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

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Generalized Guideline for Application of Nanoremediation

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1   Introduction to the Generalized Guideline for Application of Nanoremediation

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" (7th FP, NMP.2012.1.2-2). 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).

1.1   What this Guideline can achieve

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 and 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.

1.2   What this Guideline cannot achieve

This is a technical guideline focusing on nanoremediation only. While it provides a comprehensive overview on the application of 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.

1.3   Regulatory issues

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 are listed in chapter 10 to facilitate communication between consultant and regulator.

1.4   Financial issues of nanoremediation

As for the application of any other remediation technology, there is no "generic" cost calculation for nanoremediation, rather the total cost will be a function of many parameters, due to subsurface and contamination, due to geographic location and so on. Nevertheless, to facilitate cost estimation the main cost drivers are listed in chapter 11. (For more information on financial issues see Bardos and Merlin, 2017)

1.5   Examples of nanoremediation

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

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1.6   Inputs necessary to beneficially use this technical Guideline

Detailed site investigation

Prior to any remediation action a detailed site investigation needs to be performed. The goal of this investigation is to clearly describe the hydrogeology and the hydrochemistry as well as the contaminant distribution of the site. In addition, existing buildings, foundations, cables, pipelines etc potentially influencing the installation of remediation actions need to be delineated.

Based on this information a conceptual site model has to be developed.

Conceptual site model, CSM

A conceptual site model (Appendix A - Conceptual site models) describes the site and delineates potential pathways of contaminants to receptors (humans, animals, plants,…). It then defines how to control/ sever these pathways in order to protect the receptors and thus the environment. Ideally all pathways can be controlled by a single remediation technology, however, in most cases a tiered approach will be necessary (technology A to control the path to groundwater, technology B to control the path to air etc).

Overview of available nanoparticles

A whole range of nanoparticles (NP) are available commercially or are currently being developed and tested (Appendix B - Nanoparticles available in NanoRem). Different NPs have different properties with respect to migration in the subsurface, reactivity, longevity, resistance to adverse chemical subsurface conditions etc. Appendix B - Nanoparticles available in NanoRem lists NPs developed and tested in the research project NanoRem and briefly summarizes their properties.

Operating window

Like all remediation technologies, nanoremediation has its benefits but also technical limitations. These are outlined in Operating Window tables provided in Appendix C - Operating window for nanoremediation.

1.7   Structure of the Guideline

The structure of the guideline is delineated in the flow chart depicted in Figure 1. This flow chart delineates the information necessary to use this guideline (mentioned above) and also shows which parts are treated in which chapter, thus it allows the user to quickly jump to a chapter of interest.
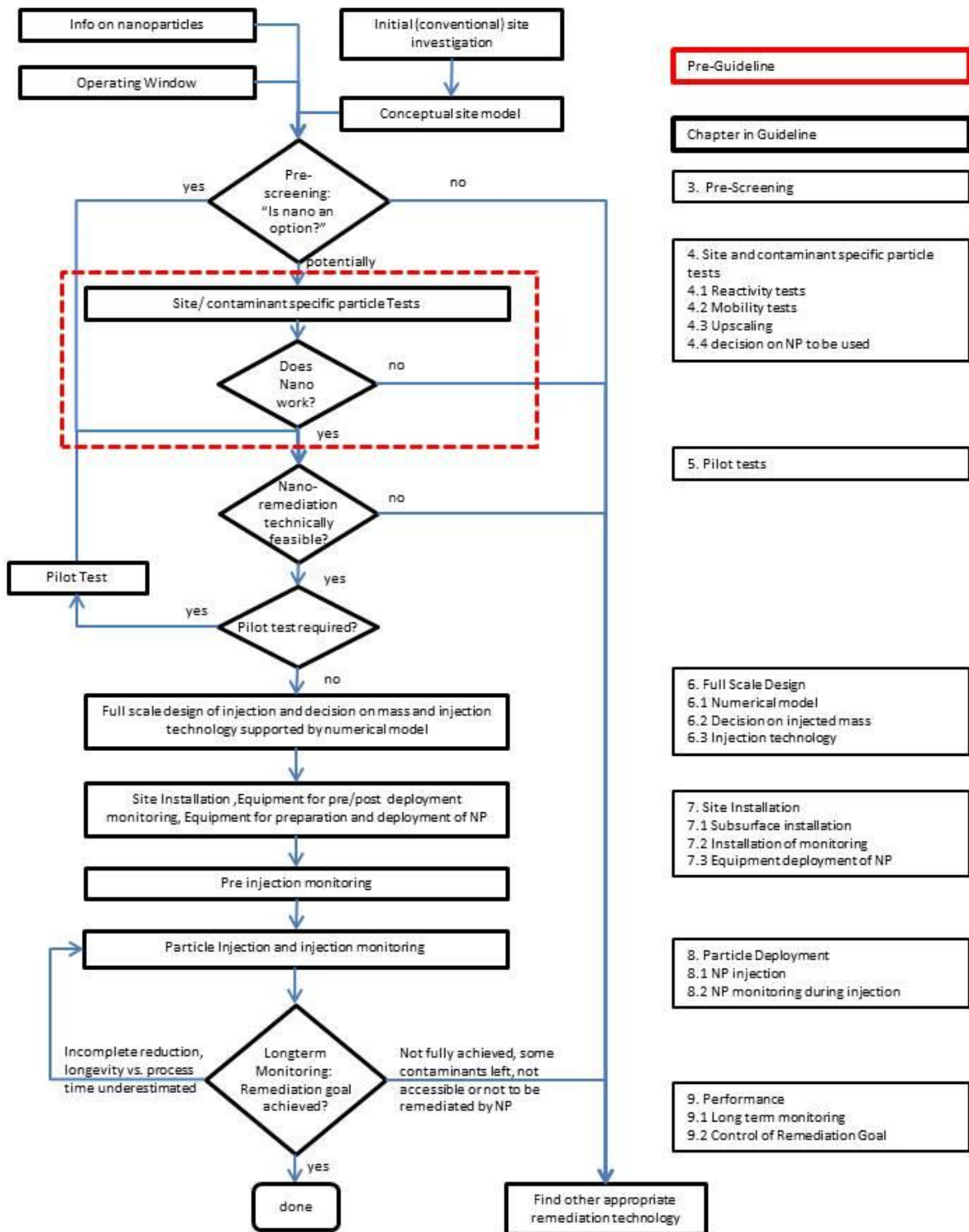
Figure 1:   Flowchart on the application of nanoremediation (details on reactivity and mobility testing, dashed box, see Figure 3)

2   Pre-Screening

A Pre-Screening tool (www.nanorem.eu) may be used to delineate if nanoremediation is a potential method of choice to remediate a given contaminated site. Prior to entering the prescreening tool the decision on a particle type has to be taken. The potentially optimum particle has to be selected based upon a sound conceptual site model (Appendix A - Conceptual site models), an in depth understanding of the properties of different nanoparticles (Appendix B - Nanoparticles available in NanoRem) and the operating window (Appendix C - Operating window for nanoremediation). The pre-screening tool will assist in verifying your choice and, if need be, point out possible obstacles.

The Pre-screening tool based on a Microsoft Excel® file where several input parameters are evaluated so that a first estimate is made, if the application of NPs is promising. In addition, the critical parameters (Figure 2) are identified which may need a closer evaluation for the site in question. Based on the contaminants dominating the site, a (pre)selection of a particle type has to be made beforehand. In the tool a distinction is made between oxidative and reductive particles and the respective set of parameters is to be filled in. The tool is subdivided into three main sections. The first section covers some general site conditions, some of which are used later to calculate composite conditions. The second section contains the hydrochemical conditions, which are essential for chemical remediation techniques. In the third section some hydrogeologic conditions are prompted, which finalize the overall picture of the case. For most parameters a direct decision is made based upon threshold values; other parameters are interconnected and a full evaluation whether the combination is favorable or not can only be given when all parameters are provided by the user. If requested parameters are not available or not relevant for the specific site the input may be omitted. The parameter is then, however, marked unfavorable.

An overall evaluation is given based on the ration between favorable and unfavorable parameters (see Figure 2). It again is favorable (=no obvious obstacles) or unfavorable (=potential obstacles/risks). In case of an unfavorable outcome the parameters identified as critical should provide a basis for further site-specific screening activities and particle specific tests that have to be performed. The more parameters are identified as critical the more additional investigations have to be made and the less likely is a successful or economically feasible application of a nano-based remediation.

CAUTION: The interplay between some of the influencing factors is very complex and cannot be exhaustively reflected in a simple tool like this. Thus, the use of the tool cannot replace the consultation of experts when deciding about the application of nanoremediation at a given site.

Based upon the outcome of the pre-screening tool the user may directly enter the technical planning phase and design the application (chapter 7). Alternatively, if one or several parameters are less favorable, additional site investigations or specific particle tests are necessary to proof the suitability of the particle under the conditions present at the site (chapter 3). The particle tests include the investigation of the transport behaviour and/or the reactivity under the conditions given at the site. Site specific tests might require taking soil and/or ground water samples while preserving relevant properties; they may even comprise the installation of additional sampling equipment and application of specific sampling strategies (chapter 4.1).

Prescreening tool

planning tool for applicability of
nanoparticles at specific sites

Particle type		Input (selection or value)	Effect of Condition	
oxidative	reductive		favorable	unfavorable
Condition				
general conditions				
access to site (select)		limited restrictions		☐ (yellow)
spatial extent of contamination (give m³)		1000	☐ (green)	
area affected (give m²)		100	☐ (green)	
legal boundary conditions (select)		injection possible	☐ (green)	
pilot application possible (select)		Yes	☐ (green)	
location of ground water table (m bgl)			☐ (grey)	
Hydraulic conductivity (kf)		1,0E-05	☐ (green)	
expected contaminant mass (kg)		3000	☐ (green)	
hydrochemical conditions				
ground water velocity (m/d)		0,1	☐ (grey)	
	redox potential (mV)	100		☐ (yellow)
stoichiometry (ration ox/cont)		1	☐ (green)	
Background consumption (NOM, factor to stoichiometry)		1		☐ (yellow)
	m-value mMol/L	10	☐ (green)	
	p-value mMol/L	0,1	☐ (green)	
	nitrate content in ground water (mg/L)	100	☐ (green)	
	sulfate content in ground water (mg/L)	100	☐ (green)	
longevity of the particles to be expected (months)		5	☐ (green)	
	enhancement of NA (sel.)	Yes	☐ (green)	
efficiency of particles (%)		20	☐ (green)	
hydrogeolocical conditions				
type particle injection (select)		direct push	☐ (green)	
depth of contamination (overburden/pressure needed)		1	☐ (green)	
contaminant distribution (select)		blobs	☐ (green)	
expected gas production (select)		moderate	☐ (green)	
	Sum		17	3
	Result	Looks good, but check yellow parameters		

Figure 2: Screen shot of pre-screening tool

3   Site and contamination specific particle tests

3.1   Site-specific particle tests and requested materials/parameters

Based on the outcomes of the pre-screening phase, one type of commercially available NPs is proposed to remediate a given contaminant type at a given site. The commercially available NPs can be supplied by the producer as a ready-to-use suspension or with a protocol for the preparation of a NP suspension. It is strongly recommended to experimentally verify the claims of the producer, including QA/QC checks for the batches and the suggestion of the pre-screening tool.

The site-specific tests account for reactivity and/or mobility of the selected NP suspension. Site-specific reactivity tests are recommended if I) the target contaminant is not on the producer's target list or II) if site conditions are slightly deviating from the optimal application window defined by the supplier and in general, if III) NP products new to the market shall be applied for which experience from previous field applications is still limited. Mobility tests need to be conducted in any case (Figure 3). The experiments ought to be carried out under laboratory conditions resembling those at the field. It is recommended that, whenever available, representative porous medium and groundwater from the contaminated site are used. If site material is not available, the laboratory tests need to be designed in accordance with the known hydrogeological and hydrogeochemical parameters at the field (Table 1). Additionally information on the groundwater flow velocity and the expected injection velocity, based on the applicable injection technology for the particular field site, is required for the design of the mobility tests.

Table 1:   On-site (input) parameters needed for site-specific tests.

Parameters for mobility tests	Parameters for reactivity tests
Availability of contaminants: pool/ residual/ plume	
Groundwater seepage velocity, v	Targeted contaminant type and content
Hydraulic conductivity, K	pH, buffer capacity
Effective porosity, n_e	Eh
Grain size distribution curve (alternatively d_{10}, d_{50}, d_{90})	O_2 content
Mean diameter of porous medium (d_c)	Major anion content
Mineral composition of porous medium	Major cation content
	Fe^{2+}, Mn^{2+} content
	NOM (natural organic matter)

The proposed workflow for the site-specific mobility and reactivity tests is presented in Figure 3.
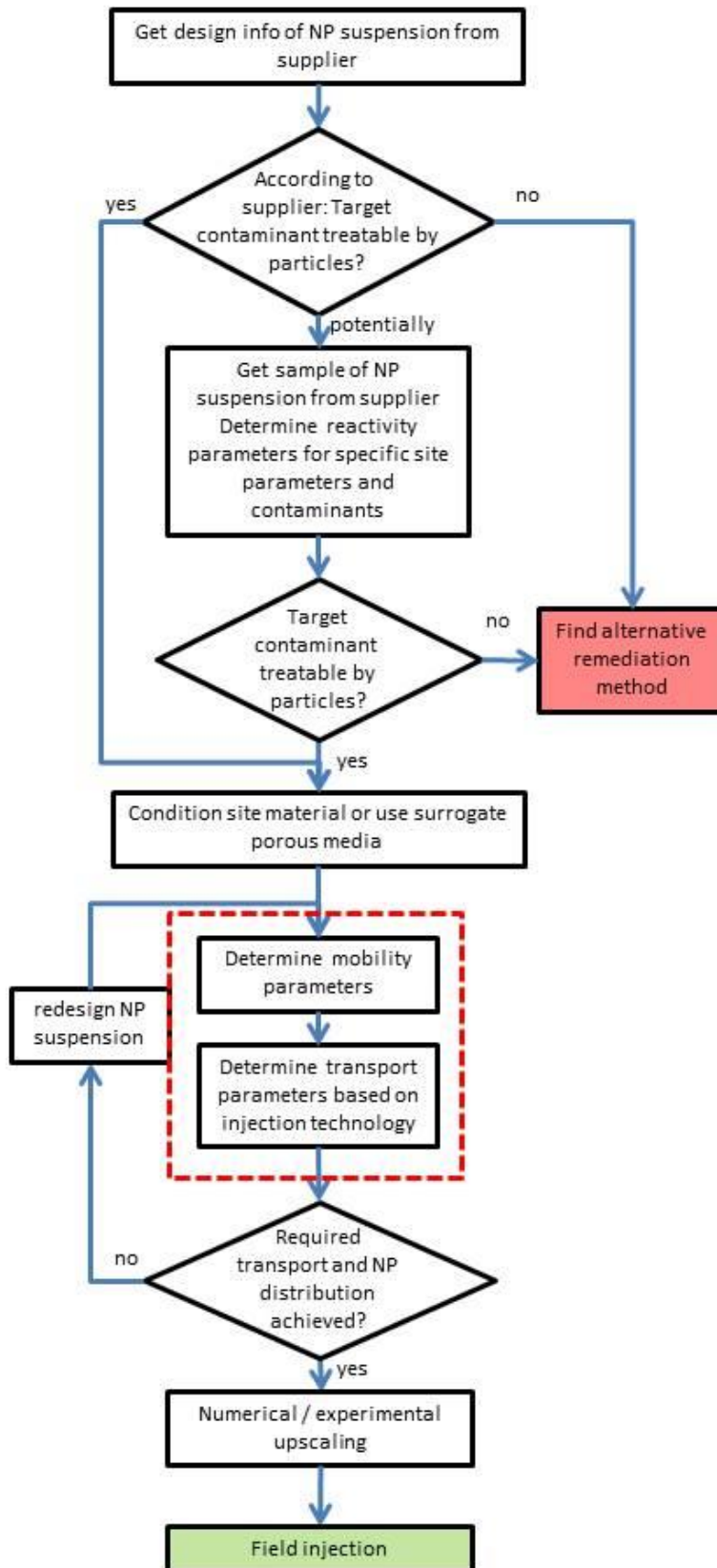
Figure 3:   Flowchart: reactivity and mobility testing (details on mobility testing, dashed box, see Figure 5

3.2   Site-specific reactivity tests

Each site is characterized by its specific contaminant spectrum and hydrogeochemical conditions which include pH, dissolved oxygen concentration, ORP, dissolved inorganic ions and organic matter (DOM) in groundwater as well as the mineral composition and the natural organic matter (NOM) content of the sediment. These site-specific factors can have substantial influence on NP reactivity, efficiency, longevity and (by)product formation. For nano iron and other ZVI-based particles, knowledge on the impact of various hydrogeochemical parameters is well established and operation windows for optimal applicability can be defined. **Figure 4** gives an example for the optimal operation window of Carbo-Iron.

	pH
3 4 5 6 7 8 9 10 11	

	ORP (mV)
+200 +100 0 -100 -200 -300	

	$c_{O2,15°C}$ (mg L^{-1})
10 9 8 7 6 5 4 3 2 1 0	

	Hydr. Conductivity (m s^{-1})
Gravel Sandy Gravel Middle Sand Fine Sand Very Fine Sand, Silt, Loess, Loam	
10^{-1}-10^{-2} 10^{-2}-10^{-3} 10^{-3}-10^{-4} 10^{-4}-10^{-5} < 10^{-5}	

not treatable	Sorption	Reduction	Treatability
Hydrophilic non-reducible substances, (such as acids, alcohols, fuel oxygenates, but also dichloromethane, dichloroethane…)	**Hydrophobic** non-reducilbe substances (such as PAHs, pollutants with aromatically bound halogen, pesticides, pharmaceuticals…)	**Reducible Pollutants** (such as halogenated hydrocarbons, metals /metalloids, pesticides and pharmaceuticals with aliphatically hound halogen, Nitro compounds…)	

Figure 4:   Pre-consideration of basic functioning of a particle type under aquifer conditions (example Carbo-Iron; green = expected to function, yellow = could function, red = not expected to function)

Site-specific reactivity testing in the lab can be omitted, if site conditions can be clearly identified to be within the optimal operation window, which should be defined by the NP producer and substantiated by publically available reports on previous lab and field testing. However, if there are deviations in one or more parameters or uncertainties about site-specific interactions, lab-scale tests can safeguard decisions before entering pilot tests. On the other hand, site-specific reactivity tests are indispensable if the target contaminants are not on the producers target list and/or no limited data from previous field tests exist for the specific NP/contaminant combination.

The simulation of field conditions through laboratory reactivity tests are common practice and allows approximation of the general particle reactivity towards the target contaminant. However, true field-like conditions can hardly be created in the laboratory. Even though experiments can be done with water and soil samples from the field, the achievable information is naturally limited since I) the experiment can only give a segmented, punctual and small-scale picture of the (heterogeneous) site regarding reactivity aspects, II) all steps of sampling, shipping, storage and experimental setup using samples from the site are prone to distort hydrogeochemical conditions. Precautions need to be adhered to e.g. in order to fully maintain anaerobic conditions, prevent loss of volatile compounds, or even more difficult, to maintain a certain indigenous microbiology. Standard methods for groundwater and soil sampling are summarized e.g. in TGM (2015).

Thus, working with synthetic water adapted to the most important parameters of the site with respect to contaminant spectrum, composition of inorganic ions, ionic strength, pH, and O_2 content can be a good alternative to using site material, depending on the specific processes which have to be considered.

In case a site is regarded as generally treatable by a particle type, the expected outcome of site-specific reactivity testing are quantitative parameters which can serve as input parameters for modelling with the final aim to determine the required volume/mass of material and the timeframe needed to reach a certain remediation goal and to identify the footprint of the remediation measure at the specific site.

3.2.1   Relevant information and output parameters from reactivity tests

Reactivity tests provide information on the expected range of reaction rate between the contaminant and the reactive particles under the test conditions, expected products/by-products/intermediates and in most cases also chemical fate/life-time of the reactive particles. Together with modelling tools these raw data can be used for the design of the field application. The input mass of the reactive NP component (e.g. as Fe(0) content) or other reagents (e.g. H_2O_2 in combination with Trap-Ox Fe-zeolites) can be estimated. If the target contaminant is not on the producer's target list, the identification of the final reaction products and intermediates is of high relevance for the evaluation of the environmental impact.

Common to all particle types is that kinetic parameters for the degradation of target contaminants are determined from concentration-over-time profiles for contaminant removal. Kinetic parameters are reaction rate constants based on fitting kinetic data to suitable models or, in case of complicated kinetics, more simple measures such as half-lives or required contact times for reaching a certain removal degree.

Key factors and measures for particle efficiency as well as interferences by site-specific conditions depend strongly on the mode of action of the considered NPs. The most important factors and parameters are discussed below for the three types of NPs action: reduction, oxidation and adsorption of contaminants.

3.2.2   Parameters for ZVI-based and other reductive particles:

Within NanoRem, this group of particles comprises NZVI products (e.g. NANOFER 25S, NANOFER STAR, FerMEG12), ZVI-based composite particles (e.g. Carbo-Iron®) and Fe(II)-containing oxides (e.g. Bionanomagnetite).

- Reaction rate constants: If the reagent (in most cases the zero-valent metal) is applied at sufficient surplus, contaminant degradation frequently follows pseudo-first-order kinetics. For nZVI-based particles, surface-area normalized reaction rate constants (k_{SA} in [L (m² · min)$^{-1}$]) are commonly reported.

- Particle life-time and/or consumption rate constants: Zero-valent metals such as NZVI are consumed not only by the reaction with target contaminants but also by anaerobic corrosion and reaction with other oxidizing species (e.g. dissolved O_2 or nitrate) if present. The rate of anaerobic corrosion can be influenced by groundwater composition (pH and inorganic ions such as sulfate and natural organic matter). Thus, in lab experiments under site-relevant conditions,

preferably with site material, the depletion in zero-valent metal content over time is monitored and if possible described by suitable kinetic models in order to derive rate constants for modelling. Anaerobic corrosion is frequently followed by detection of H_2 evolution.

- Particle efficiency (ϵ): Particle efficiency (ϵ [-]) is defined as the fraction of potentially reactive particle constituent (e.g., Fe(0) of nZVI) which is utilized to degrade a target contaminant. Particle efficiency is limited by non-target consumption processes such as Fe(0) corrosion.

- Products and intermediates: Reductive transformation generally attacks certain functionalities in organic contaminant molecules but cannot lead to degradation of the carbon backbone. Ideally, halogenated contaminants are fully converted to non-halogenated hydrocarbons with concomitant release of halogenide ions as has been shown e.g. for TCE and PCE as most important target contaminants of NZVI-based particles. However, for novel zero-valent metal type particles or 'novel' or 'emerging' halogenated contaminants the formation of hazardous dead-end products needs to be excluded. Reductive transformation and subsequent immobilization of heavy metals (e.g. Cr(VI), radionuclides U(VI), Tc(VII), Re(VII) and metalloids (e.g. Se(VI)) by ZVI-based and other reducing particles requires not only the identification of short-term reaction products but needs to take the long-term effects into account. This is due to the fact that metals or radionuclides immobilized by reducing NPs may undergo re-oxidation or remobilization depending upon changes in the biogeochemical conditions (especially redox potential) in the subsurface, although information on the long-term stability of *in-situ* stabilized contaminants is very limited up to now.

3.2.3   Parameters for NPs applied for contaminant oxidation (e.g. Nano-Goethite, Trap-Ox Fe-zeolites):

So far there are no NPs on the market which, in analogy to nZVI as reductant, would directly act as particulate oxidant. However, within NanoRem NPs were developed which either I) enhance microbial contaminant oxidation (Nano-Goethite) or II) catalyse H_2O_2-driven contaminant oxidation in combination with contaminant adsorption (Trap-Ox Fe-zeolites). Due to the different mode of action, the setup for site-specific lab-scale reactivity tests and parameters used for their evaluation are more specific.

Nano-Goethite applicability tests for enhanced microbial oxidation are performed as incubation experiments with site sediment. Sediment is sampled, stored and used in experiments with the addition of Nano-Goethite carefully avoiding disturbance (e.g. avoiding O_2 contact) of biogeochemical conditions.

- In order to evaluate whether indigenous microorganisms can reduce the Nano-Goethite for the oxidation of hydrocarbons and to allow for adaptation, experiments are performed over sufficiently long time periods (several weeks).

- Degradation rates are determined by the detection of Fe^{2+} production and reduction in contaminant (e.g. BETX aromatics) concentrations.

Trap-Ox Fe-zeolites combine two processes and act as adsorbents for contaminants and as Fenton-like catalysts to oxidize the adsorbed contaminants with H_2O_2. Relevant parameters for reactivity tests with Trap-Ox Fe-zeolites are:

- Kinetic parameters for degradation of target contaminants: As for *in-situ* Fenton oxidation processes in general, the contaminant degradation rate in case of combined application of Trap-Ox Fe-zeolites and H_2O_2 depends on I) H_2O_2 concentration available in proximity to cata-

lyst particles, II) pH of the water and III) composition of the water matrix. Different to *in-situ* Fenton with dissolved iron, the Fe-zeolite-catalyzed Fenton is active at a wider pH range (pH 3-8) and less sensitive to OH-radical scavenging species (e.g. chloride, carbonate or NOM). Nevertheless, high concentrations of divalent cations (Ca^{2+} and Mg^{2+} in very hard water) affect contaminant degradation rates and various Fe-zeolite types differ in their optimal application pH. Previously not tested, larger contaminant molecules (e.g. highly-branched aliphatics or compounds with several aromatic rings) need to be studied on a case by case basis due to the size selectivity of the various Fe-zeolites.

- Rate of oxidant depletion/Natural oxidant demand: Since H_2O_2 can be decomposed via productive (leading to the desired OH-radicals) and non-productive pathways (at the surface of some soil minerals) the rate of oxidant decomposition by site sediment alone and after deposition of the Fe-zeolite needs to be determined in order to estimate the radius of influence of the oxidant and determine the required oxidant doses.

