

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 (MNP), 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 (CeO₂) MNP 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 MNP to 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 CeO₂ MNP, that

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can be ranked amongst solid-liquid partitioning (K_d) values of bulk (micrometer sized) forms, soluble salts and other possible contaminants of soils and that account for MNP dissolution using ultrafiltration (<1kDa). After method optimisation, suspensions containing 1.24 mg kg⁻¹ Ag as Ag MNP and 1.30 mg kg⁻¹ Ce as CeO₂ 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 – 2,165 L kg⁻¹), CeO₂ MNP (1.1 – 2,828 L kg⁻¹) contrasted with K_d values of soluble Ag(I), Ce(III) and Ce(IV) salts and bulk Ag and CeO₂ powders in different soils.

Keywords: K_d , partitioning, transport, risk assessment, solubility, bulk powders

1 Introduction

[1]. 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 [2]. Due to the small size of nano-sized materials, their mechanical, catalytic, electric and optical properties are often vastly different to those of the same material with a larger particle size. However, some of the same properties that make these MNP useful in nanotechnology could possibly also result in risk to aquatic and terrestrial environment. Indeed several reviews have demonstrated potential toxicity to aquatic and terrestrial organisms specific to some MNP [1,3], 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 air-borne MNP, use of MNP in agrochemicals [7] or soil remediation [1,8]. 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 exposure of organisms to MNP suspended in porewaters, the major exposure pathway in soil systems [9], knowledge of the retention of MNP is required, 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 upon 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 invariably result in an increased mobility in soil ^[12].

Silver MNP are amongst the most widely used MNP for microbial sterilization ^[2]. The catalytic properties of CeO₂ MNP are also used extensively and they are a common additive in diesel fuels ^[2]. The potential toxic properties of Ag and CeO₂ MNP towards aquatic ^[14,15] and terrestrial organisms in case of Ag MNP ^[16] have been demonstrated. Toxic effects of Ag MNP have been related to cell membrane damage, to oxidative stress, or to interactions of Ag⁺ ions with proteins and enzymes ^[17], whereas both cytotoxic oxidative stress due to a reduction of Ce(IV) to Ce(III) within CeO₂ MNP ^[18] as well as a cytoprotective effect due to reduction of reactive oxygen species ^[19] have been observed in toxicity tests with CeO₂ MNP.

In this study we present, for the first time, a method to determine retention (K_r) values for Ag and CeO₂ 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 CeO₂ MNP in soils. The method was based on partitioning determination of solutes in soil, which 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. OECD method 106 ^[20]). Solid-liquid partitioning values are calculated by:

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

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 ^[21]) yet partitioning may be a combination of many different processes e.g. sorption, precipitation, solid-state diffusion, etc. and it is recognised that these are non-equilibrium processes, even for solutes ^[22]. Existing methods to determine solid-liquid partitioning (K_d value), such as OECD method 106 ^[20], are, however, inappropriate for metal-containing MNP that may dissolve in environmental media ^[23] and thus complicate solute *versus* 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 CeO₂ MNP with soluble and bulk forms of Ag and Ce and other possible contaminants of soils.

2 Results and discussion

2.1 Method optimisation

Table 1 lists experimental procedures undertaken to optimise Ag and CeO₂ MNP spiking suspensions, filtration and digestion procedures to determine K_r values for Ag and CeO₂ MNP and K_d values for bulk materials and soluble salts in soils.

Ag and CeO₂ MNP size characterisation

The measured particle size of Ag and CeO₂ MNP were found to be inconsistent with manufactured supplied nominal particle sizes (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 BET-N₂ adsorption specific surface area determinations and transmission electron microscopy (TEM) images of suspended Ag MNP (Figure 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 CeO₂ MNP, on the other hand, appeared to be smaller than the nominal 20 nm particle size based on XRD and BET-N₂ measurements (Table 2). Individual CeO₂ MNP could not be visualized clearly on TEM images, which showed aggregates with sizes of 100 nm (Figure 1B). This highlights the importance of MNP characterisation before experiments are undertaken to ensure results can be directly linked to the size of MNP.

