

Electronic Supporting Information

Assessing the interactions of metal nanoparticles in soil and sediment matrices – A quantitative analytical multi-technique approach

Hind El Hadri*, Stacey M. Louie and Vincent A. Hackley*

National Institute of Standards and Technology
Materials Measurement Science Division
100 Bureau Drive, Gaithersburg, MD 20899

*corresponding authors: h.el.hadri@hotmail.fr; vince.hackley@nist.gov

Humic acid extraction protocol and mixing with AuNPs

Humic acid (HA) was extracted from the SONE-1 soil following a procedure¹ developed by the IHSS with one modification (described by the IHSS^a) to apply filtration instead of hydrofluoric acid treatment for ash removal. 1 mol L⁻¹ HCl was added to 1 g of SONE-1 sample at room temperature until the slurry attained a pH between 1 and 2 (\approx 2.5 mL was required). Then, 7.5 mL of 0.1 mol L⁻¹ HCl was added to obtain a final liquid volume of 10 mL. The suspension was mixed for 1 h on an end-over-end rotator at 40 rpm, then centrifuged at 2000 rpm (500 g) for 11 min. The supernatant was collected as fulvic acid (FA) extract 1.

The soil residue was neutralized with 1 mol L⁻¹ NaOH to pH 7. In a glove bag purged with N₂, 0.1 mol L⁻¹ NaOH was added to a final liquid volume of 10 mL. The suspension was shaken every 30 min for 4 h and allowed to settle overnight. The suspension was again centrifuged at 2000 rpm (500 g) for 11 min, and the supernatant was collected. Filtration was used for ash removal. A 0.2 μ m PES membrane (Whatman)^b was pre-rinsed by passing 10 mL of 0.1 mol L⁻¹ NaOH through the membrane. Then, the supernatant of the soil suspension was

^a <http://humic-substances.org/isolation-of-ihss-soil-fulvic-and-humic-acids/>

^b The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

filtered twice through the same membrane. The filtered solution was acidified to pH 1.0 with 6 mol L⁻¹ HCl and allowed to stand overnight for (12 to 16) h to precipitate HA. The suspension was centrifuged at 2000 rpm (500 g) for 11 min, and the supernatant was collected as FA extract 2. The precipitate slurry was dialyzed against deionized water using a 100-500 Da molecular weight cutoff SpectraPor regenerated cellulose membrane with four reservoir exchanges.

The dialyzed solution was collected as HA. The initial pH of the HA solution was 3.9, and the solution was adjusted to pH 8 with 0.1 mol L⁻¹ NaOH. The two FA extracts were combined for total organic carbon (TOC) analysis but were not used for further experiments. The concentration of the HA solution was also determined by TOC analysis. TOC was measured on a Phoenix 8000 instrument (Teledyne Tekmar, Mason, OH). Calibration standards were prepared using potassium hydrogen phthalate (KHP) solutions. In the method, 4.0 mL of sample is mixed with 0.5 mL of 21 % phosphoric acid reagent and sparged with N₂ for 120 s to remove inorganic carbon. Then, 1.0 mL of 10 % persulfate/5 % phosphoric acid reagent is added to the sample in a UV reactor to oxidize the organic carbon to CO₂, which is measured by a nondispersive infrared detector. Based on the TOC analysis, the extracted masses of HA and FA from the 1 g soil sample were (1.8 and 2.5) mg as C, respectively.

To prepare AuNPs coated with HA, an aqueous mixture of Cit-AuNPs (≈ 10 mg/L) and HA (20 mg L⁻¹ as C) was allowed to equilibrate overnight. The coated AuNPs were not purified of unadsorbed HA before spiking into soil matrices.

