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Electronic Supporting Information

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

Min Li,[ab] Fei Dang,[*a] Qing-Long Fu,[c] Dong-Mei Zhou[a] and Bin Yin[d]

[a] Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, the Chinese Academy of Sciences, Nanjing 210008, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Department of Civil and Environmental Engineering, Tokyo Institute of Technology, Tokyo 152-8552, Japan

[d] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, the Chinese Academy of Sciences, Nanjing 210008, China

[*] Corresponding author, Tel: +86-25-86881179, Fax: +86-25-86881000.

E-mail: fdang@issas.ac.cn.

Summary

11 SI pages containing 2 tables and 7 figures.

Contents

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 http://humic-substances.org/#products).

Sample	H_2O	Ash[a]	C	H	O	N	S	P	Carboxyl[b]	Phenolic[c]
NOM	5.69	4.01	50.7	3.97	41.48	1.27	1.78	ND	11.21	2.47

[a]: Percentage of inorganic residue (%, w/w) in a dry sample.

[b]: Charge density (m_{eq} g^{-1} C) at pH 8.0.

[c]: Two times the change in the charge density (m_{eq} g^{-1} 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).

	$CaCl_2$ (2 min)	HNO_3 + L-cysteine (2 min)	$CaCl_2$ (10 min)	HNO_3 + L-cysteine (10 min)
Ag in washing solution (μg)	9.32 ± 1.30	12.40 ± 1.89	12.20 ± 2.05	13.88 ± 2.27
Ag remained in tissue (μg)	3.66 ± 0.82	2.90 ± 0.90	4.31 ± 0.95	2.93 ± 0.66
Ag removed (%)	72.0 ± 2.00	81.4 ± 2.80	74.1 ± 2.08	82.6 ± 2.22

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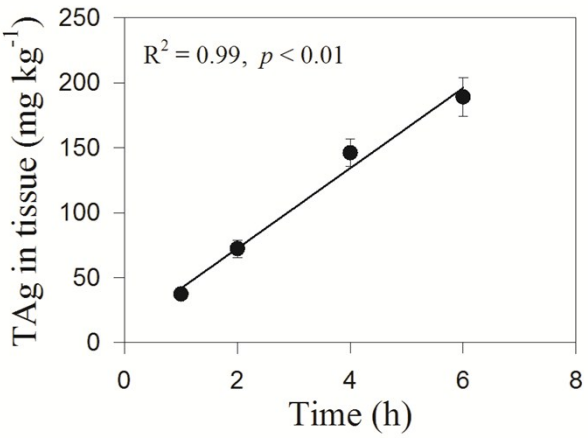

