*** Supporting Information ***

Title: Extracting metallic nanoparticles from soils for quantitative analysis: Method development using engineered silver nanoparticles and SP-ICP-MS

Authors: D. M. Schwertfeger,[†] Jessica R. Velicogna,[†] Alexander H. Jesmer,[†] Selin Saatcioglu,[‡] Heather McShane,[§] Richard P. Scroggins,[†] Juliska I. Princz[†,*]

[†] Biological Assessment and Standardization, Environment Canada, Ottawa, Canada

[‡] Department of Civil and Environmental Engineering, Carleton University, Ottawa, Canada

[§] Department of Natural Resource Sciences, McGill University, Montreal, Quebec, Canada

[*] To whom correspondence may be addressed (juliska.princz@canada.ca)

This document contains:

1. Characterization of the Nanomaterials
2. SP-ICP-MS Analytical Details
3. Experimental details of the Spike-Recovery Analysis

21 **Characterization of the Nanomaterials**

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23 *AgNP (25 nm), nanoComposix*. TEM analysis of the 20 mg L^{-1} stock suspension showed that

24 most particles fell within the supplier's size specifications of 23.1 ± 6.9 nm (Fig. S1a). Dynamic

25 light scattering (DLS) analysis of the same 25 nm stock suspension of the particles agreed with

26 the TEM results and showed a mono-modal size distribution with a z-average hydrated diameter

27 of 26.3 nm (0.3 nm standard deviation) with a polydispersivity index of 0.11. SP-ICP-MS

28 analysis performed on a diluted suspension (10 to 100 ng L^{-1}) revealed that 89% of the total Ag

29 mass consisted of detectable particles (i.e. ≥ 19 nm) showing a mono-modal size distribution

30 with mode and mean diameters of 24.8 and 30.4 nm.

31 *AgNP (40 nm), nanoComposix*. TEM analysis of the 15 g L^{-1} stock suspension showed that most

32 particles fell within the supplier's size specifications of 38.6 ± 9.8 nm with a minor presence of

33 particles approximately ≤ 19 nm (Fig. S1b). DLS analysis was conducted on a diluted suspension

34 (15 mg L^{-1}) and showed a bimodal particle size distribution with 9% of the total light intensity

35 arising from the smaller (~ < 15 nm) particle size fraction (Fig. S2). Note: z-average particle

36 sizes derived from poly-modal distributions are not accurate. SP-ICP-MS analysis performed on

37 an initial diluted suspension (~ 10 to 100 ng L^{-1}) revealed that 93% of the total Ag mass

38 consisted of detectable particles showing a mono-modal size distribution with mode and mean

39 particle diameters of 35.1 and 43.4 nm (Fig. S3). However, analysis of the suspension 48 h later

40 showed that only 35% of the total Ag mass consisted of detectable particles and mode and mean

41 particle sizes were slightly decreased to 31.2 and 39.8 nm. Presumably, the 65% of the Ag mass

42 comprising the "dissolved" fraction of the SP-ICP-MS analysis consisted not only of dissolved

43 Ag, but of particles below the particle size detection limit of 19 nm. This shift in the particle size

44 distribution and increase of Ag in the dissolved fraction after 48 h was likely because of particle

45   dissolution. It should be noted that the spiked soil samples used in this study were amended with

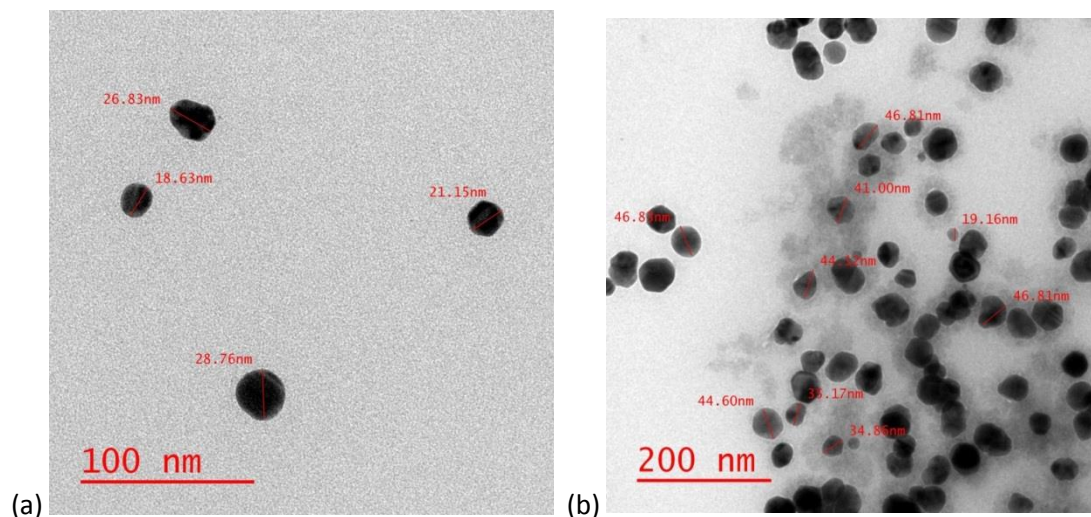46   the original 15 g L^{-1} 40 nm stock suspension.