- Contaminant mineralization and byproduct formation: Ideally radical-driven oxidation leads to full mineralization of contaminants. However, in zones of oxidant limitation mineralization may be incomplete. Commonly observed organic byproducts of Fenton-like oxidation are low molecular weight carboxylic acids and others which are non-toxic and biodegradable. In some cases heteroatoms (e.g. Cl) in the parent molecule remain in the intermediates. Thus, the potential formation of unwanted byproducts needs to be counteracted by the addition of oxidant amounts for sufficiently deep oxidation instead of just accepting the disappearance of the parent compound (determination of oxidant demand).

- Oxidant utilization efficiency: In analogy to particle efficiency for ZVI-based particles, an oxidant utilization efficiency can be determined, e.g. as ratio of moles of contaminant degraded per moles of oxidant consumed.

3.2.4   Parameters for particles with adsorption-based mode of action

Various NPs including those developed in NanoRem rely on the adsorptive removal of contaminants as dominant mode of action or as contributing step in combination with reductive or oxidative contaminant removal. For instance, NPs with iron oxide surfaces (Bionanomagnetite or Nano-Goethite) are very good adsorbents for As(V) and As(III). Carbo-Iron and Fe-zeolites act as adsorbents for organic contaminants due to their microporous supports and contaminant enrichment in the vicinity of active sites is beneficial for their degradation (by reaction with the Fe(0) component in Carbo-Iron or in combination with H_2O_2 for Fe-zeolites). However, if the contaminant cannot be degraded by a suitable abiotic reaction, the adsorbent particles can still be used as a sorption barrier to cut a plume, i.e. to prevent further spreading of contaminants and thus provide sufficient time for natural attenuation processes. If contaminants are solely immobilized by adsorption and not degraded, reversibility of the adsorption upon changes in geochemical conditions becomes an issue, which needs to be dealt with in long-term lab tests. Parameters studied in lab-scale test with adsorbent particles are:

- Adsorption isotherms which describe the equilibrium between adsorbed and aqueous phase concentration and, if applicable, maximum uptake capacity and can be fitted to isotherm models (e.g. Freundlich or Langmuir model). Competition between various contaminants and/or water matrix constituents (e.g. heavy metal species: other inorganic ions and NOM) needs to be taken into account.

- Kinetics of adsorption processes: The kinetics of adsorption processes determine to which degree the adsorbents' potential can be utilized under flow-through conditions. Batch experiments can be used to study the rate of intraparticle processes (e.g. diffusion in porous particles) and/or processes at the particle surface (i.e. rate of adsorbate formation on the surface). In column experiments, a more realistic picture of mass transfer under groundwater flow conditions is obtained including convective and film diffusion processes. Retardation factors are obtained from breakthrough curves of contaminants in comparison to inert tracers.

In general, for all three types of reactive particles, a sequence of experiments with an increasing degree of complexity is recommended. To start with screening and confirmation of NPs applicability in batch experiments with synthetic water or water from the site and, in case of positive evaluation, followed by column experiments with soil samples from the site. The detailed setup of experiments depends on the nanoparticles' mode of action and the specific questions to be answered. In the following, advantages and disadvantages of batch and column tests in site-specific reactivity testing are summarized.

Batch experiments:

- fast screening of reactivity towards a set of target contaminants and/or reaction conditions

- conditions can be easily controlled (pH adjustment)

- intense agitation can be applied and mass-transfer effects on reaction kinetics excluded or minimized in order to determine intrinsic particle reactivities

- reaction rate constants can be easily derived

- batch experiments with sediment require shaking which can cause perturbations due to mechanical stress/grinding effects

Column experiments:

- more elaborate and time-consuming

- more realistic scenario for reactivity or adsorption under flow-through conditions

- impact of sediment on reactivity well represented

- quantitative evaluation with respect to reactivity parameters, is more complex and/or calculated parameters are specific for applied conditions (flow-rate, particle loading on sediment)

3.3   Site-specific mobility tests

3.3.1   ROI vs. ROT

When looking at an injection of NPs in the field a distinction between radius of influence (ROI) and radius of transport (ROT) needs to be made. The ROI encompasses the total volume of the porous media affected by the injection, i.e. the volume reached by the transport fluid. ROT is the distance from the point of injection within which 80% of the injected nanoparticles are emplaced. This definition was chosen under the assumption that it encompasses an area with sufficient NP mass to efficiently remediate a contamination present. Given that NPs usually experience some kind of retardation ROI is larger than ROT and thus the remaining (20%) particles will be dispersed in a distance ROT > r > ROI. Of course, there will also be an effect of the injection at a radius beyond ROT, however this effect is most

likely not due to the particles injected (but rather due to e.g. dissolution etc). Two alternatives are proposed to attain an expected ROT for NPs on a large scale, at a field application (Figure 5):

- Relatively simple injection tests with short columns in conjunction with a numerical model

- Somewhat more elaborate cascading column tests to directly deduce the ROT
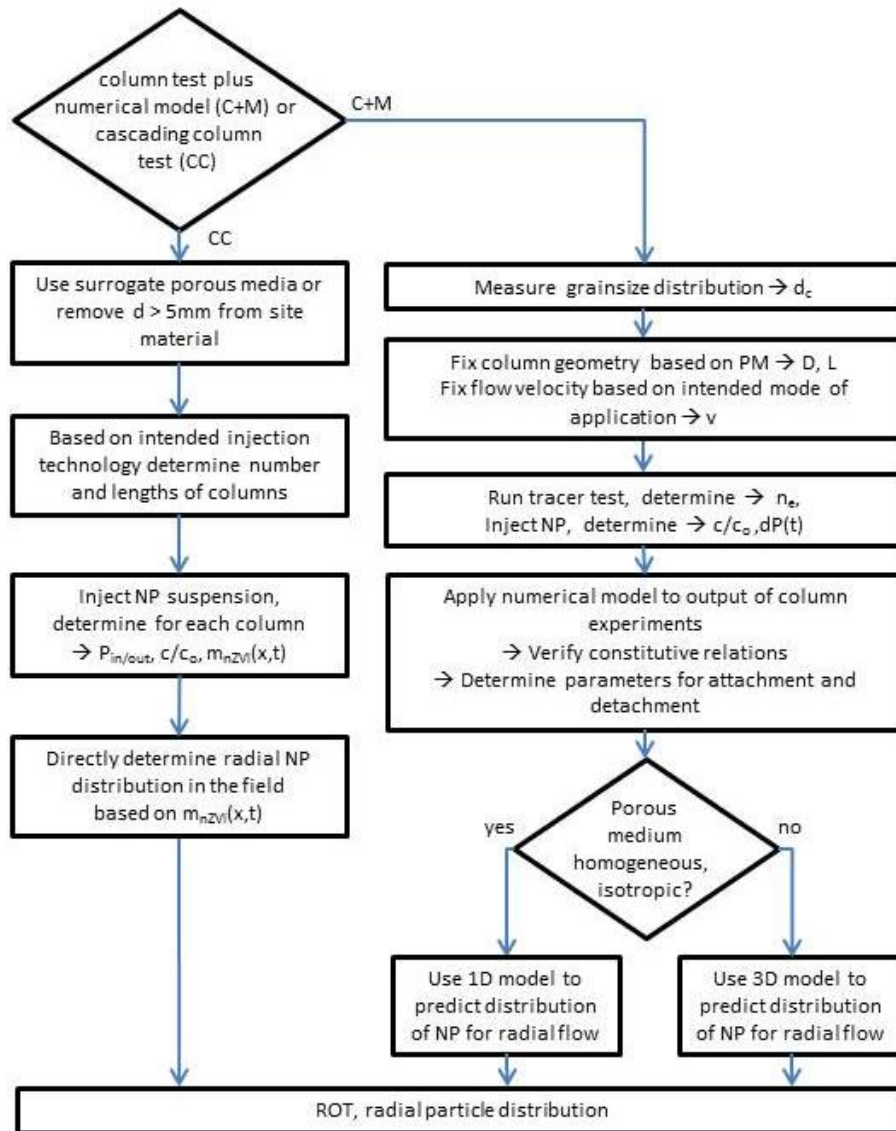
Figure 5:   Workflow of site-specific mobility tests and numerical modelling

3.3.2   Preparation of columns for particle transport tests

Column preparation for the small columns and the cascading columns is pretty similar. In the following a brief summary is offered, additional information on the preparation of column tests may be found in Appendix F - Mobility investigations of nanoparticles.

When representative porous medium from the contaminated site is available, dry the porous medium and break up the agglomerates potentially formed during the drying procedure. If possible, use the porous medium as it is (without sieving). In case that grains are present, which are not compatible with the appropriate column diameter (see below), they need to be sieved out. Determine the grain size

distribution of the porous medium. Select the column dimensions according to the porous medium (collector) diameter.

If porous medium from the contaminated site is not available, then select a surrogate porous medium with a comparable grain size distribution and a hydraulic conductivity similar to the one determined for the field site. The surrogate should also have comparable mineralogical composition to the porous medium from the contaminated site.

Column dimensions must be in agreement with the size distribution of the porous medium. Column diameter (D) to collector diameter (d_{50}, i.e. median grain) ratio D/d_{50} should be ≥ 20 (preferable ≥ 50) in order to avoid "wall effects". For the same reason, the ratio of column length (L) to diameter (D) should be $L/D \geq 4$.

The selection of column material must take into account the structural strength of the material, possible chemical interference with the NP suspension and interference with the monitoring techniques (to be avoided). Additional points to consider are the ease of installing instrumentation and material transparency (to allow for visual observation).

For small column tests with ZVI NPs Plexiglas^{TM} is recommended, since it is transparent, it is less apt to break (compared to glass), easier to modify and allows for the installation of sampling and monitoring ports throughout the column. For cascading columns usually glass columns are used for their better bending stiffness when placed horizontally.

For smaller column dimensions (length ≤ 20 cm) slurry packing is recommended. In this case the soil is saturated with water and settled at the bottom of the column either by stirring the soil into the water prior to pouring it into the column as slurry, or by filling the column with water and then slowly pouring dry soil into the column while stirring. For larger columns (length > 20 cm) dry packing is recommended. It involves loading small amounts of dry soil into the column and then mechanically packing it either by hand or with a pestle, or, for longer columns use the pluviation method proposed by Rad and Tamay (1987). Prior to the (water) saturation the porous media it is to be flushed with at least five pore volumes of CO_2 and then upwardly replaced by three to five pore volumes of de-aired water. If the length of the column does not allow for dry packing, slurry packing is necessary.

The effective porosity of the porous medium in column should be determined using a nonreactive tracer (e.g. Br$^-$). The tracer solution of a known concentration is introduced into the column with a pump at a known flow rate. The column effluents are collected in a time frequency selected in accordance with analytical limitations (regarding the effluent volume and concentration). From the tracer breakthrough curve read the elapsed time ($t_{0.5}$) at $C/C_0 = 0.5$ (where C_0 is the initial tracer concentration and C is its concentration at a given sampling time). With $t_{0.5}$ and the known flow rate, calculate the tracer volume (equal to pore volume, V_p, corrected for the volume of the tubing, if needed). With V_p and the volume of the column, V_c, ($V_c = A*L$, where A is area of the column cross section and L is the column length), calculate effective porosity (n_e) as $n_e = V_p/V_c$.

After the tracer test, flush the porous medium with at least 4 pore volumes with the chosen background solution (e.g. ultrapure water or the type of water which NP solution was prepared in) in order to remove residual tracer from the pore space.

Columns need to be kept saturated until the n_e is determined. When the relative standard deviation (RSD) of n_e measured in triplicate columns is ≤ 2%, it is considered that the columns were packed homogeneously and can be further used for the mobility tests.

3.3.3   Transport tests in short columns

The column should be oriented vertically, if the mobility test is aimed to simulate vertical particle propagation under injection or natural groundwater condition or horizontally if the mobility test is aimed to simulate horizontal propagation of particles after the injection at natural groundwater flow condition as well as to minimize gravitational effects on NP transport. In case of vertical column orientation the recommended flow is from bottom to top to prevent gas entrapment. To ensure reproducible and reliable results a minimum of three replicates is recommended.

The method of introducing NPs into the column and the chosen flow velocity depend on the subsequent data processing and, thus, ought to be defined in close conjunction with the numerical modelers. To attain parameters for the potential of the NP suspension to be delivered into the contaminated zone during the particle injection, the column test should be carried out under injection condition (flow velocity of ca. 10–100 m/d). In this case NP suspension of a known concentration is continuously injected into the column using a pump (e.g., peristaltic or piston pump) under the injection flow velocity. In order to reduce NP aggregation and sedimentation, the NP suspension must be homogenized (by e.g., sonication, dispersion unit, or agitation) prior to and during the injection. Suspension should be injected until the particle breakthrough occurred. To facilitate the use of the data in a numerical model it is required that the evolution of the pressure at the inflow and outflow of the column is continuously monitored during the mobility tests in all three replicate columns. For this purpose differential manometers or online pressure transducers are recommended.

Column effluents need to be collected at appropriately short intervals (either manually or using e.g. an autosampler) for a subsequent particle concentration analysis. The target parameter to assess NP concentration and subsequently the transport depends on the NP type. In case of ZVI or Fe oxide NPs, particle concentration is usually estimated on the basis of Fe_{tot} measured in unfiltered effluents (after acid digestion) e.g., by means of ICP-OES. The handling of samples must be in accordance with the NP Specific Safety Data Sheet, provided by the NP producer.

Results of the column tests are to be shared with the numerical modelers (chapter 5). The data should be presented as particle breakthrough curves and should also include the tracer breakthrough. The NP breakthrough curves should be constructed from the mean values including the RSD. Figure 6 shows exemplary the target parameter for NP concentration and tracer concentration presented at the y-axis, while the number of pore volume (alternatively sampling time) is placed on the x-axis.
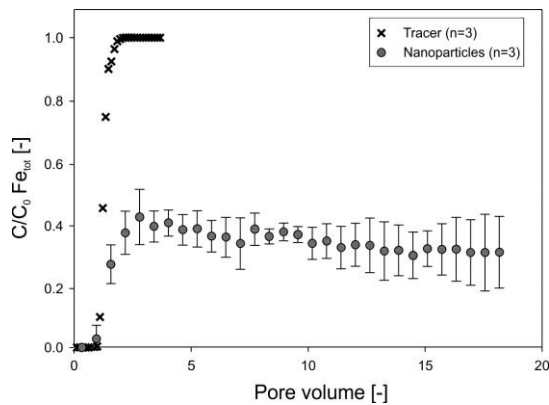
Figure 6:   An example of NP and tracer breakthrough curves where Fe_{tot} was used to assess the concentration of nZVI particles.

An additional, optional, measure to facilitate the use of the experimental data in the numerical model and to better calibrate the model would be to determine the distribution of the retained NPs along the length of the column (both in case of presence or absence of NP breakthrough). This could be carried out either via magnetic susceptibility measurements (when the NP type and column geometry allows) or via separating the porous medium into the section of defined length and analytically determining the NP content in each section separately.

3.3.4   Additional outcome of short column tests

In order to test the mobility potential of renegade particles after the injection, the column test should be carried out under natural groundwater flow conditions. This test may be carried out in the same column in which the deliverability of NPs under the injection condition was performed. Columns are to be utilized after the plateau of NP breakthrough was achieved. If no breakthrough of NPs is observed, it implies that the travel distance of renegade particles from the injection point less than the length of the column.

Based on the outcomes of the column experiments Attachment efficiency, α, and Particle deposition rate coefficient, k [s^{-1}], both calculated after Kretzschmar et al., 1999, using either the mean value (from 3 independent replicates) of the particle breakthrough at plateau (C/C$_0$) or a selected particle property (such as magnetic susceptibility or fluorescence signal) as well as Predicted travel distance (Elimelech et al. 1995) may be determined to directly compare the transport potential of different nanoparticles. While this predicted travel distance cannot be directly applied to the determination of absolute NP migration in an aquifer it is, in conjunction with numerical modelling, a good indicator for relative NP mobility for fairly stable suspensions and useful for the comparison of the migration potential of different nanoparticles.

3.3.5   Direct experimental evaluation of ROT using cascading columns

Transport of NPs strongly depends on shear forces and thus the flow velocity of the injected suspension. This flow velocity is highly variable; it hyperbolically decreases as a function of distance from the injection point. Since the investigation of a quasi-3D radial flow field is extremely time consuming and elaborate, the cascading column approach is used, which allows for the representation of a radial flow field with a number of linked column experiments (Comba S. and Braun J., 2012a,b)

A cascading columns experiment is a one dimensional method that reproduces the radial flow and transport of NPs in the proximity of an injection well in an aquifer. The length of each horizontally ori-

ented column corresponds to the thickness of a section of area between the injection well and the ROT and is determined by a velocity, a volume of injected slurry and the duration of flow of the slurry in the respective area. In order to simulate the concentration decay, slurry discharge from each column is re-injected into the next column.

With these experiments it is possible to experimentally upscale the transport process and to determine the parameters for the transport and deposition of NPs for a successful remediation on a large (field) scale (Figure 7).
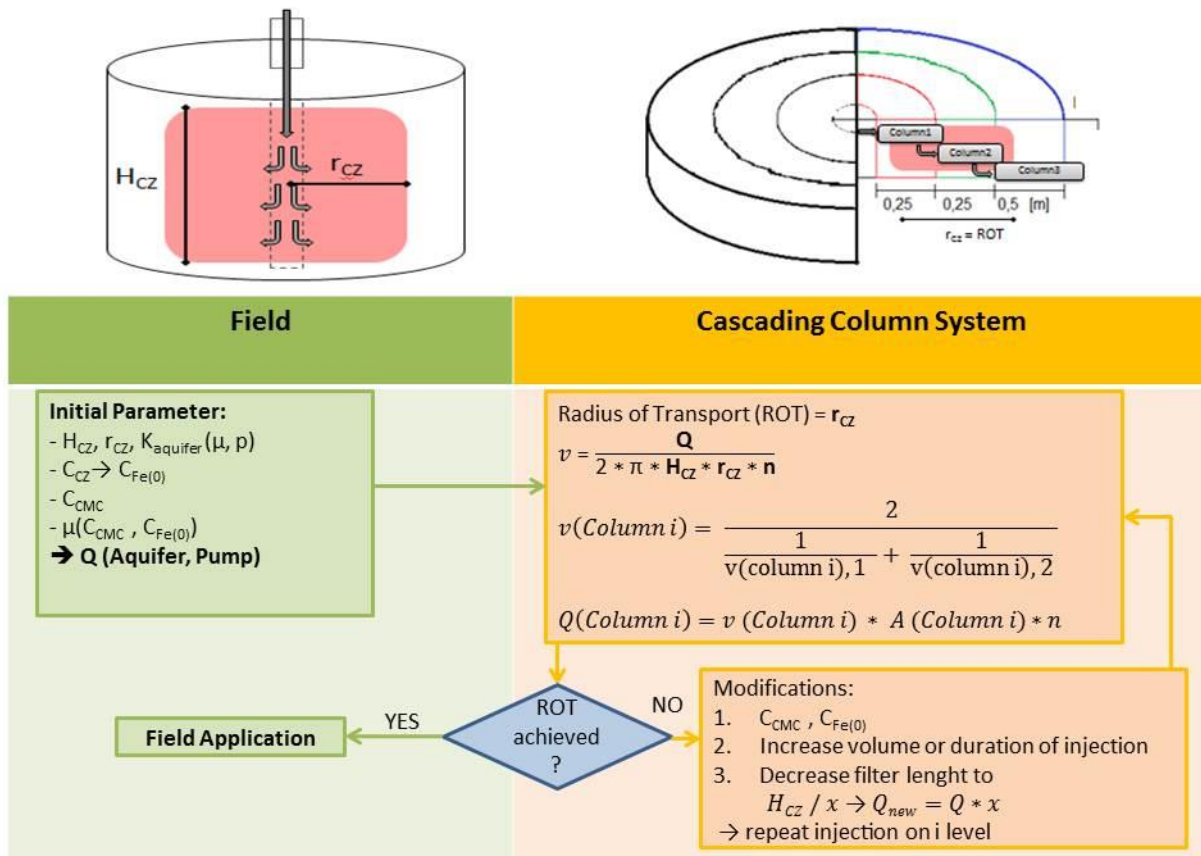
Figure 7:   Implementation path taking 3D field parameters and reproducing them with 1D Cascading Column Experiments

Flow System and Experimental Set-up

Figure 8 shows the flow chart of a cascading columns experiment. The left side shows the preparation and injection of NP suspension. A disperser (Ultra Turax T25) is used to prepare homogeneous NP suspension and to prevent agglomeration of NPs. For the injection of the NP suspension, two peristaltic pumps are used to create constant flow. The selection of the pumps depends on the flow rate necessary. The columns have an inner diameter of 44 mm. To minimize gravity effects, the columns are positioned horizontally. Various porous media are used for the cascading columns experiments. It is important, though, that d_{50} of the sand is small relative to the column diameter to reduce boundary effects along the column walls. Sampling valves are connected to the inflow and outflow of the column.

The right side of Figure 8 shows the collection of outflow (to be used as inflow of a subsequent column). A collection bag is placed on a scale to record the volume and discharge through a column dur-

ing an experiment. When injecting nZVI NP, all samples taken are analyzed for Fe^0 (to close the mass balance). During injection, the pressure difference between inflow and outflow is recorded using a differential pressure transducer. A specially designed scanner for magnetic susceptibility measurement (Hua, 2015) is used to monitor the transport and distribution of the iron slurry during injection. The movement of the susceptibility sensor along the column is controlled by a PC, thus the iron content inside the columns can be resolved in both time and space. When using the appropriate porous media and a flow rate based on the proposed injection technology migration distances for the field application may be derived directly. For non-magnetic NP, non-destructive monitoring methods are not available yet.
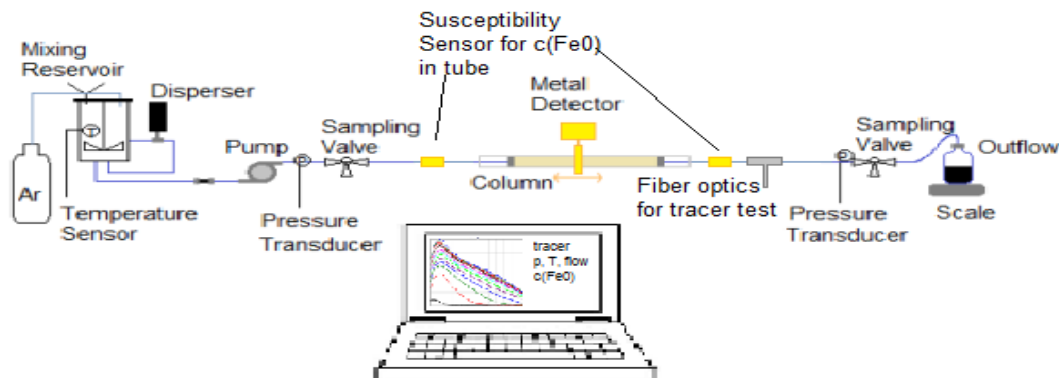
Figure 8:   Flow chart of working principle of cascading column experiments

3.3.6   Evaluation of NP transport parameters

The predicted radius of transport (ROT), i.e. the distance in which 80% of the injected particles are deposited after the injection is compared with the desired ROT. If these two coincide, the proposed NP suspension can be directly applied at the field.

In case that the predicted ROT for the required particle mass largely differs from the desired ROT, the NP suspension needs to be altered; mostly adding more or less of stabilizer for further or lesser transport distances, respectively, or even new particles need to be taken into consideration. For a newly designed NP suspension, both site-specific reactivity and mobility tests need to be repeated and the resulting parameters newly evaluated (**Figure 3**).

As pointed out above, if no NP can be detected in the column outflow it may be assumed that NP movement is restricted to the zone of injection. However, this can be confirmed by numerical modeling: the travel distance $L_{99.99\%}$ may be assumed to be the transport distance of renegade particles (0.01% of the injected NPs). It should be evaluated if this distance is shorter/equal/longer than a distance from the injection well to a possible endangered receptor (e.g. groundwater extraction well). In case that the renegade particle can reach a possible receiver, the NP suspension (including NP type) may need to be newly designed, the site-specific tests need to be repeated and the resulting parameters newly evaluated.

4   Monitoring

4.1   Monitoring strategies

A special feature of chemical remediation techniques is that a variety of substances might emerge as reaction products which have to be determined in order to demonstrate a successful remediation. The processes involved here are usually very complex and the proof that the expected processes are really taking place requires, thus, a much closer look at the conditions in the subsurface than for conventional physical technologies. Chemical techniques are based on the conversion of chemical substances to other compounds – ideally less harmful ones. One nature of chemical conversions is the fact that side reactions and competing processes can be involved, which make the interpretation of monitoring data somewhat more complicated. To deal with such complex phenomena a sophisticated monitoring is required. That means that – depending on the contaminants and particles involved - a variety of potential substances and relevant parameters have to be monitored. This may require special care during sampling, transportation to a laboratory and the choice of the analytical procedures.

Two types of approaches can be distinguished: integrative and point type strategies. Integrative methods are suitable for assessing parameters like emissions, contaminant masses and the like. Point type methods are usually used when detailed information is needed, e.g. about chemical processes like the formation of intermediates or information about the heterogeneity of the system. To obtain the relevant information a combination of approaches is necessary, which in most cases may involve different sampling equipment. Thus a thorough planning of the monitoring including the monitoring intervals is essential. Otherwise the interpretation of the findings will be difficult at a later point in time, when it is no longer possible to take the required samples.

