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A method for determination of retention of silver and cerium oxide manufactured nanoparticles in soils

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Environmental context. Soils are the environmental compartment likely to be exposed most to manufactured nanoparticles, but there is no method available at present to assess their retention, which determines potential mobility and bioavailability. Optimisation and application of a method to determine retention values for silver (Ag) and cerium oxide (CeO_2) manufactured nanoparticles in soils found in many cases that they differed from the partitioning of their bulk and soluble counterparts. Wider application of this method can assist in comparing the risk of many different manufactured nanoparticles with other contaminants in soil systems and model their relationship to soil properties.

Abstract. Methods to study the retention of manufactured nanoparticles (MNP) are lacking for soils that are likely to be increasingly exposed to MNP. In this study we present, for the first time, a method to determine retention values (K_r) of Ag and CeO_2 MNP, that can be ranked among solid–liquid partitioning (K_d) values of bulk (micrometre-sized) forms, soluble salts and other possible contaminants of soils. After method optimisation, suspensions containing 1.24 mg kg^{-1} Ag as Ag MNP and 1.30 mg kg^{-1} Ce as CeO_2 MNP were added to five soils. More than 7% of Ag MNP occurred as soluble Ag^I after 24 h and the range of K_r values of Ag MNP (77–2165 L kg^{-1}) and CeO_2 MNP (1.1–2828 L kg^{-1}) contrasted with K_d values of soluble Ag^I, Ce^{III} and Ce^{IV} salts and bulk Ag and CeO_2 powders in different soils.

Additional keywords: K_d, K_r, partitioning, risk assessment, transport.

Introduction

The field of nanotechnology is rapidly expanding, and manufactured nanoparticles (MNP) are already being used in electronics, as catalysts, for pollution control, and in personal and medical products.[1] Because of their small size, the mechanical, catalytic, electric and optical properties of nano-sized materials are often vastly different to those of the same material with a larger particle size.[2] However, some of the same properties that make these MNP useful in nanotechnology could possibly also result in risk to aquatic and terrestrial environments. Indeed, several reviews have demonstrated potential toxicity to aquatic and terrestrial organisms specific to some MNP,[2,3] but much of the toxicity evaluation of MNP has been conducted in aqueous suspensions at unrealistic environmental exposure concentrations.

The main exposure pathway of MNP to soils has been suggested to occur through the application of biosolids to amend soils.[4] This is because most of the projected increase in MNP discharge to urban wastewater treatment plants is retained by biosolids in wastewater treatment plants.[5] Other potential routes of MNP exposure to soils may be through landfill leachate,[6] accidental spills, deposition of airborne MNP, use of MNP in agrochemicals,[7] or soil remediation.[2,8] Soil exposure to MNP has thus been projected to increase, especially in the case of metallic or metal-oxide MNP, to several nanograms to micrograms per kg soil per annum.[4]

To estimate the potential exposure of organisms to MNP suspended in porewaters, the major exposure pathway in soil systems to organisms is required.[9] This requires knowledge of the retention of MNP in soils, which is the ensemble of time-dependent aggregation of MNP with other MNP and naturally occurring colloids and deposition on mineral surfaces that are all likely to determine the available fraction of MNP and thus their potential risk in soil environments. It is increasingly becoming relevant to have knowledge of the retention of MNP in soils, because of the vast array of consumer products being introduced into the market containing many different types of MNP and the ever-increasing risk of exposure of soils to MNP.[10] Moreover, the diversity of available MNP is complicated further by the likely dependence of MNP behaviour on size and coating,[11] but as yet, there are no rapid assessment methods to determine and rank the potential retention or mobility of MNP in soils. Currently available mechanistic models based on Derjaguin–Landau–Verwey–Overbeek (DLVO) theory can predict some aspects of MNP partitioning in soils, such as the increase in deposition on increase of the ionic strength of the soil solution[12] and the stabilising effect of dissolved organic matter,[13] but these models are deficient for reliable risk assessments of MNP in soils.[12] DLVO theory, for instance, predicts an increased stability of MNP suspensions as the surface potential increases, e.g. as a function of pH, but this does not invariantly result in an increased mobility in soil.[12]

Silver MNP are among the most widely used MNP for microbial sterilisation.[1] The catalytic properties of CeO_2 MNP are also used extensively and they are a common additive in diesel fuels.[1] The potential toxic properties of Ag and CeO_2 MNP towards aquatic[14,15] and in the case of Ag MNP[16] also to terrestrial organisms have been demonstrated. Toxic effects of Ag MNP have been related to cell membrane damage, to oxidative stress, or to interactions of Ag^{I} ions with proteins and enzymes,[17] whereas both cytotoxic oxidative stress due to a reduction of Ce^{IV} to Ce^{III} within CeO_2 MNP[18] as well as a cytoprotective effect due to reduction of reactive oxygen species[19] have been observed in toxicity tests with CeO_2 MNP.

In this study we present, for the first time, a method to determine retention (K_r) values for Ag and CeO_2 MNP in soils. Whereas there is a need to develop more accurate models of MNP behaviour in soils based on a sound knowledge of mechanisms of MNP deposition and transport, the K_r method can be used as a screening technique that determines likely retention of Ag and CeO_2 MNP in soils. The method was based on solid–liquid partitioning determination of solutes in soil. Such solid–liquid partition is commonly operationally defined as partitioning coefficients (K_d) that are routinely used in risk assessment models of inorganic and organic contaminants in soils and sediments (e.g. Organisation for Economic Co-operation and Development (OECD) method 106[20]). Solid–liquid partitioning values are calculated by:

$$K_d = M_{solid}[M]^{-1}\ (\mathrm{L\,kg^{-1}}) \quad (1)$$

where M_{solid} is either the geogenic or spiked solid-phase concentration of an element or contaminant expressed on a soil-weight basis (mg kg^{-1}). $[M]$ is the aqueous concentration expressed on a solution volume basis (mg L^{-1}) present in a soil–electrolyte suspension that is agitated for a short time, e.g. 24 h, followed by a phase separation. High and low K_d values thus indicate preferential partitioning to the solid and liquid phase respectively, but do not imply specific retention mechanisms. For example, metal K_d values have been extensively studied in soils (reviewed by Sauvé et al.[21]), yet partitioning may be a combination of many different processes, e.g. sorption, precipitation and solid-state diffusion. and it is recognised that these are non-equilibrium processes, even for solutes.[22] Existing methods to determine solid–liquid partitioning (K_d values), such as OECD method 106,[20] are, however, inappropriate for metal-containing MNP that may dissolve in environmental media[23] and thus complicate solute *v.* particulate retention determinations. K_r values account for potential dissolution processes of MNP, which distinguishes them from K_d values of solutes, although K_r and K_d values can still be compared. The benefits of this K_r method therefore do not lie in determining retention mechanisms of MNP, but allowing the ranking of Ag and CeO_2 MNP with soluble and bulk forms of Ag and Ce and other possible contaminants of soils.