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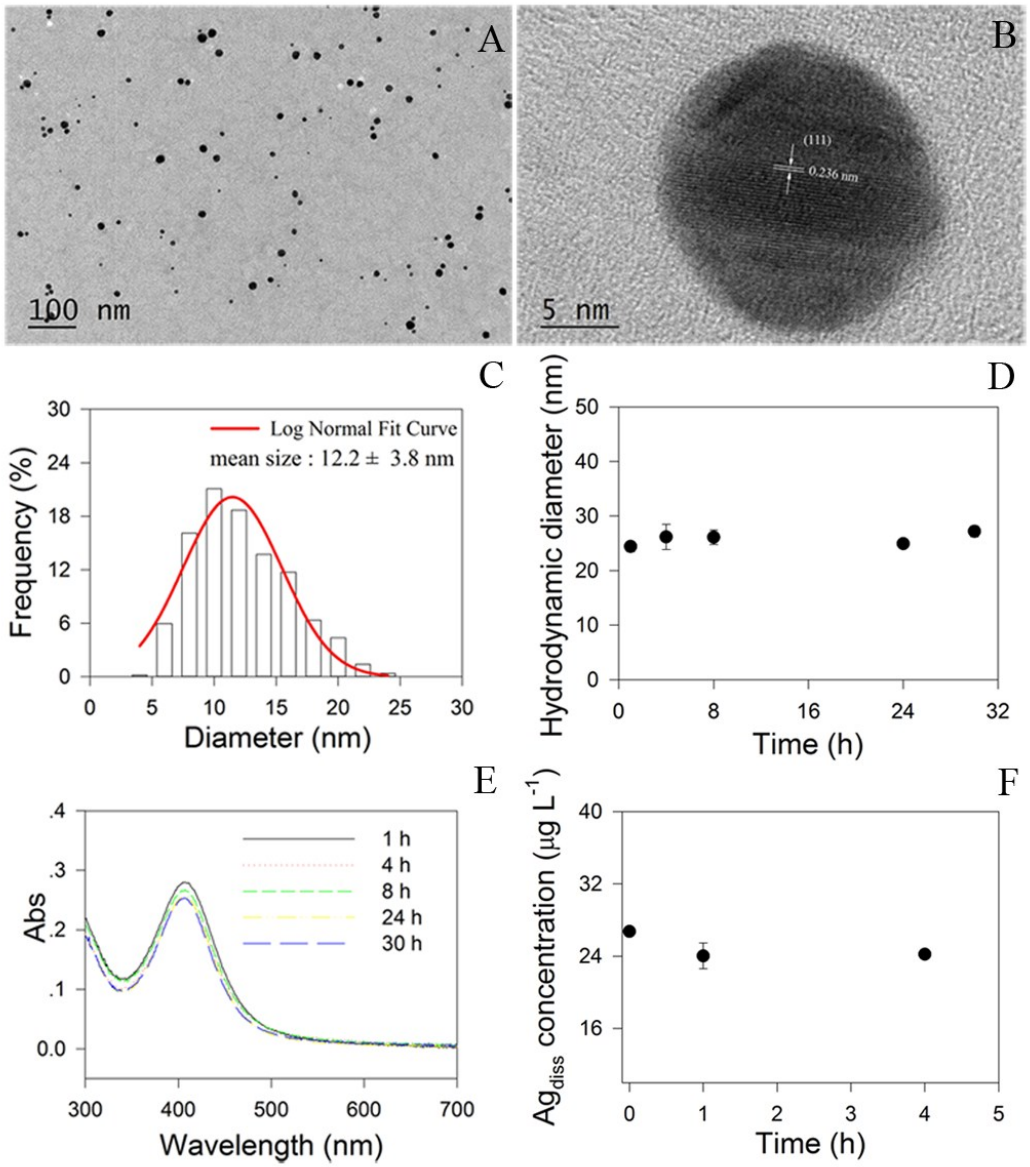
54 **Figure S1.** Linear pattern of the uptake of total Ag by rice over time. The data are presented as the

55 mean ± SD (n = 5). Exposure medium condition: 1 mg AgNPs L^{-1} in 1/4 Hoagland's medium (pH

56 5.6 ± 0.1).



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59 **Figure S2.** Representative transmission electron microscopy (TEM) image (A), high-resolution