Table 1: Optimisation of MNP spiking suspensions, filtration and digestion procedures to determine K_r and K_d values in soils.

Short-term nanosized 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 (CeO₂), sonicated for 3 min and using the following treatments:

- 1) None (no filtration or centrifugation)
- 2) Centrifuged at 2300 g for 15 min
- 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:

Treatments	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 Microsep	1 kDa	Ultrafiltration	None
5	Pall 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	Treatments	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 ₂ O ₂	5 ml HNO ₃	Closed vessel microwave
	5	3 ml H ₂ O 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

^AMolecular weight cut off: Size of a polyethylene glycol molecule that is retained for 90%; ^BOpen 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 CeO₂ 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

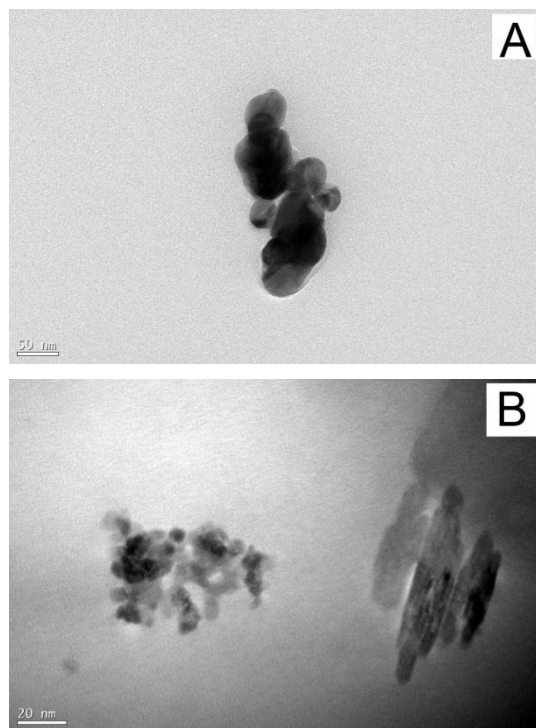


Figure 1. TEM images of A) Ag MNP suspended in water and B) CeO₂ MNP suspended in citrate at pH=10 after sonication and 0.20 μm filtration.

Ag and CeO₂ MNP suspensions for soil spiking

Reproducible spiking rates of Ag and CeO₂ MNP to soils representative of current and projected soil exposure concentrations as estimated by [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 prior to soil spiking. Water as a dispersant for MNP spiking suspensions would have a minimal impact on soil properties, but preliminary experiments using TEM, showed micrometer sized aggregates were formed in aqueous 0.01 g L⁻¹ Ag MNP and CeO₂ 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 spiking solution treatments in Table 1. In the case of CeO₂ 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 CeO₂ MNP in Table 3 therefore do not reflect the micrometer sized aggregates in these suspensions that were observed by TEM. Both centrifuging and 0.20 μ m filtration lowered d of Ag MNP suspensions significantly, but the PDI was only lowered using 0.20 μ m 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 μ m filtered Ag MNP suspensions corresponded to aggregate sizes observed in TEM (Figure 1A), but ongoing aggregation is likely to have increased aggregate sizes slightly from 1 h to 24 h.

Table 3. DLS measurements of diluted spiking suspensions

Average Z-average diameters (d) and polydispersity indices (PDI) of Ag and CeO₂ NP suspensions measured 1 h and 24 h after preparation (n=3; mean \pm standard deviation).