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48   (a)   (b)
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50   **Figure S1.** TEM images of the 25 nm AgNP prepared from a 20 mg L^{-1} aqueous suspension (a), and the
51   40 nm AgNP prepared from a 15 g L^{-1} aqueous suspension (b). Imaging was conducted using an FEI^{TM}
52   Tecnai G2 F20 TEM (FEI, Hillsboro OR) at the Carleton University Nano Imaging Facility.
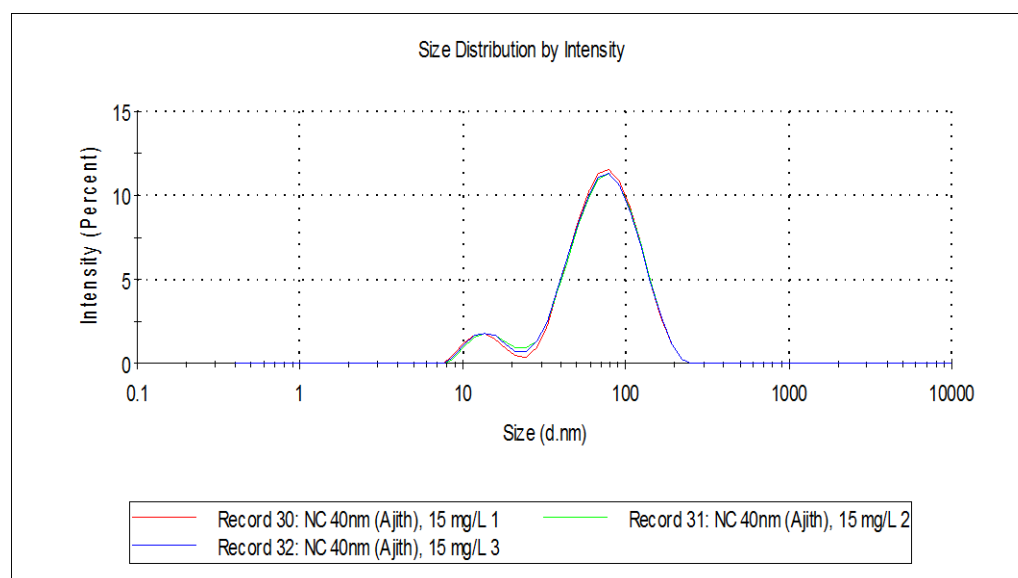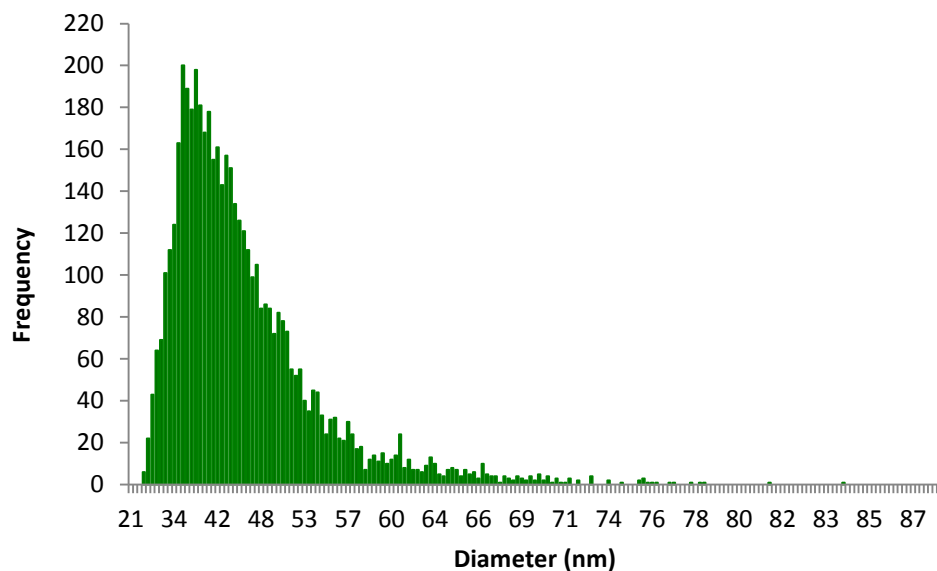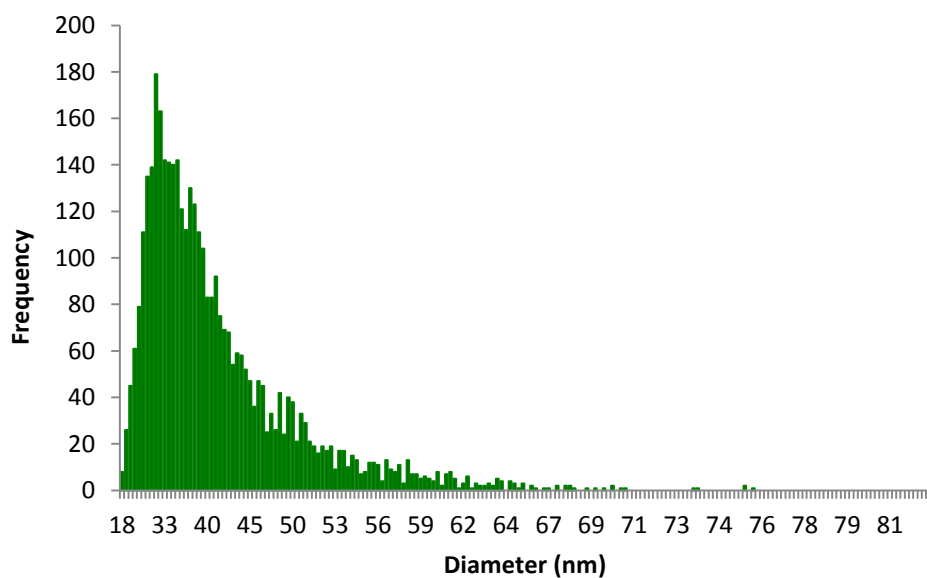
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56   **Figure S2**. Particle size distribution by DLS (based on intensity) of the 40 nm AgNP determined on three
57   replicate samples of a 15 mg L^{-1} suspension.
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59   (a)