60 TEM image (B), particle size distribution (C), number-weighted hydrodynamic diameters (D),

61 UV-Vis spectra (E), and dissolved Ag (Ag_{diss}) concentration (F) of 1 mg AgNPs L^{-1} in 1/4

62 Hoagland's medium (pH 5.6 ± 0.1).

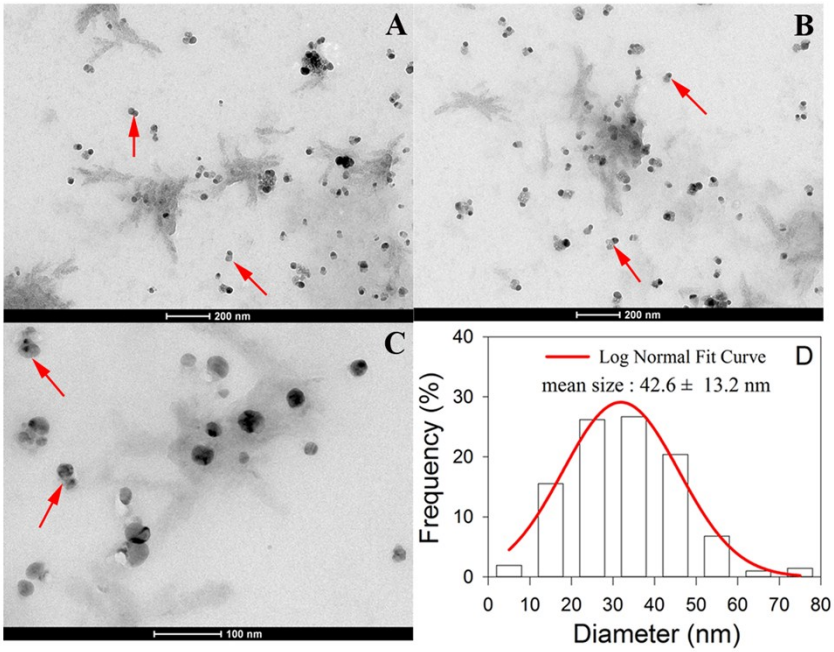


Figure S3. Representative TEM images (A, B, and C) and particle size distribution (D) of AgNPs incubated with 80 mg L^{-1} NOM. The AgNP concentration (5 mg L^{-1}) was higher than that in the exposure medium to satisfy the detection limit of TEM. Note that particle size distribution were analyzed by 200 well-dispersed nanoparticles with NOM adsorption (as indicated in the selected particles), while particles associated with large NOM aggregates were not considered.

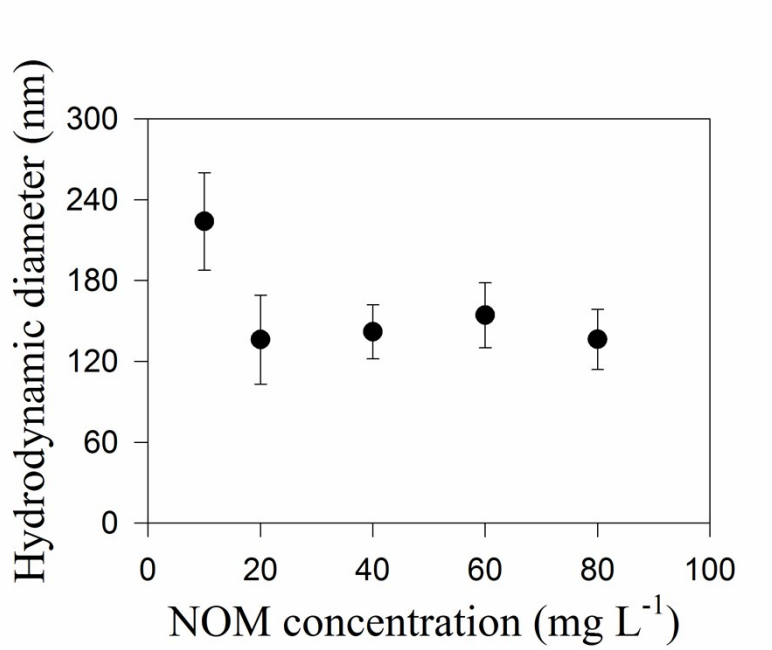
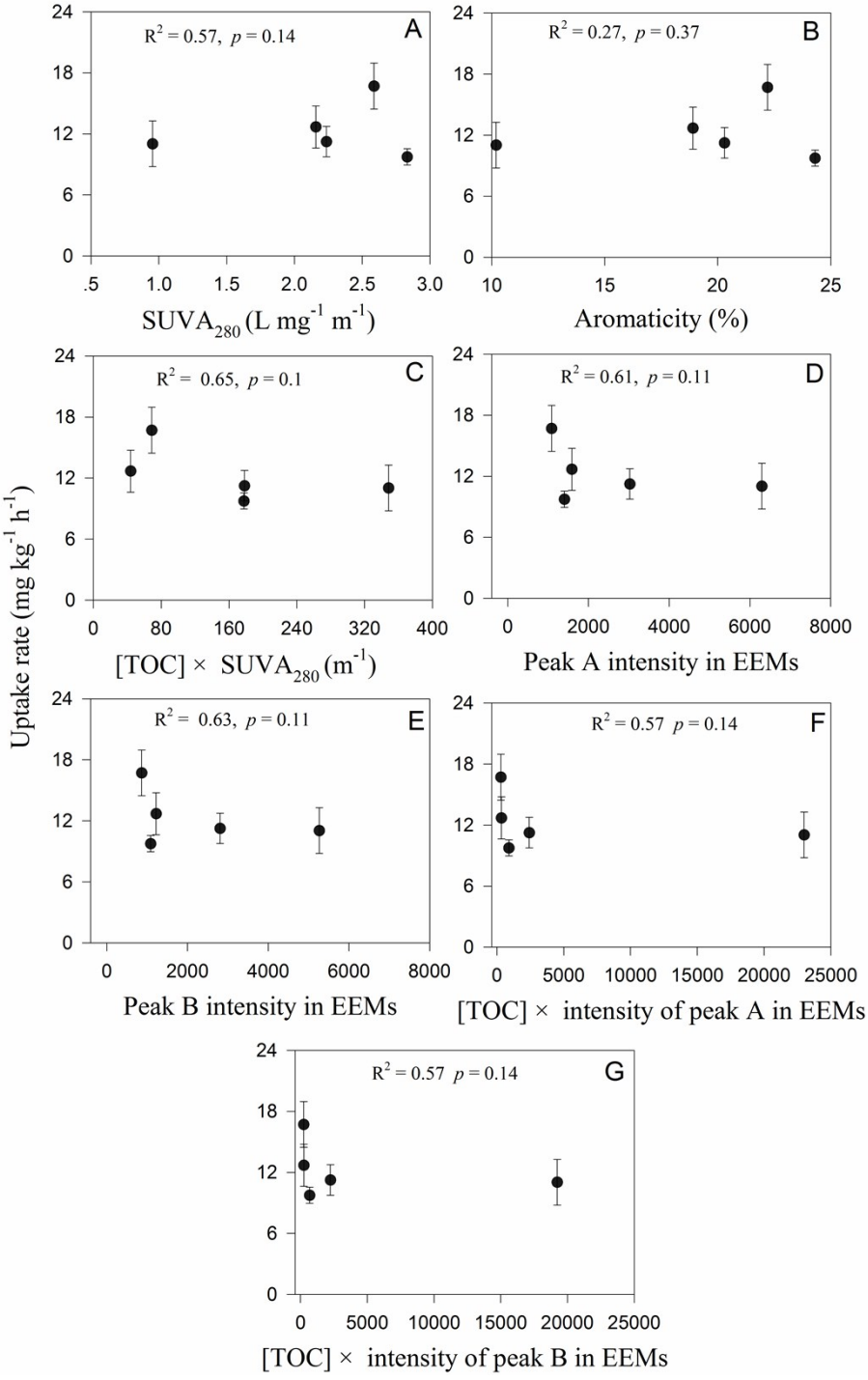