Treatments		Ag		CeO ₂	
		1 h	24 h	1 h	24 h
None	d	164 \pm 8 nm	119 \pm 2 nm	403 \pm 90 nm	157 \pm 2 nm
	PDI	0.44	0.37	0.51	0.22
Centrifuged	d	53 \pm 2 nm	68 \pm 6 nm	123 \pm 4 nm	135.7 \pm 2 nm
	PDI	0.46	0.4	0.22	0.22
0.20 μ m filtered	d	85 \pm 5 nm	66 \pm 5 nm	107 \pm 2 nm	103 \pm 2 nm
	PDI	0.27	0.39	0.19	0.18

In the case of CeO₂ MNP suspensions, filtration through 0.20 μ m 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 μ m filtration, but had not settled during centrifugation. The particle size of filtered CeO₂ suspensions was found to remain short-term stable (i.e. 24 h) for longer than filtered Ag MNP suspensions (Table 3). In addition, CeO₂ MNP aggregate sizes by DLS were found to be comparable to TEM observations (Figure 1B).

Sonication followed by 0.20 μ m filtration was hence the preferred method to prepare short-term diluted Ag and CeO₂ 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. ^[28]) and partitioning studies (e.g. ^[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 1kDa 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 MF and Pall-Gellman UF filters were found to be lower than 75% (Figure 2A). The pre-treatment 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 $\mu\text{g L}^{-1}$ solutions. Using Sartorius filters did not offer an alternative because recoveries using Sartorius MF were lower than 50% and exceeded 80% for the 1 $\mu\text{g L}^{-1}$ 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 this study to determine K_r and K_d values because they provided the minimum loss of soluble Ag onto MF and UF membranes.

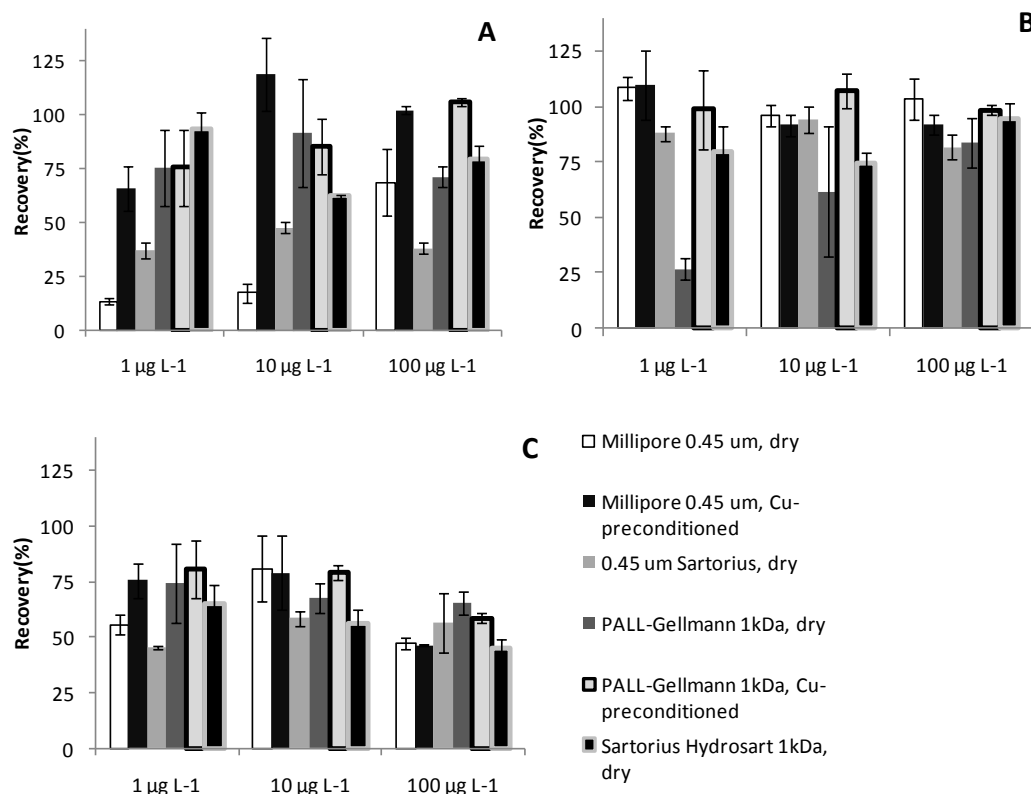


Figure 2. Recoveries of A) Ag(I), B) Ce(III) and C) Ce(IV) dissolved in artificial soil solution during MF and UF. Error bars indicate standard deviations, $n=3$.