Results and discussion

Method optimisation

Table 1 lists experimental procedures undertaken to optimise Ag and CeO_2 MNP spiking suspensions and filtration and digestion procedures to determine K_r values for Ag and CeO_2 MNP and K_d values for bulk materials and soluble salts in soils.

Ag and CeO_2 MNP size characterisation

The measured particle sizes of Ag and CeO_2 MNP were found to be inconsistent with nominal particle sizes supplied by the manufacturer (Table 2). Size estimates based on crystallite sizes calculated from X-ray diffraction (XRD) patterns are known to suffer from experimental imperfections leading to lower than actual size estimates.[24] However, sizes calculated from Brunauer–Emett–Teller (BET) N_2 adsorption specific surface area determinations and transmission electron microscopy (TEM) images of suspended Ag MNP (Fig. 1a) also suggested that at least a fraction of the Ag MNP had primary particle sizes ranging from 20 to 100 nm. The size of individual CeO_2 MNP, however, appeared to be smaller than the nominal 20-nm particle size based on XRD and BET-N_2 measurements (Table 2). Individual CeO_2 MNP could not be visualised clearly on TEM images, which showed aggregates with sizes of 100 nm (Fig. 1b). This highlights the importance of MNP characterisation before experiments are undertaken to ensure results can be directly linked to the size of MNP.

Ag and CeO_2 MNP suspensions for soil spiking

Reproducible spiking rates of Ag and CeO_2 MNP into soils representative of current and projected soil exposure concentrations as estimated by Gottschalk et al.[4] can only be achieved by diluting stock suspensions. These diluted stock suspensions need to remain for the short term stable in their nano-particle size before soil spiking. Water as a dispersant for MNP spiking suspensions would have a minimal impact on soil properties, but preliminary experiments using TEM showed micrometre-sized aggregates were formed in aqueous 0.01 g L^{-1} Ag MNP and CeO_2 MNP suspensions.

Table 3 shows Z-average hydrodynamic diameters (d) and polydispersity indices (PDI) obtained through cumulants analysis[25] of the field correlogram determined by dynamic laser scattering (DLS) of MNP suspensions prepared according to the spiking solution treatments in Table 1. In the case of CeO_2 MNP, citrate at pH = 10 was added to increase stability as it does for Ag MNP.[26] High PDI values indicate either a broad monomodal particle size distribution around d or a multimodal distribution. Cumulants analysis to calculate d does not provide valid results for highly polydisperse suspensions.[25] Calculated d values of untreated Ag MNP and CeO_2 MNP in Table 3 therefore do not reflect the micrometre-sized aggregates in these suspensions that were observed by TEM. Both centrifuging and 0.20-µm filtration lowered d of Ag MNP suspensions significantly, but the PDI was only lowered using 0.20-µm filtration. Filtration thus appears to be a more rigorous size separation in this case than centrifugation, where the separation based on the Stokes diameter is also influenced by aggregate density that may settle smaller, densely packed aggregates together with loosely packed larger aggregates. The fitted monomodal d value of 0.20-µm filtered Ag MNP suspensions corresponded to aggregate sizes observed in TEM (Fig. 1a), but ongoing aggregation is likely to have increased aggregate sizes slightly over 24 h.

Table 1. Optimisation of manufactured nanoparticles (MNP) spiking suspensions and filtration and digestion procedures to determine retention coefficients (K_r) and partition coefficients (K_d) in soils

Short-term nano-sized MNP suspensions for soil spiking

Particle size distribution of spiking solutions were examined using dynamic laser scattering (DLS) on 0.01 g L^{-1} MNP powder suspended in water (Ag) or 0.5 mM citrate at pH 10 (CeO_2), sonicated for 3 min and using the following treatments:

(1) None (no filtration or centrifugation)
(2) Centrifuged at 2300*g* for 15 min at 20°C
(3) Filtered using 0.20-μm membranes (Sartorius Minisart)

Microfiltration and ultrafiltration procedures

Different concentrations of Ag, Ce^{III} and Ce^{IV} dissolved in artificial solution were filtered using the commercially available membranes below:

Treatment	Membrane	Pore size–MWCO[A]	Type	Pretreatment
1	Millipore Millex	0.45 μm	Microfiltration	None
2	Millipore Millex	0.45 μm	Microfiltration	0.1 M $Cu(NO_3)_2$
3	Sartorius Minisart	0.45 μm	Microfiltration	None
4	Pall-Gellman Microsep	1 kDa	Ultrafiltration	None
5	Pall-Gellman Microsep	1 kDa	Ultrafiltration	0.1 M $Cu(NO_3)_2$
6	Sartorius Vivaspin 2	2 kDa	Ultrafiltration	None

MNP digestion procedures

0.1 g MNP powders were digested using the following procedures:

MNP	Treatment	Acid 1	Acid 2	Digestion[B]
Ag	1	10 mL HNO_3	–	Open vessel block
	2	9 mL HNO_3	3 mL HCl	Closed vessel microwave
	3	9 mL HCl	3 mL HNO_3	Closed vessel microwave
	4	3 mL H_2O_2	5 mL HNO_3	Closed vessel microwave
	5	3 mL H_2O_2	5 mL HNO_3	Open vessel block
CeO_2	1	10 mL HNO_3	–	Open vessel block
	2	9 mL HNO_3	3 mL HCl	Open vessel block
	3	9 mL HNO_3	3 mL HCl	Closed vessel microwave

[A]Molecular weight cut off: size of a polyethylene glycol molecule that is retained for 90%.
[B]Open vessel block digestion occurred at 175°C for 10 min and closed vessel microwave digestion occurred at 160°C for 60 min.

