



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

Project Nr.: 309517

EU, 7th FP, NMP.2012.1.2

Risk Screening Model (RSM) for Application of NanoRem Nanoparticles to Groundwater Remediation

Andy Gillett, Judith Nathanail, Paul Nathanail (LQM)

31 January 2017



[Downloaded from www.nanorem.eu/toolbox](http://www.nanorem.eu/toolbox)

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517

List of co-authors:

Name, First Name	Partner Organisation
Gillett, Andy Nathanail, Judith Nathanail, Paul	Land Quality Management Ltd

**Reviewed by PAG members:**

Name, First Name	Partner Organisation
Johannes Bruns	Intrapore GmbH

**Reviewed and agreed by PMG**

Table of Contents

List of Figures	v
List of Tables	vi
Summary	1
1 Introduction	3
1.1 <i>Background</i>	3
1.2 <i>The NanoRem Nanoparticles: Nature and intended deployment</i>	3
1.3 <i>Purpose</i>	4
1.4 <i>Scope</i>	4
2 Assessing Environmental Risk	5
2.1 <i>Legislative Context</i>	5
2.2 <i>Conceptual Exposure Scenarios</i>	5
2.3 <i>Conceptual Site Models</i>	5
2.4 <i>Transport</i>	7
2.4.1 <i>Transport in porous media</i>	7
2.4.2 <i>Transport in fractured rock</i>	8
2.4.3 <i>Estimating Transport distances for the RSM</i>	9
2.5 <i>Fate</i>	9
2.5.1 <i>NanoREM results on NP Fate</i>	9
2.5.2 <i>Evaluating Fate in the RSM</i>	9
2.6 <i>Toxicity</i>	9
2.6.1 <i>Toxicity: Human Health</i>	12
2.6.2 <i>Toxicity: Ecotoxicity</i>	12
2.6.3 <i>Toxicity: for the RSM</i>	15
3 Modelling of NanoRem nanoparticles	20
3.1 <i>Modelling approach</i>	20
3.2 <i>Important processes to model for NPs</i>	20
3.2.1 <i>Advection Dispersion of NanoRem nanoparticles</i>	20
3.2.2 <i>Attachment and Detachment of NanoRem Nano Particles (NPs)</i>	21
3.2.3 <i>Effect of ionic strength on NP deposition</i>	22
3.3 <i>Calculation of NanoRem NP transport distance</i>	24
3.3.1 <i>Environment Agency Remedial Targets Methodology (RTM)</i>	24
3.3.2 <i>Derivation of 'K_d' (K_{d,NP}) and transport retardation factor (R_{f,NP}) for NPs</i>	26
3.3.3 <i>Comparison of concentration - travel distance profile between MNMs and the RSM model</i>	28
3.3.4 <i>Travel distance and times variability/sensitivity based on plausible inputs</i>	31
3.3.5 <i>Impact of values of k_{att} and k_{det} (i.e. k_{att} : k_{det}) on retardation of NP</i>	33
3.3.6 <i>Comparison against field data</i>	35
3.3.7 <i>Large Scale Flume data (University of Stuttgart)</i>	38
3.3.8 <i>Values of k_{att} and k_{det} based on column experiments for the range of NanoRem particles</i>	38

4	Modelling Assumptions and Limitations	43
4.1	<i>Key Assumptions</i>	43
4.2	<i>Key Limitations</i>	43
5	Modelling Wish List / Ways to develop the approach	45
6	Modelling Protocol	46
6.1	<i>Legislation, Site characterization and CSM</i>	46
6.2	<i>Model Parameterisation</i>	46
6.3	<i>Using the RSM model worksheets</i>	47
6.3.1	NanoParticle_Inputs worksheet	47
6.3.2	Level3 Groundwater worksheet	48
6.3.3	Level3_1 G_ Calc_NP worksheet	49
6.3.4	Subsidiary worksheets	49
6.4	<i>Sensitivity Analysis</i>	50
7	References	51
	Appendix 1 - MNM's – 1 year simulation inputs for comparing to modified RTM model for NPs	54
	Appendix 2 – Conceptual Site Models	57

List of Figures

Figure 1:	Comparison of MNMs and the RSM predicted NP (Fe) concentration at the same distances downstream of the (continuous) injection point after approximately 1 year and 5 years30
Figure 2:	NP (Fe) Concentration Distance profiles predicted by the RSM at various times (1-50 years) assuming continuous injection at x=0m (Note: breakthrough at 100m (i.e. non-zero concentration) predicted after 23 years, see also Figure 3), see Table 11 for model inputs.....31
Figure 3:	Likely upper estimates of the number of NP (Fe) particles (assuming mean diameter of 100nm) variation with distance predicted using the Figure 2 concentration profiles and simplified assumptions (see text) (Note: log-scale for y-axis, zero concentrations not plotted on log-scale).....32
Figure 4a, b:	NP (Fe) Concentration Distance profiles predicted by the MNMs model at various times (end of 9h injection, +1day, +1week, +1month, +1year) following single injection at x=0m , see Table 11 for model inputs. a) log-scale for Y-axis, b) linear for Y-axis.....33
Figure 5a, b:	NP (Fe) concentration distance profiles predicted by the RSM for a range of $k_{att}:k_{det}$ ratios at (a) 1-year and (b) 25-years for a continuous injection upstream, see Table 11 for inputs.....34
Figure 6:	Dependence of predicted NP concentration at defined downstream distances (5, 25 & 100m) on the attachment to detachment coefficient ratio (Note: X-axis plotted as a log scale), see Table 11 for inputs35
Figure 7:	Variation of retardation parameters K_{d_NP} , R_{f_NP} and u_{NP} with values for the attachment to detachment coefficient ratio (Note: plotted on a log-log scale)35
Figure 8a, b:	Variation of total dissolved iron with approximate distance from the injection (x=0m) at the Hungary pilot site (Balassagyramat), along two transects, following injection of Carbo-Iron® NPs (Note: y-axis plotted as log scale).....37
Figure 9a, b:	Variation of derived attachment coefficient (s^{-1}) against predicted 99.9% travel distance (m) for NPs: a) at start/optimised in column experiments [Source IDL 4-2 and IDL 4-3]; b) optimised under field relevant conditions [Source DL 4-2]39

List of Tables

Table 1:	The NanoRem Nanoparticles.....	3
Table 2:	Conceptual exposure scenarios included in the RSM.....	6
Table 3:	Nanoparticle Transport Distances Recorded from Large Containers and Flume	7
Table 4:	Nanoparticle Transport Distances Recorded at Field Sites.....	8
Table 5:	Summary of the reported predicted travel distances from column experiments, ascending order of maximum $L_{t,99.9\%}$ value (see also Table 13 and Table 14) [Source: DL 4.2 (Micic Batka & Hofmann, 2016)]	8
Table 6:	Summary of findings following WP4 experiments under field conditions (on soil and groundwater samples from deployment sites) on fate relevant to risk assessment as reported within DL 4.2 (after Micic Batka & Hofmann, 2016).....	11
Table 7:	Summary of ecotoxicity testing across NanoRem NPs (EC_{50} is defined as an effect concentration at which an effect of 50% is observed) [Source: DL5-1, (Coutris et al., 2015)].....	13
Table 8:	Key toxicity outcomes (in absence of environmental matrix) from the WP5 DL5.1 report (Coutris et al., 2015) for each NP.....	14
Table 9:	Key toxicity outcomes from lab and field water samples following injections, transformation and transport from the WP5 DL5.2 report (Coutris et al., 2016) for the NPs tested	16
Table 10:	Variation of attachment (k_{att}) and detachment (k_{det}) coefficient and their ratio with ionic strength (adapted from Tiraferri et al., 2011) for negatively charged latex particles (mean size 1900nm) in micro-sized siliceous sand column experiments (shaded cells considered likely to be representative of typical aquifer ionic strengths) [see text for discussion on parameter variation at same ionic strength].....	24
Table 11:	MNM 2015 & RSM model inputs (see Environment Agency, 2006), Hungary pilot site data from NanoRem Internal Deliverable (see also CL:AIRE, 2017)	29
Table 12:	MNM 2015 and RSM outputs – see Table 11 for inputs	30
Table 13:	Attachment ('deposition') coefficients as reported by the NanoRem WP4 column experiments for the "starting" and "optimised" nano-particles investigated, plus salient meta-data [Source: IDL4-2 (Hofmann et al., 2015) or IDL 4-3 (Hofmann et al., 2016)]	40
Table 14:	Attachment ('deposition') coefficients as reported by the NanoRem WP4 column experiments for "optimised" nano-particles under field relevant conditions, plus salient meta-data [Source: DL4-2 (Micic Batka & Hofmann, 2016), some data reported is a repeat of data first reported under IDL4-2 or 4-3 – see Table 13]	41
Table 15:	Table of input parameters required for the RSM model (see also Table 11).....	47
Table 16:	Worksheet inputs and cell numbers.....	48
Table 17:	Illustration of the influence of $k_{att} : k_{det}$ ratio on predicted travel distance at which the UK EQS for Iron (100mg L^{-1}) is exceeded, based on a continuous Carbo-Iron [®] injection (example based on Hungary pilot site, see Table 11).....	50

Summary

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

Previously, Land Quality Management Ltd (LQM), as part of the NanoRem project (WP9) have provided an outline risk assessment protocol to assist the NanoRem field studies (WP10) in presenting evidence to regulators. The project delivery report and protocol included a summary of an associated workshop hosted by LQM in July 2013 and an extensive literature evidence base which informed the risk protocol (NanoRem, WP9 Internal Deliverable).

Chapter 1 outlines the background to the deployed (laboratory and/or field) nanoparticles and indicates that the RSM and protocol applies to the deployed NanoRem NPs (nZVI, Nano Goethite, milled nZVI, Carbo-Iron[®]), although it may inform risk assessment for other NPs. The RSM approach includes conceptual exposure scenarios, consideration of fate, transport and toxicity (Chapter 2).

This report draws upon relevant NanoRem findings and reports across the technical work packages (WP2-10) to present a Risk Screening Model (RSM) for application of NanoRem nanoparticles to groundwater remediation (Chapter 3). The RSM estimates the macro-scale transport of NPs within saturated media based on some of the algorithms presented within NanoRem DL7.1 (Bianco et al., 2015; Tosco et al., 2016), and integrated into the MicrosoftTM Excel spreadsheet tool Environment Agency Remedial Targets Methodology, RTM (Environment Agency, 2006a). A key assumption is that the RSM is to be applied to locations outside of the immediate source and injection zone for the NPs. The spreadsheet based model described is used to estimate NP transport distance and concentration, with some illustrative outputs and comparisons based on field site inputs and results.

The RSM methodology depends on calculating values of attachment (k_{att}) and detachment (k_{det}) using the MNMs model (Bianco et al., 2015), with the $k_{att}:k_{det}$ ratio used to estimate retardation of NPs. Outputs from the RSM spreadsheet model have also been compared against a numerical solution currently included within MNMs and indicates the simplified models can provide similar outputs for the same inputs.

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

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

impact. Hence $k_{att}:k_{det}$ ratios of between 10 and 100 may reasonably be expected to significantly reduce NP transport within the downstream aquifer.

Although, there are a number of key limitations and assumptions (Chapter 4) and a number of ways to develop the approach have been identified (Chapter 5), it is considered that the RSM approach and modelling protocol presented (Chapter 6) provides a useful basis for a cautious risk assessment methodology.

1 Introduction

1.1 Background

The NanoRem project aims to unlock the potential of nanoremediation for addressing groundwater contamination. The work is supported by considering the potential environmental impacts of using the NanoRem nanoparticles (NP). The current document considers the risk from NP, referred to as 'renegade' nanoparticles, that are injected into groundwater but either do not reach the intended treatment area or pass through it.

Earlier in the project, prior to injection of nanoparticles LQM produced a WP9 internal deliverable entitled: '*Potential Environmental Risks of Nanoparticle Deployment: Risks from Renegade Nanoparticles*'. This included an outline risk assessment protocol for NanoRem field deployments (Nathanail et al., 2016). This report (as part of WP8, DL 8.2) provides a Risk Screening Model for the Application of NanoRem Nanoparticles To Groundwater Remediation (RSM).

It also updates the approach of the LQM WP9 internal deliverable (as summarised by Nathanail et al., 2016) using available results from other parts of the project.

1.2 The NanoRem Nanoparticles: Nature and intended deployment

Table 1: The NanoRem Nanoparticles

Nanoparticles	Deployed at: Pilot Site / LSF /LSC	Suspensions added	Notes
nZVI (NANOFER 25S, NANOFER STAR)	Spolchemie I, Czech Republic (CZ); LSF (VEGAS)	PAA	Lithium chloride tracer
nZVI (NANOFER STAR)	Nitrastur, Spain (ES)		
Nano Goethite (Iron Oxide)	Spolchemie II, Czech Republic (CZ); LSC (VEGAS)	-	Potassium bromide tracer
Milled nZVI (FERMEG12)	Solvay, Switzerland (CH)	-	Lithium chloride tracer
Carbo-Iron [®]	Balassagyarmat, Hungary (HU) Neot Hovav, Israel (IL)	CMC CMC	Low concentration - goal was placement (HU) High concentration - goal was maximum potential
Bionanomagnetite (BNM) & Palladzed BNM	Not deployed (lab scale tests only)	Agar, starch, guar gum, sodium humate	
Colloidal Trap-Ox Fe-zeolites	Not deployed (lab scale tests only)	CMC, guar gum	H ₂ O ₂ can be injected at a later step (catalytic oxidation)
Fe (VI) salts (ferrates)	Not deployed (lab scale tests only)		
Non-Fe metals & alloys (Al & Mg)	Not deployed (lab scale tests only)		

Note: LSF = Large Scale Flume; LSC = Large Scale Container; PAA = polyacrylic acid; CMC = carboxymethyl cellulose

1.3 Purpose

The aim of the RSM is to evaluate the risks to identified receptors from renegade NanoRem nanoparticles applied to a site for groundwater remediation.

1.4 Scope

This protocol applies to the deployed NanoRem NPs (Table 1); whilst it may inform risk assessment for other NPs it has not been designed to address risk assessment for other NPs.

This protocol applies to renegade NanoRem NPs – i.e. those NP that are injected into polluted groundwater but either do not reach the intended treatment area or pass through it. It does not apply to fluids (e.g. CMC) used in association with the NPs (e.g. to optimise transport distances).

The protocol applied to risks from the NP once they have been injected into the polluted groundwater. It does not address risks from manufacturing or handling the NP prior to injection.

2 Assessing Environmental Risk

Risk assessments are used where the outcome of an activity is uncertain. The aim of risk assessment is to estimate and then evaluate the level and significance of the risk posed by the given activity. Assessing environmental risk from potentially hazardous substances includes consideration of exposure to (based on fate and transport) and the toxicity of the substance.

2.1 Legislative Context

The first step in assessing risks to the environment is to establish the legal context. This determines the constraints under which the work will be undertaken. It will define the standard to be achieved (the Target Concentration) and the location at which that standard must be achieved (the Compliance Point). The terms Target Concentration and Compliance Point specifically derive from guidance from the Environment Agency (UK) (Environment Agency, 2006a) and have been adopted for the RSM. However, this concept has general applicability and acceptance across all member states of the EU, though specific terminology or terms may be different.

Where available the Target Concentration (i.e. the standard not to be exceeded) would be based on an authoritative standard for the Country e.g. an Environmental Quality Standard. At least in the short term, such a standard is unlikely to be available for nanoparticles and the Target Concentration will need to be based on the available information such as toxicity data as discussed in Section 2.6.

The Compliance Point (i.e. the location at which exceedance of the standard must be determined) will vary by country; for example, in the UK the Compliance Point is generally based on the location of the receptor (e.g. a river) (Environment Agency, 2006a) although, can be based on other factors (e.g. distance from source) if no receptor is identified (Environment Agency, 2013). However, in other EU countries the Compliance Point (or pathway length to be assessed) could be considered to be the edge of the site or property boundary.

2.2 Conceptual Exposure Scenarios

Conceptual Exposure Scenarios (CES) are used to identify the receptors (the things which might be affected by the hazard) and possible pathways which may link a source to a receptor. **Table 2** identifies the CES included in the RSM.

2.3 Conceptual Site Models

A CSM should be developed for the site, to qualitatively consider risks from renegade NPs. The CSM for the RSM shows nanoparticles as the source term (in the context of the source-pathway-receptor contaminant linkage paradigm). Depending on the complexity of the site it may or may not be helpful to display the location of the groundwater contamination to be treated. The conceptual site model will identify the contaminant linkages which need consideration at the site.

This is separate from the CSM created to explain the problem that drove the need for remediation in the first place. More details on CSMs for renegade nanoparticles are provided in Appendix 2.

Evaluation of risk from a hazardous substance includes consideration of exposure to (based on fate and transport) and the toxicity of the substance.

Table 2: Conceptual exposure scenarios included in the RSM

Receptor	Possible Exposure scenario [identified in WP9 internal deliverable, see also Nathanail <i>et al.</i> (2016)]	Comments	Addressed in the RSM
Human health	Direct ingestion/ dermal uptake/ inhalation/ vegetable uptake	Would need NPs to get into the near surface soil zone	No – properly injected NPs should not get into soil zone (assuming daylighting is prevented). Might be considered via a risk register.
Human health	Drinking water/irrigation water/swimming	Would need NPs to get into abstracted water. Possible but dependant on transport distances of NPs, since public water supplies could not be drawn from the polluted groundwater the NP are intended to remediate.	Yes – NPs in groundwater have the potential to get into abstracted water
Groundwater	Migration of contaminants in groundwater	Possible but dependant on transport distances of NPs	Yes
Surface water	Migration of contaminants in groundwater	Possible but dependant on transport distances of NPs	Yes – NPs in groundwater have the potential to get into surface water
Building materials	Accumulation of H ₂ gas (e.g. nZVI dissolution under anaerobic conditions)	Speculative scenario	No – risk not due to renegade NPs. Might be considered separately.
Ecosystems	Migration of contaminants in groundwater and surface water	Micro eco-receptor exposure may be no greater than other in situ remediation techniques or the contaminants themselves. Possible impact to macro-receptors via surface water or wetlands.	Yes – NPs in groundwater have the potential to affect surface water microbiology

2.4 Transport

To reach potential receptors, NPs must be transported away from the point of injection, through the polluted groundwater and onto a relevant receptor.

2.4.1 Transport in porous media

Most of the sites and the large containers, into which NanoRem injected NPs, comprised porous (as opposed to fractured) media in which intergranular flow would be expected.

The results from the large containers and field trials have been reviewed and the maximum distances (reported in **Table 3** and

Table 4) are 2.5m and 5m, from the point of injection, respectively.

The experimental protocols outlined by WP4 outline how values for the predicted maximum travel distances by 99.9% of NPs ($L_{t\ 99.9\%}$) could be calculated using the results of the D.I and D.II column experiments¹. Early experiments showed transport distances to be just over 20m (21.8m), whilst the column experiments on optimised particles under field relevant conditions (**Table 5**) had predicted distances ($L_{t\ 50\%}$ and $L_{t\ 99.9\%}$ range estimates) of just over 30m (32.2m). These experimentally derived transport distances are estimates based on column properties (grain size, effective porosity, length of column), effective flow velocity and the initial inlet to outlet concentration ratio. Hence, these results are for controlled laboratory experiments and may not be representative of field conditions which are likely to be more heterogeneous. Typically, the reported travel distances in the NanoRem large container/flume pilot sites are less than those estimated from the small column experiments.

Table 3: Nanoparticle Transport Distances Recorded from Large Containers and Flume

Container	Particle	Max distance (m)	Notes*	Reference
LSF	ZVI - NANO-FER STAR	1.5	Most particles were transported more than 0.3m; a small amount reached 1.44m	Draft ZVI paper ²
LSC	Iron-oxides Goethite Nano-particles	2.5	1.7 m Transport during injection; no further transport detected after injection at higher levels; however maximum 2.6m further transport was observed after injection at base level	Draft LSC paper ³
LSF	Carbo Iron	0.8	Particle distribution by the injection was not uniform.	Draft Carbon Iron paper ⁴

¹ D.I) small columns (L < 20-30 cm) without spatial information; D.II) columns (L > 20-30 cm) with spatial information (including cascading columns)

² In-situ Groundwater Remediation Using NANOFER STAR Upscaling to Large Scale Flume Experiment to Investigate Transport and Reactivity in a Source Treatment Approach (Kumiko Miyajima; Jürgen Braun; Norbert Klaas; Petr Kvapil; Jan Slunsky) **In Preparation**

³ In-situ Groundwater Remediation Using Iron-oxides Goethite Nano-particles: Upscaling to Large Scale Container Experiment to Investigate Transport and Reactivity in a Plume Treatment Approach (Kumiko Miyajima; Jürgen Braun; Norbert Klaas; Rainer Meckenstock) **In Preparation**

⁴ Title: In-situ Groundwater Remediation Using Carbo-Iron®: Upscaling to Large Scale Flume Experiment to Investigate Transport and Reactivity in a Source Treatment Approach (Kumiko Miyajima; Katrin Mackenzie; Jürgen Braun; Norbert Klaas) **In Preparation**

		3.5 (diminished Fe content)	Solid particles (primarily of carbon) came out of the sampling ports 3.5m from injection point but analysis shows iron(0) content greatly diminished	Kumiko Miyajima pers comm
--	--	-----------------------------	--	---------------------------

* For full details consult the source reference(s) as indicated

Table 4: Nanoparticle Transport Distances Recorded at Field Sites

Site	Nanoparticles	Max distance from injection (m)	Notes	Reference
Spolchemie I, CZ	nZVI (NANO FER 25S)	at least 1m	NPs immobilised in treatment zone; Tracer (LiCl) moved about 4m.	NanoRem 7 (CL:AIRE, 2017a)
Spolchemie II, CZ	Nano-Goethite	at least 1m	Distance estimate based on iron concentration in nearest wells. A significant amount of NPs immobilised in treatment zone.	NanoRem 8 (CL:AIRE, 2017b)
Solvay, CH	milled iron nanoparticles	2m - 5m	Based on visual assessment of water colour.	NanoRem 9 (CL:AIRE, 2017c)
Balassagyarmat, Hungary	Carbo-Iron®	Possibly <1m	Based on greyish colour in core sample, TOC, ORP, total dissolved iron.	NanoRem 10 (CL:AIRE, 2017d)
Nitrastur, Spain	NANO FER STAR	at least 3m (less than 15m)	Based on iron (Fe total, Fe(II) and Fe(III)).	NanoRem 12 (CL:AIRE, 2017e)

* For full details consult the source reference as indicated. The NanoRem Bulletins are based on NanoRem deliverables.

Table 5: Summary of the reported predicted travel distances from column experiments, **ascending order of maximum $L_{t\ 99.9\%}$ value** (see also **Table 13** and **Table 14**) [Source: DL 4.2 (Micic Batka & Hofmann, 2016)]

Nanoparticle	$L_{t\ 50\%}$ (m)	$L_{t\ 99.9\%}$ (m)	Source
Nanofer 25S*	0.03 - 0.05	0.29 - 0.48	DL 4-2 page 10 - Table 1
Nanofer 25S optimised	0.03 - 0.18	0.32 - 1.79	DL 4-2 page 10 - Table 1
Nanofer STAR in 3% PAA	0.10 - 0.14	1.00 - 1.35	DL 4-2 page 20 - Table 4
Bionanomagnetite	0.47 - 2.13	1.09 - 4.13	DL 4-2 page 59 - Table 20
Trap-Ox Fe-Zeolite	0.6 - 1.1	6.0 - 10.8	DL 4-2 page 51 - Table 17
CMC-stabilized Carbo-Iron®	0.06 - 1.6	0.56 - 16.4	DL 4-2 page 40 - Table 11, 12
Fe-oxides (Nano-Goethite)	1.2 - 2.2	12.9 - 21.8	DL 4-2 page 65 - Table 23
Milled ZVI – agar agar stabilised	0.9 - 3.2	8.9 - 32.2	DL 4-2 page 31 - Table 7

* unoptimised; $L_{t\ 99.9\%}$ - predicted travel distance by 99.9% of NPs based on ratio of measured concentration against the initial concentration (i.e. where $C/C_0 = 0.001$); $L_{t\ 50\%}$ - predicted travel distance by 50% of NPs (i.e. where $C/C_0 = 0.5$).

