

Temporal Trends of Metal Extractability in Calcareous soils Affected by Soil Constituents and Metal Contamination Levels

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ABSTRACT: The role played by soil constituents in governing temporal trends of metal mobility in calcareous Mediterranean soils deserves special attention due to the particular soil and climate characteristics. Reactions occurring during the aging modify the metal mobility over time, and the rate of metal application and type of soil can be decisive in the outcome of aging reactions in soils. The aim of the present work was to investigate the role that both metal dose and soil constituents play in temporal trends of (potential) metal mobility in soils offering a natural gradient of carbonate and whose remaining soil constituents differed. Soil samples were spiked with a mixture of Cd, Cu, Pb and Zn at two levels and then left aging for 12 months incubation. Metals were extracted at different time intervals (1 day, 1, 3, 6 and 12 months) with one-step extraction methods to estimate immediate metal mobility (NaNO₃) and potential metal mobility (diethylene triamine pentaacetic acid –DTPA–). At both levels of contamination, NaNO₃-extractable Cd, Cu and Zn concentration values reached equilibrium within the period of incubation. Temporal trend of immediate metal mobility was governed by carbonate fraction for Cd and Cu and by the finest carbonate fraction for Zn. In the case of potential metal mobility, DTPA-extractable metal concentrations did not reach equilibrium within the incubation time. In this case, the combined action of carbonate, organic, Fe-oxide and clay fractions were decisive to define the different temporal trends observed for each metal and level.

Key words: Calcareous soils, Incubation experiment, Metal mobility, Soil properties, Temporal trends

INTRODUCTION

In any study aimed at accurately predicting the behaviour of metals in soils, it is important to know the metal sorption-desorption processes in the preliminary stages of contamination, and also to investigate the dynamics of metals over time (McLaughlin, 2001). Metal sorption processes in soils are characterized by an initial stage of relatively rapid sorption, followed by a secondary stage that may continue over weeks, months or even years (Smolders & Degryse, 2007). These processes, known as “natural attenuation” or “aging”, are caused by metal diffusion to internal sorption sites by migration, adsorption, surface precipitation or redox processes (Pueyo *et al.*, 2008). Reactions occurring during aging modify metal mobility over time, and should consequently be considered for risk assessment purposes (Sayen *et al.*, 2009).

It has been reported that the outcome of aging reactions in soils where metal loadings are higher are similar to those in metal deficient soils, although the processes may differ due to the higher metal concentrations involved, i.e. precipitation reactions may become more important at high metal loadings and at longer contact times, months or years (McLaughlin, 2001). In this context, factors such as the rate of metal application and the type of soil can be decisive (Han & Banin, 1999). In calcareous soils, due to the presence of CaCO₃ compounds and to soil pH values, aging processes can be expected to be more pronounced than in soils with a low pH (Lock & Janssen, 2003). Nevertheless, in recent works conducted in metal-spiked calcareous soils after 12 months of contact time, we observed a high potential mobility of metals despite the elevated metal sorption

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capacity of these soils (de Santiago-Martín *et al.*, 2013a,b). Furthermore, we also reported that the carbonate fraction alone could not explain the metal mobility patterns, indicating that other soil fractions may play a key role in governing the temporal trends of metal mobility.

The aim of the present work was to investigate the role that both metal dose and soil constituents play in the temporal trends of (potential) metal mobility in soils with a natural carbonate gradient and whose remaining soil components differed. With this purpose, soil samples were spiked with a mixture of Cd, Cu, Pb and Zn at two different levels, and allowed to age for 12 months under incubation before the metals were extracted with one-step extraction methods at different time intervals. Differences in temporal trends among metals, dose levels and soils are discussed.