To prove the success of a remediation a combination of two strategies is suggested: first a measurement strategy with high resolution in time and space and second an integrative measurement strategy. The high resolution strategy is used to track down the processes involved; sampling wells using a point type sampling technique are usually installed directly inside the application area. The integrative strategy is used to show the overall success by e.g. measuring the reduction of an emission. The corresponding installations for sampling are installed downstream allowing for the assessment of integrative data. Here, the installation of fully screened sampling wells is advisable (**Figure 9**).
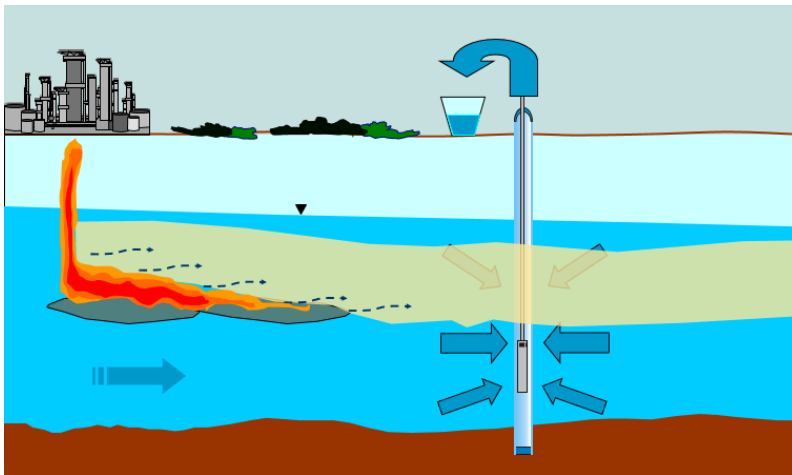
Figure 9:   Integrative sampling[1]
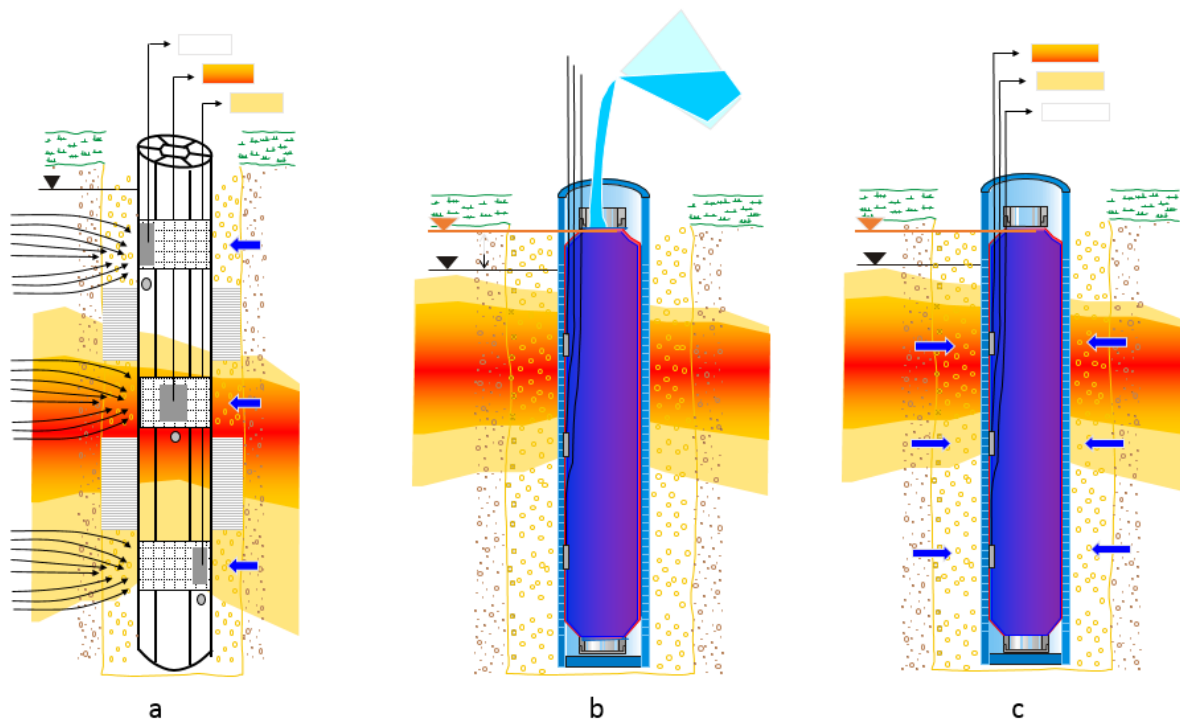
Figure 10: Examples of point type sampling: CMT sampling system (a), hose packers with low flow sampling systems during installation (b) and during sampling (c)[1]

The parameters measured within each strategy depend on the chemical mechanism (oxidative or reductive), the special type of particle as well as the specific hydrochemical and hydro-geological boundary conditions. Examples for reductive and oxidative parameters are given in Appendix D - Exemplary lists of parameters to describe chemical processes in the subsurface. The temporal and spatial resolution of the measurements (i.e. sampling campaigns) depends on site conditions such as the groundwa-

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[1] courtesy imw, Tübingen, Germany (www.im-weiss.de)

ter flow velocity, the size of the site, the expected natural fluctuations and the final set of analytical parameters to be measured.

The choice of the appropriate strategy should be made considering the specific conditions of the site. Before installing additional sampling equipment, the already available equipment should be evaluated and based upon this the necessary installations should be planned. Throughout the monitoring campaigns data and procedures are to be protocolled to ensure consistent sets of data. The goal of the monitoring as well as the corresponding techniques may be distinguished according to four different phases with specific requirements (see chapter 4.3). The requirements of all of these phases have to be included in the strategy and the protocols.

4.2   Phases of monitoring

The goal of the monitoring as well as the corresponding techniques can be distinguished according to four different phases with specific requirements.

4.2.1   Pre-injection phase

The measurement techniques applied in this phase are mostly standard methods used in chemical or hydraulic engineering. Measurement systems such as sampling and injection wells, or in-situ sensors (if needed) are either already available from the assessment for the conceptual site model or have to be installed. In the latter case, disturbances of the system and a corresponding time requirement for the system to stabilize again need to be taken into consideration. The main task is to describe the temporal and spatial concentration profiles of contaminants, but sampling can also provide background and baseline data of relevance for NP tracking. The duration of this phase and the frequency of sampling should be sufficiently long to provide a sound background for quantification of the remediation success and to identify impacts of the particle injection. Ideally this would be over a similar time scale as the post remediation monitoring phase in order to identify natural seasonal and temporal fluctuations. Since in most cases the list of parameters contains volatile substances which due to losses tend to be less reliable, a more frequent sampling or a longer duration of the phase is advisable in order to obtain sound background information.

4.2.2   NP injection phase

The requirements in this phase are very different from the previous one and also from the following phases. While this phase extends for some hours or days acute changes within minutes have to be detected. This requires not only much higher measurement frequencies, but also the application of different measurement techniques (chapter 4.3).

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 planned behaviour.

For the liquid phase (radius of influence, ROI) relatively simple methods are available such as temperature measurements (usually the temperature of the injected fluid differs from the ground water temperature) or the addition of tracer substances (dyes or tracer ions) to the suspension. For the particles (radius of transport, ROT, and homogeneity of NP distribution), unfortunately, only very few in-situ methods are available (see 4.3). Thus, in most cases the particle detection will have to be based on sampling and on-site or laboratory methods, fortunately there are a number of relatively fast and

cheap on site methods available such as turbidity or spectrophotometry measurements of iron content.

4.2.3   System recovering phase

This phase is the intermediate phase between the injections, with a considerable disturbance of the hydraulic system in the aquifer, and the recovery back to the natural ground water flow conditions. During this phase intensive analytical activities for both, particles and contaminants, are usually not justified, because the dissolved compounds are in a highly transient state. This means that during the recovery phase a reduced monitoring program is advisable where, in addition to the hydraulic parameters, only some main chemical parameters (e.g. DOC, chloride, sulfate) are monitored to determine the point in time when the natural groundwater conditions have re-established (of course some changes are to be expected due to the injected NP).

4.2.4   Long term phase (monitoring of success, reinjection)

During this phase contaminants, reaction products, metabolites and general environmental parameters of the groundwater 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 groundwater, 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 has to be chosen accordingly (see chapter 4.1; 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. The possibilities therefore are discussed in chapter 9.2.

4.3   Monitoring methods

There are three types of methods that can be used to monitor the processes in the subsurface:

- Laboratory methods

- *In-situ* measurement methods

- On site techniques.

Laboratory methods are the most widely used ones; usually they are standardized. Groundwater, soil or soil gas samples taken by appropriate techniques in the field are brought to a laboratory and analysed with standard laboratory methods. For the laboratory methods sampling is required based on the strategies described above (chapter 4.1). The results are highly precise but may be affected by the sampling procedure, or by the time lag between sampling and sample analysis. In addition, a potential disturbance of the aquifer may have to be considered, depending on the type of sampling procedure and the volume of water extracted.

Appendix D - Exemplary lists of parameters to describe chemical processes in the subsurface shows exemplary sets of parameters for reductive and oxidative technologies. These are not exhaustive, but give an idea of parameters that should be considered to describe the processes qualitatively and quantitatively.

In-situ **measurement** methods are usually sensor based techniques that allow for the determination of signals that cannot directly be compared to data obtained by laboratory methods. The advantage of these types of methods is that high measurement frequencies are possible and, thus, changes in the system can be recognized effectively. Unfortunately, suitable in-situ measurement devices are available only for very few parameters (such as pH, redox, electrical conductivity, temperature and oxygen). Since these devices will usually be lost their use is not inexpensive. For nZVI particles magnetic measurement systems can be used. These can be combined with temperature sensors and sampling systems. An example for a combined array of sensors is given in **Figure 11**. **Figure 11**a shows the measurement principle. An array with four magnetic sensors is emplaced next to an injection rod. The sensors detect the (heterogeneous) distribution of the particles during an injection. **Figure 11**b shows the location of the additional temperature sensors and the sampling ports, and **Figure 11**c depicts the final configuration of the arrays prior to installation.
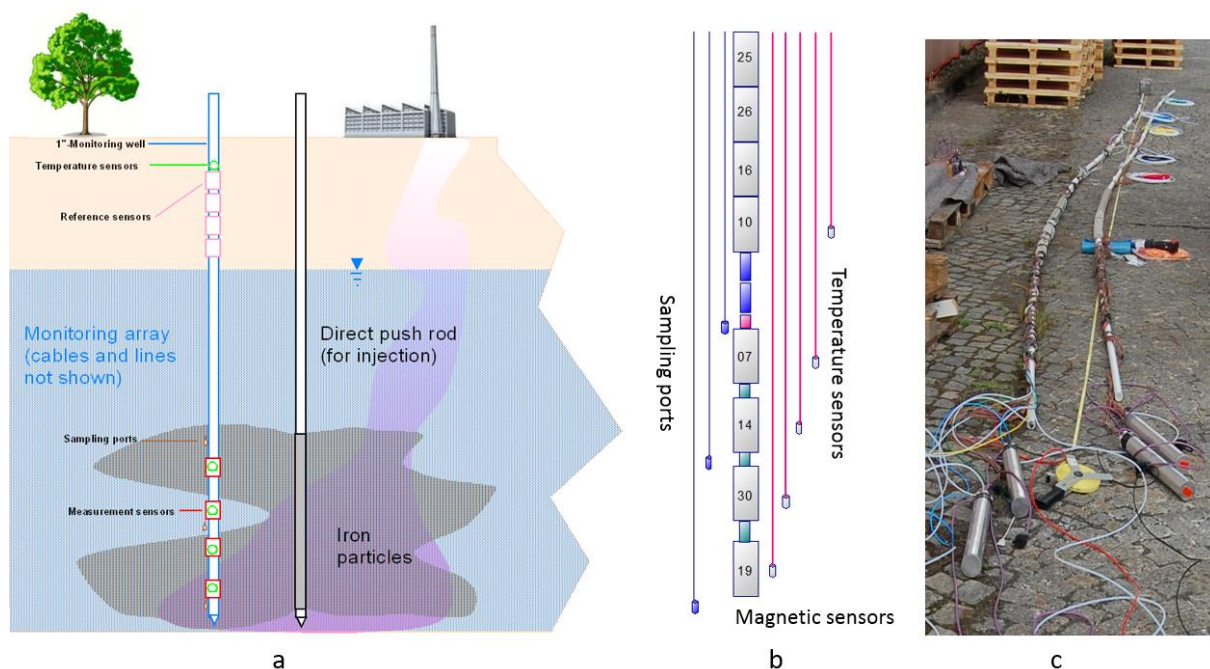
Figure 11: Magnetic susceptibility arrays: use in nano-remediation (a), components (b), photo of final assembly on site before installation (c)

On-site techniques are placed somewhere in between the former two methods; samples used are freshly taken from the subsurface and measured immediately, thus avoiding transport and sample pretreatment. Changes in Fe concentration, pH, temperature, and conductivity can provide a relatively rapid assessment of the spatial and temporal status of the particle suspensions. Providing the chemical properties of injection suspensions are significantly different from that in groundwater, a number of standard chemical techniques can be applied on site, and can give results within a few minutes of sampling. These include temperature, redox, pH, conductivity as well as turbidity and total Fe content, for which the instrumentation required for on-site measurements is portable and not expensive. Turbidity and spectrophotometry measurement of total Fe concentrations both provide a direct analysis of particle concentrations and are relatively fast and cheap methods.

Table 2 gives an overview of the advantages and disadvantages of the various types of analytical methods. Each type of method has strengths and weaknesses. To meet all requirements especially

during the different phases (chapter 4.2) a combination of methods is therefore recommended. This combination of methods should be reflected in the measurement strategy and be supported by protocols.

Table 2:   Overview of advantages and disadvantages of analytical methods

	Laboratory Techniques	*In-Situ* **Techniques**	*On-Site* **Techniques**
Advantages	Highly precise results Suitable for (almost) all parameters Accepted by authorities	Data readily available (immediate reaction possible) Remote measurements possible Well suited for injection and possibly for long term phase	Data readily available No losses during transport Well suited for injection phase
Disadvantages	Results affected by sampling and transport Time gap between sampling and results (ill-suited during injection) Repeated measurements are costly	Not suitable for some parameters High requirements with respect to personnel Results usually not accepted by authorities Installations costly	Not suitable for some parameters High requirements with respect to personnel Acceptance by authorities uncertain

An overview of relevant characterization methods for the detection of particles with their target parameters and some limitations is given in Appendix 13.5. This list shows the wide variety of methods and application windows. Some of the methods are particle-specific, others can be applied to all particles. Since these methods are restricted to the detection of the particles themselves, other methods have to be added in order to assess the processes and the overall effectivity of a remediation.

4.4   Summary of monitoring issues

As a minimum requirement the following installations are to be considered:

- Net of wells, ideally allowing to sample at defined depths, upstream/downstream samples, covering the whole injection area, considering the results of the conceptual model (see above).

- Grid of injection points sufficiently dense to cover the whole site with particles at all relevant depths. These may also be used for sampling or as measurement points in the pre-injection phase and during the long term monitoring (only if injection wells are used, not suitable if direct push methods are used).

- Sampling technology that allows taking water samples while minimizing losses for volatile or gaseous compounds.

Additional features of a monitoring concept would be beneficial:

- Online measurement capabilities for particles during injection (can be achieved via on-site and/or in-situ techniques).

- Visualisation of relevant parameters monitored during injection.

- In-situ measurement capabilities for particles and/or reaction products during long term phase.

- Remote access during long term monitoring.

The over-all goal of the monitoring is to conclusively prove the success of a remediation measure. In order to get a reliable set of information a thorough planning under consideration of all influencing factors is necessary. In addition, the strategy and concept for the monitoring should be discussed and agreed on with the responsible authorities beforehand. The possibilities for eventually assessing the success of a remediation measure are discussed in chapter 9.

5   Model-assisted upscaling of NP mobility

5.1   Role and types of models used in upscaling

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). Currently; no numerical models predicting NP reactivity in the field are available.

In chapter 3.3 it was described how NP transport parameters that adequately describe the observed breakthrough curves (BTC) are derived from laboratory column tests. These laboratory BTC parameters allow the comparison between different particles and, in combination with information on reactivity and anticipated costs, the selection of the most favourable NPs for a specific site. In most cases, however, the assumptions on NP transport mechanisms, based on which such laboratory-based BTC parameters are derived, are too simplistic. Consequently, their direct use may lead to an incorrect estimate of the Radius of Influence (ROI), Radius of Transport (ROT) and particle distribution pattern that can be expected when injecting the NPs in the field. For this reason, model-assisted upscaling of NP mobility is recommended.

When NPs dispersed in a suspension are injected into a (contaminated) aquifer, they are subject to processes like filtration, straining, physical-chemical deposition and aggregation, as they are attracted to the surfaces of the aquifer grains and to each other. The importance of the different interaction mechanisms and the associated attachment and detachment rates are strongly influenced by both operative and natural conditions, which may differ in space and time. Relevant conditions include flow velocity, NP size and aquifer pore size distributions, surface properties of both the NPs and the aquifer grains, especially surface charge, and the physico-chemical properties of the injection fluid (dielectric constant and viscosity, salt content (ionic strength) and pH). Within NanoRem, modelling tools were specifically designed to take these effects into account in a quantitative, and coupled, way, to be effective in assisting with the design of a nanoremediation field-scale application.

In case of a hydrogeologically homogeneous contaminated site, the upscaling of NP mobility tests is still relatively straightforward. The outputs of laboratory (column) tests - at relevant flow rates and NP concentrations - are fitted with a 1D model. The fitted parameters for the kinetics of NP attachment and detachment are then used in a 1D radial simulation to account for the field injection through a single screened well. This configuration takes into account the decay in flow velocity with distance from the injection well, and also allows coping with slightly changed conditions compared to the lab test, such as different pressure gradients and variations in hydraulic conditions (porosity, hydraulic conductivity, dispersivity). In case of a more heterogeneous field site, e.g. with zones or layers that have different hydraulic properties, the additional effort of building a full 3D model may be required for adequate upscaling.

For the design of a pilot injection of NP, MNMs (see chapter 5.2) can be used to fit column transport tests performed for a specific field application (Figure 5), and to predict the expected radius of influence, with two major advantages described in chapters 5.3.2 and 5.3.3.

5.2   Models developed within NanoRem

Accordingly, two macro-scale modelling tools were developed within NanoRem that take into account the operational and natural conditions mentioned above. The two models apply to different stages of complexity (see Appendix G - Numerical modelling for details and supporting references):

- MNMs, standing for **M**icro- and **N**anoparticles transport, filtration and clogging **M**odel **S**uite, is used for the assisted quantitative analysis of laboratory-scale column tests, and the preliminary design of pilot NP injections in a simplified geometry (radial 1D simulations);
- MNM3D, standing for **M**icro- and **N**anoparticles transport **M**odel in **3D** geometries, is a full 3D transport module for the simulation of particle injection (In one or more injection points) in heterogeneous domains, and for the prediction of NP fate and transport at the field scale.

If coupled with MNMs, MNM3D can be used at the final stage of the remediation design process, as a support to estimate important operative parameters including particles distribution around the injection well, radius of a target NP concentration (e.g. ROT), number of required injection wells etc.

At the heart of the models is the modified advection-dispersion equation that takes into account the mass exchanges between liquid and solid phase due to physical and physico-chemical interactions. A detailed discussion of the retention mechanisms included in MNMs and of the associated transport equations is provided in Appendix G - Numerical modelling.

Like many transport simulation models, MNMs can be run in two modes (Figure 12):

- predictive or forward mode: assuming that transport-controlling mechanisms and transport parameters are known, the model is run once to forecast particle transport;

- inverse mode: assuming transport-controlling mechanisms, and determining the transport parameters (see Appendix G - Numerical modelling) by fitting the simulation results to experimental data.
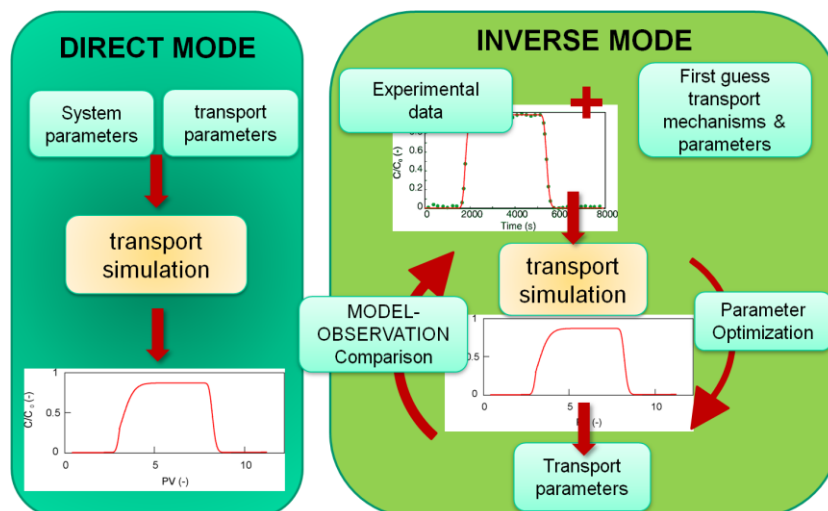
Figure 12:   Transport model run in predictive or inverse mode

It is worth mentioning here that a field injection can be performed by permeation (generating a relatively uniform NP distribution, ensuring the contact between particles and contaminants), or by fracturing (injecting fluids and particles at a pressure exceeding the porous medium critical pressure, thus generating a non-uniform distribution if the process is not properly designed and controlled) (Luna et al. 2015). Both tools described in this paragraph (MNMs and MNM3D) are based on advection-dispersion equations and are therefore applicable to the design of permeation injection of NPs.

5.3   Using the modelling tools to assist NP-based remediation

5.3.1   Getting the software

MNMs can be downloaded from the Polito website (http://www.polito.it/groundwater/software), where also step by step tutorials and example files can be found. MNM3D is a modified version of the well-known transport model RT3D[2], in which the colloid transport equations and the coupled dependencies of attachment and detachment kinetic coefficients on transients in pore water ionic strength and velocity have been implemented. MNM3D can be easily implemented in many open-source and commercial graphical interfaces which already support RT3D, like e.g. Visual Modflow. At the moment, the implementation in Visual Modflow (Waterloo Hydrogeologic) is under evaluation with the developers of the software. A detailed description of MNM3D and two examples of its application are provided in Bianco et al. (2016).

5.3.2   Limiting the number of tests to be performed in the laboratory

As discussed above, several parameters have a significant effect on the overall mobility of the nanoparticles injected at the site. Those expected to play a major role in the field-scale mobility of the particles should be identified. As an example, if the aim of the column tests is to gather information for a pilot injection through a screened well, then flow velocity is expected to be a key parameter to be investigated. As a consequence, few (typically 3 or 4) column tests will be run injecting particles at different flow rates. If the parameter of interest is the injected concentration, or the concentration of stabilizer, the same approach can be adopted, running a few column tests with different NPs or stabilizer concentrations. MNMs is then applied to extract quantitative information on the key transport features associated with the investigated parameter (inverse mode), and also to simulate NP transport under a wider set of conditions (forward mode). The latter helps to identify which range of conditions should be covered by the column experiments. Modelling may thus spare extensive cost- and time-consuming experiments, while widening the range of conditions that can be investigated.

5.3.3   Exploring different implementation scenarios

The information gathered from the modelling of the column tests, in terms of processes identified and associated rate parameters, has general validity and can thus be extended to more complex scenarios.

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[2] Clement, 1997, Clement et al., 1998

In this case simulations are run in forward mode, to forecast NP transport under various implementation scenarios, and the model results can aid in optimizing NP and slurry properties and injections schemes (e.g. based on a desired radius of influence and NP concentration in the target area, which discharge rate should be applied, how long injection should last, which concentration of NPs and stabilizers is the most effective, …). Equally important, model results can point out what crucial but still missing information would contribute most to making a better-informed decision, and therefore suggest if and which additional laboratory transport tests should be performed to fill knowledge gaps.

5.3.4   Guiding monitoring and testing assumptions

Model forecasting should always go hand in hand with adequate monitoring and vice versa. Model results can guide how, where and when to monitor, to proof that the expectations on NP placement - and remediation targets and safety – will be met. Model forecasts that cannot be verified are useless, as are monitoring data that cannot be tested against prior expectations. Any discrepancy between actual observation and previous prediction should be reason to question and revise aspects of the conceptual site model and to adjust any follow-up activities accordingly.

5.3.5   Overall strategy

As an example, Figure 13 depicts the various steps - combining experiments, modelling, and monitoring - that could be followed in the model-assisted design of a pilot injection of NPs through a screened well for the case of a fairly homogenous aquifer system:

- NP slurry and porous medium are characterized in detail;

- Columns are packed using the site porous medium, and a tracer test is run on each column to determine porosity and dispersivity;

- Few transport tests under well-defined conditions are performed at different injection rates (typically three or four);

- Based on NP and porous medium properties, a first guess of the transport-controlling mechanisms is made (e.g. data[3] indicate that ripening can be assumed);

- Transport coefficients (Appendix G - Numerical modelling) are fitted against experimental results; if model fitting is unsatisfactory, the initial guess on transport mechanisms is updated via an iterative procedure (eg. comparison of model and experimental data suggest that physical filtration may dominate over blocking);

- The trend of the NP transport parameters with flow velocity and/or other underlying factors is verified against the theoretical model formulation used (see Appendix G - Numerical modelling for details on the mathematical formulations), and the values of the underlying coefficients are determined;

- 1D- radial simulations are run in forward mode assuming the transport mechanisms and parameters as determined in the previous steps. Several radial simulations can be run, eg. assuming different injection rates, or different injection durations, thus deriving the expected

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[3] Specifically the DVLO profile, see Appendix 11.5 for details

radius of influence, particle spatial distribution and associated pressure build up for each set of operative conditions (see Tosco et al., 2014, for an example of application).

- Based on the model results, the preferred injection scenario for the pilot test is implemented.

- After the pilot test is performed, the particle distribution around the injection point and the radius of influence predicted by the model are compared to those obtained in the field. To this aim, monitoring results collected during the pilot injection and after are needed. In particular, it is crucial to have information on the particle mobility during the injection (which can be obtained, for example, by collecting water samples over time in monitoring piezometers around the injection point), and the final particle distribution after injection (to be reconstructed, for example, by analyzing the concentration of particles in soil cores collected in the proximity to the injection point, at various distances).