60   (b)

61   **Figure S3.** SP-ICP-MS particle size histograms of the 40 nm AgNP material performed on

62   suspensions in the 10 to 100 ng L^{-1} range analyzed fresh (a) and analysed after 48 h (b).

63 **SP-ICP-MS Analytical Details**

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65   SP-ICP-MS analysis requires that samples are sufficiently dilute such that analytical

66 coincidence is avoided (i.e., two or more particles making up a plasma event). Based on our

67 operating parameters, we estimated that coincidence could be avoided if sample particle

68 concentrations were ≤ 1.2 x 10^5 mL^{-1}; therefore target particle concentrations for calibration

69 suspensions and samples were approximately 10^5 particles mL^{-1}. Data processing was performed

70 within the Syngistix^{TM} Nano-Application module. The software derives the intensity threshold

71 used to discriminate a particle signal from a dissolved signal using an iterative "mean + 3σ"

72 computation, similar to that described by Hadioui et al.[1] As quantification of both the dissolved

73 and nano-particulate forms of Ag are of interest, capturing both dissolved and particle signals is

74 necessary; however, it is doubtful that one dilution/analysis can optimally capture both signals.

75 Therefore samples were analyzed using a dilution series previously described in Schwertfeger et

76 al.[2] Briefly, soil extracts were first diluted to capture the dissolved analyte reading within the

77 dissolved calibration range and above the limit of quantitation (LoQ). A second or "optimal"

78 dilution was used to optimize the particle signal by (i) reducing the dissolved signal to near

79 background levels, (ii) reducing particle counts (i.e., ≤ 1.2 x 10^5 mL^{-1}) to minimize coincidence,

80 and (iii) ensuring that the number of particles detected was sufficient for statistical power for

81 describing the particle distributions (generally ≥ 1000 particles), which sometimes resulted in our

82 extending the sampling time. Finally, a third dilution was analyzed, (usually 2x the optimal

83 dilution), which was used as a quality control. For example, a 2x dilution should not affect

84 particle intensity, but particle counts should be approximately half, otherwise samples were sub-

85 sampled again, checked for matrix interferences, and re-analyzed. Each dilution was prepared

86 such that the ionic strength of the sample matrix was maintained. This was done by using an

87 appropriate dilution of the extracting reagent. Dilutions were analyzed immediately.