2.4.2 Transport in fractured rock

One NanoRem site, Neot Hovav an industrial zone in southern Israel was in fractured chalk with high permeability fractures and a low permeability matrix. Fractures enable fast transport of contaminants. The aim of the work was to look at transport in fractured rock, rather than contamination degradation.

NanoRem Bulletin 11 reports that the NPs travelled from the injection point to the pumping well a distance of 47m (CL:AIRE, 2017). A maximum distance for NP transport in fractured rock has not been calculated.

2.4.3 Estimating Transport distances for the RSM

With the technologies deployed, at the present time, the distance NPs migrate is much shorter than likely dissolved phase plume lengths. Although, research goes on for ways to increase the migration distance. Hence, it may be useful in the longer term to be able to estimate transport distances based on the hydrogeological characteristics of the site and parameters describing key features of the NPs.

A simplified quantitative approach to estimating transport distances has been developed, as a spreadsheet, using the methodology described in Section 3. The methodology depends on calculating values of attachment (k_{att}) and detachment (k_{det}) using the MNMs model (micro-and nanoparticle transport, filtration and clogging model suite) developed by WP7 (Bianco et al., 2015; Tosco et al., 2016). Use of the current spreadsheet model is described in the Modelling Protocol in Section 6.

2.5 Fate

NPs injected into polluted groundwater will undergo various physical and chemical transformations which are likely to affect the particle properties e.g. size, reactivity, bioavailability and toxicity. They may no longer be NPs either due to aggregation or dissolution.

2.5.1 NanoREM results on NP Fate

WP4 DL 4.2 (Micic Batka & Hofmann, 2016) reported on various aspects of fate; much of it concentrated on changes in reactivity, particularly due to the composition of the suspension, as opposed to factors relevant to risk assessment such as changes to the physical and chemical properties which may be expected in the sub-surface.

Some findings on fate relevant to risk assessment were reported and are shown in **Table 6**.

2.5.2 Evaluating Fate in the RSM

Both the literature and the NanoREM experiments indicate that nanoparticles are changed in the sub surface. In general, they will increase in size, decrease in reactivity and, in many cases undergo chemical transformations to minerals common in the subsurface. As reported in DL 4.2 (Micic Batka & Hofmann, 2016) in respect of Nano-Goethite (**Table 6**), they may lose their coating as they move through the subsurface, thus decreasing their mobility.

However, there is insufficient detail to formally include changes in the nature of the particles as part of a risk model. The model therefore assumes that particles maintain their reactivity/toxicity. Assuming reactivity/toxicity decreases (no evidence has been found to indicate that reactivity/toxicity increases) this is a conservative, indeed overly conservative, assumption.

2.6 Toxicity

The inherent toxicity of a substance is used to consider how much of that substance a receptor might be able to be exposed to without 'environmental damage' in the context of the European Union Environment Liability Directive (EC, 2004) (see Box 1 below).

The receptors to be covered in the Risk Screening Model (RSM) and identified in **Table 2** are:

- Human health
- Groundwater
- Surface water

- Ecosystems

Any assessment criteria for NP concentrations in groundwater and surface water are usually based on the use of that water (e.g. WFD Annex V quality elements, HMSO, 2015a, e.g. English WFD Directions Schedule 3 (EQS) vs Schedule 5 (Groundwater), 2015a) i.e. toxicity to humans (e.g. if abstracted for drinking water) or eco-receptors (e.g. aquatic life).

Table 6: Summary of findings following WP4 experiments under field conditions (on soil and groundwater samples from deployment sites) on fate relevant to risk assessment as reported within DL 4.2 (after Micic Batka & Hofmann, 2016)

Nanoparticle	Relevant fate aspects studied	Findings	Section
Nanofer 25S	Particle oxidation and Fe speciation in groundwater from Spolchemie I	Highly sensitive to oxidation. Fast & significant losses Fe(0), especially in presence of dissolved oxygen. Under field conditions anaerobic corrosion and/or reaction with electron acceptors other than contaminant (e.g. nitrate & sulphate) can lead to less utilisation of Fe(0) for contaminant degradation.	4.1.3
Nanofer STAR (activated & CMC modified)	Long term anaerobic corrosion and Fe speciation for activated NANOFEAR STAR in groundwater from Spolchemie I, contaminated with chlorinated hydro-carbons	Transformation products (Fe oxides, Fe hydroxides and Fe carbonates) commonly found in sediment and soils. c. only 12% and 30% of initial Fe(0) remained unconsumed in groundwater samples (after 1 month) and soil samples (after 5 months) from field site.	4.2.3
Milled ZVI	Particle lifetime and Fe speciation under conditions corresponding to material from Solvay (CH) and Balassagyarmat (HU)	Reaction constants are smaller and particle lifetime is longer, compared to Nanofer 25S, and application at relatively high oxygen field sites (e.g. Solvay, CH) may be advantageous.	4.4.3
Carbo-Iron [®]	Contaminant sorption after long term aging	Sorption ability of Carbo-Iron [®] not expected to be significantly reduced in field (i.e. following NP alteration and formation of Fe precipitates (oxides)). Under test conditions <0.5% weight of Fe(0) detected after 75 days of reaction with PCE, indicating limited lifetime under field conditions. Transformation of Fe(0) comparable to nZVI e.g. into magnetite.	4.5.3
Trap-Ox Fe-zeolites (field relevant conditions)	Alteration of elemental composition, BET specific surface area, catalytic activity and MTBE adsorption after long-term aging in the presence of NOM	Changes in zeolite composition are mainly due to uptake of divalent cations (Ca ²⁺ and Mg ²⁺) from hard water, associated with the presence of alumina in the zeolite framework. This may hinder reaction rates for relatively large contaminant molecules – i.e. diffusive mass transfer within zeolite pores. On-site groundwater experiments required.	4.6.3
Bionanomagnetite/palladized bionanomagnetite	None (fate experiments addressed: Removal of Cr (VI) and Reactivity)	Not applicable (not deployed under field conditions)	4.7.3
Nano-Goethite	Long-term changes in Fe content and Fe speciation of Nano-Goethite particles exposed for 1 year to BTEX-contaminated porous medium from Spolchemie II field site, CZ	Fe _{total} content decreased along column length; after flushing low effluent Fe _{total} indicates majority of Nano-Goethite was irreversibly loaded onto porous medium. Most of the measured Fe was as Fe(III). Fe-speciation shows Nano-Goethite resistant to chemical changes after long (1 year) period. Mineral composition of particles remains the same, but the size and the crystallinity of nano-needle increased. Mobility of renegade particles is unlikely, since Nano-Goethite loses its stabilizing humic acid coating while moving through porous medium in the cascading column experiments.	4.8.2
Mg/Al particles	None (poor long term reactivity observed, hence no further fate experiments were undertaken).	N/A	4.9

BET SSA - Specific surface area determined by the BET (Brunauer, Emmett and Teller) method; NOM – Natural Organic Matter; CMC – carboxymethylcellulose.

Box 1: European Union Environmental Liability Directive (as amended 2013) definition of environmental damage (EC, 2004), most relevant section to the NanoRem context in bold

‘environmental damage’ means:

- (a) damage to protected species and natural habitats, which is any damage that has significant adverse effects on reaching or maintaining the favourable conservation status of such habitats or species. The significance of such effects is to be assessed with reference to the baseline condition, taking account of the criteria set out in Annex I;

Damage to protected species and natural habitats does not include previously identified adverse effects which result from an act by an operator which was expressly authorised by the relevant authorities in accordance with provisions implementing Article 6(3) and (4) or Article 16 of Directive 92/43/EEC or Article 9 of Directive 79/409/EEC or, in the case of habitats and species not covered by Community law, in accordance with equivalent provisions of national law on nature conservation.

- (b) ‘water damage’, which is any damage that significantly adversely affects:

- (i) **the ecological, chemical or quantitative status or the ecological potential, as defined in Directive 2000/60/EC, of the waters concerned, with the exception of adverse effects where Article 4(7) of that Directive applies;** or
- (ii) the environmental status of the marine waters concerned, as defined in Directive 2008/56/EC, in so far as particular aspects of the environmental status of the marine environment are not already addressed through Directive 2000/60/EC;

- (c) land damage, which is any land contamination that creates a significant risk of human health being adversely affected as a result of the direct or indirect introduction, in, on or under land, of substances, preparations, organisms or micro-organisms;

Notes:

Directive 2000/60/EC is the Water Framework Directive (EC, 2000)

Within England the ELD is implemented through The Environmental Damage (Prevention and Remediation) (England) Regulations 2015 (HMSO, 2015b)

2.6.1 Toxicity: Human Health

No testing in relation to toxicity to human health or animal analogues was carried out as part of the NanoRem project.

As part of earlier NanoRem work, a literature review was carried out (Internal Deliverable WP9). Whilst the findings were limited, it was concluded that the NanoRem nanoparticles were probably less harmful than those in widespread use where human exposure is more likely (e.g. nano-silver used in clothing) (Nathanail et al., 2016).

2.6.2 Toxicity: Ecotoxicity

Ecotoxicity – pristine particles

WP5 carried out eco toxicity testing on most of the pristine NanoRem nanoparticles deriving dose-response relationships for terrestrial and aquatic species exposed to aqueous suspensions of NPs (in **absence of the environmental matrix** (i.e. soil, DOC, contaminants, etc). Exposure concentrations were 0, 1, 10, 50, 100, 500, 1000, 5000 and 10,000mg L⁻¹ (note exact doses selected dependent upon test and species). The results are reported in DL 5-1 (Coutris et al., 2015). The following ecotoxicity tests-species were investigated:

1. Aquatic species: algal growth, assimilation and photosynthesis tests (green algae *Pseudokirchneriella subcapitata* or *Chlamydomonas* sp.); Daphnia immobilization test (planktonic crustacean *Daphnia magna*); aquatic worm *Lumbriculus variegatus* mortality test.
2. Bacteria species: Bacterial luminescence bioassay (*Vibrio fischeri*); *Escherichia coli* growth test; *Escherichia coli* viability cell test; *Clostridium perfringens* growth test;
3. Soil species: Earthworm survival test (adult *Eisenia fetida*); Seed germination and root elongation test (monocot ryegrass, *Lolium multiflorum* and dicot radish, *Raphanus sativus*).

In general this showed there was no adverse effect at concentrations less than 100 mg/L, and for many of the tests at concentrations of 1000 mg/L, often the highest concentration tested. A small number of higher adverse effects values were reported (~ several g/L), predominantly in relation to earthworms.

The DL5-1 report (Coutris et al., 2015) summarises the toxicity as follows:

“The low toxicities found in the standard organisms do not lead to any hazard classification according to EU regulation for any of the tested particles and the results indicate that the particles, except the milled Fe particles, can be considered non-toxic. ”

In addition, the outcome of the ecotoxicity testing in the absence of environmental matrices was provided as a summary table, reproduced as **Table 7** below.

Table 7: Summary of ecotoxicity testing across NanoRem NPs (EC₅₀ is defined as an effect concentration at which an effect of 50% is observed) [Source: DL5-1, (Coutris et al., 2015)]

	EC ₅₀ >100 mg/L	EC ₅₀ <100 mg/L	ND: not determined						
	<i>P.subcapitata</i>	<i>Chlamydomonas</i> sp.	<i>D. magna</i>	<i>L. variegatus</i>	<i>V. fischeri</i>	<i>E. coli</i>	<i>E. fetida</i>	<i>L.multiflorum</i>	<i>R. sativus</i>
	48 h growth OECD 201	48 h photosynthesis efficiency	48 h immobilization OECD 202	96 h mortality	15 min luminescence ISO 11348-3	6 h growth 24 h viability	48 h mortality OECD 207	6 day root elongation OECD 208	6 day root elongation OECD 208
NanoFer STAR (NanoIron)									
Nano-magnetite (UPOL)									
Milled Fe particles (UVR-FIA)	ND	ND	ND				ND		
Nano-goethite (HMGU)									
Fe Zeolite (UFZ)									
Carbo-Iron (UFZ)									
Bio-nanomagnetite (UMAN)	ND	ND	ND	ND	ND	ND		ND	ND

It should be noted that the above summary results relate to acute toxicity tests and provide an indication as to whether the EC₅₀ is greater or less than 100mg L⁻¹. For deriving an Environmental Quality Standard (EQS) “critical ecotoxicity data are (typically NOECs/EC10s or LC/EC50) for sensitive species and endpoints are used as the basis for extrapolation and hence determine - or strongly influence - the value of the QS [quality standard]” (European Commission & Directorate-General for the Environment, 2011). Where a deterministic approach to extrapolation is used (i.e. an Assessment Factor (AF) is applied) whereby the AF is applied to the lowest credible NOEC/EC10 or LC/EC50 (the critical datum),

with values of applied AF varying between 1 and 1000 dependent on level and type of data available (based on para 1.2.6, Annex V of EC, 2000).

Table 8: Key toxicity outcomes (in absence of environmental matrix) from the WP5 DL5.1 report (Coutris et al., 2015) for each NP

Nanoparticles	Limiting Concentration	Limiting test	Comment
nZVI (Nanofer25S)/ NanoferSTAR	100 mg/L	No adverse effect to freshwater worm (<i>Lumbriculus variegatus</i>) to the highest concentration tested of 100mg/L	
Nano-magnetite (UPOL)	100 mg/L	No adverse effect to freshwater worm (<i>Lumbriculus variegatus</i>) to the highest concentration tested of 100mg/L	
Nano Goethite (HMGU)	100 mg/L	No signs of toxicity to the bacteria <i>Vibrio fischeri</i> at the highest concentration (100mg/L) to give feasible toxicity assessment results for this particular test	
Trap-Ox Fe-Zeolite (UFZ)	100 mg/L	No signs of toxicity to the green algae <i>Pseudokirchneriella subcapitata</i> or bacteria <i>Vibrio fischeri</i> at the highest concentration (100mg/L) to give feasible toxicity assessment results for these particular tests	
Milled (nZVI) iron	EC ₅₀ 1-5 mg/L	EC ₁₀ 76 mg/L (53-108 mg/L 95% confidence interval) for bacteria <i>Vibrio fischeri</i> . EC ₅₀ between 1-5 mg/L for aquatic worm <i>Lumbriculus variegatus</i> . Root elongation of radish (<i>Raphanus sativus</i>) significantly reduced at 50mg/L.	Not all species were tested.
Carbo-Iron® and associated (UFZ)	100 mg/L	No adverse effects to the planktonic crustacean <i>Daphnia magna</i> were observed for Carbo-Iron at concentrations up to 100 mg/L. However, the activated carbon affected the mobility of the <i>Daphnia magna</i> at concentrations above 50 mg/L. No adverse effects to the green algal <i>Chlamydomonas sp.</i> were observed at concentrations up to 100 mg/L for reactive Carbo-Iron, aged Carbo-Iron, activated carbon and up to 200 mg/L for CMC.	Possible effect below 100mg/L arising from the activated carbon
Bio-nanomagnetite (UMAN)	5000 mg/L	No adverse effect to the earthworm <i>Eisenia fetida</i> was observed at Fe concentrations up to 7 g/L (420 µg/cm ²), 11 g/L (600 µg/cm ²), and 5 g/L (290 µg/cm ²), for biomagnetite, palladised biomagnetite, and commercial magnetite, respectively, which were the highest concentrations tested.	Earthworms were the only receptor tested.

Ecotoxicity – field samples following interactions with soil

The influence of transformation and transport on the ecotoxicity of some of the NanoRem NPs was reported as part of the DL 5.2 report (Coutris et al., 2016), using water samples taken from upstream and downstream wells of the NP injection from large scale experiments at VEGAS (WP8) and the field sites (WP10). Tests included time-course sampling to assess effects of ageing (i.e. prior to NP injection, a few hours after injection, two to four weeks, three months and nine months after NP injection), and account for the (assumed) reduction in toxicity caused by nanoparticles transformation and adsorption to solid matrices. Tests and species generally undertaken were on the root elongation of radish *Raphanus sativus*, growth of green algae *Pseudokirchneriella subcapitata*, growth of anaerobic bacteria *Clostridium perfringens*, and colony formation of cultivable indigenous bacteria. Microbial profiling was also undertaken in some cases. The reported outcomes are summarised in Table 9 below.

The time course of NP, contaminant concentration or other parameters were not provided as part of the DL 5.2 report, although a control (e.g. tap water) was used to give relative toxicity effects.

2.6.3 Toxicity: for the RSM

Based upon the majority of the dose-response evidence base presented by DL 5.1 (Coutris et al., 2015) and as summarised in **Table 8** above, for the purposes of this protocol, a reasonable value to use to represent potential for ecotoxicity at a contaminated Site across the spectrum of NPs within NanoRem (with the exception of milled nZVI) is 100 mg/L.

This is also a practical limit; WP6 have reasonable techniques to test for iron based particles to a detection limit of 100mg/L, for example the total Fe measurements, turbidity or trace element fingerprinting (e.g. Table 7.1, Oughton et al., 2015).

It should be noted that in assigning or deriving a regulatory Environmental Quality Standard (EQS) consideration of the spectrum of potential critical ecological receptors tested, data quality, uncertainty, etc, would need to be assessed (European Commission & Directorate-General for the Environment, 2011).

Table 9: Key toxicity outcomes from lab and field water samples following injections, transformation and transport from the WP5 DL5.2 report (Coutris et al., 2016) for the NPs tested

Nanoparticles (Location) (Source Term)	Average NP injection concentration (g/L)	Species – effect tested	Sampling times (after injection)	Reported outcome
Nano-Goethite (Large Scale Container, VEGAS) (BTEX plume, toluene 60mg/L)	20g/L (120kg NP over 8.5 hours)	Anaerobic bacteria <i>Clostridium perfringens</i> - growth rate	Prior, 8hr, 4wk	No toxicity at any sampling time (except at upstream location prior to NP injection)
		Radish <i>Raphanus sativus</i> – root length	Prior, 8hr, 4wk	No toxicity at any sampling time
Nanofer 25S (Large Scale Flume, VEGAS) (PCE plume 18mg/L)	10g/L (10kg NP)	Green algae <i>Pseudokirchneriella subcapitata</i> - growth	Not stated	No toxicity at any sampling time
		Anaerobic bacteria <i>Clostridium perfringens</i> - growth rate & percentage dead cells	Prior, 8hr, 2wk, ~3mth	No toxicity at any sampling time
		Radish <i>Raphanus sativus</i> and <i>Lolium multiflorum</i> – root length	Prior, 8hr	No toxicity at any sampling time
Nanofer 25S (Spolchemie I, CZ, 2014) (DNAPL Chlorinated hydrocarbons up to 30mg/L)	2g/L (200kg NP total applied)	Green algae <i>Pseudokirchneriella subcapitata</i> - growth	Prior, ~8hr, 3wk, 3mth, 9mth	Highest toxicity within waters of some wells 3 months after injection. At 9 months toxicity similar to Prior to injection.
		Anaerobic bacteria <i>Clostridium perfringens</i> - growth rate & percentage dead cells	Prior, ~8hr, 3wk, 3mth, 9mth	No toxicity to growth at any sampling time Higher percentage of dead cells in waters from some wells possibly due to DNAPL rebound (though uncertain)
		Radish <i>Raphanus sativus</i> – root length	Prior, ~8hr, 3wk	No significant toxicity at any sampling time
Nanofer Star (Spolchemie I, CZ, 2015) (DNAPL Chlorinated hydrocarbons up to 30mg/L)	5g/L (300kg NP over 3 days)	Microbial analysis (gene profiling)	Prior, Post, 3wk, 3mth, 9mth	Injection caused first a negative effect on selected organohalide respiring bacteria and <i>bvcA</i> and <i>vcrA</i> genes. However, this effect was transient, and groundwater was colonized again with monitored bacteria within approximately 1 month.
Nano-Goethite (Spolchemie II, CZ) (BTEX plume up to 90mg/L)	5g/L (300kg NP over 3 days)	Green algae <i>Pseudokirchneriella subcapitata</i> - growth	Prior, 8hr, 4wk, 3mth, 9mth	Transient toxicity alleviation was reported in most samples after injection, which reappeared within 3m.
		Anaerobic bacteria <i>Clostridium perfringens</i> - growth rate & percentage dead cells	Prior, 3hr, 4wk, 3mth, 9mth	Based on samples taken from one well (AW6A-1) toxicity levels decreased significantly between 4w and 3m after injection, though toxicity alleviation

Nanoparticles (Location) (Source Term)	Average NP injection concentration (g/L)	Species – effect tested	Sampling times (after injection)	Reported outcome
				was transient with levels close to pre-treatment levels by 9m
		Radish <i>Raphanus sativus</i> – root length	Prior, 8hr, 4wk, 3mth, 9mth	Toxicity alleviation (i.e. increase in root length compared to prior to injection) was maintained for at least 8h or 4w dependent on sample well location. Other well locations appeared to show no differences in toxicity.
		Microbial analysis (gene profiling)	Prior, 8hr, 4wk, 3mth, 9mth	Some inhibitory effect on organohalide-respiring bacteria (possibly due to O ₂ saturated water used to disperse NPs). Enzyme associated with aerobic BTEX degradation remained low for at least 8.5m after injection.
Milled nZVI - FerMEG12 (Solvay, CH) (DNAPL of PCE, TCE and HCA, PCE circa 10mg/L)	10g/L (500kg NP over 3 days)	Green algae <i>Pseudokirchneriella subcapitata</i> - growth	Prior, 2d, 2wk, 3mth, 8mth	Toxicity was increased in all samples at 2d post injection, which lasted for 2w in 2 out of 5 samples (associated with the deepest layers). 8 months after injection toxicity was lower compared to prior to injection.
		Anaerobic bacteria <i>Clostridium perfringens</i> - growth rate & percentage dead cells	Prior, 2d, 2wk, 3mth, 8mth	Virtually no toxicity before or after injection at any sampling time
		Radish <i>Raphanus sativus</i> – root length	Prior, 2d, 2wk	Virtually no toxicity before or after injection at any sampling time
		Microbial analysis (gene profiling)	Prior, 2d, 2wk, 3mth, 8mth	The data fail to convey significant deleterious impacts associated with the injection of FerMEG12 particles. It can be concluded that the FerMEG12 treatment had a positive effect on microbial communities and particularly on organohalide-respiring bacteria.
Carbo-Iron[®] (Balassagyarmat, HU) (DNAPL within PCE, TCE, DCE up to 15.4, 6.2 and 0.09mg/L, respectively)	13.6g/L (180kg NP over 2 days)	Green algae <i>Pseudokirchneriella subcapitata</i> - growth	Prior, 2d, 1wk, 1mth, 3mth	Toxicity alleviation was observed for up to at least 1 month in samples from 2 of 3 wells, with partial alleviation for at least 1 week in a sample from the other well. Toxicity alleviation was not observed in all samples taken from each well (i.e. those with 2 sample

Nanoparticles (Location) (Source Term)	Average NP injection concentration (g/L)	Species – effect tested	Sampling times (after injection)	Reported outcome
				depths).
		Anaerobic bacteria <i>Clostridium perfringens</i> - growth rate & percentage dead cells	Prior, 2d, 1wk, 1mth, 3mth	No toxicity effects on the growth rate. Percentage of dead cells was significantly higher in 2 (out of 3) wells, associated with highest contaminant concentrations, both prior and after injection. Though by 1 month no effects were reported.
		Radish <i>Raphanus sativus</i> – root length	Prior, 2d, 1wk, 1mth, 3mth	Little toxicity effect at any sampling time
		Microbial analysis (gene profiling)	Prior, 2d, 1wk, 1mth, 3mth, 7m	Harmful effects associated with the injection were not detected. Vinyl chloride reductase genes <i>vcrA</i> and <i>bvcA</i> and Dehalococoides, not detected prior to injection, appeared in most wells right after application. Total bacterial biomass increased in most of the monitored wells so that other bacterial groups (such as sulfate or nitrate-reducers) in addition to bacteria utilizing chlorinated hydrocarbons were supported by the newly established conditions.