MATERIALS & METHODS

The soil samples come from different plots in an Agricultural Research Station (Alcalá de Henares, Madrid, Spain), at an altitude of 588 m, on quaternary sediments (IGME, 1990), as previously reported (de Santiago-Martín *et al.*, 2013a,b). Soils classified as calcaric Fluvisol (Moreno Merino, 1998) present Anthric characteristics today (FAO, 2006). The average annual temperature is 13 °C, average annual rainfall is 401 mm/year and potential evaporation is about 760 mm/year. A set of six soil samples with different carbonate content –moderate (S1M and S2M), low (S3L and S4L) and very low (S5VL and S6VL)– was selected based on information from previous studies (de Santiago-Martín *et al.*, 2013a,b; Lafuente *et al.*, 2008). Several properties of the soil samples are shown in Table 1. The total metal contents in the selected soils were fairly small, being total Cu = 10.1 ± 1.1; total Pb = 27.2 ± 6.0 and total Zn = 56.9 ± 3.6 mg/kg. The total Cd

contents were below our quantification limit and were not quantified in the initial soil samples. These values were consistent with contents reported by other authors for low- or unpolluted agricultural soils of the Mediterranean area (Jiménez Ballesta *et al.*, 2010; Micó *et al.*, 2006; Peris *et al.*, 2007), and in no case exceeded the levels set by the European Union (Directive 86/278/EEC). Sampling was done at randomly selected points. To avoid potential bias, 30-40 kg were taken from each sampling point (0-30 cm) and homogenized. Soil samples were air-dried and passed through a 2 mm sieve.

The selected unpolluted soil samples were spiked with a multi-element salt solution of metals to mimic the situation which would occur in multi-element contaminated soils. Metal-spiking and soil aging is extensively reported in a previous work (de Santiago-Martín *et al.*, 2013a,b), but in the present paper we have used two different metal contamination levels. Briefly, two containers (40 cm wide x 59 cm long x 21 cm high), weighing 10 kg each, were set for each sample, and nitrate salts of heavy metals in aqueous solution were spiked at two different levels: the Tt1 level (3 mg/kg Cd + 140 mg/kg Cu + 300 mg/kg Pb + 300 mg/kg Zn) and the Tt2 level (20 mg/kg Cd + 875 mg/kg Cu + 600 mg/kg Pb + 2000 mg/kg Zn) within the limit values proposed by current European legislation (Directive 86/278/EEC). The soil sample and the metal solution were mixed and left to equilibrate for a period of 12 months at room temperature without cover or drainage. During this equilibration period, the soils were air-dried, mixed and rewetted with distilled water in cycles of about 2 weeks, in order to favour metal redistribution into the soil matrix (McLaughlin, 2001). Duplicate subsamples were randomly removed from each metal-spiked soil sample at different time intervals (1 day, 1,

Table 1. Physicochemical parameters of un-spiked soil samples

Soil sample	pH	Carbonate fraction		Organic fraction			Oxide fraction	Particle-size distribution			
		ECC	AL	TOC	OM	C/N	Cry-Fe	CS	FS	Silt	Clay
		g/kg		g/kg			g/kg	g/kg			
S1M	8.4	190	77	6	10	8	8	111	603	126	161
S2M	8.1	148	53	12	20	12	9	114	569	124	193
S3L	8.2	106	21	18	32	11	13	159	590	78	172
S4L	8.1	100	42	8	13	10	10	112	462	167	259
S5VL	8.2	27	15	12	21	11	12	99	386	172	344
S6VL	8.2	9	6	8	14	8	7	245	560	70	124

ECC = equivalent CaCO₃; AL = active lime; TOC = total organic C; OM = organic matter; Cry-Fe = crystalline Fe oxides; CS = coarse sand; FS = fine sand.

