping wells was installed in 2008 and the tightness of the barrier has been verified by tracer tests. The contamination originated from an old production plant contains a mix of perchloroethylene (PCE), hexachloroethane (HCA), trichloroethylene (TCE),…. The remediation of the plume downgradient of the site started in 2002 with the implementation of a pump and treat installation. The slow progress of the remediation and still high concentrations of contaminants on the other side of the wall indicate the presence of a secondary source downstream the impermeable barrier in this area, even if a clear decrease of contaminant appeared some time after the installation of the wall.
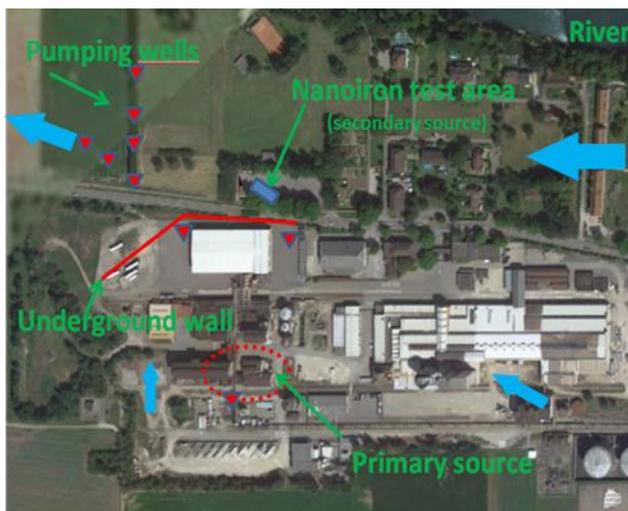
Fig 1:   Impermeable barrier (red line), pumping wells (red triangles)

The aquifer is alluvial, highly permeable with anisotropies which have been increased by the impermeable wall and the pumping wells, changing the natural flow of groundwater. The subsurface is composed of different layers made of variable composition of sand, gravel and pebble on marlstone bedrock (-16 m bgl) with some centimetres of altered marlstone at the interface. Groundwater velocity ranges from 20 m/day near the water level to less than 5 m/day close to the bedrock. The saturated zone is 3 to 4 meter high, following the level of the river.

From multilevel analysis, it appears that contamination increases with the depth to reach its maximum in the altered marlstone but also that big variations of contaminants levels occur from one well to the other at only a few meters distance (in the deepest part: from 100 mg/kg for B148 and B155 to more than 10000 mg/kg for B150, B151 and B153 (see Figure 2). We have chosen to analyse

three levels during the pilot test for the contamination (D: as "deep" in the altered marlstone, M: as "middle" in the first layer of mainly sand 0.7 meter higher, F as "flat" in the second layer of mainly pebbles – another 0.7 meter higher). These analyses have begun approximately 9 months before the injection. They have shown some linear decrease in the contaminant concentration that we have linked to the return to pre-installation conditions after the effect of the very energetic drilling activities.
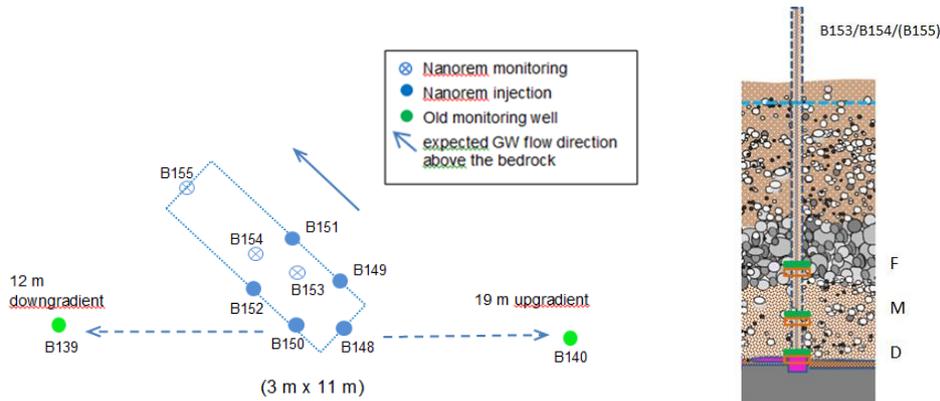
Fig 2:   Test area set-up at the Solvay DNAPL site and monitoring is made by µ-pumps directly in contact with the soil.

The injection of milled iron nanoparticles

Based on the concentration of contaminant found, it has been decided to inject 100 kg of nZVI in each of the 5 injection wells at their deepest part through the use of screens and packers (see Figure 3).

The particles were delivered in an ethylene glycol suspension. This suspension was diluted with tap water, the injected suspensions contained 10 g/l of nano-sized zero-valent iron (nZVI), 20 mg/l of LiCl (tracer) and ethylene glycol. Injection rate was 2-3 m³/h so each injection of 10 m³ took approx. 3-4 hours.
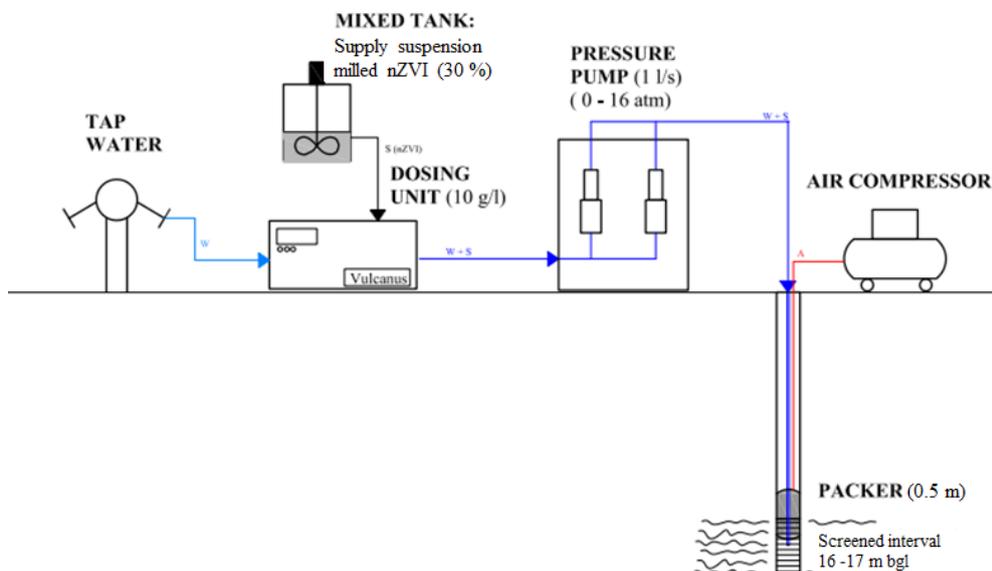
Fig 3:   Injection set-up used at the Solvay DNAPL site

We have followed up the transfer of the injected solution through three kinds of analysis: tracer (Li), the TOC (glycol used to stabilize nZVI in water), and nanoiron presence. In addition water temperature was measured to detect the front of the injection. The suspension injected has partly replaced the groundwater in the deepest part near the injection well (radius 2-3 meters), confirmed by the presence of the three components in the D and M compartment. The arrival in the F compartment was established with some delay and for the B155, only for the tracer and the TOC. Also, the concentration decreases more quickly in the F level than for the other levels confirming the higher groundwater flow velocity. Additional analyses have shown that this last piezometer B155 was not downgradient of the pilot zone as supposed initially by the water flow direction measured in the wells but just impacted by the flooding given by the injected solution. B139 appears to be the more appropriate downgradient control point.

The results

The results of the monitoring before and after the injection of nanoiron for O_2, ORP, HCA, PCE, TCE and chloride are illustrated in Figure 4.
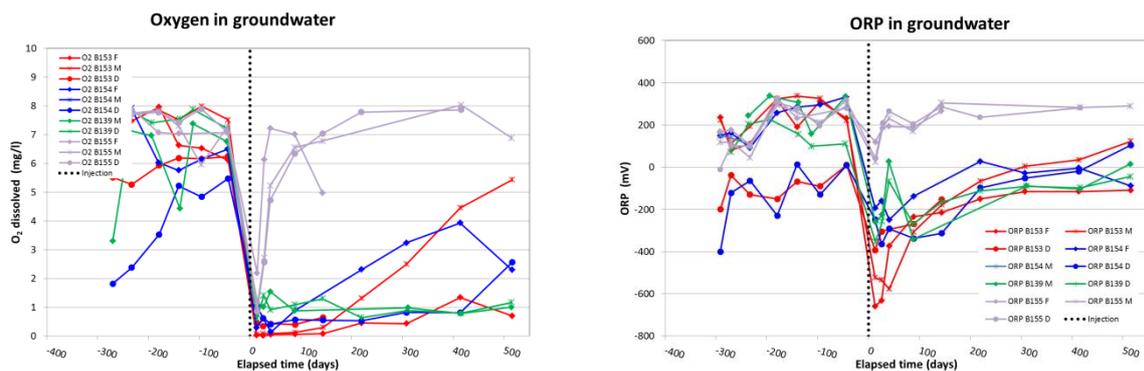
Fig 4A: Concentration of dissolved oxygen and ORP at different levels of four monitoring wells before and after injection of nanoiron.
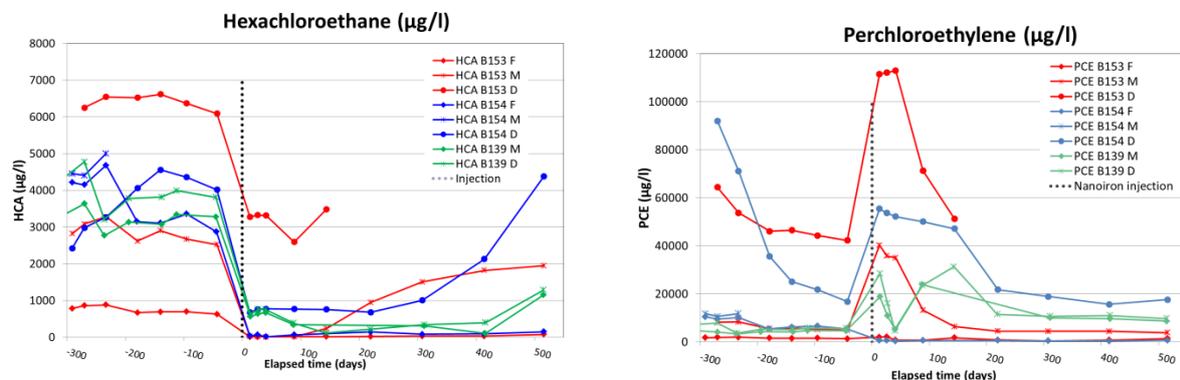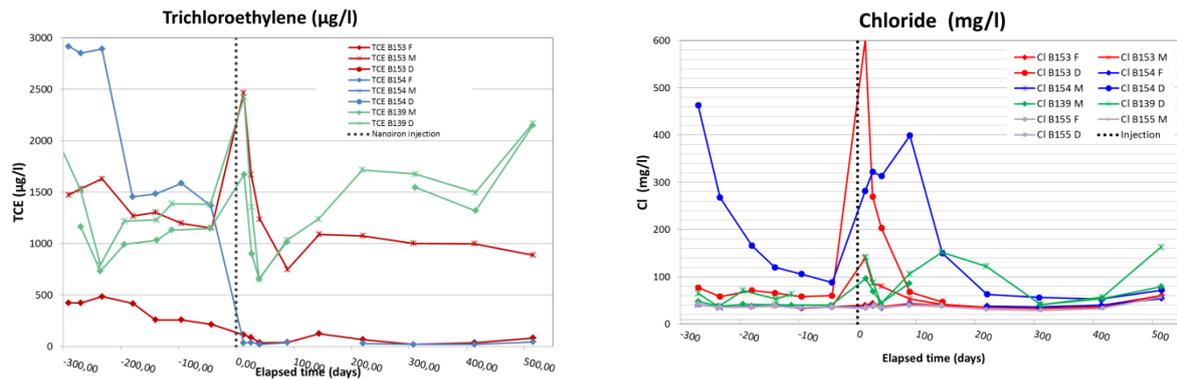
Fig 4B: Long term monitoring results from reactive zone and downstream plume.

