Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Material for

Modeling Nanomaterials Fate and Uptake in the Environment: Current Knowledge and Future Trends

Baalousha M[a*], Cornelis G[b], Kuhlbusch TAJ[c], Lynch I[d], Nickel C[c], Peijnenburg W[e,f], van den Brink NW[g]

a Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, Arnold School of Public Health, University South Carolina, Columbia, SC 29208, USA

b Department of Chemistry and Molecular Biology, University of Gothenburg, Kemivägen 10, Göteborg, 41296, Sweden

c Institute of Energy and Environmental Technology (IUTA) e.V., Unit Air Quality & Sustainable Nanotechnology, Duisburg, Germany and Centre for Nanointegration (CENIDE), University Duisburg-Essen, Duisburg, Germany.

d School of Geography, Earth and Environmental Sciences, College of Life and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

e National Institute of Public Health and the Environment, Center for Safety of Products and Substances, Bilthoven, The Netherlands

f Institute of Environmental Sciences (CML), Leiden University, Leiden, The Netherlands

g Wageningen University, division of Toxicology, Box 8000 NL-6700 EA, Wageningen, The Netherlands

Models used in NM fate modeling in terrestrial systems

Symbol list

C	Suspended NM concentration in pores
C_0	Suspended NM concentration in the feed suspension
D	Dispersion coefficient
d_{50}	Average collector diameter
ψ	Blocking or straining coefficient
k_{deti}	Detachment rate constant
S_{max}	Maximum deposition concentration
d_{50}	Average soil grain diameter
β	Straining depth dependency parameter
K_{s}	hydraulic conductivity
k_{a}	Attachment or straining rate constant
α	Attachment efficiency
η_0	Single-collector deposition efficiency
k_{d}	detachment rate constant
L	Column length
S	Deposited NM concentration
S_{max}	Maximum site deposition capacity
t	Time
u	pore water velocity
x	Depth
θ	Effective porosity
ρ	Bulk density

Formulas

Eq. 1 is the basic one-dimensional convection-dispersion equation that describes the mass transfers along the depth profile and on which much of the mechanistic transport modelling in soils is based.

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\sum_i^s \frac{\partial S_i}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} \qquad \text{(eq. 1)}$$

Deposition, i.e. interaction of particles with the soil pore wall expressed by the second term of eq. 1, is seen as the most crucial process determining NM travel distances and many different formulations of the deposition term have been used to describe deposition of NM to soil pore walls accounting for different mechanisms (Table S1).

Table S1. Equations used for transport modelling of different NMs in sand columns or stacked columns of natural soils.

eq.	Mechanism	Equation
2	Irreversible attachment	$\rho\frac{\partial S_i}{\partial t} = k_{att,i}\theta\psi C$
3	Colloid filtration theory (CFT)	eq. S2 in which $k_{att,i} = \alpha_{att}\frac{3(1-\theta)}{2d_{50}}\eta_0 u$

4	Reversible attachment	$\rho \frac{\partial S_i}{\partial t} = k_{att,i}\theta\psi C - k_{det,i}\rho S_i$
5	2nd order irreversible attachment	$\rho \frac{\partial S_i}{\partial t} = k_{atti}\theta\psi C^2$

Table S2 shows different formulations to modify the attachment rates shown in Table S1. Note that release rates are always considered to be linearly related to the solid concentration.

Table S2: Different formulae for the parameter in table S1.

6	Linear	$\psi = 1$
7	Blocking	$\psi = \left(1 - \frac{s_i}{S_{max}}\right)$
8	Straining	$\psi = \left(\frac{d_{50} + x}{d_{50}}\right)^{-\beta}$

Two other interactions, ripening and preferential flow, each reflect how a part of the effective pore volume preferentially becomes or is inaccessible to suspended NMs. In the case of ripening, the accessible pore volume is related to the solid NM concentration S. As S increases, more and more sites become inaccessible. Tosco and Sethi[1] propose a general relationship for blocking and ripening:

$$\rho \frac{\partial s}{\partial t} = \theta\left(1 + AS^{\beta}\right)k_a C - \rho k_d S \qquad \text{(eq 9)}$$

Positive coefficients A and b in eq. 9 describe a ripening mechanism, whereas β = 1 and A = -1/$S_{\max}$ describe blocking.