3, 6 and 12 months) using one-step metal extraction methods which estimate the immediate mobility (0.1 M NaNO₃) and the potential mobility (0.005 M DTPA) of metals (Gupta *et al.*, 1996). From data, differences in temporal trends among metals, dose levels and soils were discussed. Some of the analytical data of metal extractions used in the present work were obtained from data published previously. All chemicals were obtained from analytic grade reagents of Merck (Germany) and Panreac (Spain). All glassware used was pre-washed with an aqueous solution of HNO₃ 0.1 % for 24 h and rinsed with de-ionized type I water. According to ISRIC methods (2002), the following parameters were determined in un-spiked soil samples: soil pH in a 1:2.5 soil to water ratio; equivalent CaCO₃ –ECC– according to the acid neutralization method; total organic C by the Walkley and Black wet oxidation procedure; particle-size distribution by Robinson’s pipette method; crystalline Fe oxide contents by dithionite-citrate extraction; in addition to acid oxalate extraction. The active equivalent CaCO₃ or “active lime” –AL– was determined with NH₄-oxalate as described by Drouineau (1942). Total Cd, Cu, Pb, and Zn contents of the soil samples were determined after wet digestion (150 °C, 6 h) with a mixture of nitroperchloric-hydrofluoric acids under high-pressure conditions using PHAXE 2000 reactors (SISS, 1985). Metal concentration in the extracts was quantified by flame atomic absorption spectroscopy –FAAS– (Analytikjena NovAA 300). Quantification limits in

mg/L were: Fe = 0.5, Cd = 0.2, Cu = 0.2, Pb = 0.5 and Zn = 0.1. All samples were extracted and analysed in duplicate.

To determine extractable metals in metal-spiked soil samples, we used the following procedures: NaNO₃-extractable metals were determined by shaking 16 g of soil with 40 ml of 0.1 M NaNO₃ for 2 h (Gupta & Aten, 1993); DTPA-extractable metals were determined by shaking 20 g of soil with 40 ml of 0.005 M diethylenetriaminepentaacetic acid (DTPA) + 0.01 M CaCl₂ + 0.01 M triethanolamine for 2 h (Lindsay & Norwell, 1978). The samples and the extraction solution were shaken in a vibrator agitator (Vibromatic, Selecta) at 400 oscillations per minute (opm) and centrifuged at 3500 rpm for 15 min and then the supernatant was filtered (low ash filters, 5-7 µm). Dilutions were made with the corresponding extraction solution. Cadmium, Cu, Pb and Zn concentration in the extracts was quantified by FAAS.

RESULTS & DISCUSSION

Results of temporal trends of immediate metal mobility estimated using NaNO₃ extractions are shown in Fig. 1, expressed in mg/kg. Relative metal extractability is shown in Table 2, expressed in % (NaNO₃-extractable metal vs. total metal content). The temporal trends of the NaNO₃-extractable metal concentration values were substantially affected by the nature of the metal and the concentration of the mixture added. A similar temporal trend was observed