Notes: hr = hour; dy = day; wk = week; mth = month

Key:

Transient toxicity alleviation / beneficial effect reported
No toxicity effect reported
Transient toxicity effect reported
Toxicity effect reported



This page is intentionally blank



3 Modelling of NanoRem nanoparticles

3.1 Modelling approach

The approach taken is to modify an existing relatively simple transport model that is widely used as a screening tool (i.e. the Environment Agency Remedial Targets Methodology, (Environment Agency, 2006)) to account for some of the properties of Nano particles (NPs). The objective is to estimate the maximum expected transport distance for NPs injected into polluted groundwater.

The following sections present the derivation and basis for these modifications to the RTM tool, how they are implemented and some of the current results, drawing on some of the available data and results from other NanoRem work packages.

3.2 Important processes to model for NPs

This section outlines the important processes that require consideration in developing a Risk Screening Model (RSM) for the initial assessment of NPs at injection sites. The modifications made to the RTM tool to develop the RSM and its outputs from test scenarios are subsequently described in Section 3.3.

3.2.1 Advection Dispersion of NanoRem nanoparticles

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

$$\phi \frac{\partial C}{\partial t} - \sum_i \rho_b \frac{\partial S_i}{\partial t} = -U \frac{\partial C}{\partial x} + \phi D \frac{\partial^2 C}{\partial x^2} \quad (\text{eq. 10a})$$

$$\rho_b \frac{\partial S_i}{\partial t} = \phi k_{att,i} \psi_i C - \rho_b k_{det,i} S_i \quad (\text{eq. 10b})$$

Where:

i denotes the interaction type or site which have different NP – grain interaction mechanisms where the sum over all *i* terms controls overall affinity of the colloidal particles to grain surfaces;

ϕ [-] is the porosity of the medium;

U [$L T^{-1}$] is the Darcy velocity⁵;

C [$M L^{-3}$] is the NP concentration in the mobile phase;

S_i [$M M^{-1}$] is the NP concentration in the solid phase for interaction site *i*;

D [$L^2 T^{-1}$] is the dispersion coefficient;

ρ_b [$M L^{-3}$] is the bulk density of the solid matrix;

⁵ U as defined here is the Darcy (volume) flux or specific discharge [$L^3 L^{-2} T^{-1}$], typically referred to as the Darcy flux or velocity, q (Haitjema & Anderson, 2016)

ψ_i [-] in the attachment term is a generic function depending on the attachment mechanisms that have to be modelled (see Section 3.2.2)

$k_{att,i}$ [T^{-1}] is the rate coefficient of attachment of nanoparticles onto the grain surface for the interaction site i .

$k_{det,i}$ [T^{-1}] is the rate coefficient of detachment of nanoparticles off of the grain surface for the interaction site i .

As outlined in DL7.1 NP attachment and detachment are influenced by aquifer hydro-dynamic (such as pore-water velocity and injection flow-rate) and hydrochemical (such as ionic strength, pH) conditions.

3.2.2 Attachment and Detachment of NanoRem Nano Particles (NPs)

The function ψ_i in the attachment term (eq. 10b above) is a generic function depending on the attachment mechanisms that are being modelled, whilst the detachment term is always assumed to be linearly proportional to the concentration of the attached colloids (Bianco et al., 2015).

A range of attachment or kinetic mechanisms are envisaged (for details see Tosco et al., 2016) and their relevance to the screening risk model have been assessed:

- Linear – whereby NP deposition is not impacted by previously deposited particles with the particle-particle and particle-collector interaction energies being similar:

$$\psi_i = 1$$

This type of attachment behaviour is considered to be most likely to occur outside of the immediate injection zone where NP concentrations are comparatively low – i.e. where there is a ‘clean(er)’ collector bed environment with respect to NPs (rather than with respect to groundwater contaminants).

- Blocking – particle-particle interaction energies are repulsive so that deposited NPs exclude attachment in their immediate vicinity resulting in a decrease in the localised attachment rate:

$$\psi_i = 1 - (S_i / S_{i, \max})$$

Where $S_{i, \max}$ is the maximum NP concentration retainable on the solid phase at given chemical conditions. This blocking effect is considered to be most relevant to the near-field injection zone where elevated NP concentrations are more likely to lead to retained NPs on the available solid phase collector sites. Hence outside of the NP source (injection) zone it is assumed that $S_i \ll S_{i, \max}$ so that $\psi_i \rightarrow 1$ (i.e. linear attachment) and the regulatory compliance point⁶ is assumed to be located at a sufficiently distant point where blocking kinetics are unlikely to be applicable.

- Ripening - particle-particle interaction energies are attractive so that already deposited NPs attract those in suspension with a progressive increase in attachment kinetics occurs which eventually leads to clogging of pores:

$$\psi_i = (1 + A_{rip} S_i^{\beta_{rip}})$$

⁶ e.g. the location at which any agreed target concentrations for NPs with the relevant regulatory authority should be met

Where both $A_{rip} > 0$ and $\beta_{rip} > 0$ so that deposition rate increases with increasing concentration of attached NPs. This phenomenon is considered to be unlikely to be relevant at the compliance point location and excluding this kinetic process is a cautious assumption with regards to predicting the NP transport distance.

- Straining – is another kinetic process that is likely to lead to impeded transport of NPs away from the injection (source) zone such that NPs are too large to pass through individual pores and become trapped. Straining is envisaged to vary as a function of NP travel path length (x) and average diameter of the porous medium grains (d_{mean}):

$$\psi_i = (1 + x/d_{mean})^{-\beta_{str}}$$

Where β_{str} is an empirical fitting parameter, but for dilute colloidal conditions a value of 0.432 is often assumed. At large travel lengths (i.e. well away from the NP injection zone) then the straining term is likely to be relatively small and exclusion of this process is a cautious assumption with regards to predicting the NP transport distance.

3.2.3 Effect of ionic strength on NP deposition

The effects of variations of ionic strength (IS) on NP attachment and detachment and maximum blocking concentration are described within DL7.1 (eq. 15, 16 and 17, Tosco et al., 2016) and the MNMs User Manual (Eq 5-11, 5-12 and 5-13, Bianco et al., 2015). The semi-empirical equations comprise up to 14 empirical coefficients to be determined via fitting procedures for each NP type across a range of ionic strengths (e.g. Tiraferri et al., 2011). The relationships are reproduced below and have been included in the Risk Screening Model, along with some default parameters for micro-sized latex particles (Tiraferri et al., 2011), to provide an indication of potential variability of the attachment and detachment coefficients with ionic strength. However, it is currently considered that there is not sufficient data availability for the NanoRem NPs to fully implement parameterised equations at this stage in the RSM, so the user would have to select appropriate values for the attachment and detachment coefficients based on their experience.

$$k_{att,i}(C_{salt}) = \frac{k_{att\infty,i}}{1 + \left(\frac{CDC_i}{C_{salt}}\right)^{\beta_{att,i}}} \quad (\text{eq. 15})$$

$$k_{det,i}(C_{salt}) = \frac{k_{det0,i}}{1 + \left(\frac{C_{salt}}{CRC_i}\right)^{\beta_{det,i}}} \quad (\text{eq. 16})$$

$$S_{i,max}(C_{salt}) = \gamma_{s,i} C_{salt}^{\beta_{s,i}} \quad (\text{eq. 17})$$

Where subscript i recognises the possibility to have more than one active site with different energy barrier levels (interaction site). The terms $k_{att\infty,i}$, CDC_i , $\beta_{att,i}$, $k_{det0,i}$, CRC_i , $\beta_{det,i}$, $\gamma_{s,i}$ and $\beta_{s,i}$ are empirical coefficients determined via fitting procedures, where according to Tiraferri *et al.* (2011):

$\beta_{att,i}$ [-] is related to the deposition sensitivity to changes in ionic strength;

CDC_i [$M L^{-3}$] is the critical deposition concentration and is the salt concentration at which the transition occurs between favourable and unfavourable attachment regimes;

CRC_i [$M L^{-3}$] is the critical release concentration and corresponds to the ionic strength at which the detachment coefficient is half the value of the favourable regime;

C_{salt} [M L^{-3}] is the salt concentration that models the variation in pore water ionic strength;

$k_{\text{att},i}$ [T^{-1}] is the asymptotic attachment coefficient at high ionic strength (i.e. favourable attachment regime) and is affected by the solid matrix, the flow field, and grain-particle interactions;

$k_{\text{det},i}$ [T^{-1}] is the asymptotic detachment rate coefficient for low ionic strength (i.e. in favourable release regime);

$S_{i,\text{max}}$ [M^{-1}] is the maximum NP concentration retainable on the solid phase at given chemical conditions;

$\gamma_{S,i}$ [-] and $\beta_{S,i}$ [-] are empirical coefficients relating $S_{i,\text{max}}$ to changes in ionic strength.

The above equations have been validated both under constant ionic strength (see Figure 4 in Tiraferri et al., 2011) and under transient ionic strengths (Tosco et al., 2009).

The anticipated pattern of variation in the attachment and detachment coefficients with ionic strength is presented in **Table 10**, based on experiments with latex particles (Tiraferri et al., 2011). The key relationship considered is the ratio between the attachment and detachment coefficients ($k_{\text{att}}:k_{\text{det}}$) which, for ionic strengths in the range of 10-30mM, may typically be expected to lie between 100-200 (range 1 to 486). Within extremely saline aquifers the ratio ($k_{\text{att}}:k_{\text{det}}$) could be of the order of several 1000s, based on the latex particles dataset. 'Low' ionic strength aquifers are typically considered to be groundwater <0.01 mM (Wallace et al., 2012). Typical ionic strengths of natural waters are (Custodio et al., 2005)^{7,8}: surface waters, 1-5 mM; potable water / groundwater 1-20mM; alluvial aquifer, 0.8-7 mM; karst aquifer, 1.2-10mM; and seawater up to about 700mM.

As the data presented in **Table 10** demonstrates the ionic strength does not explain all of the variation in the reported values for the attachment and detachment coefficients – i.e. for the same reported ionic strength derived $k_{\text{att}}:k_{\text{det}}$ ratio's do vary. Therefore, it is clear that attachment and detachment coefficients are impacted by other factors such as the initial (inlet or injected) NP concentration, viscosity of carrier fluids, delivery parameters, NP size distribution, pore network size distribution, etc. Hence some of the variation presented will relate to both the experimental variation (between different columns or aquifers) and unaccounted for colloid interaction processes. However, for the purposes of this RSM the ionic strength provides a first approximation of one of the driving variables.

⁷ <http://www.aqion.de/site/69>, accessed October 2016

⁸ http://www.swim-site.nl/pdf/swim18/swim18_042.pdf, accessed November 2016

Table 10: Variation of attachment (k_{att}) and detachment (k_{det}) coefficient and their ratio with ionic strength (adapted from Tiraferri et al., 2011) for negatively charged latex particles (mean size 1900nm) in micro-sized siliceous sand column experiments (shaded cells considered likely to be representative of typical aquifer ionic strengths) [see text for discussion on parameter variation at same ionic strength]

Ionic Strength (mM)	k_{att} (sec ⁻¹)	k_{att} (day ⁻¹)	k_{det} (sec ⁻¹)	k_{det} (day ⁻¹)	$k_{att} : k_{det}$
1	2.40E-04	20.7	1.46E-03	126.1	0.16
1	5.78E-04	49.9	3.62E-03	312.8	0.16
3	1.59E-04	13.7	2.23E-03	192.7	0.07
3	6.42E-04	55.5	1.07E-02	924.5	0.06
10	7.39E-04	63.8	7.06E-04	61.0	1.0
10	2.87E-03	248.0	2.82E-05	2.4	102
10	9.15E-04	79.1	2.47E-05	2.1	37
30	4.71E-03	406.9	1.63E-05	1.4	289
30	3.84E-03	331.8	1.63E-05	1.4	236
30	5.30E-03	457.9	1.09E-05	0.9	486
100	5.46E-03	471.7	2.52E-07	2.18E-02	21667
100	5.06E-03	437.2	2.52E-07	2.18E-02	20079
100	4.93E-03	426.0	2.52E-07	2.18E-02	19563
300	1.09E-02	941.8	2.25E-10	1.94E-05	48444444
300	9.44E-03	815.6	5.63E-09	4.86E-04	1676732
300	6.54E-03	565.1	5.63E-09	4.86E-04	1161634

3.3 Calculation of NanoRem NP transport distance

3.3.1 Environment Agency Remedial Targets Methodology (RTM)

The basis for deriving the transport element of the Risk Screening Model (RSM) – i.e. estimating a screening level NP concentration versus distance from the NP source (injection) zone - is the Environment Agency Remedial Targets Methodology, (RTM) (Environment Agency, 2006a). The RTM is accompanied by a Microsoft[®] Excel spreadsheet tool⁹ for four Levels of Assessment: Levels 3 (saturated zone transport, attenuation and retardation); and 4 (dilution in the receptor) apply to the saturated zone.

To create a model for NP transport, the Level 3 (groundwater) RTM spreadsheet has been modified by incorporating some of the key NP parameters into one of the analytical solutions (the Ogata Banks equation) used to describe the advection-dispersion including degradation and retardation of solutes downstream of the source term. The implementation and assumptions are described in more detail in the sub-sections below, whilst the Ogata Banks equation and definition of terms is provided in **Box 2**.

⁹ Available freely from : <https://www.gov.uk/government/publications/remedial-targets-worksheet-v22a-user-manual>, last accessed 6th October 2016

Box 2: Analytical solution for transport (extracts from Environment Agency, 2006a)

Table D5 Basic equations for calculating attenuation factor (Level 3)

Calculation of concentrations downgradient of the site (time variant) using the Ogata Banks equation (Table D3 gives the steady-state solution of this equation. Table D4 gives the simplified Domenico time-variant version of this equation).

$$C_{ED} = \frac{C_0}{8} \exp\left\{\frac{x}{2a_x}\left(1 - \sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\} \cdot \operatorname{erfc}\left\{\frac{1}{2\sqrt{a_x u t}}\left(x - ut\sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\}$$

$$+ \exp\left\{\frac{x}{2a_x}\left(1 + \sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\} \cdot \operatorname{erfc}\left\{\frac{1}{2\sqrt{a_x u t}}\left(x + ut\sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\}$$

$$\left[\operatorname{erf}\left\{\frac{z + \frac{S_z}{2}}{2\sqrt{a_z x}}\right\} - \operatorname{erf}\left\{\frac{z - \frac{S_z}{2}}{2\sqrt{a_z x}}\right\}\right] \left[\operatorname{erf}\left\{\frac{y + S_y}{2\sqrt{a_y x}}\right\} - \operatorname{erf}\left\{\frac{y - S_y}{2\sqrt{a_y x}}\right\}\right]$$

Attenuation factor $AF = \frac{C_{ED}}{C_0}$

where:

C = concentration of contaminant at point x and time t (mg/l)
 C_0 = initial contaminant concentration in groundwater (mg/l)
 λ = decay constant = 0.693/half life for decay of contaminant in days
 a_x, a_y, a_z = longitudinal, vertical and lateral dispersivity (m)
 S_z, S_y = width and thickness of plume at source (in saturated zone) (m)
 u = rate of contaminant movement due to retardation (Table D2)

$$u = \frac{K i}{n R_f}$$

R_f = retardation factor Retardation factor $R_f = 1 + \frac{K_a \rho}{n}$
 n = effective porosity
 i = hydraulic gradient
 K = hydraulic conductivity (m/d)
 n = effective porosity
 i = hydraulic gradient
 k = hydraulic conductivity (m/d)
 x = distance to compliance point (m)
 z = distance (lateral) to compliance point perpendicular to flow direction (m)
 y = distance (depth) to compliance point perpendicular to flow direction (m)
 erf = error function
 exp = exponential
 erfc = complementary error function
 t = time (in days) since contaminant entered groundwater

Note: Plume thickness at source, S_y , is equal to mixing zone thickness. In order to calculate the remedial target time (t) should be set as a large number (i.e. 10^{99} d) and the lateral and vertical offset should be set as zero. This solution assumes that vertical dispersion occurs in one direction only.

Table D3 Basic analytical equations for calculating attenuation factor

Calculation of concentrations downgradient of the site (steady-state) using the Domenico equation. This is a simplified version of the Ogata Banks equation given in Table D5.

$$C_{ED} = C_0 \exp\left\{\frac{x}{2a_x}\left(1 - \sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\} \cdot \operatorname{erf}\left\{\frac{S_y}{2\sqrt{a_y x}}\right\} \cdot \operatorname{erf}\left\{\frac{S_z}{4\sqrt{a_z x}}\right\}$$

Attenuation factor $AF = \frac{C_{ED}}{C_0}$

where:

C_{ED} = concentration of contaminant at distance x (mg/l)
 C_0 = initial contaminant concentration in groundwater (mg/l)
 λ = decay constant = 0.693/half life for degradation of contaminant in days
 a_x, a_y, a_z = longitudinal, vertical and lateral dispersivity (m)
 S_z, S_y = width and thickness of plume at source (in the saturated zone) (m)
 u = rate of contaminant movement due to retardation (Table D2)

$$u = \frac{K i}{n R_f}$$

R_f = retardation factor (Table D2)
 n = effective porosity
 i = hydraulic gradient
 K = hydraulic conductivity (m/d)
 x = distance to compliance point (m)
 erf = error function
 exp = exponential

Note: For certain cases or choices of parameter value, the Domenico equation can give slightly different calculated values to the Ogata Banks equation. This is a function of the simplifications made in the Domenico solution. Plume thickness at source, S_y , is equal to mixing zone thickness (M_z) used in calculating the dilution factor. This solution assumes that vertical dispersion occurs in one direction only.

Table D4 Basic equations for calculating attenuation factor (Level 3)

Calculation of concentration downgradient of site using the Domenico equation (simplified version of the Ogata Banks equation, see Table D5).

$$C_{ED} = \frac{C_0}{2} \exp\left\{\frac{x}{2a_x}\left(1 - \sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\} \cdot \operatorname{erfc}\left\{\frac{1}{2\sqrt{a_x u t}}\left(x - ut\sqrt{1 + \frac{4\lambda a_x}{u}}\right)\right\} \cdot \operatorname{erf}\left\{\frac{S_y}{2\sqrt{a_y x}}\right\} \cdot \operatorname{erf}\left\{\frac{S_z}{4\sqrt{a_z x}}\right\}$$

Attenuation factor $AF = \frac{C_{ED}}{C_0}$

where:

C = concentration of contaminant at point x and time t (mg/l)
 C_0 = initial contaminant concentration in groundwater (mg/l)
 λ = decay constant = 0.693/half life for decay of contaminant in days
 a_x, a_y, a_z = longitudinal, vertical and lateral dispersivity (m)
 S_z, S_y = width and thickness of plume at source (in saturated zone) (m)
 u = rate of contaminant movement due to retardation (Table D2)

$$u = \frac{K i}{n R_f}$$

R_f = retardation factor (Table D2)
 n = effective porosity
 i = hydraulic gradient
 K = hydraulic conductivity (m/d)
 x = distance to compliance point (m)
 erfc = complementary error function
 erf = error function
 exp = exponential
 t = time since contaminant entered groundwater (days)

Note: Plume thickness at source, S_y , is equal to mixing zone thickness use in calculating the dilution factor. In order to calculate the remedial target, time (t) should be set as a large number (i.e. 10^{99} d) and the lateral and vertical offset should be set as zero. This solution assumes that vertical dispersion occurs in one direction only.

3.3.2 Derivation of 'K_d' (K_{d_NP}) and transport retardation factor (R_{f_NP}) for NPs

Although, the concept of a distribution coefficient (K_d) for NPs is considered to not be fully representative of the dynamic colloidal kinetic environment and nature of NP injections into aquifer systems, it could provide a useful basis for a screening level model.

Justification for the derivation of the distribution coefficient for NPs (K_{d_NP}) is as outlined below, and relies on estimates of the attachment and detachment coefficients for NPs which can be used to estimate the likely subsequent retardation between the injection and compliance point.

From eq. 10b (of DL 7.1, see Section 3.2.1 above), the rate of change of NP in the solid phase for a particular interaction type site i (S_i) is:

$$\rho_b \frac{\partial S_i}{\partial t} = \phi k_{att,i} \psi_i C - \rho_b k_{det,i} S_i \quad (\text{eq. 1})$$

At a downstream location, well outside of the injection zone, at a time period high compared to the start of the injection where there are likely to be relatively small changes in S_i, with a quasi-equilibrium conditions, then the following assumptions are likely to be valid:

$$\text{as } \partial t \rightarrow \infty \text{ and } \partial S_i \rightarrow 0 \text{ then } \frac{\partial S_i}{\partial t} \rightarrow 0 \quad (\text{eq. 2})$$

Hence eq. 1 can be re-arranged as follows:

$$0 = \phi k_{att,i} \psi_i C - \rho_b k_{det,i} S_i \quad (\text{eq. 3})$$

Or in terms of C [M L⁻³], NP concentration in the mobile phase:

$$C = \frac{\rho_b}{\phi} \left(\frac{k_{det,i}}{k_{att,i}} \right) \frac{S_i}{\psi_i} \quad (\text{eq. 4})$$

We can define a NP distribution coefficient, K_{d_NP} [L³ M⁻¹], as the ratio between NP in the solid phase S_i for interaction site i [-] and colloid (NP) concentration in the mobile (liquid) phase [M L⁻³], analogous to the solute distribution coefficient:

$$K_{d_NP} = \frac{S_i}{C} \quad (\text{eq. 5})$$

Inserting C from eq. 4 into eq. 5 gives:

$$K_{d_NP} = \psi_i \left(\frac{k_{att,i}}{k_{det,i}} \right) \frac{\phi}{\rho_b} \quad (\text{eq. 6})$$

Hence, the NP K_d can be related to the type of attachment mechanism (ψ_i) and ratio of the attachment and detachment coefficients for the NP – aquifer system.

From **Box 3** above the rate of solute contaminant movement, u [L T⁻¹], due to retardation is defined as:

$$u = \frac{Ki}{\phi R_f} \quad (\text{eq. 7})$$

with u inversely proportional to the solute retardation factor R_f [-] which is defined as:

$$R_f = 1 + K_d \frac{\rho_b}{\phi} \quad (\text{eq. 8})$$

Replacing K_d in eq. 8 with K_{d_NP} provides an estimate for the retardation factor for NPs as follows:

$$R_{f_NP} = 1 + K_{d_NP} \frac{\rho_b}{\phi} \quad (\text{eq. 8a})$$

$$R_{f_NP} = 1 + \psi_i \left(\frac{k_{att,i}}{k_{det,i}} \right) \quad (\text{eq. 8b})$$

Where the rate of NP movement, u_{NP} [$L T^{-1}$], due to retardation is defined as:

$$u_{NP} = \frac{Ki}{\phi R_{f_NP}} \quad (\text{eq. 9a})$$

$$u_{NP} = \frac{Ki}{\phi \left(1 + \psi_i \left(\frac{k_{att,i}}{k_{det,i}} \right) \right)} \quad (\text{eq. 9b})$$

Definition of terms and units used in eq. 1 to 9 above:

S_i = NP (colloid) concentration in the solid phase [-] for interaction type site i ;

C = NP (colloid) concentration in the mobile (liquid) phase [$M L^{-3}$];

$k_{att,i}$ = attachment coefficient [T^{-1}] for NP interacting with site i under aquifer conditions;

$k_{det,i}$ = detachment coefficient [T^{-1}] for NP interacting with site i under aquifer conditions;

ψ_i = is the attachment function [-] describing the attachment mechanism being described for interaction site i (linear, blocking, ripening, straining);

ϕ = effective porosity of the porous medium (aquifer) [-];

ρ_b = bulk density of the porous medium (aquifer) [$M L^{-3}$];

K_{d_NP} = NP (colloid) distribution coefficient [$L^3 M^{-1}$] describing the ratio of the solid (S_i) to liquid (C) concentration, assumed to be applicable to low concentration, quasi-equilibrium (i.e. close to “clean-bed”) conditions likely to exist in the aquifer downstream of the injection zone;

K = representative hydraulic conductivity [$L T^{-1}$] for the aquifer, between the injection and downstream regulatory compliance point;

i = representative hydraulic gradient [-] for the aquifer, between the injection and downstream regulatory compliance point;

R_{f_NP} = estimate for NP (colloid) retardation factor arising due to interaction of the NP with the aquifer matrix (via attachment and detachment processes);

u_{NP} = estimate for rate of NP (colloid) movement due to retardation following attachment and detachment.

