Supporting Information

Experimental and Numerical Investigations of Silver Nanoparticle Transport under Variable Flow and Ionic Strength in Soil

Joanna Makselon^{\dagger^*}, Dan Zhou^{\ddagger}, Irina Engelhardt^{\ddagger}, Diederik Jacques[§], Erwin Klumpp^{\dagger}

[†] Agrosphere (IBG-3), Institute of Bio- and Geosciences, Forschungszentrum Jülich GmbH, Jülich, Germany

^{*} Department of Hydrogeology and Hydrochemistry, TU Freiberg, Freiberg, Germany

[§] Institute for Environment, Health and Safety (EHS), Belgian Nuclear Research Centre (SCK•CEN),

Mol, Belgium

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*Corresponding author address: j.makselon@fz-juelich.de; 0049-2461-61-2797.

Introduction

Appendix A. Supplementary Information - The Supplementary Information provides a brief description and discussion of: (i) procedures for collecting undisturbed soil samples, (ii) running the column experiments, (iii) description of model calibration and summary of the input variables for the model (Table S1), (iv) fitted AgNP transport parameters (Table S2), (v) pH of effluent samples for experiments A, B and C (Fig. S1), (vi) measured and simulated BTCs of tracer and AgNP for experiment A (Figure S2), (vii) simulated RPs of AgNP at SWI and AWI for experiments A, B and C (Fig. S4).

Collecting undisturbed soil samples - Polyvinyl chloride columns (8 cm inner diameter and 10 cm in length) were filled with undisturbed soil from the upper 30 cm of the field. The undisturbed soil samples were collected using a metal adaptor with a sharp front attached to the bottom of the column to minimize any disturbance of the soil structure. A water balance was then used to vertically insert the column stepwise into the plowed soil. Between the insertion steps, the surrounding soil was removed, so that at the end the filled column could be easily removed from the sampling field. Before use, the undisturbed soil columns were stored at 4 °C.

Transport experiments - The bottom of the column was fitted with an acrylic glass plate with 2 mm openings covered by a polyester membrane with 21 μ m pores to support uniform flow. The pore volume in the soil column was 228 cm³, 223 cm³ and 239 cm³ for experiments A, B and C, respectively. Before running the transport experiment, the soil column was slowly saturated from the bottom with 1 mM KNO₃ for one week. All column experiments were run with a software-controlled system to achieve unit gradient, steady-state flow conditions in the columns, and to

ensure homogeneous water saturation and flow conditions.¹ In brief, the background solution, tracer and AgNP in one storage bottle were simultaneously pumped through a sprinkling head placed on the top of the column using a peristaltic pump. A constant irrigation rate was controlled and measured by recording the weight of storage bottle for the irrigation solution with a balance linked to a computer. The suction at the bottom of the column was controlled by an air pump and pressure regulation. The matrix potential inside the column was measured using two tensiometers installed 2.5 and 7.5 cm below the column surface. The soil-water tension at the lower column boundary was -7 mbar for experiment A. For experiments B and C, the soil-water tension changed from -7 mbar to -9 mbar after FI. Effluent samples (15 mL for each sample) controlled by an electric circuit with two water level sensors were collected over the course of the experiment using a fraction collector. Important parameters such as electrical conductivity (related to electrolyte concentration), irrigation rate, weight from the balance, and time were recorded automatically for each sample. The columns were irrigated with at least 18 pore volumes of 1mM KNO3 at 0.2 cm/min until unit gradient (constant matrix potential) and steady state flow and electrical conductivity (baseline conductivity) conditions were achieved. The anions such as chloride were washed out and replaced by nitrate in this equilibrium process to avoid precipitation of silver chloride, which can affect AgNP stability and the subsequent Ag concentration measurements.² After this conditioning procedure, the transport experiment was performed as described in the main article. A summary of the experimental conditions is provided in Table 1.

