Where Will Our Nanoparticles Go? Numerical Modeling of Nanoparticles Transport

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NanoRem Final Conference

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

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- Introduction
- Part I: pore scale modelling
- Part II: macro scale modelling
- Part III: examples

Why numerical modelling?

Why numerical modelling?

- Where do I inject to be the most effective?
- How many wells and at what distance?
- What injection rate? Injection duration?
- What NP concentration? Stabilizer concentration?
- Where, when and what to monitor to validate NP emplacement?
- Where, when and what to monitor to ensure the safety of relevant receptors?

➔ Modelling aims in short:

- Forecast placement of NP during injection
- Forecast long term behaviour / potential transport of particles out of remediation area during and after injection

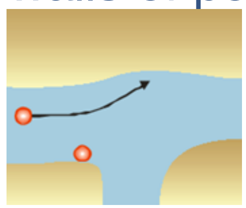
Main advantages:

- complementing / reducing laboratory testing
- ability to explore different employment options in advance
- guiding design/execution of monitoring
- testing assumptions

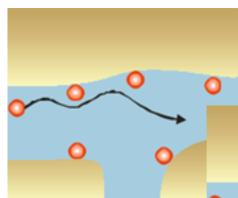
What affects NP transport?

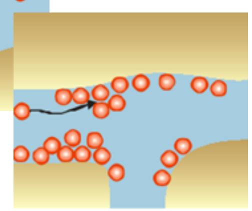
And at what scale to be described?

- Fluid flow (NP suspension)
- Interaction with walls of pores of porous medium
  - attachment
  - detachment

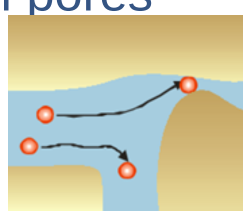


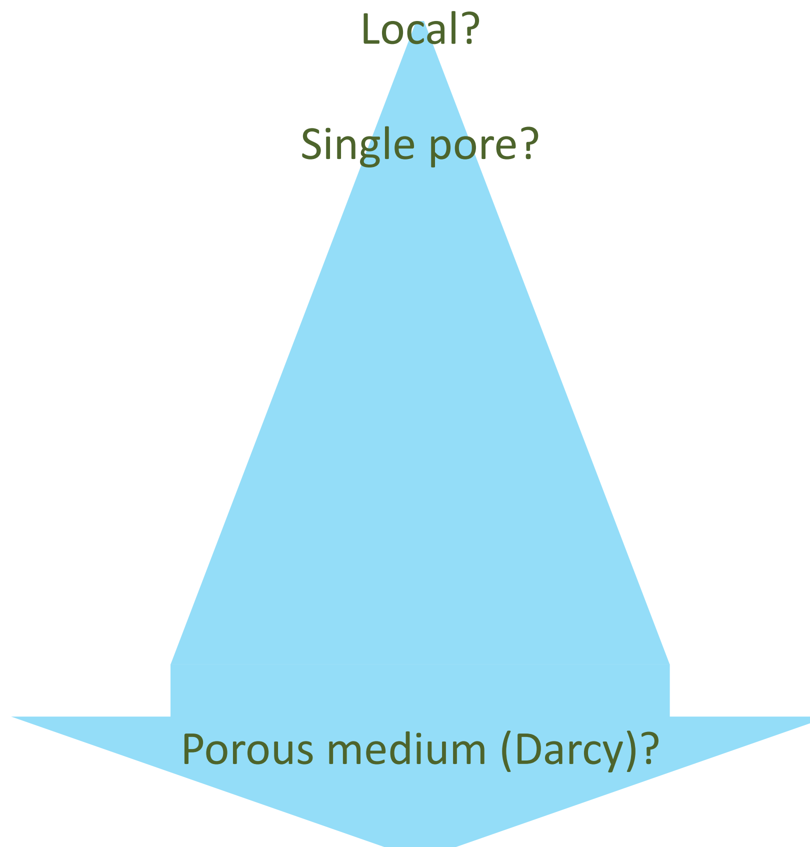
- Mutual interaction
  - blocking
  - ripening / aggregation





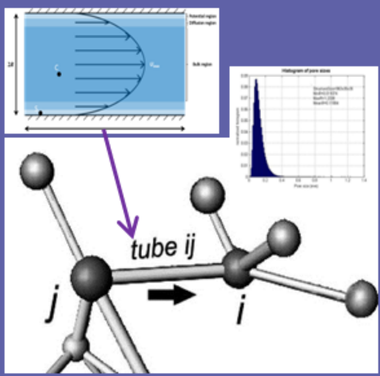
- Interaction with small pores (dead ends)
  - straining / clogging





NanoRem modelling in a nutshell

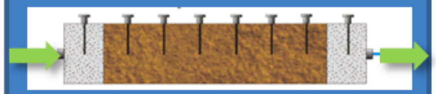
Pore scale

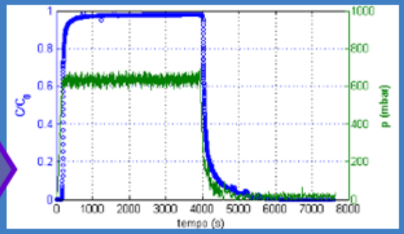


NanoPNM and **pre- and post-processing tools:**

- Monte Carlo approach
- 1st principles modelling at pore & pore-network scale
- to derive upscaled formula with physically based parameters
- validation at scale of small columns

Laboratory scale

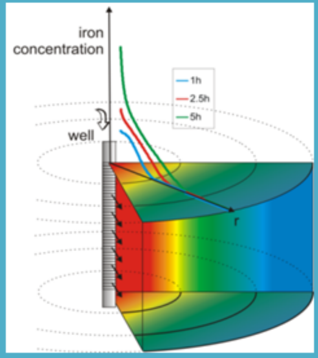




MNM1D-MNMs: tools for column test interpretation:

- Estimation of DLVO interactions and single collector efficiency
- Solute & colloid transport in 1D columns:
  - Deposition/release
  - Influence of I.S.
  - Clogging
  - Non Newtonian fluid

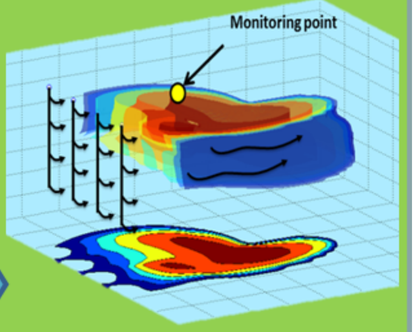
Pilot-scale



MNMs: software for simulation of particle injection via single well.

- Solute & colloid transport in radial geometry:
  - Deposition/release
  - Clogging
  - Influence of flow rate
  - Non Newtonian fluid

Large-scale



MNM3D: a MODFLOW/RT3D-based simulation tool for particle transport in large scale scenarios:

- Full-scale injection of NPs
- Long-term fate of NPs released in the subsurface
- Features included:
  - Deposition/release
  - Coupled influence of I.S. and flow rate

Part I

Pore scale modelling

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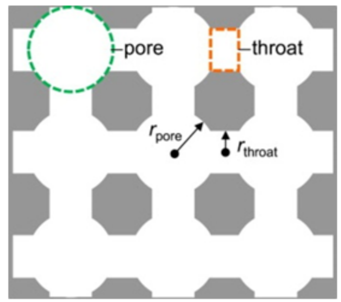
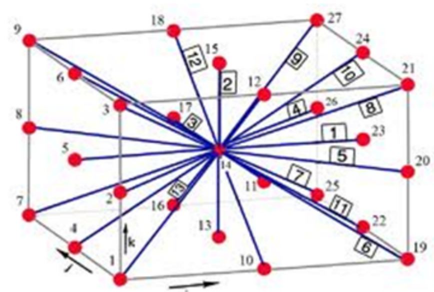
NanoPNM: a pore network model

"average" sand

represented by:

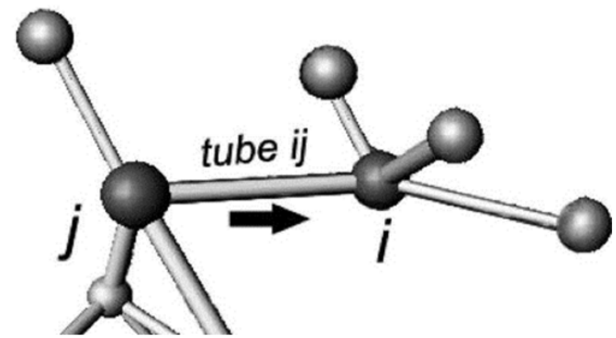


regular network of pores



can be connected to
26 neighbours (or not)

Raoof, A., & Hassanizadeh, S. M. (2010). A new method for generating pore-network models of porous media. *Transport in porous media*, *81*(3), 391-407.