Ce(III) was found to be much less retained than Ag during MF with recoveries for Millipore filters near 100% (Figure 2B). After Cu(II) pre-treatment, PALL Gellman UF membranes provided the highest recovery of Ce(III) of the tested UF membranes. Ce(IV) recoveries, on the other hand, were lower than 75%, regardless of the applied filtration or preconditioning with Cu(II), with the lowest recoveries for the $100 \mu\text{g L}^{-1}$ solution (Figure 2C). This lower recovery for Ce(IV) solutions may be due to cerium pyrophosphate ($\text{Ce}_2\text{P}_2\text{O}_7$) precipitation^[33] in the artificial soil solutions used in this 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 $\text{Ce}(\text{OH})_4(\text{aq})$ 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 this study to determine K_r and K_d values for CeO_2MNP because they provided the minimum loss of soluble Ce onto MF and UF membranes.

MNP digestion optimisation

Direct introduction of particles in ICP-MS analysis, also called slurry nebulisation, was not chosen in this study to determine Ag and CeO₂ MNP concentrations due to the possible formation of larger aggregates during storage and ICP-MS analysis. Total solution concentrations (including Ag and CeO₂ MNP) were determined by ICP-MS following acid digestion (Table 1).

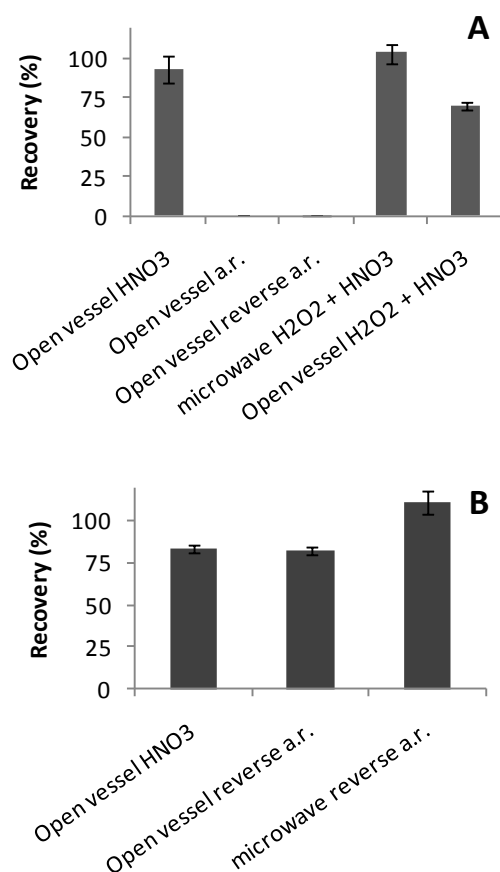


Figure 3. Recoveries of A) Ag and B) Ce during digestion of Ag or CeO₂ MNP using different methods as outlined in Table 1 (mean of 3 samples; error bars indicate standard deviations, a.r.= aqua regia).

Not all tested digestion methods provided quantitative determinations of Ag and Ce associated with Ag MNP and CeO₂ MNP (Figure 3). Recoveries of Ag were low during MNP digestions involving HCl, likely caused by to AgCl precipitation. The open vessel digestion with nitric acid and microwave digestion with nitric acid and hydrogen peroxide (H₂O₂) 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 CeO₂ MNP, only the use of microwave digestion with reverse *aqua regia* led to Ce recoveries of ~100%. The use of a speciation model, MINTEQA2 (using thermodynamic data from [38]), determined the solubility of Ce from crystalline CeO₂(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 CeO₂ MNP (Figure 3). MNP concentrations in environmental samples are, however, likely to be much lower than that. Figure 4 shows measured Ce concentrations after digestion of 10 mL of CeO₂ 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 due to its ease of use and suitability for large sample numbers.