The analyses made before injection on the groundwater confirm the presence of free phase (HCA and PCE) on the D level for some piezometers (near the solubility limit). ORP measurement and oxygen content showed that the aquifer was clearly aerobic with the exception of some deepest "D" level.

We see clearly the effect of the nZVI injection with a large decrease in the HCA concentration combined with a temporary big increase in PCE and chloride. PCE is the first intermediate in the dechlorination of HCA, but the molar increase in PCE and chloride is larger than the decrease observed for HCA. One explanation could come from the solid form of pure HCA as free phase.

O_2 and ORP measurements show that the effect of NZVI is longer than expected in such high flow aerobic groundwater, we can suppose that iron hydroxides have decreased the permeability of the treated zone (altered marlstone and first sandy layer). Hydrogen, ethane and ethene were still detected 3-5 months after injection. Some other degradation products as cis and trans-DCE have been found near the injected wells.

After three months, a significant degradation was obtained for HCA at all levels of B139, B153 and B154 and for TCE and PCE in all the upper level (F), with reduction from 50 to 100% following the compound. As these zones are downstream of the pilot zone, such results can be considered as very positive.

Some rebound appeared after 1 year but only in the deepest part (layer M and D – desorption from the marlstone), the level F which has the highest flow rate kept this high level of contaminant reduction. No clear effect has been detected one year after injection in the wells of the hydraulic barrier.

Conclusion of the pilot test

Nanoiron has been injected directly into a DNAPL secondary source zone where the contaminants are present as a residual phase and more permanently adsorbed on or into the marlstone. The unexpected large quantity of contaminant did not allow achieving a total elimination of the contaminant by the nZVI quantity applied.

However, the groundwater analyses show some very promising effects encouraging us to repeat the injection of nZVI, what has been done two months ago.

Conclusion of a site owner for nanoremediation

Remediation of chlorinated solvent with injection of nZVI allows treating quickly and efficiently such contamination. From our point of view, some preliminary conditions are required to obtain the best results:

	Optimum	Reason	Solvay site
Technical Injection	Direct push	Cost (injection radius: 2 meters so need a large number of wells to treat source)	No, well drilling required (large pebbles in a sandy matrix and too deep)
Soil	Medium permeability	Enough to inject and not too high to avoid too large dispersion	High, except at the bottom where suspension was injected
Water flow	Low	Sufficient reaction time	High, except at the bottom but iron by-products decrease flow
Oxygen	Low	Avoid consumption of nZVI to deplete oxygen	High, except at the bottom

Obviously, the test site does not provide optimum conditions for a full scale remediation but we still have very positive results.

Potential improvements (as site owner, it will be related with cost effectiveness)

- Decrease consumption of nZVI through oxygen depletion (adding of chemical reductant? or pre-treatment)
- Decrease the number of drillings by increasing the injection radius (surfactant, injection process?)
- Decrease cost of iron (development of nZVI, use of electrical field or if suitable mix of nZVI with μ-iron?)
- Improve the follow-up of the reaction zone by specific geophysical techniques?
- Combine nano and bioremediation to avoid rebound as nanoremediation results in a very suitable environment for anaerobic bioremediation?

Some drawbacks:

- Authorities' acceptance of "nano" remediation still not "automatic" even though it is evident that nZVI does not travel far in the groundwater
- Presence of unwanted degradation products or some mobilization effect when treating sources (so useful to have a hydraulic barrier downstream).

Where will our nanoparticles go? Numerical modeling of nanoparticles transport

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1. Introduction

Applying nanoremediation, nanoparticles (NP) - dispersed in a slurry – are injected into a contaminated aquifer. For nanoremediation to be effective, the NPs injected should be emplaced so that they will primarily encounter and react with the contaminants. As a consequence, the design of a field-scale injection of engineered nanoparticle (NP) suspensions for the remediation of a polluted site requires a reliable estimation of the particle distribution after injection. For nanoremediation to be safe, non-reacted NPs should preferably not travel outside the area that is to be treated and definitely not pose a threat to any receptors of concern. Regulators will require information on the long term mobility and transport of the injected particles that may remain in the subsurface after reaction with the contaminant.
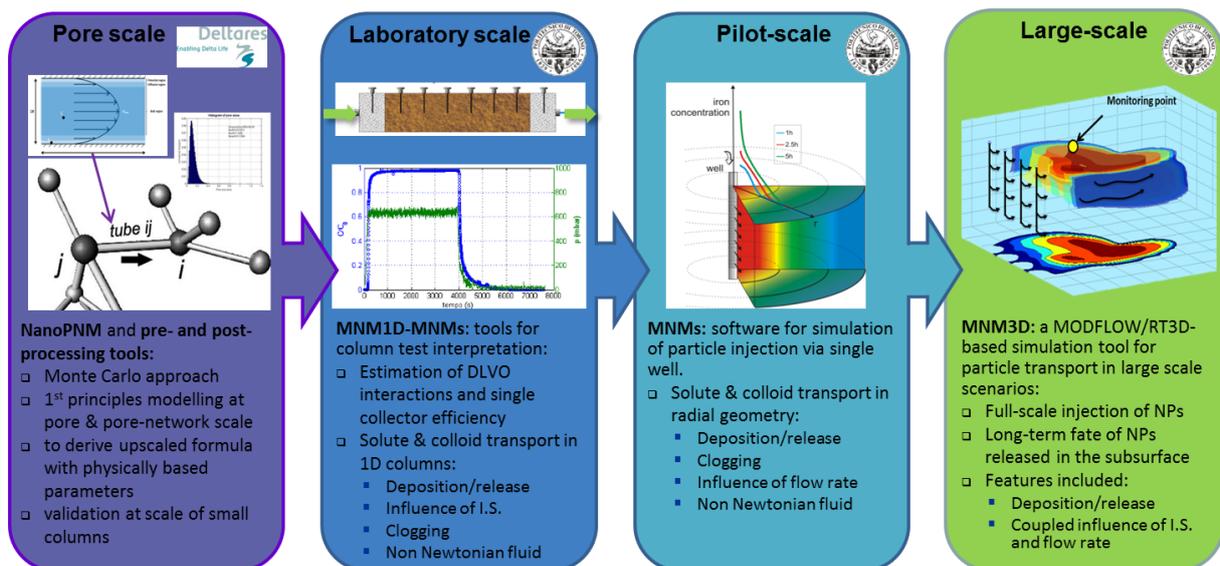
Fig 1:   NanoRem modelling research within a nutshell

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. Within NanoRem 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. The 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 employment options, in guiding the design and execution of the required monitoring and in testing assumptions.

The approach has been twofold: on the one hand we focussed 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).

2. Pore scale modelling

Our pore scale modelling built on the research by Raoof & Hassanizadeh (2010), Raoof et al. (2013), and Seetha et al. (2014, 2015). Seetha et al. (2015) performed model simulations at the scale of a single pore to derive values for NP attachment and detachment rates at this scale depending on pore size, flow velocity, NP size and surface charge, surface charge of the pore wall, and physical (temperature, viscosity, dielectric constant) and chemical (ionic strength, pH) properties of the transporting fluid. These data were used to derive simplified regression equations for the pore scale rate parameters - as a function of the variables mentioned -, to be included in the pore network model NanoPNM, that was based on the network developed by Raoof et al. (2013).

We also derived equations for porosity, hydraulic conductivity and dispersivity as a function of the NanoPNM input parameters, which enabled easy matching of these input parameters to the actual properties of a porous medium as e.g. used in a laboratory column test. These outcomes were also used to test the feasibility of predicting conductivity and dispersivity from simpler macro-scale properties like porosity and grain size. Regression statistics for these equations show that porosity and grain size alone are incomplete predictors for hydraulic conductivity and especially dispersivity. The grain packing, represented by the average pore connectivity in the pore network model, 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.

The surface charge of sandy PM is predominantly negative, according to literature the zeta potential for quartz sand varies roughly between -15 mV and -40 mV. The NPs investigated within NanoRem are engineered to also obtain a –preferably strongly– negative zeta potential, to aid both in the stabilization of the NP slurry as in NP transport within an aquifer. Their zeta potentials are reported to vary between -20 mV and -60 mV. For these conditions the fundamental modelling analysis by Seetha et al. (2014, 2015) shows very limited NP attachment at the scale of a single pore, with NP transport similar to that of a tracer. Pore network summation over all pores in a mineralogically homogeneous PM domain then also results in NP breakthrough similar to that of a tracer. Significant retention of NPs is only predicted for much lower zeta potentials. It is therefore concluded that both NP and PM are not sufficiently characterized by just their average zeta potential, as the domain averaged NP behaviour appears to be dominated by the occurrence of less negative (or even positive) surfaces. This should be taken into account when characterizing both NPs and porous media.

3. Macroscale modeling

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. When NPs are dispersed and transported in groundwater, they are subject to processes like filtration, straining, physical-chemical deposition and aggregation, as they are

attracted to the surfaces of the PM grains and to each other. These dynamic processes are governed by physical laws that operate at the pore scale, but impact the NP transport behaviour at the macro scale. 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 way (Tosco, Gastone et al. 2014).

In this context, the objectives of this work focussed on particle transport modelling for the development of user-friendly tools for the simulation of NP transport. The tools aim to aid in the design and interpretation of laboratory tests, and to enable prediction of NP fate and transport and effectiveness at the field scale. In particular, MNMs (standing for **M**icro- and **N**ano-particles transport, filtration and clogging **M**odel **S**uite) 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); MNM3D (standing for **M**icro- and **N**ano-particles transport **M**odel in **3D** geometries) has been developed for a 3D simulation of particle injection, transport and fate at the field scale in heterogeneous domains. MNMs is freely available for download on Polito's website (http://areeweb.polito.it/ricerca/groundwater/software/MNMs.php) (Bianco, Tosco et al. 2016). 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.

3.1 MNMs for 1D modelling of NP transport

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 represents the evolution of MNM1D (Tosco, Tiraferri et al. 2009) and E-MNM1D (Tosco and Sethi 2010). 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.

3.2 MNM3D for 3D NP transport modelling

MNM3D was developed coupling the transport solver RT3D with MNMs (Bianco, Tosco et al. 2016), 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 IS and velocity. In addition, MNM3D implements a new formulation of the attachment and detachment coefficients for the simulation of the simultaneous effects of pore water velocity and IS.