Table S1: Principal interfering species in ICP-MS for the monitored isotopes

Isotopes	Polyatomic interference
^{27}Al	$^{12/13}\text{C}^{15/14}\text{N}$, $^{12}\text{C}^{14}\text{N}^1\text{H}$
^{55}Mn	$^{37}\text{Cl}^{18}\text{O}$, $^{23}\text{Na}^{32}\text{S}$
^{57}Fe	$^{40}\text{Ar}^{16}\text{OH}$, $^{40}\text{Ca}^{16}\text{OH}$

Table S2: Carbon, aluminum, iron and manganese content in the solid soils and sediment ²⁻⁵

	SONE-1	San Joaquin 2709a	Estuarine sediment (1646a)
Carbon content (mass %)	1.94 ± 0.18	1.2*	1.57*
Al (mass %)	6.44 ± 0.22	7.37 ± 0.16	2.30 ± 0.02
Fe (mass %)	2.92 ± 0.02	3.36 ± 0.07	2.01 ± 0.04
Mn (mg/kg)	639 ± 59	529 ± 18	234.5 ± 2.8

*Uncertainty not determined

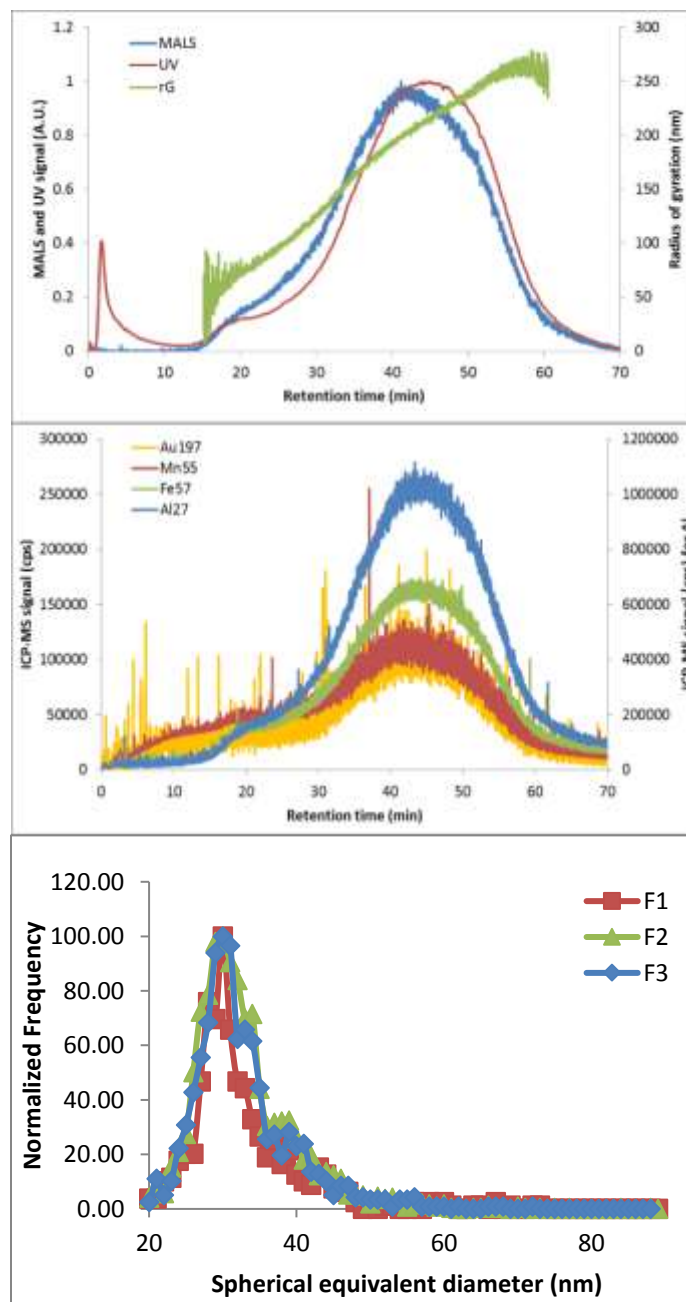


Figure S1: AF4-UV-MALS-ICP-MS fractograms for $5000 \mu\text{g kg}^{-1}$ bPEI-AuNPs spiked into SONE-1 soil in the fraction $< 0.45 \mu\text{m}$ after 24 h of agitation, and AuNP size distribution determined by spICP-MS from three collected fractions (F1, F2 and F3 were collected at $t_R = 5.5$, 16.5 and 45 min, respectively, in 1 min intervals).

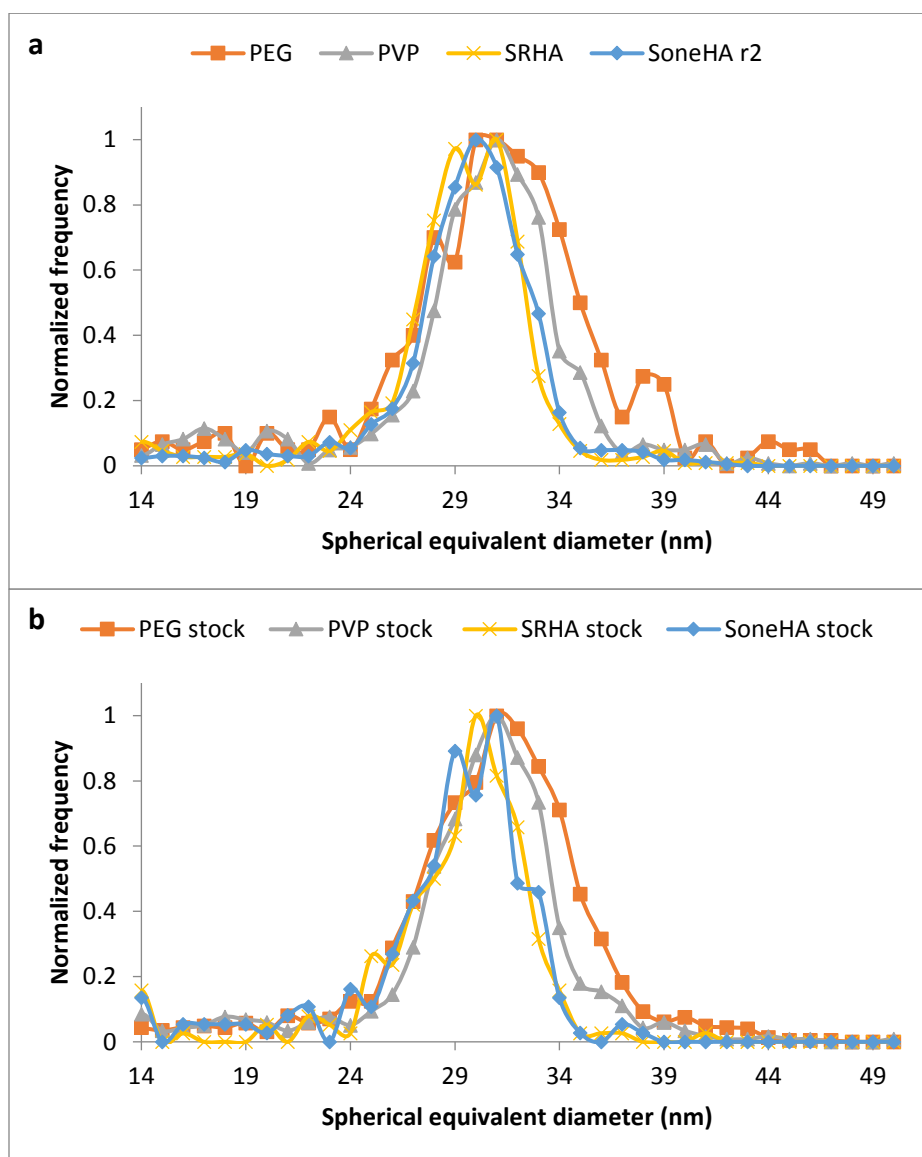


Figure S2: spICP-MS size distributions for a) soil extract (SONE-1) spiked with AuNPs coated with PEG, PVP, SRHA or SONE-HA and b) diluted stock solution of AuNPs coated with PEG, PVP, SRHA and SONE-HA. The spiked concentration was $500 \mu\text{g kg}^{-1}$.

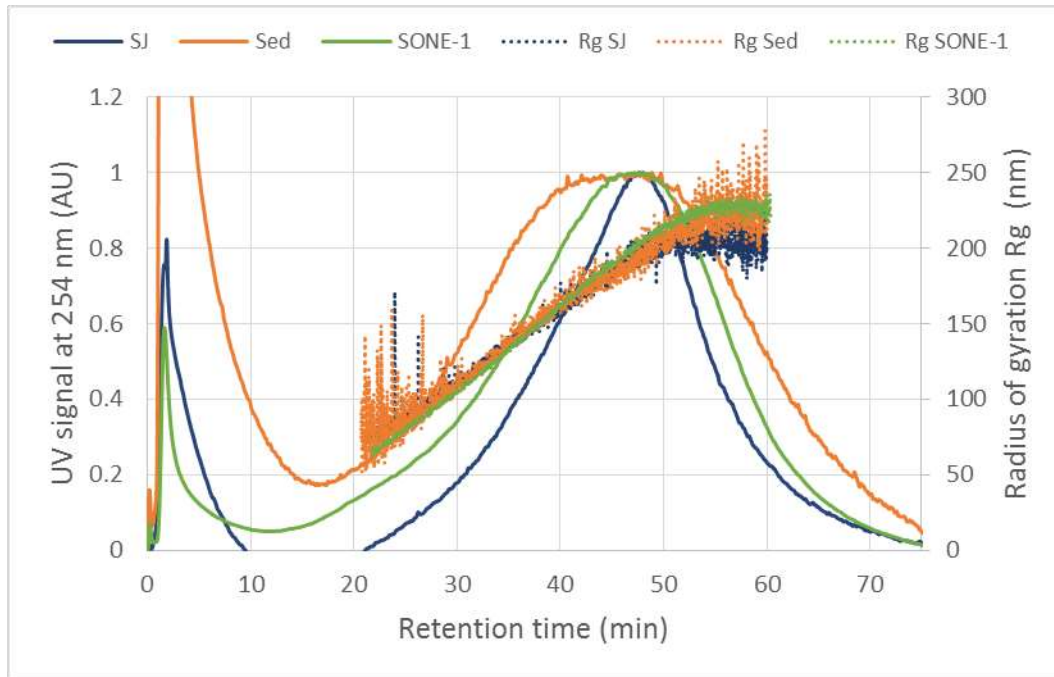


Figure S3: Fractograms obtained using AF4-UV/vis-MALS for the different sample types (SJ, Sed and SONE-1) in the $< 0.45 \mu\text{m}$ fractions. Solid lines are UV signal and dots are R_g data points. The fractograms are in relative scaling (each one is scaled against its own magnitude). SONE-1 has the highest intensity (one order of magnitude).

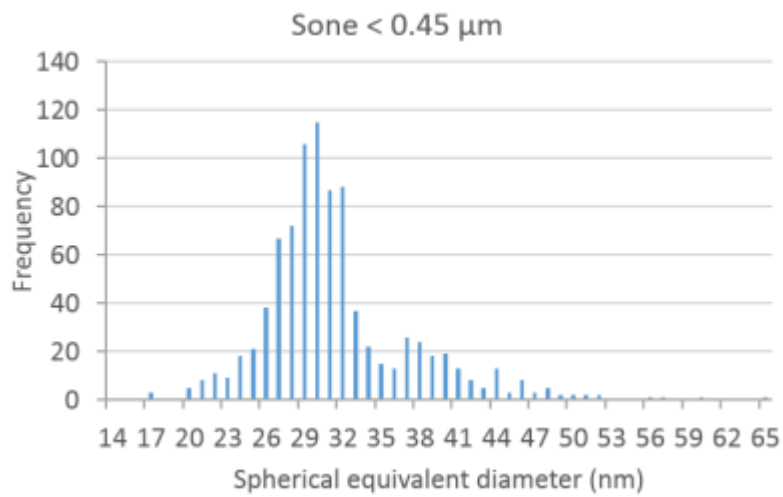
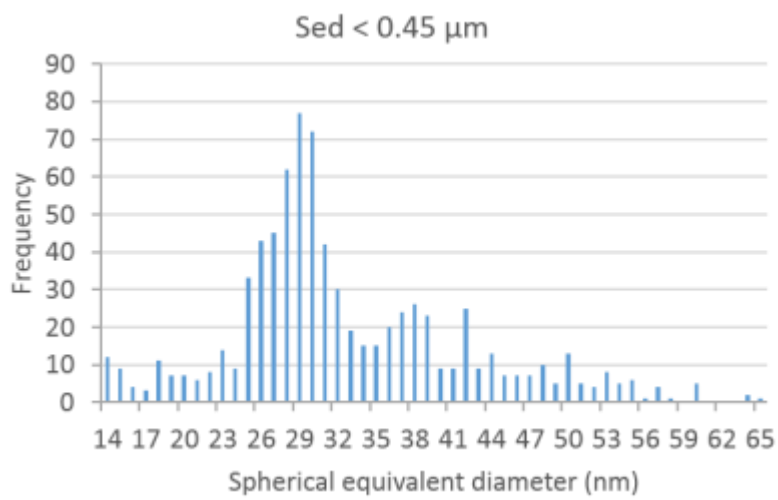
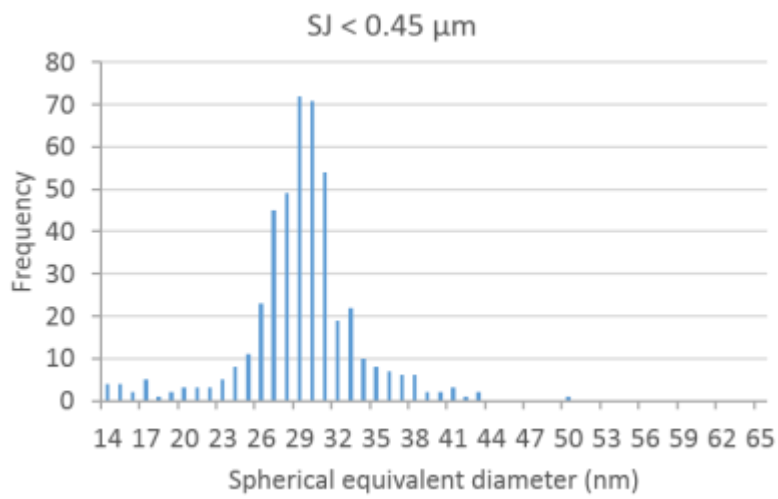


Figure S4: spICP-MS ^{197}Au frequency distributions for $< 0.45 \mu\text{m}$ fractions extracted from the three matrices used in this study.

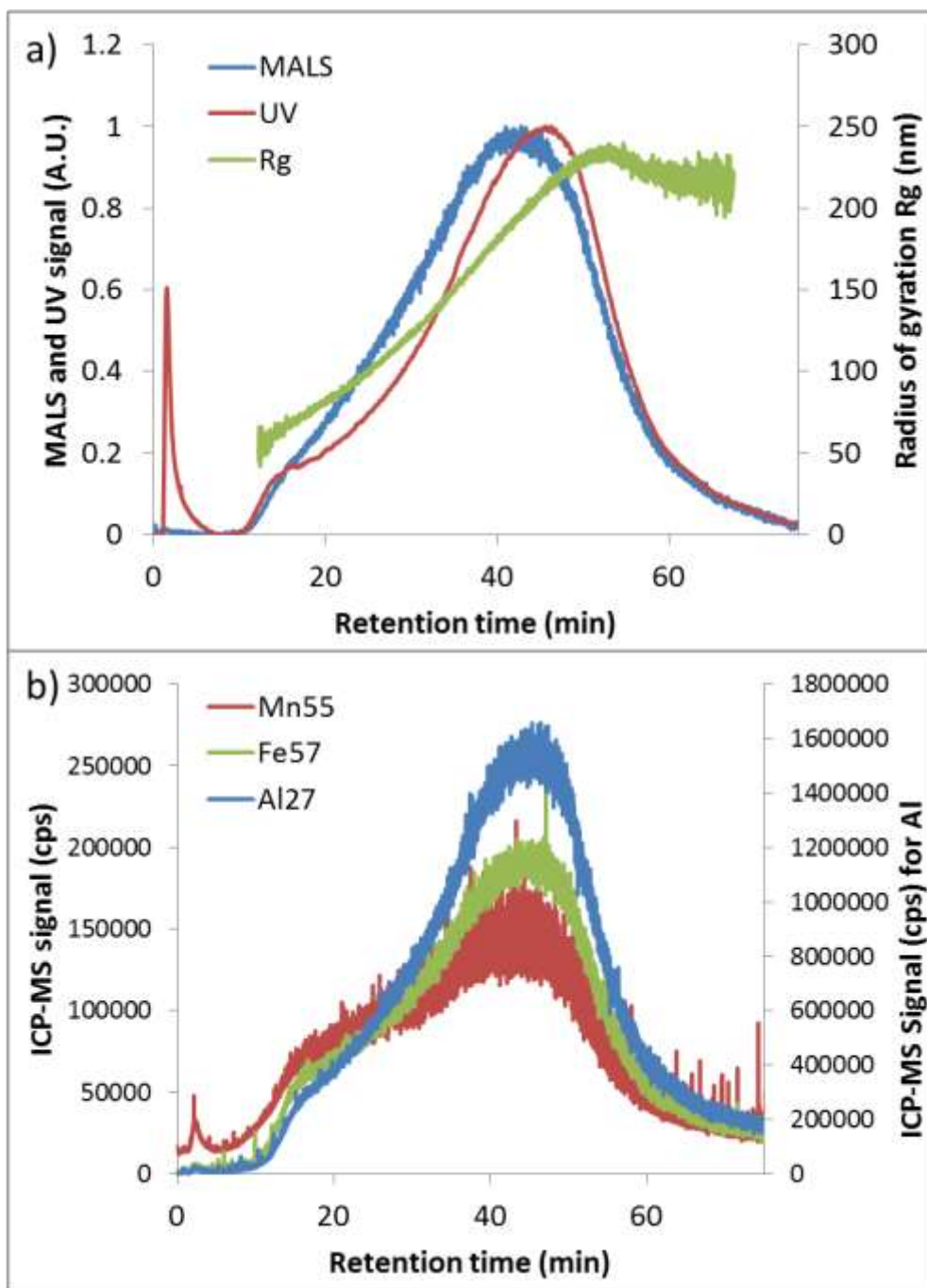


Figure S5: AF4-UV-MALS-ICP-MS fractograms for $500 \mu\text{g kg}^{-1}$ Cit-AuNPs spiked into SONE-1 soil in the fraction $< 0.45 \mu\text{m}$ after 24 h of agitation.

UV irradiation

Coating degradation under UV exposure was tested in DI water rather than MHW to avoid rapid homo-aggregation that was previously observed upon loss of PEG⁶ and that would preclude evaluation of the coating thickness by DLS. Here, a rapid decrease in layer thickness was observed within 2 h for the PEG-AuNPs in DI water, followed by a slower decrease over the next (3 to 4) days. A concomitant decrease in zeta-potential was observed (consistent with previous findings). On the other hand, the PVP-AuNPs showed minimal change within 2 h and a slower decrease in layer thickness over 3 days.