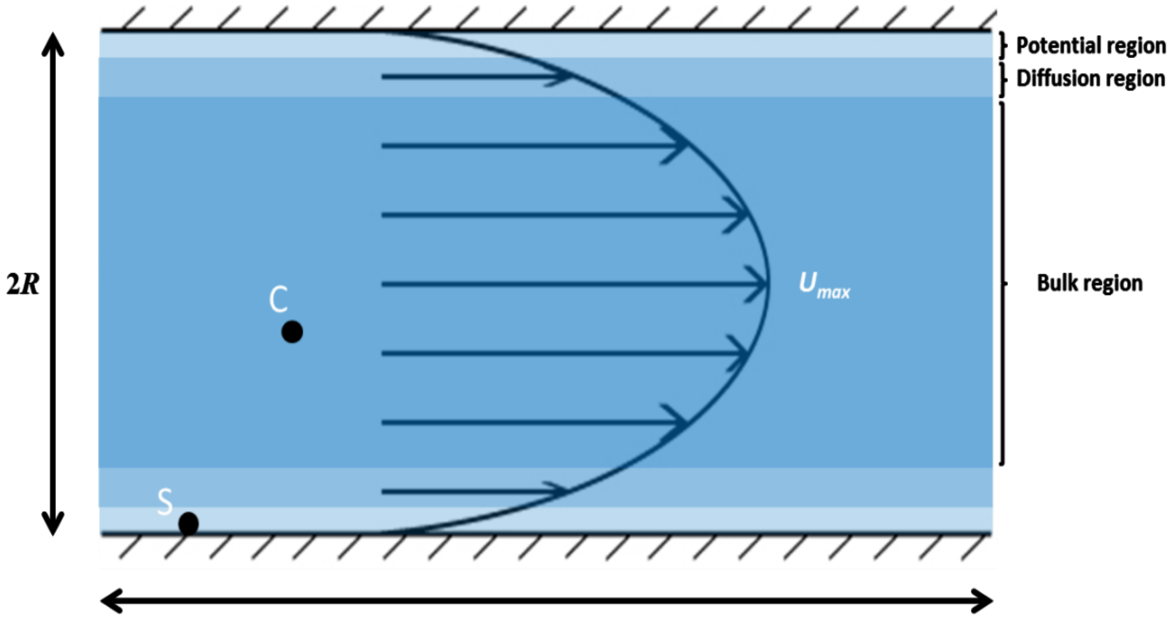


define:

- lattice distance ***LD***
- pore/throat size ***m, s***
- average # connected neighbours

CN =26(1-***E***)

Starting from a single pore throat:



Hagen-Poiseuille:

$$\bar{U} = ½\, U_{max}$$

$$q = \pi R^2\, \bar{U} = \frac{\Delta P}{l}\, \frac{\pi R^4}{8\mu}$$

Seetha, N., Majid Hassanizadeh, S., Kumar, M., & Raoof, A. (2015). Correlation equations for average deposition rate coefficients of nanoparticles in a cylindrical pore. *Water Resources Research*, *51*(10), 8034-8059.

3D simulation for range of values of pore-scale parameters

↓

Averaging 3D concentrations (C, S) to obtain 1D concentration field

↓

Fit of 1D concentration field with 1D advection-dispersion-adsorption equation to obtain pore averaged k_{att} and k_{det} or K_D

↓

Find general relationship between averaged rate coefficients at pore-scale and various pore-scale parameters

Multiple pore network simulations for range of parameters

For tracer flow:

- to obtain relations with input parameters ***LD***, ***m***, ***s***, and ***E*** for:
  - porosity **ϕ**
  - hydraulic conductivity ***K***
  - dispersivity ***α***
- that are used to easily find pore network input parameters that represent laboratory experiments
- to derive upscaled relations for ***K*** and ***α***

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Empirical relations for hydraulic parameters

Parameters	Equation	R^2	RMSQE rel.	RMSQE abs.
NanoPNM input parameters	$\phi = 26.0\,(m/LD)^{1.75}(e^{s/m})^{-0.55}\,(1-E)$	0.998	1.1%	0.0035
	$K = 3.04\cdot 10^{6}\,(m/LD)^{2.75} m^{2}\,(e^{s/m})^{-2}\,(1-E)^{2.25}$	0.997	3.2%	0.84
	$\alpha = 0.243\,Nx^{0.1}\;\mathrm{LD}\,(e^{s/m})^{1.55}\,(1-E)^{-0.7}$	0.991	1.6%	0.024
porosity and LD	$K = 650\,\phi^{2.5} LD^{1.7}$	0.979	8.2%	2.1
	$\alpha = 0.53\,\mathrm{Nx}^{\,0.1}\,\phi^{-0.5}\,LD^{0.2}$	0.720	9.3%	0.13
porosity, LD, E	$K = 395\,\phi^{2.75}\,LD^{2.1}\,(1-\mathrm{E})^{-0.5}$	0.996	3.7%	0.84
	$\alpha = 0.32\,\mathrm{Nx}^{\,0.1}\,\phi^{-0.25}\,LD^{0.6}\,(1-E)^{-0.5}$	0.885	6.0%	0.085

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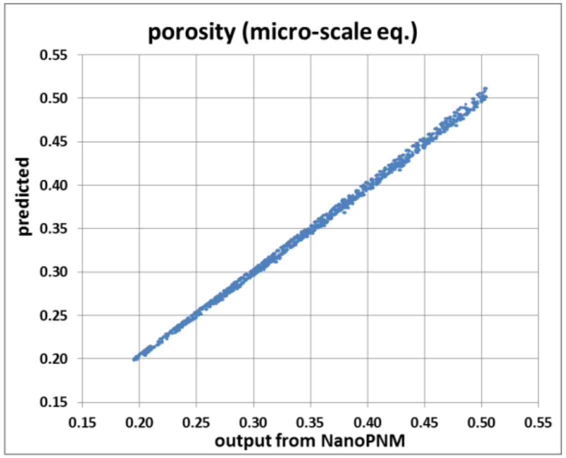