4. 3D simulation of an injection of Carbo-Iron® in a flume experiment

Carbo-Iron® (ScIDre GmbH, UFZ Leipzig) at a concentration C_{CI}=20 g/l was injected in a 2D pilot scale flume (Bleyl, Kopinke et al. 2012, Mackenzie, Bleyl et al. 2012) at the VEGAS facility (VEGAS, USTUTT). The container (LxWxH 1.0x0.12x0.7 m) was filled with homogeneous quartz sand (Dorfner, Germany) simulating a confined aquifer. Particles were stabilized with Carboxymethyl cellulose (C_{CMC}=4 g/l) and

injected in the central part of the domain through 4 delivery points for 48 minutes (Figure 2). The Carbo-Iron® injection was then simulated using MNM3D to check the capability of the code in complex and more realistic conditions. The inverse modelling of column transport tests performed before the 2D injection indicated that Carbo-Iron® retention onto the sand can be modelled assuming a single-site interaction with linear reversible attachment. The simulated maps of total particle concentration (retained and suspended) were compared to the images of the flume after 7 and 34 min of NP injection (Figure 2Fig). Refer to (Bianco, Tosco et al. 2016) for additional information.
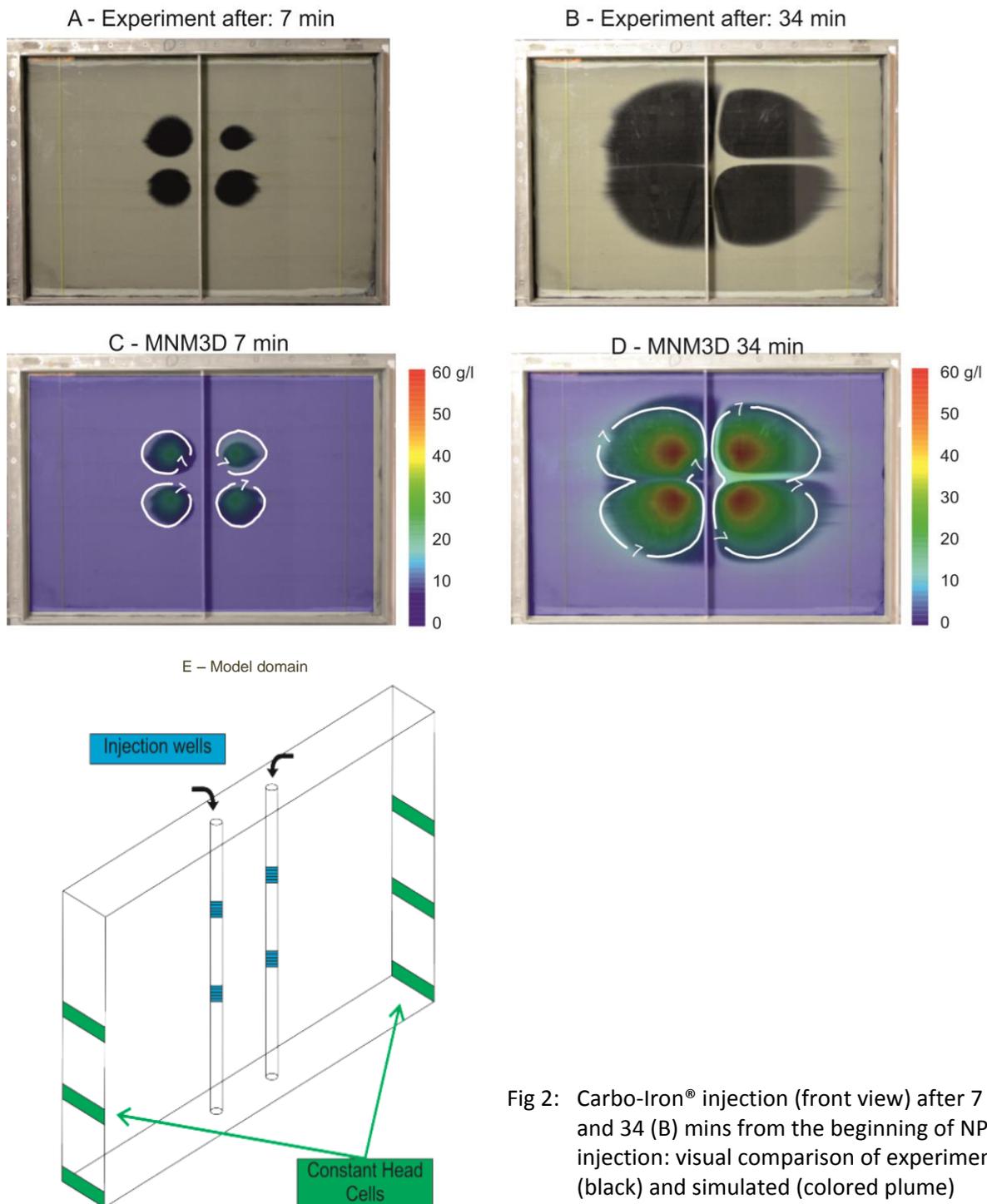

Fig 2: Carbo-Iron® injection (front view) after 7 (A) and 34 (B) mins from the beginning of NP injection: visual comparison of experimental (black) and simulated (colored plume) results of nanoparticle transport (C-D) and model domain (E). Modified from (Bianco, Tosco et al. 2016).

The velocity-dependent attachment implemented in MNM3D well reproduces the experimental plume, catching its shape and extent. The partial asymmetry observed in the experimental data is due to a slightly different injection rate in the four ports. The overall good quality of the matching between experimental and modelled plume suggests that MNM3D can correctly describe the transport of Carbo-Iron® in 2D domains in the presence of strong spatial variations of flow velocity.

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Where are our nanoparticles? At site and in-situ monitoring

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INTRODUCTION

All remediation applications need to show and document the effectiveness of the technologies. For nanoparticle-based remediation, this includes providing information on the mobility and fate of the injected nanoparticles. Monitoring the behaviour of engineered nanoparticles requires their detection in environmental media, and in particular their isolation from natural background colloidal material. This represents a potential challenge for the use of Fe-based NPs in remediation, because of relatively high levels of naturally occurring iron. Hence, the development and application of analytical methods for *in situ* measurement and detection of nanoparticles was a key objective of the NanoRem project.

One of the strengths of the NanoRem project has been the opportunity to test a wide variety of techniques, from measurement of simple chemical parameters to high-end sophisticated techniques, and to cover applications in simple laboratory experiments, large scale tank experiments, and finally field applications. This has enabled an evaluation of applicability of different methods for Fe-based NPs, as well as providing insight into specific challenges, advantages and factors influencing detection limits for field measurements.

Monitoring and characterisation requirements at different remediation phases

The applicability of the methods depends on the phase of remediation and the question to be addressed, all having different analytical requirements and issues. The most important issues for monitoring purposes are:

- The detailed field characterisation studies prior to injection.
- Monitoring the movement and distribution of particles during injection. Is the particle suspension reaching the required location, with the required concentration and state? While the NP concentrations are relatively high, there is a need for rapid feedback at relatively high resolution.
- Monitoring for transport of "fine" or "renegade" particles out of the core application area during and after injection. Low NP concentrations give rise to challenges with detection against background levels of colloids, but monitoring can be carried out with a lower spatial resolution, and less urgency for a rapid feedback.

- Post injection behaviour and information on the transformation and reactivity of the particles and their reaction products. This is particularly relevant for the assessment of the need for reinjection.

WHICH METHODS SHOW THE GREATEST POTENTIAL?

Monitoring of particle dispersion during injection phase

The main focus during the injection phase is the behaviour of the particles, namely the radius of influence (ROI), the travel distance and the homogeneity of the distribution around an injection point of well, and acute changes within minutes have to be detected. This phase has a duration of hours to days, and requires a high measurement frequency. Since particles are injected as a suspension, the liquid and the solid phases may behave differently, and methods need to address both phases in order to provide information about the overall efficiency of the injection and potential deviations from the expected behaviour.

Results from NanoRem field measurements during the injection of nZVI, FeOx and milled Fe show that the detection of particle suspension loads is relatively straightforward, and can easily be 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 via in situ methods such as magnetic susceptibility, redox (ORP) and H_2 measurements. The detection limits, in the order of 0.5-50 mg Fe/L, are sufficient to follow the dispersion of injection liquids and particles during injection. Given the relatively low toxicity of Fe-based particles to organisms, with very few effects seen below 100 mg/L, these detection limits should be sufficient to assess the potential ecological impact, both within and outside the injection area. Of the various methods tested, magnetic susceptibility, turbidity and total iron measurements are most appropriate for monitoring during injection.

Magnetic Susceptibility

Magnetic susceptibility is one of the very few *in situ* methods that can be used to detect iron nanoparticles, has the advantage of allowing for continuous monitoring, and can be combined with other sampling and monitoring arrays. The method is limited to measurement of nZVI or milled Fe particles, and at concentrations of about 50 mg/L, although laboratory tests show it can be used for other particles (e.g. Carbo-Iron®), albeit with higher detection limits. During NanoRem field tests, several susceptibility sensors were installed in arrays in the subsurface at the Spolchemie, Czech Republic (nZVI) and Solvay, Switzerland (milled Fe) field sites, together with a temperature sensor and sampling ports. The pilot studies showed the arrays were successful in detecting the iron particles during injection at both sites. Despite the fact that detection limits are slightly higher and instrumentation costs for the magnetic array sensors are greater than those for on site sampling and measurement, (ca. 1,000 EURO per array and 1,000 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 not only on the concentrations of Fe, but also on its speciation in order to understand the fate and reactivity of the injected particles. For total Fe concentration, measurements on suspensions/liquids and soils/sediments can be carried out after acid digestion and measurement using standard chemical analysis (e.g., ICP-OES or spectrophotometry). For low particle densities, pre-concentration by

centrifugation, magnetic separation (for nZVI or milled Fe particles) or filtration can be applied to improve detection limits. Specific protocols for acid digestion need to be developed for the different particles to ensure complete dissolution. The detection limits of all methods will be site specific, depending largely on the background levels, and, for Fe-based NPs, dissolved iron concentrations. Field applications have demonstrated that Mössbauer (for nZVI or milled Fe particles) can give useful additional information on the time dependent changes in particle state and reactivity, in both water and solid phases. These can be supported by other methods for measurements of structure and oxidation state (e.g. X-ray photoelectron spectroscopy, transmission/scanning electron microscopies, X-ray powder diffraction, X-ray fluorescent spectroscopy).

Mössbauer Spectroscopy

Within the NanoRem project, transmission ^{57}Fe Mössbauer spectroscopy has proven to be a useful tool for a characterization of nZVI particles and it represents a unique technique for probing the Fe_0/Fe_{tot} ratio in field samples, including the identification of nZVI particles in complex environmental and geological matrixes. While the Mössbauer spectrometer is compact and portable, the main disadvantage lies in the relatively long counting times. These are typically about 1 day per sample of nZVI, but can be up to 1 week for environmental samples with low iron content, during which time the measured sample could further oxidize. Therefore, samples need to be analyzed in a protective atmosphere (e.g., a glove box under nitrogen, see Filip et al., 2014) or pre-concentrated samples are frozen and measured at low temperatures (optimally at 150 K or simply at LN_2 temperature, see Filip et al. 2007). The method has been successfully tested during nZVI injections at Spolchemie, and measurements taken for suspensions, sediments and soil samples directly proved both the formation of nZVI reaction products and extent of nZVI migration in groundwater conditions.

Methods for Carbo-Iron® and zeolites

Methods for tracing Carbo-Iron® (CIC) and zeolites are still at the laboratory development phase, although preliminary results are promising. A combination of Temperature-programmed oxidation (TPO) with parallel CO_2-analysis seems to be the best approach to distinguish Carbo-Iron® from other particle types and background sediment, with detection limits down to 0.1 to 5 wt %. Fluorescence labelling has been proved successful for quantitative analysis of Fe-zeolite concentration in water samples. Fe-BEA35 can be detected with a LOD of ~ 1 mg/L, providing information on travel distances and particle fate.

Temperature-programmed oxidation (TPO) of solid sediment samples utilizes the fact that the immediate vicinity of the carbon has an effect on the carbon-specific oxidation temperature. In case of Carbo-Iron®, the embedment of iron decreases the incineration temperature significantly in comparison to pure powdered activated carbon (Bleyl et al. 2012). One can take advantage of this temperature shift to detect carbon-based particles within a complex matrix containing a natural carbon background. The main challenges are sample preparation of natural heterogeneous aquifer sediment to achieve representative results for the sediment loading with carbon species and the detection of low-concentrated particle fractions (<< 0.1 wt-%) in complex matrices. To quantify Carbo-Iron® particles immobilised on sediment grains, predefined loadings of aged CIC on the NanoRem standard material M.I (Dorsilit®) in a typical expected range of 0.1 wt% up to several wt% has been studied.

Monitoring for transport of particles out of the treatment area

Total Fe content and other chemical parameters can give a reliable picture of the behaviour of injected suspensions in the application area, but more sensitive methods are needed to control for the possible transport of particles outside the treatment area, often termed "renegade" particles. Demarcation of low concentrations of Fe-based NPs from background matrix requires greater sensitivity, but tests and developments of a variety of methods within NanoRem have been promising. By ICP-MS analysis of lanthanides (rare earth elements, RREs) and other trace elements in particles and background groundwater site samples, a group of elements can be selected to "fingerprint" the injected NPs. By applying Multivariate Statistics tools such as Principal Components Analysis, it is then possible to discriminate injected particles 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); however, as for all methods, the performance and applicability in the field is highly dependent on site-specific parameters. Nevertheless, field tests carried out at various NanoRem field injections show good separation of NP from background components at most sites, with the potential for detection down to ng/L levels. Although the analytical costs are higher than for total Fe measurement, by targeting selected monitoring sites, measurements can be carried out over a lower spatial and temporal frequency.

CONCLUSIONS

The NanoRem project has demonstrated that there are a number of techniques that can be applied for monitoring Fe-based nanoparticles during remediation, and that determination of concentrations at levels below those linked to ecotoxicological effects should be straightforward both within and outside the remediation area. Existing challenges include the discrimination of intact Fe particles from dissolved Fe, since increased Fe concentrations outside the treatment area do not necessarily mean movement of NP. However, fingerprinting techniques using trace element and lanthanides analysis look promising. Future work will consolidate all field experience to provide a quantitative assessment and design of standard operating protocols.

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Generalized guideline for nanoremediation application

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This Guideline was developed within the research framework "NanoRem – Taking Nanotechnological Remediation Processes from the lab Scale to End User Applications for the Restoration of a Clean Environment". It gives a comprehensive overview of the successful implementation of nanoremediation. While it is a stand-alone document it is supported by a range of publications offered in the "NanoRem Toolbox" (www.nanorem.eu).

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 technical guideline provides a comprehensive overview of the application of a nanoremediation on a given site. It is not intended to design a feasibility study to decide which technology best to apply for a given site. Of course, technical information given in this guideline will help the engineer to assess the option "nanoremediation" in comparison to other remediation technologies.

Layout of the Guideline and Prerequisites

The guideline strictly focuses on the application of nanoremediation (Figure 1). Prerequisites of a successful remediation such as a detailed site investigation, a conceptual site model (CSM), an overview of commercially available nanoparticles (NP) and the corresponding operating windows (OW) are not discussed in detail. Nevertheless, corresponding background material is being offered in the appendix of the guideline.

Pre-Screening

The pre-screening tool is an EXCEL-based application to quickly screen a contaminated site regarding the potential of nanoremediation. The application matches commercially available NP and their OW with the requirements of a site as delineated in the CSM. It gives a quick indication of "favourable"/ "unfavourable" and indicates critical parameters to be investigated in more detail.

Site and Contaminant Specific Particle Tests

Based on the outcomes of the pre-screening phase, one type of commercially available NP is proposed to remediate a given contaminant type at a given site. The commercially available NPs are supplied by the producer as a ready-to-use suspension or with a protocol for preparation of NP suspension. It is strongly recommended to site specific verify the claims of the producer experimentally since site specific parameters such as pH, dissolved oxygen concentration, oxidation reduction potential, dissolved inorganic ions and dissolved organic matter in groundwater as well as the mineral composition and natural organic matter content of the sediment can have substantial influence on NP reactivity, efficiency, longevity and (by)product formation. If 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.

Monitoring

As for all remediation the monitoring of a nanoremediation application may be divided in pre-, during, and post-deployment. For nanoremediation especially the deployment phase itself is critical since in this phase the distribution of the NP (which in the end controls success and efficiency of a given measure) in the subsurface is verified. The guideline describes the monitoring phases and suggests innovative and conventional monitoring devices associated with each phase.

Model-Assisted Upscaling of NP Mobility

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 main purpose of the modelling is to predict the NP mobility at different stages of the technology application, both in the planning and design stages (i.e. support the design of the injection plan), and later to predict the long-term particle mobility after injection (i.e. support the monitoring). The guideline describes "MNMs" (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 Tests

Pilot field tests are preferably designed based on the results of laboratory tests, or, if no such data are available, based on particle information from the supplier on hydro-geo-chemistry and contaminant information obtained in the site investigation. The main aim of pilot field tests is the definition of 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 and technical as well as economic success of a given remediation scheme.

Full Scale Design

Based on the pilot test and in conjunction with the numerical model a full scale nanoremediation can be designed. The key part of the design is to match the contaminant distribution and inventory with a targeted deployment of 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 and Particle Deployment

Site installations necessary for a successful NP deployment comprise both above ground and below ground installations. Below ground installations may be emplaced beforehand if wells are being used or during particle deployment if the subsurface allows for the use of direct push injection technology. Above ground installations are mobile equipment containing mixing containers, dispersers, pumps etc. 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.

Long Term Performance

Test and confirmation of a successful nanoremediation is achieved via long term monitoring. During this phase contaminants, reaction products, metabolites and general milieu parameters of the ground water are monitored on a regular (monthly) basis, in order to verify the success of the remediation. The main focus of the monitoring is to investigate the efficiency of the desired reaction in terms of reduction of concentrations of contaminants in the ground water, reduction of emissions or contaminant masses. The criteria for the decision on the success of a nanoremediation have to be defined beforehand and a monitoring program chosen accordingly (usually the success is measured against remediation goals, which are beforehand mutually agreed on with the responsible authorities). The monitoring results will be compared to the status defined during the pre-injection phase. Eventually, the monitoring program should be designed to give positive proof of a successful remediation or to decide if and when a reinjection of particles is required.

Regulatory Issues will be Addressed Qualitatively

In order to implement nanoremediation at different locations within the EU (and beyond) local regulatory requirements have to be fulfilled. It is beyond the scope of this guideline to address these requirements in detail. However, most frequently or most likely asked questions posed by regulators will be listed to facilitate communication between consultant and regulator.

Financial Issues of Nanoremediation

As for the application of any other remediation technology, there is no "generic" cost calculation for nanoremediation. Rather the total costs will be a function of many parameters, due to subsurface and contamination, due to geographic location and so on. Nevertheless, to facilitate cost estimation the main cost drivers will be listed and ranked in the guideline.

Examples of Nanoremediation

Within the NanoRem project six pilot site studies have been conducted successfully. The descriptions of the sites, chosen remediation approach, monitoring and the outcomes are described in dedicated NanoRem Bulletins (http://www.claire.co.uk/).

A summary of the Generalised Guideline for Application (extensive document) will be available in December 2016 as CL:AIRE/NanoRem Bulletin No 3 "Generalised Guideline for Application of Nanoremediation" at http://www.claire.co.uk/NanoRem and www.nanorem.eu.

The full guideline and its appendices will be offered for download by the end of January 2017 under http://www.nanorem.eu.
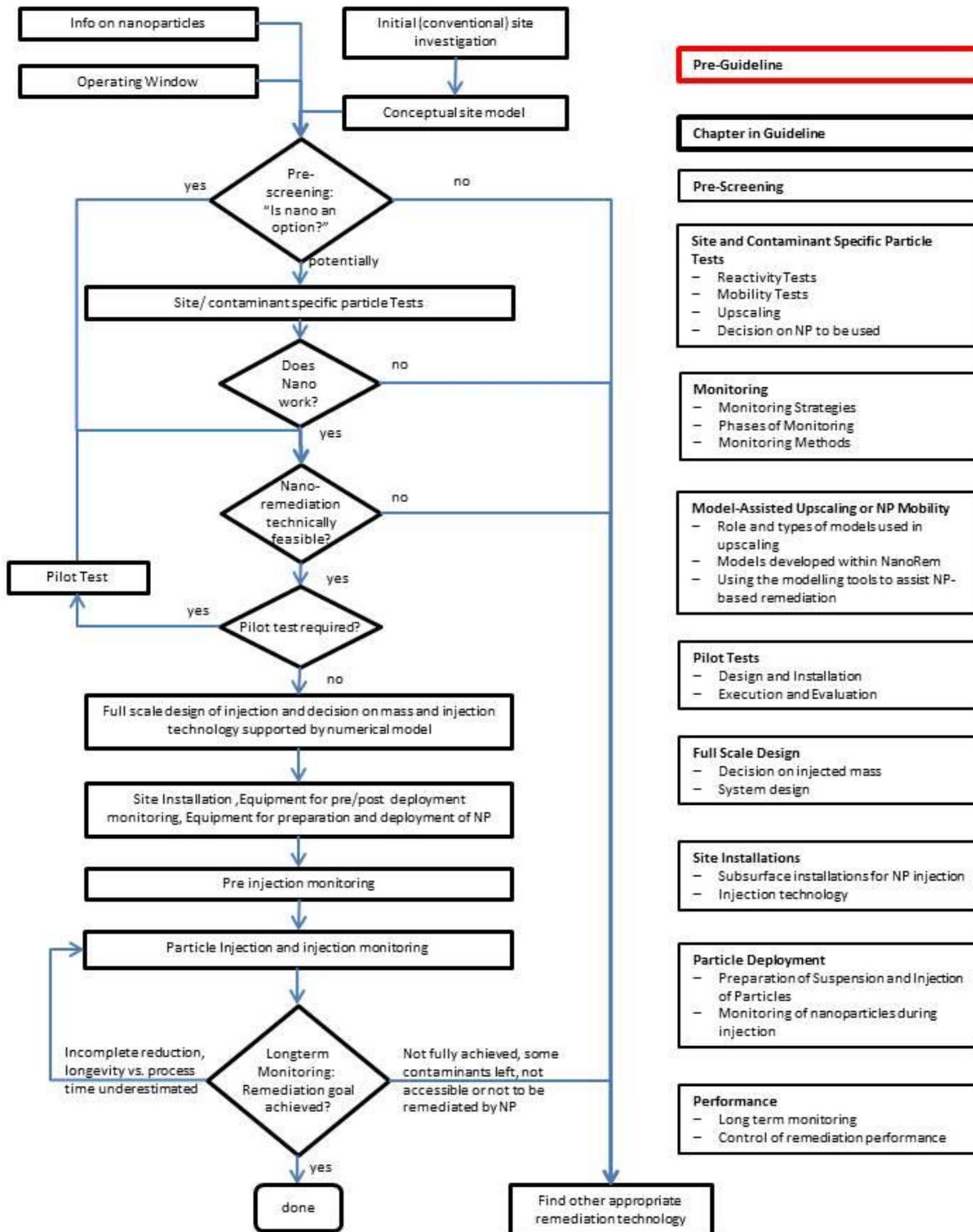
Fig 1: Flow chart of a nanoremediation

Safe application of nanoremediation

Renegade nanoparticles quo vaditis? Risk assessment = regulatory reassurance

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This paper considers what happens to nanoparticles (NPs) that are injected into polluted groundwater but either do not reach the intended treatment area or pass through it to reach parts of the aquifer that they were not intended to reach. We call such NPs 'renegade' particles.

The NanoRem European research project aims to support and develop the appropriate use of nanotechnology for contaminated land remediation by facilitating practical, economic and exploitable nanotechnology for in-situ remediation. This can only be achieved in parallel with a comprehensive understanding of the environmental risk-benefit balance for the use of the NPs being investigated. In terms of the source-pathway-receptor paradigm used in Risk Based Land Management (RBLM), renegade NPs are presumed to represent a hazard. Receptors in the form of not yet polluted groundwater are assumed to be present.

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

A more detailed risk assessment protocol in the form Technical Guidelines has been developed to provide quantitative estimates of the risks posed by renegade NPs. Technical Guidelines, including a computer based risk assessment model, to assess the level of risk, if any, posed by renegade nanoparticles has been developed within the research framework of the NanoRem project. The aim is to assist practitioners and consultants in screening and regulators in permitting nanoremediation as a possible remediation option for a given site. If nanoremediation is deemed beneficial, the guidelines will provide criteria to inform the design of successful nanoremediation. The guidelines are developed with only the NanoRem NPs in mind but they may inform risk assessment for other NPs as well.

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

The Environment Agency Remedial Targets Methodology, RTM (Environment Agency, 2006) has been used as the basis for deriving the transport element of the risk model that estimates a screening level NP concentration versus distance from the NP source (injection) zone. The RTM is accompanied by a Microsoft[TM] Excel spreadsheet tool for four Levels of assessment.

The RTM spreadsheet model has been modified at the Level 3 stage (i.e. saturated zone transport) by incorporating some of the key NP parameters into one of the analytical solutions (currently the Ogata Banks equation) used to describe the advection-dispersion including degradation and retardation of solutes downstream of the source term. The model has been compared against the numerical solution currently included within the MNMs 2015 (v 1.012) model (Bianco et al., 2015).

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

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

There are a number of ways that the current screening transport model could be improved and extended, some of which involve further investigation of current datasets that may become available during the final few months the NanoRem project.

List of posters

Lederer et al. (2016):	The application of iron oxides nanoparticles as an alternative electron acceptor for biodegradation of BTEX
Laszlo et al. (2016):	In Situ Groundwater Decontamination Using Carbo-Iron® Nanoparticles at a NanoRem pilot site in Balassagyarmat (Hungary)
Stejskal et al. (2016):	The application and behaviour of nZVI during the treatment of chlorinated hydrocarbons in the field test at Spolchemie site
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Ribas et al. (2016):	Production of abrasive milling nZVI and activation of air stable nZVI as methods to improve groundwater remediation
Otaegi et al. (2016):	Testing on emerging nanoparticles for arsenic removal under real conditions on a pilot field site, in Asturias, Spain
Tomkiv et al. (2016):	Stakeholder engagement in the NanoRem project
Cohen et al. (2016):	Nano iron particles transport in fractured rocks: laboratory and field scale
Krok et al. (2016):	Colloidal Iron Oxide Nanoparticles for Remediation of Land and Groundwater Aquifers contaminated by Heavy Metals or Organic Pollutants
Georgi et al. (2016):	Trap-Ox Fe-zeolites for in-situ trap&treat of organic contaminants: lab-scale results on mobility, performance and stability
Herrmann et al. (2016):	Metal (composite) particles for reductive aquifer remediation - reactivity tests in columns
Bleyl et al. (2016):	Carbo-Iron as colloidal microreactor in the perspective of NanoRem
Müller et al. (2016):	Cascading Column System: Closing the Mass Balances and Results for Different Particles
Wiener et al. (2016):	Cascading Column System: Improved Susceptibility sensors
Miyajima et al. (2016):	Migration and Reaction of iron oxide NP in the large VEGAS Container
Miyajima et al. (2016):	Migration and Reaction of NANOFER STAR in a Large Scale VEGAS Flume

The application of iron oxides nanoparticles as an alternative electron acceptor for biodegradation of BTEX

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A stabilized slurry of coated Nano-Goethite was developed in the framework of the NanoRem project, progressing with particle design. The original particles were bought and further processed to achieve their stability and subsequent mobility in a subsurface environment.

A special coating procedure is applied, which provides the particles with better mobility, helping to target microbial contaminant degradation. The aim of the study is to test their mobility and reaction characteristics and to optimize their performance. Characterization and mobility tests were carried out during lab scale and subsequent pilot scale tests in the VEGAS large scale container system achieved promising results.

One of the contamination plumes at the Spolchemie site was chosen as a NanoRem case study site to test iron oxide nanoparticles (NPs) for *in situ* remediation of BTEX. Nanoremediation was seen as an opportunity to enhance the remedial works that have been ongoing since 2005. Spolchemie is one of the leading synthetic resin manufacturers in Europe, located in the town of Usti nad Labem (Czech Republic) in the heart of Europe. The plant began producing synthetic resins in the middle of the last century. The production, storage and distribution of various raw materials has led to extensive contamination of the subsurface by BTEX compounds, which in many cases have dispersed widely from the original source areas.

Six contamination plumes were identified by AQUATEST at Spolchemie based on the type of contamination, geology and hydrogeology of the subsurface areas identified in the conceptual site model (CSM).

The central part of the Spolchemie site was also extensively contaminated by BTEX. A general approach in this area was to excavate the contaminated soils from the unsaturated zone in the source zone area and then remediate the underlying aquifer by pump and treat and enhanced bioremediation. The pumping of free phase from several wells is ongoing. Treated water is discharged back into the ground. Enhanced *in situ* bioremediation was identified as a suitable remedial technology to treat residual free phase product and BTEX compounds in this area based on laboratory and pilot tests. Tests confirmed the ability of natural microflora to degrade the present contamination under anoxic conditions with nitrate being used as an electron acceptor. This is being monitored in collaboration with the Technical University of Liberec. These findings have created an opportunity for the NanoRem project to look at nanoremediation and *in situ* bioremediation processes working in tandem, using newly developed stabilized oxidic NPs (based on Goethite) as another possible electron acceptor. The NanoRem partners involved in this trial are AQUATEST, University Duisburg-Essen, VEGAS Stuttgart, Norwegian University of Life Sciences and University of Vienna.

The selected area of the site as described above has been investigated in detail. Additional wells with micropumps were drilled and tracer tests undertaken before the application of NPs in order to more precisely delineate the plume. Undisturbed soil samples were taken for laboratory test verification (reactivity and migration tests) to assist with NanoRem field test design.

A number of groundwater monitoring campaigns were undertaken, followed by a preliminary site investigation. Based on this work a conceptual site model (CSM) was developed detailing the subsurface conditions followed by a preliminary risk analysis. The 300 kg of oxidic NPs were infiltrated via direct push into a contaminated zone of the pilot area in the October 2015.

The poster summarizes the first results from the pilot test application and presents the experience from field measurement.

In Situ Groundwater Decontamination Using Carbo-Iron® Nanoparticles at a NanoRem pilot site in Balassagyarmat (Hungary)

Tamas Laszlo, Matthias Kraatz, Marton Szabo

Golder Associates

In September 2015, Golder conducted a Carbo-Iron® injection into a groundwater aquifer that is contaminated with chlorinated hydrocarbons at the NanoRem Balassagyarmat pilot test site in Hungary. Significant reduction of PCE and enhanced microbiological degradation/chemical reduction only in the closest monitoring wells to the injection points can be detected. As well, a slight increase of TCE, cDCE and VC concentration but only traces of ethane and ethane have been detected, which proofs the abiotic dehalogenation induced by Carbo-Iron® injection.

According to the on-site measurement and the laboratory analyzes we assume, that the Carbo-Iron® migration could be very significant right after the injection. The aquifer porosity (n_{eff} ~ 0.3) and the low sorption potential of the gravelly layers could affect the fast transport (advection/dispersion) of injected materials. Due to the high porosity and heterogeneity of the aquifer and the overpressure that was used during the injection it is very likely that the designed reactive barrier couldn't be formed at the place of injection that hinders the effective biodegradation of the contaminants in a larger area.

The application and behaviour of nZVI during the treatment of chlorinated hydrocarbons in the field test at Spolchemie site

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The main aim of this study was a verification of migration characteristics and remedial efficiency of the new type of nZVI using advanced procedures for monitoring both ZVI nanoparticles and vertical stratification of contamination, including detailed water and soil sampling after infiltration.

The Spolchemie site was chosen as one of the NanoRem project case study sites to test zerovalent iron nanoparticles (nZVI) for *in situ* remediation of chlorinated hydrocarbons. Spolchemie is one of the leading synthetic resin manufacturers in Europe, located at Usti nad Labem (Czech Republic) in the heart of Europe. The plant started to produce resins and freons based on tetrachlormethane and tetrachlorethene from the middle of the last century in Spolchemie. The production, treatment, storage and distribution of these various raw materials and products has led to extensive contamination by chlorinated ethenes and methanes, which in many cases have dispersed widely from the original source areas.

Six contamination plumes were identified at Spolchemie, based on the type of contamination, geology and hydrogeology of the subsurface areas identified in the conceptual site model.

For one of these plumes, which is contaminated only by chlorinated hydrocarbons, an impermeable underground wall was installed as safety measure. However, recently a part of the contamination overflowed this wall. As the subject of a NanoRem field test this new contamination outside of this wall is now treated by nZVI application. Two different types of ZVI NPs were used as crucial agents (NANOFER 25S – 200 kg in November 2014 and NANOFER STAR – 300 kg in October 2015, both NANO IRON, s.r.o., Czech Republic).

A number of groundwater monitoring campaigns were undertaken followed by a preliminary site investigation. Based on this work a conceptual site model (CSM) was developed detailing the subsurface conditions followed by a preliminary risk analysis. This initial CSM was refined by further targeted investigation and subsequent updating of the risk analysis. This work indicated that remediation requirements would be complex. With further funding being secured, the CSM was expanded following delineation of the contamination, geological and hydrogeological surveys, well logging, development of a hydrogeological model of the site and a remediation feasibility study. Exploration of the site is still ongoing to further improve the conceptual site model and review further the most appropriate overall remedial strategy.

Advanced techniques are used during the NanoRem field test, especially to monitor the mobility of ZVI nanoparticles. A magnetic susceptibility array was developed (by VEGAS Stuttgart) for field site monitoring of nZVI, and test arrays were installed at the Spolchemie field site.

At Spolchemie, injection equipment, particle suspensions preparation and procedures were set up; injections into six depths (contaminated horizons) were performed by direct push after detailed

monitoring using newly developed micropumps (VEGAS Stuttgart) installed at 5 positions (5 depths). The pilot trials have been completed and the final results are evaluated.

The presented poster summarizes very positive results (e.g. 277 days lasting decrease of ORP and 222 days lasting contaminant reduction) from the first field test with NANOFER 25S and presents also results of the second nZVI injection (NANOFER STAR).

The NanoRem partners involved in this trial are AQUATEST, NANO IRON, VEGAS Stuttgart, Technical university of Liberec and Palacky University in Olomouc.

Tracing Iron Nanoparticles at Field Sites using an Multi-elemental Fingerprint approach

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Monitoring the migration of engineered nanoparticles (NPs) used for groundwater remediation is a challenging task, due to the difficulty in distinguishing between iron NPs and naturally occurring Fe colloids. Measurements of total and dissolved iron can give an indication of the possible influence of Fe-NPs, but detection limits are dependent on background levels of Fe.

In our work we established a novel approach for tracing iron NPs in the environment based on multi-element fingerprinting by ICP-MS analysis. Our hypothesis is that Fe nanoparticles used in NanoRem field injection experiments have distinctive lanthanide and other trace element signatures that, after an injection event, modify the background signature of groundwater samples towards profiles similar to that of the nanoparticles. Lanthanides appear to be one of the possible groups of elements suitable for this purpose as well as other trace elements naturally occurring in environment and constituting the NPs. The multi-elemental inorganic analysis of different engineered NPs used within the NanoRem project was done and their fingerprints were compared with the profiles of representative groundwater samples collected from the localities before and after the remediation.

This approach could be a good complement to measurements of total and dissolved iron, especially in the case of long-term monitoring of the wells outside the nanoparticle injection zone.

Can sodium humate coating on mineral surfaces hinder the deposition of nZVI?

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The affinity between nano scale zero valent iron (nZVI) and mineral surfaces hinders the mobility of nZVI injected into contaminated aquifers and thus the effectiveness of the remediation technology as a whole. The surface of nZVI particles used in remediation is often modified with a polymeric coating that stabilizes the particles via electrosteric repulsion and hinders homoaggregation. However, the attachment of stabilized nZVI to collector surfaces remains high (Laumann et al., 2013). This is probably due to a shifted contact frontier between the coated nanoparticles and collector grains, where electrical double layer interaction is weaker (Lin et al., 2012).

Previous work with polymer-coated Ag nanoparticles demonstrated that when a coating polymer was allowed to attach to the collector surfaces, the attachment efficiency of these nanoparticles and the collector was reduced due to electrosteric stabilization (Lin et al., 2012).

