Electronic Supplementary Information (ESI)

Silver Nanoparticle (Ag-NP) Retention and Release in Partially Saturated Soil: Column Experiments and Modeling

Yinon Yecheskel^{*}, Ishai Dror and Brian Berkowitz Department of Earth and Planetary Sciences Weizmann Institute of Science Rehovot 7610001 Israel

The ESI contains the following: (1) Ag-NP synthesis and characterization; (2) Experimental setup; (3) Soil column experiment detailed protocol; (4) Sample preparation procedures; (5) Quantitative analysis of BTC slope and initial breakthrough and (6) Information regarding experiment replicate variability.

*Corresponding author: Yinon Yecheskel Email: Yinon.yecheskel@weizmann.ac.il Postal address: Department of Earth and Planetary Sciences, Weizmann Institute of Science 234 Herzl St., P.O. Box 26, Rehovot 7610001, Israel Phone: +97289342542 Fax: +9729344124

(1) Ag-NP synthesis and characterization

Citrate reduction method was applied for the synthesis of Ag-NP suspension¹. Briefly, 10 mL of 0.1 M AgNO₃ (Sigma) were added to boiling citrate solution (990 mL, 7 mM, pH adjusted to 11.5 with (NaOH)) under vigorous stirring for 15 min, then deionized water was added to achieved 100 mg L⁻¹ of silver. The Ag-NP suspension was kept in a 1 L closed bottle. The silver ionic content of the Ag-NP suspension was measured during the course of experiments. A dialysis bag containing a sample of 10 mg L⁻¹ Ag-NPs, silver ion solution or a mixture of silver ions (25%) and NP (75%) was placed in 700 mL deionized water, and the water was replaced three times during 48 h of dialysis. Measurements of the silver content inside the dialysis bag indicate complete removal of free silver ions from the dialysis bag and less than 2% free silver ions in the Ag-NP suspension.

Transmission electron microscopy (TEM) and high resolution scanning electron microscopy (HR-SEM) imaging were used to determine Ag-NP shape and size. TEM imaging was performed with a Philips CM-120 instrument operating at 120kV, equipped with a CCD camera ($2k \times 2k$ Gatan Ultrascan 1000). TEM samples were prepared by placing a 5 µL drop on collodion/carbon-coated 400 mesh Cu grid and blotting after one minute. SEM imaging was performed with a Zeiss Ultra 55 HR-SEM; samples were prepared by placing a diluted Ag-NP suspension on a silicon wafer. Representative SEM and TEM images of Ag-NPs are displayed in Fig. S1. The average diameter of the spherical Ag-NPs was 40.1±8.3 nm based on SEM analysis. Note that the aggregation observed in the TEM/SEM images is due to sample preparation and does not represent the aggregation state of Ag-NPs in solution. Electron microscope imaging was used to determine the shape and size of single Ag-NPs.

Ag-NP hydrodynamic size and surface charge, as a function of pH and solution chemistry, were measured by Dynamic Light Scattering (DLS) and ζ potential (Malvern, Zetasizer Nano ZSP).

At pH 6.8, the hydrodynamic diameter was 58 nm (with polydispersity index 0.57) and the measured value of ζ potential was -43.6 mV, indicating a stable suspension. The effects of solution pH and chemical composition on hydrodynamic size and zeta potential are presented in Fig. S2, and are consistent with previous literature.²



Fig. S1. TEM (left) and SEM (right) images of Ag-NPs.



Fig. S2. Hydrodynamic diameter (A) and zeta potential (B) of Ag-NPs as function of pH, and in the presence of deionized water (blue circles), humic acid (red plus symbol), $Ca(NO_3)_2$ solution (green triangle) and soil solution (black filled/open squares). pH was adjusted using NaOH or HNO₃ solutions. Samples were equilibrated for 10 min with the pH/chemical solution, and then measured three times for hydrodynamic size followed by six measurements of zeta potential; error bars indicate +/- one standard deviation.

(2) Experimental setup

Figure S3 illustrates the partially saturated flow system for Ag-NP transport. Partially saturated conditions were achieved by controlling a pressure difference along the columns; the outlets of the columns were located in a low-pressure chamber while their inlets were exposed to atmospheric pressure. The pressure gradient, controlled by a valve and monitored by a digital vacuum meter, enabled solution flow through the columns and prevented their saturation.

Each column was fed by eight drip infiltration tips, with four connected to each of two source-solutions: the Ag-NP suspension and the flushing/background solution. A three-way valve controlled flow between the two sources.

The inlet solutions flowed downward through the soil column and eluted inside the lowpressure chamber. A plastic mesh was located at the bottom of each column to prevent escape of soil grains; preliminary testing demonstrated that it had no effect on Ag-NP transport.