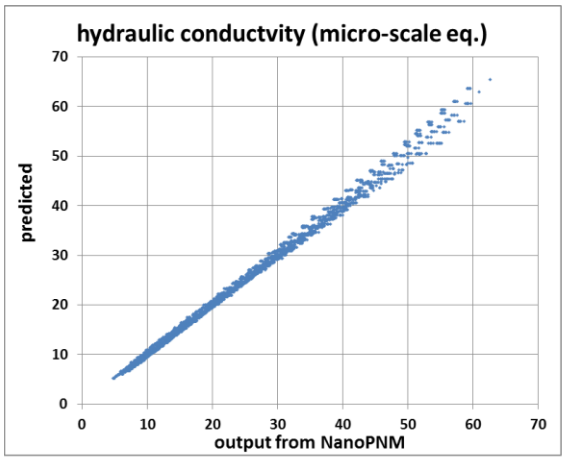

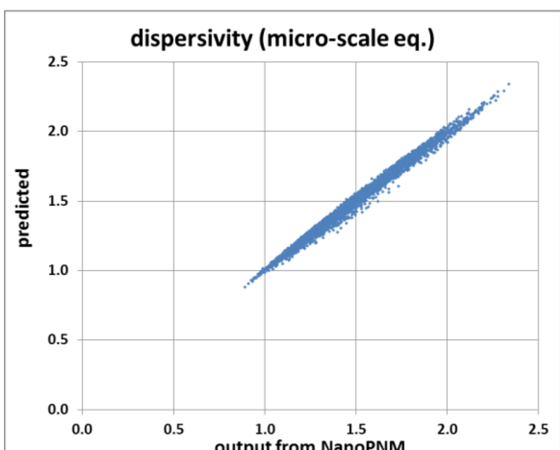

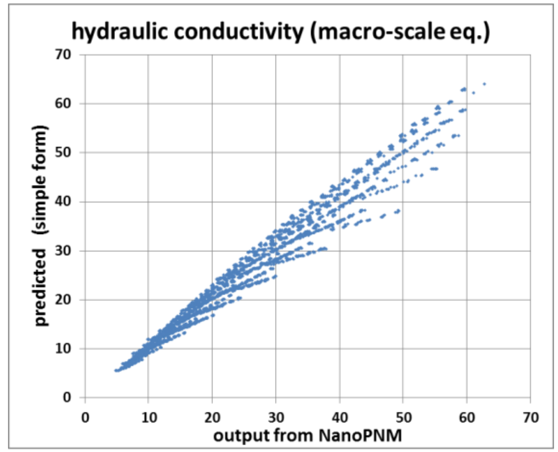

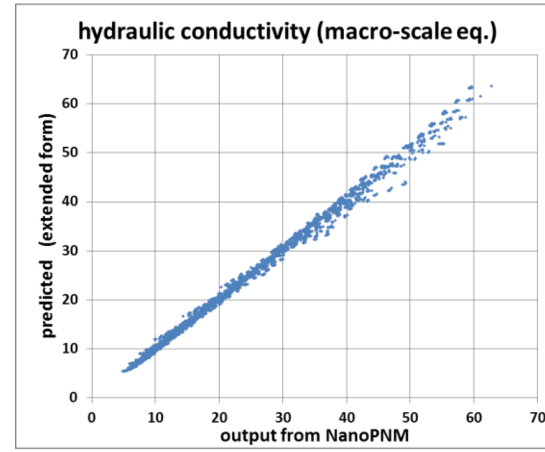

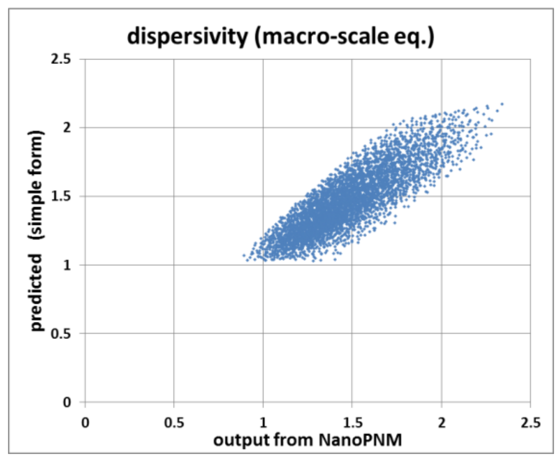

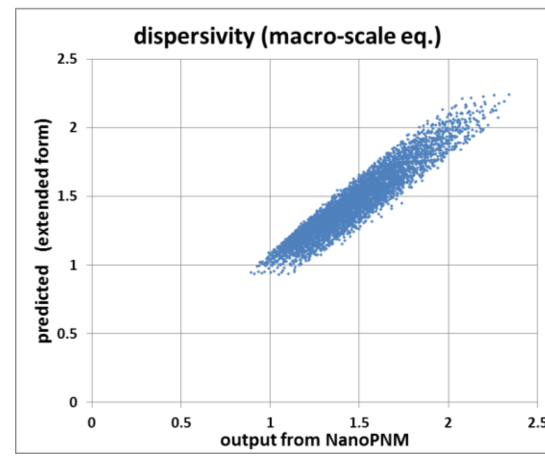

Main conclusions (I.1)

- porosity + grain size ⇏ hydraulic conductivity, dispersivity
- grain packing cannot be ignored

- Hydraulic conductivity and dispersivity from packed columns may differ between different columns
- and may differ from the actual field values!

- Ideally, laboratory tests should be performed on undisturbed columns
- At least a NP breakthrough test should always be combined with a tracer test for the exact same column

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Multiple pore network simulations for range of parameters

For NP transport:

- to obtain macro scale relations with pore network flow parameters (providing **R** and pore scale **v**) and NP parameters **a**, ***I***, and ψ_{PM} & ψ_{NP} (function of ***I*** & **pH**) for:
  - attachment rate K_{att}
  - detachment rate K_{det}
  - and/or distribution constant k_D

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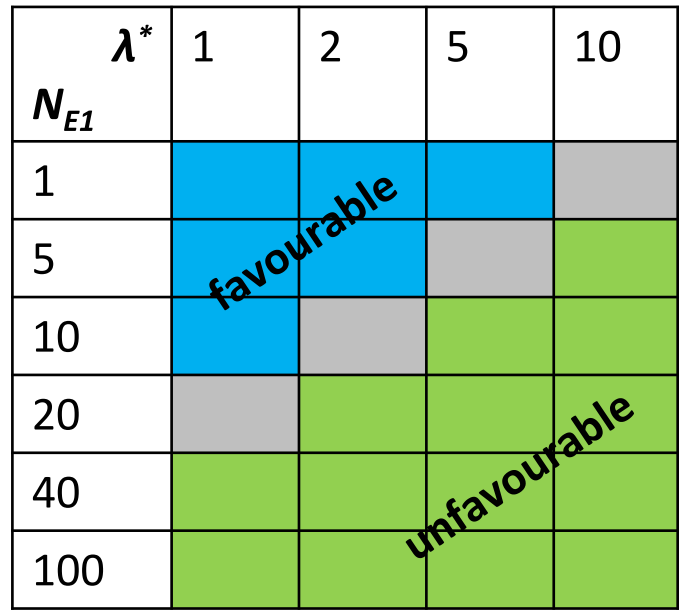
Empirical relations at single pore scale

Non-dimensional parameters

	expression	remarks
λ^*	λ/a	λ = characteristic wavelength of interaction, 100 nm
A	a/R	interception parameter
Pe	vR/D_∞	Peclet number
N_{DL}	κa	ratio of particle radius to double layer thickness
N_{E1}	$\dfrac{\pi\varepsilon\varepsilon_0 a(\psi^2_{PM}+\psi^2_{NP})}{k_B T}$	magnitude of surface potentials
N_{E2}	$\dfrac{2(\psi_{PM}/\psi_{NP})}{(1+(\psi_{PM}/\psi_{NP})^2}$	ratio of surface potentials



Seetha, N., et al. "Correlation equations for average deposition rate coefficients of nanoparticles in a cylindrical pore." *Water Resources Research* 51.10 (2015): 8034-8059.

Simplified equations

λ* x NE1 ≥ 40

$$Da_{att} = 0.158\,\lambda^{*1.5} e^{-0.5\lambda^*} A^{0.5} e^{-400A} Pe^{-1.1} N_{DL}{}^{0.5}\ N_{E1}{}^{-0.15}$$

$$Da_{det} = 6.40\,\lambda^{*0.5} e^{-0.3\lambda^*} A^{-0.1} e^{-400A} Pe^{-0.9}$$

$$k'D = 0.0124\ \lambda^{*1.0} e^{-0.2\lambda^*} A^{0.6} Pe^{-0.2}\ N_{DL}{}^{0.5}\ N_{E1}{}^{-0.15}$$

15 < λ* x NE1 < 40

$$Da_{att} = 17.8\ e^{-1.5\lambda^*}\ e^{-250A} Pe^{-1.0} e^{0.03N_{DL}} e^{-0.25N_{E1}}$$

$$Da_{det} = 1.40 \times 10^{-3} e^{0.5\lambda^*} A^{-0.8} e^{-200A} Pe^{-0.9} e^{-0.02N_{DL}} e^{0.03N_{E1}}$$

$$k'D = 6370\ e^{-2\lambda^*} A^{0.8} e^{-50A} Pe^{-0.1} e^{0.05N_{DL}} e^{-0.28N_{E1}}$$

λ* x NE1 ≤ 15

$$Da_{att} = 0.0872\ e^{-1.0\lambda^*} A^{-0.5} e^{-120A} Pe^{-1.0} N_{DL}{}^{0.1} e^{-0.1N_{E1}}$$

$$Da_{det} = 2.03 \times 10^{-11} e^{3\lambda^*} A^{-1.3} e^{-120A} Pe^{-1.0} N_{DL}{}^{-0.4} e^{1.0N_{E1}}$$

$$k'D = 2.15 \times\ 10^{9} e^{-4\lambda^*} A^{0.8} N_{DL}{}^{0.5} e^{-1.1N_{E1}}$$

