A framework for forward modelling of engineered nanomaterials in terrestrial systems

Geert Cornelis, Jenny Perez-Holmberg
University of Gothenburg (SWEDEN), Dept. Chemistry and Molecular Biology

www.Marina-FP7.EU

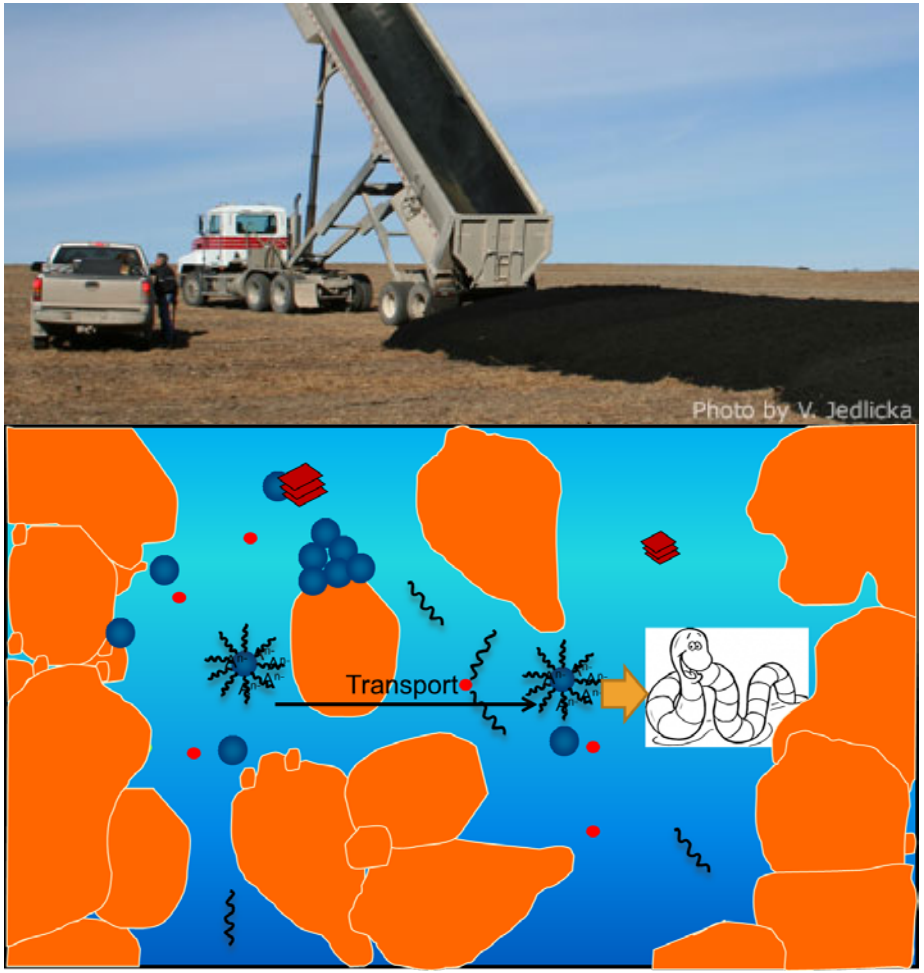
www.Marina-FP7.EU

Fate of NM in soils

Risk = **exposure** x hazard

Exposure ~ Bio-availability

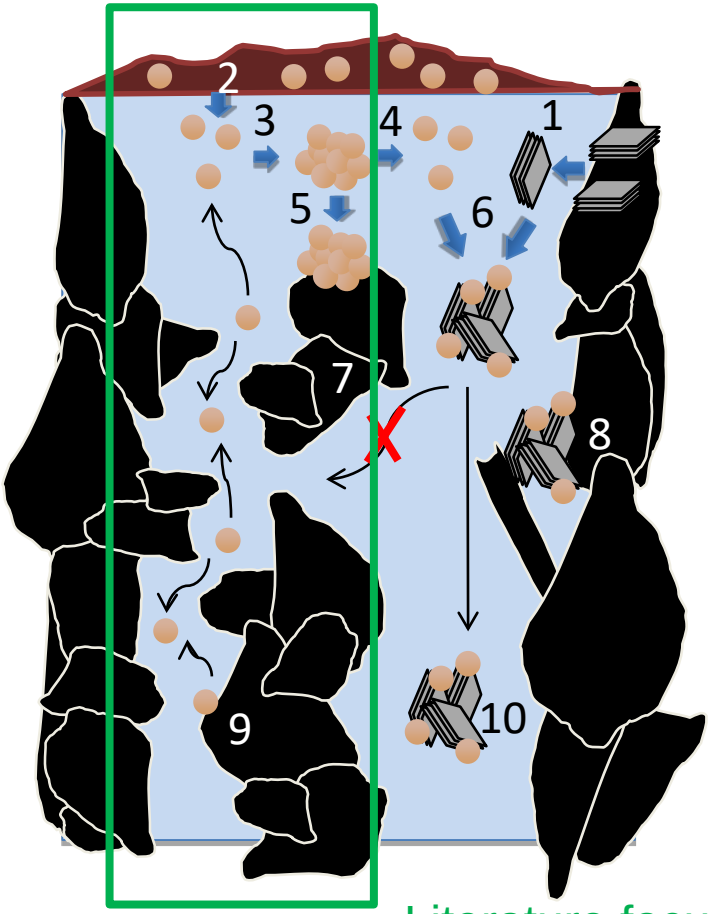
1. ”What NM **form** is the organism really exposed to”: **speciation**
2. ”What NM **concentration** is the organism really exposed to”: **transport**
3. “Is the specific NM form at its specific concentration and form hazardous”