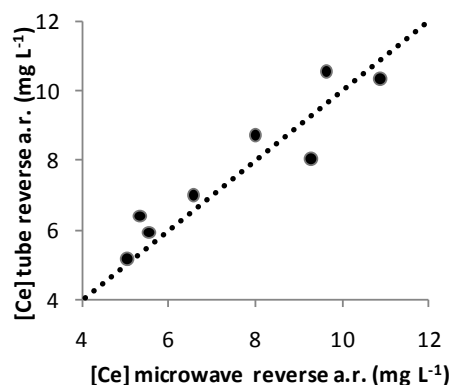


Figure 4. Comparison of Ce concentrations in suspensions of CeO₂ MNP following open vessel digestion using nitric acid and microwave digestion using aqua regia (a.r.) The dotted line signifies a 1:1 relationship.

2.2 *Kr and Kd values*

Soluble (<1Kda, UF) and nanoparticulate (1Kda to < 0.45 µm, MF and UF) Ag and Ce concentrations in soil suspensions following Ag and CeO₂ MNP addition can be found in Figure 5A and B. The soluble (MF) Ag and Ce concentrations in geogenic, bulk Ag and CeO₂ and soluble Ag and Ce species in solutions can be found in Figure 5C to G. The soluble and nanoparticulate concentrations in solutions were used to

calculate K_r values (Equation 3) for Ag and CeO₂ MNP and soluble concentrations to calculate K_d values (Equation 1) for geogenic, soluble and bulk treatments of Ag or Ce in soils (Table 4 and 5).

