# Electronic Supporting Information

# The transformation and fate of silver nanoparticles in a paddy soil: Effects of soil organic matter and redox conditions

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**Summary**

**9 SI pages containing 2 figures, 3 tables, 3 detailed descriptions and 1 reference.**

**Contents**

**Soil organic matter removal**

Subsamples of soil were reacted with sodium hypochlorite, which was less invasive for soil organic matter (OM) removal than other oxidants described previously.[1] Briefly, 100.0 g soil was reacted with 1 L 6% NaClO (pH 8.0) for 6 h at 25 $^{o}$C. The mixture was then centrifuged at 2574 × g for 5 min and washed twice using 1.0 M $NaNO_3$. The procedure was repeated twice. Finally, samples were washed with 18 MΩ water until conductivity was < 40 μS $cm^{-1}$.

**AgNP and soil characterization**

The particle size distribution and morphology of polyvinylpyrrolidone (PVP)-coated silver nanoparticles (AgNPs) were determined by TEM (JEM-2100, JEOL, Japan). Number weighted hydrodynamic diameters were measured using dynamic light scattering (DLS, BI-200SM, Brookhaven Instruments, USA). AgNPs stock suspension was sonicated in a benchtop sonicator (KQ-300VDE, China) at 45 kHz for 3 min prior to experiments.

Soils with or without OM removal were characterized for pH (0.01 mol $L^{-1}$ $CaCl_2$), OM content (Waikley-Balck method), water holding capacity (WHC), cation exchange capacity (CEC, ammonium acetate centrifugal exchange method) particle-size (Laser particle size analyzer, Beckman LS 13320) and total S (elemental analyzer, Elementar vario max cube, Germany ).

**Characteristics of soils**

The soil revealed characteristics typical of paddy soils in China (Table S1). Background Ag concentration was below detection limit (< 0.075 mg $kg^{-1}$). Sodium hypochlorite treatment decreased soil OM contents significantly from 3.8% to 1.0% (on average), and the residual refractory organic carbon was comprised of pyrogenic materials and aliphatic compounds.[1] Total S concentrations decreased, on average, from 605.8 mg $kg^{-1}$ to 212.9 mg $kg^{-1}$. Conversely, other soil properties (e.g., pH, CEC, and amorphous Fe/Mn) showed relatively little change (Table S1) after OM removal.

**References:**

1 R. Mikutta, M. Kleber, M. S. Torn and R. Jahn, *Biogeochemistry*, 2006, **77**, 25-56.

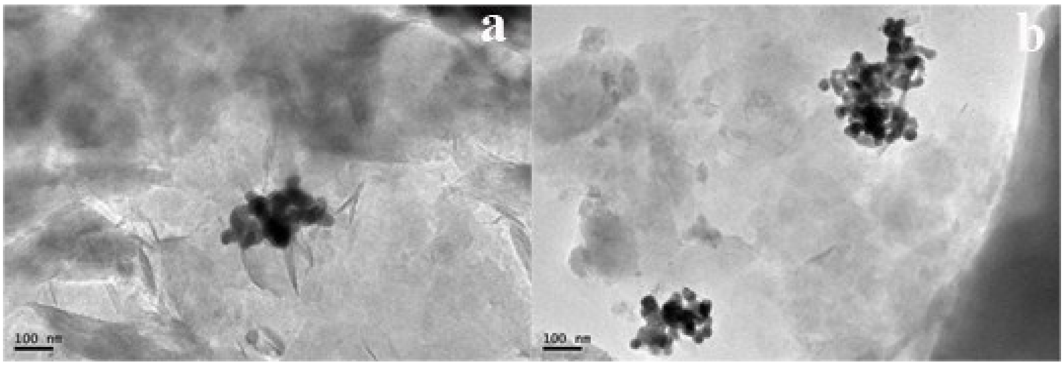


**Fig. S1.** Representative TEM images of soil without organic matter removal spiked with AgNPs and incubated for 28 days.