Calculations for attachment efficiency - The attachment efficiency α [-] is calculated with the Maxwell approach and the DLVO theory:³⁻⁵

$$\alpha = \alpha_{pri} + \alpha_{sec} = 1 - \int_{\sqrt{\phi_{sec}}}^{\sqrt{\Delta\phi}} \frac{4}{\pi^{1/2}} x^2 \exp(-x^2) dx$$
(1)

$$\phi_t = \phi_{vdw} + \phi_{el} \tag{2}$$

$$\phi_{\nu dw} = -\frac{A_{123}a_c a_p}{6y(a_c + a_p)} \left[1 + \frac{14y}{\lambda} \right]^{-1}$$
(3)

$$A_{123} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{4}$$

$$\phi_{el} = \pi \varepsilon_0 \varepsilon_r \frac{a_c a_p}{a_c + a_p} \left\{ 2\psi_p \psi_c \ln \left[\frac{1 + \exp(-\kappa y)}{1 - \exp(-\kappa y)} \right] + \left(\psi_p^2 + \psi_c^2 \right) \ln[1 - \exp(-2\kappa y)] \right\}$$
(5)

$$\kappa = \sqrt{\frac{2N_A e^2 I}{\varepsilon_0 \varepsilon_r k_B T}} \tag{6}$$

where α_{pri} [-] and α_{sec} [-] are the attachment efficiencies at primary and secondary minimum depths, respectively, $\Delta \phi$ is the sum of ϕ_{max} and ϕ_{sec} , ϕ_{max} is the maximum energy barrier and ϕ_{sec} is the secondary minimum, ϕ_t [J] is the total energy barrier, ϕ_{vdw} [J] and ϕ_{et} [J] are the attractive van der Waals potential and repulsive electrostatic potential, respectively. A_{123} [J] is the combined Hamaker constant of the system, A_{11} is the Hamaker constant for AgNP, A_{22} is the Hamaker constant for the collector surface, A_{33} is the Hamaker constant for water, λ is the characteristic wavelength of the interaction [m], y [m] is the distance between the colloid and soil grain, ε_0 [C V⁻¹ m⁻¹] is the permittivity in the vacuum and ε_r [-] is the relative dielectric permittivity. ψ_p [V] and ψ_c [V] are the zeta potentials of AgNP and the soil grain, respectively. κ [m] is the Debye length, k_B [J K⁻¹] is the Boltzmann constant, T [K] is the temperature, N_A [mol⁻¹] is Avogadro's number, e [C] is the elementary charge, and I is the ionic strength [mol L⁻¹].

Model calibration - Values of the AgNP diameter (a_p) , soil grain diameter (a_c) , bulk density (ρ) , and volumetric water flux (q) were obtained from laboratory measurements (Table S1). The dispersion coefficient (D) was estimated by the automated calibration of the volumetric water flux (q) and the BTC of D₂O using the inverse model of Hydrus-1D. The AgNP transport parameters $(M_{det}^{SWI}, f_i, S_{max} \text{ and } M_{att}^{AWI})$ were estimated using PEST.⁶ To reduce the uncertainty of the parameter estimation process, the Tikhonov regularization method implemented in PEST is used. Through this method, a parameter field of minimum error variance can be obtained when the regularization constraints are properly formulated. Using the Tikhonov regularization method, PEST minimizes a total objective function:

$$\Phi = \Phi_m + \mu^2 \Phi_r \tag{7}$$

 Φ is the target measurement objective function, provided by the user. Φ_m is the measurement objective function, the sum of the squared weighted differences between field measurements and their model-generated counterparts. Φ_r is the regularization objective function, the sum of squared weighted differences between parameters and their preferred conditions (equal to their initial values in this study). μ is the regularization weight factor, which is updated by PEST in every iteration of the inversion process such that a target level of model-to-measurement fit is achieved. Based on the Marquardt-Levenberg method, PEST minimizes the regularization objective function while keeping the measurement objective function smaller than its user-supplied target measurement objective function⁶. The target measurement objective functions in this study were obtained by using a range of parameter values to achieve an acceptable fit between model outputs and field measurements.⁷ We first estimated M_{det}^{SWI} , S_{max} and M_{att}^{AWI} based on the AgNP BTC from experiment A. Values obtained for S_{max} and M_{att}^{AWI} were directly transferred to the inversion of experiments B and C and kept fixed during the parameter estimation. f_1 and f_2 were estimated based on the calibration of experiments B and C, respectively. M^{SWI}_{det} was not directly transferred from experiment A but recalibrated in experiments B and C to account for the impact of flow rate and IS, respectively, on the mass transfer rate coefficient during detachment from the SWI according to Torkzaban.⁸