Fig. S3. Schematic illustration of the experimental system: 1) vacuum pump; 2) low pressure chamber; 3) multichannel peristaltic pump; 4) Ag-NP suspension; 5) background solution; 6) cylindrical acrylic glass columns with plastic mesh located at the bottom; 7) valve to control inlet source solution; 8) fraction collector consisting of stationary tube trays and moving arms; 9) vacuum meter, and 10) valve to control the pressure inside the chamber.

(3) Soil column experiment: detailed protocol

Each BTC experiment involved several steps. First, the column was equilibrated with background solution; solution was supplied for at least 12 h under the same condition as in the next steps, to achieve steady-state flow through the column. In parallel, Ag-NP suspension was circulated in the pumping tubes to equilibrate the tubing and achieve a stable Ag-NP concentration in the column inlet. Then the inlet source was changed from washing solution to Ag-NP suspension, with continuous step input lasting 180 min, followed by return to washing solution for an additional 180 min. The effluents were collected in plastic tubes using a fraction collector, at intervals of 6 min, and analyzed for silver concentration (see Ag-NP Quantification in the main text and Sample preparation procedures below). At the end of each experiment, the columns were weighed to calculate the total water content. To examine the vertical distribution of entrapped Ag-NPs in the column, a retention profile (RP) was determined. RP is defined here as a spatial profile of Ag-NP attached mass. S (ng Ag per g soil) was normalized to the input concentration, C_0 (ng mL⁻¹). Each column was divided into 8 segments, and each segment was first dried to determine the spatial water content and then analyzed for Ag-NP content.

This protocol was applied to determine bromide tracer transport and to explore the influence of input Ag-NP concentration, water saturation level and presence of humic acid and Ca(NO₃)₂ solutions on the mobility and retardation of Ag-NPs. Table 1 in the main text specifies the entire set of experiments, detailing the input concentration, background solution and water content (θ).

Composition and ionic strength of major cations in soil pore solutions were measured for selected experiments. The first and last fraction of the eluted solution from each experimental triplicate were diluted with nitric acid (2% final concentration) and measured for total Na, K, Mg and Ca by ICP-MS. Concentrations were then calculated based on calibration curves. The total concentrations were assumed to reflect the ionic concentration of each element. Note that pure humic acid solution was also measured to confirm negligible contribution of humic acid to total concentration. Average concentrations are shown in Table S1. The ionic strengths of soil pore water in the case of deionized water (0.71 mM) and humic acid solution (0.66 mM) were similar, and comparable to the value commonly used in electrolyte solutions in transport experiments (1 mM).²⁻⁷ The calcium concentration and the ionic strength (2.55 mM) increased when Ca(NO₃)₂ solution was used as background solution. In the case of sand, the column was flushed with deionized water (as background solution), and the cation concentrations and ionic strength were minimized (0.02 mM).

Table S1: Pore water composition and ionic strength of selected sand and soil column experiments. Note: Experiment numbers refer to Table 1 in the main text.

		Na	K	Mg	Ca	Ionic strength*
Exp. 3, soil column, deionized wter	Mean [mM]	0.13	0.15	0.05	0.17	0.71
	Standard deviation	0.017	0.018	0.005	0.017	
		n=3	n=6	n=6	n=6	
Exp. 7, soil column, humic acid solution	Mean [mM]	0.13	0.14	0.05	0.15	0.66
	Standard deviation	0.050	0.016	0.004	0.014	
		n=6	n=6	n=6	n=6	
Exp. 8, soil column, Ca(NO3)2 solution	Mean [mM]	0.03	0.12	0.25	0.95	2.55
	Standard deviation	0.002	0.035	0.012	0.056	
		n=2	n=6	n=6	n=6	
Exp.12, sand column, deionized wter	Mean [mM]	0.0008	0.0017	0.0034	0.0054	0.020
	Standard deviation	0.0002	0.0001	0.0005	0.0014	
		n=6	n=6	n=6	n=6	

* Ionic strength calculations assumed that total element concentration is equal to the ionic concentration.

(4) Sample preparation procedures

The sample preparation procedure to determine BTCs was as follows: 1.8 mL from the collected fractions were diluted with 0.2 mL thiosulfate-cupric-ammonia mixture (0.1 M ammonium thiosulfate, 0.25 M ammonium sulfate and 1 mM cupric sulfate, the mixture pH was adjusted to ca. 9 using NaOH) and then digested for 24 h to allow Ag-NP dissolution.

To determine RPs, the columns were dismantled at the end of each experiment and divided into 8 segments (about 1 cm each); then the wet segments oven-dried to determine the soil moisture. Subsequently, 20 mL thiosulfate-cupric-ammonia mixture (0.05 M ammonium thiosulfate, 0.125 M ammonium sulfate and 0.5 mM cupric sulfate, the mixture pH was adjusted to ca. 9 using NaOH) was added to each dry soil sample, followed by 24 h shaking. The soil was then separated and the supernatant was analyzed. Extraction efficacy (generally >90%) was determined for each experiment separately and accounted for in yield calculations.

