Supplementary material

Ion exchange technique (IET) to characterise Ag+ exposure in soil extracts contaminated with engineered silver nanoparticles

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Ion exchange technique (IET) theory

The principles of IET have been previously outlined [28,30]. Briefly, a sample is passed through a column containing a known mass of a negatively-charged resin (m_r) saturated with a readily exchangeable cation, usually Na^+. Exchange occurs between the free metal ions in the sample, and the exchange cation on the resin until steady-state equilibrium conditions are achieved (i.e., the concentration of resin-bound metal is constant). The resin-bound metals are then extracted by passing an exact volume of eluate (e.g., 1.5 M HNO_3) through the column from which the metal concentration can be determined. The concentration of resin-bound metal, [R-M] (mol g^{-1}), is thus determined as:

$$[R - M] = \frac{v_{el} \times [M_{el}]}{m_r} \tag{1}$$

where v_{el} is the known volume of eluate (L), $[M_{el}]$ is the concentration of metal measured in the eluate (mol L^{-1}), and m_r is the mass of resin (g). A calibration procedure, whereby solutions of known free metal ion activity (M^{z+}) are equilibrated with the resin, is then used to determine the conditional binding constant of the resin-metal complex (λ_{R-M}) given the relationship:

$$\lambda_{R-M} = \frac{\{R-M\}}{(M^{z+})} \tag{2}$$

Conditions for which the binding constant is valid are: (i) calibration solutions and samples must have a consistent temperature, pH and dominant ionic composition in the matrices; and (ii) the concentration of resin sites occupied by the exchange cation at equilibrium must greatly exceed the number of sites occupied by the metal ion (i.e., [R-M] << [R-Na]) such that [R-Na] is not affected by (M^{z+})). The latter condition is considered satisfied if the percentage of resin sites occupied by the metal is < 1% [28]. Free metal activity in the samples can thus be determined by:

$$[M^{z+}] = \frac{[M_{el}] \times v_{el}}{(\lambda_{R-M} \times m_r)} \tag{3}$$

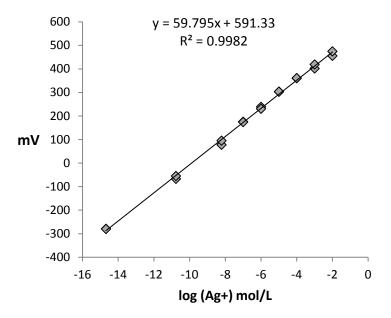## Details of the SP-ICP-MS analysis

As quantification of both the dissolved and nano-particulate forms of Ag are of interest, capturing both dissolved and particle signals is necessary; however, it is doubtful that one dilution/analysis can optimally capture both signals. We have previously developed an approach for the analysis of samples containing high levels of dissolved analyte[36], whereby a sample dilution series is used as follows:

1. The first dilution allows for the capture of the dissolved analyte signal within the dissolved calibration range and above the LoQ.

2. The second, or "optimal" dilution is used to optimize the particle signal by (i) reducing the dissolved signal to near background levels, (ii) reducing particle counts (i.e., $\leq 1.2 \times 10^5$ mL^{-1}) to minimize coincidence, and (iii) ensuring that the number of particles detected during the sampling time is sufficient for statistical power (generally ≥ 1000 particles), increasing analysis time if necessary.

3. The final dilution is generally 2x the optimal dilution and is used as a quality control check: particle intensity should remain constant, but particle counts should be approximately half of that observed for the optimal dilution.
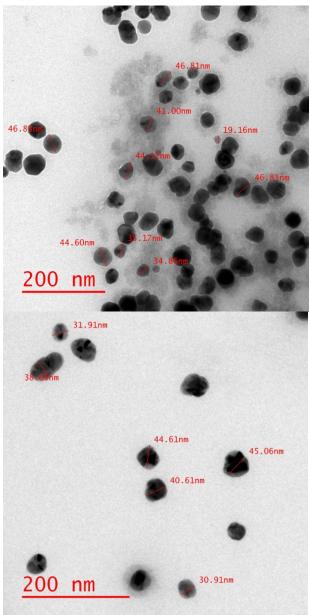
Each dilution was prepared from the original sample (i.e., not from a dilution) and analyzed immediately.
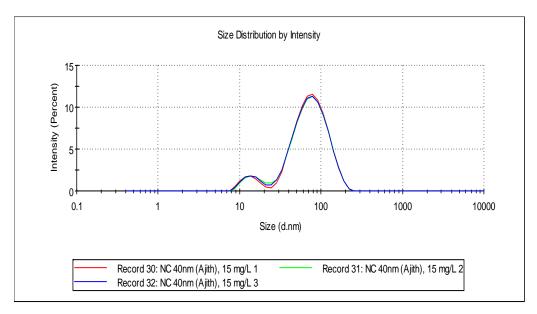
Ag$^+$ ISE Calibration