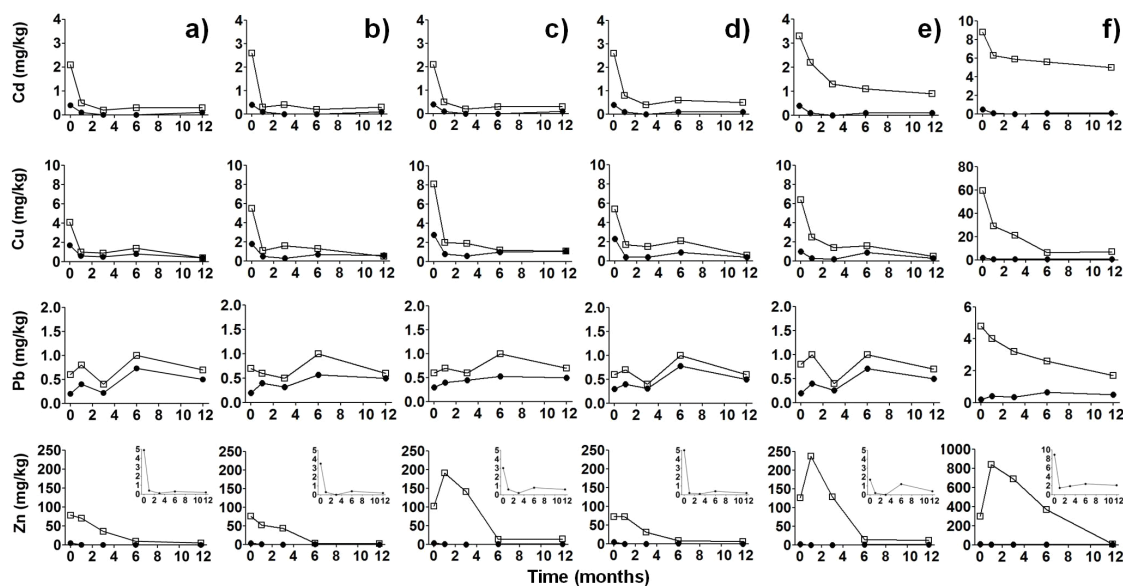


Fig. 1. Temporal trends of Cd, Cu, Pb and Zn extractability with NaNO₃ (mg/kg) in metal-spiked S1M (a), S2M (b), S3L (c), S4L (d), S5VL (e) and S6VL (f) soil samples at the Tt1 (●) and at the Tt2 level (□)

Table 2. Relative metal extractability with NaNO₃ (% extractable metal vs. total metal content) in metal-spiked soil samples at the Tt1 and Tt2 levels at different contact times (1 day, 1, 3, 6 and 12 months)

Level	Sample	Cd					Cu					Pb					Zn				
		1d	1m	3m	6m	12m	1d	1m	3m	6m	12m	1d	1m	3m	6m	12m	1d	1m	3m	6m	12m
Tt1	SIM	14.34	2.61	0.00	1.54	3.00	1.18	0.42	0.39	0.58	0.31	0.08	0.14	0.07	0.24	0.16	1.64	0.13	0.04	0.10	0.08
	S2M	14.00	2.71	0.09	1.49	2.75	1.28	0.34	0.21	0.49	0.45	0.07	0.14	0.11	0.19	0.16	1.18	0.09	0.00	0.12	0.07
	S3L	14.05	2.76	1.07	1.71	2.92	1.97	0.58	0.44	0.71	0.75	0.09	0.14	0.15	0.18	0.15	1.01	0.20	0.08	0.27	0.21
	S4L	14.40	2.71	0.13	2.08	3.02	1.67	0.28	0.28	0.65	0.31	0.09	0.15	0.10	0.26	0.17	1.66	0.07	0.02	0.13	0.07
	S5VL	14.34	2.59	0.16	2.19	2.84	0.73	0.21	0.17	0.67	0.21	0.07	0.15	0.09	0.24	0.16	0.56	0.05	0.00	0.41	0.13
	S6VL	16.05	3.06	0.86	3.30	3.93	1.25	0.34	0.40	0.54	0.41	0.07	0.15	0.12	0.22	0.16	2.95	0.49	0.65	0.80	0.72
Tt2	S1M	10.70	2.61	1.20	1.67	1.65	0.47	0.11	0.10	0.16	0.05	0.10	0.13	0.07	0.17	0.11	3.93	3.53	1.80	0.48	0.27
	S2M	13.19	1.45	2.19	1.17	1.43	0.62	0.13	0.18	0.15	0.05	0.12	0.09	0.07	0.17	0.10	3.78	2.59	2.18	0.16	0.09
	S3L	16.11	5.86	4.53	3.40	3.35	0.93	0.23	0.22	0.14	0.12	0.09	0.12	0.10	0.17	0.11	5.10	9.51	7.04	0.68	0.76
	S4L	13.20	4.17	1.98	2.90	2.65	0.62	0.19	0.17	0.24	0.07	0.10	0.12	0.07	0.17	0.11	3.63	3.60	1.54	0.43	0.31
	S5VL	16.67	10.90	6.29	5.55	4.42	0.74	0.29	0.16	0.19	0.05	0.14	0.17	0.07	0.17	0.11	6.27	11.83	6.39	0.73	0.57
	S6VL	44.07	31.50	29.60	28.06	25.24	6.81	3.34	2.39	0.73	0.82	0.80	0.67	0.53	0.43	0.28	14.85	41.88	34.31	18.39	0.50

for Cd, Cu and Zn extractability, mainly at the Tt1 level, and a different trend for Pb.

At the Tt1 level, we observed a sharp decrease (~ 64-96 % decrease) during the first month of contact time of NaNO₃-extractable Cd, Cu and Zn concentrations. Concentration values reached equilibrium and remained constant in all soil samples over the subsequent 11 months. Results suggest a rapid redistribution of the metals in the different soil fractions (McLaughlin, 2001).

The influence of some soil constituents on metal extractability with incubation time was revealed mainly at the highest contamination level (Tt2). At this level, carbonate and fine mineral fractions appeared to play an important role in Cd, Cu and Zn extractability. Thus, NaNO₃-extractable Cd and Cu concentration values at the Tt2 level reached equilibrium at different contact times (Fig. 1) depending on the ECC content (Jalali & Khanlari, 2008). Indeed, in soil samples with higher ECC content (S1M, S2M, S3L, and S4L samples), NaNO₃-extractable Cd and Cu values sharply decreased (~ 65 % decrease), and equilibrium was reached during the first month (Fig. 1a,b,c,d). Thereafter concentrations of both levels (Tt1 and Tt2) tended to equalize despite the fact that Cd and Cu concentrations added in the mixture were ~ 6 times higher at the Tt2 level than at the Tt1 level. This pattern was more evident in the case of Cu, suggesting a higher Cu sorption capacity in calcareous soils than for Cd (Jalali & Moharrami, 2007). Nevertheless, as the ECC content decreases (S5VL and S6VL samples), a longer contact time was required to reach equilibrium –up to 6 months for Cu and > 12 months for Cd– and differences in concentrations between the two levels were more evident (Fig. 1e,f). In the case of Zn extractability at the Tt2 level (Figure 1), equilibrium was reached within the incubation time (> 6 months, ~ 90 % decrease), except in the S6VL sample (Fig. 1f), and Zn concentrations at this level were approaching those of the Tt1 level. However, two clear temporal trends could be distinguished during the first month of incubation, highlighting the key role played by soil constituents in Zn redistribution. Thus in S1M, S2M and S4L soil samples (Fig. 1a,b,d), a gradual decline in Zn extractability was observed from the beginning of the experiment. Conversely, in S3L, S5VL and S6VL soil samples (Fig. 1c,e,f), extractable Zn values increased during the first month of contact time and then subsequently decreased sharply. This pattern could be due to the proportion of carbonate fraction in the samples. Thus, a rapid Zn redistribution in the carbonate fraction could explain the temporal trend

observed in the case of samples with higher ECC content (S1M and S2M). In soil samples with very low ECC content (S5VL and S6VL) (Fig. 1e,f), the competitive processes exerted by other metals (Cd and Cu) or major cations (Ca and Mg) in soil solution with a higher affinity to the carbonate fraction could account for the initial increase in extractable Zn concentration values. In this regard, the longer time required for extractable Cd and Cu concentrations to reach equilibrium in these soil samples would support this hypothesis. As previously reported, the simultaneous presence of metals can increase the amount of metals released in the exchangeable fraction (Morera *et al.*, 2001). In our case, this behaviour was more evident as the ECC content decreased. Nevertheless, S3L and S4L samples do not follow this pattern and showed an opposite temporal trend (Fig. 1c,d), despite the fact that the ECC content was the same in these samples, ~ 100 g/kg. The different concentration of active lime (AL) between S3L and S4L samples is particularly worth noting. Thus, the concentration of AL in the S4L sample is about twice that in the S3L sample (Table 1). So, we hypothesize that AL was the soil constituent that defined these trends, assigning a dominant role to the finest carbonate fraction in governing the temporal trend of NaNO₃-extractable Zn concentration in the shorter term. During the following 11 months, Zn may be redistributed to other soil mineral fractions such as the phyllosilicate fraction, explaining the subsequent decrease in Zn extractability (Jacquat *et al.*, 2009). In previous works we reported that the fine mineral fraction was the main factor in explaining Zn extractability patterns in calcareous soils at 12 months of contact time (de Santiago-Martín *et al.*, 2013a,b). Finally, it should be noted that in the S6VL soil sample (Fig. 1f), NaNO₃-extractable Zn values did not reach equilibrium within 12 months of incubation, probably due to the fact that this sample has the peculiarity of presenting poor ECC, AL and clay contents (Table 1). In the case of Pb, despite the slight increase in its extractable concentration with contact time at both the Tt1 and Tt2 levels, the Pb concentrations extracted with NaNO₃ were too low to assess the temporal trend (Fig. 1), except in the case of S6VL soil at the Tt2 level (Fig. 1f). The low Pb concentration extracted was attributed to the high Pb retention in these soils, probably through the formation of lead oxide carbonate, as stated in previous works (de Santiago-Martín *et al.*, 2013a). This could also explain the different pattern observed in the S6VL soil sample, which can be attributed to its very low proportion of carbonate fraction.

Table 3. Relative metal extractability with DTPA (% extractable metal vs. total metal content) in metal-spiked soil samples at the Tt1 and at the Tt2 levels at different contact times (1 day, 1, 3, 6 and 12 months)

Level	Sample	Cd					Cu					Pb					Zn				
		1d	1m	3m	6m	12m	1d	1m	3m	6m	12m	1d	1m	3m	6m	12m	1d	1m	3m	6m	12m
Tt1	S1M	68.76	65.43	41.79	44.31	35.74	64.93	54.14	50.86	74.10	79.79	62.25	53.40	45.93	50.93	55.73	60.45	53.23	50.27	66.05	66.30
	S2M	65.59	56.90	41.49	49.37	55.57	50.77	42.38	41.32	62.60	80.50	53.88	42.00	39.09	42.32	57.07	49.62	42.97	41.63	58.39	70.00
	S3L	88.41	77.53	66.02	77.50	73.25	58.31	69.01	60.70	79.61	86.43	64.36	68.00	49.06	48.07	55.40	64.37	73.60	78.27	82.60	81.53
	S4L	77.21	62.11	46.65	64.86	56.71	59.65	55.41	41.71	77.66	74.93	61.65	57.80	42.59	56.45	52.57	58.39	56.90	49.97	76.62	71.07
	S5VL	85.10	70.60	64.89	71.03	68.48	60.41	52.22	56.43	67.80	77.57	66.17	56.24	55.26	42.20	53.53	59.19	56.27	70.90	80.64	74.47
	S6VL	86.19	90.40	55.73	70.73	77.96	63.19	79.29	53.04	83.07	98.71	67.15	80.07	48.34	48.17	62.50	61.12	76.70	55.30	89.38	86.77
Tt2	S1M	44.33	27.10	25.04	32.27	43.62	37.36	32.31	28.37	32.72	30.72	3.20	2.92	3.62	6.33	6.48	26.29	29.96	28.84	23.65	20.97
	S2M	42.18	28.31	27.95	44.16	48.63	30.76	33.47	30.91	32.90	30.22	17.97	5.53	5.07	8.25	9.36	19.96	26.64	26.51	20.67	18.63
	S3L	51.06	24.61	27.40	34.20	23.97	30.87	30.88	32.72	32.49	30.17	6.82	3.82	2.78	3.54	3.77	24.40	36.18	34.32	27.46	26.06
	S4L	57.27	38.13	32.09	39.22	25.55	36.06	32.41	27.79	33.63	31.62	4.73	4.32	4.53	5.04	5.77	24.23	22.82	23.33	22.95	21.09
	S5VL	50.91	28.55	31.34	40.08	28.90	43.58	38.10	32.70	35.50	32.85	1.04	2.24	3.65	4.81	5.60	28.97	27.22	24.49	23.51	22.13
	S6VL	60.80	39.37	37.14	33.96	38.67	58.75	54.46	54.34	58.61	53.77	3.13	3.16	2.36	2.92	3.65	20.51	48.92	46.66	52.99	45.72

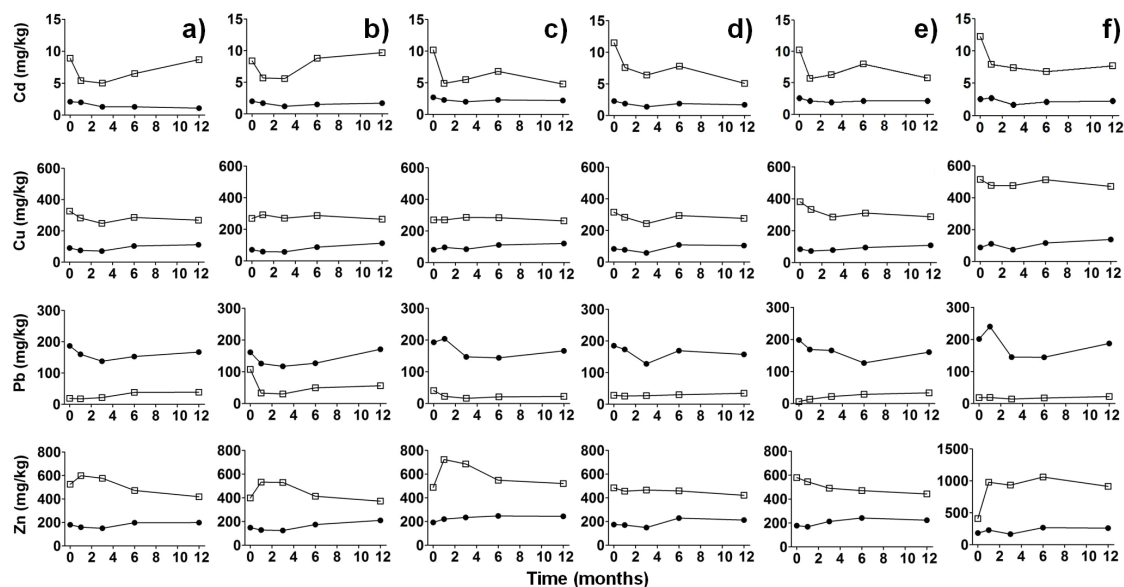


Fig. 2. Temporal trends of Cd, Cu, Pb and Zn extractability with DTPA (mg/kg) in metal-spiked S1M (a), S2M (b), S3L (c), S4L (d), S5VL (e) and S6VL (f) soil samples at the Tt1 (●) and at the Tt2 level (□)

Results of temporal trends of potential metal mobility estimated using DTPA extractions are shown in Fig. 2, expressed in mg/kg. Relative metal extractability is shown in Table 3, expressed in % (DTPA-extractable metal vs. total metal content). As shown in the Fig. 2, the temporal trends of DTPA-extractable metal concentration values varied widely among metals and for each contamination level.

At the Tt1 level, the DTPA-extractable Cd concentration showed an overall decrease ~ 10-48 % at 12 months, without reaching equilibrium during the time experienced (Fig. 2). The lowest Cd extractability at both 1 day and 12 months of contact time was recorded for S1M, S2M and S4L soil samples (Fig. 2a,b,d), probably due to their higher proportion of carbonate fraction, and specifically of AL (Rajaie *et al.*, 2006).

In the case of DTPA-extractable Cu and Zn at the Tt1 level, their concentration values did not reach equilibrium within the contact time of the incubation experiment, and showed ~ 23-59 % increase for Cu and ~ 10-44 % increase for Zn at 12 months when compared to day 1 (Fig. 2). These wide ranges of variation in metal extractabilities among soil samples highlighted the key role that soil constituents play in affecting metal extractability with this method (Reyhanitabar & Gilkes, 2010). Both the increase in Cu and Zn concentrations and the decrease in Cd could be due to Cu and Zn redistribution from the carbonate fraction to the soil fractions for which these metals have high affinity –

such as the organic fraction, mainly in the case of Cu, and the fine mineral fraction, predominantly for Zn – probably through organo-mineral associations (Besnard *et al.*, 2001; Dabkoska-Naskret, 2003). In this scenario, soluble Cd species could be more easily diffused in the crystal defects and pores of the lime, occupying the sites left free by Cu and Zn, and resulting in stable bonds (Buekers *et al.* 2007), leading to decreased Cd extractability.