Note: for the purposes of a screening model assessing potential risks to receptors located at length scales likely to be at least an order of magnitude higher than the distance over which visible evidence for injections are reported in the field or lab-scale (typically 1-5m), it has been assumed that a single interaction type mechanism is relevant so that:

- a single value for k_{att} and k_{det} can be used, which is representative of the interaction environment in the aquifer near to the regulatory compliance point;
- a linear attachment mechanism is applicable akin to a “clean bed” early stage attachment situation in a low-concentration NP environment, such that a value of $\psi=1$ can be assumed.

3.3.3 Comparison of concentration - travel distance profile between MNMs and the RSM model

The results of the analytical solution¹⁰ for the RSM incorporating NP retardation (Section 3.3.2) can be compared against the results of the numerical solution¹¹ currently included within the MNMs 2015 (v 1.012) model (Bianco et al., 2015)¹². The list of inputs used in the MNMs 2015 and RSM and how they relate to one another are provided in **Table 11**. Appendix 1 provides screen dumps for each of the main input screen steps for the MNMs model with the salient assumptions and justification as follows:

1. **Main Processes** screen: Micro- and nano-particles transport (numerical solution), Column transport test: 1D simulation option selected.
2. **Problem definition** screen: Single fluid (Newtonian) option selected (applicable to the 'far-field' compliance point zone where the groundwater viscosity is unlikely to be impacted by the injection fluids); Constant ionic Strength selected (representative value for the aquifer transport zone between injection and compliance point); Single active interaction site (NP attachment mechanism), with Linear Attachment assumed (i.e. 'clean-bed' low concentration quasi-equilibrium aquifer conditions close to compliance point).
3. **System Properties** screen: Flow field defined by 'Darcy's Velocity' (assume a constant flow field within the aquifer driven by the local groundwater velocity based on hydraulic gradient and conductivity); see **Table 11** for input values (Column length, Darcy velocity, Dispersivity, Clean Bed Effective porosity, Density of sand grains, Mean diameter of sand grains).
4. **Interaction Parameters** screen: see **Table 11** for input values (Attachment rate, Detachment rate).
5. **Initial and Boundary Conditions** screen: see **Table 11** for input values (Initial salt concentration, Stress (injection) period duration, NP concentration in the liquid phase and Ionic strength).
6. **Solver settings and output control** screen: time interval for breakthrough curve every 100s, number of (numerical solution calculation) points along the profile 200.

Comparison of the NP (iron) concentration - distance profile predicted by the two models after approximately 1 year (370 days) and 5 years (1850 days) has been undertaken and is shown in **Figure 1**. There is a good level of agreement between the analytical (RSM) and numerical approach (MNMs model) with the RSM predicting higher NP concentrations especially within the vicinity of the injection (see **Table 12**). [Note: the simulation period comparison was limited to 5 years as the MNMs model became unstable beyond this probably due to PC memory / processing limitations].

¹⁰ An analytical solution is one in which your variable(s) of interest can be represented and solved in an explicit expression – i.e. equations in Box 2 represent analytical solutions

¹¹ A numerical solution is often used for solving (or approximating) complex (partial) differential equations for which an explicit analytical solution is not available or multiple parameters are vary with the derivative (e.g. Equation 10a, Section 3.2.1 above)

¹² <http://areeweb.polito.it/ricerca/groundwater/software/MNMs.php>, accessed September 2016

Table 11: MNM 2015 & RSM model inputs (see Environment Agency, 2006), Hungary pilot site data from NanoRem Internal Deliverable (see also CL:AIRE, 2017)

Parameter Type	Input Parameter, abbreviation	Units	MNMs value	RSM value	Notes / Justification
Aquifer	Column length (distance to compliance point), x	m	100	100	user defined value, set according to site circumstance
Aquifer	Width of plume in aquifer at source, S_z	m	n/a	5	typical injection scale for NanoRem pilot sites (e.g. Hungary site), not important for this comparison as transverse dispersivity set to negligible value and zero lateral offset (z) assumed for compliance point
Aquifer	Plume thickness at source, S_y	m	n/a	10	typical scale for NanoRem pilot sites (e.g. Hungary site), not important for this comparison as transverse dispersivity set to negligible value and zero vertical offset (y) assumed for compliance point
Aquifer	Hydraulic gradient, i	Fraction	n/a	2.78×10^{-4}	value estimated for NanoRem Hungary pilot site, based on reported groundwater velocity (0.3 m d^{-1})
Aquifer	Hydraulic conductivity, K	m/d	n/a	4.320×10^2	mid-point value reported for NanoRem Hungary pilot site
Aquifer	Darcyan velocity (specific discharge), q	$\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$	1.390×10^{-6}	1.390×10^{-6}	derived as product of hydraulic conductivity and hydraulic gradient values for the NanoRem Hungary pilot site
Aquifer	Dispersivity (longitudinal), a_x	m	10	10	set at 10% of distance to compliance point (pathway length)
Aquifer	Dispersivity (transverse), a_z	m	n/a	1×10^{-14}	negligible low value assumed for RTM model
Aquifer	Dispersivity (vertical), a_y	m	n/a	1×10^{-14}	negligible low value assumed for RTM model
Aquifer	Clean bed (aquifer) effective porosity, n	-	0.4	0.4	value reported for NanoRem Hungary pilot site
Aquifer	Density of sand grains (aquifer materials), ρ_b	kg m^{-3}	1600	1600	assumed value for NanoRem Hungary pilot site (sand and gravel)
Aquifer	Mean diameter of sand grains (for straining)	m	0.001	n/a	straining not assumed applicable at compliance point, not a RTM input
Aquifer	Initial salt concentration (ionic strength), C_{i0}	mM	10	n/a ^b	select appropriate values of k_{att} and k_{det} to yield a $k_{att} : k_{det}$ ratio value determined at similar ionic strength value (e.g. see Table 10)
NP	Attachment coefficient (rate), k_{att}	s^{-1}	2.3148×10^{-3}	$2.3148 \times$	assumed values, same values used in each model
NP	Detachment coefficient (rate), k_{det}	s^{-1}	1.1574×10^{-5}	$1.1574 \times$	assumed values, same values used in each model
NP	Half-life for degradation of NP in water, $t_{1/2}$	days	n/a	1×10^{99}	assume negligible degradation of metal based NPs – i.e. set at infinitely large half-life to predict an infinitely small NP decay rate - could be used to account for oxidation, etc processes
Injection	Stress period duration (length of injection), t	s	3.2×10^7 or 16×10^7	3.2×10^7 or 16×10^7	continuous injection assumed whereby the stress period duration is the same as the time period since NPs entered the groundwater (i.e. over which the calculation is made), set to 370 days or 1850 days.
Injection	NP concentration in liquid phase (concentration at source), C_0	kg m^{-3}	4.76	4.76	average Iron NP concentration injected into Hungary pilot site (i.e. 35% of total Carbo-Iron [®] injected)

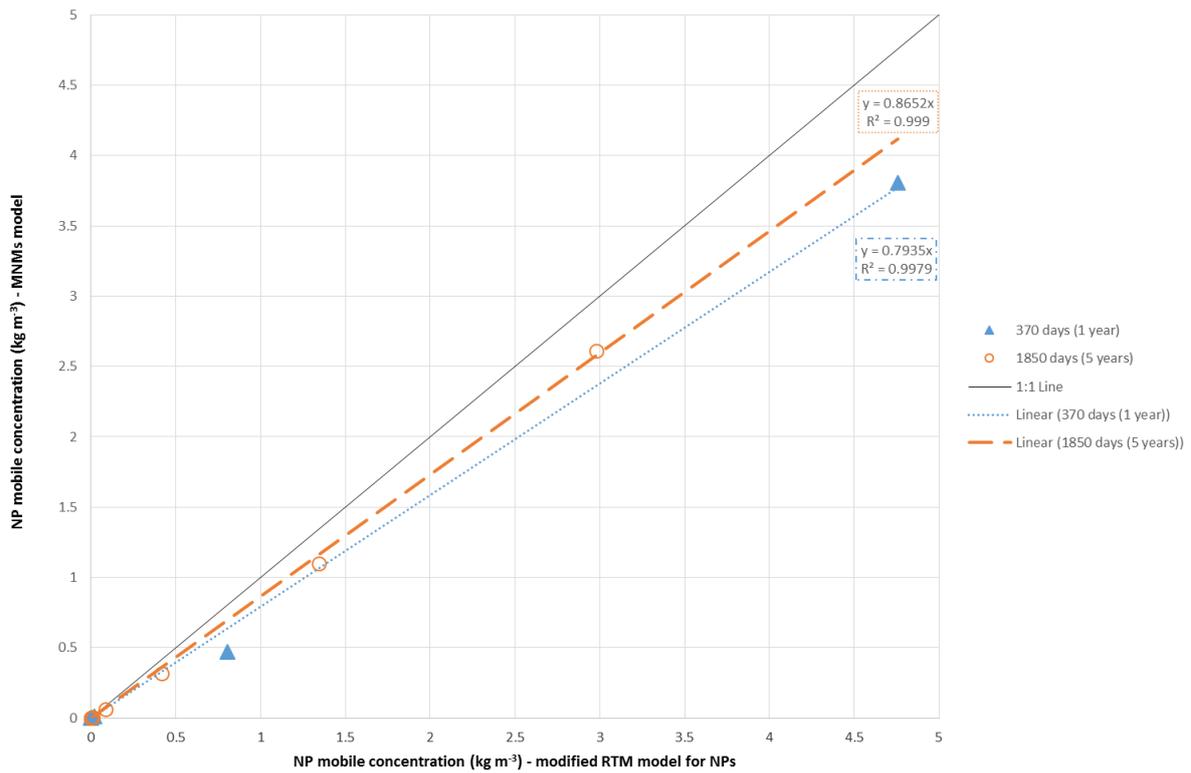


Figure 1: Comparison of MNMs and the RSM predicted NP (Fe) concentration at the same distances downstream of the (continuous) injection point after approximately 1 year and 5 years

Table 12: MNM 2015 and RSM outputs – see **Table 11** for inputs

Distance (m)	NP concentration (kg m ⁻³) 370 days (1 year)		NP concentration (kg m ⁻³) 1850 days (5 years)	
	RSM	MNMs	RSM	MNMs
0	4.76E+00	3.81E+00	4.76E+00	
5	8.03E-01	4.71E-01	2.98E+00	2.61E+00
10	2.04E-02	1.16E-02	1.34E+00	1.10E+00
15	6.40E-05	7.33E-05	4.17E-01	3.21E-01
20	0.00E+00	1.53E-07	8.73E-02	6.40E-02
25	0.00E+00	1.30E-10	1.21E-02	8.74E-03
30	0.00E+00	5.21E-14	1.09E-03	8.19E-04
35	0.00E+00	1.11E-17	6.43E-05	
40	0.00E+00	1.38E-21	1.30E-06	4.65E-06
45	0.00E+00	1.06E-25	0.00E+00	
50	0.00E+00	5.37E-30	0.00E+00	4.10E-09
55	0.00E+00	1.87E-34	0.00E+00	
60	0.00E+00	3.98E-38	0.00E+00	1.04E-12
65	0.00E+00	7.73E-43	0.00E+00	
70	0.00E+00	1.13E-47	0.00E+00	8.56E-17
75	0.00E+00	1.27E-52	0.00E+00	
80	0.00E+00	1.13E-57	0.00E+00	2.52E-21
85	0.00E+00	8.02E-63	0.00E+00	
90	0.00E+00	4.05E-69	0.00E+00	2.91E-26
95	0.00E+00	2.20E-73	0.00E+00	
100	0.00E+00	8.77E-79	0.00E+00	1.44E-31

3.3.4 Travel distance and times variability/sensitivity based on plausible inputs

For the continuous injection scenario as defined in **Table 11** the RSM can be used to estimate the time at which 'breakthrough' (very low but non-zero concentration, $7.95 \times 10^{-8} \text{ kg m}^{-3}$) occurs at a distance 100m downstream (23 years), with the NP concentration distance profiles at specific times (1-50 years) as shown in **Figure 2**. Clearly, a continuous injection for the lengths of time assumed is unrealistic but even for such a cautious assumption the travel time is predicted to be relatively high and travel distance limited, for this scenario.

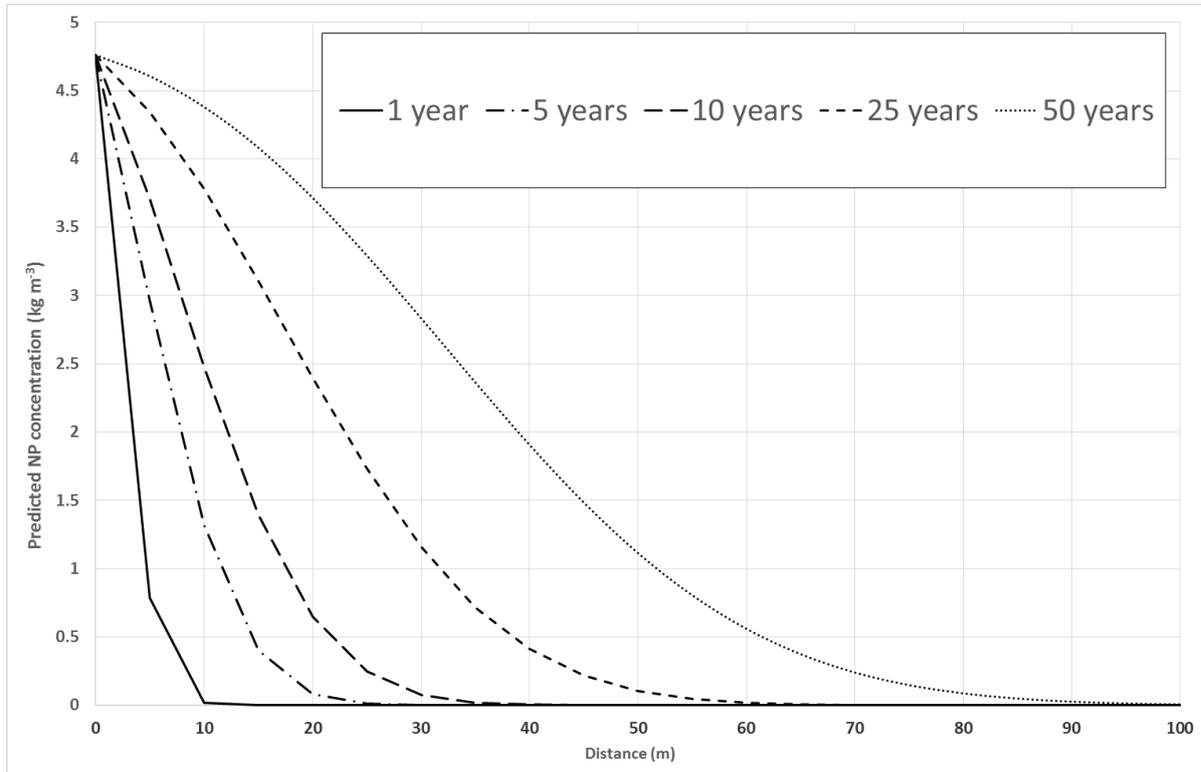


Figure 2: NP (Fe) Concentration Distance profiles predicted by the RSM at various times (1-50 years) assuming continuous injection at $x=0\text{m}$ (**Note:** breakthrough at 100m (i.e. non-zero concentration) predicted after 23 years, see also **Figure 3**), see **Table 11** for model inputs

Number of NPs

Assuming NPs are spherical with a mean diameter of 100nm (upper limit for definition of a NP) and comprising solely of iron (density of 7870 kg m^{-3}) an estimate of the number of particles can be made – a simplistic (i.e. original NPs may be dissolved and/or reacted with the aquifer or co-substances present) but likely cautious assumption with respect to particle number (i.e. injected NPs will generally aggregate resulting in a larger mean diameter and so lower aggregated particle number). The concentration profiles of **Figure 2** can be used to generate the mobile particle number (NP L^{-1} water) estimates shown in **Figure 3**. Given the assumptions about small particle size (100nm) and purity the number of particles estimated to reach 100m after 25 years is relatively high ($9.7 \times 10^7 \text{ NP / L}$).

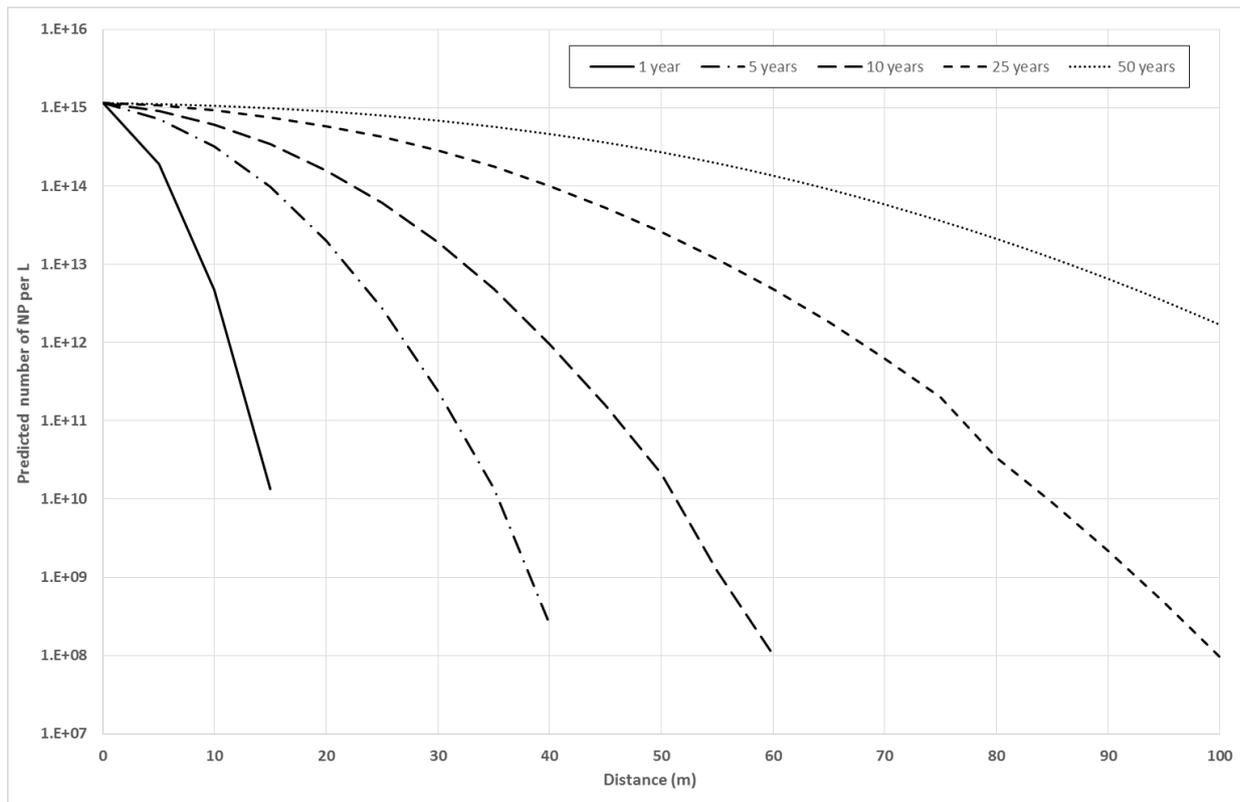


Figure 3: Likely upper estimates of the number of NP (Fe) particles (assuming mean diameter of 100nm) variation with distance predicted using the **Figure 2** concentration profiles and simplified assumptions (see text) (**Note:** log-scale for y-axis, zero concentrations not plotted on log-scale)

Concentration distance profile

For the aquifer and NP inputs in **Table 11** the MNMs model was used to provide an estimate for the Concentration Distance profile (e.g. cumulative injection time at the NanoRem Hungary pilot site) at an average injection concentration of $4.76 \text{ kg Fe m}^{-3}$ (i.e. 35% of Carbo-Iron[®] injected at a concentration 13.6 kg m^{-3}). The profiles at the end of the injection period and at +1 day, +1 week, +1 month and +1 year following the single injection are shown in **Figure 4**, with only very low concentrations estimated even at 20m downstream after 1 year ($1.653 \times 10^{-9} \text{ kg m}^{-3}$).

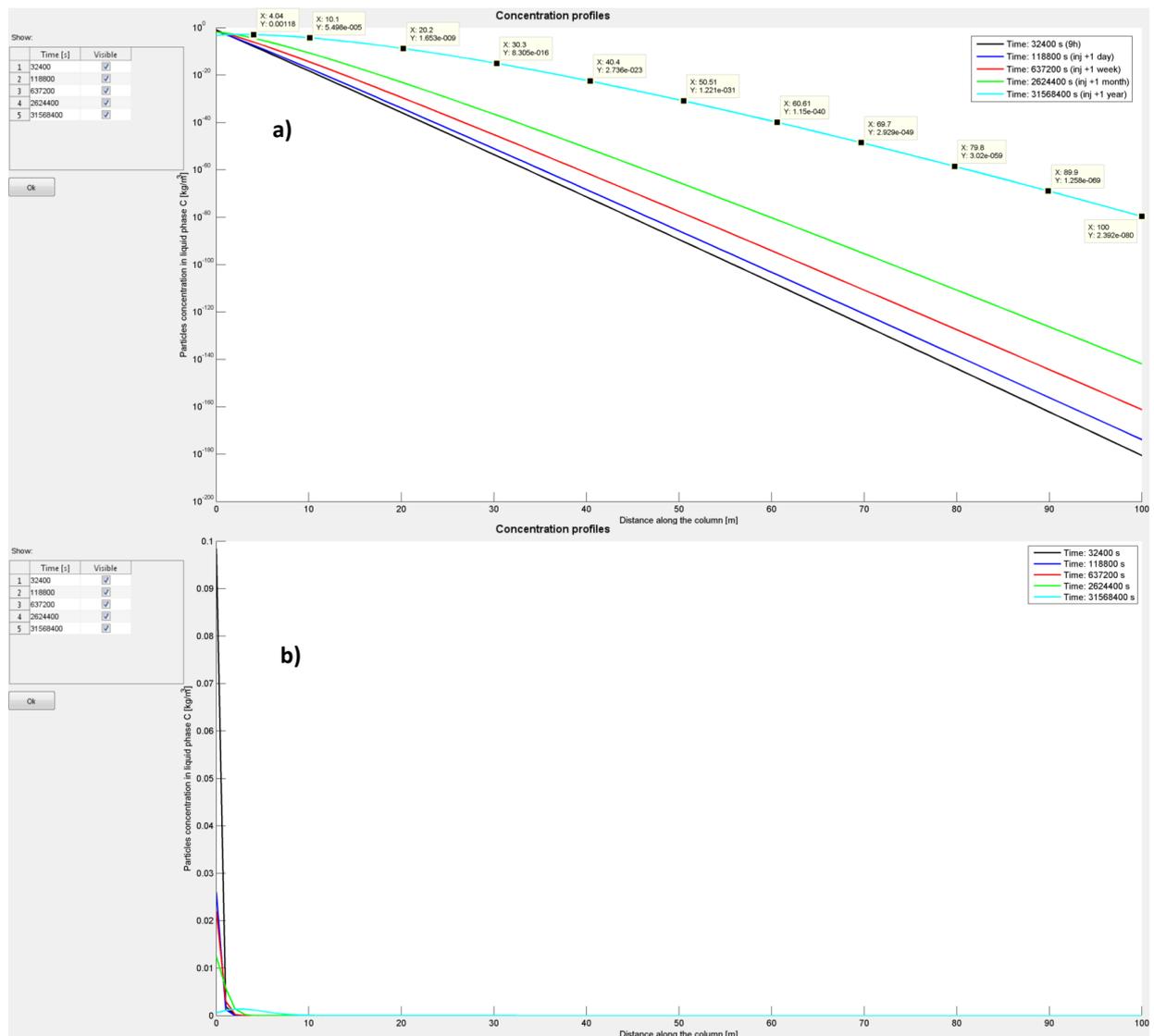


Figure 4a, b: NP (Fe) Concentration Distance profiles predicted by the MNMs model at various times (end of 9h injection, +1day, +1week, +1month, +1year) following **single injection at x=0m**, see **Table 11** for model inputs. a) log-scale for Y-axis, b) linear for Y-axis.