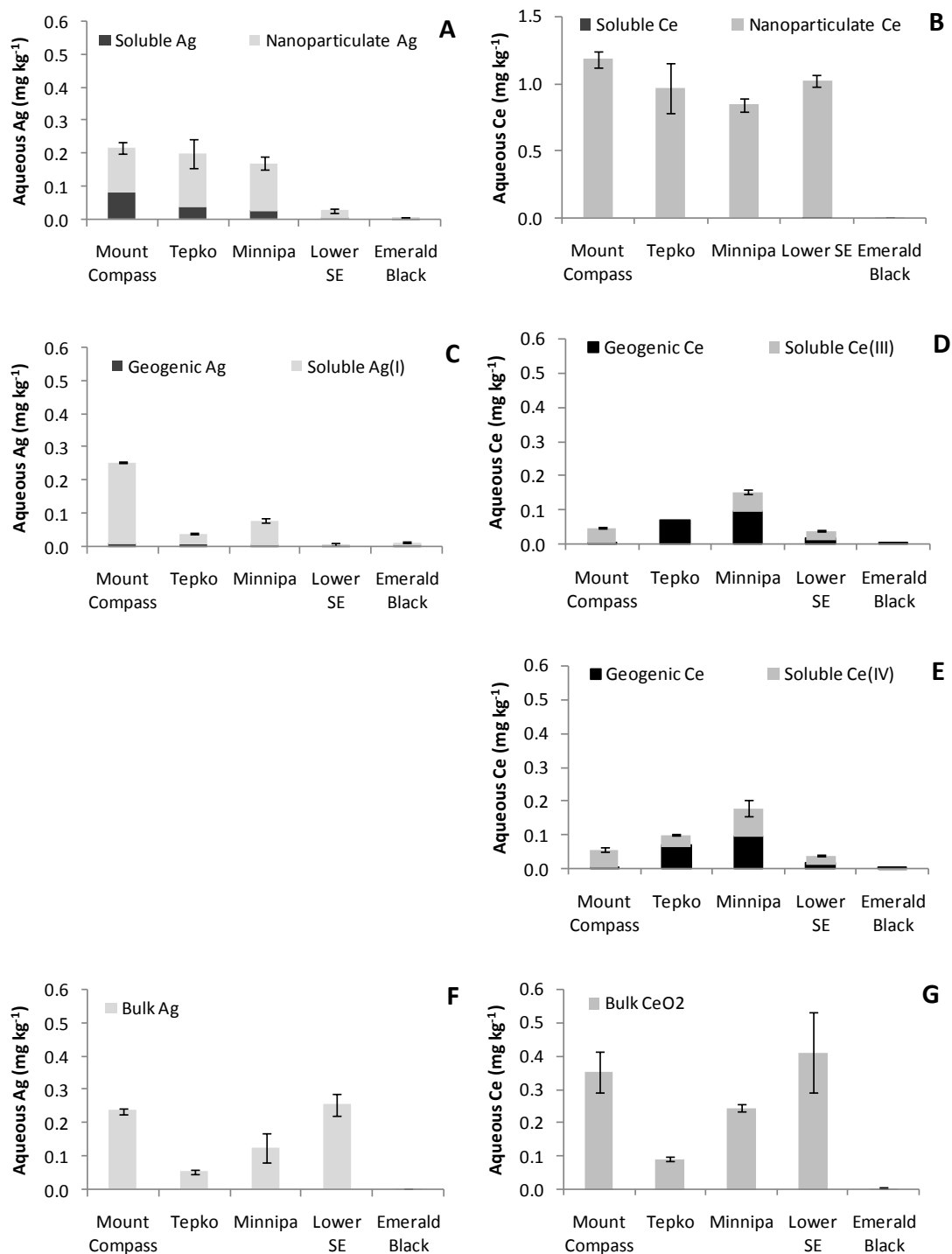


Figure 5. Ag and Ce concentrations remaining in solution after membrane filtration upon addition of A) Ag MNP, B) CeO₂ MNP, C) soluble Ag, D) soluble Ce(III), E) soluble Ce(IV), F) bulk Ag, and G) bulk CeO₂ (mean ± error bars indicate standard deviations).

Table 4. K_r values for Ag MNP and K_d values for geogenic, soluble and bulk Ag treatments in soils (mean \pm standard deviation).

Soil	Ag MNP	Geogenic Ag	Soluble Ag	Bulk Ag
(L kg ⁻¹)				
Mount Compass	77 \pm 13	110 \pm 41	35 \pm 1	88,667 \pm 2,823
Tepko	68 \pm 20	48 \pm 2 ^A	331 \pm 7	443,911 \pm 60,817
Minnipa	76 \pm 12	79 \pm 18 ^A	131 \pm 13	180,967 \pm 46,644
Lower SE	541 \pm 91	212 \pm 35 ^A	1,816 \pm 42	84,140 \pm 11,168
Emerald Black	2,165 \pm 5	79 \pm 10 ^A	1,548 \pm 347	33,559,688 \pm 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. K_r values for CeO₂ MNP and K_d values for geogenic, soluble, and bulk Ce treatments in soils (mean \pm standard deviation).

Soil	CeO ₂ MNP	Geogenic Ce	Soluble Ce(III)	Soluble Ce(IV)	Bulk CeO ₂
(L kg ⁻¹)					
Mount Compass	1.1 \pm 0.6	5,334 \pm 563	263 \pm 18	226 \pm 23	58,897 \pm 10,096
Tepko	4.1 \pm 0.7	13,207 \pm 680	3,763 \pm 52	351 \pm 25	850,444 \pm 204,889
Minnipa	5.6 \pm 0.9	242 \pm 12	209 \pm 24	155 \pm 47	136,355 \pm 10,497
Lower SE	2.8 \pm 0.6	10,948 \pm 408	478 \pm 27	500 \pm 26	55,785 \pm 22,854
Emerald Black	8,282 \pm 741	144,990 \pm 0	5,187 \pm 25	5304 \pm 11	10,738,547 \pm 3,457,283

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 CeO₂ 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 (Table 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

CeO₂ MNP, on the other hand, 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 CeO₂ MNP were more stable in soil suspensions than Ag MNP. The lower solid phase partitioning of CeO₂MNP 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 CeO₂ MNP in soil suspensions as it did in stock aqueous suspensions. Bulk powder additions were much higher than MNP additions for both Ag and CeO₂, 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 (Figure 5). Due to their small size and apparently limited aggregation, MNP can pass 0.45 μ m 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.

Table 6. Soil properties.