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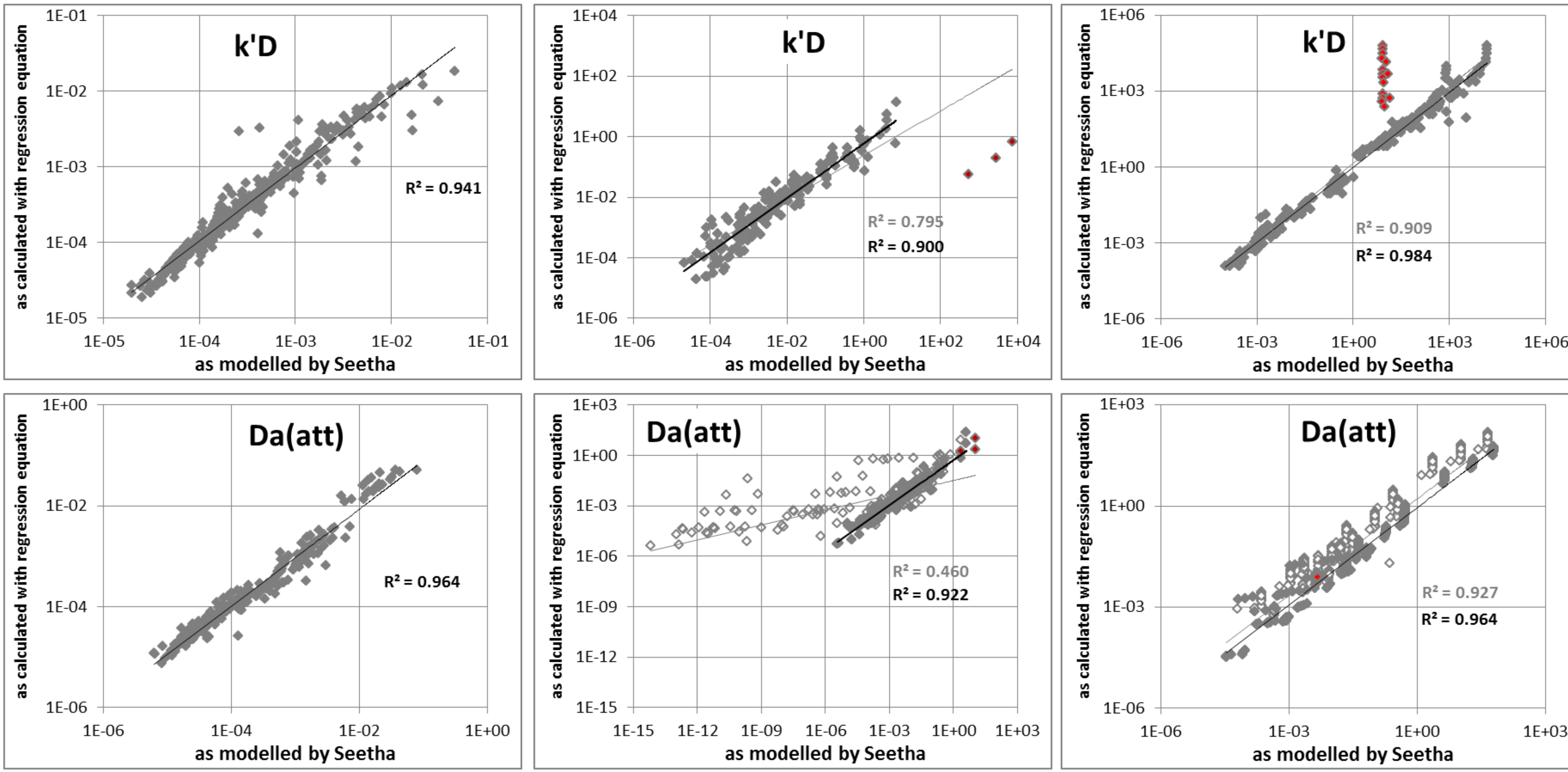
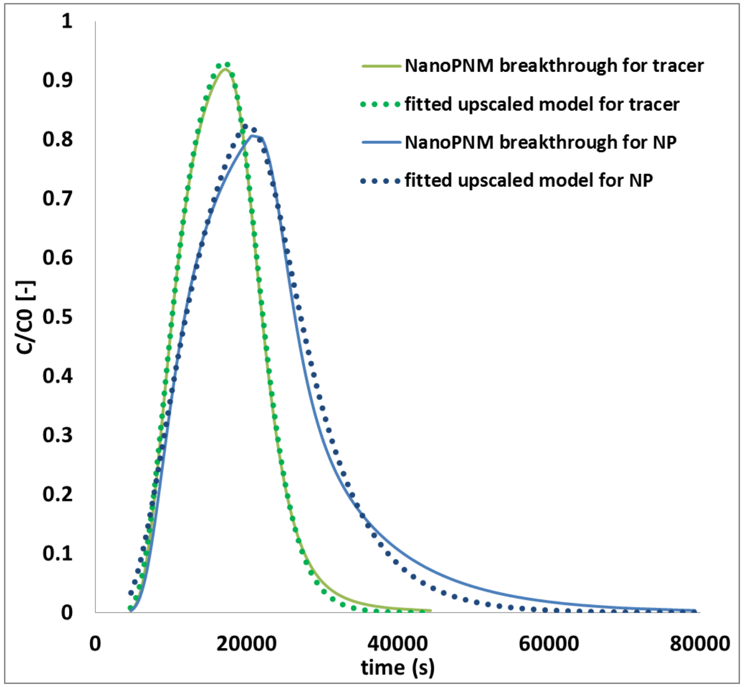
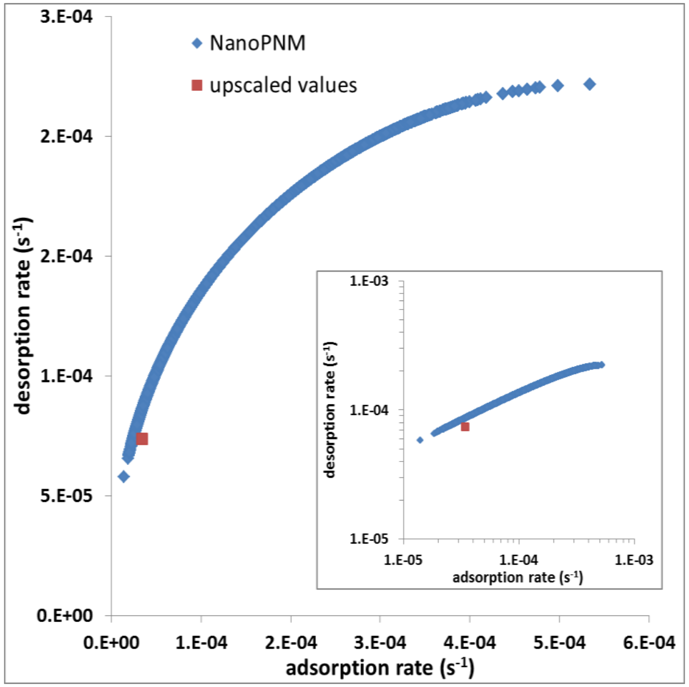
◇ all simulation data
◆ simulation data resulting in k'D, outliers for Da(det) and k'D
◆ simulation data resulting in k'D, used in regression

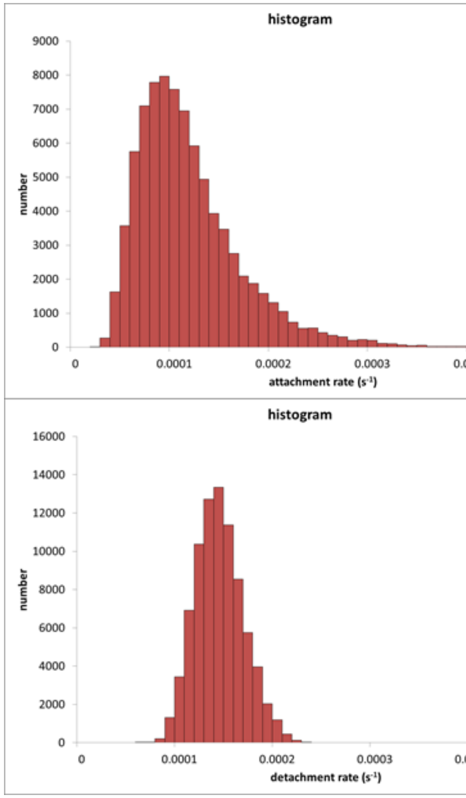
Large surface charges | Intermediate range | Small surface charges



Some NanoPNM results







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However, …..

- When using the equations in NanoPNM for conditions relevant for Nanoremediation, we predict no significant attachment!
- Attachment only occurs if surface potentials are small
- Even then, attachment rates are small compared to advective process

λ^* / N_{E1}	1	2	5	10
1				
5				
10				
20				
40				
100				

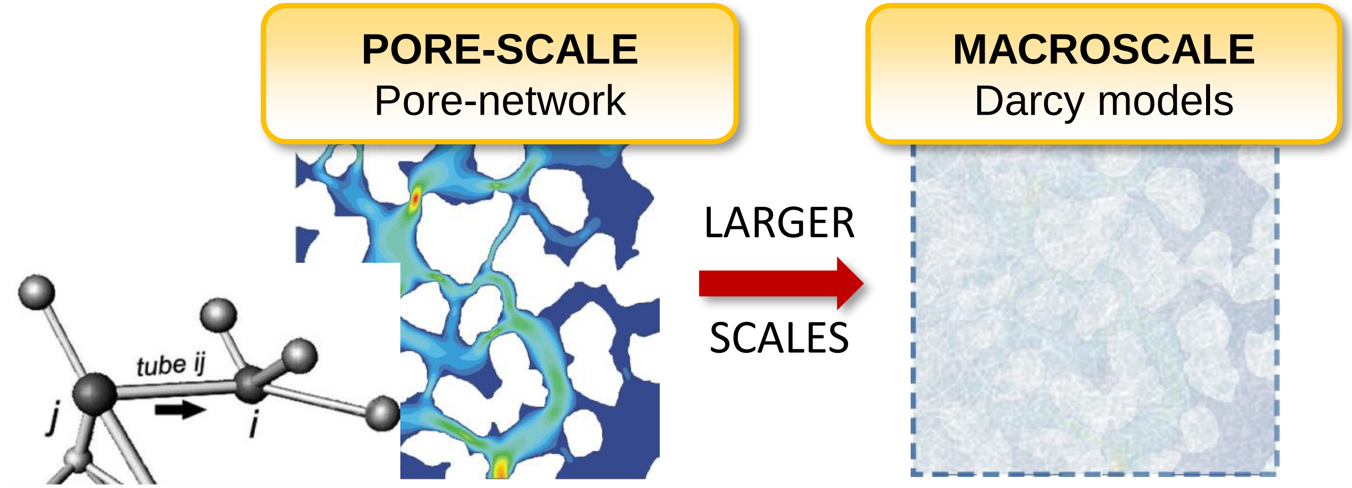
Main conclusion (I.2)

- Upscaling of fundamental description of electrostatic interaction between NP and PM at pore scale does not adequately describe NP attachment and detachment at Darcy scale

Part II

Macro scale modelling

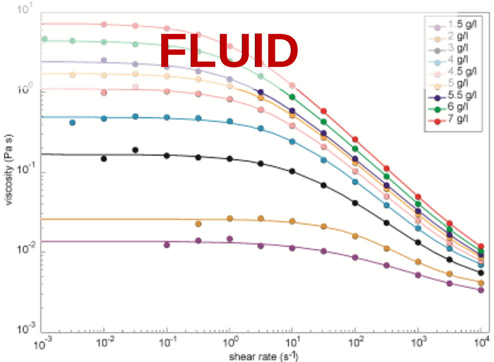
Macro-scale modeling



- Challenge: NP transport coupled with porous medium clogging and non Newtonian flow of NP slurries → not possible to use “classic” advection-dispersion-deposition models

Macro-scale modeling

SHEAR THINNING FLUID



Darcy's law:

$$q_m = -\frac{K(s)}{\mu_m(\dot{\gamma}_m, c, c_x)}\frac{\partial p}{\partial x}$$

Transport equations:

$$\begin{cases} \frac{\partial}{\partial t}(\varepsilon_m c_x) + \frac{\partial}{\partial x}(q_m c_x) - \frac{\partial}{\partial x}\left(\varepsilon_m D \frac{\partial c_x}{\partial x}\right) = 0 \\ \frac{\partial}{\partial t}(\varepsilon_m c) + \frac{\partial(\rho_b s_1)}{\partial t} + \frac{\partial(\rho_b s_2)}{\partial t} + \frac{\partial}{\partial x}(q_m c) - \frac{\partial}{\partial x}\left(\varepsilon_m D \frac{\partial c}{\partial x}\right) = 0 \\ \frac{\partial(\rho_b s_1)}{\partial t} = \varepsilon_m k_{a,1} c - \rho_b k_{d,1} s_1 \\ \frac{\partial(\rho_b s_2)}{\partial t} = \varepsilon_m k_{a,2}\left(1 + A_2 s^{\beta_2}\right) c \end{cases}$$

Porosity:

$$\varepsilon_m(s) = n - \frac{\rho_b}{\rho_s} s$$

Fluid viscosity:

$$\mu_m(\dot{\gamma}_m, c, c_x) = \mu_{m,\infty} + \frac{\mu_{m,0}(c, c_x) - \mu_{m,\infty}}{1 + [\lambda_m(c) \cdot \dot{\gamma}_m]^{\chi_m(c)}}$$

$$\dot{\gamma}_m = \alpha_\gamma \frac{q_m}{\sqrt{K(s)\varepsilon_m(s)}}$$

Permeability:

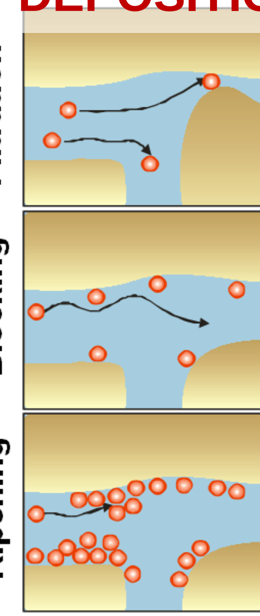
$$K(s) = \left[\frac{\varepsilon_m(s)}{n}\right]^3 \left(\frac{A_0}{A_0 + \vartheta A_c \frac{\rho_b}{\rho_c} s}\right)^2 K_0$$

PARTICLE DEPOSITION

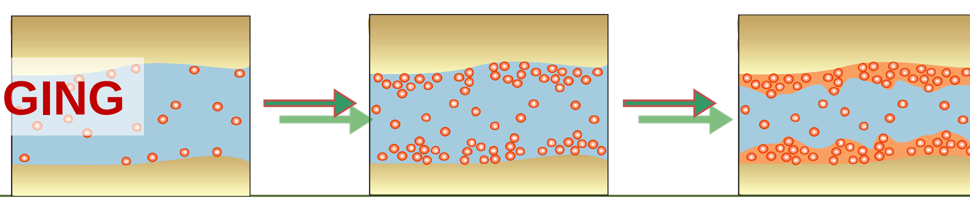
Filtration

Blocking

Ripening

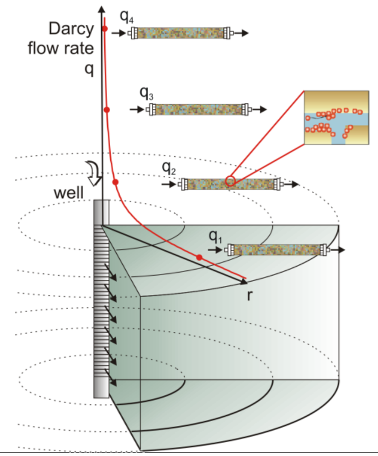


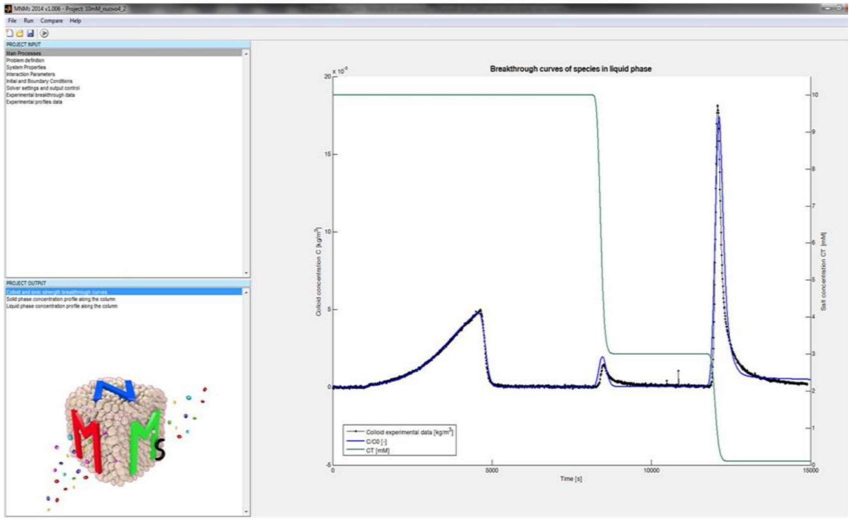
CLOGGING



Modeling tools: MNMs

- Graphical interface for
  - lab-scale transport problems
  - Pilot scale preliminary design
- User-friendly input/output
- Availaible on Polito's website





Modeling tools: MNM3D

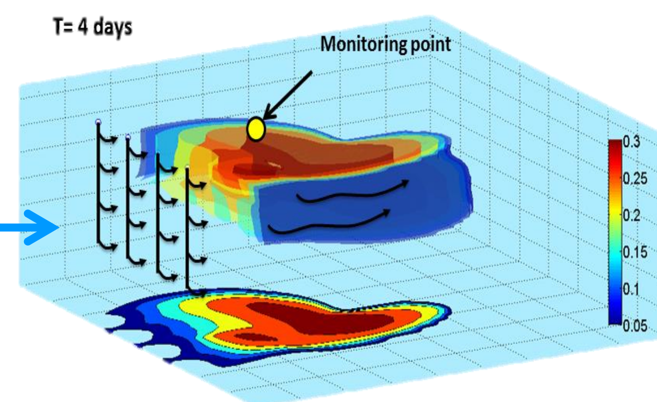
- Particle transport equations implemented in MNM3D:
  - Modified advection-dispersion equation
  - Ionic strength dependency
  - Flow velocity dependency

  } Coupled solution
- Modeling tool available in the next release of Visual Modflow

MNMs → MNM3D

MODFLOW + RT3D → MNM3D

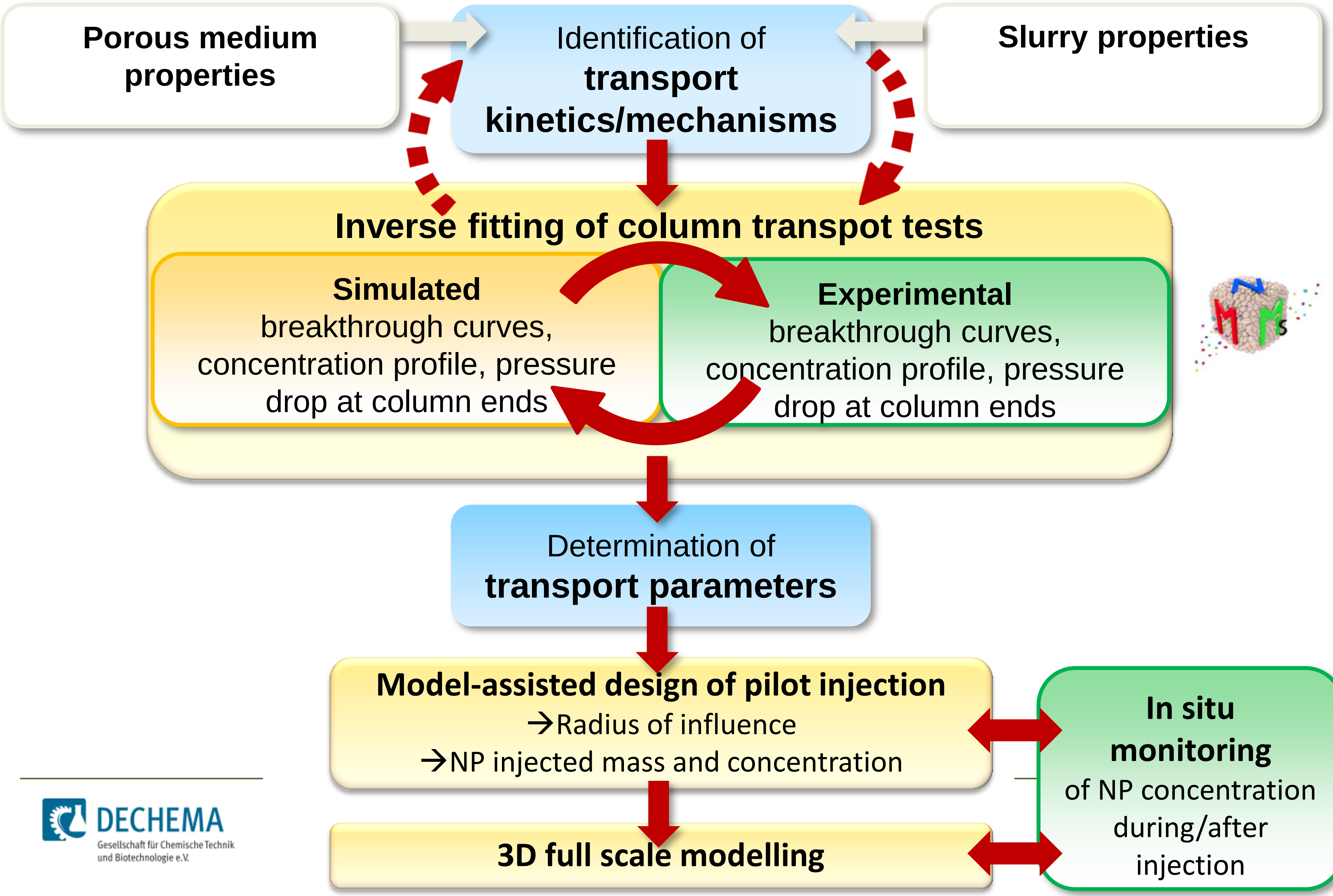
MNM3D →



Part III

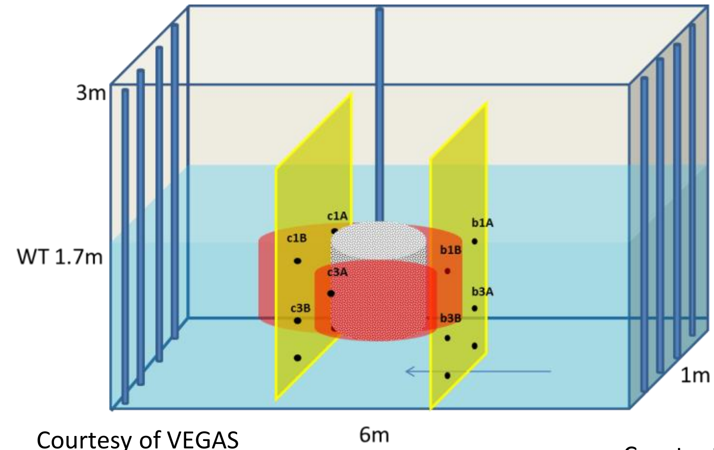
Examples

From laboratory to field scale

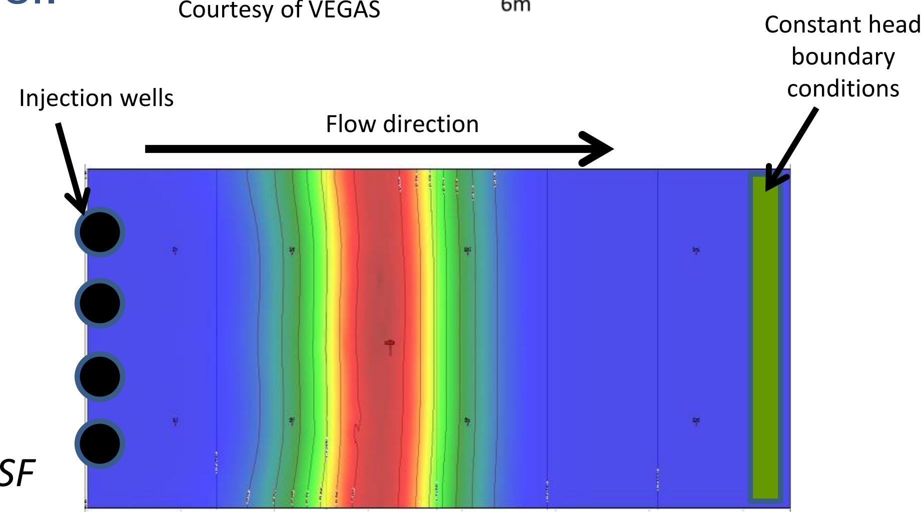


Example 1 – injection of CarboIron in a large-scale flume

- Modeling steps:
  - Flow model: developed in collaboration with USTUTT
  - Simulation of tracer injection from the left side of the domain to calibrate the numerical model.
    - Steady state flow
    - Simulation time = 720 h
    - Injection flow rate = 0.54 m^3/d



Courtesy of VEGAS

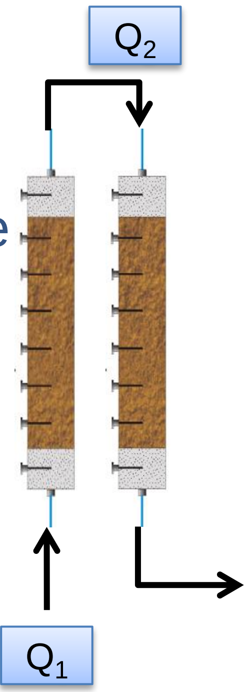


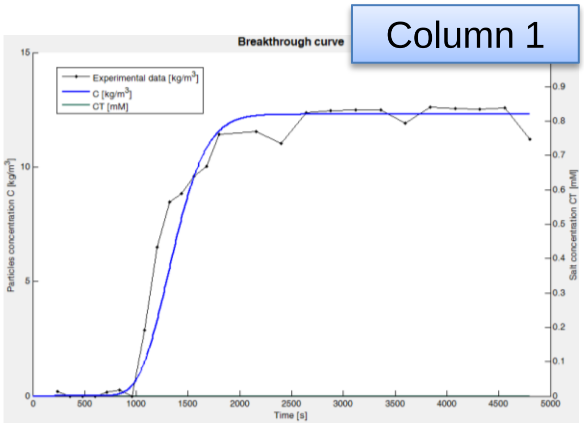
Simulation of tracer injection in the LSF

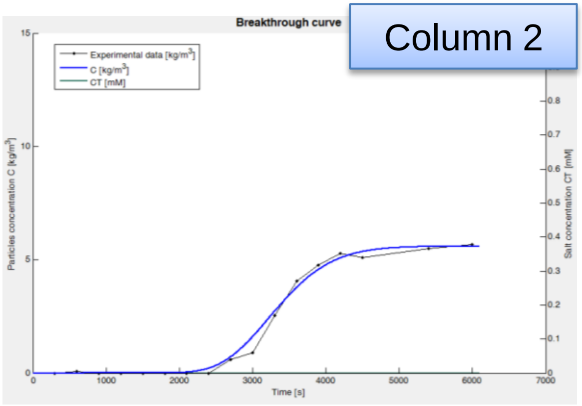
Example 1 – injection of CarboIron in a large-scale flume

- Modeling steps:
  - Column tests: inverse modeling of one cascading column tests (WP8) using MNMs to determine velocity-dependent coefficients.

	Column 1	Column 2
Length [cm]	25	
Diameter [cm]	4.4	
Porosity	0.34	
Dispersivity [m]	0.0039	
Q [ml/min]	5.7	2.3
Inlet concentration [g/l]	14.8	8.75