$$y = 59.795x + 591.33$$
$$R^2 = 0.9982$$

Fig. S1. Calibration for Ag$^+$ ISE. Measured potential (mV) of the Ag ISE as a function of the log [Ag$^+$] activity (mol L^{-1}) measured in samples with a 0.1 M NaNO$_3$ matrix. Data plotted are from two separate calibration procedures performed two months apart. Note: readings corresponding to Ag$^+$ activities below 10^{-7} M were achieved using buffered solutions (i.e., Cl$^-$, Br$^-$, I$^-$).
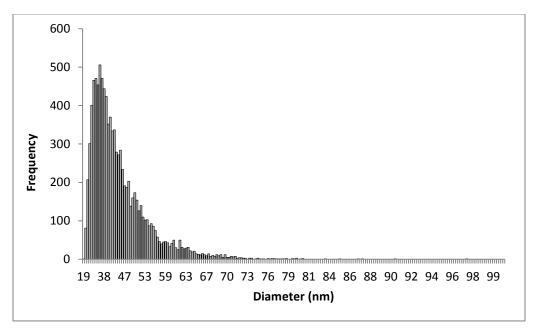
Supporting data for Ag nanomaterial characterization

Fig. S2. TEM images of Nanocomposix Ag 40 nm nanomaterial prepared in a 15 g L^{-1} suspension.

Fig. S3. Particle size distribution by DLS (based on intensity) of the 40 nm AgNP (Nanocomposix) determined on three replicate samples of a 15 mg L^{-1} suspension.
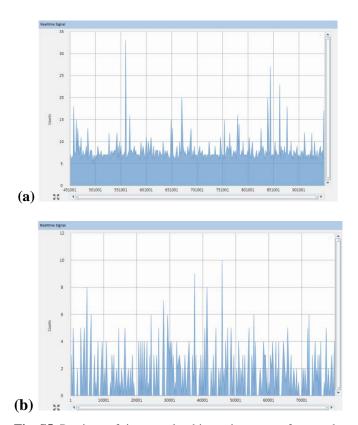

Fig. S4. Particle size histogram of the 40 nm AgNP material (Nanocomposix) determined by SP-ICP-MS. Analysis performed on a 15 ng L^{-1} suspension. The total particulate Ag mass detected represents 35% of the total Ag mass detected.
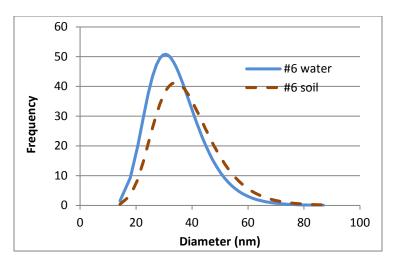
Table S1. Nominal and measured total Ag concentrations in test samples

Measured values were obtained by ICP-MS (standard mode) on acidified samples

#	Nominal (μg L^{-1})	Meas. water matrix (μg L^{-1})	Meas. soil matrix (μg L^{-1})
1	2	1.9	1.7
2	12.5	14.0	13.2
3	200	209	188
4	2	2.7	2.3
5	20	23.7	23.6
6	200	224	217
7	20	19.3	18.3
8	20	19.3	20.4
9	12.5	12.6	13.9
10	200	248	243

(a)

(b)

Fig. S5. Portions of time-resolved intensity scans of a sample containing both dissolved and nano-particulate Ag. The first scan (a) shows the elevated baseline of the SP-dissolved fraction, and the second scan (b) shows the same sample after dilution to obtain the optimal particle signal.

Fig. S6. Example of SP-ICP-MS particle size frequency distribution data, fitted to log normal curve. This graph shows data for samples #6 (water matrix) and #6 (soil extract matrix). Samples have been diluted to achieve optimal particle signals. Note: the particles detected in the water sample were slightly smaller than particles detected in the soil extract matrix, possibly due to greater AgNP dissolution.