

NanoRem Bulletin

CL:AIRE's NanoRem bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater using nanoparticles. This bulletin describes how numerical tools can support the various stages of the design, implementation and evaluation of a nanoremediation.

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Forecasting Nanoparticle Transport in Support of *In Situ* Groundwater Remediation

1. BACKGROUND

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) was a research project, funded through the European Union Seventh Framework Programme. The NanoRem project focused on facilitating practical, safe, economic and exploitable nanotechnology for *in situ* remediation. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), market demand, overall sustainability, and stakeholder perceptions. The NanoRem Toolbox, available at www.nanorem.eu, provides outputs which address all these issues.

This bulletin explains how numerical tools can support the various stages of the design, implementation and evaluation of a nanoremediation, focussing on two such tools that were developed within NanoRem Work Package 7. In section 2 the motivation for using modelling tools in support of nanoremediation decision making is elaborated. Section 3 provides background on the fundamental pore-scale processes that are assumed to govern the mobility of NPs injected for nanoremediation. Sections 4 to 6 describe and illustrate

how macro-scale models, that use empirical relations, can aid in the various phases of the design of a nanoremediation.

2. MODELLING FOR DECISION MAKING

Performing a nanoremediation, like any other technology implementation, is a stepwise process where successive choices or decisions are being made, then implemented, and their outcomes verified afterwards. The following main stages can be discerned in a nanoremediation application:

- 1) An initial pre-screening stage
- 2) The planning and design stage
- 3) The implementation and injection stage
- 4) The actual remediation stage
- 5) The post-remediation stage

In the pre-screening stage it has to be decided if nanoremediation is, at least theoretically, a feasible option, expected to outcompete more conventional remediation approaches. A wide range of choices have to be made in the design stage, many of which require insight into NP mobility as a function of the aquifer conditions and NP slurry properties. Ultimately of course, a decision must be made over

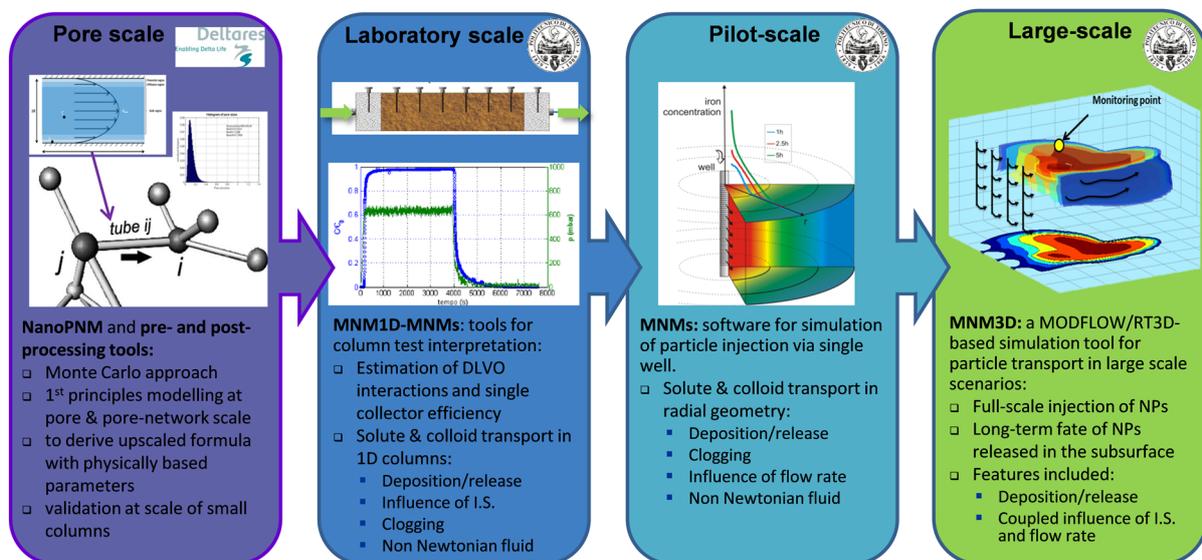


Figure 1. Summary of NanoRem modelling research



Taking **Nanotechnological Remediation Processes** from Lab Scale to End User Applications for the Restoration of a Clean Environment. This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517.