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

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 CeO₂ MNP, a much higher K_r value was found for the emerald black soil, with the highest clay content, which explains the high variability on this K_r value as Ce concentrations in digested MF filtrates were very low (Figure 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 eq. (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 CeO₂ 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 this 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 spiked metal concentrations ^[1] 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 CeO₂ MNP in soils corresponds with observations in aquatic environments ^[14,15], which suggests that whereas Ag MNP are retained more than CeO₂ 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 CeO₂ in soils, examining retention behaviour of Ag and CeO₂MNP over a wider concentration range and develop models to predict the mobility of Ag and CeO₂MNP in soils through an examination of retention behaviour in soils with a wider set of physico-chemical characteristics.

3 Conclusions

A method was developed to study the retention and dissolution of Ag and CeO₂ 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 CeO₂ 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 CeO₂ 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.

4 Material and methods

4.1 Ag and CeO₂ MNP spike solutions

Ag MNP (Nanostructured & Amorphous Materials, Inc., Houston, TX) were suspended in water and CeO₂ 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 1h and again with DLS after 24 h in untreated suspensions or after centrifugation or 0.20 μm filtration. 20 μL suspensions drops were air-dried on a 400 mesh Cu-grid covered with an electron-transparent Formvar film and images were obtained according to [44]. The chosen centrifugation settings sediments Ag and CeO₂ MNP aggregates with an equivalent Stokes diameter of ca. 0.20 μm.

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

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 AgNO₃ (Sigma-Aldrich), Ce(NO₃)₃.6H₂O (Aldrich) and (NH₄)₂Ce(NO₃)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 [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, 2 ml of the solution was filtered with centrifugal devices at 3800 g for 15 min. The Ag and Ce concentrations of working solutions and MF and UF filtrates were then measured using inductively coupled plasma-mass spectrometry

(ICP-MS, Agilent 7500ce). In addition, Ag and Ce recoveries were determined using MF and UF membranes that were pre-treated by filtering 2 ml of a 0.1 M copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) solution, followed by 2 ml ultrapure water.

All concentration determinations were performed using ICP-MS. To ensure complete dissolution of MNP prior to 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 prior to digestion. In the methods involving H_2O_2 , this acid was added and left overnight prior to addition of acid 2.

4.2 *MNP size characterization*

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 g cm^{-3} 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 brining 0.05 g in 50 mL water or 0.05 g CeO_2 MNP suspensions in 50 mL 0.5 mM sodium citrate brought at pH=10 using 0.1 M NaOH. After sonication for 3 minutes using a microprobe, these suspensions were either left untreated, centrifuged at 3800 g for 15 min to sediment aggregates larger than 200 nm or filtered using 0.20 μm membrane filters (Sartorius). After 1 h or 24 h, the hydrodynamic diameter of MNP aggregates in 1 mL of these suspensions 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]. Results were averaged over triplicate runs.

4.3 *Soil characterization*

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 over 2 mm. Soil EC, pH, 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) and measurement by ICP-MS. A calcareous soil (ERM-CC690) with a certified Ce concentration of 49.1 +/- 2.5 mg kg⁻¹ and a sediment (NRC-CNRC PACS-2) with a certified Ag concentration of 1.22 +/- 0.14 mg kg⁻¹ were used as quality controls. Discrete determinations of Ag or Ce concentrations in these certified reference materials, 49.2 and 1.20 mg kg⁻¹ respectively, were in close agreement with certified values.