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Input variables	Values	Unit	Literature/ measured/	
	A, B, C ^a		estimated/ constant	
AgNP diameter, a_p	20 ^b	nm	measured	
Median soil grain diameter, a_c	160 ^c	μm		
Ionic strength, I	$0.001, 0.001/0.001, 0.001/0.0002^{d}$	mol L ⁻¹		
Zeta potential of AgNP, ψ_p	1.1269* <i>I</i> -0.0161 ^e	V	⁹ / measured	
Zeta potential of soil grain, ψ_c	-0.375* <i>I</i> - 0.0371 ^e	V	⁹ / estimated	
Temperature, T	293.15	K	measured	
Porosity, n	0.468, 0.465, 0.469	-		
Hamaker constant, A	2.37×10^{-21}	J	9	
Characteristic wavelength, λ	100	J	10	
Boltzmann constant, k_B	1.38×10^{-23}	$J K^{-1}$		
Permittivity in vacuum, ε_0	8.85×10^{-12}	$C V^{-1} m^{-1}$		
Relative permittivity, ε_r	78.5	_	constant	
Elementary charge, e	$1.60 imes 10^{-19}$	С	constant	
Avogadro's number, N_A	6.02×10^{23}	mol ⁻¹		
Gravitational constant, g	9.8	$\mathrm{m~s}^{-2}$		
Fluid density, ρ_f	0.988	g m ⁻³	10	

Table S1 Summary of the input variables for the model

^a Input variables for scenario A, B, C, respectively.

^b AgNP diameter determined by TEM.

^c Median soil grain diameter determined by sieve analysis.

^d Ionic strength before and after flow interruption.

^e Analytical relation between zeta potential and ionic strength.

٨	В			С		
Falameters A	I.	II.	III.	I.	II.	III.
2.51×10 ⁻⁵	2.51×10 ⁻⁵	2.51×10 ⁻⁵	2.51×10 ⁻⁵	2.51×10 ⁻⁵	2.51×10 ⁻⁵	2.51×10 ⁻⁵
60.99	60.99	5.00	60.99	60.99	5.00	1137.89
1.83×10 ⁻⁹	1.83×10 ⁻⁹	1.83×10 ⁻⁹	1.83×10 ⁻⁹	1.83×10 ⁻⁹	1.83×10 ⁻⁹	1.83×10 ⁻⁹
0	0	0.7^{a}	0.8 ^b	0	0.7^{a}	3×10 ^{-2 c}
	A 2.51×10 ⁻⁵ 60.99 1.83×10 ⁻⁹ 0 0.073	$ \begin{array}{c cccc} A & I. \\ \hline 2.51 \times 10^{-5} & 2.51 \times 10^{-5} \\ \hline 60.99 & 60.99 \\ 1.83 \times 10^{-9} & 1.83 \times 10^{-9} \\ \hline 0 & 0 \\ 0.073 & 0 \end{array} $	A I. II. 2.51×10^{-5} 2.51×10^{-5} 2.51×10^{-5} 60.99 60.99 5.00 1.83×10^{-9} 1.83×10^{-9} 1.83×10^{-9} 0 0 0.7^a 0.073 0.059	A I. II. III. 2.51×10^{-5} 2.51×10^{-5} 2.51×10^{-5} 2.51×10^{-5} 60.99 60.99 5.00 60.99 1.83×10^{-9} 1.83×10^{-9} 1.83×10^{-9} 1.83×10^{-9} 0 0 0.7^a 0.8^b 0.073 0.059 0.059	A I. II. III. II. I. 2.51×10^{-5} 60.99 60.99 5.00 60.99 60.99 1.83×10^{-9} 1.83×10^{-9} 1.83×10^{-9} 1.83×10^{-9} 0 0 0.7^a 0.8^b 0 0.073 0.059 0.8^b 0	A I. II. III. I. II. 2.51×10^{-5} 60.99 60.99 5.00 60.99 60.99 5.00 1.83×10^{-9} 0 0 0.7^a 0.8^b 0 0.7^a 0.073 0.059 0.076 0.076 0.076

Table S2 Fitted AgNP transport parameters

^{*a*} Fraction of retained colloids at SWI that is not released by the decrease of flow rate $(f_1^{I,II})$.

^b Fraction of retained colloids at SWI that is not released by the increase of flow rate $(f_1^{II,III})$.

^c Fraction of retained colloids at SWI that is not released by the decrease of IS $(f_2^{II,III})$.

^d Normalized root mean square error between measured BTCs and corresponding model results

I.: Irrigation with AgNP and tracer, II.: flow interruption, III.: irrigation with electrolyte solution



Figure S1: pH of effluents samples for experiments A, B and C.



Figure S2: Measured and simulated BTCs of AgNP and tracer for experiment A.



Figure S3: Simulated RPs of AgNP at SWI and AWI for experiments A, B and C. The attached AgNP at SWI overlapped for experiments A and B due to their similar values.



Figure S4: The total DLVO interaction energy curve at 1 mM IS and 0.2 mM IS.