The most used approach for modelling NM transport is colloid filtration theory (CFT), where NM are assumed to only irreversibly deposit on pore walls from the soil pore solution.(e.g.[1,2]):

$$\frac{\rho}{\theta}\frac{\partial S}{\partial t} = \alpha_{att}\frac{3(1-\theta)}{2d_{50}}\eta_0 u C \qquad \text{(eq 10)}$$

The attachment or collision efficiency, α_{att} is a crucial parameter in CFT that theoretically quantifies the extent by which deposition is altered from the ideal case, i.e. absence of all repulsive NM – pore wall interactions[3]. η_0 is the single-collector contact efficiency that accounts for all physicochemical parameters determining deposition efficiency under favorable conditions, i.e. in the absence of repulsive barriers. α_{att} is obtained without fitting eq. 1 in most cases and is estimated directly from experimental breakthrough curves obtained after a step NM input according to eq. 10[1].

$$\alpha_{att} = \frac{2d_{50}}{3(1-\theta)\eta_0 L}\ln(C/C_0) \qquad \text{(Eq. 11)}$$

C is the column outflow plateau concentration that is reached after a certain time, whereas C_0 is the input NM concentration. There are similar equations that can be applied when a pulse NM input is applied to soil columns[4]. CFT relies conceptually on DLVO theory in describing particle-wall interactions. There are correlation equations to calculate η_0, the single-collector contact efficiency, a coefficient that accounts for the transport of suspended particles to deposition sites as a result of gravity, diffusion and advection or a combination thereof[5].

Model formulations used in NM uptake modeling

First order rate model for uptake of NMs in daphnids[6]:

$$[organism] = [water] * \left(\frac{ku}{ke}\right) * \left(1 - \mathrm{e}^{-\mathrm{ke}*\mathrm{time}}\right) \qquad \text{Eq. 12}$$

with ku: uptake rate constant ($L*kg^{-1}*h^{-1}$); ke (elimination rate constant (h^{-1}); time in hours

First order rate model for uptake of NMs in daphnids, including effect of decreasing NM-concentrations due to sedimentation[6]:

$$[organism] = [water] * \left(\frac{ku}{ke-\gamma}\right) * \left(\mathrm{e}^{-\gamma\mathrm{t}} - \mathrm{e}^{-\mathrm{ke}*\mathrm{time}}\right) \qquad \text{Eq. 13}$$

with γ: linear regression slope of concentration in time (h^{-1})

Accumulation of NMs in organisms according to the concepts of Figure 3 (main manuscript) can be modelled by:

$$\left[NM_{org}\right] = [NM_{env}] * e^{-k_{dis}*t} * \frac{k_{NMup}}{(k_{NMout}-k_{meta})} * \left(1 - e^{-(k_{NMout}+k_{meta})*t}\right) \qquad \text{Eq. 14}$$

with: NM_{env} the initial environmental concentrations of the NM; t the duration of the test or residence time in the environment; k_{NMup}: uptake rate constant for particulate form ($kg_{soil}*kg_{worm}^{-1}*day^{-1}$), k_{NMout}: elimination rate constant for particulate form (day^{-1}), k_{dis}: dissolution rate in environmental compartment (day^{-1}); k_{meta}: dissolution rate in organism (day^{-1})

Accumulation of the ionic species of the NMs can be modelled by

$$\left[Ion_{org}\right] = [NM_{env}] * e^{-(k_{dis}*t)} * \frac{k_{NMup}}{(k_{NMout}+k_{meta})^2} * k_{meta} * ((k_{NMout} + k_{meta}) * t + \left(1 - e^{-(k_{NMout}+k_{meta})*t}\right) - 1) + [NM_{env}] * \left(1 - e^{-(k_{dis}*t)}\right) * \frac{k_{Ionup}}{k_{Ionout}} * \left(1 - e^{(-k_{Ionout}*t)}\right) \qquad \text{Eq. 15}$$

with: k_{Ionup}: uptake rate constant for ionic form ($g_{soil}*g_{worm}^{-1}*day^{-1}$); k_{Ionout}: elimination rate constant for ionic form (day^{-1})

Reference List

(1) Tufenkji, N.; Elimelech, M. Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. *Environ. Sci. Technol.* **2004,** *38* (2), 529-536.

(2) Logan, B. E.; Jewett, D. G.; Arnold, R. G.; Bouwer, E. J.; O'Melia, C. R. Clarification of clean-bed filtration models. *J. Environ. Eng.* **1995,** *121* (12), 869-873.

(3) Tosco, T.; Papini, M. P.; Viggi, C. C.; Sethi, R. Nanoscale zerovalent iron particles for groundwater remediation: a review. *J. Clean. Product.* **2014,** *77*, 10-21.

(4) Harvey, R. W.; Garabedian, S. P. Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer. *Environ. Sci. Technol.* **1991,** *25* (1), 178-185.

(5) Petosa, A. R.; Jaisi, D. P.; Quevedo, I. R.; Elimelech, M.; Tufenkji, N. Aggregation and Deposition of Engineered Nanomaterials in Aquatic Environments: Role of Physicochemical Interactions. *Environ. Sci. Technol.* **2010,** *44* (17), 6532-6549.

(6) Skjolding, L. M.; Kern, K.; Hjorth, R.; Hartmann, N.; Overgaard, S.; Ma, G.; Veinot, J. G. C.; Baun, A. Uptake and depuration of gold nanoparticles in Daphnia magna. *Ecotoxicology* **2014,** 1-12.