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whether a technically optimised design is also economically feasible. In addition, regulators will decide on permits based on information regarding the remediation safety. During implementation and monitoring new information may become available that gives rise to adaptations of the design or implementation procedures.

Decision making is always based on a combination of general knowledge and specific data for the situation at hand. Examples of generally available information in the context of nanoremediation are that nano zero-valent iron (nZVI) can be applied for reductive dechlorination of chlorinated volatile organic compounds (CVOC) but not to stimulate oxidative biodegradation of BTEX; and that low permeable aquifers are less conducive for nanoremediation in general, due to intrinsic difficulties in an effective emplacement of the particles. The type of contaminants present at a site and the local aquifer hydraulic properties form part of the site specific information that must be known in order to produce a robust conceptual site model. Informed decision making is not just based on 'facts' and direct measurements or observations, but also on expectations (beliefs), inferences (reasoning), and quantitative forecasts (modelling). During the technology implementation process, the nature of the required information may become more and more detailed, quantitative, and site specific.

Given that NP mobility is a key issue for nanoremediation, the use of a numerical model can be of significant value, both in the planning and design stages (1-2) and in the verification stages (3-5), to ensure effectiveness and safety of the remediation. In the first stages of the evaluation of the technology applicability, a NP transport model can be used in combination with column transport tests performed for a specific field application. By fitting the experimental results of selected tests with the model, the key transport features of the NPs can be extrapolated and used to simulate NP transport under a wider set of conditions. Modelling thus spares extensive costly and time-consuming experiments, and widens the range of conditions that can be investigated through actual laboratory testing. In a second step, a NP transport model will be used to forecast placement of the NP with the injection, and to forecast NP long term mobility, i.e. the potential transport of particles out of the core area during and after injection. When doing so for various implementation scenarios, the model results can aid in optimising NP and slurry properties and injection schemes (e.g. based on a desired radius of influence and NP concentration in the target area, which discharge rate should be applied, how long injection should last, which concentration of NPs and stabilisers is the most effective, etc.). Equally important, model results can point out what crucial but still missing information would

contribute most to making a better-informed decision. Regarding verification, model forecasts can guide how, where and when to monitor, to prove that the expectations on NP placement - and remediation targets and safety - are met. It should be noted that model forecasting should always go hand in hand with adequate monitoring and vice versa. Model forecasts that cannot be verified are useless, as are monitoring data that cannot be tested against prior expectations.

At this point, it is important to emphasise that general knowledge regarding NP mobility in porous media (PM) is still incomplete. Whilst transport of dissolved contaminants is thoroughly understood and many numerical models are commercially available to assist the design of a remediation intervention, fundamental factors that control the transport of NPs in PM are as yet largely unknown. The basic processes (filtration, straining, blocking, ripening) have more or less been identified and can in principle be simulated at the scale of the surface interactions between NP and PM, i.e. at the scale of a single pore. However, a rigorous framework of physical laws that describe these processes as a function of the relevant fundamental parameters at the macro (Darcy) scale is lacking. Various empirical approaches are currently used, that include parameters of which the exact meaning varies with the formula used and that have to be calibrated each time. The knowledge gap could be closed by generating an increasing number of well-documented observations from laboratory or field tests that are supported by modelling exercises.

In view of the above, NanoRem Work Package 7: *Modelling Tool for Nanoparticle Mobility and Interaction with Contaminants* set out to develop a user-friendly simulation tool, both for the design, interpretation and supplementation of laboratory tests, and for predicting transport and emplacement of NPs at the field scale. The research aim was approached from two sides: from the pore scale to increase fundamental knowledge and from the macro scale to be of practical use (Figure 1).

3. INCREASING FUNDAMENTAL KNOWLEDGE ON NP TRANSPORT

When NPs are dispersed and transported within groundwater, they are subject to processes like filtration, straining, physical-chemical deposition and aggregation, as they are attracted to the surfaces of the PM grains and to each other (Figure 2). The dynamic processes of attachment and detachment of NPs are governed by physical laws that operate at the scale of grains and pores, but impact the

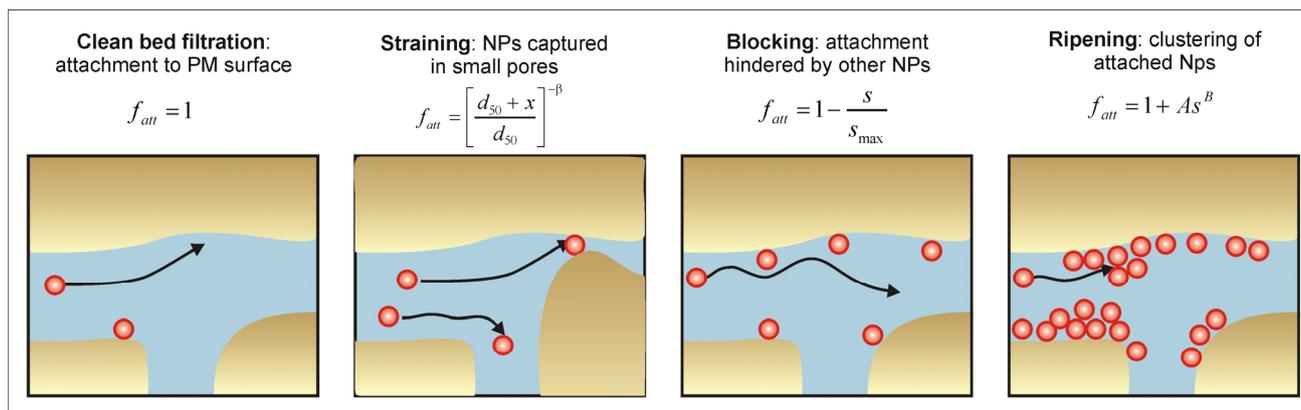


Figure 2. Pore scale particle retention processes (Modified from Tosco *et al.*, 2014b); d_{50} is median grain size of the PM; x is distance travelled in the PM domain from the inlet point; β , A , B are fitting parameters.

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transport behaviour of NPs at the macro (Darcy) scale. NP transport in PM at the Darcy scale is usually described by a modified advection-dispersion equation (Box 1) that takes into account the mass exchanges between the liquid and solid phase due to physical and physico-chemical interactions.

Box 1. Modified advection-dispersion equation for NP transport

$$\Phi \frac{\partial c}{\partial t} + \rho_b \frac{\partial s}{\partial t} + v \frac{\partial c}{\partial x} - \Phi(\alpha v + D_{\infty}) \frac{\partial^2 c}{\partial x^2} = 0$$

$$\rho_b \frac{\partial s}{\partial t} = \Phi k_{att} f_{att} c - \rho_b k_{det} s$$

with:

c	NP number concentration in the liquid phase [L ⁻³]
s	NP number concentration in the solid phase [M ⁻¹]
Φ	porosity of PM [-]
ρ_b	bulk density of the PM solid matrix [M L ⁻³]
v	Darcy velocity [L T ⁻¹]; $v = K \Delta h$
K	hydraulic conductivity [L T ⁻¹]
Δh	hydraulic gradient [-]
α	dispersivity [L]
D_{∞}	NP bulk diffusion coefficient [L ² T ⁻¹]
k_{att}, k_{det}	NP attachment and detachment rate coefficients [T ⁻¹]
f_{att}	function [-] depending on the process(es) being described, see Figure 2

The parameters ϕ , K , and α for a given PM must be measured/calibrated from a tracer breakthrough test, or estimated from grain size and/or pore size distributions.

The parameters k_{att} and k_{det} must be calibrated from a NP breakthrough test, or estimated as a function of flow velocity and NP, PM, and slurry physiochemical properties.

The interaction kinetics, resulting in NP deposition onto and release from the solid matrix, have been proven to be strongly influenced by both operative, e.g. injection flow rate, and natural conditions, e.g. pore-water ionic strength. These parameters can substantially vary according to the field of application and the involved subsurface formations (e.g. nZVI injected in contaminated aquifers, NPs released with leachate from a landfill, NPs injected in a reservoir for enhanced oil recovery, etc.). The approach within NanoRem WP7 has therefore been to increase understanding of NP behaviour through pore-scale modelling, aimed at defining upscaled relationships for k_{att} and k_{det} that can be validated using experimental or field data at the macro-scale.

