Electronic Supporting Information

Effects of Molecular-Weight-Fractionated Natural Organic Matter on the Phytoavailability of Silver Nanoparticles

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Summary

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Table S1 Elemental composition and acidic functional groups of Suwannee River natural organic
matter (NOM) as provided by the International Humic Substance Society (available at

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O</th>
<th>Ash&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Carboxyl&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Phenolic&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOM</td>
<td>5.69</td>
<td>4.01</td>
<td>50.7</td>
<td>3.97</td>
<td>41.48</td>
<td>1.27</td>
<td>1.78</td>
<td>ND</td>
<td>11.21</td>
<td>2.47</td>
</tr>
</tbody>
</table>

<sup>a</sup>: Percentage of inorganic residue (% w/w) in a dry sample.

<sup>b</sup>: Charge density (m<sub>eq</sub> g<sup>-1</sup> C) at pH 8.0.

<sup>c</sup>: Two times the change in the charge density (m<sub>eq</sub> g<sup>-1</sup> C) between pH 8.0 and pH 10.0.

ND: not determined.
Table S2 Washing efficiencies of two washing methods (HNO$_3$ + L-cysteine and CaCl$_2$). HNO$_3$ + L-cysteine: tissues were soaked thoroughly in Milli-Q water for 10 min, rinsed with 10 mM HNO$_3$, soaked thoroughly in 10 mM of freshly prepared L-cysteine for 20 min, and finally rinsed with Milli-Q water after soaking in AgNP medium for 2 or 10 min. CaCl$_2$: tissues were soaked thoroughly in Milli-Q water for 10 min, 10 mM CaCl$_2$ for 20 min, and finally rinsed with Milli-Q water after soaking in AgNP medium for 2 or 10 min. Exposure medium condition: 10 mg AgNPs L$^{-1}$ in 1/4 Hoagland’s medium (pH 5.6 ± 0.1). The data are presented as the mean ± SD (n = 5).

<table>
<thead>
<tr>
<th></th>
<th>CaCl$_2$ (2 min)</th>
<th>HNO$_3$ + L-cysteine (2 min)</th>
<th>CaCl$_2$ (10 min)</th>
<th>HNO$_3$ + L-cysteine (10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag in washing solution (µg)</td>
<td>9.32 ± 1.30</td>
<td>12.40 ± 1.89</td>
<td>12.20 ± 2.05</td>
<td>13.88 ± 2.27</td>
</tr>
<tr>
<td>Ag remained in tissue (µg)</td>
<td>3.66 ± 0.82</td>
<td>2.90 ± 0.90</td>
<td>4.31 ± 0.95</td>
<td>2.93 ± 0.66</td>
</tr>
<tr>
<td>Ag removed (%)</td>
<td>72.0 ± 2.00</td>
<td>81.4 ± 2.80</td>
<td>74.1 ± 2.08</td>
<td>82.6 ± 2.22</td>
</tr>
</tbody>
</table>
Figure S1. Linear pattern of the uptake of total Ag by rice over time. The data are presented as the mean ± SD (n = 5). Exposure medium condition: 1 mg AgNPs L$^{-1}$ in 1/4 Hoagland’s medium (pH 5.6 ± 0.1).
Figure S2. Representative transmission electron microscopy (TEM) image (A), high-resolution TEM image (B), particle size distribution (C), number-weighted hydrodynamic diameters (D), UV-Vis spectra (E), and dissolved Ag ($\text{Ag}_{\text{diss}}$) concentration (F) of 1 mg AgNPs L$^{-1}$ in 1/4 Hoagland’s medium (pH 5.6 ± 0.1).
Figure S3. Representative TEM images (A, B, and C) and particle size distribution (D) of AgNPs incubated with 80 mg L$^{-1}$ NOM. The AgNP concentration (5 mg L$^{-1}$) was higher than that in the exposure medium to satisfy the detection limit of TEM. Note that particle size distribution were analyzed by 200 well-dispersed nanoparticles with NOM adsorption (as indicated in the selected particles), while particles associated with large NOM aggregates were not considered.
Figure S4. Number-weighted hydrodynamic diameters of NOM alone in the exposure medium: 1/4 Hoagland solution at pH 5.6. Samples were prepared using unfractionated NOM ranging from 10 to 80 mg L$^{-1}$. The data are presented as the mean ± SD (n = 5).
Figure S5. Correlation between total Ag uptake and the compositional differences in the NOM fractions. A: specific ultraviolet absorbance at 280 nm (SUVA$_{280}$), B: aromaticity, C: [TOC] × SUVA$_{280}$, D: peak A intensity in the excitation-emission matrix spectra (EEMs), E: peak B intensity in the EEMs, F: [TOC] × intensity of peak A in EEMs, G: [TOC] × intensity of peak B in EEMs.
Figure S6. Chemical structural formulas of small-NOM models.

- L-cysteine
- L-serine
- Malic acid
- Citric acid
Figure S7. Effects of NOM concentration (A), NOM fractionation (B), and small-NOM models (C) on the pH of the exposure medium. Exposure medium condition: 1 mg AgNPs L\(^{-1}\) in 1/4 Hoagland’s medium (pH 5.6 ± 0.1). The data are presented as the mean ± SD (n = 5).