Take home messages

- ”NM are very often hitchhikers on natural colloids in soils.”
- ”We should be focussing on developing forward models including fate descriptors for detachment, NOT only attachment.”
- ”Batch tests provide unprecise fate descriptors for NMs in soils.”

Fate of NM in terrestrial media

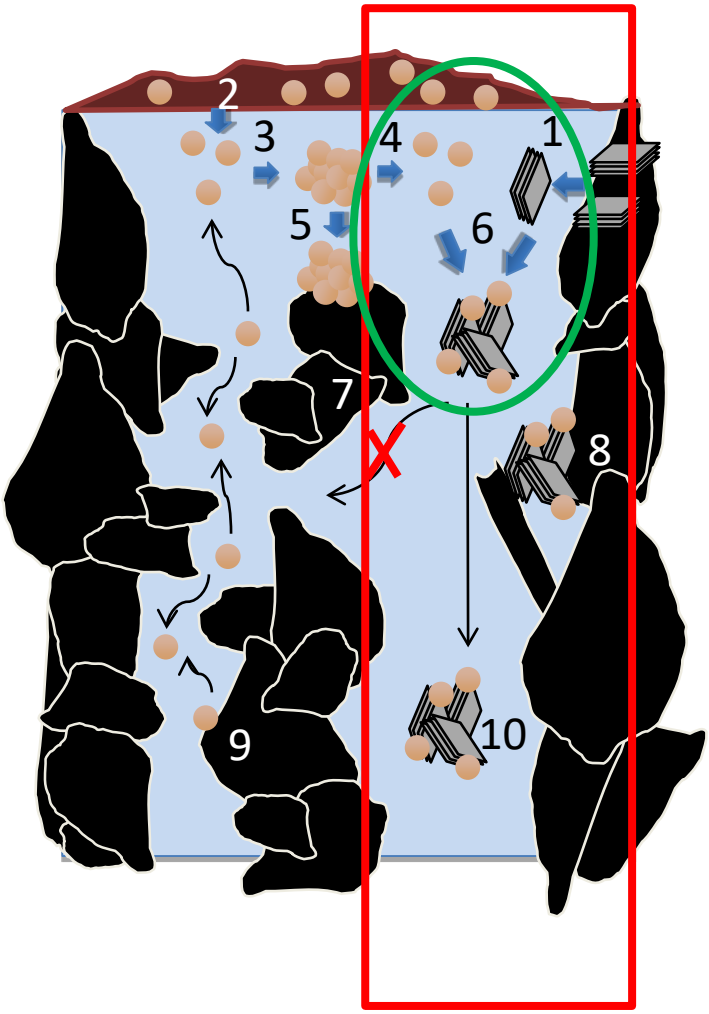


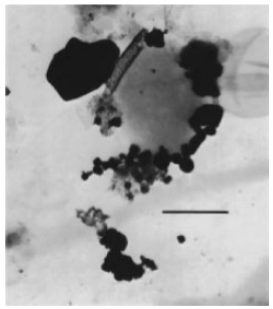
1. Colloid generation
2. NP detachment
3. Homoaggregation
4. Resuspension
5. Sedimentation
6. Heteroaggregation
7. Size exclusion
8. Straining
9. Attachment
10. Preferential transport

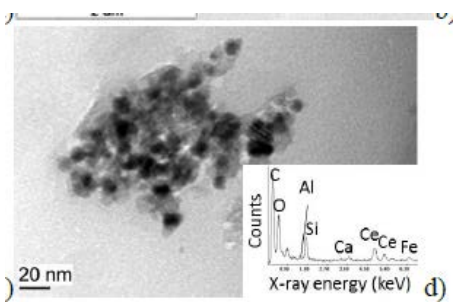
Literature focus:NM – NM; NM - soil

Cornelis et al., 2014. Crit. Rev. Environ. Sci. Technol. 44: 2720-2764.