Fundamental pore-scale modelling built on previous research by Raouf (Raouf and Hassanizadeh, 2010; Raouf *et al.*, 2010, 2013) and Seetha *et al.* (2014, 2015). Results from Seetha's model simulations at the scale of a single pore were implemented in the pore network model NanoPNM that was based on the pore network developed by Raouf. Pre-processing and post-processing tools were developed to allow the generation of large numbers of simulations for tracer and NP breakthrough in PM columns, and the automated interpretation of the resulting breakthrough curves (BTC) in terms of fitted hydraulic parameters (Φ , K , α) and the kinetic parameters for NP attachment and detachment (k , f). The upscaled equations were derived via statistical regression.

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

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

4. NP TRANSPORT IN COLUMN TESTS

Based on the upscaled equations for tracer flow that were derived from the pore-scale modelling, an optimisation tool was also developed to generate the pore network input parameters that best represent real-world column experiments in terms of porosity, hydraulic conductivity and dispersivity. This enables quick reproduction of laboratory column tests with NanoPNM. The pore network can then be used to investigate slightly different conditions, both with respect to the PM hydraulic parameters and NP surface properties and slurry composition. The combination of laboratory tests with NanoPNM simulations can aid in focussing limited laboratory availability to critical tests.

The final stage of the upscaling process involves the implementation of the macro-scale equations in numerical codes for direct application in typical laboratory and field-scale problems. The software MNMs was developed in NanoRem to incorporate the features relevant for NP transport simulation at the macro-scale both in 1-D Cartesian (e.g. NP transport column test interpretation) and 1D radial geometries (e.g. simulation of pilot-scale injection of NP). These features include (see Figure 3) i) the calculation of interaction energy profiles to forecast micro- and nano-particles behaviour in terms of aggregation and mobility; ii) calculation of single collector attachment efficiency (Messina *et al.*, 2015); iii) simulation of the transport of a dissolved species accounting for equilibrium sorption and first order degradation; iv) simulation of particle transport under transient ionic strength conditions (Tosco *et al.*, 2009); v) simulation of porous medium clogging phenomena; vi) simulation of particle transport in the presence of Non-Newtonian carrier fluids (Tosco *et al.*, 2010); and vii) simulation of pilot-scale injection of NP slurries through a single well via a radial simulation tool (Tosco *et al.*, 2014). MNMs represents the evolution, combination and extension of other numerical codes developed at Politecnico di Torino in previous projects, such as MNM1D and E-MNM1D. MNMs is embedded in a user-friendly graphical interface for an easy and direct application to practical problems (Figure 4). MNMs can be downloaded, free of charge, from <http://areeweb.polito.it/ricerca/groundwater/software/MNMs.php>, the website of the Groundwater Research Group of Politecnico di Torino.

The mechanisms controlling NP transport (see Box 1 and Figure 2) are the same regardless of the scale (1D, radial or 3D) and as a consequence they can be determined on smaller scales (namely columns) and then applied to larger scales (radial or full 3D). Parameters calibrated by using the 1D model for laboratory column tests are directly transferable to the 3D model. When applied to the

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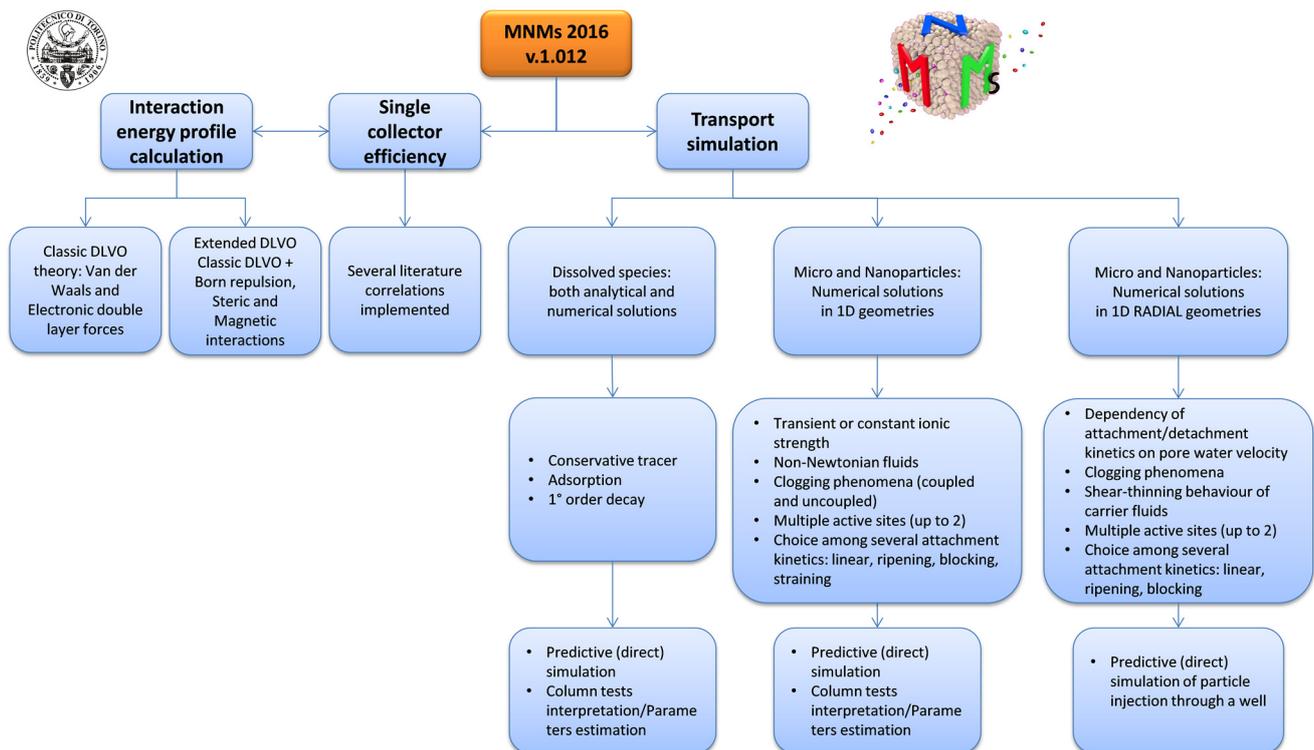


Figure 3. Structure and main features of MNMs.

design of a NP-based remediation, MNMs can be used to assist and integrate laboratory column tests. First, the size-specific and particle-specific properties are assessed, and a few preliminary column tests are run using the site material (sand) to explore how particles are transported under different conditions (e.g. different flow rates). The experimental results are then modelled using MNMs, and the kinetics (i.e. k_{att} , k_{det}) are obtained by fitting the experimental data. When the NP transport features have been characterised, a few additional column tests can also be run to verify the predictive capability of the model (i.e. tests are run in the lab and the results are compared to the prediction of the model for the specific conditions). Such integrated use of MNMs allows limiting the number of column tests, and directly provides the NP transport mechanisms and kinetics which can be implemented at large scale to assist the design of full-scale applications.

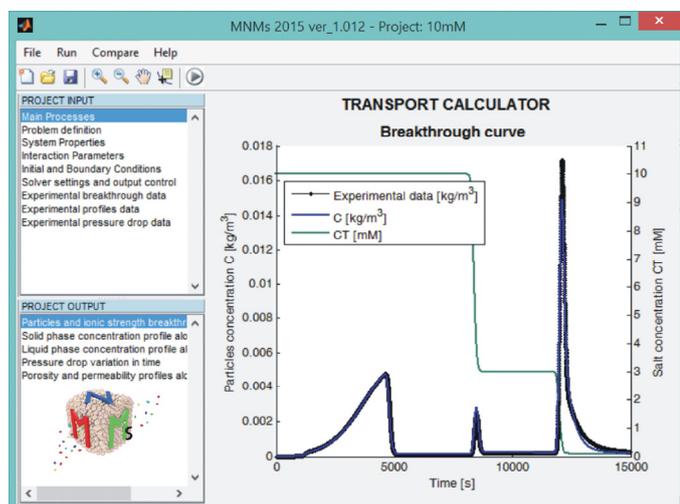


Figure 4. Graphical interface of MNMs. Fitting example of experimental data of a column transport test of ferrihydrite nanoparticle under transient ionic strength conditions.

5. FORECASTING NP EMPLACEMENT WITH INJECTION

When moving from the lab to the field, a first step in the design of a full-scale intervention is represented by a pilot injection. In field applications NP suspensions are typically injected into the subsurface via wells or direct push systems, generating a radial or radial-like flow, where velocity decreases with increasing distance from the delivery point (Tosco *et al.*, 2014). To simulate this condition, the radial tool included in MNMs can be used, which incorporates all the information on NP mobility generated from the column tests, namely, the influence of flow velocity (and consequently of the injection flow rate) on the kinetics of the particle-porous medium interactions, the eventual clogging, and the non-Newtonian (shear thinning) rheological properties of the carrier fluid used to improve stability and mobility of particle suspensions. The empirical relationships proposed in Tosco *et al.* (2014) have been used to express the dependence of the deposition and release parameters on the flow velocity. A modified formulation of the Cross rheological model has been implemented to account for the shear thinning behaviour of polymeric stabilisers usually employed for particle injection.

The radial tool of MNMs can be used for the preliminary design of the field injection, namely to evaluate how injection rate, particle concentration, injection duration may result in a different radius of influence and particle concentration in the emplacement area. However, for the design of the full-scale injection, more complex modelling tools are necessary. To this aim, the key features of MNMs were also implemented in MNM3D (Bianco *et al.*, 2016), which combines MNMs with the well-known transport model RT3D (Clement, 1997; Clement *et al.*, 1998), for the full 3D numerical simulation of field-scale injection and transport of NPs in PM (<http://areweb.polito.it/ricerca/groundwater/software/MNM3D.php>).

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MNM3D is a standalone numerical code developed at Politecnico di Torino. The tool can be employed in the design of *in situ* aquifer remediation (accounting for dependency of NP transport on the injection flow rate, and on the local heterogeneities of the contaminated aquifer) and to estimate important operative parameters, including particle distribution around the injection well, influence radius for a target concentration, number of required injection wells, etc. MNM3D was successfully tested to simulate the injection of Carbo-Iron® NPs in a 2D pilot-scale flume (Figure 5). The injection was carried out at the VEGAS facilities at the University of Stuttgart (NanoRem WP8). A simplified version of MNM3D was also implemented in Visual Modflow for the simulation of ionic strength dependent transport of NPs in groundwater (Bianco *et al.*, 2016).

6. PREDICTING LONG TERM NP MOBILITY

Understanding and modelling the transport and the deposition of NPs injected for groundwater remediation is a key aspect both in the short-term (for the design of the field-scale injection) and the long-term (to understand if and to what extent NPs can spread in the environment during and after remediation).

The injection of NPs for groundwater remediation is usually performed at high flow rates to promote the spreading of particles around the injection well. However, when the injection is stopped, the particles are subjected only to the natural flow and the transport velocities become usually much smaller. In such conditions, the geochemical properties of groundwater and the aquifer heterogeneities become the main driving force governing the particle deposition and release processes. In this sense, MNM3D proves to

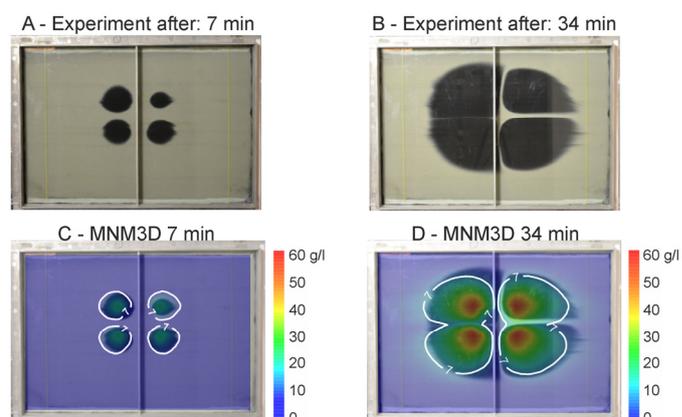


Figure 5. Application of MNM3D to the simulation of Carbo-Iron® NP injection in a 2D pilot scale flume. The particles were injected at the VEGAS facilities (NanoRem WP8). Visual comparison between experimental (black plume) and simulated (coloured) results of nanoparticle transport (C, D) (modified from Bianco *et al.*, 2016).