Table 2. Nominal size provided by manufacturer and measured Ag and CeO_2 manufactured nanoparticles (MNP) characteristics

Property	Ag	CeO_2
Mineralogy	Silver	Cerianite
Specific surface area	5 $m^2 g^{-1}$	104 $m^2 g^{-1}$
Nominal size	10 nm	20 nm
Diameter (BET-N_2 – estimate)	58 nm	4 nm
Crystallite size (Scherrer equation)	41 nm	9 nm

In the case of CeO_2 MNP suspensions, filtration through 0.20-μm filters did not result in lower PDI values than following centrifugation (Table 3). However, lower *d* values were observed in filtered suspensions, which may again be due to loosely packed aggregates that were removed during 0.20-μm filtration, but had not settled during centrifugation. The particle size of filtered CeO_2 suspensions was found to remain stable in the short term (i.e. 24 h) for longer than filtered Ag MNP suspensions (Table 3). In addition, CeO_2 MNP aggregate sizes by DLS were found to be comparable with TEM observations (Fig. 1b).

Sonication followed by 0.20-μm filtration was hence the preferred method to prepare short-term diluted Ag and CeO_2 MNP suspensions for soil spiking, because reproducible nano-sized MNP aggregates were generated. This was even the case for the slightly less stable Ag MNP suspensions, because addition of this suspension to soils always occurred within 1 h after filtration. The method may further be adapted by using filters with a lower pore size (e.g. 0.10 μm) than 0.20 μm to investigate the effect of average aggregate size on retention.

Microfiltration and ultrafiltration optimisation

Although 0.45-μm microfiltration (MF)[27] is an arbitrary cut-off for determination of the dissolved fraction of metals in waters and soil solutions, it was applied in the present study because of its use in many regulatory schemes (e.g. Ure et al.[28]) and partitioning studies (e.g. Sauvé et al.[21]), thus allowing comparison of K_r values with K_d values of other contaminants. In the case of K_r values, the MF step was followed by ultrafiltration (UF) using 1-kDa centrifugal UF devices to determine soluble Ag and Ce concentrations in solutions. Nanoparticulate metals or their aggregates are too large to pass through these UF filters.[14,29]

The loss of metals on MF and UF membranes has been reported to occur in the literature,[30] which can lead to an underestimation of both MNP partitioning and dissolution. The recovery of soluble Ag and Ce on various MF and UF membranes was tested to determine possible artefacts on K_r and K_d value determinations (Table 1). Recovery of Ag during both MF and UF using Millipore (Billerica, MA) and Pall-Gellman (Port Washington, NY) filters was found to be lower than 75% (Fig. 2a). The pretreatment of filters with Cu^{II} was found to increase Ag recoveries, especially in the case of Millipore MF membranes. In the case of Pall-Gellman UF filters, the increase in recovery was only significant for 100 μg L^{-1} solutions. Using

Sartorius filters did not offer an alternative because recoveries using Sartorius MF were lower than 50% and exceeded 80% for the 1 $\mu g\,L^{-1}$ solutions only. The Ag^{I} ion has a high affinity for organic ligands,[31] but so does the Cu^{II} ion,[32] which possibly occupied specific binding sites on membranes, thus preventing subsequent Ag^{I} adsorption. Filtering Ag solutions with Millipore MF and Pall-Gellman UF filters that were preconditioned with Cu^{II} was the preferred method in the present study to determine K_r and K_d values because they provided the minimum loss of soluble Ag onto MF and UF membranes.

Ce^{III} was found to be much less retained than Ag during MF, with recoveries for Millipore filters near 100% (Fig. 2b). After Cu^{II} pretreatment, Pall-Gellman UF membranes provided the highest recovery of Ce^{III} of the tested UF membranes. Ce^{IV} recoveries, however, were lower than 75%, regardless of the applied filtration or preconditioning with Cu^{II}, with the lowest recoveries for the 100 $\mu g\,L^{-1}$ solution (Fig. 2c). This lower recovery for Ce^{IV} solutions may be due to cerium pyrophosphate ($Ce_2P_2O_7$) precipitation[33] in the artificial soil solutions used in the current study that contained phosphate. Alternative explanations such as electrostatic repulsion of Ce^{IV} by charged membranes[34] are unlikely, because dissolved Ce^{IV} predominantly occurs as $Ce(OH)_{4(aq)}$ at pH values higher than 3.[35,36] In soil solutions, Ce is, however, expected to be present as $Ce^{III}_{(aq)}$, because Ce^{IV} generally forms sparingly soluble precipitates under normal environmental conditions.[36,37] The filtering of Ce solutions with Millipore MF and Pall-Gellman UF filters that were preconditioned with Cu^{II} was therefore the preferred method in the present study to determine K_r and K_d values for CeO_2 MNP because they provided the minimum loss of soluble Ce onto MF and UF membranes.

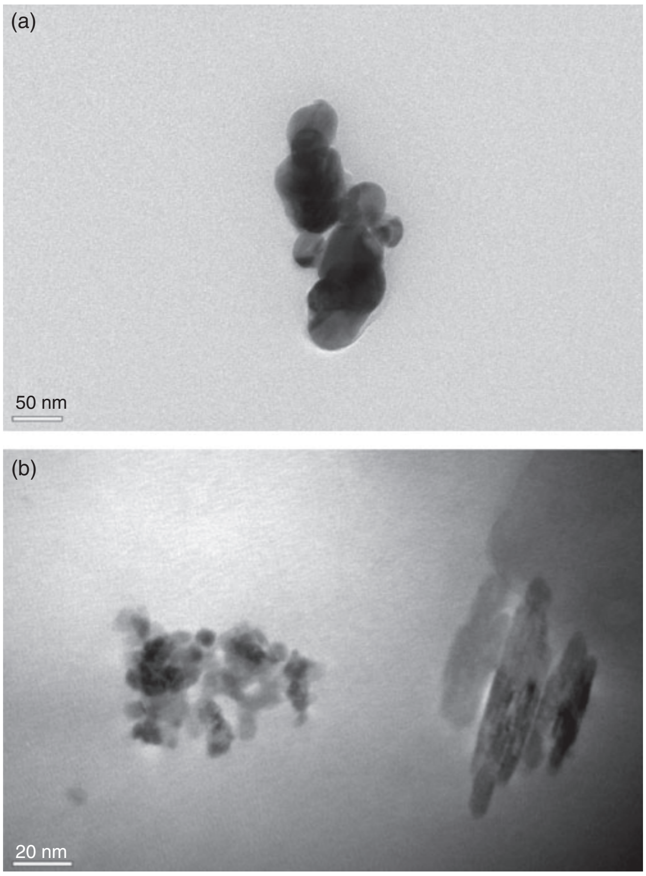

Fig. 1. Transmission electron microscopy (TEM) images of (a) Ag manufactured nanoparticles (MNP) suspended in water, and (b) CeO_2 MNP suspended in citrate at pH = 10 after sonication and 0.20-µm filtration. The scale in (a) indicates a 50-nm length, whereas the scale in (b) indicates 20 nm.

MNP digestion optimisation

Direct introduction of particles in inductively coupled plasma–mass spectrometry (ICP-MS) analysis, also called slurry nebulisation, was not chosen in this study to determine Ag and CeO_2 MNP concentrations owing to the possible formation of larger aggregates during storage and ICP-MS analysis. Total solution concentrations (including Ag and CeO_2 MNP) were determined by ICP-MS following acid digestion (Table 1).

Not all tested digestion methods provided quantitative determinations of Ag and Ce associated with Ag MNP and CeO_2 MNP (Fig. 3). Recoveries of Ag were low during MNP digestions involving HCl, likely because of AgCl precipitation. The open-vessel digestion with nitric acid and microwave digestion with nitric acid and hydrogen peroxide (H_2O_2) both provided Ag recoveries approaching 100%, but the nitric acid digestion was the preferred method because of its ease of use.

In the case of CeO_2 MNP, only the use of microwave digestion with reverse aqua regia led to Ce recoveries of ~100%. The use of a speciation model, MINTEQ (using thermodynamic data from Bratsch[38]), determined the solubility of Ce from crystalline CeO_2(c) in concentrated nitric acid to be only 22.5 $mg\,L^{-1}$. Although the solubility of MNP is expected to be higher than that of large minerals,[32] limited solubility may explain the 78% recovery that was obtained using a nitric acid digestion of 100 mg CeO_2 MNP (Fig. 3). MNP concentrations in environmental samples are, however, likely to be much lower than that. Fig. 4 shows measured Ce

Table 3. Dynamic laser scattering (DLS) measurements of diluted spiking suspensions

Average Z-average diameters (d) and polydispersity indices (PDI) of Ag and CeO_2 manufactured nanoparticles (MNP) suspensions measured 1 and 24 h after preparation ($n = 3$; mean ± standard deviation)

Treatments		Ag		CeO_2	
		1 h	24 h	1 h	24 h
None	d	164 ± 8 nm	119 ± 2 nm	403 ± 90 nm	157 ± 2 nm
	PDI	0.44	0.37	0.51	0.22
Centrifuged[A]	d	53 ± 2 nm	68 ± 6 nm	123 ± 4 nm	135.7 ± 2 nm
	PDI	0.46	0.4	0.22	0.22
0.20-µm filtered	d	85 ± 5 nm	66 ± 5 nm	107 ± 2 nm	103 ± 2 nm
	PDI	0.27	0.39	0.19	0.18

[A]Centrifuged at 2300*g* for 15 min at 20°C.

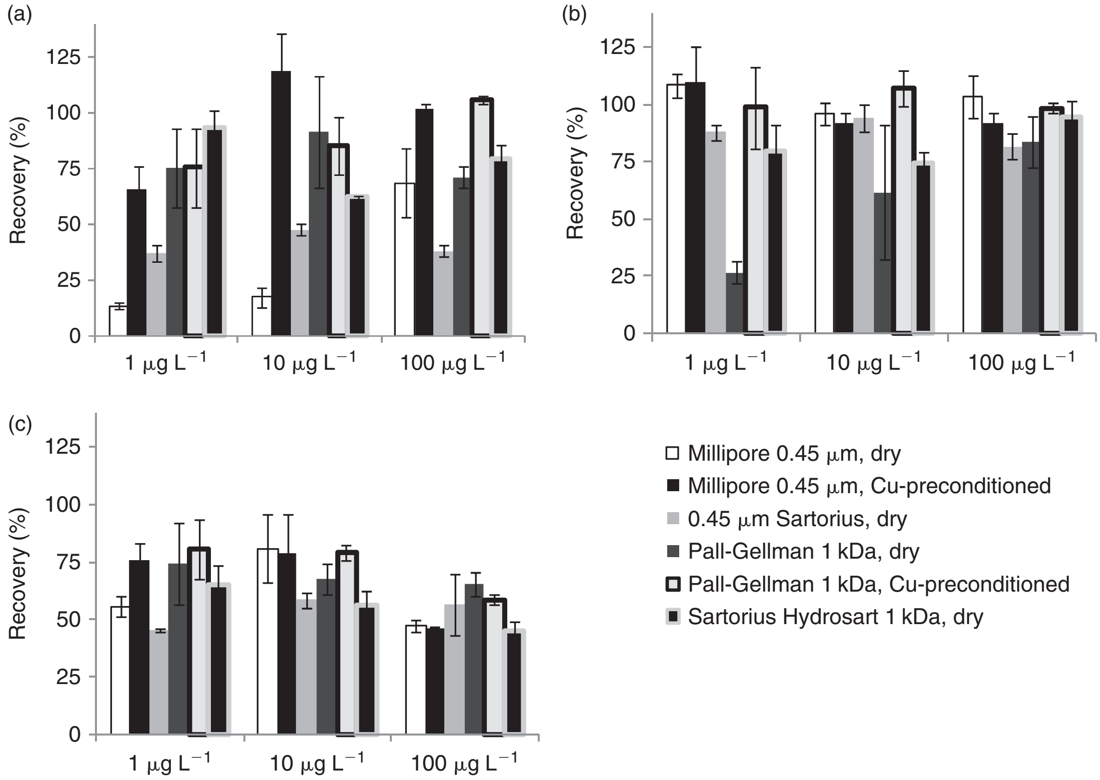

Fig. 2. Recoveries of (a) Ag^{I}; (b) Ce^{III}; and (c) Ce^{IV} dissolved in artificial soil solution during MF (microfiltration) and UF (ultrafiltration). Error bars indicate standard deviations, $n = 3$.

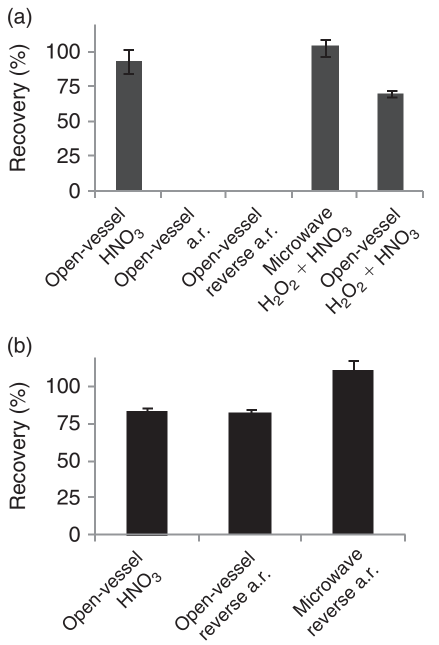

Fig. 3. Recoveries of (a) Ag, and (b) Ce during digestion of Ag or CeO_2 manufactured nanoparticles (MNP) using different methods as outlined in Table 1 (mean of three samples; error bars indicate standard deviations; a.r. = aqua regia).

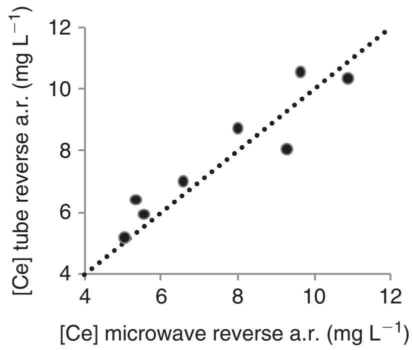

Fig. 4. Comparison of Ce concentrations in suspensions of CeO_2 manufactured nanoparticles (MNP) following open-vessel digestion using nitric acid with Ce concentrations in CeO_2 MNP suspensions digested using aqua regia (a.r.) in closed vessels. The dotted line signifies a 1 : 1 relationship.

concentrations after digestion of 10 mL of CeO_2 MNP suspensions with nitric acid in open-vessel tubes or using closed-vessel microwave reverse aqua regia, the method that led to 100% Ce recovery. The total Ce concentrations that were digested ranged between 50 and 120 μg. It can be seen that in the case of these environmentally more relevant lower concentrations, similar concentrations were measured using either digestion method. Nitric acid was therefore again preferred owing to its ease of use and suitability for large sample numbers.

K_r and K_d values

Soluble (< 1 kDa, UF) and nanoparticulate (1 kDa to < 0.45 μm, MF and UF) Ag and Ce concentrations in soil suspensions following Ag and CeO_2 MNP addition can be found in Fig. 5a, b. The soluble (MF) Ag and Ce concentrations in geogenic, bulk Ag and CeO_2 and soluble Ag and Ce species in solutions can be found in Fig. 5c–g. The soluble and nanoparticulate concentrations in solutions were used to calculate K_r values (see

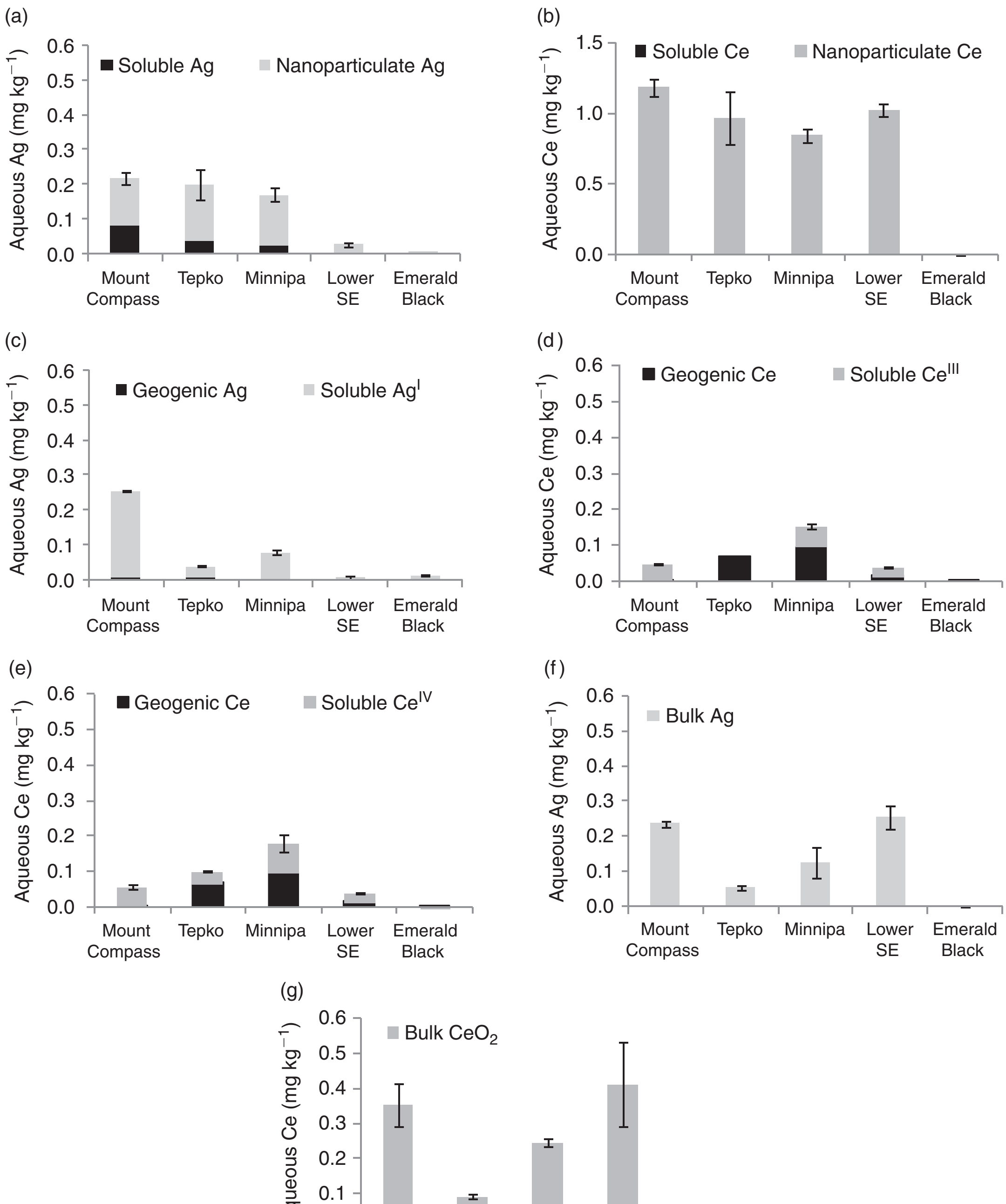

Fig. 5. Ag and Ce concentrations remaining in solution after membrane filtration on addition of (a) Ag manufactured nanoparticles (MNP); (b) CeO_2 MNP; (c) soluble Ag; (d) soluble Ce^{III}; (e) soluble Ce^{IV}; (f) bulk Ag; and (g) bulk CeO_2 (mean ± error bars indicate standard deviations).

below) for Ag and CeO_2 MNP and soluble concentrations to calculate K_d values (Eqn 1) for geogenic, soluble and bulk treatments of Ag or Ce in soils (Tables 4 and 5).

The average coefficient of variation expressed as a percentage of the mean of replicate K_r determinations was 16 and 33% for Ag MNP and CeO_2 MNP respectively. This sample variability contrasts with the high variability of K_r values for different soils and with the difference between K_r values and K_d values of dissolved Ag and Ce, despite similar spiking rates (Tables 4 and 5). This suggests that K_r values are indicative of general trends in the retention behaviour of MNP.

Some general trends in differences between K_r and K_d values can be identified. This is the largest benefit of the present method because the single-point K_r values for MNP and K_d values of soluble Ag and Ce were obtained at similar spiking rates. It has to be noted that higher K_r and K_d values were found for all Ag and Ce additions in Emerald Black relative to other soils. The present K_r values and K_d values of soluble Ag for the same soil were in the same order of magnitude. Dissolved Ag preferentially interacts with natural occurring colloids such as organic matter or clays,[39] but the aggregation of Ag MNP with these soil constituents remains to be investigated. The K_r values for CeO_2 MNP, however, were two orders of magnitude lower than K_d values of dissolved Ce^{III} and Ce^{IV}, and were also consistently lower than those of Ag MNP, which suggested that CeO_2 MNP were more stable in soil suspensions than Ag MNP. The lower solid-phase partitioning of CeO_2 MNP in soils found in this study may be due to the addition of citrate in spiking solutions as an organic stabiliser.[40] Although citrate in soil solutions is likely to be degraded in soils within a few hours, adsorption to mineral surfaces reduces its bioavailability markedly.[40,41] Citrate may thus still have provided additional stabilisation to CeO_2 MNP in soil suspensions as it did in stock aqueous suspensions. Bulk powder additions were much higher than MNP additions for both Ag and CeO_2, because these powders could not be added as suspensions. Very high K_d values were calculated, because despite the very high addition rate of bulk powders, relatively low Ag or Ce concentrations were measured in MF filtrates, in many cases lower than those measured in MNP retention experiments (Fig. 5). Owing to their small size and apparently limited aggregation, MNP can pass through 0.45-μm membranes much more than bulk forms of Ag and Ce. This highlights the relevance of the small particle size of MNP in terms of their retention behaviour.

The K_r values of Ag MNP appear to be higher in the two soils with the highest clay content (Table 6). In the case of CeO_2 MNP, a much higher K_r value was found for the Emerald Black soil, with the highest clay content, which explains the high variability of this K_r value, as Ce concentrations in digested MF filtrates were very low (Fig. 5b). More than any other soil parameter, the texture thus appears to influence K_r values, but the limited number of soils studied prevents an elaborate discussion to relate observed K_r values to soil properties.

The dependence of M_{solid} with $[M]$ in Eqn 1 can be non-linear, depending on the retention mechanism.[21,42] Solid–solution partitioning and K_r values can thus be concentration-dependent, and to ensure a wider applicability of the present method, K_r values should be obtained at varying spiking rates. The applied soil Ag and CeO_2 MNP exposure rates in this study were higher than current estimated exposure rates to soils in the ng kg^{-1} range.[4] The MNP spiking rates in the present study can be lowered by diluting the stock solutions but this would lead to metal concentrations below ICP-MS detection limits even with low partitioning to the solid phase. Hence, other sensitive techniques such as radioactive isotopic labelling of MNP will be needed in order to distinguish MNP, geogenic and

Table 4. Retention coefficient (K_r) values for Ag MNP and partition coefficient (K_d) values for geogenic, soluble and bulk Ag treatments in soils (mean ± standard deviation)

MNP, manufactured nanoparticles. Values are L kg^{-1}

Soil	Ag MNP	Geogenic Ag	Soluble Ag	Bulk Ag
Mount Compass	77 ± 13	110 ± 41	35 ± 1	88 667 ± 2823
Tepko	68 ± 20	48 ± 2^A	331 ± 7	443 911 ± 60 817
Minnipa	76 ± 12	79 ± 18^A	131 ± 13	180 967 ± 46 644
Lower SE	541 ± 91	212 ± 35^A	1816 ± 42	84 140 ± 11 168
Emerald Black	2165 ± 5	79 ± 10^A	1548 ± 347	33 559 688 ± 84 876

^A K_d values of these soils were calculated based on a total Ag concentration of 0.05 mg kg^{-1}.

Table 5. Retention coefficient (K_r) values for CeO_2 manufactured nanoparticles (MNP) and partition coefficient (K_d) values for geogenic, soluble and bulk Ce treatments in soils (mean ± standard deviation)

Values are L kg^{-1}

Soi1	CeO_2 MNP	Geogenic Ce	Soluble Ce^{III}	Soluble Ce^{IV}	Bulk CeO_2
Mount Compass	1.1 ± 0.6	5334 ± 563	263 ± 18	226 ± 23	58 897 ± 10 096
Tepko	4.1 ± 0.7	13 207 ± 680	3763 ± 52	351 ± 25	850 444 ± 204 889
Minnipa	5.6 ± 0.9	242 ± 12	209 ± 24	155 ± 47	136 355 ± 10 497
Lower SE	2.8 ± 0.6	10 948 ± 408	478 ± 27	500 ± 26	55 785 ± 22 854
Emerald Black	8282 ± 741	144 990 ± 0	5187 ± 25	5304 ± 11	10 738 547 ± 3 457 283

Table 6. Soil properties

EC, electrical conductivity; Clay, clay weight percentage; Silt, silt weight percentage; Sand, sand weight percentage; CEC, cationic exchange capacity; DOC, dissolved organic carbon; Total Ag, total silver concentration; Total Ce, total cerium concentration

Soil	pH	EC (mS)	Clay (%)	Silt (%)	Sand (%)	CEC (cmol kg^{-1})	Total C (%)	DOC (mg kg^{-1})	Total Ag (mg kg^{-1})	Total Ce (mg kg^{-1})
Mount Compass	4.85	0.01	1	0	99	0.2	0.1	31	0.10	1.8
Tepko	6.09	0.09	8	3	89	5.2	1.0	261	<0.05	87.6
Minnipa	5.90	0.03	1	<1	99	1.7	0.2	168	<0.05	2.4
Lower South East	4.21	0.04	14	10	75	3.4	1.6	163	<0.05	16.2
Emerald Black	6.41	0.1	59	14	27	65.7	0.9	68	<0.05	34.8

spiked metal concentrations[2] in solutions at sub-mg kg^{-1} concentrations.

In MF filtrates of MNP-spiked soils, more than 20% of the total Ag concentration in soil solutions was present as soluble (<1 kDa) Ag and <1% in the case of Ce. The higher dissolution of Ag MNP relative to CeO_2 MNP in soils corresponds with observations in aquatic environments,[14,15] which suggest that whereas Ag MNP are retained more than CeO_2 MNP in soils, Ag MNP are less persistent, because they are easily oxidised.[43] Future research should be directed towards examining the influence of MNP coatings that may explain the lower partitioning of CeO_2 in soils, examining retention behaviour of Ag and CeO_2 MNP over a wider concentration range and developing models to predict the mobility of Ag and CeO_2 MNP in soils through an examination of retention behaviour in soils with a wider set of physicochemical characteristics.

Conclusions

A method was developed to study the retention and dissolution of Ag and CeO_2 MNP in soil environments that led to reproducible K_r values. In addition, the accuracy was tested and confirmed for the spike concentration, phase separation and MNP detection. Application of the method to five soils revealed contrasting retention behaviours and solubilities of Ag and CeO_2 MNP that differed in many cases from the K_d values of bulk materials and soluble salts. The method should, however, be applied to a wider concentration range to extend the applicability of the K_r values, and values should be determined for a larger set of soils in order to specify the most important soil properties that influence retention of Ag and CeO_2 MNP. The method could possibly also be extended to other metal and metal oxide MNP and environmental matrices such as sediments or possibly even natural colloids in aquatic systems.

Material and methods

Ag and CeO_2 MNP spike solutions

Ag MNP (Nanostructured & Amorphous Materials, Inc., Houston, TX) were suspended in water and CeO_2 MNP (MTI Cooperation, Richmond, CA) in 0.5 mM citrate adjusted to pH 10 with sodium hydroxide, both at 0.01 g L^{-1}, followed by sonication for 3 min. The average hydrodynamic diameter was determined with DLS (Malvern Nanosizer) and TEM (Phillips CM200 at 120 keV) after 1 h and again with DLS after 24 h in untreated suspensions or after centrifugation or 0.20-μm filtration. Suspensions drops (20 μL) were air-dried on a 400-mesh Cu-grid covered with an electron-transparent Formvar film and images were obtained according to Mavrocordatos et al.[44] The chosen centrifugation setting sedimented Ag and CeO_2 MNP aggregates with an equivalent Stokes diameter of ~0.20 μm.

Table 1 shows the commercially available MF and UF membranes that were tested for recovery of soluble Ag^{I}, Ce^{III} and Ce^{IV} concentrations after filtration. Freshly prepared 1000 mg L^{-1} aqueous stock solutions prepared from $AgNO_3$ (Sigma–Aldrich), $Ce(NO_3)_3{\cdot}6H_2O$ (Aldrich) and $(NH_4)_2Ce(NO_3)_6$ (Fluka) were diluted in artificial soil solutions to obtain working solutions with final metal concentrations of 1, 10 or 100 μg L^{-1}. The artificial soil solutions were prepared starting from soluble salts based on McLaughlin et al.[45] to obtain compositions shown in Table 7. Nitrate was added instead of the same molar concentration of chloride in the case of Ag to avoid AgCl precipitation. During UF, the solution (2 mL) was filtered with centrifugal devices at 3800*g* for 15 min at 20°C. The Ag and Ce concentrations of working solutions and MF and UF filtrates were then measured using ICP-MS (Agilent 7500ce). In addition, Ag and Ce recoveries were determined using MF and UF membranes that were pretreated by filtering 0.1 M copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$; 2 mL) solution, followed by ultrapure water (2 mL).

All concentration determinations were performed using ICP-MS. To ensure complete dissolution of MNP before ICP-MS determinations, total Ag or Ce concentrations were determined in digests using procedures in Table 1. Both acids were added concomitantly to the MNP powders in either Teflon microwave digest tubes or glass digest tubes and left overnight before digestion. In the methods involving H_2O_2, this acid was added and left overnight before addition of acid 2 (Table 1).

MNP size characterisation

The primary particle sizes of Ag and CeO_2 MNP powders were calculated from N_2-BET adsorption surface area determinations, assuming a spherical shape and densities of 10.4 and 7.21 g cm^{-3} for Ag and CeO_2 MNP respectively. Primary particle sizes were also estimated from crystallite sizes calculated from XRD patterns using the Scherrer equation.[24] Ag MNP suspensions were prepared by adding 0.05 g in 50 mL water or 0.05 g CeO_2 MNP suspensions in 50 mL 0.5 mM sodium citrate adjusted to pH 10 using 0.1 M NaOH. After sonication for 3 min using a microprobe, suspensions were either left untreated, centrifuged at 3800*g* for 15 min at 20°C to sediment aggregates larger than 200 nm or passed through a 0.20-μm membrane (Sartorius). After 1 or 24 h, the hydrodynamic diameter of MNP aggregates in these suspensions (1 mL) was determined using DLS (Malvern Zetasizer). Field correlograms of backscattered light (173°) from a He-Ne laser at a wavelength of 633 nm were recorded, which allowed estimation of hydrodynamic diameters and polydispersity indices using cumulants fitting.[25] The results were averaged over triplicate runs.

Soil characterisation

The physical and chemical properties of the five selected soils from South Australia can be found in Table 7. The soils (0–10-cm depth) were air-dried and sieved through 2 mm. Soil electrical conductivity (EC), pH and dissolved organic carbon (DOC) were measured in a 1 : 10 soil : solution ratio using 2 mM KNO_3 suspension as a background electrolyte. Total carbon, cation exchange capacity (CEC), particle size and oxalate-extractable iron (Fe) and aluminium (Al) were determined according to standard methods.[46] Total elemental Ag and Ce concentrations were determined after digestion of soil samples in aqua regia (US-EPA 3051A[47]) and measurement by ICP-MS. A calcareous soil (ERM-CC690[48]) with a certified Ce concentration of

Table 7. Composition of artificial soil solutions
Values are in mg L^{-1}

Component	Ag	Ce
Ca	400	400
Mg	146	146
K	381	382
Cl	0	710
SO_4	577	577
PO_4	24	24
NO_3	1800	590

$49.1 \pm 2.5\,mg\,kg^{-1}$ and a sediment (NRC-CNRC PACS-2[49]) with a certified Ag concentration of $1.22 \pm 0.14\,mg\,kg^{-1}$ were used as quality controls. The determined total Ag or Ce concentrations in these certified reference materials, 49.2 and $1.20\,mg\,kg^{-1}$ respectively, were in close agreement with the aforementioned certified values.

K_d *and* K_r *value calculations*

The K_d values for geogenic, soluble Ag, soluble Ce^{III}, Ce^{IV} and bulk Ag and Ce were determined using Eqn 1. Geogenic Ag and Ce^{III} partitioning in soluble and bulk treatments were taken into account in calculations to avoid underestimation of K_d values of spiked elements.[42] Approximately 2.5 g of each soil ($n = 3$) was weighed into 50-mL centrifuge tubes and 25 mL of 2 mM KNO_3 or appropriate amounts of stock solution diluted in 2 mM KNO_3 were added to obtain final concentrations of 1.10 mg Ag kg^{-1}, 1.25 mg Ce^{III} kg^{-1} or 1.28 mg Ce^{IV} kg^{-1} to determine geogenic, soluble Ag, Ce^{III} or Ce^{IV} K_d determinations respectively. The samples were shaken end over end for 24 h, followed by centrifugation at 2300*g* for 15 min. The partitioning of bulk powders in soils was examined by adding 0.1 g of metallic Ag (Fluka) or CeO_2 (Aldrich) powders to five replicates of 50 g of each soil, equilibrated for 24 h with 2 mM KNO_3 (500 mL), which resulted in addition rates of 2027 mg Ag kg^{-1} and 2462 mg CeO_2 kg^{-1}. Filtration and centrifugation were performed similarly to those in MNP retention determination, but the UF step was not applied. Total Ag and Ce concentrations were determined in <0.45-μm filtered solutions by ICP-MS.

The K_r values for Ag and CeO_2 MNP were determined by weighing 2.5 g of each soil ($n = 5$) into 50-mL centrifuge tubes to which 2.22 mM KNO_3 (22.5 mL) was added. While sonicating stock Ag MNP or CeO_2 MNP stock suspensions, 2.5 mL of these suspensions was added to all soils (final concentration of 2 mM KNO_3) and shaken end over end for 24 h. In addition, 10 replicates of 2.5-mL stock solutions were digested and analysed for total Ag and Ce to confirm MNP addition rates. Final spike concentrations were determined to be $1.24\,mg\,kg^{-1}$ Ag and $1.30\,mg\,kg^{-1}$ Ce for Ag and CeO_2 MNP respectively. After the MNP spike equilibration period, the samples were centrifuged at 2300*g* for 15 min at 20°C (sedimentation of MNP aggregates >200 nm). The supernatants were then filtered using the optimised MF and UF procedures. The MF filtrates (10 mL) were then added to digest vessels for digestion and total Ag or Ce determination by ICP-MS.

Eqn 1 can be rewritten using Fig. 6 to express Ag and CeO_2 MNP retention as K_r values ($mg\,kg^{-1}$):

$$K_r = \frac{M_{solid}}{M_{NP}} \times L/S\,(L\,kg^{-1}) \qquad (2)$$

M_{NP} represents the MNP concentration that is not deposited on soil surfaces, or shows only limited aggregation after 24 h and thus passes through the 0.45-μm membrane. The dissolved MNP fraction (M_{NP_diss}) is not included in the denominator of Eqn 2, because high K_r values would otherwise be attributed to relatively soluble MNP regardless of whether they remained suspended or formed large aggregates and regardless of whether or not they deposited on soil surfaces. Despite the limited dissolution of Ag MNP and CeO_2 MNP in soils, the inclusion of M_{NP_diss} in Eqn 2 leads to a different ranking (solid–solution partitioning) of soils in terms of K_r values of Ag MNP (Table 8). Not including M_{NP_diss} in Eqn 2 ensures that K_r values can be used to rank MNP in different soils in terms of MNP retention rather than in terms of MNP solubility. This may be relevant, especially for MNP that dissolve in environmental media, such as ZnO.[23] We, however, argue that dissolution also determines the fate of MNP, which is evaluated using the K_r method, but needs to be distinguished from retention. The unknown retained MNP concentration (M_{solid}) was thus calculated as $M_{added} - M_{NP} - M_{NP\_diss}$. The concentrations M_{NP} and M_{NP_diss} are both measured in the MF fraction (M_{MF}), but so is geogenic Ag or Ce (M_{geo}). Dissolved geogenic Ag or Ce were therefore measured in separate experiments as M_{geo}, which allows calculation of the term M_{solid} as $M_{added} - M_{MF} + M_{geo}$ and M_{NP} in the denominator of Eqn 2 as $M_{MF} - M_{UF}$ because M_{geo} is already included in M_{UF}. The final equation to determine K_r values for Ag and CeO_2 MNP in soils can be expressed as:

$$K_r = \frac{M_{add} - M_{MF} + M_{geo}}{M_{MF} - M_{UF}} \times L/S\,(L\,kg^{-1}) \qquad (3)$$

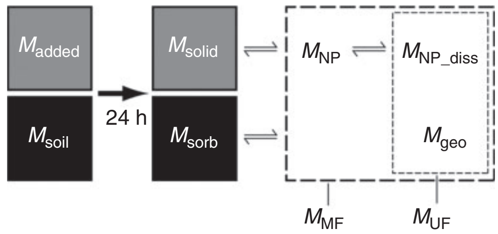

Fig. 6. Schematic representation of reactions occurring during a retention experiment. Initially, the soil suspension contains geogenic metals (M_{soil}) and metals added as suspended manufactured nanoparticles (MNP) (M_{added}). After a 24 h shaking period, part of the added MNP will remain suspended or form small aggregates that pass 0.45 μm MF (M_{NP}), whereas some will aggregate or deposit on soil mineral or organic matter, producing particulates that do not pass 0.45 μm MF (M_{solid}). Some metals may also dissolve from suspended MNP and pass UF (UF, ultrafiltration; M_{NP_diss}). Dissolved geogenic metals partition to the soil solution (M_{geo}) or remain in the solid phase (M_{sorb}). M_{MF} and M_{UF} represent the MF and UF fractions respectively that are measured during MNP partitioning experiments.

Table 8. K_r values for Ag manufactured nanoparticles (MNP) calculated including dissolved MNP (mean ± standard deviation)
Values are L kg^{-1}

Soil	Ag MNP
Mount Compass	60 ± 5
Tepko	68 ± 18
Minnipa	76 ± 9
Lower SE	489 ± 101
Emerald Black	2165 ± 5

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