88

89 **References**

90 (1) Hadioui, M.; Peyrot, C.;Wilkinson, K. J., Improvements to Single Particle ICPMS by the Online
91 Coupling of Ion Exchange Resins. *Anal. Chem.* **2014,** *86* (10), 4668-4674.
92 (2) Schwertfeger, D. M.; Velicogna, J.; Jesmer, A.; Scroggins, R. P.;Princz, J. I., SP-ICP-MS Analysis
93 of Metallic Nanoparticles in Environmental Samples with Large Dissolved Analyte Fractions. *Anal.*
94 *Chem.* **2016**. DOI: 10.1021/acs.analchem.6b02716

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96 **Spike-Recovery Analysis**

97 **Experimental Set-up**. Ag recovery for the optimal extraction procedure was investigated using

98 a control soil sample to which AgNP was added. Triplicate samples were prepared by adding an

99 aliquot of a 150 mg L^{-1} AgNP (40 nm) suspension to 50-mL test tubes containing 0.5 g soil and

100 50 mL 2.5 mM TSPP to achieve a nominal total Ag concentrations of 1.5 mg L^{-1} which

101 corresponded to 150 µg Ag per g soil. The spiked samples were treated as regular samples and

102 followed the finalized method protocol: 30 min mixing, 1.5 min ultrasonication with the wand,

103 18 h settling, followed by sampling extracts between a depth of 0.5 to 1.0 cm from sample

104 surface and diluting 100x in Nanopure^{TM} water within minutes prior to initial SP-ICP-MS

105 analysis. Triplicate AgNP-spiked method blanks were also prepared in the same manner as

106 above, except they did not contain any soil (i.e., TSPP reagent only). The reference sample to

107 which Ag recovery in the spiked samples/blanks was assessed was a 1.5 mg L^{-1} AgNP

108 suspension prepared fresh from the 15 g L^{-1} stock suspension and analyzed immediately.

109 Recovery was assessed based on three parameters: particle number concentration (particles mL^{-1}

110 ^{1}), particulate Ag mass (µg L^{-1}) and total Ag mass (µg L^{-1}) (i.e., particulate Ag mass + dissolved

111 Ag mass) obtained by SP-ICP-MS.

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114 **Table S1.** SP-ICP-MS results for the spike-recovery samples. Bracketed values show the standard
115 deviation derived from three replicate samples.

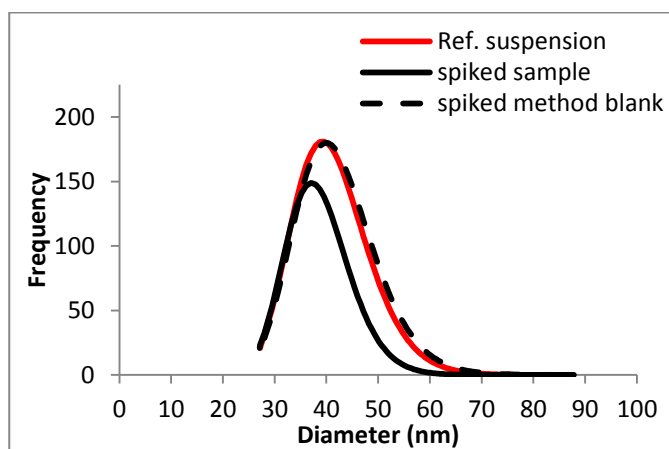| Sample	nominal total Ag conc. $\mu g\ L^{-1}$	measured total Ag conc. $\mu g\ L^{-1}$		particulate Ag mass conc. $\mu g\ L^{-1}$		dissolved Ag mass conc. $\mu g\ L^{-1}$		Particle # conc. particles mL^{-1}		mean part. size nm
AgNP Ref. suspension	1500	1443	*(86)*	1201	*(32)*	242	*(19)*	2.4E+09	*(5E+07)*	43.4
spiked soil sample	1500	1397	*(165)*	1018	*(48)*	379	*(118)*	2.0E+09	*(7E+07)*	42.7
spiked method blank	1500	1523	*(127)*	1218	*(38)*	345	*(165)*	2.5E+09	*(6E+07)*	42.8

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120 **Fig. S4.** Particle size distributions of Ag particles recovered in spiked samples and spiked method blanks
121 compared to distribution of the reference sample. Note: these distributions represent one of the three
122 replicates samples.