Multi-scale biogeochemical Assessment of Soil Denitrification Process Impacted by Nanosilver

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Abstract

Silver nanoparticles (AgNPs) continue to increase in popularity in both consumer goods as well as industrial and medical applications, posing concerns about their effect on ecosystems in the inevitable case of environmental release. Once released to the environment, soils are one of primary sinks for AgNPs, ranking second only to landfills in several modeling scenarios. In this study, the effect of AgNPs on ($[Ag]_T$: 1-100 mg/kg, 13-58 nm with/without polyvinylpyrrolidone (PVP) capping agent) on soil denitrification kinetics was investigated in redued agricultural soils along with the chemical fate of AgNP using synchrotron based X-ray techniques. Although the effects on denitrification kinetics were variable among the AgNPs, some NPs exhibited kinetically limited the antimicrobial effect that resides at the soil-water interface as sorbed-AgNP aggregates or -Ag(I) species. The strong AgNP sorption was observed in soils (Freundlich isotherm K_d: 686- 77,390) that was independent of particle properties (size, zeta potential, and capping agent). However, each AgNP underwent the particle specific chemical transformation. Substantial fraction of PVP coated AgNPs(15nm) were transformed into Ag_2S and or humic acid (HA) complexed Ag, whereas only HA fraction was dominant in uncoated AgNPs (50nm). Changes in solid-state chemical speciation of sorbed AgNPs was promoted by particle specific sorption/aggregation process in soils, suggesting the critical role of soil absorbents in predicting the fate of AgNPs in terrestrial environments.

Material and Methods

ID	Source	Silver purity	Avg. particle size (nm)	Density (g/cm³)	Capping agent
pAg15	NanoAmor	10%	13 +/- 5	2.13	90% PVP (by wt.)
uAg50	Inframat Adv. Materials	99.95%	48 +/- 14	10.49	None
pAg60	NanoAmor	99.9%	58+/- 12	10.49	0.3% PVP (by wt.)
uAg35	NanoAmor	99.9%	35 +/- 21	10.49	None
pAg50	NanoAmor	99.9%	53 +/- 21	10.49	0.3% PVP (by wt.)

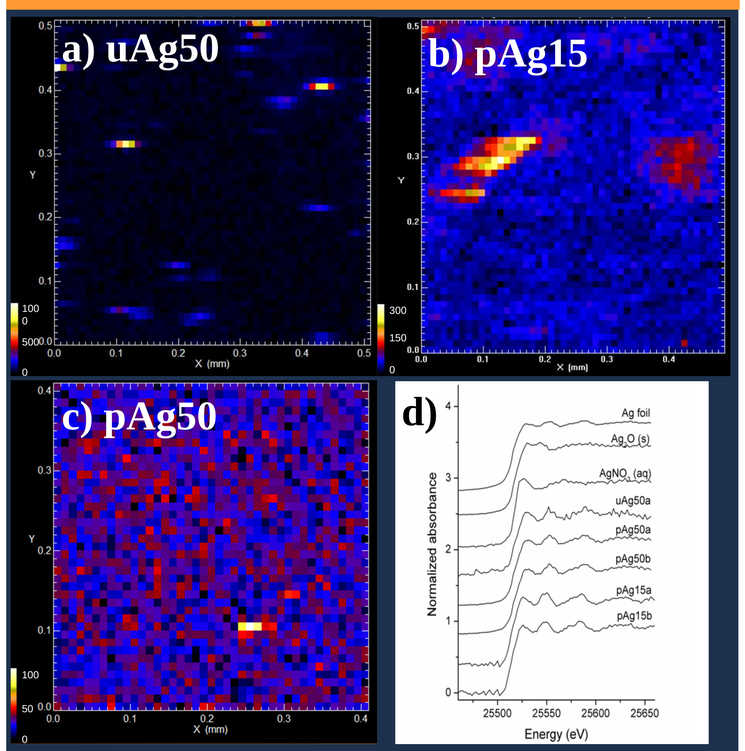
Table-1: Physiochemical characterization of silver nanoparticles

Batch denitrification experiments were conducted in an anaerobic chamber using 50 g of Toccoa entisol (top soil at field capacity), to which 200 mL of a solution containing 1% glucose (C source), 0.005 M Na_2SO_4 , and 1 to 100 mg/L of Ag(I) (as $AgNO_3$) or AgNPs were added. Samples were retrieved every 4 to 8 hrs, and measured for pH, nitrate, and Eh. The kinetic rate (k) was determined from the best fit of a linear regression line of nitrate concentration over time (zero-order). Sorption experiments were conducted in batch mode (33 g/L, 0.005 M Na_2SO_4). A centrifugation technique was used to separate sorbed from unsorbed components. Freundlich isotherm model was used to determine overall distribution coefficient, or K_d. Synchrotron based X-ray analysis was conducted at National Synchrotron Light Source (Beamlines X18B and X27A, Upton, NY) and Stanford Synchrotron Radiation Laboratory (Beamline 4-1, Menlo Park, CA).

pH	Clay	% OM	CEC ($cmol_c$/kg)	Exchangeable Cations ($cmol_c$/kg)		
				K	Ca	Mg
5.2	K, HIV, H, G	1.53	7.4	0.22	1.62	0.37

Table-2: Characterization of Toccoa entisol sandy loam. K: Kaolinite, HIV: Hydroxy interlayered vermiculite, H: hematite, G: gibbsite. CEC: Cation exchange capacity.