4.4 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 Equation 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 25ml of 2 mM KNO₃ or appropriate amounts of stock solution diluted in 2mM KNO₃ 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 24h 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 CeO₂ (Aldrich) powders to five replicates of 50 g of each soil, equilibrated for 24 h with 500 ml of 2 mM KNO₃ which resulted in addition rates of 2027 mg Ag kg⁻¹ and 2462 mg CeO₂ kg⁻¹. Filtration and centrifugation were performed similar to 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 CeO₂ MNP were determined by weighing 2.5 g of each soil (n=5) into 50 ml centrifuge tubes to which 22.5 ml of 2.22 mM KNO₃ was added. While sonicating stock Ag MNP or CeO₂ MNP stock suspensions, 2.5 mL of these suspensions was added to all soils (final concentration of 2 mM KNO₃) and shaken end over end for 24 h. In addition, ten 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 CeO₂ MNP respectively. After the MNP spike equilibration period, the samples

were centrifuged at 2300 g for 15 min, again sedimenting MNP aggregates larger than 200 nm. The supernatants were then filtered using the optimised MF procedure followed by the UF procedure. Ten mL of the MF filtrates was then added to digest vessels for digestion and total Ag or Ce determination by ICP-MS.

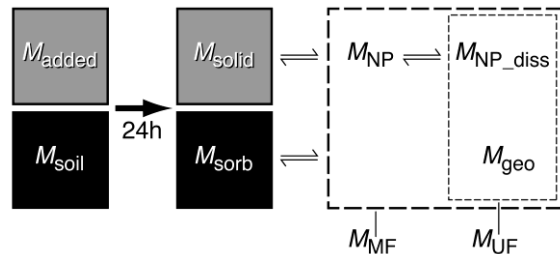


Figure 6. Schematic representation of reactions occurring during a retention experiment. Initially, the soil suspension contains geogenic metals (M_{soil}) and metals added as suspended MNP (M_{added}). After a 24 h shaking period, part of the added MNP will remain suspended or form small aggregates that pass $0.45 \mu\text{m}$ MF (M_{NP}), whereas some will aggregate or deposit on soil mineral or organic matter producing particulates that do not pass $0.45 \mu\text{m}$ MF (M_{solid}). Some metals may also dissolve from suspended MNP and pass UF ($M_{\text{NP_diss}}$). 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.

Equation (1) can be rewritten using Figure 6 to express Ag and CeO_2 MNP retention as K_r values (mg kg^{-1}):

$$K_r = \frac{M_{\text{solid}} * L/S}{M_{\text{NP}}} \quad [\text{L kg}^{-1}] \quad (2)$$

M_{NP} represents the MNP concentration that is not deposited on soil surfaces or shows only limited aggregation after 24 h and thus passes the $0.45 \mu\text{m}$ membrane. The dissolved MNP fraction ($M_{\text{NP_diss}}$) is not included in the denominator of eq. (2), because high K_r values would otherwise be attributed to relatively soluble MNP regardless of whether they remain suspended or form large aggregates or regardless of whether or not they deposit on soil surfaces. Despite the limited dissolution of Ag MNP and CeO_2 MNP in soils, the inclusion of $M_{\text{NP_diss}}$ in equation (2) leads to a different ranking of soils in terms of K_r values of Ag MNP (Table 8). Not including $M_{\text{NP_diss}}$ in equation (2) thus 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 this method, but needs to be distinguished from retention. The unknown retained MNP concentration (M_{solid}) was thus calculated as $M_{\text{added}} - M_{\text{NP}} - M_{\text{NP_diss}}$. The concentrations M_{NP} and $M_{\text{NP_diss}}$ 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 $M_{\text{added}} - M_{\text{MF}} + M_{\text{geo}}$ and M_{NP} in the denominator of equation (2) as $M_{\text{MF}} - M_{\text{UF}}$ because M_{geo} is already included in M_{UF} . The final equation to determine K_r values for Ag and CeO₂ MNP in soils can be expressed as:

$$K_r = \frac{M_{\text{add}} - M_{\text{MF}} + M_{\text{geo}}}{M_{\text{MF}} - M_{\text{UF}}} * \frac{L}{S} \quad [\text{L kg}^{-1}] \quad (3)$$

Table 8. K_r values for Ag MNP calculated including dissolved MNP (see text) (mean \pm standard deviation).

Soil	AgMNP (L kg ⁻¹)
Mount Compass	60 \pm 5
Tepko	68 \pm 18
Minnipa	76 \pm 9
Lower SE	489 \pm 101
Emerald Black	2,165 \pm 5

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