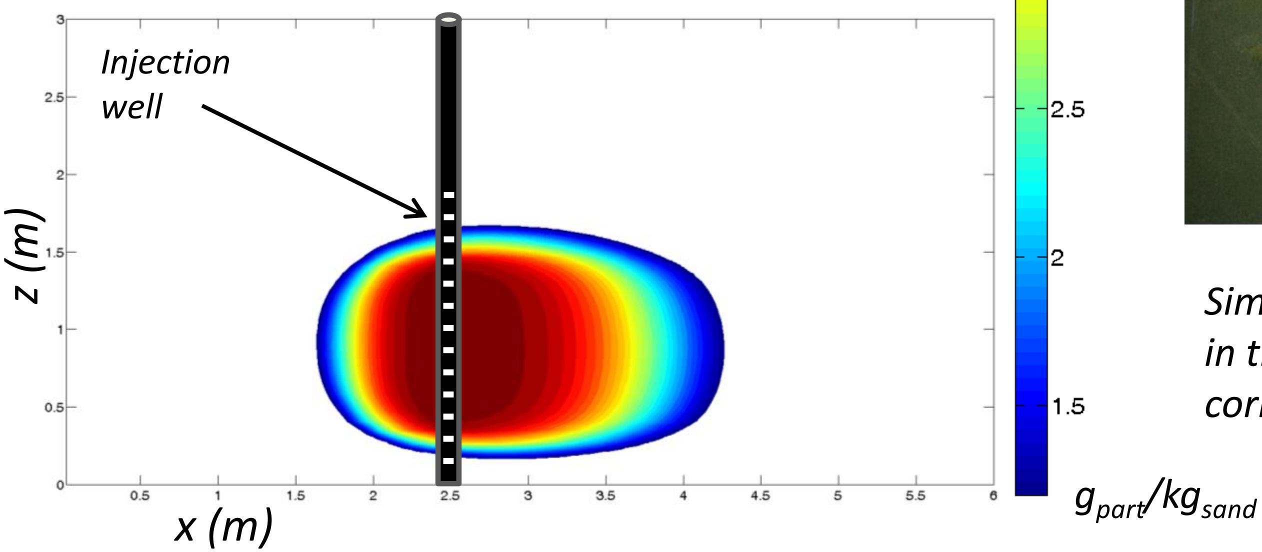


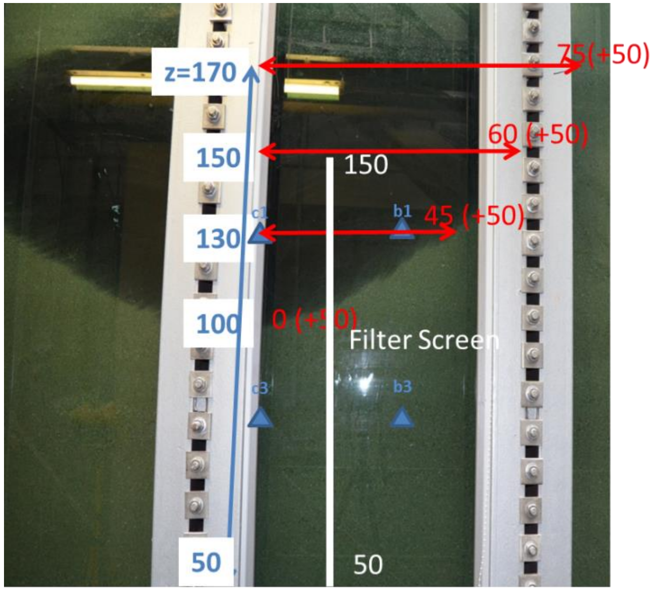


- Fitting model: 1 site with irreversible attachment (k_a = 1.35^{-4} s^{-1})
- No effect of flow velocity

Example 1 – injection of CarboIron in a large-scale flume

- Modeling steps:
  - Simulation of the injection of CarboIron through the central well
  - Vertical section



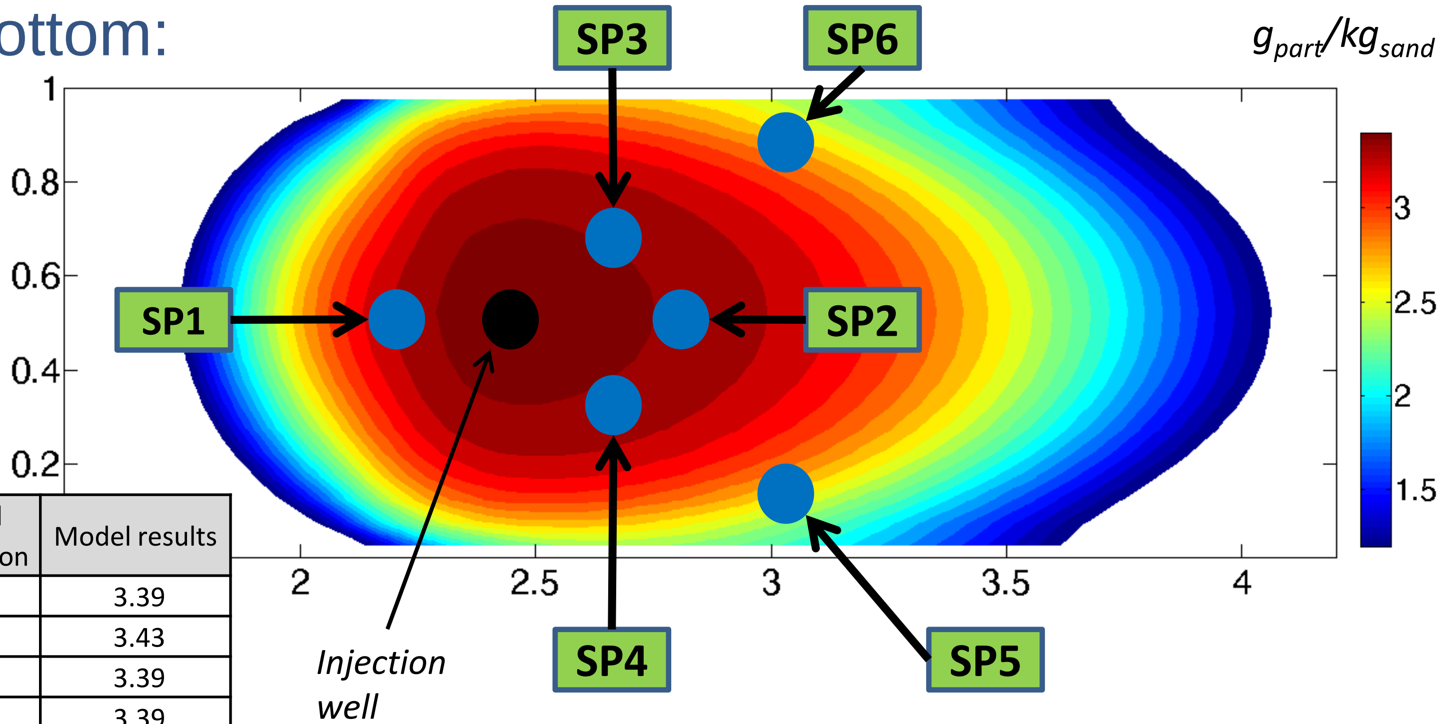


Simulation of CarboIron injection in the LSF. Plume edge corresponds to 1.2 g/kg

Example 1 – injection of CarboIron in a large-scale flume

- Core sampling at 1.3 m from the LSF bottom:

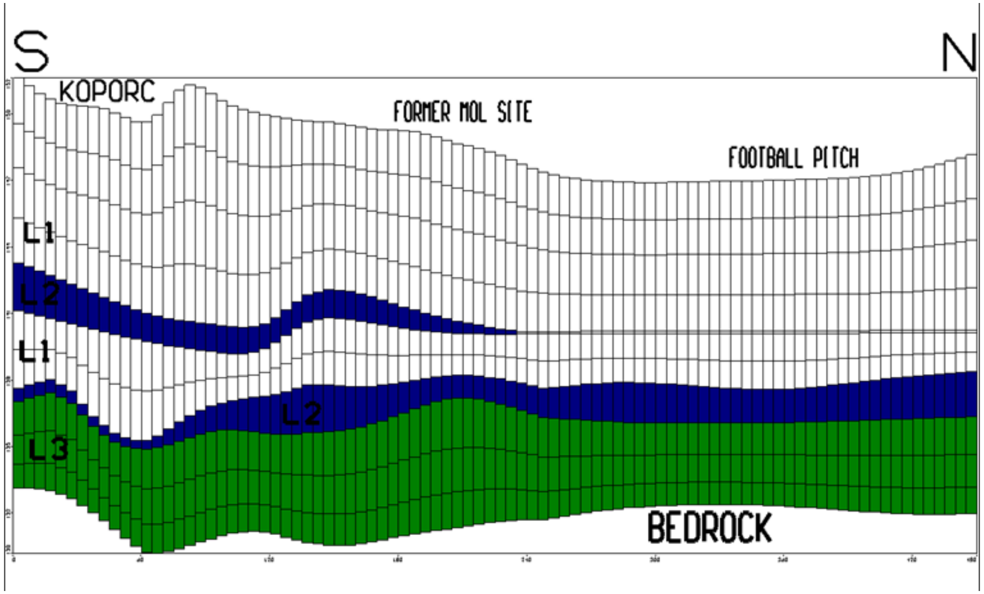
Simulation of CarboIron injection in the LSF. Plume edge corresponds to 1.2 g/kg



Monitoring point		Observed concentration	Model results
SP 1	g/kg	3.40	3.39
SP 2	g/kg	3.30	3.43
SP 3	g/kg	2.20	3.39
SP 4	g/kg	3.30	3.39
SP 5	g/kg	4.90	3.19
SP 6	g/kg	NO data	3.05

Example 2 – simulation of field scale injection

- Field location: Balassagyarmat, Hungary
- Original flow model provided by GOLDER, further refined around the injection points



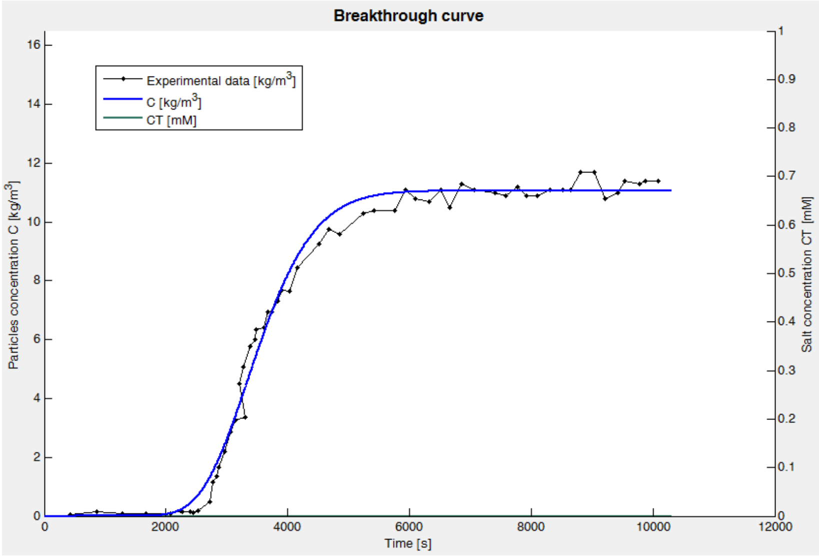
Courtesy of Golder

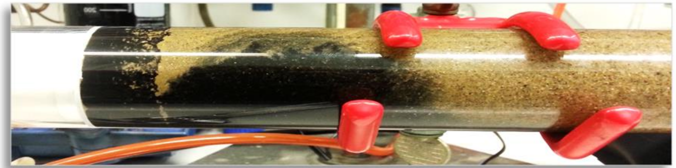
Example 2 – simulation of field scale injection