At the Tt2 level, DTPA-extractable Cd concentration values in samples with low and very low ECC content (S3L, S4L, S5VL and S6VL samples) (Fig. 2c,d,e,f) decreased during the first month (~ 33-52 % decrease), followed by a tendency toward equilibrium. The highest crystalline Fe-oxide content of S3L, S4L, S5VL samples (Table 1) could be the factor responsible for this behaviour, since reactive oxide phases may play a significant role in decreasing Cd solubility after adsorption or coprecipitation (Martínez & McBride, 2001). However in samples with higher ECC content (S1M and S2M samples) (Fig. 2a,b) DTPA-extractable Cd concentration values decreased during the first three months within the contact time of the incubation experiment, and then increased to levels similar to the starting values, showing that other soil fractions were also affecting the temporal trends of extractable Cd.

In the case of DTPA-extractable Cu at the Tt2 level, lower concentrations were extracted in S2M

and S3L samples (Fig. 2b,c) at 1 day of contact time, agreeing with the higher ECC and TOC contents of these samples. However, at 12 months, similar amounts of Cu were quantified in all samples at the Tt2 level (~ 264-287 mg/kg Cu) (Fig. 2), except in the particular case of the S6VL soil sample (~ 471 mg/kg Cu) (Fig. 2f).

In the case of Zn, its extractability with DTPA at the Tt2 level was highly dependent on the fine mineral fraction, clay and silt, as indicated above for NaNO₃ extractions. In fact, in soil samples with a higher clay content (S4L and S5VL samples) (Table 1) Zn concentration values decreased slightly (~ 13-24 % decrease) throughout the incubation time without reaching equilibrium (Fig. 2d,e). In the same way, the highest Zn extractability at 12 months was found in soil samples with a lower silt content (S3L and S6VL samples) (Fig. 2c,f), as previously reported (de Santiago-Martín *et al.*, 2013a,b). Considering that Zn redistribution with contact time to the fine mineral fraction is via specific adsorption, DTPA may exert a weak capacity to extract Zn from the adsorption sites of mineral surfaces. In soil samples with a lower fine mineral proportion, Zn extractability could be affected by the combined action of other soil fractions where Zn was weakly bound. However, due to the non-specificity of the DTPA method we were unable to distinguish them. In any case, these results indicate that in coarser textured soil samples a large percentage of Zn is present as a potentially mobile form, without attaining equilibrium, throughout most of the duration of our experiment.

With regard to DTPA-extractable Pb at the Tt1 level, slight variations in Pb concentrations (~ 11 % net decrease) were observed over the course of the incubation experiment (Fig. 2). This suggested a rapid Pb redistribution in the soil matrix during the first hours of contact time (Jalali & Khanlari, 2008). At the Tt2 level, the results were surprising, since Pb extractability was much lower than at the Tt1 level. The formation of lead oxide carbonate, as stated above, could explain its lower extractability when Pb is added at higher concentrations. Thus in these calcareous soils, lower concentrations of Pb added as soluble salts may involve greater potential mobility, entailing an increased environmental risk.

CONCLUSION

Results showed that the carbonate fraction was the main factor governing temporal trends of immediate metal mobility, estimated using the NaNO₃-method. This fraction thus determined the temporal trend of Cd

and Cu extractability with this method, whatever the contamination level, which led to concentrations of both levels tending to equalize at 12 months. Although the level of contamination was a determining factor in the case of temporal trends of NaNO₃-extractable Zn, the finest carbonate fraction was observed to play an important role in both cases. The low Pb concentrations extracted, attributed to precipitation processes, did not allow us to study the temporal trends of this metal. In the case of potential metal mobility, estimated using the DTPA method, extractable metal concentrations did not attain equilibrium within the incubation time. The combined action of carbonate, organic, Fe-oxide and clay fractions determined the different temporal trends observed for each metal at both levels. Since this has provided evidence for the possible occurrence of competitive processes governed by the differing affinities of these metals to different soil fractions, further research in this direction would be of great interest.

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