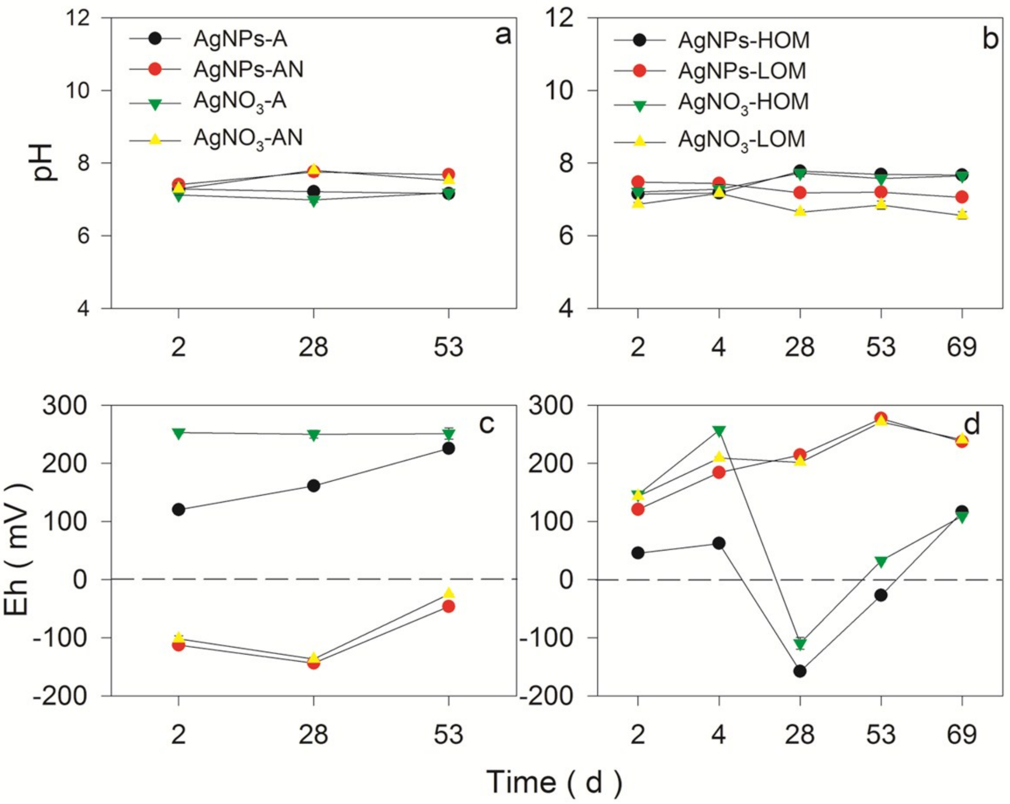


**Fig. S2.** Eh and pH in the liquid phase of all treatments (same legends for a and c, b and d). Data are presented as mean ± SD (n=3).

**Table S1.** Soil properties in this study.

| Property | Soil without OM removal (HOM) | Soil with OM removal (LOM) |
|---|---|---|
| pH[a] | 7.1 ± 0.4 | 7.9 ± 0.2 |
| CEC (cmol/kg) | 22.0 | 15.5 |
| Sand (%) | 19.4 | 3.8 |
| Silt (%) | 43.0 | 56.2 |
| Clay (%) | 37.6 | 40.0 |
| Amorphous Fe (mg/kg) | 7736 | 7137 |
| Amorphous Mn (mg/kg) | 196 | 211 |
| OM (%)[a] | 3.73 ± 0.04 | 0.959±0.001 |
| WHC (%) | 44.1 | 33.4 |
| Total S (mg/kg)[a] | 605.8±21.3 | 212.9±11.3 |
| Ag concentration (mg/kg) | < 0.075 | < 0.075 |

[a]Data are given as mean ± SD (n=3).