The aim of this study was to assess how the coating of collector surfaces with a polymer influences the attachment of polyacrilic acid coated nZVI (PAA-nZVI) used in groundwater remediation. Sodium humate, a water soluble sodium salt of humic acid derived from leonardite (an oxidation product of lignite) was applied as the coating polymer. The effect of sodium humate on the deposition of polyacrilic acid coated nZVI (PAA-nZVI) was studied in flow-through columns packed with (i) uncoated/coated permeable silica collectors with varying surface roughness (ii) uncoated/coated glass beads with different ferrihydrite content to account for the surface charge heterogeneity and (iii) uncoated/coated less permeable heterogeneous collectors from the contaminated aquifers.

A permeable silica collector with rough surfaces allows homogeneous attachment of sodium humate, which provides electrosteric stabilization and hinders deposition of polymer coated nZVI onto collector grains. Sodium humate does not attach to smooth surfaces of the silica collector grains, even if their surface contains charge heterogeneity. In low permeable natural collectors sodium humate does not attach effectively, even to rough surfaces of the collector grains which contain surface charge heterogeneity (such as Fe oxide and carbonates), and is not able to prevent the attachment of PAA-nZVI.

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Production of abrasive milling nZVI and activation of air stable nZVI as methods to improve groundwater remediation

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Two approaches were developed in order to increase the reactivity of nZVI against Cr (VI), trichloroethylene (TCE) and tetrachloroethylene (PCE).

In a first approach, a new milling method for nZVI production at lab scale was developed. Several alternatives were tested. Only the addition of micronized alumina during the milling process lead to the production of particles at the nanoscale. Abrasion of the grinding media and breakage of flakes were the main mechanisms for the nZVI production. An important challenge was the optimisation of the milling parameters such as alumina concentration, grinding media load, chemical composition and diameter. These parameters have a key effect on nZVI throughput and properties.

After a long period of further testing, several milling configurations were selected, and a detailed characterization of the produced nZVI was performed. The results were compared to the properties of other commercial products. Granulometry, morphology, chemical composition and suspension stability was assessed for all samples.

The developed particles showed excellent properties in all studied parameters, highlighting reactivity and suspension stability. For example, the NA 84 sample had a mean particle diameter of 0.16 μm (by SEM), a specific surface area of 29.6 $m^2 \cdot g^{-1}$ and its reactivity showed to be several times higher than the commercial nZVIs, also when reactivity is normalized to specific surface area and Fe (0).

In a second approach, the study assessed the effect of a passivating oxide layer on a commercial nZVI. It was concluded that the oxide shield of surface-passivated nZVI particles significantly decreases the performance in terms of reactivity. An activation procedure to recover the reactivity of air-stable nZVI particles was consequently evaluated. The method consists of exposing nZVI to water for 36 hours at a concentration of 0.2 w/w iron to water just before the reaction with the pollutants.

To assess the increase in nZVI reactivity with the activation procedure three types of nZVI particles with different oxide shell thicknesses were tested for Cr(VI) removal. The two types of air-stable nZVI particles with an oxide shell thickness of around 3.4 and 6.5 nm increased their reactivity by a factor of 4.7 and 3.4 after activation, respectively. However, the pyrophoric nZVI particles displayed no significant improvement in reactivity. In order to validate the activation process, additional tests with selected chlorinated compounds were performed. They demonstrated an increase in the degradation rate of contaminants by activated nZVI particles.

The improvement in reactivity in this second approach is related mainly to the degradation of the oxide shell, which enhances electron transfer and secondarily leads to an increase in the specific surface area of the nZVI after the activation process.

Testing on emerging nanoparticles for arsenic removal under real conditions on a pilot field site, in Asturias, Spain

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The Spanish test site is an abandoned 20ha brownfield in Asturias (Northern Spain), used historically for the production of fertilizers during 48 years (1950 – 1998). Contaminants include predominantly heavy metals both in soil and groundwater. Metals are associated to the madeground's materials: pyrite ashes and furnace slags; whereas in groundwater, leaching processes from contaminated madeground result in high levels of dissolved heavy metals, particularly arsenic, lead, copper, cadmium and zinc.

With all that, solved arsenic has been selected as the target contaminant to be treated with nanoparticles (NPs), given its high groundwater concentration (up to 5,500 ppb) and the lack of pilot test or field cases in the literature that pay attention to this element, which makes this field experiment particularly groundbreaking. Still, the study has also considered the effects of the treatment of the other metals and compounds like organic matter and dissolved anions such as nitrates, sulphates and phosphates.

As a result, the effect of NPs injection on natural biogeochemical processes of the soil-groundwater interface and therefore the sustainability of the treatment with NPs has been better understood. According to reactivity tests results, activated nano-scale zero valent iron (nZVI) (NANOFER STAR) was more efficient than other NPs such as iron oxides (goethites) in terms of the presence of arsenic in solution; consequently, it has been selected as the most appropriate product to be injected in the field test.

The injection plan included a total of 3 injection points and 8 control points in a flat, cleared area of 150m^2 approximately. A total of 250kg of nZVI dry product (15mt of solution) have been injected in the aquifer zone, 5 to 7 meters below ground level, at low pressure (<5 bars), from the 23rd until 27th of February 2016. Together with the iron, Lithium (LiCl at 50mg/l) was also added to help to trace the injected liquid. Before, during and 24 weeks (6 months) after the injection application, real-time geochemical measurements (pH, temperature, redox potential, electrical conductivity and dissolved oxygen) have been recorded and periodic groundwater samples have been taken in order to understand nZVI's behavior under real conditions.

In terms of technology efficiency, although dissolved total As levels initially diminished, at the end of the monitoring period, overall As concentrations increased in most wells. Considering the site's conceptual model, the increase of As concentration in groundwater sometime after the injection (2 weeks) is anticipated. The main source of As in the groundwater comes from the fill rich in pyrite ashes. Since the source is active while the nanoremediation takes place, dissolved As is

uninterruptedly generating as rainfall recharges the aquifer, so there is a counteracting effect of the active source against nZVI NPs injection. When nZVI NPs start to precipitate and their effectivity is reduced, the effect of the active source is more noticeable as an increase in As concentration. Yet, their effectivity is reduced to some extent, considering six months after the injection application geochemical groundwater conditions are indicative of the existence of a chemically reducing reactive zone.

Regarding nZVI's spatial distribution in the subsurface, iron particles have been detected in all wells as iron total, including well CP-7, 3 meters downgradient from the injection zone, following 3 days after the injection application, and in well MW-2, 15m downgradient from the injection zone, 2 months after the injection application. Unfortunately, some of the other metal levels increased after the application of nZVI, exceeding their reference value for groundwater (Dutch intervention value). This was the case for mercury, total chromium and lead. Nevertheless, last sampling campaigns concentrations for these metals are again below the intervention reference value for groundwater.

According to existing literature (Yan, W. Ramos, M.A.V., Koel, B.E. and Zhang, W, 2012; Ling, L. and Zhang, W. 2014,) , both arsenates As(V) and arsenites As(III) can be fully transformed into metalloid arsenic As(0) by reaction with nZVI, forming iron complexes. As(0) is insoluble, thermodynamically stable, and this reaction is not expected to be reversible. A priori, the desorption of the reduced arsenic from the iron complex is not expected, since current geochemical conditions (pH, ORP, phosphates) have been stable for the last 5 months and sudden changes affecting As behavior are not expected. In terms of increased toxicity due to nZVI's presence, the results already available with cultivable bacteria isolated before and after nZVI addition, show that a significant percentage tolerate the effect of nanoparticles. In summary, although in general terms results are encouraging (initial and occasionally persistent As levels reduction in some wells, reactive zone's continuity and minimal toxicity of NPs), the effect of NPs application to mixtures of dissolved heavy metals should be further investigated.

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Stakeholder engagement in the NanoRem project

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Introduction

Stakeholder engagement is an important part of the governance of the emerging technologies. It can help inform decision-making and collect perceptions, opinions, and attitudes towards a certain technology. Nanotechnology and nanoremediation, have received much attention in recent years. The use of nanoparticles in remediation offers potentially significant environmental benefits but there are uncertainties regarding the associated risk. Nanoremediation is also a field where theoretical research is closely linked to practical application. Therefore, it is important to engage stakeholders in the discussions about this technology. NanoRem is an EU-supported project that focuses on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation of groundwater and soil. This abstract discusses how stakeholder engagement was used in the context of the NanoRem project.

The NanoRem project supported dialogue and engagement with various European and international stakeholders in order to explore the extent of any consensus about appropriate uses of nanoremediation, understand its environmental risk-benefit, market demand, and overall sustainability and stakeholder perceptions. Stakeholder engagement in the NanoRem project followed a substantive rationale. It aimed at producing better decisions through inclusion of all the relevant expertise. NanoRem engaged in a variety of activities involving stakeholders. Besides two elicitation workshops held in Nottingham and Oslo, several special sessions and focus groups were organized during relevant conferences and meetings. All the events brought together regulatory, industry and academic experts and other stakeholders interested in nanoparticle-enhanced remediation. This presentation relates to opinions surveyed, which in a number of cases have now been addressed by the practical outcomes of the NanoRem project.

Risk

When discussing risks with stakeholders, the issue of 'renegade' nanoparticles was raised a number of times. 'Renegade' nanoparticles are those particles that are deliberately injected into the polluted groundwater, but either survive beyond the duration of the pollution or are transported out of the polluted area. In this context, the risk is driven by where nanoparticles get to (transport); what happens to them (fate); and the potency with which they can harm human health or specific environmental receptors (toxicity) or impact on natural waters outside of the site. Stakeholders agreed that elemental iron nanoparticles were unlikely to penetrate into the aquifer more than a few metres from the point of injection and were likely to interact with the aquifer matrix, groundwater and each other to rapidly lose mobility. They thought there was a potential for the NanoRem nanoparticles to be toxic, but they would be substantially less potent than nano-silver, widely used in

consumer products. There was a common agreement that possible risks arising from renegade nanoparticles should be addressed through the conceptual site model. This model should be developed for any site with polluted soil or groundwater and have the deployed nanoparticles added to the CSM. The outcomes of the Nottingham expert elicitation workshop, supported with evidence from the literature, formed the basis for a simple and conservative protocol for use during NanoRem field trials to control the risk posed by NP deployment and to reassure regulators that trials would be safe. This qualitative risk assessment protocol will be updated once the results of the NanoRem field trials and other experiments are available. It will be available by the end of the project on www.nanorem.eu.

Sustainability

The discussions on sustainability revealed a need for a broad perspective on the relationship between environmental, social and economic factors applied in a site-specific context. They also showed that there is little difference between nanoremediation and other *in situ* technologies when the generic sustainability issues are considered. Uncertainties in risks and benefits related to the use of nanoparticles were found to be the most important factor that will influence its future development and hence sustainability. Additional challenges include reduction of production costs for the different nanoparticles and increasing the lifetime of the product in order to justify these costs. It is also important to enhance the mobility of the particles in the subsurface, identify possible synergies with other *in situ* remediation techniques, and establish appropriate methods to determine the environmental fate of particles. The findings of the Oslo workshop were used to frame sustainability assessments for a NanoRem trial site in the Czech Republic and a potential deployment site in the UK.

Market

NanoRem has applied a "scenario" approach to give insights into the diversity of factors that potentially influence the future development of the nanoremediation market system - including its institutional setting. Dialogue with stakeholders has been a crucial step in the scenario development process. The discussions focused on identification and evaluation factors that are likely to drive or inhibit the development of the nanoremediation market and the relationship between them. The expert stakeholders discussed not only factors influencing the market development, but also the relationship between them. A factor can be active or passive depending on whether it is more likely to influence other factors or get influences by them. The Sustainability Workshop (Oslo, 2-4 December 2014) found that the most active factors that would be expected to determine development of the nanoremediation market were science-policy-interface and availability of validated information on nanoparticle application potential. This finding was confirmed in several expert workshops, including focus groups in Germany and the UK. The results of the scenario investigation emphasize that any improvement of the market uptake of nanoremediation in Europe by 2025 is closely linked to the existence of validated data on case studies – in particular if this information can be told as success stories. In addition, dialogue between the stakeholders (science – industry – policy – general public) is crucial.

Nano iron particles transport in fractured rocks: laboratory and field scale

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The study deals with the transport potential of nano iron particles (NIPs) in fractured media. To explore this subject, we used two systems:

(1) laboratory flow system constructed from a naturally discrete fractured chalk core 0.43 m long and 0.18 m in diameter; and

(2) field system of hydraulically connected boreholes penetrating a fractured chalk aquifer, in which there is a distance of up to 50 m between injection and pumping wells. Preliminary tracer tests revealed that the boreholes are well-connected by a fracture network.

First, in order to compare the transport potential of various NIPs under different conditions, a set of preliminary experiments were conducted using different NIPs and different stabilizers in two salinities. Four different NIPs were tested. We tested particle and solution properties (stability, aggregate/particle size, viscosity and density) in batch experiments, and we ran transport experiments in the fractured chalk core to observe breakthrough curves (BTCs) and measure recovery (mobile percentage of particles). We have learned that the most crucial parameters dominating particle transport are the particles/aggregate size and stability, governing NIP settling rate and ultimately their migration distance. The governing mechanism controlling NIP transport was found to be sedimentation and to a much lesser extent processes like diffusion, straining or interception. The NIP BTCs and recovery rates could be predicted from the batch experiments where settling rates were defined. Once Carbo-Iron® particles were selected for the field test injection, a series of laboratory experiments were conducted to assess the correlation between stabilizer (CMC)/Carbo-Iron® ratio and particle recovery.

Next, a field experiment was conducted with Carbo-Iron® particles using excess stabilizer concentration to ensure maximum recovery. High Carbo-Iron® recovery and fast arrival time, similar to the ideal tracer (iodine), were observed in the field. As in the laboratory experiments, particle recovery was mostly influenced by advection and hydrodynamic dispersion. An additional factor influencing recovery in the field was the mixing and dilution with the natural groundwater. The high recovery of the very viscous and stable particle solution indicated the importance of particle stability for transport in fractures. To control the Carbo-Iron® mobility and simulate a more realistic scenario, a second field experiment was conducted. The only difference between the two experiments was that the CMC – Carbo-Iron® ratio was reduced from 0.8:1 to 0.05:1 in the second field experiment. As expected, the lower amount of stabilizer resulted in a lower recovery of the particles. Interestingly, it was found that a sudden increase in the hydraulic gradient between the injection and pumping well resulted in the release and remobilization of Carbo-Iron® particles that had settled within the fractures.

Colloidal Iron Oxide Nanoparticles for Remediation of Land and Groundwater Aquifers contaminated by Heavy Metals or Organic Pollutants

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Heavy metals such as arsenic, chromium, copper, lead, zinc etc. are frequent and hazardous pollutants of groundwater. However, there are no sustainable and economically feasible technologies available to remove heavy metals from aquifers. Pumping groundwater and treating above ground by adsorption to iron oxides is an option which, however, is very costly and needs operation for very long time. Nano-iron oxides (nanogoethite) are well-suited to support microbial iron-reducing activity for oxidation of organic pollutants. Thus, we developed an *in situ* technology for heavy metal removal by adsorption barriers. In contrast to other proposed nanoparticle technologies our new iron oxide particles are true colloids which can be injected into sediments like liquids over several meter distances where they precipitate and cover the sediment matrix. Polluted groundwater can then flow through the barrier and heavy metals adsorb to the iron oxide releasing purified water.

Advantages of our new technology are the cost-effective *in situ* treatment of heavy metal contaminated sites by implementing adsorption barriers through the use of existing or newly implemented wells or direct push technology including the application even in difficult areas (industrial sites). A single and quick injection of colloidal iron oxides secures the migration of the particles in the conductive zone and leads to an efficient removal of heavy metals including a long lasting adsorption and operation of the barrier.

Trap-Ox Fe-zeolites for *in-situ* trap&treat of organic contaminants: lab-scale results on mobility, performance and stability

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Trap-Ox Fe-zeolites is a colloidal particle family tailored for *in-situ* <u>trapping</u> of organic contaminants by adsorption and catalytic <u>oxidation</u> in combination with oxidants such a hydrogen peroxide. Zeolites can be synthetized at large scale in various modifications differing in channel structures and Si/Al ratio. The best fitting choice of Trap-Ox Fe-zeolites is based on the type of contaminants and conditions at the field site. Within NanoRem, optimized injectable suspensions were developed for two zeolite types: Trap-Ox Fe-BEA35 and Trap-Ox Fe-MFI120.

Application of Fe-zeolites combined with H_2O_2 is an alternative to Fenton-like *in-situ* chemical oxidation (ISCO) with dissolved iron where acids or complexing agents (EDTA, citric acid) need to be applied in order to keep iron in solution. Fe-zeolites are active in a much wider pH-range. Thus, Trap-Ox Fe-zeolites can be injected in suspension together with the oxidant H_2O_2 for immediate oxidation of aqueous phase contaminants in the targeted aquifer zone at the native pH of the groundwater. In addition, due to their ability to adsorb organic contaminants, Trap-Ox Fe-zeolites can be used to form an *in-situ* sorption barrier after deposition on the aquifer sediment. This is highly desirable in case of extended and expanding plumes of contaminants where a sorption barrier can stop migration of contaminants and protects sensitive receptors. Furthermore, they can act against rebound of aqueous phase contaminant concentrations which often occurs by matrix back diffusion of contaminants from dense or sorption-active aquifer sediments after an initial ISCO measure. In this case, Trap-Ox Fe-zeolites trap contaminants by adsorption, which stops any further migration. H_2O_2 solution can be injected for degradation of adsorbed contaminants without any additional activator/catalyst, which avoids any vigorous reactions (gas and heat production) known from injection of conventional Fenton reagents (i.e. dissolved iron salts + H_2O_2).

For particle optimization regarding suspension stability and transport various modifications were tested: a) pre-treatment of the Fe-zeolite to increase the stability of the iron loading, b) addition of stabilizers (CMC, guar gum) and c) adjustment of suspension pH. Finally, optimal suspensions were obtained by a combination of a) oxidative pre-treatment and c) adjustment of slightly alkaline conditions (pH 8 to 8.5). Under slightly alkaline conditions (pH 8.5) suspensions are stable even at high particle concentration (10 g/L) and without addition of stabilizers. Particle transport in clean sand was not significantly affected by pH in the range of pH 5.5 to pH 8.3 with 76 to 88% mobile fractions (20 cm-columns, u = 10 m/d) for the two Fe-zeolites. In contrast, particle breakthrough curves in native sand were vastly different under acidic and slightly alkaline conditions. The blocking-type deposition at pH 5.5 for Fe-BEA35 with strongly retarded breakthrough of particles is explained by a limited number of Fe-oxide clusters in the natural sand which are positively charged at pH 5.5 and facilitate attractive electrostatic interactions with the Fe-zeolite particles. For optimal subsurface mobility suspensions of Trap-Ox Fe-zeolites should be adjusted to slightly alkaline conditions (pH 8.5) close to the pH of groundwater. Under these conditions mobility in native sand was shown to be excellent (≈ 80 % breakthrough for 20 cm columns) even for suspensions with high particle

concentrations (10 g/L Fe-BEA35) in very hard synthetic groundwater (F.l.h) and at moderate flow velocity (10 m/d). Based on these results it is anticipated that Trap-Ox Fe-zeolites can be injected by simple injection techniques (direct push or well injection) without the need for additional additives such as organic suspension stabilizers. For tracing of particles during injections a fluorescence-labelled zeolite was synthesized [1].

In batch experiments Trap-Ox Fe-BEA35 showed high catalytic activity in Fenton-like oxidation even in very hard water (pH 8.2). Reaction rates of the model contaminants were increasing in the order dichloromethane (CH_2Cl_2) < 1,2-dichloroethane < methyl *tert*-butyl ether (MTBE) < trichloroethylene (TCE) < toluene ≈ m-xylene which is in accordance with the selectivity predicted for a reaction driven by OH-radicals. The highly reactive and unselective OH-radicals degrade a wide spectrum of chemicals whereby the pore structure of zeolites adds steric selectivity. Therefore, Trap-Ox Fe-zeolites are applicable in cases where biodegradation or *in-situ* chemical reduction fails, e.g. in case of fuel oxygenates (MTBE, ETBE), halogenated aromatics (e.g. chlorobenzene) or halogenated alkanes (e.g. dichloroethane). Due to their narrow pores, Trap-Ox Fe-zeolites add some selectivity to the radical-driven oxidation by virtue of size exclusion and adsorptive enrichment. Macromolecules such as natural organic matter are excluded from access to the catalytic sites minimizing their impact as competitors for target contaminant degradation. With respect to contaminant selectivity the two Trap-Ox Fe-zeolites are complementary. Fe-MFI120 belongs to the group of hydrophobic MFI type zeolites [2] and is a high performance adsorbent for small organic molecules including many typical groundwater contaminants. Fe-BEA35 is a more universal adsorbent and catalyst allowing adsorption and degradation also for larger contaminant molecules.

Column experiments simulating the cycle of catalyst infiltration and immobilization, contaminant adsorption and degradation were conducted using MTBE as model contaminant. Trap-Ox Fe-BEA35 which was loaded on washed quartz sand at a mass fraction of 1 wt% showed stable adsorption and catalytic properties over three cycles of infiltration of MTBE-contaminated water (10 mg/L MTBE in F.l.h) with intermittent regeneration by H_2O_2 infiltration (10 g/L H_2O_2 in F.l.h). The Fe-zeolite deposited on the sediment was active for MTBE adsorption and oxidation over the four tested adsorption/regeneration cycles with in total 320 exchanged pore volumes of water. Based on the results of the lab tests, it can be anticipated that after injection and deposition on the sediment Fe-BEA35 remains active for contaminant adsorption and catalytic oxidation by subsequent H_2O_2 injections within a period of at least two months under these 'worst case' conditions. During this period the Fe-zeolite can eliminate (trap) contaminants from the aqueous phase resulting from migrating plumes or matrix back diffusion (e.g. from dense or sorption-active aquifer sediments) and allows catalytic oxidation of adsorbed contaminants. Further lab tests with water from potential field sites are needed in order to predict longevity of Fe-zeolites over extended time periods.

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Metal (composite) particles for reductive aquifer remediation - reactivity tests in columns

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Zero-valent iron (nano)particles are most commonly used for the chemical reduction of chlorinated ethenes like for example tetrachloroethene (PCE). As alternative reducing agents offering a better stoichiometry, the use of aluminium (Al^0), magnesium (Mg^0) and silicon (Si^0) might be promising. Moreover, these materials have a lower material density which is identified as one of the crucial properties for subsurface transport. In order to investigate the reactivity of aluminium, magnesium and silicon towards PCE column experiments have been performed under flow-through conditions. The columns (having a total length of 200 cm and an inner diameter of 3.6 cm) were filled with porous medium (crystal quartz sand) and the respective particles. According to the setup either an aqueous PCE solution was passed through the columns (plume remediation) or only degassed water with a flow velocity similar to a ground water situation. In the latter case PCE was placed directly in the front part of the column next to the particles (source zone remediation). Before and after the columns sampling ports have been installed for determining the PCE concentration as well as the concentration of degradation products in solution. Quantitation of gaseous reaction products or by-products (H_2 formed as a consequence of anaerobic corrosion) was enabled by means of gas traps. pH and ORP were measured online. Major findings of the column experiments (performed over a two month period) are summarized below:

- Silicon is not suitable for PCE degradation.

- PCE degradation (in terms of chloride formation) by means of aluminium could be improved by using mechanically activated particles (by ball milling them together with e.g. Al_2O_3 prior to use). However, the use of aluminium might raise some concerns regarding possible associated environmental risks.

- Al/Mg metal alloy particles showed a higher selectivity towards the contaminant than pure Al and Mg particles.

- Combining a small amount of aluminium with iron led to promising preliminary results.