Figure S4. Number-weighted hydrodynamic diameters of NOM alone in the exposure medium: 1/4 Hoagland solution at pH 5.6. Samples were prepared using unfractionated NOM ranging from 10 to 80 mg L^{-1}. The data are presented as the mean ± SD (n = 5).



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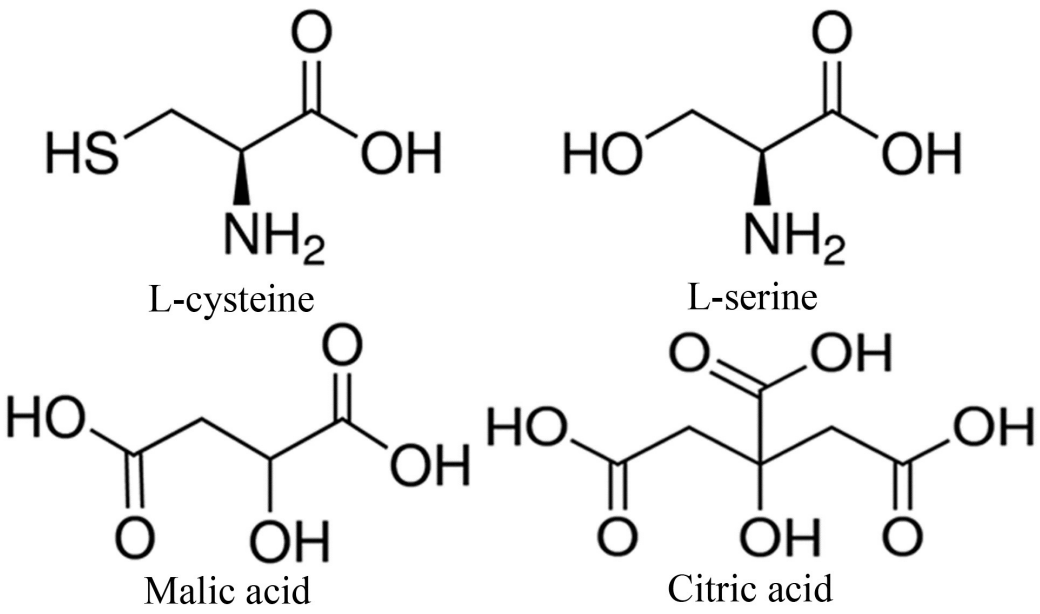
78 **Figure S5.** Correlation between total Ag uptake and the compositional differences in the NOM