- Data from UFZ (WP4)
- Column tests of CarboIron transport in site material.
- Fitting model: 2 sites, irreversible attachment.
- Variation of porosity due to clogging is relevant

Length [cm]	20
Diameter [cm]	3.5
Porosity	0.33
Dispersivity [m]	0.0041
Q [ml/min]	2
Seepage Velocity [m/d]	10
Inlet concentration [g/l]	14.8

Parameter		Value
K_{a1}	$[s^{-1}]$	$3.29\ 10^{-2}$
K_{d1}	$[s^{-1}]$	$7.15\ 10^{-2}$
K_{a2}	$[s^{-1}]$	$1.24\ 10^{-4}$

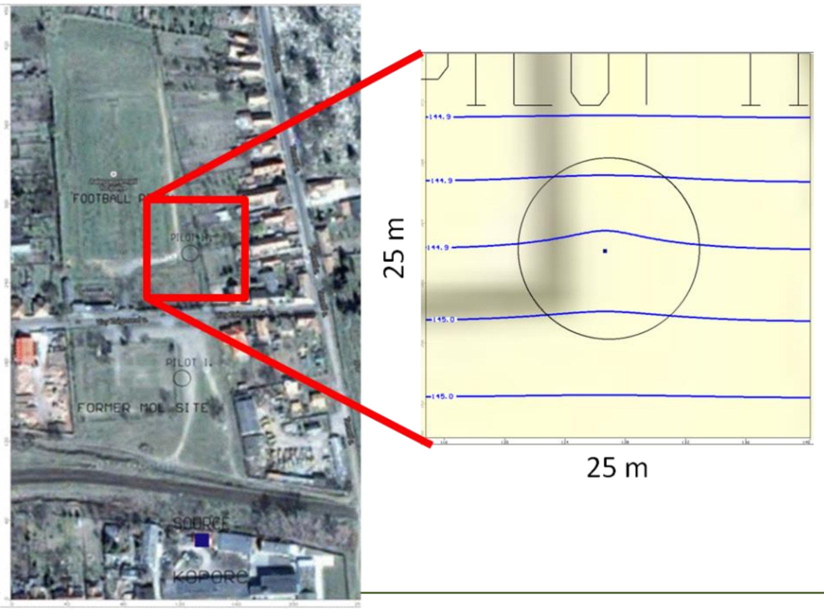


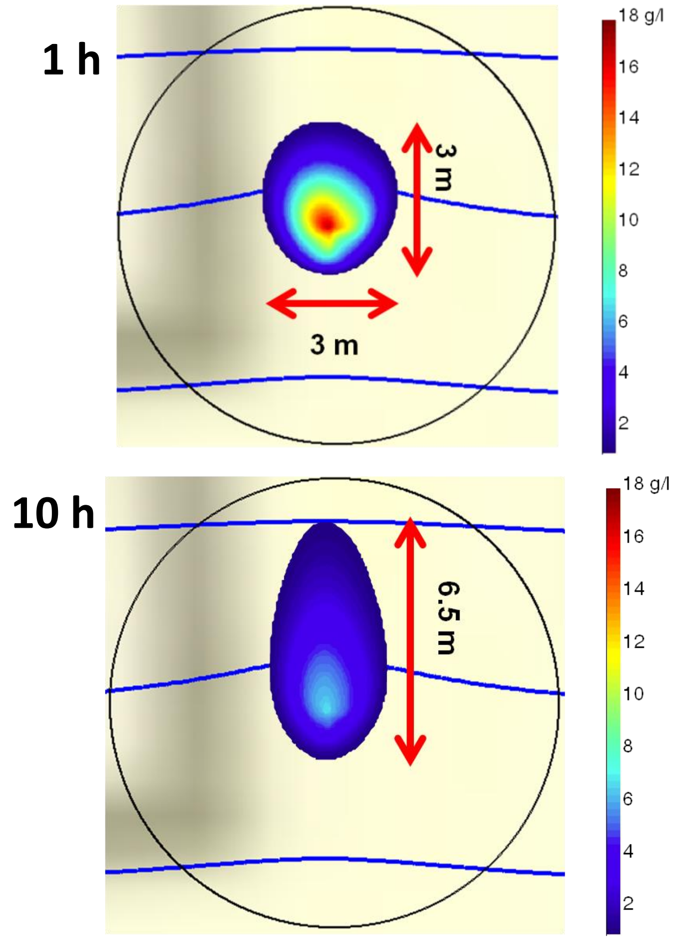


Courtesy of UFZ

Example 2 – simulation of field scale injection

- Simulation of CarboIron expected mobility in the field - radial injection
  - Kinetic coefficients from column test
  - Q = 25 l/min
  - Injection duration = 1 h

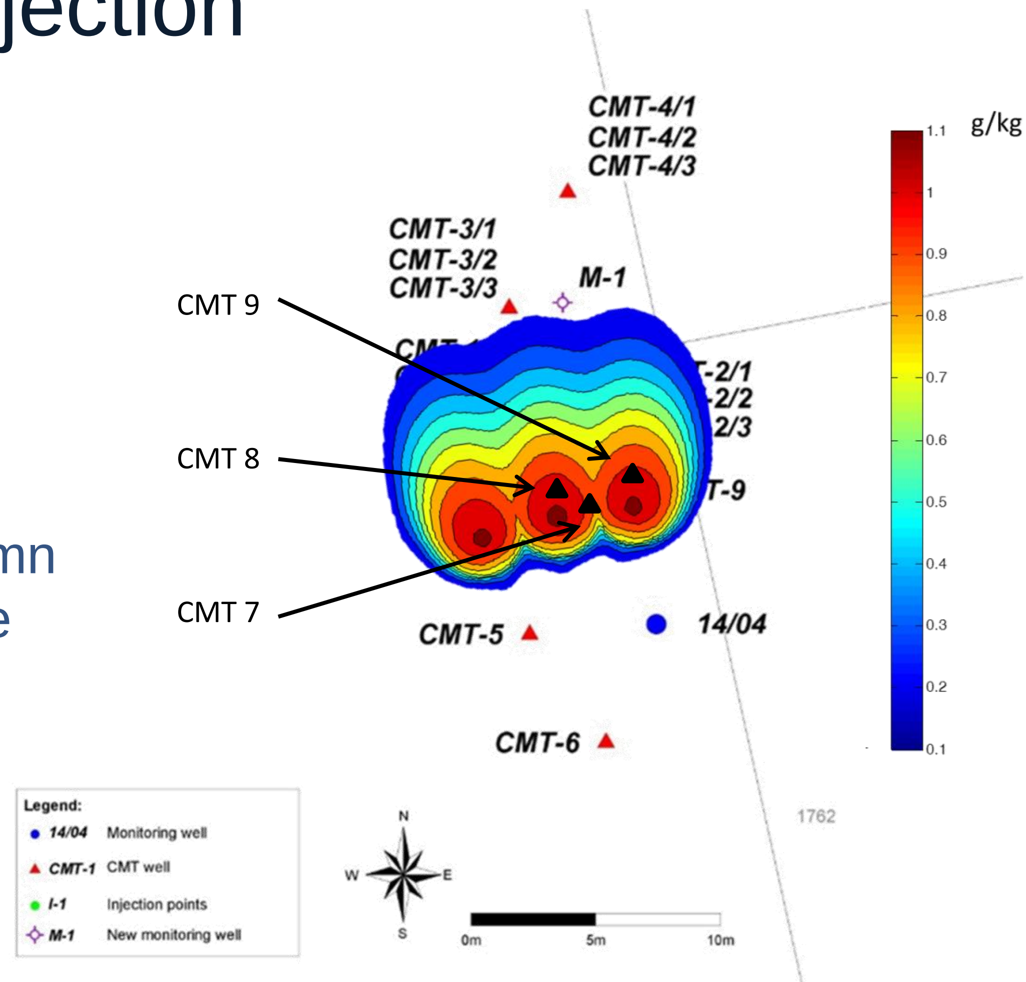




Example 2 – simulation of field scale injection

- Background GW flow 2 m/d
- 3 Injection points
  - Particles = 15 g/L
  - CMC = 1.5 g/L
- ROI = 5 m

- Model based on more column tests may be more accurate



Monitoring point		Observed concentration	Model results
CMT 7	g/kg	0.8	0.8
CMT 8	g/kg	2	1
CMT 9	g/kg	3	1

Thank you for your attention

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