(5) Quantitative analysis of BTC slope and initial breakthrough

The results and discussion in the main text consider the relationship between Ag-NP input concentrations, the BTC shape and model results. Fig. S4 provides quantitative analysis of the initial breakthrough (C/C_0 , step 1 of the BTC), BTC slope (step 2 of the BTC), and fitted attachment coefficient (K_{a2}), as a function of Ag-NP input concentration.



Fig. S4. Quantitative analysis (dots) and linear fit (lines) of (A) initial breakthrough (step 1 of the BTC), (B) BTC slope (step 2 of the BTC), and (C) attachment coefficient (K_{a2}) as a function of Ag-NP input concentration. The initial breakthrough was determined by the measured data point around 1.5 EPV in the BTC. The slope was calculated from the same point as the initial breakthrough and an additional point around 5.5 EPV.

(6) Experimental replicate variability

All transport experiments were performed in triplicate. The main text exhibits one representative replicate of each experiment, but we note that the same pattern and similar values were obtained for each replicate among the triplicate experiments. Relatively small variations between replicates are due to soil heterogeneity and the development of varying preferential flow patterns. Figures S5 to S112 provide the full triplicate data of each experiment, including BTC and RP patterns, water content and input concentration.



Fig. S5. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns, related to experiment 1 in Table 1 (see main text). The input concentrations were 94.4, 93.8 and 92.7 (C_0 in ng mL⁻¹) and the saturation levels were 74%, 78% and 76% for columns A, B and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.



Fig. S6. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns, related to experiment 2 in Table 1 (see main text). The input concentrations were 576, 593 and 598 (C_0 in ng mL⁻¹) and the saturation levels were 72%, 82% and 75% for columns A, B and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.



Fig. S7. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns, related to experiment 3 in Table 1 (see main text). The input concentrations were 889, 876 and 884 (C_0 in ng mL⁻¹) and the saturation levels were 73%, 77% and 82% for columns A, B and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.



Fig. S8. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns, related to experiment 4 in Table 1 (see main text). The input concentrations were 1820, 1817 and 1836 (C_0 in ng mL⁻¹) and the saturation levels were 73%, 77% and 74% for columns A, B and C, respectively. Experimental data are given as relative concentration, $^{C/C_0}$ for the BTCs and $^{S/C_0}$ for the RPs.



Fig. S9. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns, related to experiment 5 in Table 1 (see main text). The input concentrations were 914, 986 and 1000 (C_0 in ng mL⁻¹) and the saturation levels were 79%, 94% and 92% for columns A, B and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.



Fig. S10. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns, related to experiment 6 in Table 1 (see main text). The input concentrations were 898 and 915 (C_0 in ng mL⁻¹) and the saturation levels were >99% for columns A and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.



Fig. S11. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns in the presence of 30 mg L⁻¹ humic acid, related to experiment 7 in Table 1 (see main text). The input concentrations were 926, 936 and 917 (C_0 in ng mL⁻¹) and the saturations level were 71%, 78% and 78% for columns A, B and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.



Fig. S12. (a) Breakthrough curves (BTCs) and (b) retention profiles (RPs) of Ag-NP transport in partially saturated soil columns in the presence of 425 mg L⁻¹ Ca(NO₃)₂ solution, related to experiment 8 in Table 1 (see main text). The input concentrations were 809, 793 and 810 (C_0 in ng mL⁻¹) and the saturation levels were 67%, 69% and 68% for columns A, B and C, respectively. Experimental data are given as relative concentration, C/C_0 for the BTCs and S/C_0 for the RPs.

References

- 1. X. Dong, X. Ji, H. Wu, L. Zhao, J. Li and W. Yang, *The Journal of Physical Chemistry* C, 2009, 113, 6573-6576.
- 2. S. K. Kumahor, P. Hron, G. Metreveli, G. E. Schaumann and H. J. Vogel, *Science of the Total Environment*, 2015, 535, 113-121.
- 3. D. Kasel, S. A. Bradford, J. Simunek, M. Heggen, H. Vereecken and E. Klumpp, *Water Res*, 2013, 47, 933-944.
- 4. Y. Liang, S. A. Bradford, J. Simunek, M. Heggen, H. Vereecken and E. Klumpp, *Environ Sci Technol*, 2013, 47, 12229-12237.
- 5. Y. Liang, S. A. Bradford, J. Simunek, H. Vereecken and E. Klumpp, *Water Res*, 2013, 47, 2572-2582.
- 6. D. Wang, L. Ge, J. He, W. Zhang, D. P. Jaisi and D. Zhou, *J Contam Hydrol*, 2014, 164, 35-48.
- 7. Y. Xiao and M. R. Wiesner, *Environ Sci Technol*, 2013, 47, 2246-2253.