Carbo-Iron as colloidal microreactor in the perspective of NanoRem

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The principle applicability of nano-sized zero-valent iron (nZVI) materials for *in-situ* groundwater remediation could be shown in several lab and field studies within the last decade(s). Bare nZVI itself proved to have high reactivity towards a large number of reducible water pollutants. However, its high intrinsic tendency to form agglomerates therefore provides only limited subsurface mobility. This behavior generated worldwide extensive efforts over the last decade on the optimization of its applicability and performance. Most commonly, suppression of the agglomeration was counteracted by organic coatings and addition of suspension stabilizers.

Within the NanoRem project a new material was introduced where nanoiron structures are embedded in microscale activated carbon grains ($d_P \approx 1$ µm) where the carbon framework acts as spacer between the built-in iron which prevents the iron-iron interactions driven by the magnetic forces, thus preventing particle agglomeration. This composite material, named as Carbo-Iron®, inevitably unifies properties of both components. The carbon not only enables Carbo-Iron® to form stable suspensions over longer times but acts as sorbent to support the performance of the reagent at the same time. The hydrophobic, porous carbon grain has the ability to enrich the contaminants of concern by several orders in concentration and easily supply them to the reactive sites.

Carbo-Iron® was subject of investigations at different scales and relevant scientific issues in terms of

- optimization of material production,
- development of analytical methods for particle tracing in natural environments and
- particle migration from column to large-scale experiments (flume and field application) and screening of its reactivity towards a variety of organic water contaminants.

The presented poster shows achievements and lessons learnt using the material which reach from upscaling of the production process to finding specific analytical methods for Carbo-Iron® tracing in field sediment samples. Distinct application modes were found for selectively placing the particles near contaminant sources or forming broad plume-treatment zones. The most important results of the work carried out during the project period are summarized and insight is given into the progress of the tailored design of the colloidal *in-situ* "microreactors".

Cascading Column System:
closing the Mass Balances and Results for Different Particles

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The radial flow field around an injection well of a 3-D aquifer can be represented by using quasi 1-D cascading column system. It is made up of a number of columns filled with porous media. By reinjection of slurry discharged from one column into the next one with an appropriate, decreased flowrate a time and space dependent concentration of nZVI suspension will be reproduced.

Data collected during the experiments were induced voltage measured by susceptibility scanner, pressure, mass flux and concentrations of nZVI of suspensions sampled at the inflow and outflow.

As yet, the magnetic susceptibility in the column measured with the scanner only shows the qualitative concentration of iron in the column. To link the measured magnetic susceptibility with the iron amount in the column mass balances were performed. Therefore the analytically detected Fe^0 concentrations of liquid samples were related to the qualitative Fe^0 concentration determined by susceptibility measurement. Results show a linear relation between both concentrations. Thus, after calibration of the susceptibility sensor the determination of quantitative nZVI deposition is possible.

Experiments were conducted with three different nanoparticles - Nanofer 25S, Nanofer 25P and Nanofer Star – produced by NANO IRON, s.r.o. The goal is to find optimal conditions (concentration of Fe^0, concentration of stabilizer, injection rate) to achieve best migration and sedimentation of particles for end-user application at a field site.

Different nZVI particles were evaluated based on handling, achieved migration distance and deposition. For an injection via filtered well (L: 1 m) with an injection rate of Q_{well}: 1 m³/h/m Nanofer Star and Nanofer 25S showed similar behavior. Since Nanofer Star is easier to handle on site and no additional stabilizer (PAA) was added which might affected transport Nanofer Star is recommended for the next injections.

For details of the data recording and processing see the poster by Anke Wiener "Cascading Column System: Improved Susceptibility sensors".

Cascading Column System: Improved Susceptibility sensors

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Influencing factors (Table 1) which determine the migration and sedimentation of nanoparticles can be measured with the optimized setup of the cascading column system (see poster by Friederike Müller "Cascading Column System: Closing the Mass Balances and Results for Different Particles"). Velocity of propagation and mass of iron remaining in the porous media of the column can be detected with a specially developed susceptibility measuring device. Using this non-destructive measurement method, during each experiment a number of scans in high spatial and temporal resolution can be recorded. These scans give a quantitative estimation of the sedimentation and distribution of nanoparticles in the column. For a complete balance of the deposited amount of nanoparticles in columns, iron concentration of soil samples and liquid samples (in- and outflow) can be analyzed.

Tab 1: Factors influencing migration and sedimentation of nanoparticles

Properties	Parameter	Methods
porous media	$q_{aquifer}$	flushing column with water $q_{aquifer}$ after NP –injection – verification of mobilisation deposited NP
	porosity n	filling columns with porous media from aquifer
	k_f	falling head permeability tests before and after each measurment
	dispersitvity	tracer test
radius of transport	lenght of each column	adaption of lenght according to radius of interest
nano particles	shape, size, density, agglomeration	manufaturer information
suspension	temperature	PT100 in injection vessel
	differential pressure	pressure transducer inflow and outflow
	Viscosity	rotational viscometer
	nanoparticle concentration	stoichiometric equations empirical equations
	addition of stabilizer	empirical determination
	NP– transport and sedimentation 1. Fe^0 2. Al/Mg, Ferrate	1.) nondestructive measurement via specially developed susceptibility method: induced voltage ~ $c(Fe^0)$ 2.) extra mass balances by analysing NP-concentrations of liquid and soil samples

This compact set up facilitated investigations of transport behavior of different nanoparticles. The poster shows operation and evaluation methods of developed measurement technology.

For details to the experimental setup see poster by Friederike Müller "Cascading Column System: Closing the Mass Balances and Results for Different Particles".

Migration and Reaction of iron oxide NP
in the large VEGAS Container

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To test the performance of iron oxide (Goethite) nanoparticles for the remediation of a BTEX contamination a large scale container experiment (LSC) was set up at VEGAS, University of Stuttgart. In a large artificial aquifer (L x W x H = 9 x 6 x 4.5m) a BTEX plume was emplaced which is to be remediated with iron-oxides nanoparticle (Goethite) that enhance microbial degradation. The accurate description of the aquifers and the contaminant distribution as well as a dense monitoring system allows for the testing of these nanoparticle materials, and will provide insight in particle transport in porous media and knowledge on degradation products under field relevant conditions.

The goals of the experiment are to explore transport and targeted deposition of Goethite nanoparticles in the subsurface, to remediate the BTEX plume (toluene concentration of 60 mg/L) utilizing iron-oxide nano particles (Goethite NP), and to quantify the remediation (degradation) rates and longevity of NP (reinjection intervals).

The artificial aquifer in the container consists of a heterogeneous flow domain plus inflow/outflow sections. Inflow and outflow boundary conditions are established using 12 communicating wells each to obtain constant head conditions. The flow domain (7.0m x 6.0m x 4.5m (L x W x H)) extends between the boundary sections and shows a heterogeneous soil structure which was realised by randomly distributing 60 sand blocks of two types of sands (medium and coarse). The aquifer thickness is 3.7 m during base flow (v = 0.4 m/d). The large scale container offers a total of 378 sapling ports distributed in six horizontal planes, seven vertical planes parallel to the direction of flow and nine planes vertical to the flow direction.

The toluene plume in the experiment was established with a continuous injection of a concentrated toluene solution (~400 mg/L) into selected wells of the inflow boundary (mass flux of toluene ~1600 mg/h) resulting in a flume with a cross-sectional area of 4m² (2 m x 2 m). The distribution of toluene concentration in the aquifer became stable after 50 days and the recovery rate of toluene break through at the outflow was reached 0.6 before NP injection.

6m³ of Goethite NP suspension (c = 20 g/L) was successfully injected on 15th October 2014 with injection rate at 0.7m³/h, duration of injection 8.5 h. 120 kg of Goethite particles were transported in the target zone of ROT 1.5 m with sufficient concentration.

After the injection of iron oxide NP a distinct increase in m_{TIC} and decrease of m_{tolu}, hence increase of biodegradation can be observed. However, this increase in biodegradation lasted for approx. 100 days.

During this time interval, 1394.1 g of TIC was produced due to toluene degradation. During the same time interval, toluene mass flux in the outflow of the container decreased from 1.2 g/h to 0.6 g/h, hence 1440 g Toluene (15.6 Mol) was degraded.

1 Mol Toluene (C_7H_8 = 92.14 g/Mol) needs 36 electrons to be degraded, so 36 x 1440/92.14 = 562 electrons are necessary for remediation of 1440 g toluene. If these electrons were provided by Goethite only (FeO(OH) = 88.8 g/Mol) then 88.8 * 562 = 49,905 g ~ 50 kg of Goethite was utilized.

Migration and Reaction of NANOFER STAR
in a Large Scale VEGAS Flume

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To test the performance of NANOFER STAR in a source-remediation approach, a large scale flume experiment in a container of stainless steel (L x W x H = 6 x 1 x 3m) was set-up at VEGAS, University of Stuttgart. The aquifer was contaminated with a perchloroethene (PCE) source and chemically reduced utilizing an injected NANOFER STAR suspension. The accurate description of the aquifers and the contaminant distribution as well as a dense monitoring system allow for the testing of these nanoparticle materials and provide insight in particle transport in porous media and knowledge on degradation products under field-relevant conditions.

Goals of the experiment were

(1)   remediation of PCE source (3kg) utilizing NANOFER STAR

(2)   design, set-up and test of NANOFER STAR injection system

(3)   transport and targeted deposition of NP in the subsurface

(4)   quantification of remediation (degradation) rates and longevity of the NP.

In the large scale flume an artificial aquifer was set up consisting of a flow domain of 5.6 x 1.0 x 3.0 m (L x W x H) of medium sized homogeneous sand. Inflow and outflow boundaries were established using hydraulically communicating wells, with constant flux and constant head control, respectively. The aquifer is unconfined and its thickness during base flow (v = 0.2 m/d) is at approximately 1.7 m, resulting in an unsaturated zone of approx. 1.3 m. The flume offers a total of 36 sampling ports, distributed in six horizontal planes and six vertical planes to the flow direction.

The PCE source was emplaced by injecting pure PCE into the aquifer. A total mass 3 kg of PCE was injected at six locations placed at equal distances on a hexagonal shape of r = 30 cm, at 10 different depths at 10 cm vertical intervals starting at the groundwater table. After 20 days, the PCE concentration of outlet became stable around 50 mg/L (mass flux ~ 0.25 g/h).

1m³ of aqueous suspension containing c = 10g/L NANOFER STAR was injected on 7th June 2016. The injection was done by direct push at 5 different depths with 15 cm intervals from upper to lower (from at 1.30 m to at 0.70 m height). At each depth around 200 L of suspension was injected with an injection rate of 0.5 m³/h (~ 8.3 L/min).

The transport distance of NANOFER STAR due to injection was found to be more than 38 cm for whole injection depth (1m).

After the injection of NANOFER STAR, an increase in PCE degradation could be observed. Production of degradation products Cl^-, ethene and ethane were also observed immediately after the injection. Even 90 days after the injection, the PCE degradation is still in progress. As a preliminary result, the STAR particles had degraded m = 190.3 g of PCE after 90 days, based on the produced mass of Cl^- in the outlet.

List of partners

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1 Coordinator	University of Stuttgart (VEGAS)	DE
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3	Solvay (Schweiz) AG	CH
4	Helmholtz-Zentrum für Umweltforschung GmbH	DE
5	Ben-Gurion University of the Negev	IL
6	Fundació CTM Centre Tecnològic	ES
7	University of Vienna	AT
8	University of Manchester	UK
9	Fundacion Tecnalia Research & Innovation	ES
10	Helmholtz Zentrum München (*Has left the consortium 31/03/2015*)	DE
11	Norwegian Institute of Bioeconomy Research *Name change (formerly "Bioforsk")*	NO
12	Technical University of Liberec	CZ
13	Norwegian University of Life Sciences	NO
14	Aquatest	CZ
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23	Contaminated Land: Applications in Real Environments (CL:AIRE)	UK
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