79 fractions. A: specific ultraviolet absorbance at 280 nm ($SUVA_{280}$), B: aromaticity, C: [TOC] ×

80 $SUVA_{280}$, D: peak A intensity in the excitation-emission matrix spectra (EEMs), E: peak B

81 intensity in the EEMs, F: [TOC] ×intensity of peak A in EEMs, G: [TOC] ×intensity of peak B in

82 EEMs.



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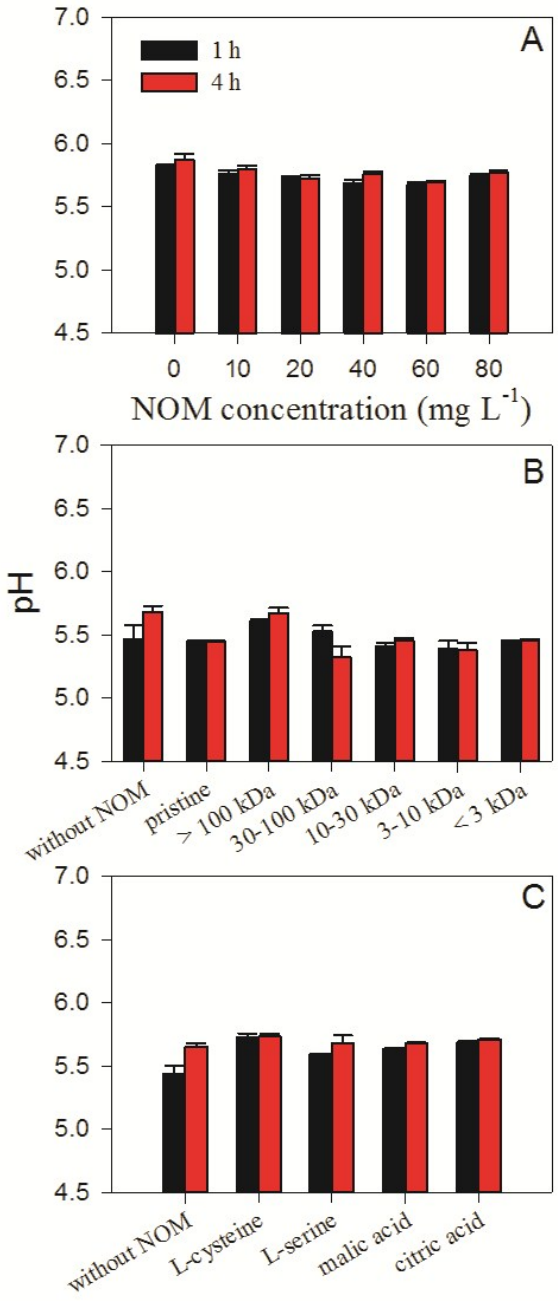
84 **Figure S6.** Chemical structural formulas of small-NOM models.



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87 **Figure S7.** Effects of NOM concentration (A), NOM fractionation (B), and small-NOM models

88 (C) on the pH of the exposure medium. Exposure medium condition: 1 mg AgNPs L^{-1} in 1/4

89 Hoagland's medium (pH 5.6 ± 0.1). The data are presented as the mean ± SD (n = 5).