be a useful tool to evaluate the post-remediation fate of particles employed in groundwater remediation, by providing useful information on the foreseen migration distances and pathways of particles. Figure 6 shows an example of application of MNM3D to long term simulation of particle transport subject to transient ionic strength conditions. The simulation highlights how the particle behaviour and the foreseen travel distance can vary according to the applied model, proving once again that the influence of the geochemical properties of the groundwater on the attachment and detachment rates cannot be neglected.

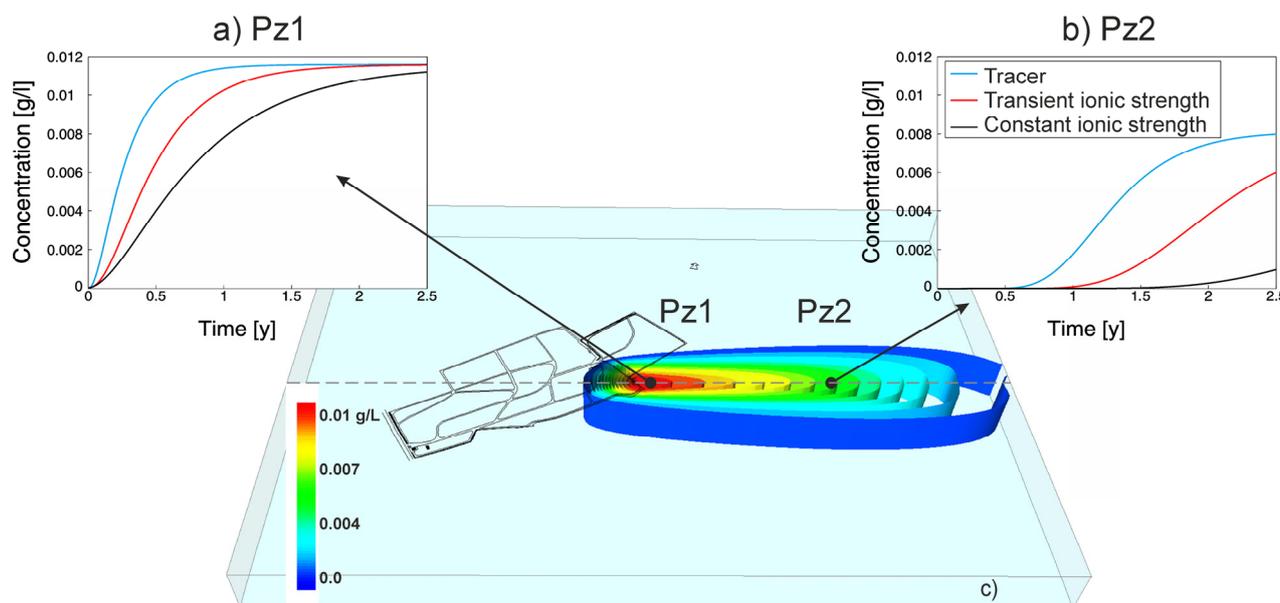


Figure 6. Example of simulation of nanoparticle release in the environment using the ionic strength dependent kinetics implemented in MNM3D. (a,b) concentration as a function of time at two observation points assuming no attachment (tracer, blue curves), constant ionic strength model (black curve) and transient ionic strength model (red curve); (c) NP plume of particles after 2.5 years from the start of the release with the transient ionic strength model (modified from Bianco *et al.*, 2016).

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7. CONCLUDING REMARKS

The numerical codes that were developed in NanoRem enable adequate and realistic macro-scale simulation of injection and transport of NPs in groundwater. They offer practical aids in the design and interpretation of laboratory tests, field pilots, and full-scale nanoremediation, as well as in the assessment of potential long term risks. MNMs, developed for quantitative analysis of laboratory-scale column tests and NP injections in simplified geometries is a useful tool for the preliminary optimisation of pilot injections in the framework of a nanoremediation design. MNM3D is a full 3D numerical code for the simulation of the velocity and ionic strength dependent transport of NPs in complex aquifer systems. It was developed as a support tool for the design of full-scale nanoremediation and to assess the long term behaviour of NPs after injection. The code is currently being implemented in the Visual Modflow graphical interface, and will be included as a transport simulation package in the next release of Visual Modflow in 2017. This will make it easily available to practitioners and consultants and promote its diffusion in the remediation field.