Fate of NM in soils

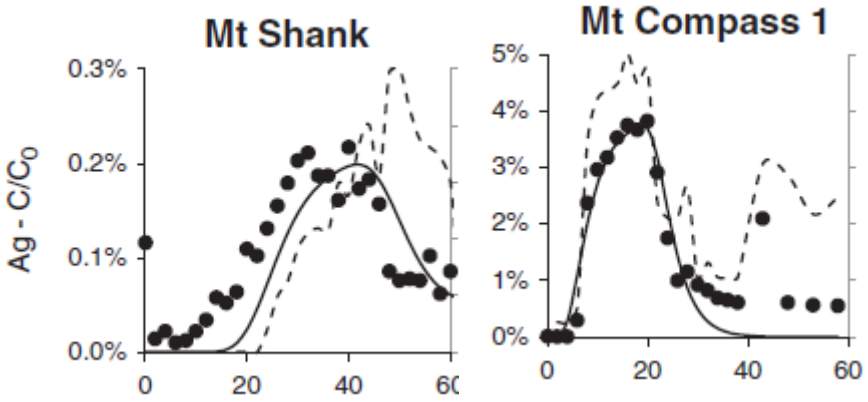






Buffle et al. 1998. ES&T, 32, 2887-2899.

Cornelis et al. 2011. ES&T, 45(7), 2777-2782

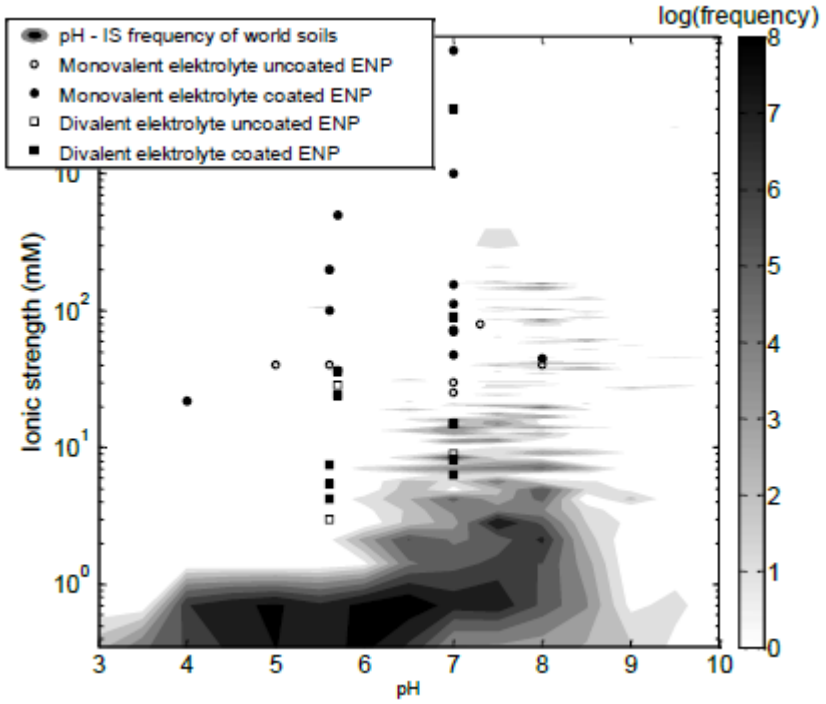


22 % clay

<1 % clay

Cornelis et al. 2013. J.Tot:Environ 463-464. 120-130.