The PEG-AuNPs were further assessed for possible effects of UV irradiation because a more significant change in layer thickness was observed. The PEG-AuNPs were irradiated for 96 h in DI water to obtain nearly complete removal of the PEG coating, followed by 2 h of mixing with the SONE-1 soil slurry to test the effect on hetero-aggregation. The irradiation was performed in DI water (rather than directly in the soil slurry) for controlled testing of the PEG-AuNP with well-defined coating loss. In the soil slurry, the attenuation of the UV light intensity by the soil colloids would need to be accounted for, and evaluation of the remaining PEG coating on the AuNPs would be difficult after mixing with the soil. However, it is noted that irradiation in the soil slurry rather than in DI water would be more environmentally relevant.

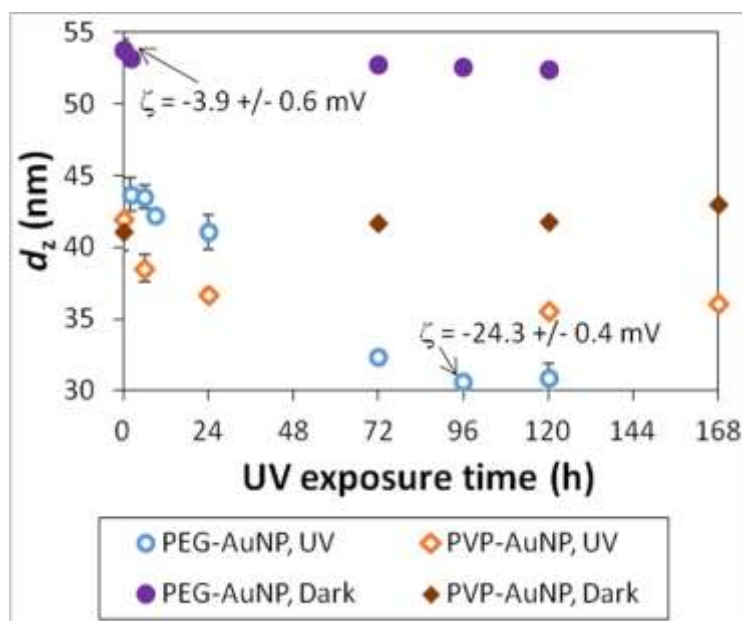


Figure S6: Transformation of hydrodynamic diameter and zeta-potential for the PEG-AuNPs and PVP-AuNPs under UV irradiation in DI water. Error bars on d_z for the UV exposed samples represent the standard deviation of measurements from duplicate experiments (only one experiment was run for the dark controls). The zeta potentials denoted for the PEG-AuNPs are the mean \pm one standard deviation for three measurements on a single sample.

References

1. R. S. Swift, *Methods of Soil Analysis Part 3—Chemical Methods*, 1996, 1011-1069.
2. NIST, *Standard Reference Material 1646a, Estuarine Sediment, Certificate of Analysis*, National Institute of Standards and Technology, U.S. Department of Commerce, 2004.
3. NIST, *Standard Reference Material 2709a, San Joaquin Soil, Certificate of Analysis*, National Institute of Standards and Technology, U.S. Department of Commerce, 2009.
4. N. S. Simon, S. A. Hatcher and C. Demas, *Chemical Geology*, 1992, **100**, 175-189.
5. D. B. Smith, W. F. Cannon, L. G. Woodruff, F. Solano, J. E. Kilburn and D. L. Fey, *Geochemical and mineralogical data for soils of the conterminous United States*, Report 801, Reston, VA, 2013.
6. S. M. Louie, J. M. Gorham, E. A. McGivney, J. Liu, K. B. Gregory and V. A. Hackley, *Environmental Science: Nano*, 2016, **3**, 1090-1102.