REFERENCES

- Bianco, C., Tosco, T., Sethi, R. 2016. A 3-dimensional micro- and nanoparticle transport and filtration model (MNM3D) applied to the migration of carbon-based nanomaterials in porous media, *Journal of Contaminant Hydrology*, 193, pp. 10-20. DOI: 10.1016/j.jconhyd.2016.08.006
- Clement, T.P. 1997. RT3D - A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers, Pacific Northwest National Laboratory, Richland, WA, USA. PNNL-11720.
- Clement, T.P., Sun, Y., Hooker, B.S. and Petersen, J.N. 1998. Modeling multispecies reactive transport in ground water. *Ground Water Monitoring and Remediation* 18(2), 79-92.
- Crevacore, E.; Tosco, T.; Sethi, R.; Boccardo, G.; Marchisio, D.L. 2016. Recirculation zones induce non-Fickian transport in three-dimensional periodic porous media. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 94(5), pp.
- Júnior, J.A.A., & Baldo, J.B. 2014. The behavior of zeta potential of silica suspensions. *New Journal of Glass and Ceramics*, 4(02), 29.
- Messina, F., Marchisio, D.L. and Sethi, R. 2015. An extended and total flux normalized correlation equation for predicting single-collector efficiency. *Journal of Colloid and Interface Science* 446(0), 185-193.
- Micic Batka, V., and Hofman, T. 2016. Stability, Mobility, Delivery and Fate of optimized NPs under Field Relevant Conditions. NanoRem deliverable DL 4.2.
- Raouf, A., & Hassanizadeh, S.M. 2010. A new method for generating pore-network models of porous media. *Transport in porous media*, 81(3), 391-407.
- Raouf, A., Hassanizadeh, S.M., & Leijnse, A. 2010. Upscaling transport of adsorbing solutes in porous media: Pore-network modeling. *Vadose Zone Journal* 9(3), 624-636.
- Raouf, A., Nick, H.M., Hassanizadeh, S.M., & Spiers, C.J. 2013. PoreFlow: A complex pore-network model for simulation of reactive transport in variably saturated porous media. *Computers & Geosciences*, 61, 160-174.
- Redman, J.A., Walker, S.L., & Elimelech, M. 2004. Bacterial adhesion and transport in porous media: Role of the secondary energy minimum. *Environmental Science & Technology*, 38(6), 1777-1785.
- Seetha, N., Kumar, M.M., Hassanizadeh, S.M., & Raouf, A. 2014. Virus-sized colloid transport in a single pore: Model development and sensitivity analysis. *Journal of contaminant hydrology*, 164, 163-180.
- Seetha, N., Majid Hassanizadeh, S., Kumar, M., & Raouf, A. 2015. Correlation equations for average deposition rate coefficients of nanoparticles in a cylindrical pore. *Water Resources Research*, 51 (10), 8034-8059.
- Tosco, T., Gastone, F. and Sethi, R. 2014. Guar gum solutions for improved delivery of iron particles in porous media (Part 2): Iron transport tests and modeling in radial geometry. *Journal of Contaminant Hydrology* 166(0), 34-51, doi: 10.1016/j.jconhyd.2014.06.014.
- Tosco, T., Papini, M.P., Viggi, C.C., Sethi, R. 2014b. Nanoscale zerovalent iron particles for groundwater remediation: a review, *Journal of Cleaner Production*, Volume 77, Pages 10-21, ISSN 0959-6526, doi: 10.1016/j.jclepro.2013.12.026.
- Tosco, T. and Sethi, R. 2010. Transport of non-newtonian suspensions of highly concentrated micro- and nanoscale iron particles in porous media: A modeling approach. *Environmental Science and Technology* 44(23), 9062-9068.
- Tosco, T., Tiraferri, A. and 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.

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