Results



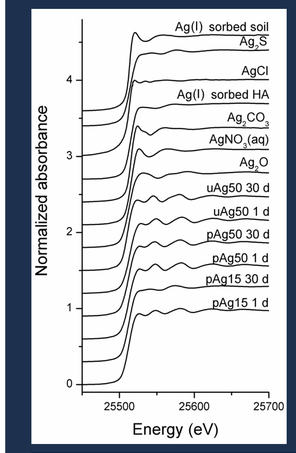


Figure-1 (top 4 panels). Micro-XRF (Ag kα) maps of AgNP reacted soils. A) uAg50, b) pAg50 and c) pAg15. d) Micro-X-ray absorption near edge structure spectroscopy (XANES) spectra of reference compounds and Ag hotspots.

Figure-2 (left). Bulk XANES spectra of Ag reference compounds and AgNP reacted whole soils after 1-30 d aging in reduced soils (E_h: -185 to – 280mV).

Table-3 (below). Linear combination of reference spectra fit of AgNP reacted soils (shown in Figure-3).

Sample	Respective ref. AgNP	AgCl	Ag_2O	Ag_2CO_3	$AgNO_{3(aq)}$	Ag_2S	Ag(I) sorbate	Red. χ^2
uAg50 1 day	0.9019 ± 0.0012	0.0981 ± 0.0012	-	-	-	-	-	1.501 x 10^{-5}
uAg50 30 days	0.8527 ± 0.0016	-	-	-	-	-	0.1476 ± 0.0016[a]	1.088 x 10^{-4}
pAg50 1 day	0.9084 ± 0.0027	-	0.0573 ± 0.0031	0.0343 ± 0.0022	-	-	-	2.334 x 10^{-5}
pAg50 30 days	0.8245 ± 0.0015	-	0.0881 ± 0.0019	-	0.0134 ± 0.0013	0.0743 ± 0.0023	-	5.378 x 10^{-6}
pAg15 1 day	0.7075 ± 0.0026	-	0.0580 ± 0.0030	0.0845 ± 0.0046	0.1501 ± 0.0059	-	-	1.983 x 10^{-5}
pAg15 30 days	0.2245 ± 0.0035	-	-	-	-	0.3414 ± 0.0078	0.4340 ± 0.0065[b]	2.827 x 10^{-5}

[a]The result of fit with Ag(I)-sorbed soil component. [b]The result of fit with Ag(I)-sorbed humic acid component.

Discussion and Important Findings

Condition	K_d	Conc. (mg/L)	Average k value (mg NO_3^- /hr)	T-test Diff. from ctrl († indicates sig. diff.)
Ctrl	N/A	0	1.486 (0.289)	N/A
Ag(I)	282.9	1	0.748 (0.019)	**0.042**†
		10	0.881 (0.244)	**0.095**†
pAg15	686.2	1	1.085 (0.212)	0.197
		10	0.581 (0.069)	**0.026**†
		100	0.425 (0.065)	**0.017**†
uAg50	20,450	1	1.517 (0.062)	0.897
		10	1.309 (0.023)	0.472
		100	0.939 (0.063)	**0.087**†
pAg50	77,390	1	1.182 (0.298)	0.337
		10	1.136 (0.323)	0.292
		100	1.027 (0.007)	0.123

Table-4: Relationships between the distribution coefficient (K_d) and denitrification kinetic rate in AgNP systems.

- Ag(I) and AgNPs exhibit strong sorption onto Toccoa entisoil
- The most toxic AgNP, pAg15, shows the lowest K_d value of any AgNP
- Micron scale chemical speciation of Ag at hot spots (aggregates) shows metallic Ag ➔ NPs are intact
- Changes in bulk chemical speciation of silver in AgNP spiked soils is particle specific
- Conversion to Ag_2S as well as sorption to soil components (e.g., humic substances) might predict the chemical fate of AgNPs
- The overall toxicity of both Ag(I) and AgNPs in the presence of soil are lower than expected from a literature search of pure-component studies.

- The relationship between toxicity, K_d, chemical transformation and size for AgNPs is explored in the image below: