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5 Maria del Carmen Hernández-Soriano, Aránzazu Peña and M. Dolores Mingorance*

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■ Environmental hazard of cadmium, copper, lead and zinc in metal-contaminated soils remediated by sulfosuccinamate formulation

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Accumulation of metals in soil at elevated concentrations causes risks to the environmental quality and human health for more than one hundred million people globally. The rate of metal release and the alteration of metal distribution in soil phases after soil washing with a sulfosuccinamate surfactant solution (Aerosol 22) were evaluated for four contaminated soils. Furthermore, a sequential extraction scheme was carried out using selective extractants (HAcO , $\text{NH}_2\text{OH} \cdot \text{HCl}$, $\text{H}_2\text{O}_2 + \text{NH}_4\text{AcO}$) to evaluate which metal species are extracted by A22 and the alteration in metal distribution upon surfactant-washing. Efficiency of A22 to remove metals varied among soils. The washing treatment released up to 50% of Cd, 40% of Cu, 20% of Pb and 12% of Zn, mainly from the soluble and reduction soil fractions, therefore, greatly reducing the fraction of metals readily available in soil. Metal speciation analysis for the solutions collected upon soil washing with Aerosol 22 further confirmed these results. Copper and lead in solution were mostly present as soluble complexes, while Cd and Zn were present as free ions. Besides, redistribution of metals in soil was observed upon washing. The ratios of Zn strongly retained in the soil matrix and Cd complexed with organic ligands increased. Lead was mobilized to more weakly retained forms, which indicates a high bioavailability of the remaining Pb in soil after washing. Comprehensive knowledge on chemical forms of metals present in soil allows a feasible assessment of the environmental impact of metals for a given scenario, and possible alteration of environmental conditions, and a valuable prediction for potential leaching and groundwater contamination.

Introduction

Soil contamination is a worldwide environmental concern due to the potential risks for human and environmental health. Soils are prone to contamination with trace metals by anthropogenic activities associated with agricultural, industrial, mining and waste disposal sectors. Trace metals originating from these sources largely accumulate in soil and may pose a greater risk to

the environment¹ than those from pedogenic or lithogenic sources as they are present in more mobile fractions and are, consequently, more available.² One permanent solution for soil pollution abatement could be the removal of contaminants from the soil in order to minimize environmental and health risks.

Several approaches can be applied for the remediation of contaminated soils, namely chemical treatment, soil flushing and washing, electrokinetic methods, bioremediation, phytoremediation techniques and thermal treatment.³ Among these strategies, chemical extraction, *i.e.* washing the soil with an appropriate reagent, represents a very promising method. There are four major ways for mobilizing metals in soils: (a) changes in the acidity, (b) changes in solution ionic strength, (c) changes in the redox potential and (d) formation of complexes. Concerning

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Environmental impact

Accumulation of metals in soil at elevated concentrations causes worldwide risks for environmental quality and human health. This study provides a comprehensive evaluation of the metal partitioning and soil solution speciation upon soil washing with an anionic surfactant solution. The washing treatment removed a large amount of the metals present in the soils, mainly those present as readily available forms, but the redistribution of the remaining amounts of metals in soil that differed among soil metal type is essential for risk assessment and successful application of remediation strategies.

the last one, among the numerous reagents evaluated in the literature, anionic surfactants have been largely used due to their intrinsic properties,⁴ the relatively low product cost and the wide range of application.^{5,6}

Among the anionic-surfactant types, sulfo-carboxylic compounds comprise the largest group of synthetic surfactants, accounting for approximately 50% of the world's production.⁴ Sulfo-dicarboxylic surfactants, such as sulfosuccinamate compounds, are commonly applied for the complexation of trace metals^{7,8} and their ability to release metals from multi-metals contaminated soil has been recently evaluated.⁹ Moreover, mobilization of metals in soils by anionic surfactants (*i.e.* sulfosuccinamate) has been recently demonstrated to directly depend on metal-surfactant complexation reactions and, indirectly, on the effects of the surfactant on soil organic matter solubility.⁹ Therefore, the introduction of co-solutes (*i.e.* surfactants) alters metal solid-phase fractions of the soil and, consequently, the availability of the remaining metals.^{10,11} Additionally, these compounds can also reach the soil unintentionally through disposal of wastes and wastewater, which contain large amounts of anionic surfactants due to the extensive use of detergents, increasing metal hazard to different environmental compartments and to living organisms.

A comprehensive evaluation of the chemical binding forms of metals in soil is a consistent approach for estimating the potential environmental hazard associated with metals release from soil.¹² Thus, sequential chemical extraction techniques provide a reliable tool for characterizing the different bonding fractions of a given metal in the soil.^{13,14} Such techniques are an analytical multi-step procedure that chemically leaches metals from soil mimicking the release of the metals into solutions under various environmental scenarios.

Hence, the aim of this study was to determine the chemical species of Cd, Cu, Pb and Zn in metal-contaminated soils and to predict the potential availability of these metals after washing with Aerosol 22, a sulfosuccinamate model compound. Batch extraction tests were performed on four soils with contrasting properties and a wide range of multi-metal contents, before and after washing the soils with the Aerosol 22 solution. Redistribution of metals and the environmental hazard related to remediation of metal-contaminated soils were evaluated.

Materials and methods

Soil samples

Four contaminated soils with a wide range of metal contents were selected for this study (Table 1). Main soil properties were

measured by standard methods described elsewhere.⁹ For pseudo-total metal analysis, samples of 0.1 g of soil were treated with 3 mL of *aqua regia* in pressurized PFA digestion vessels in a microwave digester (Milestone 1200 Mega, Italy). Digestion was carried out in quadruplicate.

Water soluble metals were extracted (soil : solution ratio 1 : 10 kg L⁻¹) at 20 °C in an end-over-end shaker at 30 rpm with MilliQ-Plus water (MQ). After 24 h, suspensions were centrifuged at 3000 rpm for 20 min. The supernatant was sampled and analyzed for total dissolved organic carbon (DOC) using a Total Organic Carbon (TOC) analyzer (Analytical Sciences Thermalox). Total DOC comprises carbon corresponding to soil soluble organic matter plus the carbon in solution due to the presence of A22. The DOC concentration derived from the soil can be calculated from the measurement of the UV absorbance at 254 nm and the total DOC concentration of the solutions as described elsewhere.⁹ A subsample was acidified to pH 1 with HNO₃ and analysed for metals concentration with ICP-OES.

Soil washing

The anionic surfactant Aerosol 22 (tetrasodium *N*(1,2-dicarboxyethyl)-*N*-octadecyl sulfosuccinamate, C₂₆H₄₃NO₁₀Na₄S), a sodium ester with a dicarboxylic functional group (sulfo-succinamate), was purchased from Sigma (Madrid, Spain). Most relevant characteristics of Aerosol 22 (from now on named A22) are: molecular weight, 653 g mol⁻¹; critical micellar concentration (CMC), 0.653 g L⁻¹; 48% of organic carbon in the commercial aqueous solution; pH 8 at a concentration corresponding to 14 times the surfactant CMC (14× CMC).

The soil washing procedure was performed by mixing soil and A22 solution (14 CMC ≈ 9 g L⁻¹) at a soil : solution ratio of 1 : 100 kg L⁻¹ and shaken end-over-end at 20 °C for 24 h.

The optimization of these experimental parameters is thoroughly described elsewhere.¹⁵ Samples were then centrifuged at 3000 rpm for 20 min and the supernatant was acidified with HNO₃ for analysis of Ca, Cd, Cu, Fe, Mg, Mn, Pb, and Zn contents. Total DOC and solubilized soil organic carbon were estimated as described above. After centrifugation, each remaining solid was washed with MQ and air-dried. Then, the total metal content was determined as indicated for native soils.

Sequential extraction procedure

The distribution of metals in the solid-phase was estimated by performing the 3-step sequential extraction scheme proposed by the Standard Measurements and Testing Programme (BCR).

Table 1 Selected physical and chemical properties and total metal content ($n = 4$) of soil samples. Standard deviation values are between brackets^a

Soil name	pH _{H2O}	OC (%)	CEC/ cmol _c kg ⁻¹	CaCO ₃ (%)	Cd/ mg kg ⁻¹	Cu/ mg kg ⁻¹	Pb/ mg kg ⁻¹	Zn/ mg kg ⁻¹	Total metal load/ mmol kg ⁻¹
S1	6.2	11	10	1.2	36.4 (3)	362 (12)	501 (47)	987 (37)	24
S2	7.4	2.5	5.1	35	34.0 (2)	690 (33)	233 (14)	6775 (308)	116
S3	8.4	2.0	12	8.1	41.7 (1)	114 (2)	1162 (31)	350 (5)	13
S4	8.5	0.92	7.9	25	18.0 (2)	247 (5)	638 (18)	877 (22)	21
Target ^b					0.8	36	85	140	
Intervention ^b					12	190	530	720	

^a EC: electrical conductivity; OC: organic carbon; CEC: cation exchange capacity. ^b Dutch guidelines.

Details on the experimental conditions are available elsewhere;^{16,17} and described in Table 2. Briefly, an aliquot of soil is mixed with the extractant in a centrifuge tube for the established time, the suspensions are then centrifuged at 3000 rpm and the supernatants carefully removed and stored in polyethylene bottles at 4 °C until analysis. The residues are washed with MQ water before the addition of the next extracting agent. Blanks were included to evaluate contamination sources. All tests were performed in triplicate. Relative standard deviations of the results at each step were typically below 10%.

Metal analysis

Metal concentrations in the extracted/digested solutions were determined by ICP-OES. Detection limits were: Cd, 0.01 mg L⁻¹; Cu, 0.03 mg L⁻¹; Pb, 0.15 mg L⁻¹; and Zn, 0.02 mg L⁻¹. All chemicals used were of analytical reagent grade. MQ water was used for all preparations of solutions. All labware used was previously soaked in a nitric acid 4 M solution for at least 24 h and then rinsed with MQ.

Data analysis

The partition index of each metal, *I*, and the reduced partition index (*I_R*) were calculated according to eqn (1) and (2), respectively.¹⁸ This parameter provides a quantitative estimation of the availability of metals in soils, simplifying the comparison of the binding intensity of a given metal among soils or of different metals in the same soil. Extractants used in the sequential extraction scheme ranged from 1 to 4. The value of *i* in eqn (1) increases in accordance with the gradual increase in the aggressiveness of extractants (1: least aggressive, *k*: most aggressive). The *F_i* is the fractional content of the element in the solid-phase *i* and *n* is an integer number of value set to 2.¹⁸

$$I = \sum_{i=1}^k F_i \times (i)^n \quad (1)$$

$$I_R = \frac{I}{(k)^n} \quad (2)$$

Low *I_R* value for a given metal indicates the presence of the metal in the soluble and exchangeable fraction, whereas a high value (close to one) points to a large proportion of the metal strongly retained in the residual fraction. Intermediate values suggest metal partitioning among all solid-phase components.

Table 2 Sequential extraction scheme (BCR) soil metal fractionation^a

Nominal target phase	Extractant	(L/S)/mL g ⁻¹	Shaking time/h
Exchangeable + acid- and water-soluble (SOL)	HAcO 0.11 M (pH = 2.85)	40/1	16
Reducible (RED)	NH ₂ OH·HCl 0.5 M (pH = 1.5)	20 mL	16
Oxidable (OX)	H ₂ O ₂ (8.8 M) + NH ₄ AcO 1 M (pH = 2)	(a) 10/1 (b) 50/1	(a) 2 (b) 16
Residual (RES)	(pseudo-total) – (F ₁ + F ₂ + F ₃)		
Pseudo-total (T)	<i>Aqua regia</i>	10/0.2	—

^a L/S: extractant volume to soil mass ratio.

Removal efficiency with the A22 solution was calculated for each metal (*M*) as the amount of the metal extracted (mg kg⁻¹) related to the total content of the given metal (mg kg⁻¹).

$$\text{Removal (\%)} = \frac{M_{A22}}{M_{\text{total}}} \times 100 \quad (3)$$

The speciation analysis of the solutions collected upon extraction with Aerosol 22 was carried out using the speciation model WHAM VI¹⁹ as described by Van Laer *et al.* (2006).²⁰

The relationship between variables was determined by correlation or regression analysis. For all tests, correlation was considered significant for *p* < 0.05. Statistical analysis was performed with the software package SPSS 17.0 (Illinois, USA).

Results and discussion

Four soils with contrasting properties were selected for this study (Table 1). The soils studied can be considered as low quality soils.^{21,22} Soils S2 and S4 present a significant concentration of CaCO₃. Low organic matter contents and CEC values indicate a short capacity for retaining metals, except for S1, and a larger susceptibility of these soils to environmental changes.

Total metal concentrations in the soils (Table 1) exceed the reference value for all metals and the intervention values in all cases, except Zn and Cu in S3 and Pb in S2, according to the Dutch guidelines.²³ The “intervention values” compiled in the Dutch guidelines are maximum tolerable concentrations above which remediation is required. The Dutch guidelines were used on the basis that they are a long established, tried and tested scheme, where intervention values are based on extensive studies of both human and eco-toxicological effects of contaminants.

Soils evaluated can be considered as severely contaminated and constitute an environmental and human health risk requiring the implementation of a remediation scheme.

Soil washing with MQ water was carried out to estimate the fraction of metal that is weakly bound to the soil particles or adsorbed on easily reachable coordination sites on the outer surface of soil particles. The metal content in the water extract was below the detection limit of the analytical method for the metals considered, suggesting a low concentration of metals in the soluble phase.

Soil washing with A22 solution

The ability of A22 for metal extraction has been previously reported to depend on the concentration of A22 in the washing solution, the soil/solution ratio and the pH.¹⁵ Selection of the

adequate concentration of A22 and soil/solution ratio to release metals is essential for minimal environmental damage and utmost feasibility.¹⁵ However, these constraints may result in a substantial amount of metals remaining in soil after washing treatment, especially for heavily contaminated soils. The experimental conditions to perform extraction with A22 have been previously optimized, and soil washing was performed accordingly, using A22 aqueous solution at a concentration corresponding to 14× CMC (about 9 g L⁻¹).

Surfactant-mediated release of metals from soil differed for the metals considered, with a general trend Cd > Cu > Zn > Pb (Table 3), although the efficiency of A22 for metal removal was particularly low for S2. On the other hand, a positive correlation ($r = 0.669$, $p = 0.009$) was determined between metals leached by A22 and the total metal contents in the soils. No significant relation was found with soil physicochemical properties but the removal efficiency of A22 can be ranked as follows: S4 (40%) > S1 (14%) > S3 (13%) > S2 (8%), when the simultaneous extraction of the different metals is considered and expressed as mmolar concentration (Table 3).

Chemical composition of the leached A22 solution showed a significant release of some macroelements (Fe, Ca, Mg and Mn), described in Table 3, which play a structural role in soil organic matter and minerals. Similar results are described by other authors for soil washing with EDTA solutions.²⁴

Solid-phase distribution of metals

The application of the BCR speciation scheme allows determination of the concentration of metals associated with the exchangeable + water- and acid-soluble phases (SOL), the reducible phase (bound to iron and manganese oxides, RED) and the oxidizable phase (bound to organic matter and sulfides, OX). Metals associated with the residual fraction (RES), correspond to the metals occluded in the soil mineral phase. The selectivity and specificity of this methodology have been discussed in the literature. A major objection for sequential-extraction methods is that the pools of metals extracted are usually considered as operationally defined and the extraction is not completely selective.²⁵ In addition, solutions used in sequential-extraction methods may create reaction artefacts that do not occur *in situ*.²⁶ Despite the limitations considered, these methods have been proved as useful for determining the potential bioavailability of metals.²⁵

Fig. 1 summarizes the initial metal distribution in the four soils assayed and the distribution of remaining metals in the soils after washing with A22, expressed as the percentage of metal extracted related to total metal concentration and according to the

fractions. Despite the different behaviour observed for each metal, a linear relationship ($p < 0.001$) was determined between metals leached by A22 washing and metals in the SOL for the four soils evaluated ($A22 = 0.47 \times SOL$, $R^2 = 0.926$). This equation demonstrates that A22 solutions remove, on average, 47% of the metal linked to the SOL fraction, *i.e.* the most soluble species of metals.²⁷

Comparison of the relative retention strength of several metals in a given soil and that of a particular metal among soils was evaluated by means of the reduced partition index (I_R) as defined by Han and Banin in 1999.¹⁸ This parameter estimates the distribution of a given metal amongst the soluble fraction and the strongly retained forms in soil.

The I_R values determined for Cd, Cu, Pb and Zn and the studied soils are summarized in Table 4. The I_R values obtained prior to the washing treatment indicate that for soil S2 the four metals are mostly present as readily available forms. For S1 and S4 soils, Cd and Zn are also highly available, while Cu and Pb might be retained in less available phases. Finally, I_R values for S3 point to Cd as the only metal readily available while the other three metals are mostly retained on the solid-phases. These results were further confirmed with a cluster analysis (data not shown), which showed that I_R values in soils before the washings are mostly related to soil CEC and OC values. The cluster analysis also suggests that I_R values after washing with A22 are related to soil carbonate content and pH. The I_R values determined after the washing treatment indicate that, for all soils, the remaining amounts of Cd and Zn present low availability. Particularly, a 3-folded decrease in Zn availability was observed in S2 after the washing treatment. The surfactant may remove the soluble Cd and Zn during the washing treatment by direct complexation, and therefore the remaining amount of these metals corresponds to the less available forms, which explains the decrease in bioavailability. The affinity of A22 for Cd and Zn has been previously described⁹ and is comparable to that of succinate for divalent cations ($\log K$ 2.6 and 2.5 for Cd and Zn, respectively). A slight increase in Pb availability was observed in all cases after washing. Finally, changes in Cu availability largely differed among the soils studied (Table 4).

Distribution of metals in soils before washing

Despite the variability on Cd concentrations among soils, the largest concentration of this metal was determined in the soluble fraction (35–81%), confirming the anthropogenic origin of this metal in the soils studied² and the RED fraction (19–65%) related to Fe/Mn oxides.²⁸ The Cd-SOL tends to increase with soil pH ($r = 0.952$, $p = 0.048$) while Cd-RED tends to decrease ($r =$

Table 3 Total metal and dissolved organic carbon (DOC) extracted by A22 washing for the four soils and the experimental setup (soil : solution ratio 1 : 100 kg L⁻¹; A22 solution at 9 g L⁻¹). Average values of three replicates are shown (relative standard deviation <10% in all cases). Percentages of extracted metal related to total content are indicated in brackets

Soil name	Cd/ mg kg ⁻¹	Cu/ mg kg ⁻¹	Pb/ mg kg ⁻¹	Zn/ mg kg ⁻¹	Total removal/ mmol kg ⁻¹	Fe/ mmol kg ⁻¹	Mn/ mmol kg ⁻¹	Ca/ mmol kg ⁻¹	Mg/ mmol kg ⁻¹	DOC/ mg kg ⁻¹
S1	9.1 (25)	106 (29)	<	112 (11)	3.5	6.2	0.5	98.1	5.5	440
S2	7.8 (23)	59 (8.5)	<	558 (8)	9.5	5.6	0.1	158.6	6.4	262
S3	20.5 (58)	33 (29)	157 (14)	24.4 (7)	1.8	3.0	0.3	70.5	11.2	298
S4	8.9 (61)	100 (46)	121 (19)	400 (46)	8.3	10.1	0.5	44.9	24.2	305

Fig. 1 Relative metal amount leached by A22 soil washing and distribution of metal in the different soil phases according with BCR sequential extraction scheme. SOL: exchangeable + water- and acid-soluble fraction; RED: reducible fraction; OX: oxidizable fraction; RES: residual fraction.

Table 4 Reduced partition index (I_R) for the total metal content in four soils before and after A22 washing

Soil	A22 washing	Cd	Cu	Pb	Zn
S1	Before	0.19	0.53	0.45	0.18
	After	0.21	0.43	0.34	0.21
S2	Before	0.17	0.31	0.31	0.22
	After	0.27	0.45	0.29	0.68
S3	Before	0.14	0.55	0.47	0.56
	After	0.22	0.74	0.37	0.68
S4	Before	0.10	0.53	0.45	0.18
	After	0.13	0.49	0.33	0.36

0.966, $p = 0.034$). The small amount of Cd associated with OX (1–4%) is consistent with the lower affinity of Cd for organic matter compared with the other metals studied.²⁹ Finally, Cd in RES fraction was consistently lower than 5%. Besides, speciation analysis carried out with WHAM for the solution obtained upon washing with A22 (Table 5) estimated that around 17–30% of Cd in the solution was associated with carbonate ions. For high pH values $\text{Cd}(\text{CO}_3)_2$ aqueous complexes have been described as the dominant species in solution.³⁰

Copper distribution in soil largely varies with soil type, but this metal was mostly associated with RED (22–73%) and OX (14–40%), while in soil S3 *circa* 40% of Cu was found in RES fraction (Fig. 1). The large amount of Cu determined in the reducible fraction may result from the preferential retention of a certain amount of metal in the inorganic soil phases through weak interactions.³¹ The presence of Cu in the SOL fraction was generally low, the highest value determined for S4 (20%). Despite the high affinity of Cu for organic matter, low Cu-OX was found due to both the low soil OC content and the large soil carbonate levels that lead to overloading of available organic ligands with

Ca.³² Finally, Cu-RES was correlated with soil CEC ($r = 0.986$, $p = 0.014$).

Lead partitioning (Fig. 1) showed also the low (<15%) rate of Pb-OX, except for soil S4 (34%) as indicated for Cu. The presence of Pb in the soluble fraction and associated with carbonates was up to 27% (Fig. 1) while 35–86% was determined in the RED fraction (Fig. 1), except for soil S3, suggesting a major role of Fe–Mn oxides in Pb retention.³³ No association was found among Pb fractions and soil properties.

Zinc was mostly located in fractions SOL (12–58%) and RED (37–77%), with <13% associated with OX (Fig. 1), as expected by the lower affinity of Zn for organic ligands compared with the other metals studied.²⁹ The amount of Zn determined in the

Table 5 Percentages of metal as a free ion (M^{2+}), complexed with soluble soil organic matter (ML) and inorganic ligands (MI) estimated with WHAM in the soil solutions collected upon washing with Aerosol 22. Values in *italic* indicate that the main inorganic ligand was hydroxide, otherwise carbonate

		Soils			
		S1	S2	S3	S4
Cd	M^{2+}	29	33	30	34
	ML	35	11	37	11
	MI	17	30	33	17
Cu	M^{2+}	6	12	6	19
	ML	86	68	87	52
	MI	<10	<10	<10	20
Pb	M^{2+}	nd	nd	4	13
	ML	nd	nd	92	66
	MI	nd	nd	<10	20
Zn	M^{2+}	29	33	30	34
	ML	35	11	37	11
	MI	27	38	40	38/16

residual fraction was negligible in soils with lower pH (S1 and S2) but in alkaline soils 20 and 40% of the total Zn was determined in RES (S3 and S4, respectively). The higher mobility of Zn in acid and slightly acids soils has been previously described in the literature.^{27,29}

Redistribution of metals in soils after washing with A22

The remaining amounts of Cd in the SOL phase (18–56%) after A22 washing were lower than before treatment suggesting that soil washing with A22 released Cd from the SOL phase for all soils (Fig. 1). Partial relocation of the remaining Cd in the RED phase was observed for all soils and also in the OX phase (15%) for S4, probably due to complexation of Cd with the fraction of surfactant adsorbed or precipitated in the soil.⁹ The speciation analysis (Table 5) suggests that around 30% of Cd extracted with A22 is present as a free ion (M^{2+}) while 11–37% is complexed with organic ligands (ML) and the rest of Cd is present as soluble carbonates (MI), which further confirms that A22 release more soluble forms of Cd from soil.

After washing, most of the Cu-SOL and part of the RED (up to 50%) in native soil were leached (Fig. 1). On the other hand, Cu-OX did not change or increase as a consequence of the Cu migration from RES (in S1) and from RED (in S2), which could be also attributed to the complexation of Cu with the surfactant retained in the soil. The large percentage of Cu complexed with organic ligands (50–90%) in solution (Table 5) largely explains the great increase of Cu mobility in soils²⁷ and therefore the redistribution of this metal in soil fractions (Fig. 1).

On the other hand, incorporation of Cu onto the RES phase after washing, especially for S3 (Fig. 1), can be explained by the increase of Na^+ ions supplied by A22. The Na^+ ions compete with heavy metals for adsorption on the low affinity planar sites, resulting in the adsorption of heavy metals on the high affinity edge sites.³⁴ This effect is particularly relevant at high pH (Table 1). Besides, precipitation of Cu–organic matter complexes under the influence of an increase in the pH or the ionic force has been previously described.³⁵ Formation of negatively charged complexes between organic ligands, *i.e.* A22 or solubilized soil organic matter, and the Cu^{2+} ion, may enhance the adsorption due to interaction with positively charged surface sites.³⁴ Formation of positively charged metal–ligand complexes, which can be retained through ion exchange, might also occur, and it is consistent with the larger mobilization of Cu to the RES fraction in soil S3, which presents the largest value for cation exchange capacity (Table 1). Mass balance for S3 indicated that increase of RES (Cu +22%; Zn 11%) after washing is consistent with the decrease in RED (Cu –23%; Zn –13%), and confirms that metals are mobilized from the Fe/Mn oxides fraction and adsorbed on the soil mineral phase.

Surfactant washing removed Pb initially present in the SOL fraction (Fig. 1), as previously observed for Cd and Cu. About 66–92% of the Pb in solution was present as soluble organic complexes (Table 5), while only 4–13% is released as a free ion, similarly to the results obtained for Cu. Moreover the metal occluded in RES fraction shifts into more weakly bound forms associated with the OX and RED phases (Fig. 1). Similar Pb relocation has been reported in previous studies.^{36,37} The increase in the concentration of soluble organic matter in solution due to

the washing treatment with A22, and therefore of humic substances, is expected to solubilize Pb-phosphate minerals, decreasing the concentration of Pb in the residual fraction and mobilizing the metal to more available fractions, a process previously described, and particularly relevant at high pH.³⁸

Furthermore, in the case of S2, Pb-RED (40%) shifted to a less accessible form (OX) with an increase of 50% Pb linked to the OX phase. The low concentrations of Pb determined in the SOL fraction (0–27%) suggest that Pb is more retained by soil constituents compared with the other metals studied. Similar results were recently described for the retention of Pb in calcareous soils,³⁹ suggesting a general adsorption of Pb forming hydroxides at the surfaces in the different components of soils. It was found that 20% of Pb complexed with carbonates in soil S4 (25% carbonates) while for S3 *circa* 10% of Pb in solution was forming hydroxides (Table 5). The presence of carbonates leads to the co-precipitation of $PbCO_3$ -like phases, suggesting the substitution of Ca with Pb in $CaCO_3$.

Washing with A22 resulted in a decrease of Zn-SOL for all soils (Fig. 1) in agreement with the large amount of Zn as a free ion (Table 5) found in leached solution. The effect of washing with A22 in Zn partitioning was low (<10%) compared with the other metals (Fig. 1). Zinc not only forms complexes with organic ligands from dissolved soil organic matter (Table 5) but also with A22,⁹ which affects adsorption reactions with the soil surface. As described above for Cu, formation of such complexes and the increase of the concentration of Na^+ ions due to the washing treatment with A22 mobilizes Zn to the RES fraction. Besides, solubility of Zn hydroxides decreases at $pH > 7.7$, which is also consistent with the behaviour of Zn in soils S3 and S4, and a fraction of the species generated by washing with A22 (Table 4) may be strongly adsorbed onto soil surfaces.

Changes in metals availability

For a given environmental scenario of concern, mobilization of metals from soil may result in the contamination of other environmental compartments, *e.g.* groundwater and food chains, ultimately threatening human health. The environmental risk of metal exposure to groundwater hampers the optimization and implementation of washing procedures. In this context, speciation analysis was performed with WHAM for the solutions collected upon washing with A22 (Table 5). Results indicated that Cd and Zn are present in the leached solution as free ion species,⁴⁰ *i.e.* the most mobile forms, representing a high risk for the biota. In contrast, Cu and Pb are present as aqueous complexes showing less availability and consequently lower risk. Though, Degryse *et al.* (2006)⁴¹ suggested that aqueous complexes, when present, can increase metal uptake by plants.

Moreover, the availability of metals in soil can be assessed on the basis of the relative content of metal fractions derived from sequential extraction. The metals present in solid-phase components have been grouped into the *readily available* (exchangeable and carbonate fractions), *potentially labile* (easily reducible oxides and organic fractions), and *non-available* with little or no environmental significance (residual fraction) groups.⁴²

The metals hereby evaluated are highly bioreactive and can induce toxicity due to their high tendency to form mobile complexes. Currently, the absence of a valid general EU

Table 6 Available metals in soils before and after washing soil with Aerosol 22 (A22) and trigger concentrations based on Dutch values and Contaminated Land Exposure Assessment (CLEA 2000) guidelines. In bold values higher than ones before washing soils

	Available Cd/mg kg ⁻¹			Available Cu/mg kg ⁻¹			Available Pb/mg kg ⁻¹			Available Zn/mg kg ⁻¹		
	Readily	Potentially	Leachable ^d	Readily	Potentially	Leachable ^d	Readily	Potentially	Leachable ^d	Readily	Potentially	Leachable ^d
<i>Native soil</i>												
S1	13	24	14	20	254	22	^e	399	^e	449	538	500
S2	15	19	17	28	662	31	7	209	8	1421	5351	1583
S3	30	11	33	5	68	6	308	452	343	40	174	45
S4	15	3	17	48	102	53	116	306	129	505	340	563
<i>Soil A22 washing</i>												
S1	7	21	8	8	239	9	^e	501	^e	322	544	359
S2	5	21	6	2	596	2	^e	233	^e	630	5586	702
S3	9	7	10	1	32	1	143	703	159	24	127	27
S4	5	3	6	10	101	11	^e	517	^e	208	156	232
<i>CLEA threshold</i>												
	15 ^a				130 ^b			1000 ^a			300 ^b	
<i>Groundwater^c</i>												
			0.006			0.075			0.300			0.800

^a Metal which may pose hazards to health when planned uses are parks, playing fields, open space. ^b Metals which are phytotoxic but not normally hazardous to health. ^c Dutch intervention values in groundwater (mg L⁻¹). ^d Free ion in soil solution in mg L⁻¹. ^e Values lower than the detection limit.

framework still hampers the evaluation of metal risk by means of available fraction data. Therefore, for the assessment of the potential contamination degree of soils washed, guidelines from the Contaminated Land Exposure Assessment²³ and the Dutch Ministry for soil have been used. CLEA generates data based on human toxicology and uses Montecarlo simulation to model the potential pathway for human exposure.²³

Results summarized in Table 6 demonstrate that the readily available fraction of metals has been considerably reduced after the washing treatment for the metals and soils evaluated. Following soil washing, Cu showed lower availability, with values below the Dutch Target.⁴³ Lead was also below (except for S3) the Dutch Target, while Cd and Zn values are higher than the Dutch Target but below the intervention values (Table 1).

International environmental groups as the Blacksmith Institute or Green Cross Switzerland situate Pb first in the ranking of toxic threats that impact the health of more than ten million people in the world. Lead can be classified as a “class B” contaminant according to its biological and chemical reactivity, and is considered more toxic than Cd, Cu and Zn, classified as “borderline”. Lead was reduced up to 100% in soils S1, S2 and S4 but only 46% in S3 soil, which contains the highest Pb total content. Besides, the pool of Pb potentially available became more hazardous due to the relocation of Pb from the RES fraction to more soluble fractions (Table 6).

Metal thresholds provided by CLEA²³ in 2000 are given according to phytotoxicity (Cu and Zn) or human toxicity (Cd and Pb). In this case, readily available Pb and Cd values for all soils are below those reported to be hazardous to health, and Cu and Zn (except S2 and S4) are below those values showing some phytotoxicity.

The maximum amount of readily available metals which could reach groundwater is estimated considering an annual average precipitation of 350 mm and assuming that this volume of water enters the soil profile. The term leachable metal refers to the free ions determined in the soil solution (Table 6). Comparing the calculated values with Dutch intervention thresholds for groundwater, the four soils can be considered as prone to leach high amounts of metals, which would compromise groundwater quality.

Conclusions

Washing soil with a sulfosuccinamate formulation resulted in a significant decrease of the readily available metal content constituting a promising option for remediation purposes for soils with contrasting properties and different levels of contamination and, even when a very high metal content was present. Although, in some cases, Cd and Zn concentrations remained above those considered as a potential risk for phytotoxicity and changes in soil condition rapidly increase the mobilization of metals towards groundwater. The high affinity of the metals for the carboxylic groups of A22 causes redistribution of the remaining soil metals among solid phases, which might still pose an environmental hazard, *i.e.* migration of Pb to a more weakly adsorbed phase that may increase its potential availability. The hazard posed by the toxic metals in the environment is determined by their specific physicochemical forms and the soil properties. The generally large concentrations of Ca and low amounts of organic matter in nearly all the soils studied explain the low rates of metals determined in the oxidizable fraction.

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