Fate of NM in soils

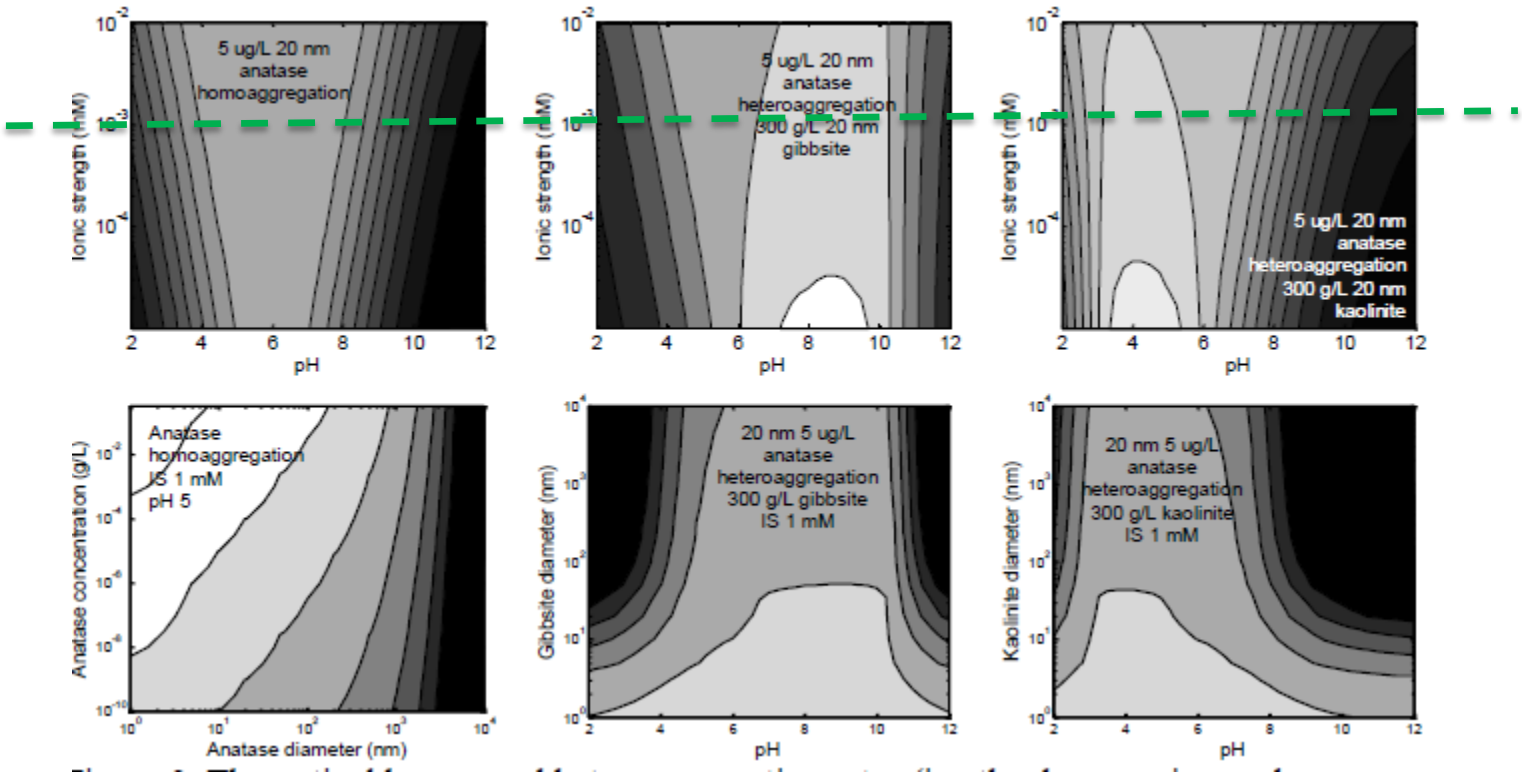


- pH-dependent CCC values of NMs vs. IS of world soil pore waters:

Homoaggregation unlikely unless NM concentrations are high

Cornelis et al., 2014. Crit. Rev. Environ. Sci. Technol. 44: 2720-2764.

Heteroaggregation rates – DLVO/Smoluchowski



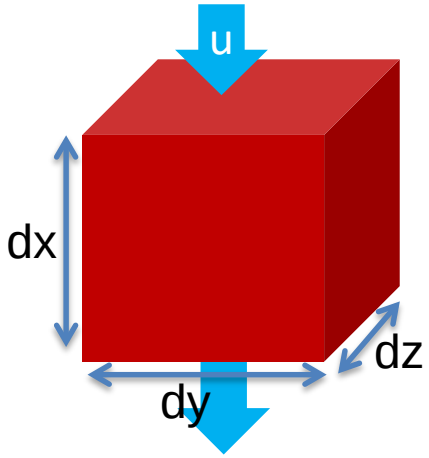
Effect of pH, IS, colloid diameter

Cornelis et al., 2014. Crit. Rev. Environ. Sci. Technol. 44: 2720-2764.

Take home message 1

” NM are very often hitchhikers on natural colloids in soils ”

➔ Transport models for NM ~ transport models for colloids



Particle transport models (PTM)

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\boxed{\sum_{i}^{s}\frac{\partial S_i}{\partial t}} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x}$$

soil surface – colloid interaction term

- C: aqueous concentration
- ρ: bulk density
- θ: porosity
- S: solid concentration
- D: dispersivity
- u: pore flow veclocity

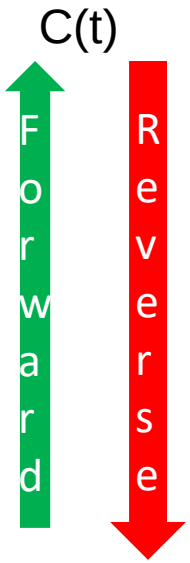
Mechanism	Equation
Irreversible attachment	$\rho \frac{\partial S_i}{\partial t} = k_{att,i} \theta \psi C$
Colloid filtration theory (CFT)	$k_{att,i} = \alpha_{att} \frac{3(1-\theta)}{2 d_{50}} \eta_0 u$
Reversible attachment	$\rho \frac{\partial S_i}{\partial t} = k_{att,i} \theta \psi C - k_{det,i} \rho S_i$
Dual deposition	$\rho \frac{\partial S_1}{\partial t} = k_{att,1} \theta \psi C - k_{det,1} \rho S_i$ $\rho \frac{\partial S_2}{\partial t} = k_{att,2} \theta \psi C$
2nd order irreversible attachment	$\rho \frac{\partial S_i}{\partial t} = k_{atti} \theta \psi C^2$
Blocking	$\psi = \left(1 - \frac{s_i}{S_{max}}\right)$
Straining	$\psi = \left(\frac{d_{50} + x}{d_{50}}\right)^{-\beta}$
Blocking/straining	$\psi = \left(1 - \frac{s_i}{S_{max}}\right)\left(\frac{d_{50}+x}{d_{50}}\right)^{-\beta}$

Symbols:

k_{atti}	Attachment or straining rate constant
α_{att}	Attachment efficiency
η	Single-collector deposition efficiency
ψ	Blocking or straining coefficient
k_{deti}	Detachment rate constant
S_{max}	Maximum deposition concentration
d_{50}	Average soil grain diameter
β	straining shape parameter

Baalousha, Cornelis et al. ES Nano. Submitted

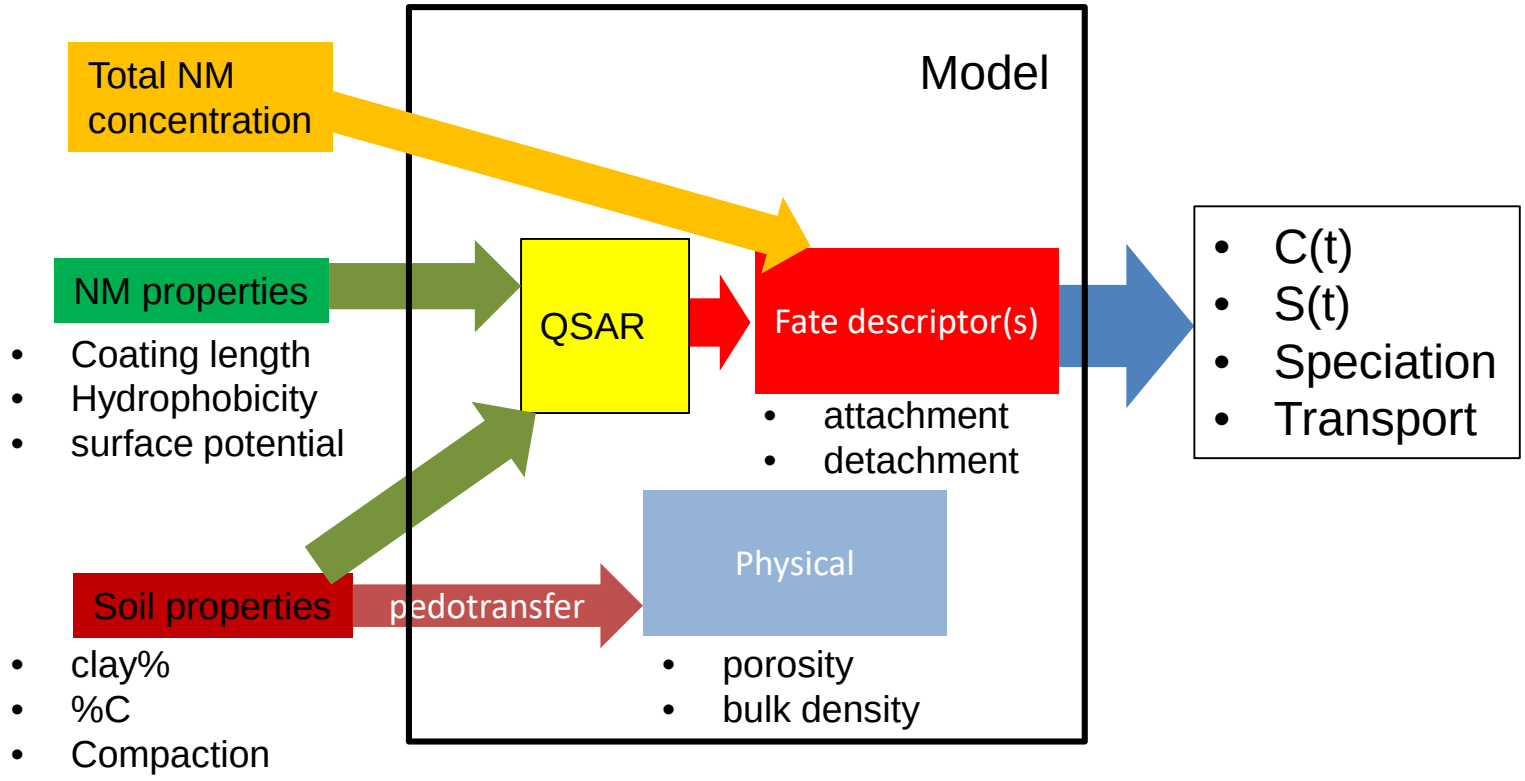
PTM



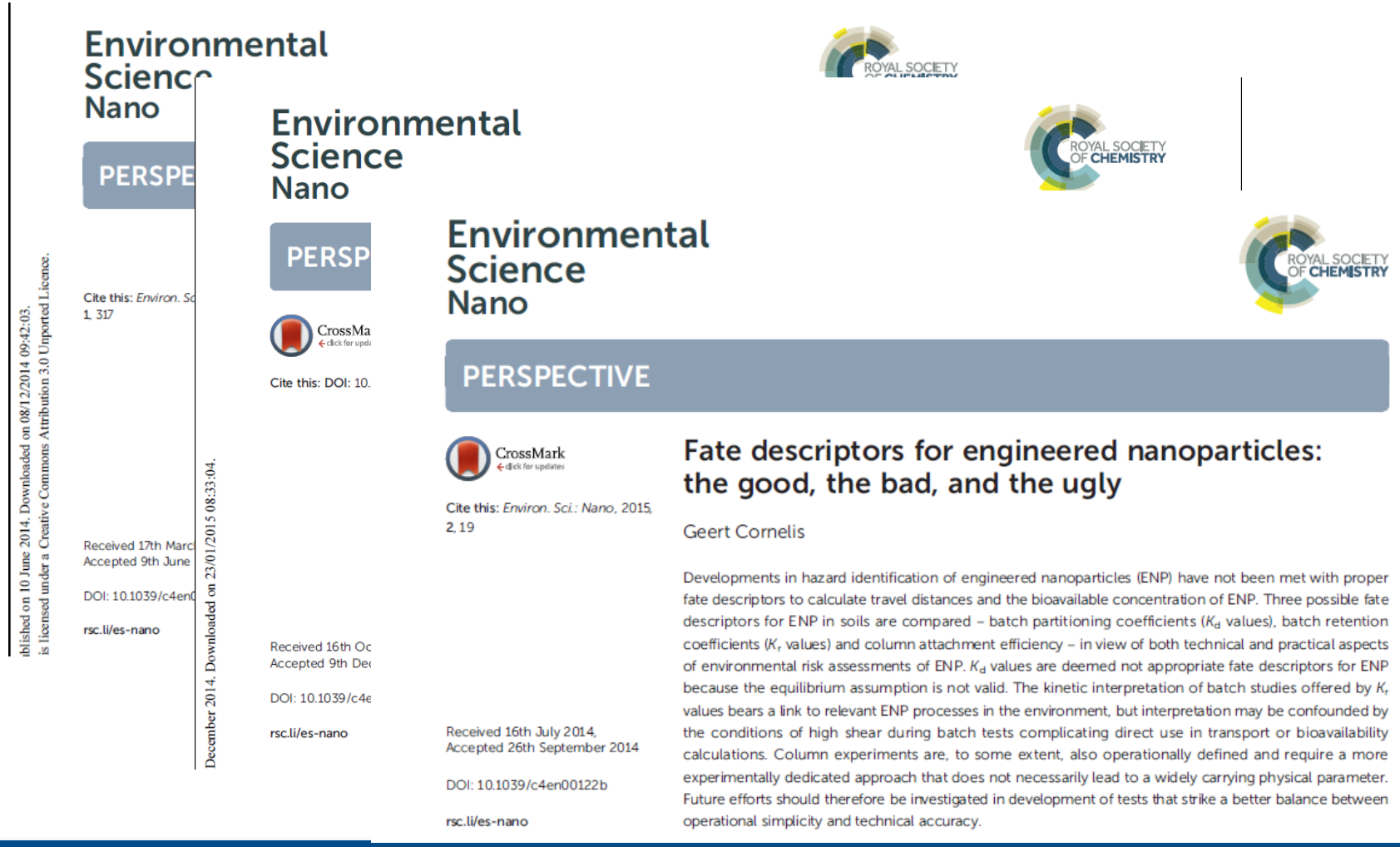
- Column test
  - Breakthrough curve inert tracer ➔ θ, D
  - Breakthrough curve ➔ C(t)
  - Depth profile ➔ S(x)
- Choose model
- Fit model and obtain parameters

Fate descriptors

Forward models



Fate descriptors



Environmental Science Nano

PERSPE

Cite this: *Environ. Sc*
1, 317

Received 17th Marc
Accepted 9th June

DOI: 10.1039/c4en0

rsc.li/es-nano

Environmental Science Nano

PERSP

CrossMa
click for upd

Cite this: DOI: 10.

Received 16th Oc
Accepted 9th De

DOI: 10.1039/c4e

rsc.li/es-nano

Environmental Science Nano

PERSPECTIVE

CrossMark
click for updates

Cite this: *Environ. Sci.: Nano*, 2015, 2, 19

Fate descriptors for engineered nanoparticles: the good, the bad, and the ugly

Geert Cornelis

Received 16th July 2014,
Accepted 26th September 2014

DOI: 10.1039/c4en00122b

rsc.li/es-nano

Developments in hazard identification of engineered nanoparticles (ENP) have not been met with proper fate descriptors to calculate travel distances and the bioavailable concentration of ENP. Three possible fate descriptors for ENP in soils are compared – batch partitioning coefficients (K_d values), batch retention coefficients (K_r values) and column attachment efficiency – in view of both technical and practical aspects of environmental risk assessments of ENP. K_d values are deemed not appropriate fate descriptors for ENP because the equilibrium assumption is not valid. The kinetic interpretation of batch studies offered by K_r values bears a link to relevant ENP processes in the environment, but interpretation may be confounded by the conditions of high shear during batch tests complicating direct use in transport or bioavailability calculations. Column experiments are, to some extent, also operationally defined and require a more experimentally dedicated approach that does not necessarily lead to a widely carrying physical parameter. Future efforts should therefore be investigated in development of tests that strike a better balance between operational simplicity and technical accuracy.

α values

$V_{max} = k_{max}*[NP]_{aqueous}$

$V_{attach} = k_{attach}*[NP]_{solid}$

$\alpha = k_{attach}/k_{max}$

- The probability that a particle will ”stick” to other particles or surfaces

$$k_{att,i} = \alpha_{att} \frac{3(1-\theta)}{2d_{50}} \eta_0$$

+

- related to mechanistic principles
- kinetic parameter
- ONE parameter

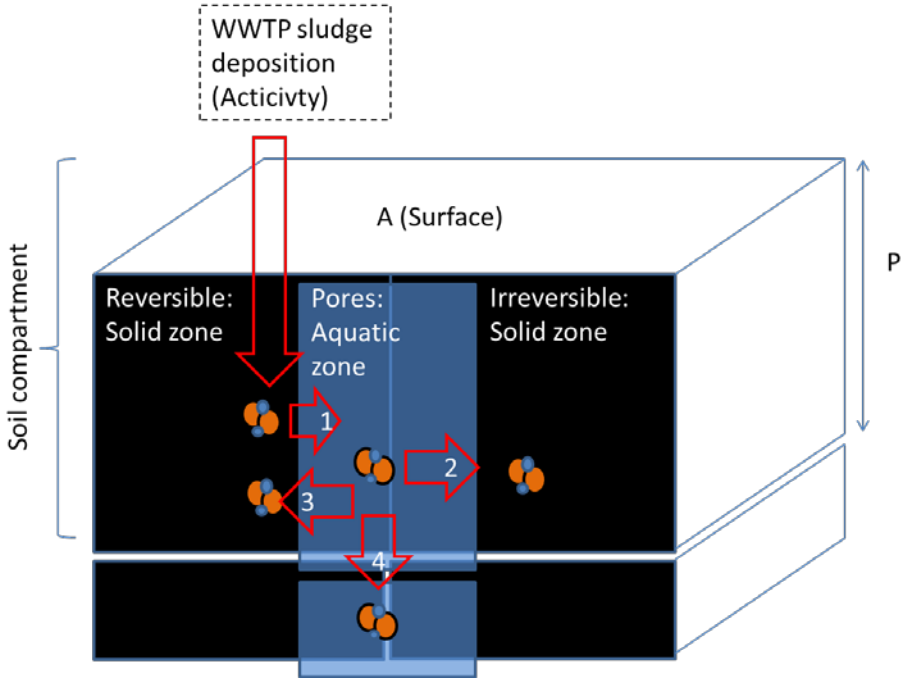
-

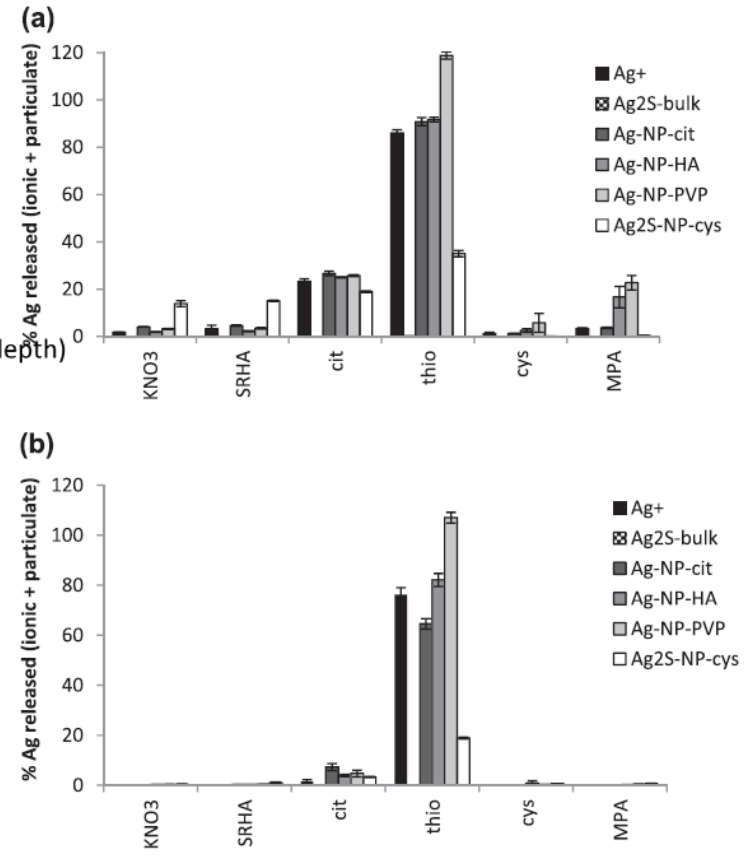
- Have to be obtained from expensive column tests
- Are (also) operationally defined
- Assumes only irreversible attachment

Take home message 2

”We should be focussing on developing forward models including fate descriptors for detachment, NOT only attachment”

Forward model





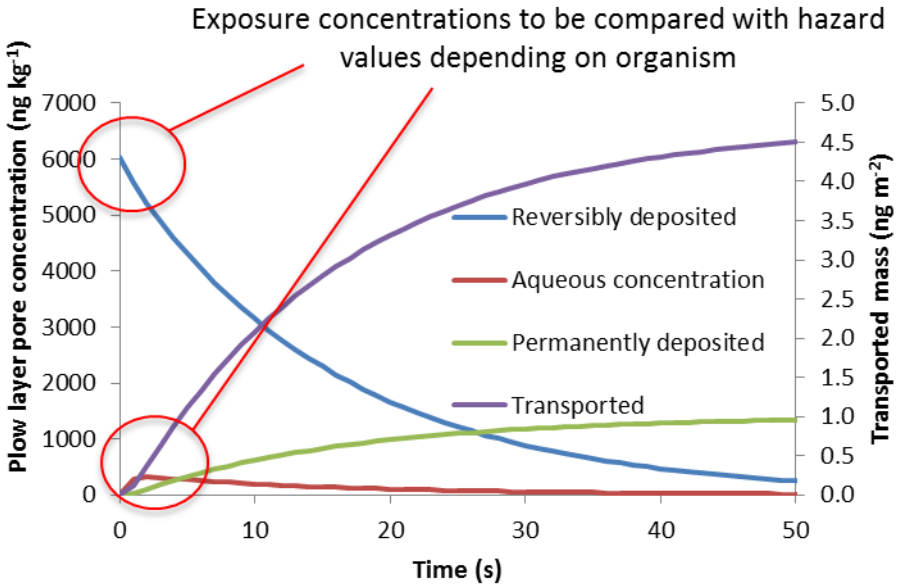
Navarro et al., Environ. Poll. 193: 102-110

Forward model

Differential equation:

$$\theta \frac{\partial C}{\partial t} = -u\theta \frac{\partial C}{\partial z} - k_{det}\rho S - k_{att}\theta C - k_{transf}\theta C$$

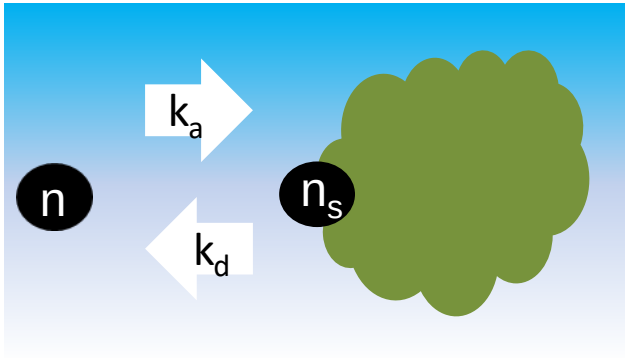
Solution:



Batch studies

$$\frac{\mathrm{dn}}{\mathrm{dt}} = -\alpha k_a \mathrm{nB} + \mathrm{k_d}(\mathrm{n_0} - \mathrm{n})$$

$$n = n_i exp(-(\alpha k_a B + k_b)t) + \frac{k_b n_0}{\alpha k_a B + k_b}\left(1 - exp(-(\alpha k_a B + k_b)t)\right)$$



Attachment initially negligible

$$\ln\left(\frac{n_0 - n_i}{n_0 - n}\right) = k_b B t$$

SOME UNPUBLISHED MATERIAL HAS BEEN CUT OUT

Take home message 3

Batch tests provide unprecise fate descriptors for NMs in soils

- Batch test provides results that vary highly with
  - Mixing technique
  - L/S ratio
- 1 Parameter models usually are best
- Batch test overestimate detachment

See also:

Sadeghi et al. (2013) J. Contam. Hydrol. 152. 12-17
Treumann et al. (2014) J. Contam. Hydrol. 164. 219-229.

How to move forward

- Focus on heteroaggregation ➔ coupling fate colloids and fate of NMs
- Focus on forward models predicting NM detachment
- Improve fate descriptors of NMs batch ⇔ column studies

UNIVERSITY OF GOTHENBURG

Thank you

Contact:
Geert.Cornelis@chem.gu.se