3.3.5 Impact of values of k_{att} and k_{det} (i.e. $k_{att} : k_{det}$) on retardation of NP

The importance of the $k_{att} : k_{det}$ ratio on NP retardation downstream of any injection, as predicted by the RSM, is illustrated by **Figure 5**, **Figure 6** and **Figure 7**. For inputs see **Table 11**.

Figure 5 shows following 1 year of continuous relatively high injection concentration (4.76kg m^{-3}) of NPs (equivalent Fe concentration injected as Carbo-Iron[®]) an attachment to detachment coefficient ratio ($k_{att}:k_{det}$) of 10 or greater is sufficient to significantly retard the movement of NPs downstream. Following 25 years (continuous injection) a value of $k_{att}:k_{det}$ of 100-200+ is required to have the same impact. Given that a continuous injection at such high concentrations is unlikely to be economically or scientifically justified (i.e. injections would usually last a few days) then ratios for the attachment to detachment coefficient of between 10 and 100 may reasonably be expected to significantly reduce NP transport within the downstream aquifer over the period of 1 – 25 years (Note: the RSM does not currently model a single injection event and assumes a continuous NP ‘source’ term). **Figure 6** indicates

the importance of time following the start of the injection in combination with the assumed value for the $k_{att} : k_{det}$ ratio.

Figure 7 illustrates the variation in the NP "distribution coefficient" (K_{d_NP}), retardation factor (R_{f_NP}) and rate of NP flow due to retardation (u_{NP}) with assumed value for the ratio of attachment to detachment coefficient ($k_{att}:k_{det}$).

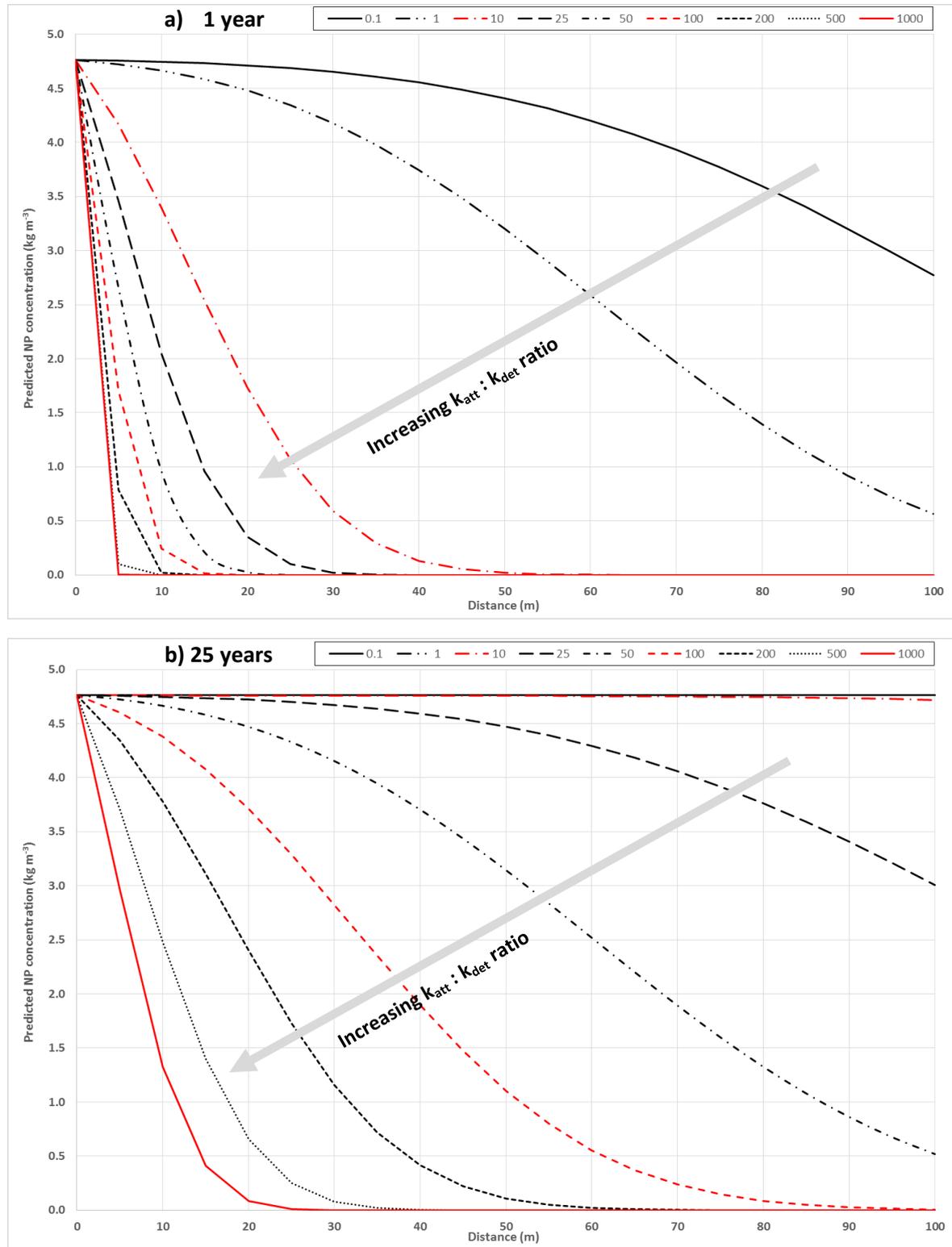


Figure 5a, b: NP (Fe) concentration distance profiles predicted by the RSM for a range of $k_{att}:k_{det}$ ratios at (a) 1-year and (b) 25-years for a continuous injection upstream, see **Table 11** for inputs

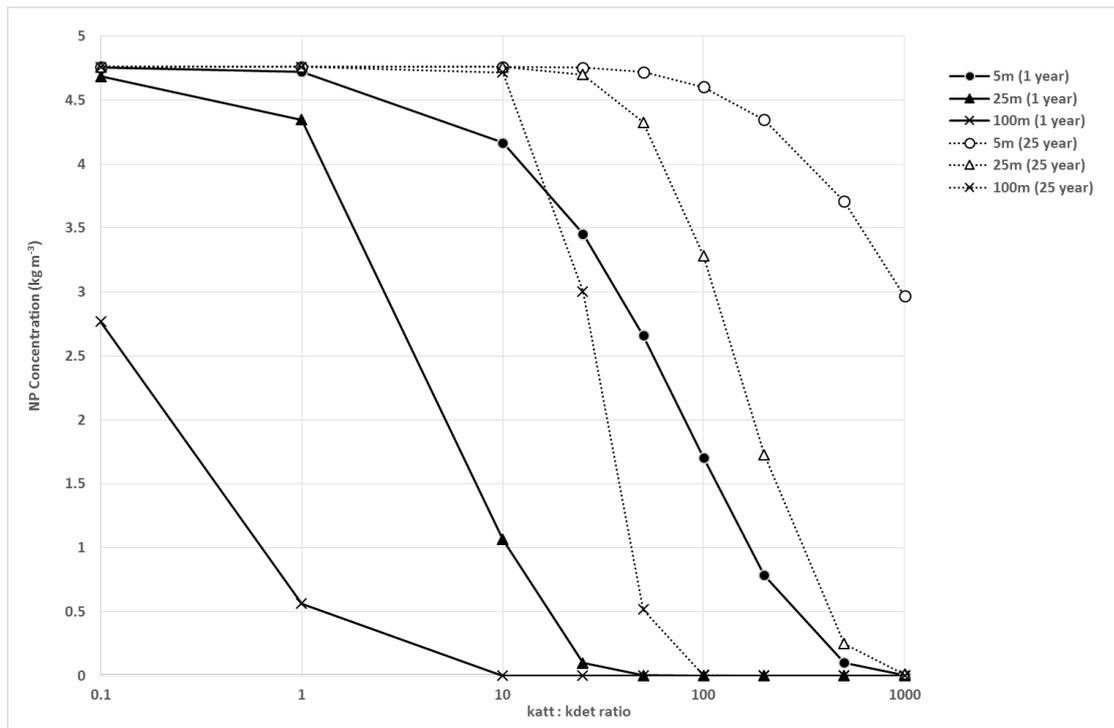


Figure 6: Dependence of predicted NP concentration at defined downstream distances (5, 25 & 100m) on the attachment to detachment coefficient ratio (**Note:** X-axis plotted as a log scale), see **Table 11** for inputs

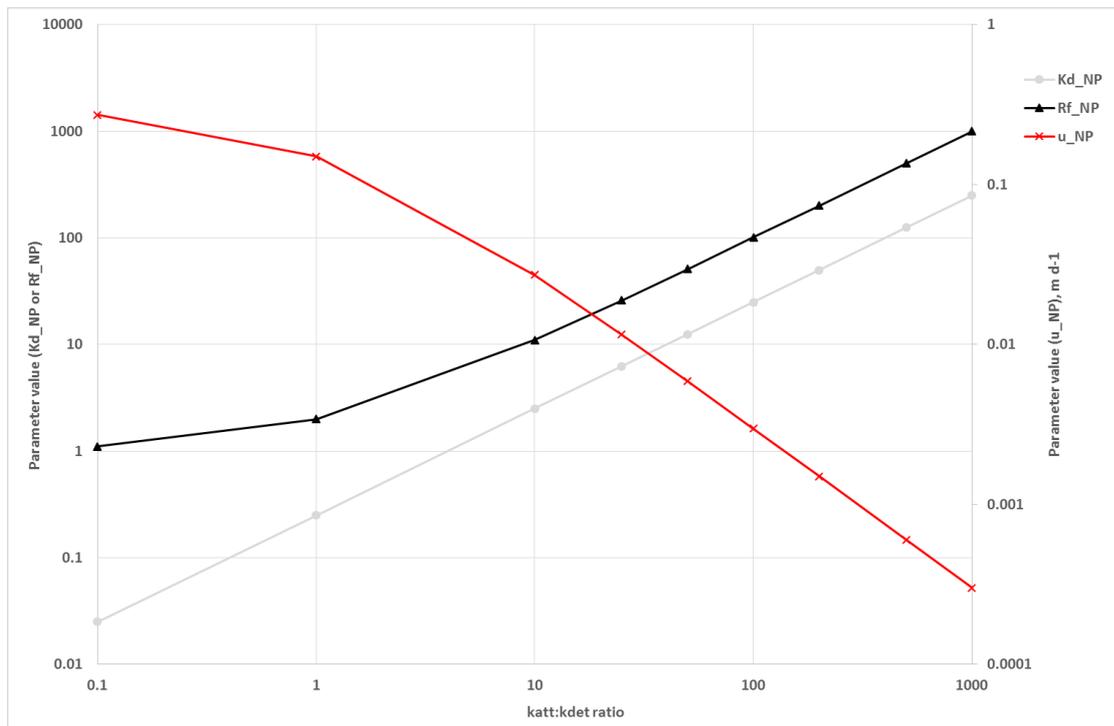


Figure 7: Variation of retardation parameters K_{d_NP} , R_{f_NP} and u_{NP} with values for the attachment to detachment coefficient ratio (**Note:** plotted on a log-log scale)

3.3.6 Comparison against field data

The Hungary field pilot site (Balassagyramat) field parameters (see **Table 11** and CL:AIRE (2017)) have been used as inputs to generate some of the model outputs presented. This site provides Iron concen-

tration distance profiles along two approximately parallel transects (A and B, insets of **Figure 8**), for the period immediately prior to the Carbo-Iron[®] injection, 10 September 2015, through to the 13th July 2016 (Fe reported as dissolved total in units of mg dm^{-3} , i.e. mg L^{-1})¹³. The two concentration transects (A and B) (**Figure 8**) provide some comparison to current NP model predictions, assuming the dissolved iron field data is an indicator of the mobile NPs predicted by the model (Note ideally total iron, including any mobile colloids/sediments, would be used although this data has apparently not been reported). Within the UK an Environmental Quality Standard (EQS) of 1mg L^{-1} for dissolved Iron (HMSO, 2015) has been applied in accordance with the Water Framework Directive (Iron is an Annex VIII specific pollutant). The UK EQS is only significantly exceeded (maximum reported concentration of 80.7mg L^{-1}) within close proximity of the injection zone (circa 2m) with elevated levels persisting for circa 10 months (July 2016). Monitoring wells CMT-4/2 and CMT-4/3 (approximately 12m downstream) show an increase in dissolved iron one month following injection (21 October 2015 sampling $0.98\text{--}2.09\text{mg L}^{-1}$, **Figure 8a**) though by 9 December 2015 concentrations were well below the UK EQS ($0.04\text{--}0.06\text{mg L}^{-1}$, **Figure 8a**).

The observations from the Hungary field pilot site (**Figure 8b**, Transect B) indicate that by 10 months post injection (July 2016) dissolved iron concentrations at up to 8m downstream were well below the UK EQS value of 1mg L^{-1} (i.e. $1 \times 10^{-3}\text{kg m}^{-3}$).

The data for Transect A (**Figure 8a**) appears to report more significant transport within a few metres (i.e. higher dissolved Fe concentrations) of the injection, although no data is available for July 2016 to confirm the temporal trend.

However, the available data at 8m along Transect A (CMT-3/2 and CMT-3/3, 0.02mg L^{-1}) is of the same order of magnitude to that predicted by the MNMs model at 10m after 1 year following a single injection ($5.5 \times 10^{-5}\text{kg m}^{-3}$ or 0.05mg L^{-1} , **Figure 4a**). Although, it should be noted that the MNMs model is predicting the mobile nanoparticles rather than the dissolved iron (cf Hungary reported data), and so a direct comparison may not be applicable.

Analysis of soil samples taken from the standard diameter wells CMT-9 (approximately 6 months after the injection) approximately 0.5m downstream of the injection point I-3 (Balassagyarmat pilot site) confirmed the presence of Carbo-Iron[®] particles using TOC (Total Organic Carbon) as a marker, with a mean particle loading at CMT-9 ($12.8\text{--}13.7\text{mbgl}$) of about 0.4 wt-%. This suggests limited lateral movement away from the injection zone (CL:AIRE, 2017).

¹³ Raw data supplied by Tamas Lazlo (Golder Associates, August 2016)

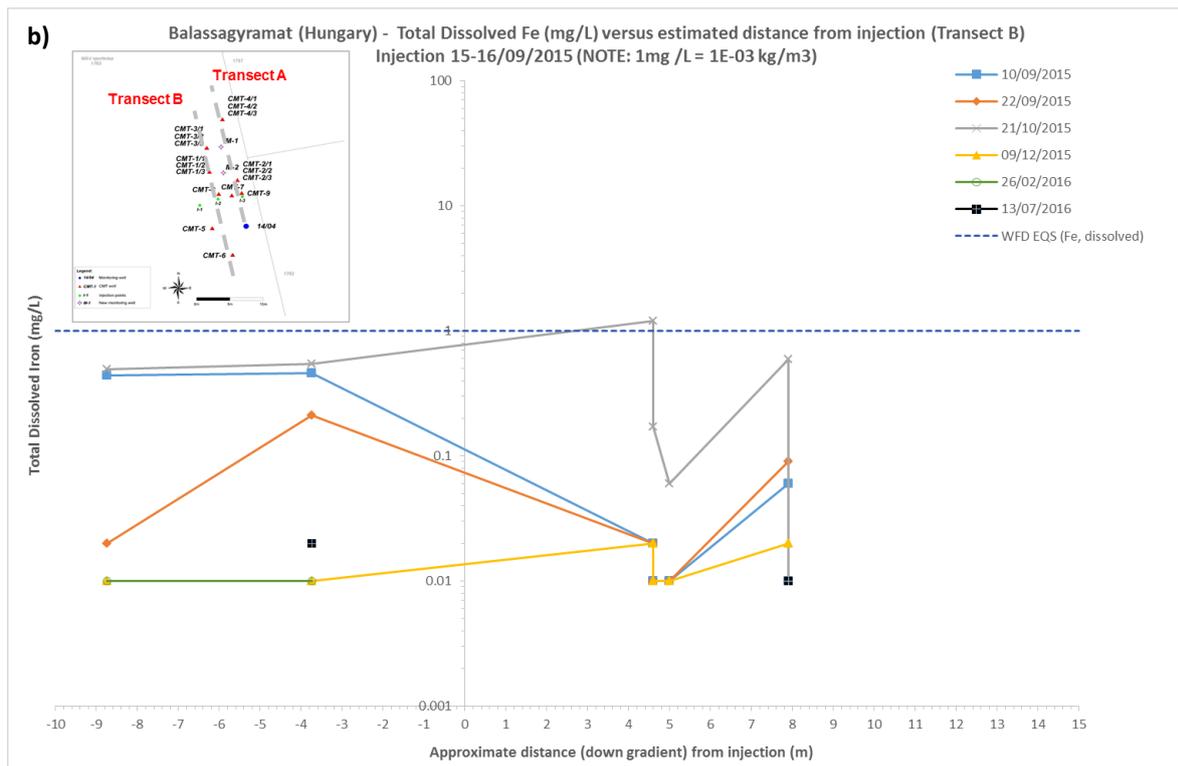
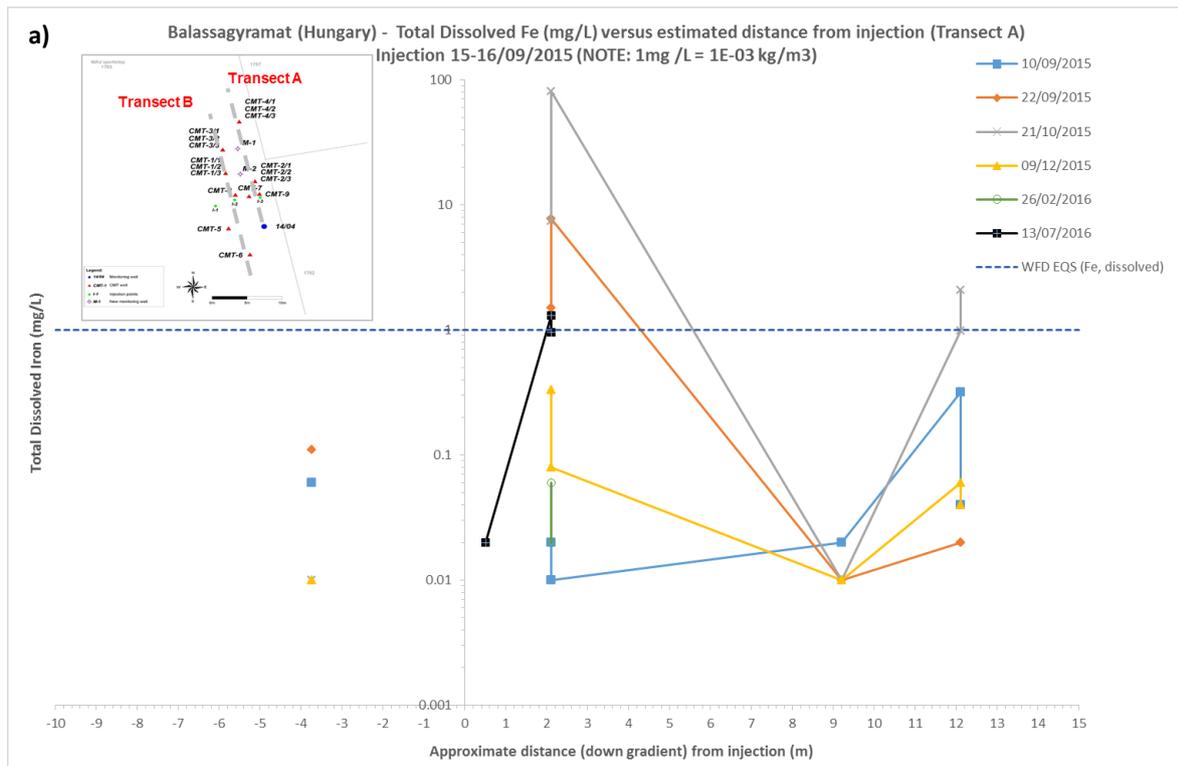


Figure 8a, b: Variation of total dissolved iron with approximate distance from the injection (x=0m) at the Hungary pilot site (Balassagyramat), along two transects, following injection of Carbo-Iron® NPs (Note: y-axis plotted as log scale)

3.3.7 Large Scale Flume data (University of Stuttgart)

The Large Scale Flume Carbo-Iron[®] experiment data developed under NanoRem WP8 (see footnote 4 above) could potentially provide some useful data to which the MNMs model could be used to derive values for k_{att} or k_{det} values.

3.3.8 Values of k_{att} and k_{det} based on column experiments for the range of NanoRem particles

Table 13 provides a summary of the attachment coefficients derived from the WP4 NanoRem column experiments investigating the mobility of the initial NPs and those subsequently 'optimised' with the addition of stabilisers (as indicated) and as reported under internal deliverables IDL 4-2 and IDL 4-3 of WP4. More recently reported data for column experiments, under field relevant conditions, is provided as **Table 14**.

Generally, the reported NP attachment coefficients¹⁴ for Nanofer 25S were higher than most other NPs types (**Figure 9a, b**), with attachment coefficients varying across all NPs between $4.9 \times 10^{-5} \text{ s}^{-1}$ (CMC stabilised Carbo-Iron[®]) and $5.4 \times 10^{-2} \text{ s}^{-1}$ (Carbo-Iron[®]).

The NPs with the lowest attachment coefficients and highest predicted transport distances of up to circa 20-30m (as indicated by the predicted $L_{t,99.9\%}$ travel distances)¹⁵ were the unmodified Fe-Oxides or Trap-OX Fe-Zeolites, milled ZVI (agar-agar) and CMC Carbo-Iron[®] NPs (**Table 13, Table 14**). Generally there was an inverse relationship between k_{att} and $L_{t,99.9\%}$, although the unmodified Carbo-Iron[®] results appear to deviate from this relationship (**Figure 9a**) as reported under IDL 4-2 and IDL 4-3. A similar pattern without the deviations for the modified Carbo-Iron[®] is reported under DL 4-3 under field relevant conditions (**Figure 9b**).

Only the attachment coefficients have been reported as part of IDL 4-2 and IDL 4-3 and no detachment coefficients were reported, hence the $k_{att}:k_{det}$ ratio cannot be currently calculated from these sources. A set of attachment and detachment coefficients were reported under DL4-2 (Table 24, Micic Batka & Hofmann, 2016) for Fe-oxides (Nano-Goethite), though no variation was reported between the attachment and detachment coefficients in the cascading column experiments (i.e. $k_{att} = k_{det} = 1 \times 10^{-4} \text{ s}^{-1}$). However, following an email discussion between LQM, WP7 (Politecnico di Torino) and WP4 (University of Duisburg-Essen) (22-25 November 2016, the most recent discussions), it is likely that the experimental set-up (e.g. variation in packing density of materials) may not be optimised for deriving k_{att} and k_{det} and the values reported are default MNM values – i.e. assumed rather than fitted parameters. It is considered unlikely that the rate of attachment and detachment would be exactly the same in an environment where low NP concentrations and hence non-equilibrium conditions would be expected.

¹⁴ Reported as particle deposition rate coefficient (k) and calculated after Kretschmar *et al.* (1999) and Tufenkji & Elimelech (2004) as described in IDL 4-1 (Section 3.3.1, Hofmann, 2013)

¹⁵ Predicted NPs travel distances derived using column properties and concentration breakthrough curves after Elimelech *et al.* (1998) as described in IDL 4-1 (Section 3.3.1, Hofmann, 2013)

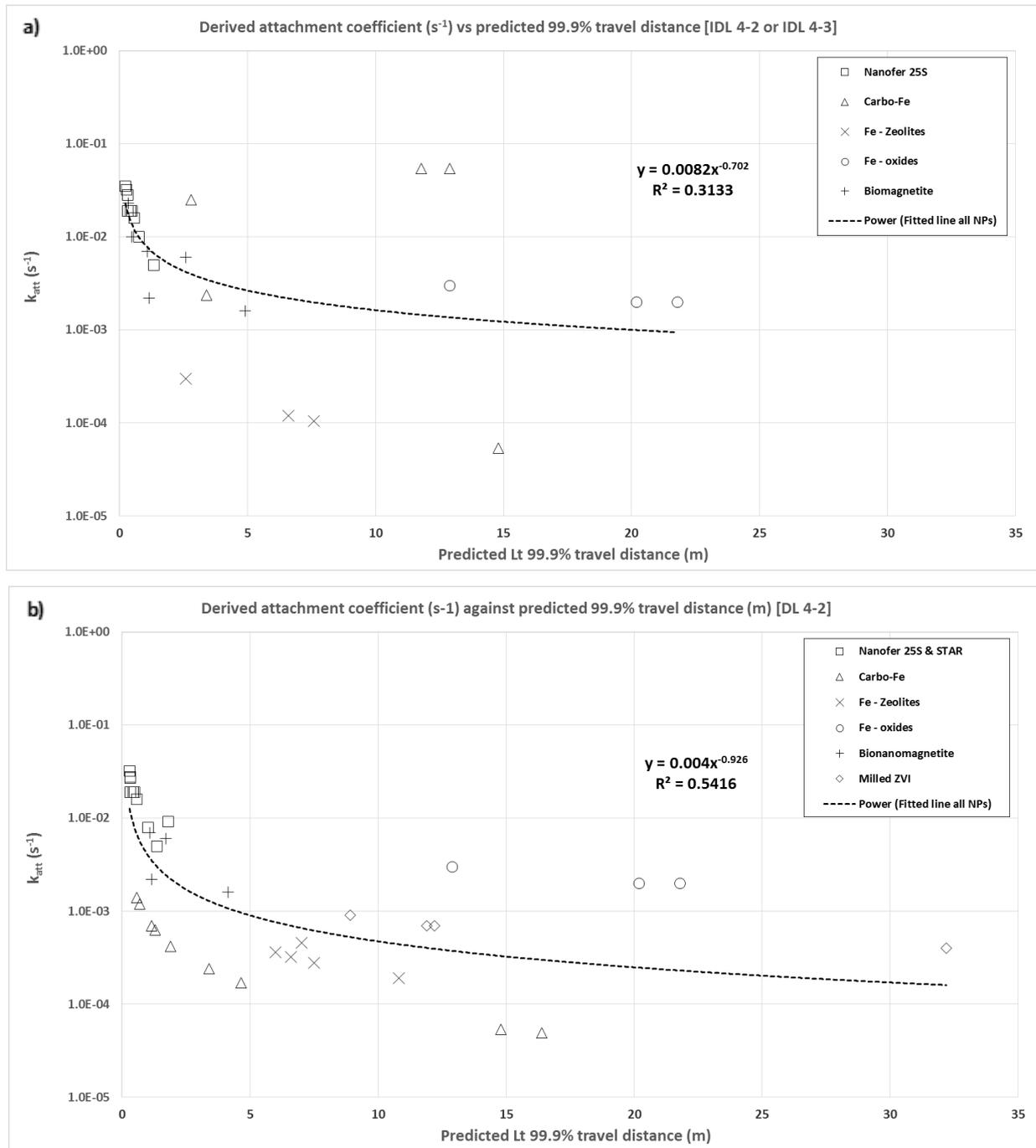


Figure 9a, b: Variation of derived attachment coefficient (s^{-1}) against predicted 99.9% travel distance (m) for NPs: **a)** at start/optimised in column experiments [Source IDL 4-2 and IDL 4-3]; **b)** optimised under field relevant conditions [Source DL 4-2]

Table 13: Attachment ('deposition') coefficients as reported by the NanoRem WP4 column experiments for the "starting" and "optimised" nano-particles investigated, plus salient meta-data [Source: IDL4-2 (Hofmann et al., 2015) or IDL 4-3 (Hofmann et al., 2016)]

Optimised NP (Y/N)	NP Type	NPs injection conc (g/L)	Type of porous media	Effective porosity	Type of fluid	Column dimensions (D x L, cm)	flow velocity (m d ⁻¹)	α (-)	$L_{t,99.9\%}$ (m)	k_{att} (s ⁻¹) (reported as k in IDL or DL)	k_{att} (d ⁻¹)	Source
N	Nanofer 25S	1	M.I	0.40	F.l.s	2.5x10	100	0.28	0.77	1.00E-02	864	IDL 4-2 page 4 - Table 3
N	Nanofer 25S	1	M.II	0.30	F.l.s	2.5x10	100	0.93	0.23	3.50E-02	3024	IDL 4-2 page 4 - Table 3
N	Carbo-Iron®	5.7	M.I	0.33	F.l.s	1.6x25	10	n/a	11.8	5.40E-02	4666	IDL 4-2 page 4 - Table 3
N	Carbo-Iron®	5.7	M.I	0.33	F.l.m	1.6x25	10	n/a	12.9	5.40E-02	4666	IDL 4-2 page 4 - Table 3
N	Carbo-Iron®	5.7	M.I	0.30	F.l.h	1.6x25	10	n/a	2.8	2.50E-02	2160	IDL 4-2 page 4 - Table 3
N	Trap-Ox Fe- Zeolites	1	M.I	0.42	F.l.s	1.7x20	10	0.33	2.6	3.00E-04	26	IDL 4-2 page 4 - Table 3
N	Fe-oxides (Nano-Goethite)	1	M.II	0.35	F.l.s	3.6x20	43	n/a	20.2	2.00E-03	173	IDL 4-2 page 4 - Table 3
N	Fe-oxides (Nano-Goethite)	1	M.II	0.33	F.l.m	3.6x20	43	n/a	12.9	3.00E-03	259	IDL 4-2 page 4 - Table 3
N	Fe-oxides (Nano-Goethite)	1	M.II	0.33	F.l.h	3.6x20	43	n/a	21.8	2.00E-03	173	IDL 4-2 page 4 - Table 3
N	Biomagnetite	1	M.I	n/a	F.l.s	2.8x11.6	100	n/a	0.48	1.00E-02	864	IDL 4-2 page 4 - Table 3
Y	Nanofer 25S	1	M.I	0.40	F.l.m	2.5x10	100	0.142	0.313	1.90E-02	1642	IDL 4-3 page 79 - Table A 5
Y	Nanofer 25S + 10mg/L humate	1	M.I	0.40	F.l.m	2.5x10	100	0.142	0.313	1.90E-02	1642	IDL 4-3 page 80 - Table A 6
Y	Nanofer 25S	1	M.II	0.40	F.l.m	2.5x10	100	0.139	0.287	3.20E-02	2765	IDL 4-3 page 81 - Table A 7
Y	Nanofer 25S + 10mg/L humate	1	M.II	0.40	F.l.m	2.5x10	100	0.122	0.326	2.80E-02	2419	IDL 4-3 page 82 - Table A 8
Y	Nanofer 25S	1	P.M.3	0.27	F.l.m	2.5x10	100	0.133	0.484	1.90E-02	1642	IDL 4-3 page 83 - Table A 9
Y	Nanofer 25S + 10mg/L humate	1	P.M.3	0.27	F.l.m	2.5x10	100	0.112	0.574	1.60E-02	1382	IDL 4-3 page 84 - Table A 10
Y	Nanofer 25S	1	P.M.4	0.28	F.l.m	2.5x10	100	0.125	0.313	2.80E-02	2419	IDL 4-3 page 85 - Table A 11
Y	Nanofer 25S + 10mg/L humate	1	P.M.4	0.28	F.l.m	2.5x10	100	0.088	0.443	1.90E-02	1642	IDL 4-3 page 86 - Table A 12
Y	Activated Nanofer Star-PAA	1	M.I	0.39	F.l.s	2.5x10	100	0.442	1.352	5.00E-03	432	IDL 4-3 page 87 - Table A 13
Y	Activated Nanofer Star-PAA	1	M.II	0.39	F.l.s	2.5x10	100	0.442	1.352	5.00E-03	432	IDL 4-3 page 88 - Table A 14
Y	Carbo-Iron® + CMC	5.7	M.I	0.37	F.l.s	1.6x25	10	0.05	14.8	5.40E-05	5	IDL 4-3 page 90 -Table A 17
Y	Carbo-Iron® + CMC	5.7	M.I	0.38	F.l.h	1.6x25	10	0.21	3.4	2.36E-03	204	IDL 4-3 page 90 -Table A 17
Y	Trap-Ox Fe - Zeolites (Fe-BEA-35)	10	M.I	0.38	F.l.h	1.7x20	10	0.1	6.6	1.20E-04	10	IDL 4-3 page 95 - Table A 19
Y	Trap-Ox Fe - Zeolites (Fe-MFI-120)	10	M.I	0.38	F.l.h	1.7x20	10	0.09	7.6	1.05E-04	9	IDL 4-3 page 95 - Table A 19
Y	Biomagnetite	1	M.I	0.40-0.45	F.l.s	2.8x11.6	1, 10, 100	0.1936	0.349	2.29E-02	1979	IDL 4-3 page 96 - Table A 20
Y	Biomagnetite + guar gum	1	M.I	0.40-0.45	F.l.s	2.8x11.6	100	0.0261	1.09	7.00E-03	605	IDL 4-3 page 96 - Table A 20
Y	Biomagnetite + agar	1	M.I	0.40-0.45	F.l.s	2.8x11.6	100	0.0053	1.1581	2.20E-03	190	IDL 4-3 page 96 - Table A 20
Y	Biomagnetite + starch	1	M.I	0.40-0.45	F.l.s	2.8x11.6	100	0.2716	2.59	6.00E-03	518	IDL 4-3 page 96 - Table A 20
Y	Biomagnetite + humic salt solution	1	M.I	0.40-0.45	F.l.s	2.8x11.6	100	0.0943	4.903	1.60E-03	138	IDL 4-3 page 96 - Table A 20

Notes: $L_{t,99.9\%}$ = predicted travel distance, 99.9% NP removal; α = attachment efficiency; M.I = pre-treated reference material fine grained quartz sand Dorsilit® Nr. 8; M.II = commercial available quartz material; P.M.3 = sand from Usti nad Labem, Písečná, Czech Republic; P.M.4 = sand from the Bad Zurzach site, Switzerland; F.l.s = soft water (40-48 mgCaCO₃ L⁻¹); F.l.m = moderately hard water (80-100 mgCaCO₃ L⁻¹); F.l.h = hard water (280-320 mgCaCO₃ L⁻¹).

Table 14: Attachment ('deposition') coefficients as reported by the NanoRem WP4 column experiments for "optimised" nano-particles under field relevant conditions, plus salient meta-data [Source: DL4-2 (Micic Batka & Hofmann, 2016), some data reported is a repeat of data first reported under IDL4-2 or 4-3 – see **Table 13**]

Optimised NP (Y/N)	NP Type	NPs injection conc	Type of porous media	Effective porosity	Type of fluid	Column dimensions (D x L, cm)	flow velocity (m d ⁻¹)	α (-)	$L_{t,99.9\%}$ (m)	k_{att} (s ⁻¹) (reported as k in DL)	k_{att} (d ⁻¹)	Source
N	Nanofer 25S	1	M.I	0.397	F.I.m	2.5x25 or 50?	100	0.14	0.31	1.90E-02	1642	DL 4-2 page 10 - Table 1
Y	Nanofer 25S	1	Na humate-coated M.I	0.397	F.I.m	2.5x25 or 50?	100	0.12	1.79	9.20E-03	795	DL 4-2 page 10 - Table 1
N	Nanofer 25S	1	M.II	0.267	F.I.m	2.5x25 or 50?	100	0.14	0.29	3.20E-02	2765	DL 4-2 page 10 - Table 1
Y	Nanofer 25S	1	Na humate-coated M.II	0.267	F.I.m	2.5x25 or 50?	100	0.12	0.32	2.80E-02	2419	DL 4-2 page 10 - Table 1
N	Nanofer 25S	1	Spochemie I, CZ	0.266	F.I.m	2.5x25 or 50?	100	0.13	0.48	1.90E-02	1642	DL 4-2 page 10 - Table 1
Y	Nanofer 25S	1	Na humate-coated Spochemie I, CZ	0.266	F.I.m	2.5x25 or 50?	100	0.11	0.57	1.60E-02	1382	DL 4-2 page 10 - Table 1
N	Nanofer 25S	1	Solvay, CH	0.283	F.I.m	2.5x25 or 50?	100	0.12	0.31	2.70E-02	2333	DL 4-2 page 10 - Table 1
Y	Nanofer 25S	1	Na humate-coated Solvay, CH	0.283	F.I.m	2.5x25 or 50?	100	0.09	0.44	1.90E-02	1642	DL 4-2 page 10 - Table 1
Y	Nanofer STAR in 3% PAA	1	M.I (Dorsilit®)	0.40	F.I.s	2.5x25 or 50?	100	0.442	1.35	5.00E-03	432	DL 4-2 page 20 - Table 4
Y	Nanofer STAR in 3% PAA	1	M.II (VEGAS)	0.30	F.I.s	2.5x25 or 50?	100	0.621	1	8.00E-03	691	DL 4-2 page 20 - Table 4
Y	Milled ZVI - agar agar-stabilised	1	M.I (Dorsilit®)	0.397	F.I.s	2.5x22	100	0.0023	11.9	7.00E-04	60	DL 4-2 page 31 - Table 7
Y	Milled ZVI - agar agar-stabilised	1	M.II (VEGAS)	0.298	F.I.s	2.5x22	100	0.0048	8.9	9.00E-04	78	DL 4-2 page 31 - Table 7
Y	Milled ZVI - agar agar-stabilised	1	Spolchemie I, CZ	0.262	F.I.s	2.5x22	100	0.0032	32.2	4.00E-04	35	DL 4-2 page 31 - Table 7
Y	Milled ZVI - agar agar-stabilised	1	Solvay, CH	0.274	F.I.s	2.5x22	100	0.00024	12.2	7.00E-04	60	DL 4-2 page 31 - Table 7
Y	CMC-stabilized Carbo-Iron®	1	M.I	0.35	F.I.m	1.6x25	10	>1	0.56	1.40E-03	121	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=0.1g/L)	1	M.I	0.43	F.I.m	1.6x25	10	0.45	1.9	4.20E-04	36	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=1.1g/L)	5.7	M.I	0.37	F.I.s	1.6x25	10	0.05	16.4	4.90E-05	4	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=1.1g/L)	5.7	M.I	0.37	F.I.m	1.6x25	10	0.05	14.8	5.40E-05	5	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=1.1g/L)	5.7	M.I	0.37	F.I.h	1.6x25	10	0.22	3.4	2.40E-04	21	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=1g/L)	20	M.I	0.34	F.I.m	1.6x25	10	≈ 1	0.68	1.20E-03	104	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=2g/L)	20	M.I	0.42	F.I.m	1.6x25	10	0.72	1.14	7.00E-04	60	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=4g/L)	20	M.I	0.41	F.I.m	1.6x25	10	0.64	1.28	6.30E-04	54	DL 4-2 page 40 - Table 11
Y	CMC-stabilized Carbo-Iron® (CMC=1.5g/L)	15	Balassagyarmat, HU site (<2 mm)	0.26	F.II	1.6x25	10	0.09	4.65	1.70E-04	15	DL 4-2 page 40 - Table 12
Y	Trap-Ox Fe-BEA35 (Zeolite)	10	M.I	0.38	F.I.s/ 8.3	1.7x20	10	0.25	6	3.60E-04	31	DL 4-2 page 51 - Table 17

Optimised NP (Y/N)	NP Type	NPs injection conc	Type of porous media	Effective porosity	Type of fluid	Column dimensions (D x L, cm)	flow velocity (m d ⁻¹)	α (-)	$L_{t,99.9\%}$ (m)	k_{att} (s ⁻¹) (reported as k in DL)	k_{att} (d ⁻¹)	Source
Y	Trap-Ox Fe-BEA35 (Zeolite)	10	M.I	0.38	F.l.h/ 8.5	1.7x20	10	0.22	6.6	3.20E-04	28	DL 4-2 page 51 - Table 17
Y	Trap-Ox Fe-BEA35 (Zeolite)	10	M.II	0.27	F.l.h/ 8.5	1.7x20	10	n/a	7	4.60E-04	40	DL 4-2 page 51 - Table 17
Y	Trap-Ox Fe-MFI120 (Zeolite)	10	M.I	0.38	F.l.s/ 8.3	1.7x20	10	0.09	10.8	1.90E-04	16	DL 4-2 page 51 - Table 17
Y	Trap-Ox Fe-MFI120 (Zeolite)	10	M.I	0.38	F.l.h/8.5	1.7x20	10	0.14	7.5	2.80E-04	24	DL 4-2 page 51 - Table 17
Y	Bionanomagnetite in guar gum (3 g/L)-	1	M.I	0.38	F.l.s	2.8x11.5	100	0.005	1.09	7.00E-03	605	DL 4-2 page 59 - Table 20
Y	Bionanomagnetite in starch (2 g/L)- modified suspension	1	M.I	0.38	F.l.s	2.8x11.5	100	0.005	1.71	6.00E-03	518	DL 4-2 page 59 - Table 20
Y	Bionanomagnetite in agar agar (2 g/L)- modified suspension	1	M.I	0.35	F.l.s	2.8x11.5	100	0.026	1.15	2.20E-03	190	DL 4-2 page 59 - Table 20
Y	Bionanomagnetite in Na humate (0.5 g/L)- modified suspension	1	M.I	0.38	F.l.s	2.8x11.5	100	0.049	4.13	1.60E-03	138	DL 4-2 page 59 - Table 20
Y	Fe-oxides (Nano-Goethite)	1	M.II	35	F.l.s	3.6x20	43	0.002	20.2	2.00E-03	173	DL 4-2 page 65 - Table 23
Y	Fe-oxides (Nano-Goethite)	1	M.II	33	F.l.m	3.6x20	43	0.003	12.9	3.00E-03	259	DL 4-2 page 65 - Table 23
Y	Fe-oxides (Nano-Goethite)	1	M.II	33	F.l.h	3.6x20	43	0.002	21.8	2.00E-03	173	DL 4-2 page 65 - Table 23

Notes: $L_{t,99.9\%}$ = predicted travel distance, 99.9% NP removal; α = attachment efficiency; M.I = pre-treated reference material fine grained quartz sand Dorsilit® Nr. 8; M.II = commercial available quartz material (VEGAS); F.l.s = soft water (40-48 mgCaCO₃ L⁻¹); F.l.m = moderately hard water (80-100 mgCaCO₃ L⁻¹); F.l.h = hard water (280-320 mgCaCO₃ L⁻¹).

4 Modelling Assumptions and Limitations

4.1 Key Assumptions

The following key assumptions apply to the RSM model:

- The receptor or regulatory compliance point is located downstream of the injection zone.
- The RSM provides an indication of the likely maximum transport distance for NPs only and does not describe the near injection zone variation –it is a screening model only useful for initial risk assessment at potential injection sites.
- Linear attachment ($\psi = 1$) in a low NP concentration environment (“clean-bed”) at the downstream receptor so that deposition is not limited nor affected by the amount of already deposited particles. Hence blocking mechanisms are assumed to be insignificant.
- ‘Equilibrium’ constant attachment and detachment conditions (rates) whereby the concentration of NPs are relatively low, at a sufficiently large time period after injection so that changes of the colloid concentration retained on the solid phase (i.e. $\delta S/\delta t$) with time are likely to be very small.
- Parameters for the attachment (k_{att}) and detachment (k_{det}) of NPs will be both site-specific and vary across NP types and injection fluids or stabilisers used. Within a heterogeneous aquifer k_{att} and k_{det} will vary spatially. However, the attachment and detachment parameters input into the RSM does not incorporate variation with longitudinal distance (or vertical or lateral offset) from the NP injection (source) zone. Hence user inputs should be suitably cautious values for the attachment and detachment coefficients which are representative of the regulatory compliance zone (deposition) conditions.
- No degradation or weathering (e.g. dissolution of iron NPs) of the NPs between the injection zone and compliance point.
- NP size does not directly influence the transport so that the assigned or derived values for the attachment and detachment coefficients (k_{att} and k_{det}) are assumed to incorporate NP weathering, variation in particle size and interaction with the surrounding aquifer material.
- The transport of NPs is assumed to be primarily impacted (retarded) by the ratio of the attachment to detachment coefficients (i.e. $k_{att} : k_{det}$ ratio). Hence different NPs which may have different values for k_{att} and k_{det} but similar values of the $k_{att}:k_{det}$ ratio would be predicted to have the same value for the retardation parameters (K_{d_NP} , R_{f_NP} and u_{NP}).

4.2 Key Limitations

Currently it has been difficult to extract relevant information from the deliverables available at the time of writing in order to try and further validate and parameterise the approach being taken – especially the variation with distance of the concentration of NP within the field injection pilot sites and large lab-scale tank tests.

There is a limited published database of values available for the attachment and detachment coefficient based on NanoRem deliverables, with a particular lack of detachment coefficients available. Cur-

rently, the absolute value of the attachment (or detachment) coefficient does not influence the retardation rather it is the ratio of attachment to detachment.

The modelling approach outlined in Section 3 above has been discussed between LQM (Andy Gillett and Judith Nathanail) with the Politecnico di Torino (Skype call, 6th September 2016; Tiziana Tosco and Carlo Bianco). It is understood that a similar approach may be considered for future development by the latter as part of the MNMs suite of models.

Therefore, it is considered that the approach outlined provides a useful basis for a suitably cautious screening methodology at this stage. The comparison of the RSM model (analytical solution) output with that provided by the MNM's (numerical solution) output provides an indication that the simplified models can provide similar outputs for the same inputs with the more complex models. This means that the risk evaluations for 'renegade' NPs based on travel distance predicted by the RSM are robust and defensible.

5 Modelling Wish List / Ways to develop the approach

There are a number of ways that the RSM could be improved and extended, some of which involve further investigation of current datasets that may become available towards the end, or even after, the NanoRem project.

1. For testing or validating the approach in the field a series of borehole transects with distinct sample ports covering the main NP transport zone with complete time series data covering as a minimum the total and dissolved mobile phase NP concentration and ionic strength (see also inputs required as per **Table 11**). Installation of boreholes post- injection would allow the solid NP concentration to be determined. Such a network from the injection zone through to the downstream receptor would ensure a more consistent and extensive spatial and temporal analysis of the NP concentration and flux profiles.
2. Laboratory flume experiments (e.g. NanoRem project involving nZVI, Carbo-Iron® and Goethite injections) with multichannel sampling port networks could be used to estimate the important transport parameters such as k_{att} and k_{det} and estimates for the maximum retained colloid concentration (S_{max}) at aquifer ionic strength conditions. Sampling transects at different injection depths could be used to parameterise the transport models within MNMs assuming vertical and transverse dispersivity were negligible compared to longitudinal dispersivity (i.e. using 1-D transport model in MNMs) as a first assumption. Any derived parameters could be used to populate and further inform the screening level model.
3. As part of a pre-deployment risk assessment for field trials at real sites, aquifer materials obtained from installed (downstream) boreholes could be collected from the main injection zone and column batch experiments undertaken to derive the important transport parameters such as k_{att} and k_{det} and S_{max} . This site-specific data could be used to inform the screening risk assessment model to provide indicative travel distances and concentration profiles downstream of the injection zone ahead of a full scale NP remediation scheme.
4. An improved collated database for attachment and detachment coefficients along with relevant metadata (experimental - aquifer conditions) would allow a more detailed analysis of how these transport parameters vary and further develop the screening level model – i.e. extend and develop **Table 13**. Ideally it would be possible to categorise different types of NPs into 'low', 'medium' and 'high' risk particles in terms of their ability to be transported away from the injection zone.
5. Incorporating the impact of a range of other controlling factors on NP transport such as the contaminant source strength, NP concentration, stabilisers used in the injection, degradation of NPs outside the source zone and aquifer ionic strength on the screening level model would improve applicability across sites and variable injection conditions.
6. Consideration of the WP7 nano-particle fate and transport model and how it compares in terms of predicted NP concentration profile with distance with the screening level model.

6 Modelling Protocol

6.1 Legislation, Site characterization and CSM

For each site in which you intend to inject NPs into polluted groundwater plumes:

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

The above protocol has been modified from that initially developed earlier in the NanoRem project (WP9 internal deliverable) and subsequently published (Nathanail et al., 2016).

6.2 Model Parameterisation

The parameters required to run the RSM model are listed in **Table 15** and where they might be sourced or derived from.

Table 15: Table of input parameters required for the RSM model (see also **Table 11**)

Parameter	Source of Data
Initial NP concentration in groundwater at plume core	Remediation design and injection strategy or Site investigation
Width of injection plume at source	Remediation design and injection strategy
Thickness of injection plume at source	Remediation design and injection strategy
Groundwater flow (seepage) velocity	Site investigation (e.g. tracer test, calculated from hydraulic conductivity, gradient and effective porosity)
Darcyan velocity (specific discharge)	Site investigation (calculated from hydraulic conductivity and hydraulic gradient)
Hydraulic conductivity	Site investigation
Hydraulic gradient	Site investigation
Effective porosity	Site investigation
Bulk density of aquifer materials	Site investigation
Saturated aquifer thickness	Site investigation
Aquifer ionic strength	Site investigation (used to help select appropriate values for attachment and detachment coefficients)
Attachment coefficient	Assumed value or derived from column experiments using site specific aquifer material and groundwater conditions (as far as practicable) and the NPs of interest. Parameter derived by fitting of breakthrough curves using a tool such as MNMs.
Detachment coefficient	Assumed value or derived from column experiments using site specific aquifer material and groundwater conditions (as far as practicable) and the NPs of interest. Parameter derived by fitting of breakthrough curves using a tool such as MNMs.
Retention or attachment term	For the risk level model, well outside of the injection zone, a linear attachment term is likely to be relevant whereby a value of 1 can be assumed.
Half-life for degradation of NP in water	Assumed value is very high such that negligible degradation is assumed for metal based NPs
Distance to regulatory compliance point	Value agreed with regulator or relates to the agreed critical (possibly nearest) receptor
Distance (lateral) to compliance point perpendicular to flow direction	Cautious assumption would be to assume a value of 0m
Distance (depth) to compliance point perpendicular to flow direction	Cautious assumption would be to assume a value of 0m
Time since pollutant entered groundwater	User defined value to be agreed with regulator
Longitudinal Dispersivity (x dir)	typically set at 10% of distance to compliance point (pathway length)
Transverse Dispersivity (z dir)	typically set at 1% of longitudinal dispersivity
Vertical Dispersivity (y dir)	typically set at 0.1% of longitudinal dispersivity

6.3 Using the RSM model worksheets

A brief outline of the relevant worksheets utilised in the RSM model and how the user can produce outputs is provided in the sections below. The terminology used and calculations are outlined in Section 3 above.

6.3.1 NanoParticle_Inputs worksheet

This worksheet is an addition to those existing in the Remedial Targets Methodology (RTM) spreadsheet model (Environment Agency, 2006b). Given that the RTM is based on well understood hydrogeo-

logical principles and is freely available, the RSM should be useful to other EU member states which can use it as is, or adapt it to be used within their chosen hydrogeological models.

The cells highlighted with blue shading in this worksheet are the input cells for the relevant NP specific inputs. Currently, only a single interaction site mode is implemented within subsequent calculation worksheets so the users ability to modify model outputs is limited to entry of the attachment coefficient (cell D13), detachment coefficient (cell D14) and retention/attachment term (cell D15).

Site specific inputs (from the 'Level3 Groundwater' worksheet) and derived parameters (NP retardation factor, NP distribution coefficient and NP retardation velocity) are highlighted with green shading (cells D16 through to D20). Again only the derived parameters for a single interaction site mode are fully implemented in the model. These derived parameters are used in subsequent calculations, as required.

Algorithms and relevant inputs for calculating the retention or attachment term (Section 3.2.2 above) and relationships between the attachment or detachment coefficient and aquifer ionic strength (Equations 15 to 17, Section 3.2.3 above) are also provided in this worksheet. These algorithms are not currently implemented in the model since they require a number of empirical parameters derived from experiments involving the NPs of interest. Some example parameters, based on latex micro-sphere experiments (Tiraferri et al., 2011), are included as indicative illustrative values at this time and can be used to estimate the key NP inputs, assuming latex micro-spheres are a suitable surrogate. These algorithms have the potential to be fully implemented if the relevant parameter inputs were to become available.

6.3.2 Level3 Groundwater worksheet

This worksheet is a modified version of that existing in the Remedial Targets Methodology spreadsheet model (Environment Agency, 2006b).

The cells highlighted with blue shading in this worksheet are the input cells for the relevant site-specific aquifer and user defined scenario inputs (**Table 16**).

Table 16: Worksheet inputs and cell numbers

Parameter	Worksheet cell
Initial NP concentration in groundwater at plume core	D20
Half life for degradation of NP in water	D21
Width of injection plume at source	D23
Thickness of injection plume at source	D24
Saturated aquifer thickness	D25
Bulk density of aquifer materials	D26
Effective porosity of aquifer	D27
Hydraulic gradient	D28
Hydraulic conductivity of aquifer	D29
Distance to (regulatory) compliance point	D30
Distance (lateral) to compliance point perpendicular to flow direction	D31
Distance (depth) to compliance point perpendicular to flow direction	D32
Time since pollutant entered groundwater	D33
Soil water partition coefficient (dissolved metal species only)	K10
Dispersivity (option selected from pull down list)	H26:K26
Longitudinal dispersivity (for user defined option)	K29
Transverse dispersivity (for user defined option)	K30
Vertical dispersivity (for user defined option)	K31

These values can be defined by the user for the site-specific situation.

The user can compare the predicted solute concentration of the dissolved metal species of the NP (e.g. iron) against its NP counterpart by defining a value for the soil water partition coefficient (K_d) in Cell K10.

The Ogata Banks solution (selected via pull down list, cell C13:E13) is the only analytical transport solution option implemented at the present time.

Model outputs of interest to the user are provided as a graph of predicted NP concentration versus distance (up to user defined regulatory compliance point) which is located within this worksheet at cell N2:W23. The predicted NP concentration at each 1/20th increment of the (regulatory) compliance distance (Cell Y14:Y34) is provided as Cell AA14:AA34 (units of mg L^{-1}), Cell AF14:AF34 (units of kg m^{-3}). This data is calculated within the '*Level3_1 G_ Calc_NP*' worksheet (Section 6.3.3). A (simplistic) estimate of number of NPs per L (Cell AD14:AD34) is derived based on user defined values for NP diameter (Cell AE8) and density (Cell AE9).

The predicted solute concentration assuming the user defined (NP) concentration behaves as a dissolved metal species is also included as a series on the graph, representing an indicator of the lower limit of travel of NP away from the injection zone. This data is calculated within the pre-existing '*Level3_1 G_ Calc*' worksheet.

6.3.3 Level3_1 G_ Calc_NP worksheet

This worksheet is an addition to those existing in the Remedial Targets Methodology spreadsheet model and is based upon the '*Level3_1 G_ Calc*' worksheet. This sheet breaks down and calculates the separate terms of the Ogata Banks analytical solution presented as Box 3 above.

The estimated values for the NP retardation factor (R_{f_NP}) and NP retardation velocity (U_{NP}) are passed into this worksheet (Cell 29 and Cell 30, respectively) with the latter being used as one of the inputs for the Ogata Banks analytical solution for the transport of the NP away from the injection point (Cells G5:X48), with the values carried forward into the '*Level3 Groundwater*' worksheet listed via Cells W56:X75.

6.3.4 Subsidiary worksheets

Additional worksheets have been added as follows:

- '*Parameter_workings*' worksheet – contains some useful reference tables for model parameter values from the literature and NanoRem project;
- '*Outputs & Comparison with MNMs*' worksheet – this tabulates some of the outputs and comparisons with the MNMs model that have been presented in this report as charts or tables;
- '*Chart -*' worksheets – comprises a series of charts that have been generated and used in this report as charts and tables linking to the data in the '*Outputs & Comparison with MNMs*' worksheet; and
- '*NOTES – README*' worksheet – provides some notes to the relevant worksheets relating to the RSM NP implemented model.

6.4 Sensitivity Analysis

The sensitivity of the predicted concentration versus (transport) distance and derived parameters against values of the attachment and detachment coefficients ratio ($k_{att} : k_{det}$) is provided within Section 3.3.5 above (**Figure 5**, **Figure 6** and **Figure 7**).

Table 17 provides an illustration of travel distances at which the UK EQS for Iron (100 mg L^{-1}) is predicted to be exceeded based on the example scenario described in Section 3.3 assuming continuous injection of Carbo-Iron[®] NPs, across a broad range of assumed $k_{att}:k_{det}$ ratio values. After 1 year of continuous injection a $k_{att}:k_{det}$ ratio of only 10 would predict that the EQS was not exceeded beyond a distance of 65m (**Table 17**). After 25 years continuous injection a $k_{att}:k_{det}$ ratio of 200 would be required to ensure the EQS was not exceeded to a distance of 75m. Hence the travel distance is critically determined by a combination of time period for the injection and assumed ratio of attachment to detachment of the NPs.

Nevertheless, the travel distances are well short of reported plume lengths for dissolved phase hydrocarbons and chlorinated solvents.

Table 17: Illustration of the influence of $k_{att} : k_{det}$ ratio on predicted travel distance at which the UK EQS for Iron (100 mg L^{-1}) is exceeded, based on a continuous Carbo-Iron[®] injection (example based on Hungary pilot site, see **Table 11**)

$k_{att} : k_{det}$ ratio	Travel distance (m) to which UK EQS is exceeded (to nearest 5m)	
	after 1 year	after 25 years
0.1	0	0
1	0	0
10	65	0
25	40	0
50	30	0
100	20	0
200	15	75
500	10	45
1000	10	35

7 References

ASTM. (1995). *Standard Guide for Developing Conceptual Site Models for Contaminated Sites* (No. E1689-95). ASTM International (West Conshohocken, PA).

ASTM. (2014). *Standard Guide for Developing Conceptual Site Models for Contaminated Sites* (No. E1689-95 (2014)). ASTM International (West Conshohocken, PA).

Bianco C, Tosco T, & Sethi R. (2015). *MNMs 2015 Micro- and Nanoparticle transport, filtration and clogging Model- Suite. A comprehensive tool for design and interpretation of colloidal particle transport in 1D Cartesian and 1D radial systems.* Politecnico di Torino (Torino, Italy).

BSI. (2013). *BS10175:2011+A1:2013 - Investigation of potentially contaminated sites - code of practice.* British Standards Institution: London, UK.

CL:AIRE. (2017a). *NanoRem Bulletin 7. NanoRem Pilot Site – Spolchemie I, Czech Republic: Nanoscale zero-valent iron remediation of chlorinated hydrocarbons.* CL:AIRE (London). Accessed from www.nanorem.eu

CL:AIRE. (2017b). *NanoRem Bulletin 8. NanoRem Pilot Site – Spolchemie II, Czech Republic: Remediation of BTEX compounds using Nano-Goethite.* CL:AIRE (London). Accessed from www.nanorem.eu

CL:AIRE. (2017c). *NanoRem Bulletin 9. NanoRem Pilot Site – Solvay, Switzerland: Nanoscale zero-valent iron remediation of chlorinated solvents.* CL:AIRE (London). Accessed from www.nanorem.eu

CL:AIRE. (2017d). *NanoRem Bulletin 10. NanoRem Pilot Site – Balassagyarmat, Hungary: In Situ Groundwater Remediation Using Carbo-Iron® Nanoparticles.* CL:AIRE (London). Accessed from www.nanorem.eu

CL:AIRE. (2017e). *NanoRem Bulletin 12. NanoRem Pilot Site – Nitrastur, Spain: Remediation of Arsenic in Groundwater Using Nanoscale Zero-valent Iron.* CL:AIRE (London). Accessed from www.nanorem.eu

CL:AIRE. (2017f). *NanoRem Bulletin 11. NanoRem Pilot Site – Neot Hovav, Israel: Transport of Iron Nanoparticles in Fractured Chalk.* CL:AIRE (London). Accessed from www.nanorem.eu

Coutris C, Boothman C, Hjorth R, & Sevcu A. (2016). *DL 5.2: Influence of Transformation and Transport on Ecotox* (NanoRem Deliverable No. DL5.2) (p. 43).

Coutris C, Nguyen N, & Hjorth R. (2015). *DL 5.1: Dose Response Relationship, Matrix Effects on Ecotox* (NanoRem Deliverable No. DL5.1) (p. 50).

Custodio E, Araguas L, & Manzano M (Eds.). (2005). *Groundwater and saline intrusion: selected papers from the 18th Salt Water Intrusion Meeting : 18 SWIM, Cartagena (Spain), 31-May to 3-June 2004.* Instituto Geológico y Minero de España: Madrid.

EC. (2000). *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy. Official Journal of the European Communities L327/1 22 December 2000.*

EC. Directive 2004/35/CE of the European Parliament and of the Council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage. OJ L 143, 30.4.2004, p56 (2004). Accessed from <http://ec.europa.eu/environment/legal/liability/>

Elimelech M (Ed.). (1998). *Particle deposition and aggregation: measurement, modelling and simulation*. Butterworth-Heinemann: Oxford.

Environment Agency. (2004). *Model procedures for the management of land contamination*. Environment Agency: Bristol, UK. Accessed from <http://publications.environment-agency.gov.uk/pdf/SCHO0804BIBR-e-e.pdf>

Environment Agency. (2006a). *Remedial targets methodology: hydrogeological risk assessment for land contamination*. Environment Agency: Bristol, UK. Accessed from <http://cdn.environment-agency.gov.uk/geho0706bleq-e-e.pdf>

Environment Agency. (2006b). *Remedial Targets Worksheet v3.1: User Manual*. Environment Agency: Bristol, UK.

Environment Agency. (2013). *Groundwater protection: Principles and Practice (GP3) (No. Version 1.1)*. Environment Agency (Bristol, UK). Accessed from https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/297347/LIT_7660_9a3742.pdf

European Commission, & Directorate-General for the Environment. (2011). *Technical guidance for deriving environmental quality standards No 27. No 27*. Publications Office: Luxembourg. Accessed from <http://bookshop.europa.eu/uri?target=EUB:NOTICE:KH3110536:EN:HTML>

French Ministry of the Environment (MEDD). (2007). *Schéma conceptuel et modèle de fonctionnement*.

Haitjema HM, & Anderson MP. (2016). Darcy Velocity Is Not a Velocity. *Groundwater*, 54(1), 1–1. doi:10.1111/gwat.12386

HMSO. (2015). *Water Framework Directive (Standards and Classification) Directions (England and Wales) 2015*. Accessed from http://www.legislation.gov.uk/uksi/2015/1623/pdfs/uksiod_20151623_en_auto.pdf

HMSO. The Environmental Damage (Prevention and Remediation) Regulations 2015. , No. 810 Statutory Instrument 2015 (2015). Accessed from http://www.legislation.gov.uk/uksi/2015/810/pdfs/uksi_20150810_en.pdf

HMSO. Water Resources, England and Wales The Water Environment (Water Framework Directive) (England and Wales) (Amendment) Regulations 2015. , No. 1623 Statutory Instrument 2015 (2015). Accessed from http://www.legislation.gov.uk/uksi/2015/1623/pdfs/uksi_20151623_en.pdf

Hofmann T. (2013). *IDL 4.1: Standardized Experimental Protocols for mobility, Reactivity and Ecotoxicity Studies* (NanoRem Internal Deliverable No. IDL4.1) (p. 47).

Hofmann T, Micic Batka V, & Schmid D. (2016). *IDL 4.3: Report on the stability, mobility, and enhanced delivery of NPs, for NPs that are accessible at the beginning of the project* (NanoRem Internal Deliverable No. IDL4.3) (p. 106).

Hofmann T, Wagner S, Velimirovic M, Micic Batka V, & Schmid D. (2015). *IDL 4.2: Report on the stability, mobility, and enhanced delivery of NPs, for NPs that are accessible at the beginning of the project* (NanoRem Internal Deliverable No. IDL4.2) (p. 72).

ISO. (2015). *ISO 11074 Soil quality -- Vocabulary*. ISO .

Kretzschmar R, Borkovec M, Grolimund D, & Elimelech M. (1999). Mobile Subsurface Colloids and Their Role in Contaminant Transport. In *Advances in Agronomy* (Vol. 66, pp. 121–193). Elsevier. Accessed from <http://linkinghub.elsevier.com/retrieve/pii/S0065211308604277>

Micic Batka V, & Hofmann T. (2016). *DL 4.2: Stability, Mobility, Delivery and Fate of optimized NPs under Field Relevant Conditions* (NanoRem Deliverable No. DL4.2) (p. 89).

Nathanail CP, Gillett A, McCaffrey C, Nathanail J, & Ogden R. (2016). A Preliminary Risk Assessment Protocol for Renegade Nanoparticles Deployed During Nanoremediation: A Preliminary Risk Assessment Protocol for Renegade Nanoparticles. *Remediation Journal*, 26(3), 95–108. doi:10.1002/rem.21471

Oughton D, Auffan M, Bleyl S, Bosch J, Filip J, Klaas N, Lloyd J, & van der Kammer F. (2015). *DL 6.1: Feasibility and Applicability of Monitoring Methods* (NanoRem Deliverable No. DL6.1) (p. 38).

Rainer Dinkel, (2009). *Groundwater Investigation Strategy*. UW Umweltwirtschaft GmbH, 70499 Stuttgart.

Tiraferrri A, Tosco T, & Sethi R. (2011). Transport and retention of microparticles in packed sand columns at low and intermediate ionic strengths: experiments and mathematical modeling. *Environmental Earth Sciences*, 63(4), 847–859. doi:10.1007/s12665-010-0755-4

Tosco T, Bianco C, Sethi R, Fujisaki A, van Gaans P, Raouf A, & Hassanizadeh M. (2016). *D7.1 Beta Version of Nanoparticle Simulation Module for WP7 (Modelling Tool for Nanoparticle Mobility and Interaction with Contaminants) of the NanoRem Project*. European Union 7th Framework Programme, NMP.2012.1.2, Grant Agreement No. 309517. (Deliverable No. DL7.1).

Tosco T, Tiraferrri A, & Sethi R. (2009). Ionic Strength Dependent Transport of Microparticles in Saturated Porous Media: Modeling Mobilization and Immobilization Phenomena under Transient Chemical Conditions. *Environmental Science & Technology*, 43(12), 4425–4431. doi:10.1021/es900245d

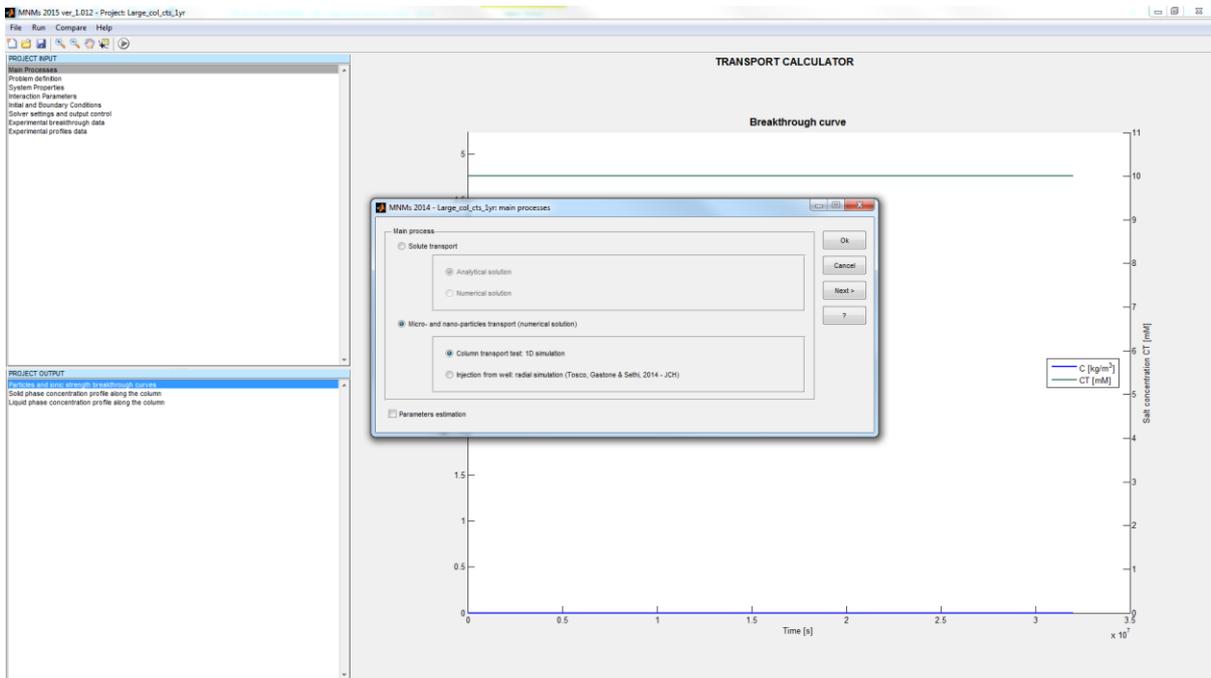
Tufenkji N, & Elimelech M. (2004). Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. *Environ Sci Technol.*, 38(0013–936X (Print)), 529–536.