**Table S2.** Dissolved TAg and Ag(I) levels in the liquid phase

| treatment | Time (d) | TAg levels in liquid phase (μg $L^{-1}$) | Ag(I) levels in liquid phase (μg $L^{-1}$) |
|---|---|---|---|
| | 2 | 33.28±4.14 | 22.15±1.19 |
| AgNPs-A | 28 | 7.04±0.42 | 6.12±0.26 |
| | 53 | 9.41±3.06 | 23.01±2.23 |
| | 2 | 14.74±10.17 | 1.42±0.48 |
| AgNPs-AN | 28 | 6.82±0.67 | 2.51±1.52 |
| | 53 | 66.71±18.79 | 20.59±0.29 |
| | 2 | 48.09±3.75 | 45.11±8.79 |
| $AgNO_3$-A | 28 | 25.45±0.34 | 26.31±2.34 |
| | 53 | 40.10±3.58 | 27.94±2.47 |
| | 2 | 14.65±1.21 | 0.49± 0.09 |
| $AgNO_3$-AN | 28 | 7.96±0.17 | 5.65±0.36 |
| | 53 | 24.43±7.45 | 23.45±1.70 |
| | 2 | 36.15±23.36 | 1.39±0.20 |
| | 4 | 58.09±11.24 | 1.25±0.46 |
| AgNPs-HOM | 28 | 4.91±0.15 | 1.30±0.57 |
| | 53 | 25.96±2.54 | 21.71±0.91 |
| | 69 | 5.52±1.61 | 2.95±0.29 |
| | 2 | 172.72±48.32 | 53.20±5.76 |
| | 4 | 37.55±0.87 | 56.39±7.36 |
| AgNPs-LOM | 28 | 229.11±42.34 | 54.25±10.53 |
| | 53 | 109.86±31.43 | 60.53±12.17 |
| | 69 | 44.32±9.22 | 40.09±0.77 |
| | 2 | 53.77±7.78 | 32.41±1.23 |
| | 4 | 43.19±4.69 | 31.56±6.00 |
| $AgNO_3$-HOM | 28 | 44.65±14.86 | 7.18±1.14 |
| | 53 | 30.80±7.36 | 27.74±3.75 |
| | 69 | 30.40±10.81 | 1.86±0.66 |
| | 2 | 71.07±16.13 | 46.44±1.59 |
| | 4 | 63.60±18.74 | 51.72±2.76 |
| $AgNO_3$-LOM | 28 | 67.67±6.65 | 78.54±2.61 |
| | 53 | 70.21±7.16 | 72.88±3.91 |
| | 69 | 75.30±21.91 | 74.70±8.45 |

**Table S3.** Results of Two-way Analysis of Variance (ANOVA) among treatments.

| Experiment | Time (d) | Factor | TAg | | Ag(I) | | $K_d$ | |
|---|---|---|---|---|---|---|---|---|
| | | | F | Sig. | F | Sig. | F | Sig. |
| Experiment 1[a] | 2 | Ag form | 0.386 | 0.557 | 9.707 | 0.017 | 3.892 | 0.096 |
| | | Eh | 21.595 | 0.004 | 138.955 | 0.000 | 0.880 | 0.384 |
| | 28 | Ag form | 926.128 | 0.000 | 163.705 | 0.000 | 6.342 | 0.036 |
| | | Eh | 751.022 | 0.000 | 181.069 | 0.000 | 3.659 | 0.092 |
| | 53 | Ag form | 0.000 | 0.998 | 1.166 | 0.312 | 32.540 | 0.004 |
| | | Eh | 1.663 | 0.245 | 0.137 | 0.720 | 22.250 | 0.014 |
| Experiment 2[a] | 2 | Ag form | 7.481 | 0.026 | 56.855 | 0.000 | 14.541 | 0.007 |
| | | OM | 20.611 | 0.002 | 501.865 | 0.000 | 74.725 | 0.000 |
| | 4 | Ag form | 9.770 | 0.014 | 103.810 | 0.000 | 0.235 | 0.642 |
| | | OM | 2.567 | 0.148 | 248.439 | 0.000 | 9.634 | 0.017 |
| | 28 | Ag form | 45.478 | 0.000 | 7.534 | 0.025 | 25.012 | 0.002 |
| | | OM | 136.700 | 0.000 | 338.283 | 0.000 | 40.214 | 0.000 |
| | 53 | Ag form | 8.486 | 0.019 | 0.053 | 0.824 | 15.899 | 0.004 |
| | | OM | 30.767 | 0.001 | 75.488 | 0.000 | 20.248 | 0.002 |
| | 69 | Ag form | 7.633 | 0.025 | 17.138 | 0.003 | 4.649 | 0.074 |
| | | OM | 32.384 | 0.000 | 604.329 | 0.000 | 1.682 | 0.242 |

[a]See text for details of experiments 1 and 2.