- If the model and experimental results of the pilot injection are in good agreement, then the model is validated, and the transport mechanisms and coefficients derived from the laboratory tests can be assumed valid also at the large (field) scale. If the agreement is not satisfactory, the model parameters have to be adjusted in order to match the pilot monitoring results, and the new set of parameters is used for further steps of the remediation design (eg. for modelling the full scale injection of NPs).

A similar procedure applies in case the radial domain considered in MNMs is an oversimplification, and a full 3D modelling tool (i.e. MNM3D) is to be used. Examples are the design of a pilot injection in a strongly heterogeneous medium, or in the presence of a strong background natural flow. Also in this case the 1D model is to be run in inverse mode to derive the transport-controlling parameters from column tests and the full 3D model in predictive mode to explore the possible range of scenarios.

Other examples where a full 3D model is called for are the full scale design of a field injection in a heterogeneous aquifer with multiple wells or to forecast the NP mobility on a longer time frame. Here, specifically the modelling-monitoring feedback system can be used to guide an adaptive remediation strategy.
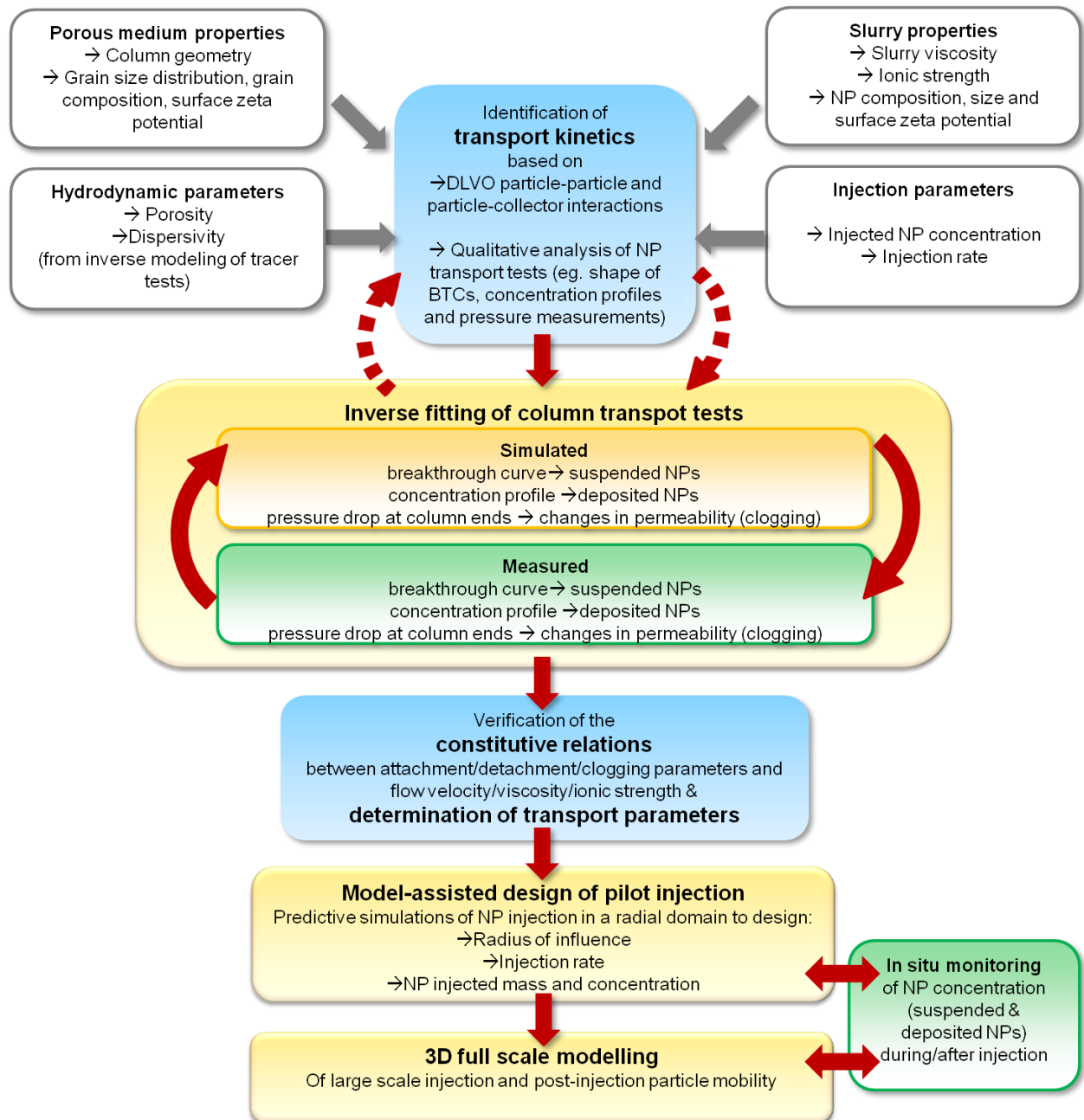
Figure 13: Procedure for the interpretation of column transport tests to derive information for the simulation at larger scales. Color legend: in white, preliminary information; in yellow, model application (MNMs or MNM3D); in blue, verification of modelling assumptions; in green, collection of experimental data.

6   Pilot tests

6.1   Design and installation

Pilot field tests are designed based on the results of laboratory tests. If no such data are available, it is possible to carry out the field test with a certain level of risk on the basis of particle information from the supplier, of hydro-geo-chemistry information, and of contamination analysis obtained in the site investigation (CSM) and based on analogies with other sites of a similar nature.

6.1.1   Aims of the pilot test

The main aim of pilot field tests is the investigation and identification of specific conditions for the design and implementation of operational applications of nanoparticles at the area of interest with respect to the following factors:

•   Confirmation of the appropriateness of the selected nanomaterial, evaluation of its efficiency and the longevity of selected particles

•   The reduction in contamination and other dissolved organic - inorganic substances in the aquifer, formation of intermediate products

•   Distribution of the particles in the given aquifer (determination of ROT), and based upon this the determination of the distance of the application wells

•   Influence on aquifer properties (permeability, microbial activity, chemistry); certain nanomaterials may also contain small amounts of organic modifier in order to maintain the migration properties of the nanoparticles

•   Verification of the method of application (direct push, well infiltration,…) verification of technological parameters and the capacity of the proposed equipment; verification of dosing unit and of the method of their injection into the target zone

•   Assessment of the impact on the surrounding objects (static or geotechnical assessment)

•   Cost estimation for a full scale remediation

All of the above-mentioned information forms a basis for the design of the full scale remedial system: The proposal of the definitive method for injecting the nanoparticles into the target zone, the application network and the monitoring wells, the amount and concentration of nanoparticles, or the estimation of the number of application rounds needed. In the case of complex hydrogeological conditions, the remedial system should be verified through hydraulic modelling.

6.1.2   Main activities during the pilot tests

It is recommended to perform the pilot test in a similar system as the real field application i.e. method of handling reagents, method of preparing the suspension, method of infiltration. The pilot test can be divided into several steps:

(a)   Building the system of pilot (application and monitoring) wells: this will vary for each site depending on local natural and technical conditions, and financial and time constraints. For the pilot test it is necessary to select a location that best represents the area of concern, and which allows to subsequently carry out long-term monitoring. It is also necessary to characterize the pi-

lot test location in terms of groundwater flow. When designing the system of pilot wells, it is necessary to determine the effect of the infiltrated reagent not only in the application wells but also in the neighbouring monitoring wells. It has been shown that in most cases the degradation of contamination in the application wells is conclusive. But without confirming the natural contaminant degradation in some of the neighbouring monitoring wells it might be difficult to evaluate pilot test.

(b) Tracer tests: The objective of tracer tests is to verify the rate of groundwater flow and the presence of preferential pathways. Tracer tests also confirm mutual communication between infiltration and monitoring wells. For the performance of tracer tests it is recommended to use a combination of two different tracers (e.g. NaBr + Na-fluorescein); one having a distinctive colour for visual inspection and the other allowing for simple and cheap measurements to obtain accurate and well evaluable results. Some tracers may react with the reagents used and may therefore change their properties during the test e.g. they become unmeasurable. The tracer is added to the dosed suspension of NPs and monitored during and after the application. The monitoring time can be typically 1-2 months. Monitoring intervals should be adapted to cover both hydraulic regimes - 1) for accelerated flow (simulating conditions during the application) and 2) natural flow (simulating the situation after the application and return of natural flow).

(c) Installation of the system for the preparation of suspension, reagent dosing and the distribution network: To implement the pilot tests it is possible to have a very simple technological system. Depending on financial resources, it is recommended to have it as close as possible to the real operating conditions of the remediation. A number of shortcomings related to the local specifics of the location may be removed during the pilot tests.

(d) Preparation of the suspension and the administration of the reagent: The migration properties and the reaction capacity of the nanoparticles depend on the method of preparation and the quality of the suspension. The aim is to prepare and infiltrate material into the aquifer that provides a maximum radius of transport (ROT) from the infiltration wells, a homogeneous NP distribution in the reactive zone and a maximum reactive capacity (with respect to a given contamination) of the reaction agent. The concentration of the reagent should be derived from laboratory tests and from the expected infiltration rate of the injection wells. When preparing the suspension, it is essential to follow the manufacturer's instructions. For nZVI NP contact with atmospheric oxygen should be kept to a minimum. Based on the preliminary analysis of process water, water treatment may be required before it is used.

(e) Monitoring: The basis for successful pilot tests is an appropriately designed monitoring system (both in terms of the measured parameters and the correct dimensioning of time steps). During the monitoring, it is best to combine the sampling (and laboratory analysis of samples) with continuous measurement of physical and chemical parameters in the wells (with the use of data loggers). Time steps of sampling for analysis should be derived based on the information on the groundwater flow velocity and the expected migration rate of the reagents. Monitoring of pilot tests should focus as a minimum on the following parameters: Concentration of contaminants monitored until after the final products of decay, total chemical analysis of inorganic parameters, concentration of Fe^{2+} and Fe_{total}, COD, pH Eh, dissolved oxygen, and groundwater level (see chapter 4 for more details).

(f)   Evaluation: Monitoring is carried out throughout the pilot tests until pre-injection conditions in the aquifer are re-established (sometimes including increased contaminant concentrations). In this way it is possible to estimate the duration of action of the infiltrated mass of reagent, the area influenced by the infiltration of the reagent and the area influenced by the reaction. Balancing calculations are then used to estimate the mass of reagent required for decontamination of a given contaminated aquifer or of a volume of contaminated groundwater. It will also be possible to estimate the longevity of the reagents, and the point in time when the maximum reduction of concentration has been achieved. This information can then be used to estimate the number of injections required to achieve the remedial target parameters. Generally, depending on the site conditions, at least two rounds of reagent application will be necessary. Assessment of remediation success is discussed in detail in chapter 9.

6.1.3   Systems of pilot tests

The method of injecting nanoparticles into the porous media is one of the fundamental parameters of the remediation, which affects both the reach and effectiveness of the remedial system. For this reason, it is advisable to design a pilot test that imitates the real remediation as closely as possible. The pilot system may be divided according to the following parameters:

Injection and monitoring wells: the system of pilot field test is designed based on the financial and technical capabilities of the project. Pilot tests can be performed in one or more wells. The explanatory power of the results increases with an increasing number of monitoring wells. Depending on the local conditions and possibilities of the project the following elements can be used for the pilot system:

- Direct push rods are considered to be the most effective method for dispensing reagents into the porous media. The recommended application system is top down into defined layers with a verified presence of contamination. For repeated application it is important to consider the greater range of technical work associated with the repeated implementation of direct push wells. The application of direct push wells is limited to fairly fine unconsolidated material, thus they are not appropriate for consolidated rock and materials with large boulders or large rock fragments.

- Standard cased wells are the only solution for the remediation and pilot systems in places where it is not possible to use direct push wells. The emphasis in this case is put on the correct casing of these wells, which must reflect the hydrogeological conditions of the porous medium and the extent and occurrence of contamination. Standard cased wells do not allow for simple depth-limited, zonal, targeted application and monitoring. This disadvantage can be slightly reduced by special equipment enabling applications in tight depth intervals between two packers. To increase the accuracy of the monitoring of the zonality of the contamination the standard wells can be cased with a micropump system or a similar effect can be achieved by placing piezometers into the backfill.

- Low-profile boreholes (e.g. direct wells D32mm, micropump monitoring wells) are used at places where repeated direct push is not feasible. Low profile borehole installation might follow a direct push injection at the same place and thus the injection points are ready for the next injection campaigns. For this type of well the same disadvantages as for standard cased wells apply. To delineate the contamination distribution these boreholes might be equipped by a micropump system.

- Horizontal application/extraction drains may be used for mobile NP in shallow geological structures or in places with restricted accessibility from the surface (under used building or other construc-

tions). The disadvantage of horizontal systems is relatively low control on the system construction (difficulty to install well sealed multi-screened casings in the case of drilled wells). Accordingly, the control of the spatial distribution of injected nanomaterial is less accurate as it is injected through whole opened (screened) interval. In the case of heterogeneous soil the well may penetrate layers of different permeabilities; zones with lower permeability will thus not be influenced.

Distance of the wells: correct adjustment of the distance between the application and the monitoring wells minimizes the risk of failure of the pilot tests and of the depreciation of the performed work. The distance between the application and the monitoring wells is based on the groundwater flow velocity, the quantity (volume) of injected material, the speed of transport of the injected supporting substances through the rock, the expected range of application of the wells and the time available for the pilot field tests. The distance between the application and monitoring wells is typically in the range of 1 to 5 m.

Groundwater flow regime: Application of nanomaterials is recommended to be performed under an increased hydraulic gradient, which will accelerate the groundwater flow. In this way it is possible to guarantee a better distribution and a larger range of nanomaterial in the subsurface. The response of the infiltration in monitoring wells can be expected sooner. An increased groundwater level gradient is achieved by the implementation of the reagent at an elevated pressure, while pumping water from wells adjacent to the application at the same time increases the desired effect. Changing the flow conditions can, if necessary, adjust the groundwater flow direction. The natural flow regime should be restored after applying the agent. In this case, the groundwater flow once again slows down, and a slower response from the monitoring system to work performed in the application wells have to be expected. Maintaining an accelerated and streamlined flow regime can be achieved by continuing the pumping.

Method for injecting the reagent into the porous media: As mentioned above, it is strongly recommended to perform pilot tests on selected reasonable techniques for injecting the nanoparticles into the porous media, which are planned for the full scale remediation. Methods of application of the agent into the porous media are listed in the following section.

Type of application: During the remediation there are two basic types of application: spatial application and reactive zone (barrier). In the event that the aim is to remove a hotspot or contaminant plume then overall spatial application of the reagent is performed. In the case a reactive zone is required in the porous media to protect the surroundings of the contaminated area from migrating pollution then limited spatial application is performed with an increased dose of reagent based on the duration of action and the amount of contaminated water flowing through. In the same way, the pilot test with a system of application and monitoring points should then be designed.

Scope and frequency of pilot test monitoring: The purpose of monitoring the pilot test is to demonstrate the achievement of the above-mentioned objectives. In terms of the scope of the monitoring the basis is monitoring the parameters specified in the chapter Remedial Monitoring. In the case of the pilot tests, it is necessary to have a higher monitoring frequency. The spacing between the monitoring rounds especially in the initial phases of the pilot tests (shortly after infiltration of the nanoparticles) should be shorter and the interval should then be gradually increased. In the case of less stable reagents, the initial interval should be derived from the half-life of the reagent. In the case of nano iron, which is a lot more stable than oxidizing agents, the intervals between the monitoring rounds should

be distributed so as to determine the characteristics of the dechlorination curves and to capture the process and the possible intermediate products of decomposition. There should be at least five time points in order to achieve a representative evaluation of the pilot test. The first sampling should therefore be done 2-3 days after the application of the NP, the second two weeks after the application of the NP, and the following rounds of monitoring can then be with a month delay. In principle, the following parameters should be monitored and recorded:

- Concentration of contaminants of interest including their potential decomposition and intermediate products

- Physical and chemical parameters measured in the field: pH, E_h, temperature, conductivity, dissolved O_2

- Groundwater level

- Concentration of Fe_{total} and Fe^{2+} or the respective reaction products of the particles

- Determination of oxidizable substances - COD (chemical oxygen demand), TOC (total organic carbon)/DOC (dissolved organic carbon), TIC (total inorganic carbon)

- Comprehensive analysis of inorganic basic parameters - total chemical analysis

- Other parameters such as selected heavy metals and other parameters depend on the results of laboratory tests, input monitoring and state authorities if necessary

The following figures are examples of pilot systems:
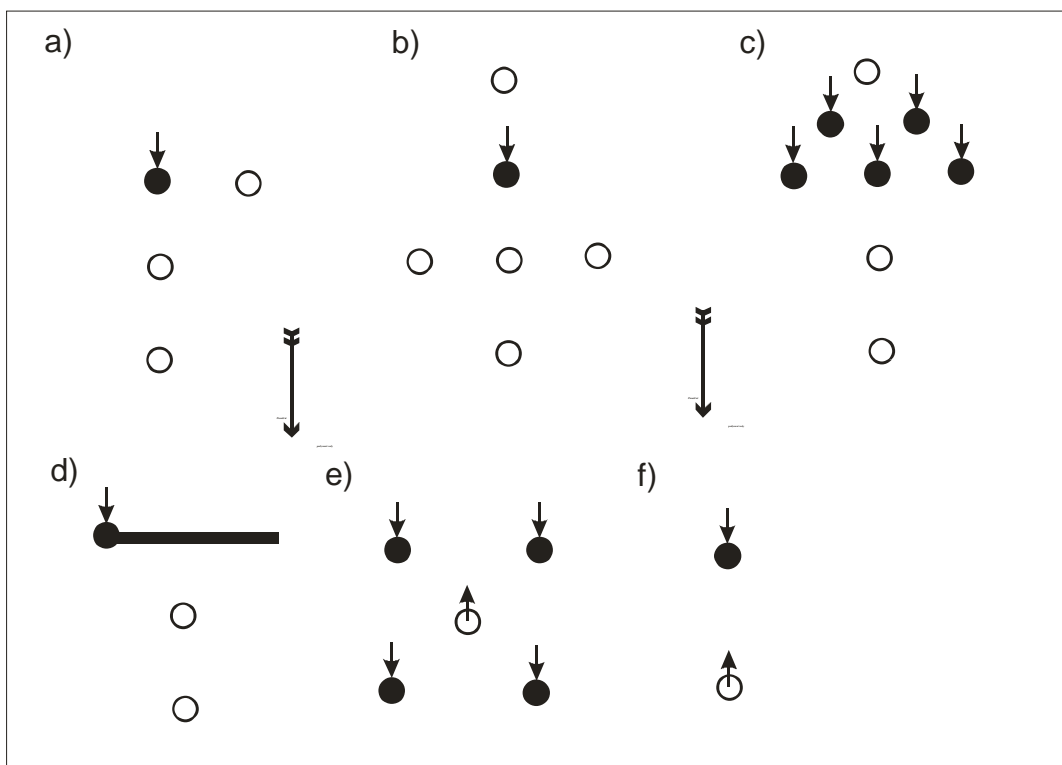
Figure 14: Examples of layouts of pilot test systems a) to d) - passive systems, e) to f) active systems, a) minimum number of monitoring points when there is a lack of space and funds, b) captured water and outflow c) simulation of a reactive barrier, a direct push system can be used, d) simulation of an application system with an infiltration cut e) "five-spot" system -

one monitoring well between four application wells, f) one pumped and one application well (solid dots indicate injection points, circles indicate extraction points).

6.2   Execution and Evaluation

The main operating parameters are derived based on the results of the field and laboratory tests, which are then used to design the remedial system. During and after the pilot test the concentrations of the monitored substances over time are determined for each contaminant and monitored well.
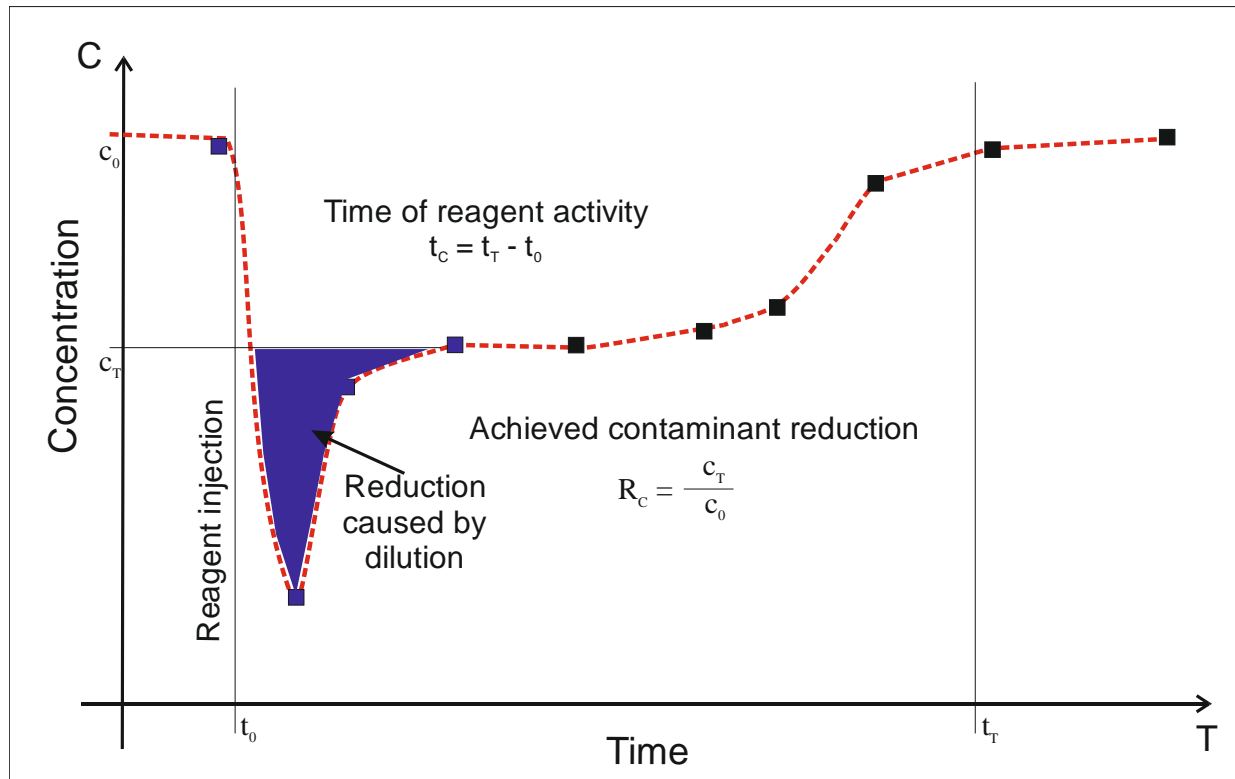
Figure 15: Expected development of contaminant concentrations during the pilot test (with rebound if an insufficient mass of NP was injected)

Infiltration capacity of the porous media: This value is essential for an estimate of the operating time of the infiltration (duration of the injection) of nanoparticles into the porous media. The infiltration of nanoparticles into the porous media can also include a hydrodynamic test. This is used to calculate the basic hydraulic properties of the aquifer (hydraulic conductivity). Alternatives for obtaining the hydraulic parameters of the aquifer are geophysical measurements, slug-tests or other forms of hydrodynamic tests. These values are used to calculate the amount of water which the environment is capable of holding at a given time.

Range: This is a figure which determines the density of the network of application wells. This is the distance from the well at which the nanoparticles reach an acceptable reduction of pollution after infiltration. The rate of reduction of contamination also depends on the applied dose of the reagent. The range, the time of action of the reagent and the applied dose are combined, and in order to optimize the remedial system it is necessary to take into account such values in order to achieve maximum reductions of concentrations in an acceptable time. The rate of reduction of contamination is derived based on the network of monitoring wells in the vicinity of the application wells. Based on this result it is possible to spatially approximate the distance from the well which achieves an acceptable rate of

contamination decrease. This distance can be regarded as the range of the wells. To estimate the range, we use an evaluation of the slowest degradable target contaminant.

The rate of reduction of contamination: This value determines what maximum reduction in contaminant concentration can be achieved at a given dose of reagent and at a given distance from the application well. The rate of reduction of concentrations for each remedial well and each contaminant is derived from the time dependence of the concentration of the monitored pollutant (relative to the initial value of the concentration) as a first indication of contaminant inventory reduction. To derive this value, the maximum level of reduction of concentrations (see the figure above) is used for each well (see also chapter 9).

Duration of action (durability) of nanoparticles in the porous media: This determines the most appropriate moment to inject further doses of the reagent into the porous media in case the initial dose did not yield the desired remediation result. The longevity (duration of action) of nanoparticles in an environment is derived in a similar way. This value is derived for each target contaminant (and possibly for intermediate degradation products). For plume treatment this corresponds to the time from administration of the reagent at which the initial concentration levels (or values close to the concentration) are reached is used.

Estimation of quantities of reactive material: At a single point, a certain reduction is achieved in a certain concentration at a certain distance from the application well using a certain amount of reagent. From here it is possible to deduce how many infiltration rounds will be required to achieve the desired reduction and, consequently, how much reagent will be needed to achieve this level of reduction of concentrations. It must be decided whether a denser network of wells or more rounds of infiltration of nanoparticles will be used. This data results from the remedial conditions and in particular the terms of remediation deadlines. Generally, a 50-70% reduction in concentrations is acceptable. It is expected that further applications rounds will gradually reduce the substances with which reagent will react in the porous media and will therefore gradually increase the efficiency of the technology. On the other hand, it is necessary to expect unforeseeable factors associated with a lack of detailed knowledge of the hydrogeological and hydro-chemical conditions of the porous media.

7   Full scale design

7.1   Remediation systems

From an operational point of view, depending on the extent of the clean up, several types of remedial systems can be considered.

Clean up of the contamination plume where contamination is mainly available in dissolved and adsorbed form: In this case, the technology is applied to large contaminated areas and large aquifer volumes. The density and shape of the network of application points must be adapted to the groundwater flow direction and velocity and to the reactive properties of the reagent (residence time). Usually several rounds of reagents infiltration and, correspondingly, long-term monitoring is required.

Clean up of the locally persisting occurrence of contaminant concentrations above target limits: in this case, if possible, a single administration of the reagent to individual remedial wells where concentrations of contaminants are still over the limits is envisaged. This method is mainly used in the final stages of the remediation, and emphasis will likely be placed on the financial point of view.

Clean up of the contamination source (e.g. with an expected occurrence of DNAPL phase): in this case an invasive remedial approach is used on a relatively small area. In addition to higher doses of reactive particles, it is advisable to select the most appropriate formulation of pure/surface modified nanoparticles for this type of contamination (which will guarantee sufficient efficiency especially in areas with free phase organic product).

Performing a nanoremediation, like any other technology implementation, is a stepwise process where successive choices or decisions are being made, then implemented, and their outcomes verified afterwards. Informed decision making is always based on a combination of general knowledge and specific data for the situation at hand. Numerical modelling (chapter 5) might improve planning and evaluation of a remediation and assist in quantitative forecasting.

7.2   Decision on injected mass

Decision on injected mass is taken based on preliminary theoretical evaluations and calculations confirmed by field and laboratory pilot tests (see chapters 3 and 6). A first estimation of the required mass is to be made based on stoichiometry (based on contaminant inventory, knowledge of which is mostly very vague) with safety factors for competing reactions, and heterogeneity of aquifer and contamination distribution. A decision on the mass can only be made based on the effect (success) of actual injections on a given site.

7.3   System design

A remedial system is designed based on the following (see also Appendix A - Conceptual site models):

•   Remedial target parameters (concentrations, deadline)

•   Predominant form and distribution of the contaminants in the aquifer environment

•   Predominant form of contamination

•   Expected particle migration to determine layout and spacing of the remedial wells

•   Estimated amount and dosage of nanoparticles

Remedial target parameters: The remedial system is primarily designed with respect to the valid remedial target limits (see chapter 9). This target may be defined for a whole area, or it might be defined for the outflow from the contaminated area. Accordingly, the approach will differ. In addition, different remediation limits might be defined according to local conditions, legal requirements or requirements of local water authorities. If the target concentrations are defined for a whole area (volume) of contaminated aquifer the goal has to be to capture the whole contaminant body and the contaminated layers of the aquifer (injection of NPs into the source (source removal) accompanied by plume treatment). In the case of effluent control from the contaminated area it is possible to propose an alternative remedial action in the form of a chemical reactive barrier on the boundary of the contamination plume (see **Figure 16**).

For source removal, spacing and injected mass of NPs are a function of mass of contaminant in the source, for plume treatment the groundwater flow velocity has to be taken into account (reasons of economics).

For plume removal the implementation of a reactive barrier might be considered, however while this might provide the required protection of a downstream property, it will, in the long run, not be economical as long as the source has not been removed due to the required periodic reinjections…
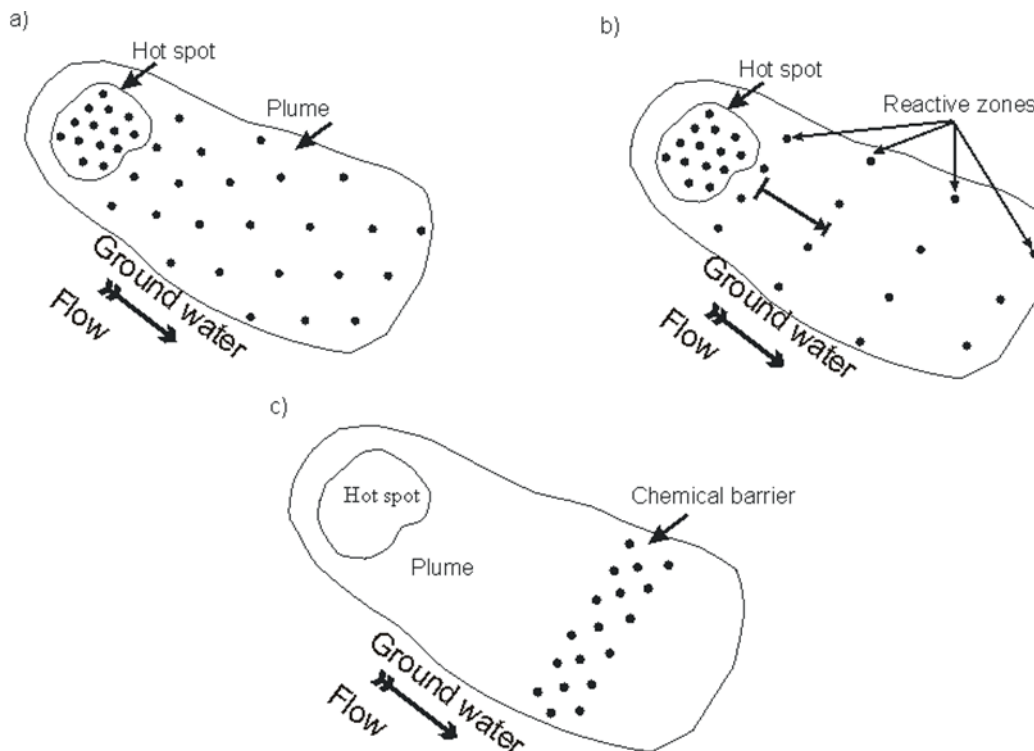
Figure 16: Design of a system of remedial wells. a) system for hotspots (source) and contamination plume under a slow flow regime, b) system for a fast flow regime where the reaction zone corresponds to the distance of the groundwater runoff between two application rounds, c) system of chemical barriers

Distribution of contaminants in an aquifer: Aquifer remediation using nanoparticles involves the chemical or biological degradation of the contaminant to a nontoxic or less toxic form. To ensure sufficient effectiveness of the remedial system it is therefore necessary to ensure direct contact between the contaminant molecules and the nanoparticles. Exact knowledge of contaminant distribution in the

aquifer is very important - both for the choice of the most suitable technique of infiltration/injection of nanoparticles and for the distribution of the application wells and their geometry (screened sections for the infiltration of the reagent/ nanoparticles).

Predominant occurrence of contamination: as mentioned above, it is necessary for the degradation to provide direct contact between the contaminant and the reagent for a sufficiently long time. The design will be different if the predominant contaminant is in a dissolved or adsorbed form or in the form of residual organic phase (NAPL). Predominantly dissolved contaminants (plume) will be mobile, and the choice of either the placement of remedial wells equally spaced throughout the site or placement as a reactive barrier will be decided depending on the velocity of groundwater flow (see **Figure 16**). Adsorbed contaminants will require a surface-modified mobile form of nanoparticles and a complete cover of the contaminated porous media by reactive nanoparticles. The elimination of residual organic phase (NAPL) will require a similar approach, however since NAPL needs to be in an aqueous solution to be treated by nanoparticles and since this is a diffusion controlled process it will take a certain amount of time and thus multiple injections might be necessary, alternatively the use of particles with a higher longevity is indicated..

Layout and spacing of remedial wells: Depending on the type of application and the expected radius of influence it is required to cover the contaminated area by a sufficient number of remedial wells. For application covering the whole site (**Figure 16**a) the area should be covered with a grid of equilateral triangles with application wells at their tops. Infiltration cuts and horizontal wells should be placed perpendicular to the flow direction in order to influence the flow field as much as possible. The layout of the infiltration wells depends in various, site specific factors. The usual distance between the application wells is 10 m (or less).

Construction of reactive zones (**Figure 16**b) is more complex. The extent of the constructed reaction zones is determined by the number of lines of application points depending on the radius around a single borehole, the groundwater flow velocity (contaminant transport) and the contact time between the contaminant and the nanoparticles (obtained from laboratory tests) required to achieve the desired decease in concentrations. Usual distance between the reaction zones depends on the lifetime of the nanoparticles used in the given physical and chemical environment. The expected life of the nanoparticles depending on the reagent dose is usually in the range of 6 months to 3 years from the application of the nanoparticles. This time, and the corresponding groundwater flow distance, corresponds to the desired distance of the line of reactive barriers (zones).

Constructing a single reactive barrier (**Figure 16**b) is also an option and needs to follow similar criteria. However, now the longevity of the particles (or number of reinjections) will be substantially increased which might prove uneconomic in the long run.

8   Site installations and particle deployment

8.1   Injection technologies

As with other *in-situ* remediation technologies, it is possible to use all of the usual application methods to infiltrate the nanoparticles into the aquifer environment. Maximum emphasis in this case should be placed on ensuring maximum communication with the aquifer and minimizing connections between aquifers, as well as placing screened intervals of wells mainly to demonstrably contaminated layers. The following systems can be used for the infiltration: Classic cased or uncased wells, direct push into unconsolidated aquifer material, infiltration drains, existing wells, hydraulic fracturing (where allowed), or dosing the reagent directly into trenches (for nanoparticles suitable for injections in oxidic or aerobic conditions (iron oxides). Material constraints are not yet known. Given that this deals with the infiltration of solid material in the form of fine suspensions, the wells must provide good communication with the aquifer, to avoid separation of the reagent during infiltration and its accumulation in the well. The usual spacing between the individual application wells should be in the range of several meters.

Type and design of infiltration wells: The incorporation of reagents into the contaminated aquifer environment is one of the basic conditions for the successful application of in-situ degradation using reactive nanoparticles. In order to promote chemical reduction of a contamination, a direct contact between the (dissolved) contaminant and the reagent is essential. If an enhancement of biodegradation is the goal, a direct contact between the contaminant and the nanoparticles is not required. For these purposes, a method of injecting the reagent is selected, which allows for sufficient spreading in the aquifer. Different techniques are chosen for consolidated and unconsolidated materials. Different techniques are also chosen for shallow and deep contaminated horizons. From this perspective, we distinguish several common ways of dosing nanoparticles into the aquifer environment (Table 3).

The location of infiltration wells can be determined by mathematical modelling of the groundwater flow (chapter 5) and reactive transport of contaminants. A reactive suspension of nanoparticles can be applied to wells either by gravity or pressure. The advantage of pressure injection is that the reactive substance spreads faster laterally. The risk of pressure injection is the deployment of the NPs in the unsaturated zone rather than in the aquifer and thus limiting its interaction with the contamination. Pressure injection may also be accompanied by the creation of fissures in the porous media.

Table 3:   Overview of the types of NP deployment methods and their basic parameters.

Dose method	Description	Depth / suitable material	Comment
Penetration boreholes	Pressure injection of the suspension of nanoparticles using uncased penetration wells with short, about 1m long perforated sections.	Up to 25 m bgl/ permeable to low permeable porous media in the saturated and unsaturated zone	Can only be used in loose material, precise dosage of reagents allows the extent of contamination to be determined, e.g. using CPT/MIP equipment

Dose method	Description	Depth / suitable material	Comment
Hydraulic fracturing (where allowed, might be restricted in certain regions and subsurface conditions)	Pressure injection of reagent to create in the porous media fissures filled with sand, followed by saturation with the reagent solution or direct suspension of elemental Fe.	To 200 m bgl, usually to 20 m bgl / low permeable materials with low elasticity.	Can be used in hard and very hard materials, application creates a subhorizontal infiltration system or horizontal reactive zone. It is possible to combine nanoscopic, micro- and macroscopic Fe. Disadvantage is the low control about the distribution of the particles.
Injection by vertical / horizontal wells	Reagent dosing using vertical / horizontal injection wells, usually in combination with the pumping from horizontal or vertical wells	Usually to 30 m bgl or more / permeable heterogeneous porous media	The network of application wells must be adapted to the site conditions It is possible to create a passive or semi-passive chemical barrier to prevent horizontal spreading.
Reactive barriers	Dosage of reagents to suspend or remove contamination plume. A suspension of the iron is dosed in liquid form using a dense network of vertical wells or infiltration cuts	To 30 m bgl / permeable porous media without substantial heterogeneity.	It is possible to create a passive or semi-passive chemical barrier to prevent horizontal spreading
Soil mixing (for iron filings, most likely not economical for NP!)	Machine mixing contaminated material with an oxidizing reagent in an aqueous suspension. Spiral drills are used for a deeper application. This can be used to remediate the hotspot as well as create a chemically reactive barrier.	To 15 m bgl / medium to low permeable porous media in the saturated and unsaturated zone	Can only be used in loose material. Creates a very good contact between the contaminated soil and reagents, highly invasive technique cannot be used in built-up and heavily used areas. It is possible to combine nano-, micro- and macro-sized particles.

8.2   Preparation of suspension and injection of particles

8.2.1   Preparation of nanoparticle suspension

The aim of this step is to prepare the reactive material for the application. All of the activities must be carried out so as to preserve as much of the original properties of the nanomaterials as possible (high reactivity, mobility, for nZVI a high fraction of active species etc.). Generally, the following conditions should be ensured:

Fresh nanomaterial (primatily for nZVI NPs): Due to their high reactivity particle age is the basic requirements for the use of nZVI. It is recommended to use NP directly from the production. The volume of operating supply of materials must conform to the shelf life of the product which depends on the surface treatment of the NPs (for nZVI usually a matter of days for untreated material and a week for surface-stabilized material).

Protective atmosphere (primarily for nZVI NPs): The high reactivity of Fe NPs causes their rapid oxidation in contact with oxygen. The nanoparticles in the aqueous suspension are therefore to be protected from direct contact with atmospheric oxygen as much as possible; if possible, process water should be de-oxidized. Dosing with a concentrated suspension should be continuous and made directly to the water flow at the desired concentration. In the event of an expected longer manipulation time of the

NP suspension prior to injection it is recommended to use a protective atmosphere of inert gas (N2, Ar) for storage in stirred tanks. Of course, for all NP suspensions the manufacturer's recommendations are to be adhered to.

Continuous dispersion: NP when in contact with each other tend to clump into larger aggregates. The level of aggregation may be reduced by mixing the working suspension and keeping the NPs uniformly dispersed in the liquid. This minimises sedimentation of the NPs and ensures a constant concentration of the dosed material during application.

Removal of unwanted substances from the process water: Nanoparticles are often supplied in a highly concentrated suspension which needs to be diluted (10-200x) to achieve the desired injection concentration. For these purpose, highly oxygenated drinking water sources are often available. Alternatively, less oxygenated groundwater may be used. If nZVI particles are to be used it is recommended to pretreat the process water before applying the nanoparticles, which ensures the removal of oxygen and possibly other competing reducible substances (such as nitrate) dissolved in the groundwater (necessary for nZVI, not relevant for oxidic NP).

The following figure shows (as an example for nZVI) a simplified diagram of the preparation of nanoparticle suspension technology:
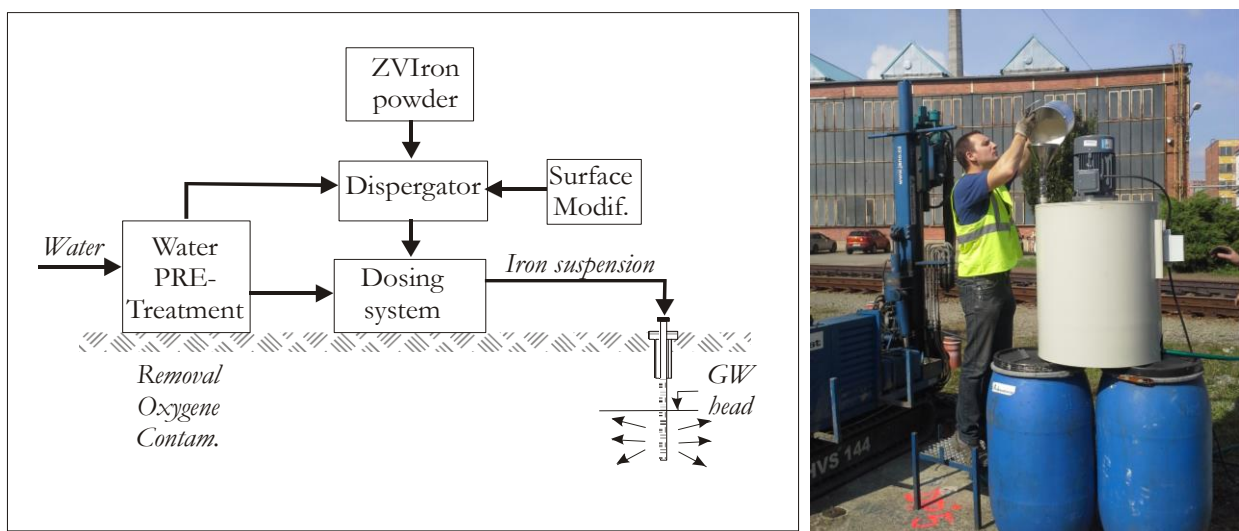
Figure 17: Simplified diagram of the preparation of nanoparticle suspension.

8.2.2   Application of nanoparticles

Once the system for dosing the reagents into the subsurface is prepared (infiltration wells, technological equipment for the preparation and application of nanomaterials, monitoring system) the injection of nanoparticles can begin. For the application, it is necessary to define in advance the basic operating parameters, which are: the concentration of reagents, the total dose of reagent and the regime for the infiltration of reagent.

Concentration and total mass of nanoparticles: There are two basic kinds of concentration: effective and dose

- The *effective concentration* of the reagent for the given type of contaminant, water and aquifer material results from laboratory tests. The effective concentration is expressed in g/g of

aquifer material or in g/l of groundwater depending on the nature and the predominant form of the contaminant present. The effective concentration is not equal to the dosage concentration in groundwater. The speed of migration of the nanoparticles is considerably smaller than the natural groundwater flow. The effective concentration is used to deduce the total reagent dose by considering the basic assumptions such as the volume of aquifer material in contact with the nanoiron and the volume of contaminated water that comes in contact with the nanoiron and type and mass of contaminant to be degraded.

- The *dose concentration* is an important operating parameter. The dose concentration can be influenced by the reach of the application wells and the size of the affected area. The rate of migration of nanoparticles in the rock environment depends on the size of the nanoparticles and the properties of the rock environment (permeability and groundwater flow). Generally, the faster the groundwater flow, the greater the expected reach of the application wells and hence the greater the distance the infiltrated nanoparticles reach. From this perspective, it is best to carry out the application of nanoparticles in a sufficiently diluted form and use an artificial hydraulic gradient to intensify the rate of migration of nanoparticles and enlarge the range of the application wells. The infiltration is usually performed in a concentration range from 1 to 10 g/l. The final value of the concentrations of nanoparticles is determined by the operational and technical conditions of the site. In some cases, it is difficult to achieve low concentration values due to the increasing demands on the accessibility of the site, and flow rates of infiltration wells etc. with decreasing dose concentrations of nanoparticles.

Regime of reagent infiltration: The infiltration of nanoparticles into an aquifer and the degradation of contaminants are significantly influenced by the regime of infiltration of reagents into the aquifer.

Pressure vs. gravitational infiltration: firstly, it is to be decided whether to apply pressure or gravity infiltration to place NPs into an aquifer. The advantage of pressure infiltration over gravitational is undoubtedly the increased efficiency of penetration of the porous material by the nanoparticle suspension. Due to the high pressure gradient during the infiltration we can assume a higher water flow velocity, and a larger range of the infiltration wells can also be expected. Increasing the injected pressure may also accelerate the infiltration process and thus shorten the time necessary for the operation of the technology at the site. The disadvantage is reduced control over the migration of nanoparticles in the porous medium. Increasing the pressure will increase the groundwater level, and thereby increase the risk of penetration and capture of nanoparticles in parts of the aquifer above the groundwater level. There is thus a risk of material losses by immobilization of nanoparticles outside the contaminated area. These negative effects can be reduced by the appropriate choice of the type and suitable casing of infiltration wells.

Number of infiltration cycles (rounds) and remediation time: The total dose of reagent to be infiltrated into a contaminated aquifer in order to achieve the remedial target value is estimated based on the results of laboratory and pilot field tests. The proposed dose is divided according to the expected effectiveness of the required number of infiltration cycles (rounds). The procedure is as follows: First, the average reduction rate of contamination (RC) by infiltration of NP to a single well is estimated from the pilot field tests. In an first approximation it may be assumed that each round of infiltration of NP will approximately decrease the contamination compared to the baseline around each infiltration well at the same rate.

The estimated number of infiltration rounds N can be calculated as follows (see also **Figure 16** and **Figure 18**):

$$N = \frac{\ln c_{limit} - \ln c_0}{\ln R_c}$$

where c_{limit} is the required concentration (remedial target limit), c_0 is the initial concentration prior to the remediation, R_c is the anticipated average reduction of contamination during a single infiltration cycle. The total remediation time can then be estimated from the following equation.

$$T = t_c * N = t_c * \frac{\ln c_{limit} - \ln c_0}{\ln R_c}$$

Where t_c is the exposure time in the aquifer and N is the anticipated number of injection cycles.
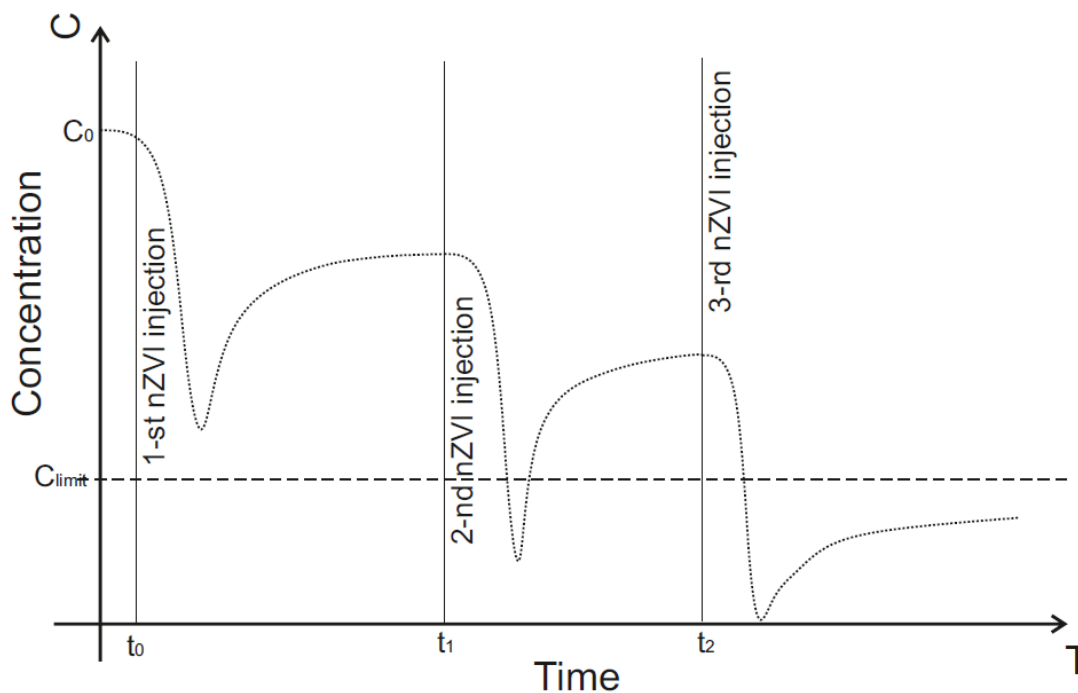
Figure 18: Expected development of the concentrations and required number of application of nano-particles (shown for the example of nZVI) to achieve the remedial target limit c_{limit}.

Simultaneous groundwater pumping: The application of nanoparticles can be operated either independently in the natural groundwater flow regime or by supporting the infiltration by increasing the hydraulic gradient. To some extent, the hydraulic gradient is affected by the infiltration of the suspension into the application well (by increasing the groundwater level). The groundwater flow conditions can be modified by simultaneously pumping groundwater from selected wells. This can significantly increase the hydraulic gradient and also increase the level of control over the direction of migration of nanoparticles in the surroundings of the application wells. Pumping from selected wells can also maintain the injected reagent in the designated area.

The pumping yield from the individual wells during the application of the reagent and the monitoring and evaluation of the modified flow conditions are established through numerical modelling.

9   Assessment of remediation success

Monitoring before, during and after injection has been discussed in detail in chapter 4, and has to comply with client or regulatory requirements. The evidence obtained in each of the monitoring stages allow predictions on the success (or failure) of a remediation.

9.1   Strategies

To assess the effect of a remediation measure the use of some sort of comparison between the situation before and after the measure is most obvious. Based on the facts outlined in chapter 4 this can be done by three different strategies (this holds for any assessment of a remediation measure):

• Determination of a reduction of the concentration of contaminants with a test field downstream of the contaminant source zone via point type samples (→ Test Field)

• Determination of the reduction of the emission from a contaminant source zone with pumping tests (→ Emission Control)

• Determination of a decrease of the mass of contaminants inside the contaminant source zone based upon soil samples (→ Soil Samples)

Each of the methods has certain strengths, but also weaknesses, which are shown in Table 4.

Table 4:   Characteristics, strengths and weaknesses of strategies for assessing a remediation success

	Test Field	Emission Control	Soil Samples
Target medium	ground water	ground water	soil
Type of information	point type	integrative	point type
Strengths	- cost effective - existing test field can be used - can be repeated at moderate costs	- Higher spatial certainty - Information compatible with legal demands - Can be repeated (at higher costs)	- Addressing inventory directly (contaminant mass) - High temporal certainty
Weaknesses	- High spatial and temporal uncertainty - Information may not be sufficient for authorities - Emission can only be deduced with high uncertainty - No information on inventory	- More costly (depending on aquifer) - The installation of new wells may be necessary - Large volumes of water have to be pumped - Long duration of pumping test at low hydraulic conductivities of aquifer - No information on seasonal fluctuations or inventory	- Cannot be repeated (at same location) - High uncertainty due to heterogeneity - Expensive (at higher numbers of samples) - Comparison before – after difficult (heterogeneity) - No (little) information on emission

The table shows that there can be no single strategy suitable for all sites. Rather a closer consideration of the strengths and weaknesses of the strategies before the background of the site-specific conditions and legal factors has to be made. Beyond these considerations, the final decision on a strategy or a combination thereof should always include an agreement with the responsible authorities in order to avoid later controversial situations.