Wallace SH, Shaw S, Morris K, Small JS, Fuller AJ, & Burke IT. (2012). Effect of groundwater pH and ionic strength on strontium sorption in aquifer sediments: Implications for 90Sr mobility at contaminated nuclear sites. *Applied Geochemistry*, 27(8), 1482–1491. doi:10.1016/j.apgeochem.2012.04.007

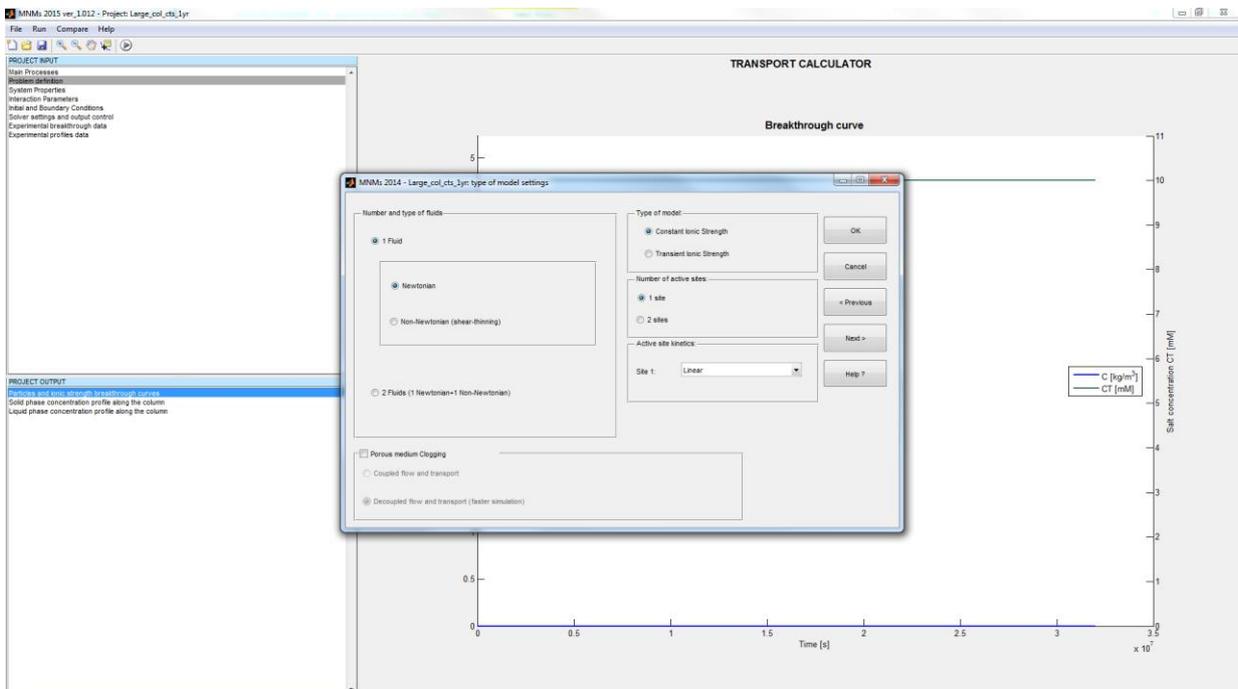
Appendix 1 - MNM's – 1 year simulation inputs for comparing to modified RTM model for NPs

MNM's – 1 year simulation inputs for comparing to modified RTM model for NPs

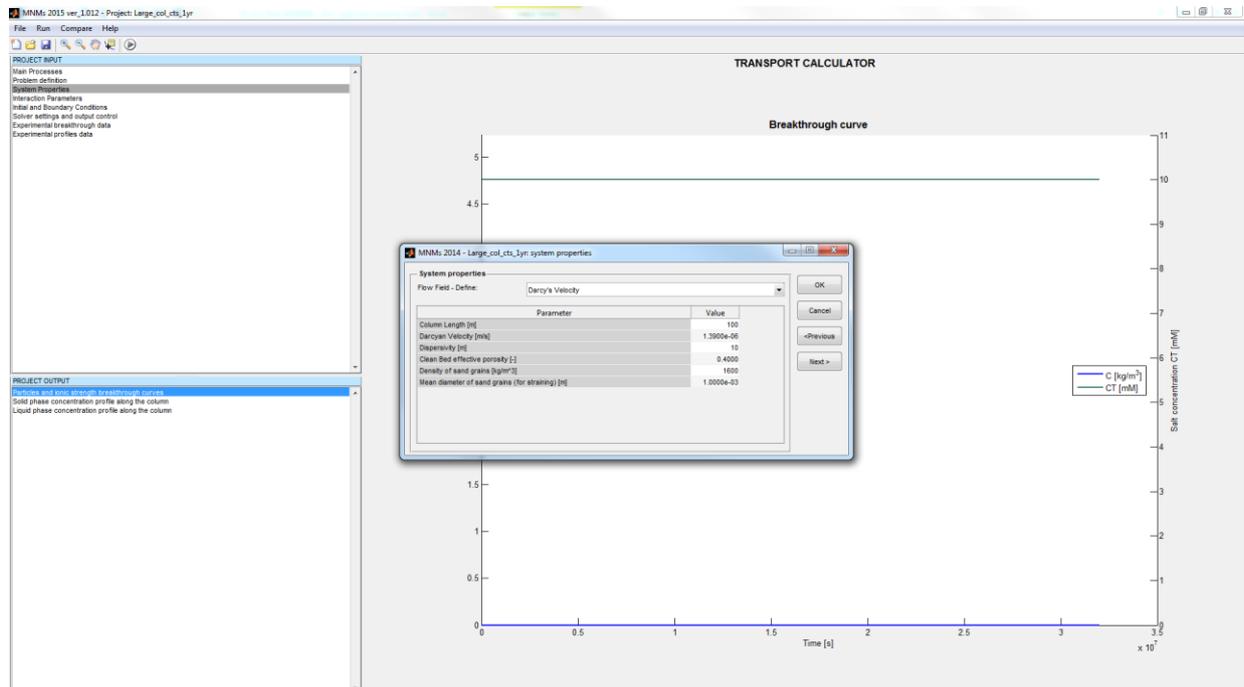
Step 1 – Main Process



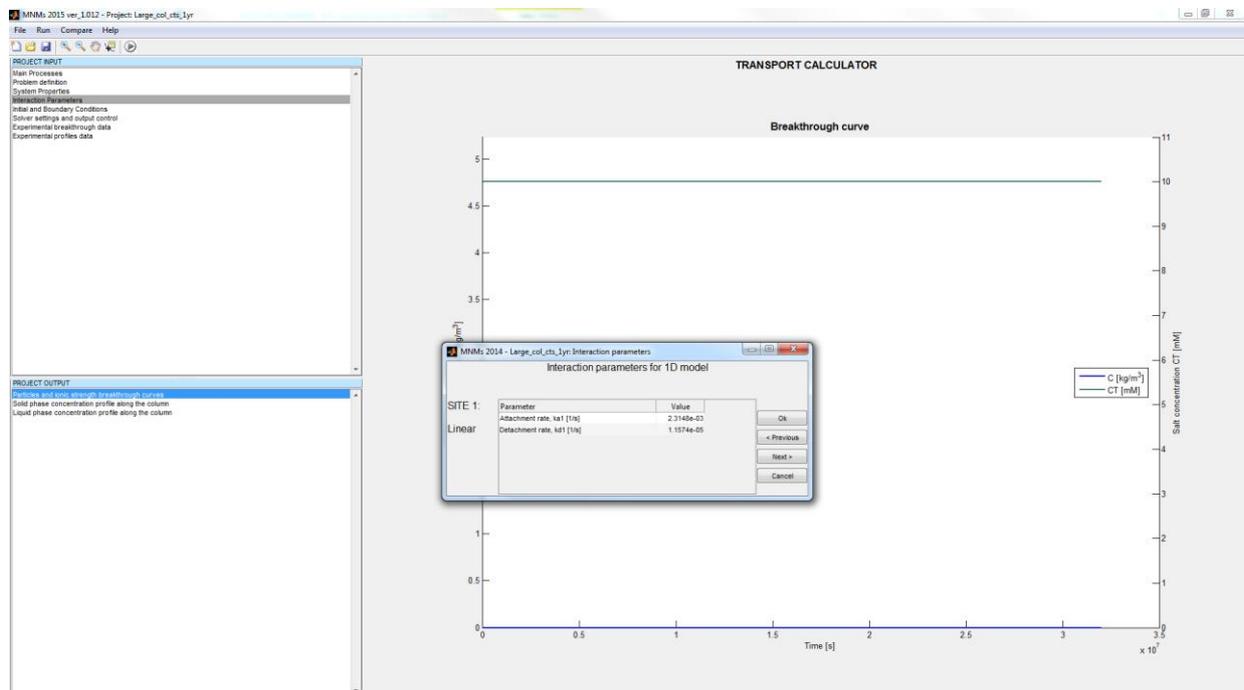
Step 2 – Problem definition



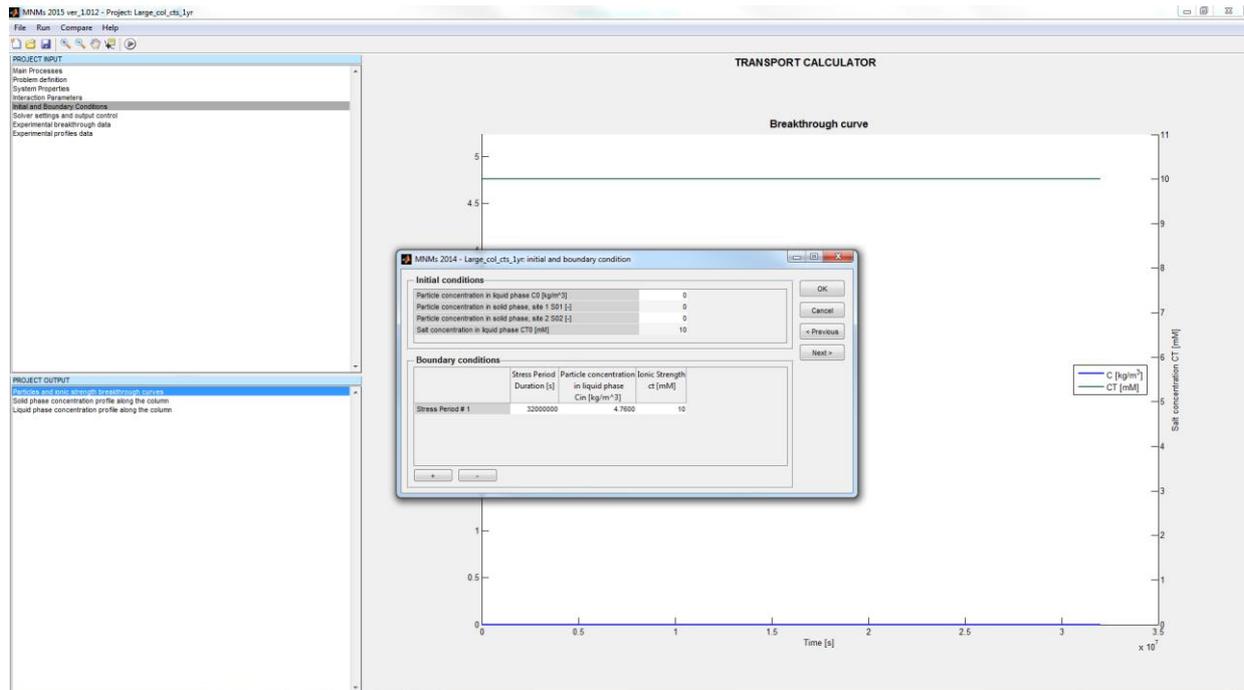
Step 3 – System Properties



Step 4 – Interaction Parameters

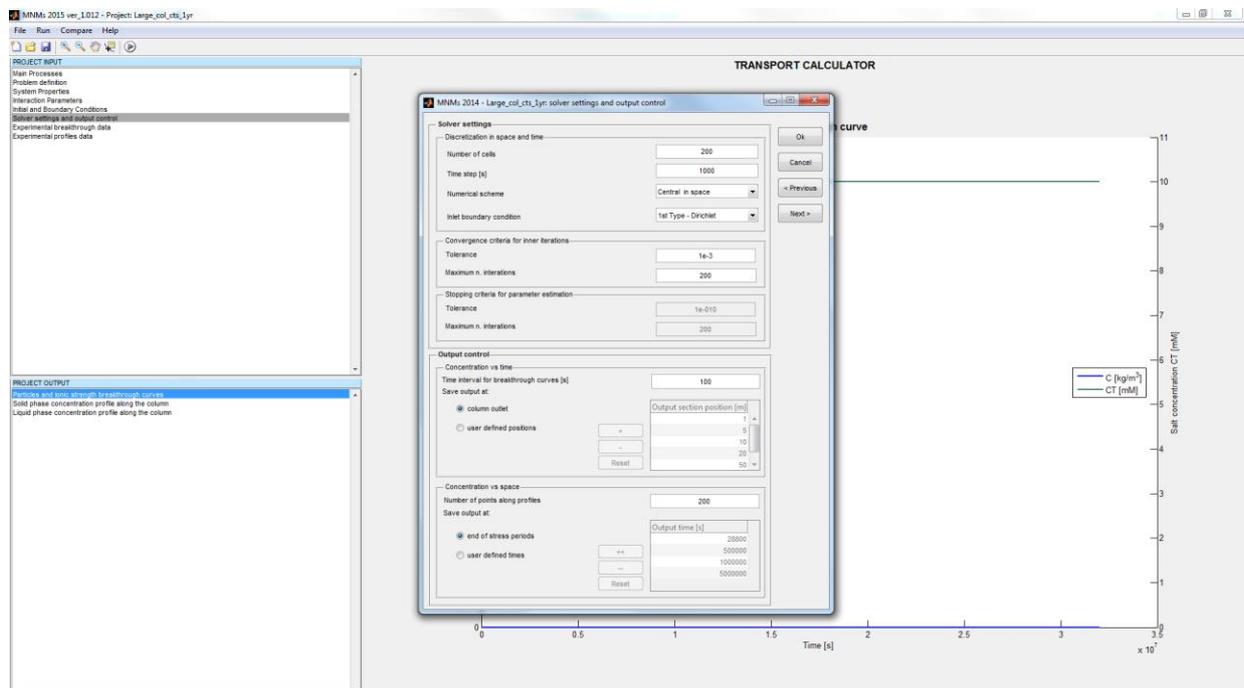


Step 5 – Initial and Boundary Conditions



reset stress period to 5 years for longer time prediction

Step 6 – Solver Settings and Output Control



Step 7 – Experimental breakthrough data

None / Not applicable

Step 8 – Experimental profiles data

None / Not applicable

Appendix 2 – Conceptual Site Models

Introduction

Risk based contaminated land management depends on a thorough understanding of the spatial distribution of contaminant sources, contaminant toxicity, fate and transport and the nature and behaviour of human, environmental and water receptors. A Conceptual Site Model (CSM) is a representation of relevant information, and remaining uncertainties, relating to contamination at a site. It is used throughout a project and is the central tool driving risk assessment and risk management.

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 contaminant 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). In the UK, CLR11 (Environment Agency, 2004) states that 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 contaminant linkages.

Example definitions offered in other British, European and International standards are in Box A2-1.

Box A2-1 Example descriptions of CSMs

The British Standards Institution, describes the process of site investigation as *“one that seeks to reduce the uncertainty in the conceptual model”* (BSI, 2013).

The State Institute for Environment, Measurements and Nature Conservation (Baden-Wuerttemberg) states that 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)

ISO defines a CSM as a *“Summation of all information about a site relevant to the task in hand”*. (ISO, 2015).

In France the CSM makes it possible to: *“precisely 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) (Ministry of the Environment (MEDD), 2007)

The Content of Conceptual Site Models

In general a complete CSM should comprise a plan view and cross section to illustrate the main site features; matrix or network diagrams to specify the contaminant linkages present and text to describe the features and linkages, as shown in Figure A2-1.

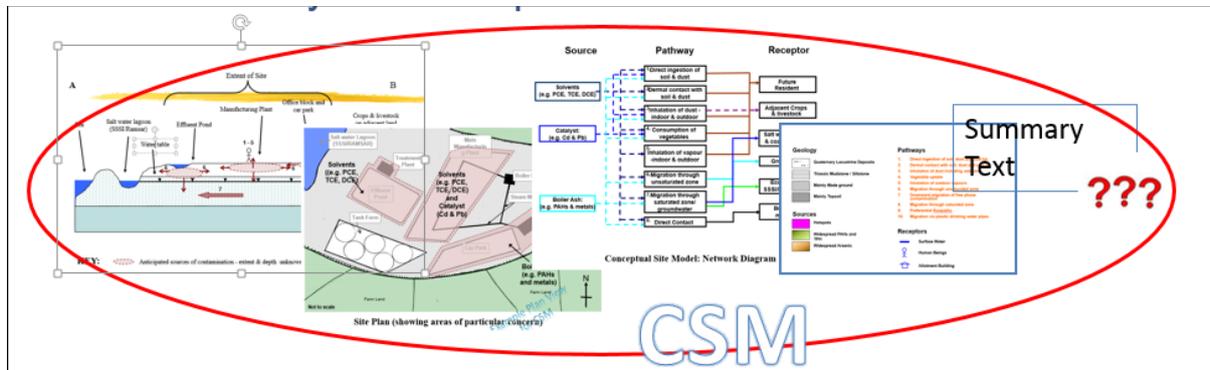


Figure A2-1 A CSM comprises multiple elements including text and diagrams

One way to think of a CSM is as a means to capture “what you know plus what you don’t know” (M de Freitas, 1987) pers comm, originally applied to ground models in engineering geology). The information that is not known should be listed as uncertainties and assumptions; these can later be the target of further investigation. The typical contents that should be included in the parts of a conceptual model are listed in Table A2-1.

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 contaminant linkages.

Table A2-1 Information to show on the various elements of a conceptual model (after Nathanail et al 2007)

Information	Text	Graphic elements	
		Drawings	Diagrams
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 contaminant linkages	Y	possibly	Y
Limitations	Y	possibly	possibly

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; i.e. even though the river is still 100m away, the pathway is only 40m.

Site description, Geology, hydrology and hydrogeology

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 contaminant linkages

The CSM should state:

- the sources of contamination e.g. benzene, arsenic;
- pathways through which the contaminants might migrate eg unsaturated zone; and
- receptors e.g. river or well.

Where source, pathway and receptor are present they form a contaminant linkage that represents a potential risk to human health or the environment. Identifying the contaminant linkages present is an important function of the CSM; they 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 are uncertain and inferred from evidence such as historical maps. As work progresses, the SPR are supported by evidence such as soil testing.

Uncertainties

The CSM should include a section for listing uncertainties and assumptions. Uncertainties are things that are not known e.g. thickness of made ground. Assumptions are things on which a reasonable guess has been made but it could be wrong e.g. the types of contaminants present.

Example Conceptual Site Models

The example CSM below comprises a plan view (Figure A2-2), cross section (Figure A2-3), and a network diagram sub divided to show the contaminant linkages to human health (Figure A2-4) and water receptors (Figure A2-5). On the plan view the line of cross section has been marked by the dashed line.

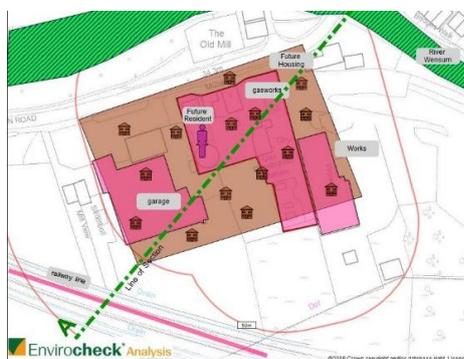


Figure A2-2 Example Plan View

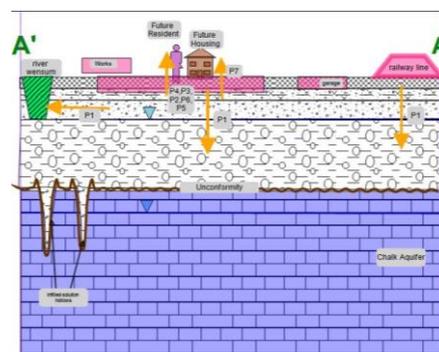


Figure A2-3 Example Cross Section

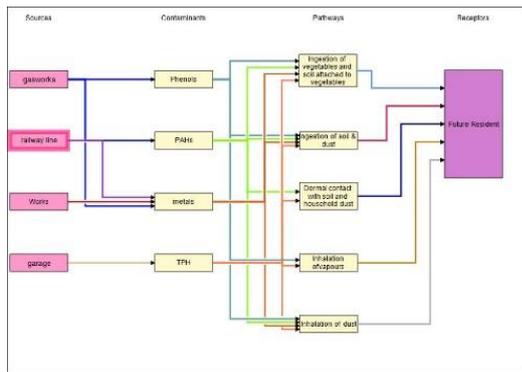


Figure A2-4 Network Diagram: Human Receptors

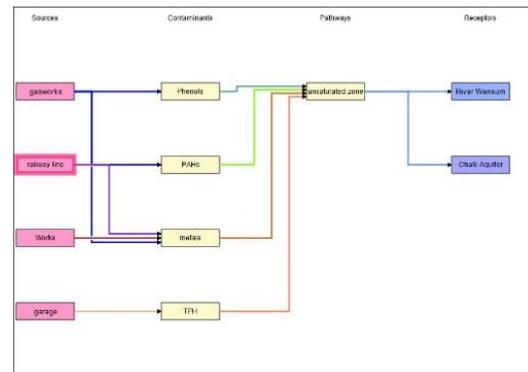


Figure A2-5 Network Diagram: Water Receptors

Use of Conceptual Site Models

CSMs are used and updated throughout the lifetime of a project Figure A2-6. 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 contaminant 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.

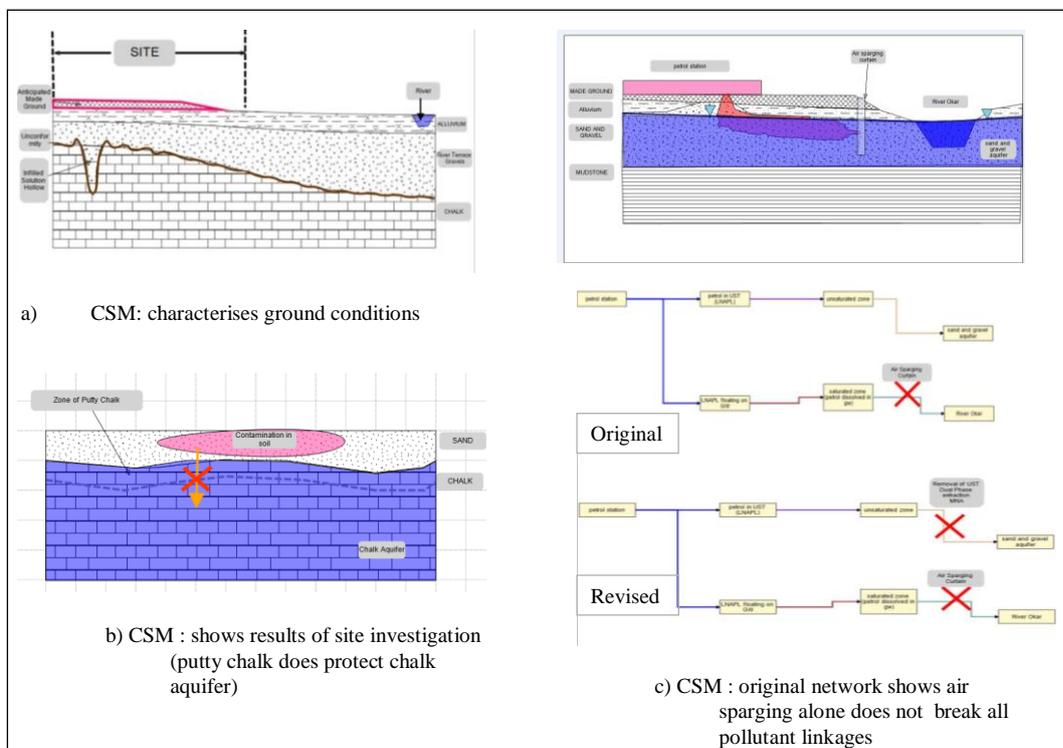


Figure A2-6 Some examples of how CSMs are used in contaminated land management

CONCLUSIONS

The purpose of a CSM of a (potentially) contaminated site is to identify, communicate and justify the (potential) source-pathway-receptor contaminant linkages by presenting succinct relevant environmental information in three dimensions in order to drive the risk assessment and risk management processes. The CSM presents the best hypothesis of what is going on at a site and formally states the key uncertainties that are used to inform the design of the next phase of investigation. The CSM is updated throughout the project as new information becomes available.

The CSM may be prepared by different organizations at different stages of the investigation. It is beneficial to those creating conceptual site models and stakeholders receiving and/or reviewing CSMs for there to be a consistent approach to the presentation of CSMs. The standardized approach proposed still leaves room for site specific design decisions to best represent environmental conditions at a particular site.

This Appendix has outlined proposals for a consistent approach to presenting CSMs in terms of content and formats and highlighted the use of conceptual modelling software – KeyCSM – which can enable the CSM to become a tool not just a product.