For chemical remediation methods - in this case nanoremediation - a fourth strategy can be considered: The determination and balancing of degradation products, usually by analyzing groundwater samples. This method alone is very uncertain with respect to the information needed by authorities, but can effectively be used to assert that the desired reactions are induced and maintained over a certain period of time. Since the respective parameters are analyzed anyway during the long term monitoring phase, the information gathered here can be used to at least support the assessment of the final success.

9.2   Remediation performance

As for all chemical remediation technologies, it cannot be expected that after the application of the particles the remaining contamination will be down to a zero (non-detect) level. However, what can be expected is that the majority of the contaminants will be removed during the remediation process and that the hazardous potential of the site could be reduced to a tolerable degree. Ideally, by adding the particles and intervention in the hydrochemical milieu, the conditions are changed such that the microorganisms present at the site prior to or having developed during the measure will effectively continue the degradation of the remaining contaminants after the direct impact of the particles has ceased. In cooperation with the authorities the property might be deleted from the list of contaminated sites or at least the value of the property can be increased considerably and further actions can be avoided.

10 Regulatory issues

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 are listed below to facilitate communication between consultant and regulator. An "impact indicator" gives an indication on the importance of the question (green = lesser importance, red = higher importance)

- Description of technology
    - General mode of operation
    - Site installations
    - NP deployment / injection technology to be applied
    - Necessity of pilot test
    - Detailed description of monitoring system

- Description of suspension
    - Particles
    - Additives
    - Stabilizers

- Description of chemical processes
    - Applicability to given contaminants
    - Reaction kinetics, degradation products

- Risk / Risk Management
    - to ecology
    - to humans
- Options for risk mitigation
    - Stakeholder involvement

- Alternative Technologies
    - Technical aspects
    - Combination with other technologies / treatment trains

- Financial aspects

- Long Term Risk
    - Stability of NPs in subsurface
    - Change of land use (zoning) due to nanoremediation?
    - Stakeholder involvement

- Best Practice
    - Well documented sites with comparable NP application

11 Financial issues

As for the application of any other remediation technology, there is no "generic" cost calculation for nanoremediation, rather the total cost will be a function of many parameters, due to subsurface and contamination, due to geographic location and so on. Nevertheless, to facilitate cost estimation the main cost drivers are listed below. An "impact indicator" gives an indication on the importance of the question (green = lesser importance, red = higher importance). Financial issues are discussed also in Bardos and Merlin (2017).

- Regulatory Aspects

  – Injection permit

  – Monitoring

  – Reporting

Cost for monitoring and reporting requirements are highly site (and country) dependent

- Remediation Goal

- Time Horizon / Time Limitations

- Site Installation and Mobilization of Personnel and Equipment

- Additional site Investigations

- Cost for Nanoparticles and Suspension

- Hydrogeological Conditions

  – Injection system and operation

  – Aquifer pre-treatment

- Geometry, Inventory, and Accessibility of Contaminants

- Miscellaneous

  – Shipping costs, customs

  – Compensation for land owners

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13 Appendices

13.1   Appendix A - Conceptual site models

Introduction

Risk based contaminated land management depends on understanding the spatial distribution of contaminant sources, their fate and transport and the nature of human, environmental and water receptors. A Conceptual Site Mode (CSM) is a representation of relevant information, and uncertainties, relating to contamination on a site.

What are conceptual site models?

Conceptual Models are used in many disciplines including weather forecasting, software development, and ecology. They summarise and simplify complex information to provide a concise and usually spatial presentation of the system being modelled so that the critical features and the relationships between them are highlighted. Within contaminated land, the system being modelled is the Site (history, current/proposed use, sub surface) and the critical features are the sources, pathways and receptors and whether or not they are linked up to form pollutant linkages.

Conceptual site models in the context of contaminated land

The United States have had detailed guidance on what should be in a CSM since 1995 (ASTM 1995) which has been updated several times, the most recent being 2014 (ASTM 2014). Some definitions offered in British, European and International standards are listed in Table A1.

Table A1: Example descriptions of CSMs

ISO	A CSM is a "Summation of all information about a site relevant to the task in hand". (ISO 2015).
Germany	The CSM "describes the hydrogeological situation and the presumed transfer of contaminants from the centre of pollution to the groundwater and threatened uses." (Rainer Dinkel, 2009)
France	The objective of the CSM is to make it possible to: "determine the linkages between: • the sources of pollution, • the various transport media and their characteristics, which determines the extent of contamination, and • the receptors that must be protected: nearby populations, people using the media and the environment, the exposure media, and vulnerable natural resources " (translated) (French Ministry of the Environment (MEDD) 2007)
UK	A CSM includes information which: • Represents the characteristics of the site • Shows possible relationships between contaminants, pathways and receptors. • Supports the identification and assessment of pollutant linkages. (Environment Agency 2004)

The content of conceptual site models

In general a complete CSM should comprise a plan view and cross section to illustrate the main features at a site; matrix or network diagrams to specify the pollutant linkages present, text to describe the features and linkages and a key, as shown in Figure A1.
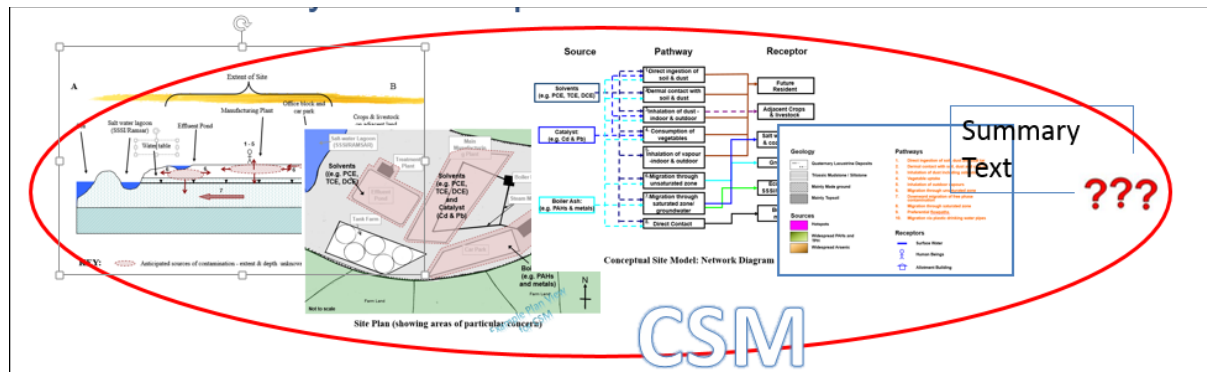
Figure A1: A CSM comprises multiple elements including text and diagrams

The typical contents of a conceptual model are listed in Table A2. One way to think of a CSM is as a means to capture "what you know plus what you don't know" (M de Freietas, 1987) pers comm, originally applied to ground models in engineering geology). The unknown information should be listed as uncertainties/ assumptions; and can later be the target of further investigation.

Table A2:   Information to show the elements of a conceptual model (after Nathanail et al 2007)

Information	Tex	Graphic elements	
		Plan View and Cross section	Network /Matrix Diagram
Legal Context of CSM	Y		
Site description	Y	Y	
Geology, hydrology and hydrogeology	Y	Y	
Potential sources (contaminative activity e.g. tank; manufacturing area)	Y	Phase 1	Y
Potential contaminants	Y	Phases 2, 3	Y
Potential pathways	Y	Y	Y
Potential receptors	Y	Y	Y
Potential/ significant pollutant linkages	Y	Possibly	Y
Limitations	Y	Possibly	Possibly

This level of detail may not be required for all sites, but should be considered as the norm, only to be departed from when a reduced format provides sufficient information to understand and evaluate the pollutant linkages.

Legal Context

The CSM should be clear on the legal context it is addressing as this affects the elements to be included in the CSM. For example, in one country; the legislation may require that the assessment is whether the contamination will migrate to the river (say 100m away) and the pathway is then 100m. In another; it may be that the assessment needs to consider the receptor as the boundary of the site (say 40m away); resulting in a shorter pathway; ie even though the river is still 100m away, the pathway is only 40m.

Site description, Geology, hydrology and hydrogeology (Figure A2, Figure A3)

The Site description, geology, hydrology and hydrogeology should be shown (as far as possible) on both the plan view and cross section with a succinct summary in the CSM text (and not a repetition of what is in the report). For example, whilst the report may describe the geology in some detail and reference other documents; in the CSM text a summary statement such as 'The site is underlain by River alluvium over up to 5m for Thanet Sand, followed by the Chalk' is sufficient.

Sources, Pathways, Receptors (SPR) and pollutant linkages (PL) (Figure A4, Figure A5)

The CSM should state:

•   Sources of contamination eg fuel tank, or benzene, arsenic (if the contaminants are known);

•   Pathways through which the contaminants might migrate eg unsaturated zone; and

•   Receptors eg river or well.

Where all three parts S-P-R are present a pollutant linkage is said to exist which represents a potential risk to human health or the environment. Identifying the PLs present is an important function of the CSM; PLs can be depicted on the cross section, but also need to be clearly listed in a network or matrix diagram.

In the early stages of an investigation the SPR and PLs are uncertain and inferred from evidence such as historical maps; as the work progresses, the SPR and PLs are supported by evidence such as testing of the ground.

Uncertainties

The CSM should include a section for listing uncertainties and assumptions. Uncertainties are things that are not known eg thickness of made ground. Assumptions are things on which a reasonable guess has been made but it could be wrong eg that no other sources of contamination are present.

Example conceptual site model

The example CSM below comprises a plan view, cross section, and a network diagram sub divided to show the pollutant linkages to human health and water receptors. On the plan view the line of cross section has been marked.
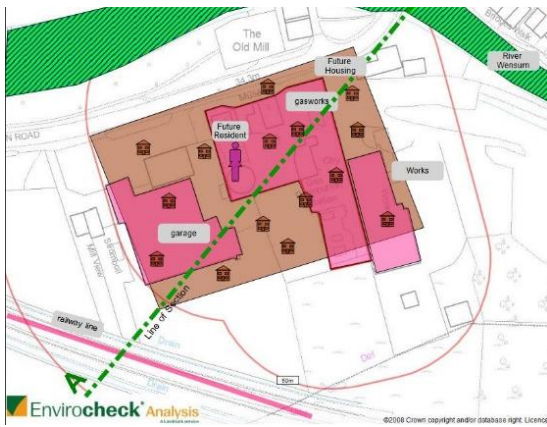
Figure A2:   Plan View
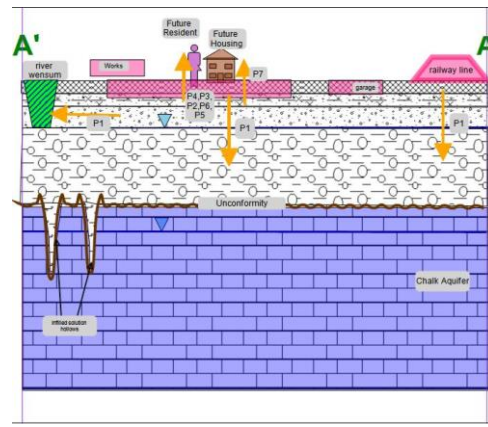
Figure A3:   Cross Section
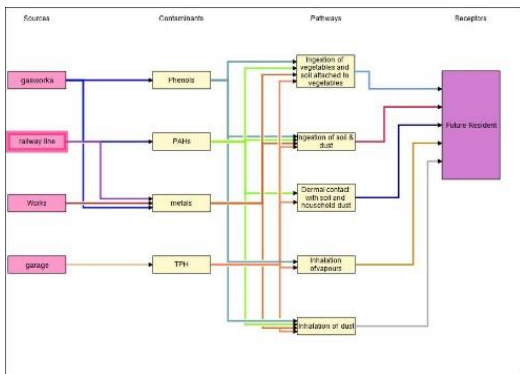
Figure A4:   Human Receptors
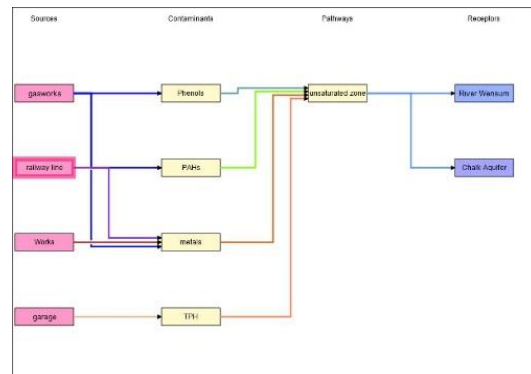
Figure A5:   Water Receptors

Use of conceptual site models

CSMs are used and updated throughout the lifetime of a project (Figure A6). An initial CSM is created at the end of a desk study and developed using the results of the site investigation and risk assessment. It is then used to guide the remediation options appraisal and remediation design. Finally, when the remediation is verified, the CSM should show that all pollutant linkages have been demonstrably broken.

A CSM is relevant in any situation where the risk in relation to a possible pollutant is being evaluated and so can also be applied to the scenario of injecting nanoparticles into the subsurface. This would be a separate CSM to the CSM which shows the results of the site investigation or the proposed remediation design.
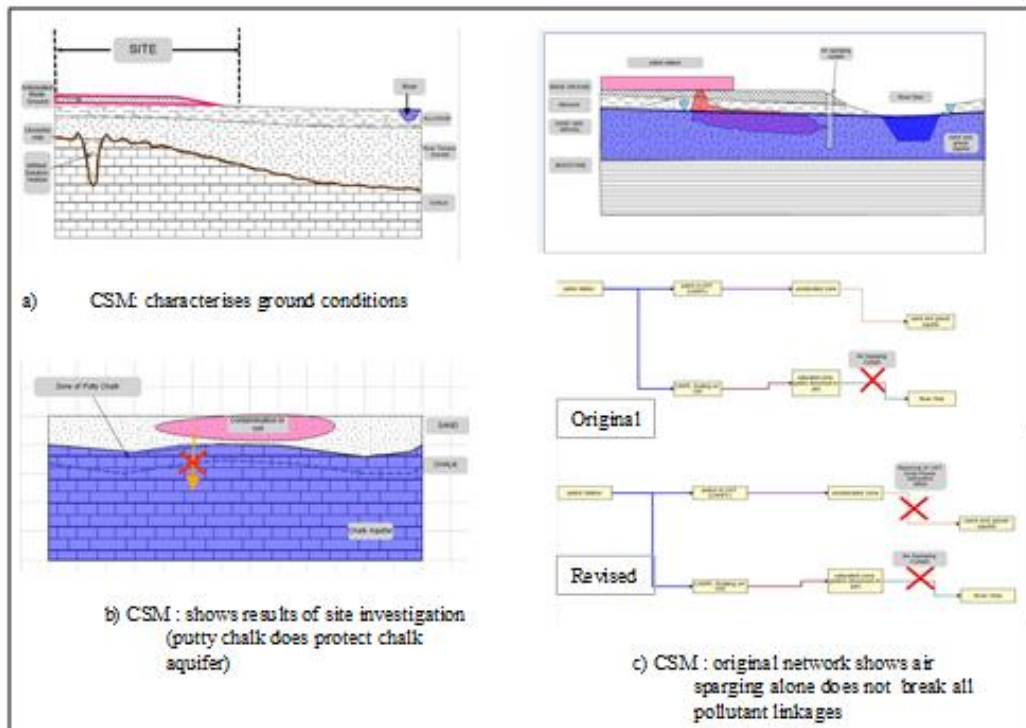
Figure A6: Some examples of how CSMs are used in contaminated land management

Conclusions

The aim of a CSM is to identify (potential) pollutant linkages by presenting summary environmental information in three dimensions. The CSM presents the best hypothesis of what is going on at a site and formally states the uncertainties which are used to design the next phase of the investigation. The CSM is updated throughout the project as new information becomes available.

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13.2　　Appendix B - Nanoparticles available in NanoRem

Table B1:　Overview of identified application areas/potential of particles

Particle Type	Oxidation	Reduction	Hydrophobic sorption	Sorption of metals/metalloids	Support of biology. treatment	Hydrolysis	Reactive compon. consumed	Additional reagents needed	Gaseous products formed	Anaerobic	Aerobic	pH <<7	pH ≈7	pH >7	yes	no	Inertization of susp. needed	Disperser needed			wastewater			Tested at field scale	Ready for up-scaled testing	Research at laboratory scale
Nano-Goethite	X			X	X										X											
Carbo-Iron	(X)	X	X	X	X	(X)	X		X	X			X	X	X		X	X			X			X		
Trap-Ox Fe-BEA35	X		X					X	X	X	X		X	X		X					X				X	
Trap-Ox Fe-MFI120	X		X					X	X	X	X	X	X			X					X					X
Bionanomagnetite (Bnm)		X		X						X			X			X					X					X
Pd-Bnm		X		X					X	X			X	X		X					X					X
Al, Mg		X					X	(X)	X	X			X	X												X
BaFeO₄	X						X		X	X	X	X	X								X					X
NANOFER (25P, 25S, STAR)		x	x	x			x		x	x			x	x		x		x			x			x	x	X
FerMEG12		x	x	x			x		x	x			x	x	x			x			x			x	x	X
Milled iron with alumina		x	x	x			x		x	x			x	x	x			x			x					x

Table B2:　List of selected contaminants degradable (+ successfully tested, - not applicable, L likely, but not tested), adsorbed or otherwise treatable (t)

Particle Type	Chlorinated Olefins (e.g. C2Cl4, C2HCl3, C2H2Cl2)	Brominated Olefins (e.g. C2H3Br)	Halomethanes (e.g. CCl4, CHBr3, CHBr2Cl ...)	Saturated polyhalogenated (e.g. C2H3Cl3)	Dichloroethane, Dichloromethane	Aromatics, Phenols (low substitution degree, e.g. dichlorobenzene)	Aromatics, Phenols (high halogenation degree, e.g. PCBs, Pentachlorophenol)	Herbicides and pesticides (e.g. DDT, Lindane)	Pharmaceuticals (e.g. Iopromid)	BTEX	PAHs	Fuel oxygenates (MTBE, ETBE)	Petroleum hydrocarbons	Metals/Metalloids (e.g. Cr(VI), Cd(II), As(III))	Nitro compounds (e.g. TNT, nitrobenzene)	Perchlorate	Further contaminants tested[1]
Nano-Goethite	-	-	-	-	-		L	-		+	L	L	L	t	L		
Carbo-Iron	+	+	+	+	-	-	L	L	L	t	t		t	t	L	L	
Trap-Ox Fe-BEA35	+	L	+/-[2]	+	+	+	L	L	+/-[3]	+	L/-[3]	+	L	-	L	-	Triton-X100
Trap-Ox Fe-MFI120	+	L	+/-[2]	+	+	+	-	-	-	+	-	+	L/-	-	L	-	+
Bionanomagnetite (Bnm)														+	+		
Pd-Bnm	+																Ramazol black
Al	+		L	-	-											-	
Al/Mg	+		L													-	
BaFeO₄						L				+					L		
NANOFER (25P, 25S, STAR)	+	+	+	-	+	-	+	+	-	-	-	-	-	+	+	L	
FerMEG12	+	+	+	-	-	-	-	L	-	-	-	-	-	+	L	L	
Milled iron with alumina	+	L	L	-	-	-	-	L	-	-	-	-	-	+	L	L	

[1] Further substances are listed in the individual particle descriptions in chapters 3.1 to 3.7; [2] not applicable for CCl4, [3] depending on molecule size

Table B3:   Reactivity data for typical target contaminants

NPs	NP concen-tration [g L⁻¹]	Contami-nant	Initial contaminant concentration [mg L⁻¹]	Type of background solution	pH of background solution	Contaminant degradation k_{obs} [h⁻¹]	k_{SA} [L m² h⁻¹]	Corrosion k_{H2} [h⁻¹]	Fe⁰ efficiency ∈ [%]	Additional data
Nano-Goethite	1	Toluene	20	F.I.S	6.5	1.9×10^{-2}				$0.47\ \mu M/day$
	1	Benzoate	72	F.I.S	5	7.75×10^{-2}				$1.86\ \mu M/day$
Carbo-Iron®	1	PCE	50	F.I.m	7.6	7.6×10^{-3}	1.3×10^{-3}	2.1×10^{-3}	5.2	
Trap-Ox Fe-BEA35	50	MTBE	500	F.I.s	8.2	1.3				with $C_{H2O2,0} = 8\ g\ L^{-1}$: $A_{pseudMTBE} = 0.025\ L\ g^{-1}\ h^{-1}$
Trap-Ox Fe-MFI120	10	MTBE	100	F.I.s	6.5	1.1				$A_{pseudMTBE} = 0.11\ L\ g^{-1}\ h^{-1}$
Bionanomagnetite (Bnm)	0.75	Cr	46.8	Deion. water +NaOH	12	0.066	3.85×10^{-5}			$A = 1.1 \times 10^{-3}\ L\ g_{NP}^{-1}\ min^{-1}$
Pd-Bnm	0.32	Cr	46.8	Deion. water +NaOH	12	1.5				Non-linear at high concentration
Al (Column)		PCE	≈ 55 mg/L	F.II	≈ 8	3.1×10^{-3}				Dechlorination (41 d): PCE → Cl⁻: 7%, PCE → TCE: 1.5% Traces of DCE Anaerobic corrosion (41 d): $m_{corroded, Al(0)}/m_{overall\ consumed\ Al(0)}$: 97%
Al/Mg (Column)		PCE	≈ 55 mg/L	F.II	≈ 8					Dechlorination (41 d): PCE → Cl⁻: 53% Traces of TCE + DCE
BaFeO₄ (Batch)		Toluene	54	Deion. water	≈7	7.6×10^{-4}				Ferrate(VI)/toluene ≈ 1.5/1 (mol/mol)
NANOFER 25S	1.1	PCE	50	F.I.s	7.6	2.6x10-3	1.0x10-4	5.3x10-4		
				F.I.m	7.8	1.9x10-3	0.76x10-4	5.4x10-4	5.2	
				F.I.h	8.2	1.7x10-3	0.68x10-4	4.8x10-4		
NANOFER 25S	0.25	Cr	46.8	F.I.m	12	0.034	1.4x10-3			A = 2.3×10-3 L gNP-1 min-1
Optimized NANOFER STAR	1	PCE	50	F.I.m	n.a.			1.79x10-5		For activated NANOFER STAR: $k_{SA} = 1.67 \times 10^{-5}$ [L m² h-1]
FerMEG12	1	TCE	11	Soft (F.I.s)	7.64	1.58x10-3	8.80x10-5		18	

13.3   Appendix C - Operating window for nanoremediation

Process Acronym	Requirements / Limitations	ReduNP, generel	OxiNP	ReduNP, Carbo-Iron®	Zeolite NP
Requirements / Limitations	saturated zone				
	unsaturated zone				
	plume				
	residual				
	pool				
	sorbed				
Process	Main Process	Primarily Reduction Based	Primarily Oxidation Based, anaerobic biodegradation enhanced by ferric oxide	Primarily reduction based (by Fe(0) component) in combination with adsorption by	Primarily adsorption + catalytic oxidation (in combination with hydrogen peroxide)
	Description	enhanced NZVI reduction based process with the use of small size and migrating particles.	Nanogoethite serves as terminal electron aceptor during the degradation of organic contaminants through bacterial	Composite of Fe(0) and microscale activated carbon (Fe/AC) applied in aqueous suspensions with stabilizers	Microporous alumosilicate particles loaded with Fe(III) which act as adsorbent and oxidation catalyst
	Tiered approach	According to site conditions is recommended nanoremediation as part of treatment train. Generally the technology is convenient after free phase removal or / and to intermediate area between	According to site conditions is recommended nanoremediation as part of treatment train. Generally the technology is convenient for polishing after source, and high contaminant concentrations removal.	> Source zones: contaminant phase or saturated soil should be removed previously by alternative methods (excavation, phase separation...), > Carbo-Iron application is usually followed by subsequent	Mainly used for formation of a barrier against spreading of plumes which can be regenerated by injection of hydrogen peroxide, can be used as polishing after source removal
	Synergies	Reductive bioremediation	Bioremediation	> Contaminant retardation in reactive zone due to sorption by AC-component > Bioremediation	sorption by zeolite leads to retardation + collects contaminants which are slowly released from sorbed/trapped
	risk management	source control/Plume	plume management	source control/Plume	plume management
	Contaminant outcome	Destruction of organic compounds, immobilisation or stabilisation of metals	Destruction of organic compounds, immobilisation or stabilisation of metals	Destruction	Destruction
Deployment	Direct Push	optimal, preferably when design is based on detailed contaminant prospection (for	optimal	optimal range of permeability 10E-3 to 10E-5 m/s	optimal range of permeability 10E-3 to 10E-5 m/s
	Well injection	feasible, screened intervals correctly designed and splitted in shorter parts, preferably targetted injection into most contaminated parts of the	feasible, screened intervals correctly designed and splitted in shorter parts, preferably targetted injection into most contaminated parts of the	optimal range of permeability 10E-2 to 10E-4 m/s	optimal range of permeability 10E-2 to 10E-4 m/s
	Emplacement	for NP not economically feasible	for NP not economically feasible	for NP not economically feasible	for NP not economically feasible
	Heath and safety	low risks when manipulationg with liquid suspension	see MSDS/ CAS 20344-49-4 LCA is in progress	see MSDS	see MSDS

Process Acronym / Operational Boundaries		ReduNP, generel	OxiNP	ReduNP, Carbo-Iron®	Zeolite NP
	Site requirements	available and accessible space for mesh of injection and monitoring wells, source of technological water and electricity, place for safe material storage during injection, used underground facilities and network might limit the process, geological, hydrogeological and contaminant characterisation done, conception model done, legal and local permits acquired,	available and accessible space for mesh of injection and monitoring wells, source of technological water and electricity, place for safe material storage during injection, used underground facilities and network might limit the process, geological, hydrogeological and contaminant characterisation done, conception model done, legal and local permits acquired, neutral	available and accessible space for mesh of injection and monitoring wells, source of technological water and electricity, place for safe material storage during injection, used underground facilities and network might limit the process, geological, hydrogeological and contaminant characterisation done, conception model done, legal and local permits acquired,	available and accessible space for mesh of injection and monitoring wells, source of technological water and electricity, place for safe material storage during injection, used underground facilities and network might limit the process, geological, hydrogeological and contaminant characterisation done, conception model done, legal and local permits acquired,
	treatable depths	no physical and chemical limits, but must be well characterized in advance	no physical and chemical limits, but must be well characterized in advance	technically limited at about 60 - 70 m bgl	technically limited at about 60 - 70 m bgl
	Footprint	no physical and chemical limits, but must be well characterized in advance	no physical and chemical limits, but must be well characterized in advance		
	Health and safety issues	use protective equipment to avoid direct contact with nanoparticles.	use protective equipment to avoid direct contact with nanoparticles.	use protective equipment to avoid direct contact	use protective equipment to avoid direct contact when handling particles, follow common safety instructions when working with H2O2
	Duration	Half-life: according to contaminant type is in range of weeks - months Source remediation duration: 3 - 5 years if NAPL was previously removed and depending on quality of pre-remediation site characterisation performed Plume remediation duration: the same 3 - 5 years ifsource was successfully removed and depending on quality of pre-remediation site characterisation performed.	Half-life: expected in range of moths Duration of plume removal: expected in range of 5-20 years if source was successfully removed and depending on quality of pre-remediation site characterisation performed.	fast removal of contaminants from groundwater by adsorption (within hours/days), reduction of adsorbed contaminants (within few weeks), longevity of reactive Fe(0) component depends on site conditions (pH, natural oxidants) and can last up to several months, re-injection of particles is possible	fast removal of contaminants from groundwater by adsorption (within hours), effective sorptive barrier function depending on contaminant and groundwater flow rate (for several weeks/months), injection of H2O2 leads to fast degradation of adsorbed contaminants (within hours), periodic adsorption/oxidation phases can be repeated as required, longevity of Trap-Ox Fe-zeolite depends on site conditions (pH,
	Cost drivers	Pre-remediation site characterisation costs, injection system - injection points nettwork density depending on soil characteristics, nano material costs depending on required nanomaterial doses,	Pre-remediation site characterisation costs, injection system - injection points network density depending on soil characteristics, time - required number of injection campains rise remediation costs	Mainly: Carbo-Iron production costs, required amounts depend on contaminand mass + natural reductand demand, in addition: site characterization and monitoring, repeated operations	Fe-zeolite production costs + demand of hydrogen peroxide (which depends on site conditions), costs of repeated operations (H2O2 injection), site characterization and monitoring

Process Acronym		ReduNP, generel	OxiNP	ReduNP, Carbo-Iron®	Zeolite NP
Treatable Contaminants	Halogenated	Prime targets: Cl-ethenes, Cl-methanes, brominated aliphatics, HCH, lindane Possible targets: Cl-ethanes,Cl-benzenes,	NONE	prime targets: chlorinated ethenes (PCE, TCE, DCE, VC), chlorinated methanes (CCl4, CHCl3), brominated aliphatics (vinyl bromide, dibromoethane, mixed chlorobromo compounds...) possible targets: polychlorinated substances (e.g. lindane, tetrachloroethane)	prime targets: chlorinated ethenes (PCE, TCE, DCE, VC) (but alternative: reduction with Fe(0)), halogenated ethanes (e.g. 1,2-DCA) chlorinated aromatic compounds (chlorobenzene)
	non-halogenated		BTEX	possible targets: very hydrophobic compounds (e.g. ≥ 3ring PAHs) by strong adsorption	prime targets: fuel oxygenates (MTBE, ETBE), BTEX, possible targets: aliphatic hydrocarbons, surfactants
	PCBs	efficient for some congeneres, must be tested in laboratory in advance,	NONE	mainly by adsorption, reactivity to be tested (=possible targets)	to be tested, possible targets: PCBs with lower Cl-substitution degree
	Heavy Metals	Cr, As, Cu, durability/stability/permanency of metal stabilisation must be evaluated.	e.g. zinc, copper, nickel, mercury, cadmium, lead, chromium	possible targets: As(V), Cr(VI), Pb(II)	not recommended
	Comments/restrictions	Prime and possible targets strongly dependent on soil and water chemistry, must be tested and evaluated in advance.	NONE	possible targets: nitrate, perchlorate	broad application range due to radical-driven oxidation, unsaturated compounds and compounds with low degree of halogen substitution are degraded most easily, restrictions: size exclusion by zeolite pores for larger contaminant molecules (e.g.
		Other: Nitrates		aromatic halogenated compounds (e.g.chlorobenzenes) and some aliphatic halogenated compounds (e.g.dichloroethane, dichloromethane) are not	compounds with high halogen substitution degree untreatable (e.g. CCl4)
				stabilization of metals/metaloids: potential long-term remobilisation	

Process Acronym		ReduNP, general	OxiNP	ReduNP, Carbo-Iron®	Zeolite NP
Hydrogeology	Permeability	lower limit 10^{-6} m/s	lower limit 10^{-6} m/s	soil and fissured rock, permeability coefficient 10E-2 to 10E-5 m/s, in soil homogeneous grain size distribution favourable, effective pore space	soil and fissured rock, permeability coefficient 10E-2 to 10E-5 m/s, in soil homogeneous grain size distribution favourable, effective pore space
	TOC	n/a	n/a	n.a.	best at low TOC (< 0.1 Ma%)
		feasible for porous and fractured aquifers, detailed aquifer characterisation with joint contaminant evaluation must be performed in advance (including vertical description of layers and contaminant	feasible for porous and fractured aquifers, detailed aquifer characterisation with joint contaminant evaluation must be performed in advance (including vertical description of layers and contaminant		best at low content of iron (and Mn) minerals in soils (< 0.1 Ma%) otherwise higher demand of hydrogen peroxide
		must be evaluated in horizontal as well as in vertical directions, injection system must be adapted to that information.	must be evaluated in horizontal as well as in vertical directions, injection system must be adapted to that information.		
Hydrochemistry	pH	different injection systems and different material modifications might be applied in aquifers with low groundwater flow velocity (<1m/day) and in aquifers with preferably higher pH to extend longevity of iron, but not feasible at pH bellow 4.5. At low pH conditions pretreatment is recommended.	neutral to basic conditions, pretreatment for acidic sites is in progress	best: pH≥6, reduced efficiency due to Fe(0) corrosion at lower pH	various Trap-Ox Fe-zeolite types applicable within pH 5 to 8.5
	TOC		no limitation, if not causing acidic pH	no limitation, if not causing acidic pH	DOC from NOM best < 10 mg/L, non-target contaminants (of similar size as targets) can lead to competitive adsorption
	buffer capacity	n/a	n/a	no limitation	no limitation
	Comments/restrictions	n/a	n/a	dissolved oxygen best: ≤2 mg/L, reduced efficiency due to Fe(0) corrosion at higher	no limitation regarding dissolved oxygen
		complex chemistry and high concentrations of reductible compounds lead to numbers of competitive reactions and might cause high iron consumption or fai of the treatment		no limitation up to 500 mg/L (CaCO₃), except of need for higher stabilizer concentrations	best: < 100 mg/L (CaCO3), possible up to 500 mg/L (CaCO3)

Process Acronym / Additional Information	ReduNP, generel	OxiNP	ReduNP, Carbo-Iron®	Zeolite NP
Application manuals/guidelines	see homepage supplier	patent US 8,921,091 B2	see NanoRem DL3.2, further material in preparation	see NanoRem DL3.2, further material in preparation
Best practice	well characterized sites	well characterized sites		
Citations		•Bosch J, Heister K, Hofmann T, Meckenstock RU. (2010). Nanosized iron oxides strongly enhance microbial iron reduction. Applied and Environmental Microbiology (76) 184-289 •Braunschweig J, Bosch J, Heister K, Meckenstock RU. (2013). Iron oxide nanoparticles in geomicrobiology: from biogeochemistry to bioremediation. New Biotechnology (30). 793-802 •Höss S, Fritzsche A, Meyer C, Bosch J, Meckenstock RU, Totsche KU. (2015). Size- and Composition-Dependent Toxicity of Synthetic and Soil-Derived Fe Oxide Colloids for the Nematode Caenorhabditis elegans. Environmental Science and Technology (49). 544–552	Mackenzie, K., Bley, S., Georgi, A., Kopinke, F.-D. (2012): Carbo-Iron – an Fe/carbon composite – as alternative to nano-iron for groundwater treatment Water Res., 46 (12) 3817-3826. (doi:10.1016/j.watres.2012.04.013) Bleyl, S., Kopinke, F.-D., Mackenzie, K. (2012): Carbo-Iron®—Synthesis and stabilization of Fe(0)-doped colloidal activated carbon for in situ groundwater treatment Chem.Eng.J. 191, 588 – 595 (doi:10.1016/j.cej.2012.03.021) Bleyl, S., Kopinke, F. D., Georgi, A., & Mackenzie, K. (2013). Carbo-Iron®–ein maßgeschneidertes Reagenz zur In-situ Grundwassersanierung. Chemie Ingenieur Technik, 85(8), 1302-1311.(doi: 10.1002/cite.201300009) Georgi, A., Schierz, A., Mackenzie, K., Kopinke, F.-D., (2015): Colloidal activated carbon for in-situ groundwater remediation — Transport	Gillies, G., Mackenzie, K, Kopinke, F D, Georgi, A (2016) Fluorescence labelling as tool for zeolite particle tracking in nanoremediation approaches. Sci. Tot. Environ. 550, 820-826. Georgi, A, Gillies, G, Mackenzie, K, Kopinke, F-D (2015) Colloidal Fe-zeolites - A novel material for sorption-supported in-situ chemical oxidation (ISCO), Extended Abstract, 5 Pages, Proceedings of AquaConSoil 2015, 9–12 June, Kopenhagen http://www.aquaconsoil.org/proceedings.html. Gonzalez-Olmos, R, Kopinke, F D, Mackenzie, K, Georgi, A (2013) Hydrophobic Fe-zeolites for removal of MTBE from water by combination of adsorption and oxidation. Environ. Sci. Technol. 47, 2353-2360.
Web-Pages		https://www.uni-due.de/biofilm-centre/mikro_projekte_nanorem_en.php	http://www.carboiron.de/ http://www.intrapore.com/	
Suppliers	www.nanoiron.cz	UDE	SciDre GmbH, http://www.scidre.de/	Helmholtz-Center for Environmental Research - UFZ
MSDS	see homepage supplier	https://www.uni-due.de/biofilm-centre/mikro_projekte_nanorem_en.php	upon request from SciDre GmbH, http://www.scidre.de/	upon request from UFZ

13.4 Appendix D - Exemplary lists of parameters to describe chemical processes in the subsurface

Table D1: Parameters to be monitored when applying reductive methods (Fe based)

Parameter	Indicator for	Remarks
Chloride	Degradation product	Essential for assessment of remediation success, but a background of ~50 mg/l will make it difficult to evaluate (no information about the natural variability at the moment)
PCE	Main contaminant	Important to detect changes in emission
TCE	Contaminant, possible intermediate product	Possibly difficult to evaluate
DCE	Intermediate product	Indicators for incomplete degradation, difficult to sample!
VC	Intermediate product	
Ethene	Final product	THE parameter for assessment, difficult to sample!
Hexaclorthane, Hexachlorbutadiene		Special contaminants at site
H_2	Corrosion	Assessment of ration corrosion/reaction, difficult to sample!
E_h	Redox milieu	Important parameter for lifetime of particles
pH	Corrosion + reaction	
O_2	Redox milieu	Indicator for changing flow regime
EC		Nice to have
Dissolved organic and inorganic carbon		DOC – nice to have (indicator for surfactants…) DIC-microbial activity
NH_4^+	Redox sensitive cation	Indicator for Nitrate reduction by iron (can be dropped, if constantly absent)
NO^{3-}, NO_2^-, SO_4^{2-}, PO_4^{3-}	Redox sensitive anions	
Acid/base capacity	Change in pH-milieu	Indicator for stability of pH-milieu
$Fe_{dissolved}$	Degradation product	Degradation product (corrosion + reaction), concentration not directly transferable due to precipitates

Table D2: Parameters to be monitored when applying oxidizing methods (iron-oxide based)

Parameter	Indicator for	Remarks
Toluene	Main contaminant	Volatile
Intermediates	Incomplete degradation	Not to be expected
CO_2, p/m-value, DOC/DIC	Main degradation product	Important, problems due to background
pH	Important parameter	Buffer capacity (p/m-value)
Fe^{2+} (dissolved)	Degradation product	Difficult to quantify due to precipitates ($Fe(OH)_2$, FeS, $FeCO_3$)
Fe^{3+} (solid)	Consumption of agent	Background in "soil", depending on acid type and concentration
Ratio Fe^{2+}/ Fe^{3+} (solid)		difficult

13.5   Appendix E - List of characterisation methods

Table E1: Characterisation methods applicable for on site or *in-situ*

Method	Concentra-tion range	Size Range	Particles	Comments/Limitations
Turbidity (TurbiScan)	0.5 mg – 1 g/L		all NP	Tested for FeOx and Fe-zeolites. Applicable in the field but detection limits depend on background turbidity measurements.
Metal-content (ICP-OES, spec-trophotometry)	µg – g/L	NR	all NP	Applicable in the field (spectrophotometer), but detection limits are dependent on site background concentrations. Restricted to water samples, solid samples affected by background content.
Magnetic susceptibility	50 mg/L – g/L		nZVI, Car-bo-Iron®	*In situ* measurements, but low mobility of nZVI means that detection will be contingent on the sensor being placed in a location where the particles will migrate. Some limitations in placement, e.g. under buildings.
Direct H_2 Meas-urement	> 10 mg/L	NR	nZVI, Car-bo-Iron®, Al, Mg	Cannot trace oxide/hydroxide reaction products. On site applications dependent on background measurements and redox
Ultrafiltration	µg – g/L	ca 10 – 450 nm	all NP	Field sampling technique. Used in combination with other techniques for separating dissolved and particulate Fe, and for insight into size distribution measurements and changes over time. Avoids problems with particle aggregation and dissolution between sampling and measurement.
C/Fe ratios	n.a.	NR	Carbo-Iron®	Preliminary *in situ* test

Table E2:   Characterisation methods: laboratory analysis only

Method	Concentration range	Size Range	Particles	Comments/Limitations
Mossbauer	>100 mg/L		nZVI	Lab technique, but can be applied to field samples that are frozen after collection.
H_2 after Acid digestion		< 500 nm	nZVI, Carbo-Iron®, Al, Mg	When combined with total Fe measurements, Fe^0/Fe_{tot} ratios can be used to follow reactivity.
Laser diffraction (Mastersizer)	> 500 mg/L	0.6 – 1 µm	all NP	FeOx below the limit of detection for size
Time of Transition (EyeTech)	< 500 mg/L	0.6 – 600 µm	Carbo-Iron®	Sedimentation problems with nZVI (Nanofer) and milled Fe. FeOx below the limit of detection for size
Dynamic light scattering, DLS (Zetasizer)	< 200 mg/l	1 nm - 1 µm	all NP	Sedimentation problems with nZVI (Nanofer) and milled Fe.
Particulate organic carbon	5 mg/L	NR	Carbo-Iron®	Filtration of water sample.
Total organic carbon	ca 0.3 % wt		Carbo-Iron®:	Sediments. Test on NanoRem porous media
Fe-Zeolites: target adsorption	0,01 % wt		Test on M:1 (Dorsilit)	

NR – Not relevant

13.6   Appendix F - Mobility investigations of nanoparticles

Excerpt from NanoRem IDL 4.1: Standardized experimental protocols for mobility and reactivity studies.

Orientation, Packing and Saturation

Columns may be oriented horizontally or vertically based upon the specific question addressed in the experiment. In case of vertical orientation movement of the flow will be from bottom to top in order to prevent the build-up of preferential flow paths and to support degassing (Lewis and Sjöstrom, 2010). In order to prevent potential dry falling of the porous media in case of pump failure or an insufficient reservoir volume it is recommended to place the column below the influent and effluent reservoir and to control the inflow pump by a pressure sensor at the column inflow which automatically shuts down the pump, if a pressure drop caused by air bubbles in the inflow occurs.

The goal of packing is to produce a homogeneous porous media, having a bulk density similar to that observed naturally, while avoiding the formation of stratifying layers or preferential flow pathways. The average range of bulk densities and porosities of typical unconsolidated soils may be found for example in Domenico and Schwartz (1998). Depending on the size of the experiment different packing procedures are suggested:

1.   <u>For small columns (L < 20 – 30 cm):</u> Wet or slurry packing is applied. It involves saturating the soil with an excess of water, then letting it settle at the bottom of the column. This is achieved either by stirring the soil into the water prior to pouring it into the column as a slurry, or by filling the column with water and then slowly pouring or sprinkling dry soil into the column while stirring (Lewis and Sjöstrom, 2010). Slurry packing appears superior to other methods for small soil columns because dry packing is both labour intensive and prone to causing heterogeneities (Corwin, 2000). Another advantage of wet packing is that no gas will be entrapped and the additional saturation procedure can be omitted.

2.   <u>For longer columns (L > 20 - 30 cm):</u> Dry or damp packing is applied. It involves loading small discrete amounts or "lifts" of dry or damp soil into the column and then mechanically packing it either by hand or with some type of ram or pestle. In order to produce homogeneous sand packing, dry deposition must be in small increments, followed by compaction with a metal pestle (Oliveira et al., 1996). Alternatively dry packing proposed by Rad and Tamay (1987) may be used. This method allows for a continuous homogeneous and isotropic soil packing if applied properly. Packing density may be adjusted using appropriate shutters.
     Prior to water saturating the porous media it is to be flushed with 4 or 5 pore volumes (PVs) of CO_2. The CO_2 is then upwardly replaced by 4 or 5 PVs of de-aired water. Due to the high solubility of CO_2 in water gas entrapment can be avoided. An alternate method to avoid gas entrapment is to water saturate the experiments in vacuum cells (only possible for columns with maximum length of 50 cm). Avoiding entrapped gas is of importance since it will provide oxygen (competing reactions) and, thus falsify the reactivity experiments and it will change the relative permeability, thus falsify flow and transport experiments.

     After packing, the columns are closed carefully to ensure that no redistribution of porous media can take place either while handling the column or due to subsequent water flow (erosion).

3.   <u>For flume or radial flow experiments:</u> As in column experiments a homogeneous isotropic packed porous media is of utmost importance. Especial care has to be employed to ensure that planned heterogeneities (lenses), wells and monitoring equipment is properly hydraulically connected and that disturbances due to these implements are minimized. Dry packing proposed by Rad and Tamay (1987) is used in flume and radial-flow experiments. This method allows for a continuous homogeneous and isotropic soil packing if applied properly. Packing density may be adjusted using appropriate shutters.

If a confined aquifer is to be set up, subsequent to packing the porous media flow domain its upper surface should be covered with bentonite pellets prior to emplacing the lid of the experiment. Swelling of these pellets during saturation of the experiments will seal the annulus along the lid and, thus, prevent preferential flow. Caution: Using inappropriate bentonite material or inadequate bentonite mass might lead to the destruction of the setup due to high swelling pressures.

Experimental procedure

NP mobility is determined for injection conditions (i.e., 10 and 100 m/d) and natural groundwater flow conditions (i.e., 1 m/d). The number of replicates depends on the scope of the experiment and should be selected according to best scientific practice.

Injection conditions:

NP suspension of a known concentration is continuously injected into the column (step input) using e.g., a peristaltic or a piston pump with the effective flow velocity of v_{eff} = 10 and 100 m/d. The given flow conditions represent only the minimum requirements of the injection tests. If NPs delivery is not sufficient additional injection conditions can be tested. In small column experiments NP suspension will be injected until the breakthrough occurred or at least 5 PVs are exchanged.

In order to reduce NP aggregation and sedimentation, the NP suspension needs to be homogenized (by e.g., sonication, dispersion unit, or agitation) prior to and during the injection. Total amount of injected particles has to be determined. The procedure is particle type dependent e.g., mass of injected ZVI-NPs is calculated from the combination of Fe(0) content by $H_2(g)$ formation after acidification of a sub-sample from the inflow NP suspension and total iron measurement.

Following column saturation, and determination of effective porosity, difference in hydraulic head between the two ends of the column are determined prior to injection and after injection of NP suspensions into the column. If the mobility data is further used for modelling it is required that the evolution of the pressure at the inflow and outflow is continuously monitored during mobility or reactivity experiments. For this purpose differential manometers (Dalla Vecchia et al., 2009), or online pressure transducers, can be applied.

Natural groundwater flow conditions:

For determination of the mobility of NPs in porous media either the experimental setup from "Injection Conditions" can be used or a new column has to be set up. If a new column is set up the column is filled with porous media and saturated. Then NPs are distributed in the porous media applying one of the following procedures:

- NP suspension of a known concentration is mixed with the porous media in an anaerobic chamber prior to column packing to provide a homogeneous mixture.

- NP suspension of a known concentration is injected into the column (from bottom to top and from top to bottom). In order to reduce NP aggregation and sedimentation, NP suspension should be homogenized (by e.g., sonication, dispersion unit or agitation) prior to and during the injection.

Figure F1 illustrates the sequence of injection and subsequent natural groundwater flow conditions. The effective groundwater flow velocity for natural flow conditions is set to v_{eff} = 1 m/d. The hydraulic head at the inflow and outflow of the column is determined at the beginning and at the end of the mobility experiment. If the data is further used for modelling continuous monitoring of the hydraulic gradient is required.
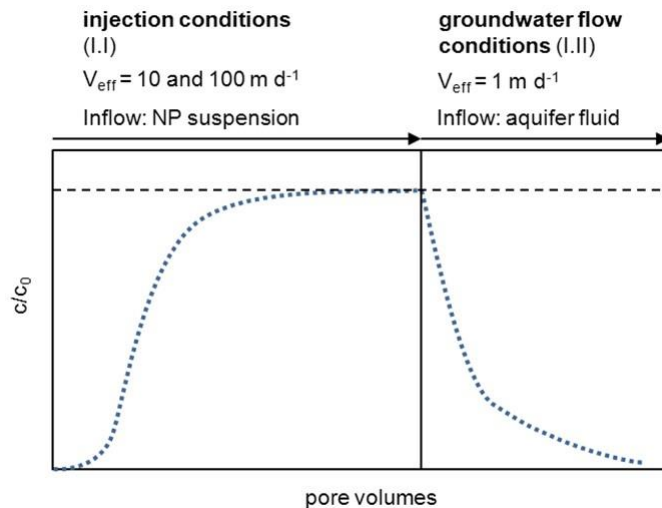
Figure F1: NPs breakthrough curve during injection conditions and NP elution during groundwater flow conditions

For vertical experimental setups the direction of flow is from bottom to top in order to reduce gas entrapment. In case of specific experimental objectives (e.g., size dependent sedimentation of NP) the column orientation can also be horizontal. The column effluent fractions are continuously collected (using e.g., an autosampler) for subsequent chemical analysis. Target parameters are again dependent on the injected NP type. In case of nZVI total iron concentration is measured in unfiltered samples e.g., by means of ICP-OES. Visual inspection and monitoring of the column is done by photography of at least the initial conditions in the column and after the experiment. Additionally for longer column experiments with nZVI particles magnetic susceptibility measurements are recommended for the determination of the spatial mass distribution in the pore space.

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13.7　　Appendix G - Numerical modelling

Introduction

Performing a nanoremediation, like any other technology implementation, is a stepwise process where successive choices or decisions are being made, then implemented, and their outcomes verified afterwards. Informed decision making is always based on a combination of general knowledge and specific data for the situation at hand, and is not just based on 'facts' and direct measurements or observations, but also on expectations (beliefs), inferences (reasoning), and quantitative forecasts (modelling). The implementation of a NP-based remediation technology at a contaminated site requires the support of quantitative modelling tools to predict the NP mobility at different stages of the technology application, both in the planning and design stages, and later on in a later stage, to predict the long-term particle mobility after injection.

In this context, the objectives of NanoRem work package WP7, focussed on particle transport modelling, are to provide user-friendly tools for the simulation of NP transport, which should:

- aid in the design and interpretation of laboratory tests
- enable prediction of NP fate and transport and effectiveness at the field scale.

To this aim, two macro-scale modelling tools, each applicable at a different scale of the problem, were developed:

- MNMs, for the assisted quantitative analysis of laboratory-scale column tests and preliminary design of pilot NP injections in a simplified geometry (radial 1D simulations)
- MNM3D, a full 3D transport module for the simulation of particle injection in heterogeneous domains, and for the prediction of NP fate and transport at the field scale.

The macro-scale modelling tools were developed following a twofold approach: on the one hand by increasing understanding of NP behaviour at the pore-scale, with the aid of pore-scale models, and on the other hand by defining up-scaled relationships valid at the macro-scale and implemented in the modelling tools for the assisted design of NP-based remediation (Figure G1).

In this appendix, an overview of the modelling approach to Darcy-scale NP transport in porous media and of the modelling tools developed in WP7 is provided. A more detailed discussion of the topics is available in NanoRem DL 7.1/7.2 and in the cited literature.

Mechanisms controlling particle transport in porous media

When NPs are dispersed and transported within 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 (Figure G2). The dynamic processes of attachment and detachment of NPs are governed by physical laws that operate at the scale of grains and pores, but impact the transport behaviour of NPs at the macro (Darcy) scale.
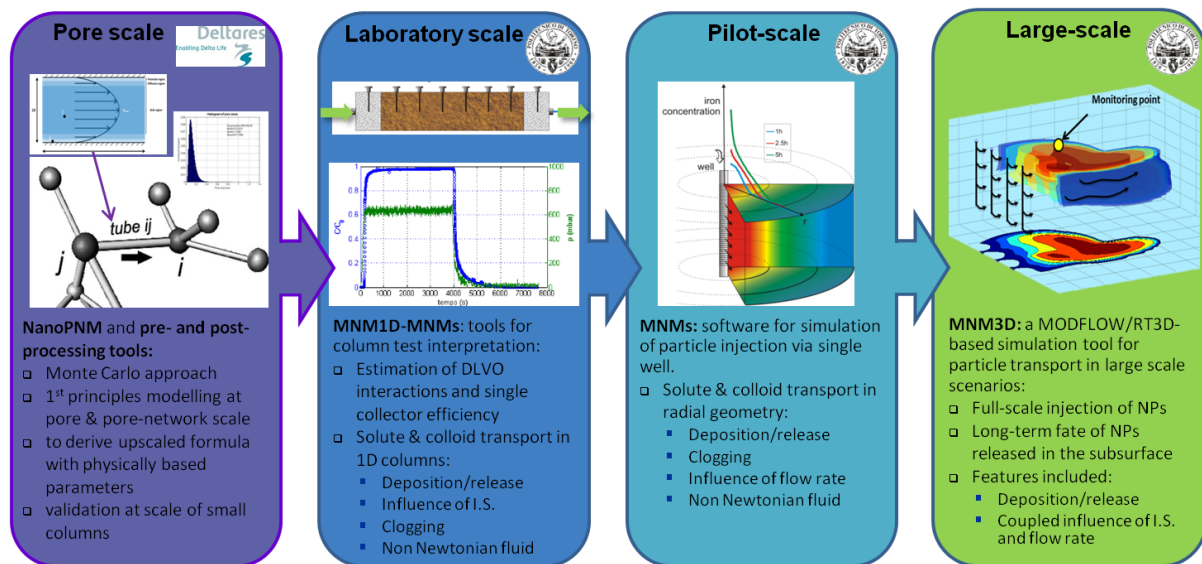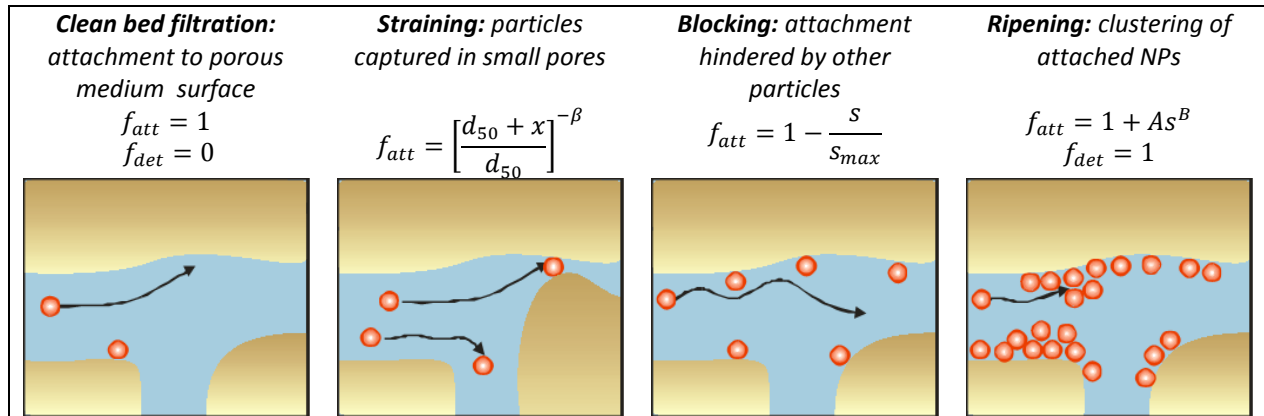
Figure G1: Modelling NP transport across the scales in NanoRem

NP transport in porous media 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:

$$n\frac{\partial c}{\partial t} + \sum_i \rho_b \frac{\partial s_i}{\partial t} + q\frac{\partial c}{\partial x} - nD\frac{\partial^2 c}{\partial x^2} = 0 \qquad \text{eq. G1}$$

$$\rho_b \frac{\partial s_i}{\partial t} = nk_{att,i}f_{att,i}c - \rho_b k_{det,i}s_i \qquad \text{eq. G2}$$

where c is the NP concentration in the liquid phase [L^{-3}], s is the NP concentration in the solid phase [M^{-1}], n is porosity [-], ρ_b bulk density of the PM solid matrix [M L^{-3}], q is the Darcy velocity [L T^{-1}], D is the dispersion coefficient [L^2 T^{-1}], k_{att}, k_{det} are the NP attachment and detachment rate coefficients [T^{-1}], f_{att} is a function [-] depending on the process(es) being described (Figure G2). The subscript i refers to the i-th retention mechanism: NP retention may be due to more than one mechanism, for eg. due to heterogeneities in the porous medium, or to different concurrent phenomena (eg. straining due to the presence of large particles, and blocking due to particle-particle interactions). An additive effect of concurrent phenomena is usually assumed, $\rho_b \frac{\partial s}{\partial t} = \rho_b \frac{\partial s_1}{\partial t} + \rho_b \frac{\partial s_2}{\partial t}$. Usually, a maximum of two concurrent phenomena is adopted (i = 1,2).

Clean bed filtration: attachment to porous medium surface	Straining: particles captured in small pores	Blocking: attachment hindered by other particles	Ripening: clustering of attached NPs
$f_{att} = 1$ $f_{det} = 0$	$f_{att} = \left[\dfrac{d_{50} + x}{d_{50}}\right]^{-\beta}$	$f_{att} = 1 - \dfrac{s}{s_{max}}$	$f_{att} = 1 + As^B$ $f_{det} = 1$

Figure G2: Pore scale particle retention processes; d_{50} is median grain size of the PM; x is distance travelled in the PM domain from the inlet point; β, A, B are fitting parameters. Modified from Tosco et al. (2014b).

The type of interaction mechanisms and the magnitude of attachment and detachment kinetics are strongly influenced by both operative and natural conditions, which include flow velocity, NP and pore size distributions, surface properties of both the NP and the aquifer grains, especially surface charge and composition, chemical properties of the fluid, such as salt content (ionic strength) and pH, and the viscosity of the injected suspension. A NP transport simulation tool effective in assisting the design of a field-scale application of nanoparticles has to take into account these effects in a quantitative, and coupled, way (Tosco et al., 2014a). In particular, when considering the injection of a NP suspension in the field, changes in space and time of three parameters can have a major impact on particle transport:

- *flow velocity*: during particle injection for eg, through a screen well, flow velocity decreases hyperbolically with increasing distance from the injection point. The concept of the single collector removal efficiency can be used to quantify the dependence of the attachment rate on pore water velocity v (Yao et al. 1971). In the current version of MNMs, the formulation of k_{att} and k_{det} as a function of *U* proposed by Tosco et al. (2014a) is implemented:

$$k_{att}(v) = \frac{3}{2} \frac{(1-n)}{n \, d_s} \, p_{att} \, \eta_0 v \qquad \text{(eq. 3)}$$

$$k_{det}(v) = p_{det} \, \mu v \qquad \text{(eq. 4)}$$

where d_s is the average grain size of the porous medium p_{att} [-] and p_{det} [T M^{-1}] are parameters to be determined from fitting of experimental data, μ [M L^{-1} T^{-1}] is the fluid viscosity, and η_0 [-] is the single collector efficiency.

- *ionic strength*: ionic strength (IS) significantly affects the particle-particle and particle-porous medium interactions. As a consequence, on a longer time frame eventual changes in the groundwater salt content may lead to immobilization or re-mobilization of the particles, thus affecting their long term behaviour. In MNMs the semi-empirical constitutive equations proposed by Tosco et al. (2009) are currently implemented:

$$k_{att}(C_{salt}) = \frac{k_{att\infty}}{1+\left(\frac{CDC}{C_{salt}}\right)^{\beta_{att}}} \qquad \text{(eq. 5)}$$

$$k_{det}(C_{salt}) = \frac{k_{det0,}}{1+\left(\frac{C_{salt}}{CRC}\right)^{\beta_{att}}} \qquad \text{(eq. 6)}$$

$$S_{i,max}(C_{salt}) = \gamma_S \, C_{salt}{}^{\beta_S} \qquad \text{(eq. 7)}$$

where the terms k_{att}, CDC, β_{att}, k_{det0}, CRC, β_{det}, γ_S, and β_S are empirical coefficients determined via fitting procedures; C_{salt} is the salt concentration in pore water.

- *fluid viscosity*: NPs suspended in water are in most cases not stable and need to be stabilised by addition of polymers in order to be injected in groundwater. The polymers commonly used in field applications (e.g. guar gum, xanthan gum, CMC, etc.) are characterized by a non-Newtonian rheological behaviour (shear thinning - viscosity changes with changing flow velocity) which influences the overall injection of the suspension. It is known that particle colloidal stability - and consequently mobility in the porous medium - is significantly affected by the viscosity of the carrier fluid. Moreover, the viscosity of the injected fluid also affect the fluid pressure in the aquifer system during injection. In MNMs the Cross model for shear thinning fluids is available, and the mutual dependence of pore pressure, particle concentration and polymer concentration is solved coupling flow and transport equations as discussed into details in Tosco et al. (2014a).

Additionally, *clogging*, due to the accumulation of significant amounts of particles in the pores of the aquifer, is simulated through the reduction of permeability and porosity induced by deposited particles. In the approach proposed by Tosco and Sethi (2010), the pressure build up arising from the particle deposition is calculated using a modified formulation of the Darcy's law (Tosco et al. 2014a), which takes into account both the reduction in porosity, permeability, and the eventual non-Newtonian nature of the fluid.

Within NanoRem WP7, alternative formulations for k_{att} and k_{att} as a function of fundamental parameters are currently being explored with the aid of first principle modelling at the pore scale (see 6.1.2.1). Parameters investigated include NP size and surface potential, pore size and packing characteristics and surface potential of the porous medium, flow velocity, fluid viscosity, ionic strength and pH. These alternative formulations will/can also be made available within MNMs.

Modelling tools

Numerical models to simulate the transport of dissolved contaminants in aquifer systems are widely available. Several particle transport simulation tools have been proposed and validated to simulate laboratory-scale processes (e.g. column transport tests, represented in 1D geometry). A number of modifications to classical Colloid Filtration Theory (CFT) have been proposed to incorporate all phenomena discussed above, and several modelling tools have been successfully applied for the simulation of NZVI transport (Hendren et al. 2013, O'Carroll et al. 2013, Tosco et al. 2014c). In the absence of clogging processes, Hydrus (Simunek et al. 2005), Stanmod (Van Genuchten 1981) and E-MNM1D under constant (Tiraferri et al. 2011) and transient pore water composition (Tosco et al. 2009, Becker et al. 2015) have been used in 1D geometries. MT3DMS-based models were proposed to simulate NZVI

transport in more complex geometries (Johnson et al. 2013), recently accounting also for particle ag-glomeration (Babakhani et al. 2015). NZVI transport as density-driven process was simulated using SEAWAT (Kanel et al. 2008). The only coupled flow and particle transport model able to account for the shear thinning nature of the fluid and the progressive clogging of the porous medium is E-MNM1D (Tosco and Sethi 2010).

However, well established field-scale NP transport models are not yet available, and the definition of proper approaches and numerical tools, usually based on the up-scaling from simpler geometries and smaller scales, is a current research topic. The approach within NanoRem WP7 has therefore been to increase understanding of NP behaviour through pore-scale modelling, aimed at defining up-scaled relationships for k_{att} and k_{det} that can be validated using experimental or field data at the macro-scale. In this paragraph, modelling approaches and tools developed in Nanorem to solve the modelling issues discussed above are briefly discussed.

Pore-scale modelling

The dynamic processes of attachment and detachment of NPs that impact the transport behaviour of NPs at the macro (Darcy) scale are actually governed by physical laws that operate at the scale of grains and pores. Therefore, physically based ensemble modelling at the pore scale was performed to investigate, from a theoretical perspective, how these fundamental laws propagate towards the macro-scale.

To this end, an existing pore network model [Raoof and Hassanizadeh, 2010; Raoof et al., 2010, 2013)] was adapted to develop NanoPNM, a numerical code for pore-scale simulation of NP transport. The pores, for which a lognormal size distribution is defined with mean pore size m and standard deviation s, are positioned at a regular grid with lattice distance LD. Each pore can potentially be connected to 26 neighbouring pores (Figure G3), actual connectivity is randomly defined by an elimination rate E ($0.8 \leq E < 0.9$).
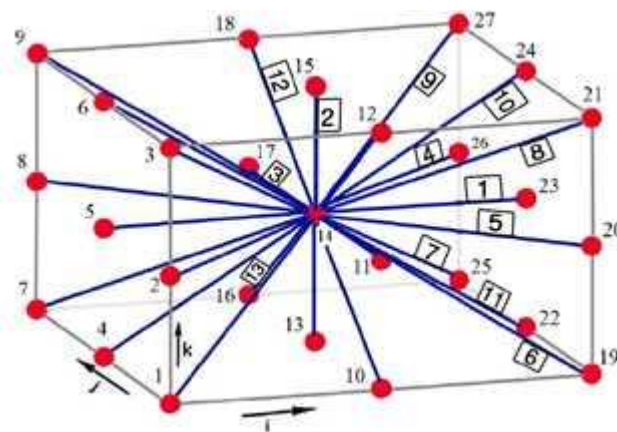
Figure G3: The 26 possible pore throats (pipes) for central pore nr. 14 in 3-dimensions (Raoof and Hassanizadeh, 2010). Numbers in a box represent the direction number 1-13.

Pre-processing and post-processing tools were developed to allow the generation of large numbers of simulations for tracer and NP breakthrough in porous medium columns, and the automated interpre-tation of the resulting breakthrough curves (BTC) in terms of fitted hydraulic parameters (Φn, K, α) and the kinetic parameters for NP attachment and detachment (*katt, kdet and fatt* in eq. 2). Upscaled

equations of these macro-scale parameters as a function of the fundamental inputs were derived via statistical regression.

The fundamental laws for tracer flow at the pore scale in NanoPNM are derived from the Poiseuille equation for laminar flow and the Hagen-Poiseuille equation that relates pore discharge/velocity to the pressure gradient, fluid viscosity, and the pore dimensions (length L and radius R). For NP attachment and detachment kinetics, we used results from model simulations at the scale of a single pore performed by Seetha et al. (2015), to derive basic laws for NP attachment and detachment at this scale as a function of pore size, flow velocity, NP size and surface charge, surface charge at the pore wall, and physical (temperature, viscosity, dielectric constant) and chemical (ionic strength, pH) properties of the transporting fluid. These rules were then implemented in NanoPNM, to simulate a large number of very small column tests. From the simulated column tests, upscaled rules were derived for hydraulic parameters and NP attachment and detachment rates at the Darcy scale of a porous medium subdomain. These in turn can be implemented in a macro scale flow and transport model.

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

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

1D macro-scale modelling of NP transport with MNMs

MNMs stands for **M**icro- and **N**ano-particles transport, filtration and clogging **M**odel **S**uite. It is a complete tool for the simulation of particle transport in 1D saturated porous media and for the interpretation of laboratory column transport test. MNMs represents the evolution of MNM1D (Tosco and Sethi 2009, Tosco et al. 2009) and E-MNM1D (Tosco and Sethi 2010), whose features are here integrated and extended in a user-friendly Matlab-based graphical interface. The structure and main features of the last release of MNMs are provided in Figure G4. MNMs is compiled as a standalone executable file and can be downloaded from the web page of the Groundwater Engineering research group of Politecnico di Torino (http://areeweb.polito.it/ricerca/groundwater/software/MNMs.php). The reader can refer to the manual of MNMs for a detailed description of tools and equations.

The main features included in MNMs are (Figure G4):

- **Interaction energy profiles**: to estimate particle-particle and particle-collector interaction energy profiles using the DLVO and Extended-DLVO (Derjaguin and Landau, Verwey and Overbeek) and

Extended-DLVO theory accounting for Born repulsion, steric and magnetic interactions). It is useful to forecast the micro- and nano-particles behaviour in terms of aggregation and mobility.

- Calculation of **single collector attachment efficiency η_0**, one of the most important parameters for the assessment of the mobility of micro- and nanoparticles in porous media. MNMs implements a dedicated tool to easily compute η_0 using up to 7 different formulations.

- Simulation of the **transport of a dissolved species** with equilibrium sorption and first order degradation**,** for simulation of contaminant transport and interpretation of column tracer tests.

- Simulation of **particle transport under constant or transient ionic strength.** Four different types of attachment kinetics can be simulated: linear, Langmuirian with blocking, ripening and straining (see Figure G2).

- Simulation of **porous medium clogging phenomena**, when the modification of the column porosity and permeability due to deposition of NPs strongly influences the flow field and cannot be neglected. MNMs takes into account the variation of pressure drop along the column due to the medium clogging and solves the differential system coupling flow and transport equations.

- Simulation of **particle transport in the presence of Non-Newtonian carrier fluids**: MNMs can be used for the interpretation of column transport test where the influence of the suspension rheology cannot be neglected. A generalized Darcy law is used to estimate the pressure build-up due to the non-Newtonian nature of the injected fluid, which is a critical issue for field injections.

- Simulation of **pilot-scale injection of micro- and nanoparticle slurries through a single well** (radial simulation tool). In field applications fluids are typically injected into the subsurface via wells or direct push systems, generating a radial or radial-like flow, with decreasing velocity with increasing distance from the delivery point (Tosco et al. 2014a). Therefore, MNMs solves the transport of injected particles in a homogeneous infinite porous medium assuming a 1D geometry with radial symmetry (Figure G5). The radial tool takes into account the influence of flow velocity (and then of the injection flow rate) on the kinetics of the particle-porous medium interactions (deposition and release processes), the eventual clogging, and the non-Newtonian (shear thinning) rheological properties of the carrier fluid used to improve the colloidal stability of the suspensions. The empirical relationships proposed in Tosco et al (2014a) have been used to express the dependence of the deposition and release parameters on the flow velocity. A modified formulation of the Cross rheological model has been implemented to account for the shear thinning behaviour of polymeric stabilizers usually employed for particle injection.

3D NP transport modelling with MNM3D

MNM3D, standing for **M**icro- and **N**ano-particles transport **M**odel in **3D** geometries, is a modified version of the transport model RT3D (Clement 1997), in which the NP transport equations are solved in 3D accounting for simultaneous dependency of the attachment and detachment kinetics on the groundwater ionic strength and velocity (Bianco et al. 2016). In particular, MNM3D solves the NP transport equations 1-2, accounting for dependency of the attachment and detachment kinetics on the groundwater ionic strength (eq. 5-6-7) and velocity (eq. 3-4). 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 ionic strength (Bianco et al. 2016). To this

purpose, the dependency of the empirical parameters $C_{a,i}$ and $C_{d,i}$ on the ionic strength has been explicitly expressed by coupling eq. 3-4 with eq. 5-6:

$$k_{att,i}(v, c_{salt}) = \frac{3}{2}\frac{(1-n)}{\epsilon d_{50}}\frac{C'_{att,i}}{1+\left(\frac{CDC_i}{c_{salt}}\right)^{\beta_{att,i}}}\eta_0 v \quad \text{(eq. 8)}$$

$$k_{det,i}(v, c_{salt}) = \frac{C'_{det,i}}{1+\left(\frac{c_{salt}}{CRC_i}\right)^{\beta_{det,i}}}\mu v \quad \text{(eq. 9)}$$

where $C'_{att,i}$ [-] and $C'_{det,i}$ [T M^{-1}] are fitting parameters which embed all the other phenomena not explicitly considered here.
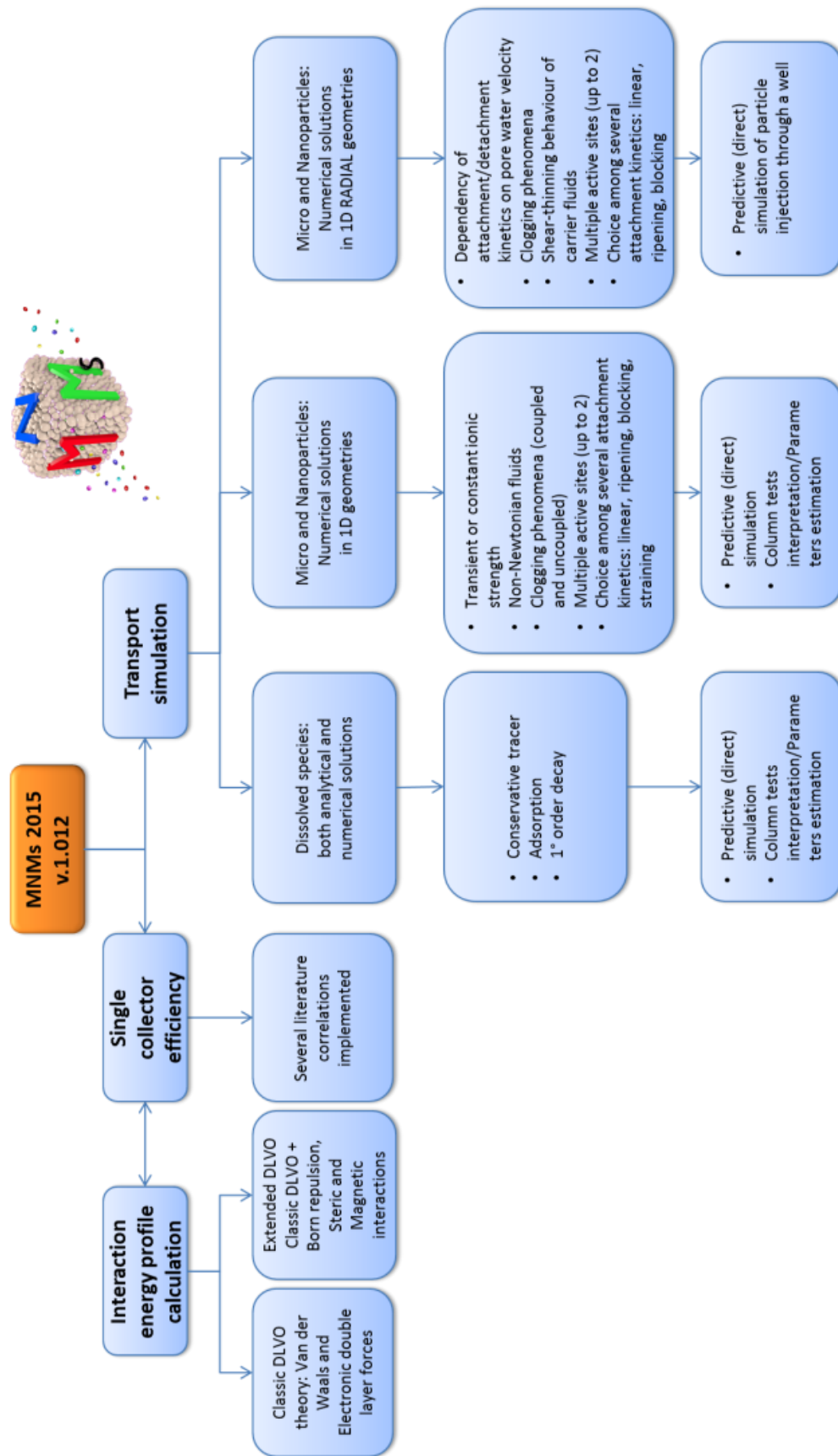
Figure G4:   Structure and main features of MNMs

The particle concentration is solved in space and time for both particles suspended in the liquid phase and attached to the porous medium. Heterogeneities in the hydrodynamic properties of the porous medium and of the particle-soil interactions can be taken into account by implementing space-variable hydrodynamic, transport and kinetic parameters.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.

MNM3D can be applied both for the short term evaluation of particles distribution around one or more injection points, and for the long term particle spreading prediction. It overcomes many limitations and approximations of the other simplified numerical codes and offers the opportunity to fill the gap between the controlled conditions of laboratory tests and the more complex scenarios typical of field-scale applications. If coupled with MNMs, MNM3D can be used at the final stage of the remediation design process, as a support to estimate important operative parameters, including particles distribution around the injection well, influence radius for a target concentration, number of required injection wells, etc.

(a)   (b)
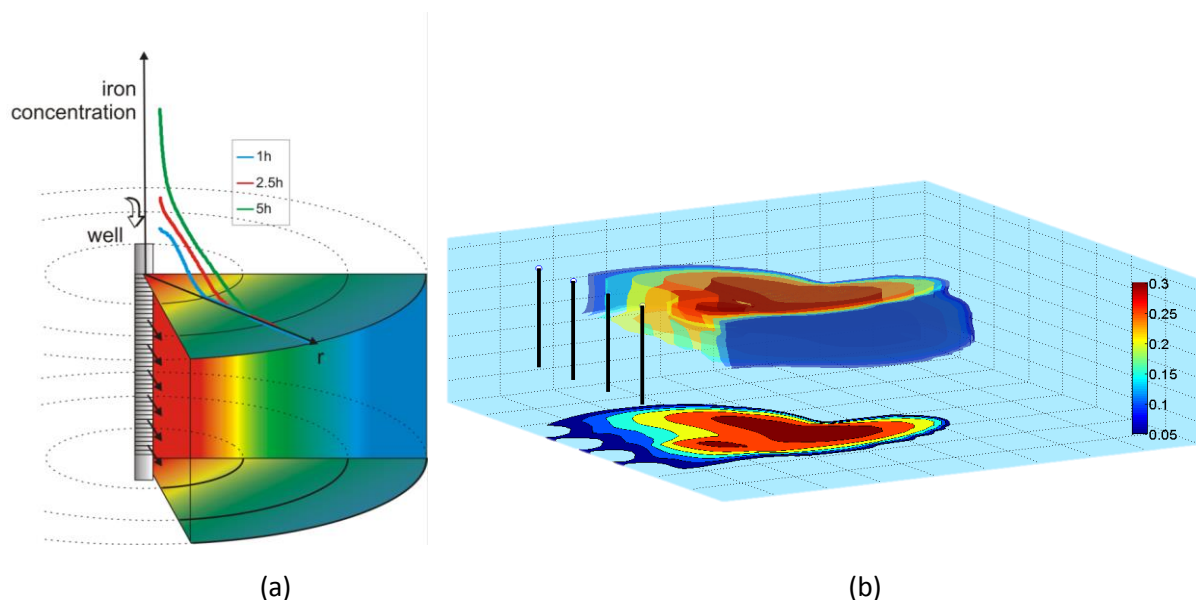
Figure G5: (a) Conceptual model and example of simulation results using MNMs radial tool [modified from Tosco et al. (2014a)]. (b) Example of simulation results of MNM3D: injection of NPs through 4 wells in the large-scale container at VEGAS

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