



Carbonate, organic and clay fractions determine metal bioavailability in periurban calcareous agricultural soils in the Mediterranean area



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ABSTRACT

A set of periurban calcareous agricultural Mediterranean soils, with a natural gradient in the content and composition of organic matter (OM), was spiked with a mixture of Cd, Cu, Pb and Zn at two levels – designated Tt1 and Tt2 – within the limit values proposed by the current European legislation and incubated for ≤12 months. We conducted bioassay experiments with romaine and iceberg varieties of lettuce (*Lactuca sativa* L.). Metal bioavailability patterns were evaluated as a function of soil constituents and extractable metals.

Metal contamination produced a decrease in plant biomass (up to 50%) and nutrient imbalance. The redundancy analysis showed that the carbonate, OM and fine mineral fractions account for up to 85% of the variance in metal bioavailability patterns in lettuce plants. Carbonate and fine mineral fractions were negatively related to Cd and Zn bioavailability in plants respectively. Organic matter explained Cu and Pb bioavailability, although patterns varied between plant tissues according to their organic composition. The labile fraction limited metal absorption of Pb by roots at the Tt2 level and Cu at both levels, but Cu and Pb translocation was enhanced at both levels. There were significant correlations between metals in leaves and metals extracted with both neutral salts and complexing agents. The high rate of metal translocation and the considerable influence of soil properties may indicate that the limiting values of metals in soils proposed by the current European legislation should be revised in the case of multi-component systems, and/or be established according to the soil characteristics.

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1. Introduction

A large part of Spain's periurban agricultural areas is threatened by heavy metal contamination caused by the recent increase in urban and industrial expansion; this is now a widespread phenomenon throughout most European Mediterranean regions (Maas et al., 2010). The increased metal content in agricultural soils raises concern about potential damage to human health through crop intake (Kabata-Pendias and Pendias, 2001; Peris et al., 2007). This is a common scenario in the calcaric Fluvisols in the southeast of the Madrid region (central Spain), which have a high agricultural and economic value.

Mobility patterns in soils differ for each metal and are strongly influenced by soil parameters such as soil pH, organic matter (OM)

content, clay mineralogy, and the concentration and combination of metals in the soil (Adriano, 2001). Our recent work involved research into metal extractability patterns in a set of metal-spiked calcaric Fluvisols in the Madrid region. We reported a decrease in metal mobility over time due to adsorption and ageing processes, governed both by the carbonate fraction and also largely by the organic and clay fractions (de Santiago-Martín et al., 2013a). However, these processes may be reversed by changes in soil physicochemical properties and/or by the rhizosphere environment, leading to a release of (bio)available metals (Fernández et al., 2005; Liao et al., 2006).

Despite the fact that ~45% of European soils have a low OM content – mainly in southern Europe (European Commission, 2006) – the organic fraction could play a key role in these metal remobilisation processes. Organic matter can immobilise metals through the formation of stable metal–humus complexes and can also enhance their availability to plants by increasing soils' cation exchange capacity and providing metal chelates and enhancing metal solubility in the soil solution (Clemente et al., 2006; Zeng et al., 2011). This dual role depends on OM composition, the metal's characteristics and/or the conditions of metal deficiency or excess in plant uptake (Cattani et al., 2006; Inaba and Takenaka, 2005). The dual role of the organic fraction has yet to be satisfactorily explained. In calcareous agricultural soils – typically poor in OM content – the carbonate fraction could be expected to

Abbreviations: DTPA, diethylene triamine pentaacetic acid; TEA, triethanolamine; EDTA, ethylene diamine tetra-acetic acid; LMWOA, low molecular weight organic acids; ECC, equivalent CaCO₃; CEC, cation exchange capacity; TOC, total organic C; OM, organic matter; LPI, labile pool I of organic matter; LPII, labile pool II of organic matter; RP, recalcitrant pool of organic matter; AAS, atomic absorption spectroscopy; XRD, X-ray diffraction; TI, tolerance index; TF, translocation factor; ANOVA, Analysis of Variance; SPSS, Statistical Package for the Social Sciences; RDA, redundancy analysis; CANOCO, Canonical Community Ordination.

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mask the role of OM, and yet we have observed that metal availability patterns are not explained by the carbonate fraction alone but rather by combined action with other soil fractions such as OM (de Santiago-Martín et al., 2013a,b). Although several authors have demonstrated the role of the organic fraction in metal (bio)availability in organically-amended calcareous soils (Clemente et al., 2007; Kaschl et al., 2002), there is little information on soils with a natural OM content gradient.

This work contributes to the knowledge of this subject by examining the interactions between metal ions and crop plants in periurban calcareous agricultural soils in the Mediterranean area with a natural gradient in their OM content and composition. We conducted bioassay experiments with two varieties of lettuce (*Lactuca sativa* L.), romaine and iceberg. Metal bioavailability patterns were assessed as a function of soil constituents and extractable metals with several different-strength methods.

2. Materials and methods

2.1. Study area, soil characteristics and sampling

The soil samples were taken from various plots in an Agricultural Research Station (Alcalá de Henares, Madrid, Spain) in the periurban axis that is home to the region's main agricultural activities, as well as being a substantial residential and industrial hub, at an altitude of 588 m, on quaternary sediments (IGME, 1990). Soils classified as calcareous Fluvisol (Moreno Merino, 1998) today present Anthric characteristics (FAO, 2006). The average annual temperature is 13 °C, average annual rainfall is 401 mm year⁻¹ and potential evaporation is about 760 mm year⁻¹.

We selected a set of ten soil samples with differing OM contents: ~30 g kg⁻¹ (H1, H2 and H3 soils), ~20 g kg⁻¹ (M1, M2, M3 and M4) and ~10 g kg⁻¹ (L1, L2 and L3), and differing carbonate content and textural class. Some of the soil sample properties are shown in Table 1. Total metal content values were similar to those obtained by other authors for agricultural soils in 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 was taken from each sampling point (0–30 cm) and homogenised. Soil samples were air-dried and passed through a 2 mm sieve.

2.2. Experimental design

The environmental impact from metal accumulation in periurban agricultural areas was simulated by adding a multi-elemental heavy metal salt solution to the soil samples as described elsewhere

(de Santiago-Martín et al., 2013b). Cadmium, Cu, Pb, and Zn were selected for their different speciation, mobility and bioavailability in soils. Briefly, three containers (40 cm wide × 59 cm long × 21 cm high) of 10 kg each were used for each sample: one un-spiked sample with the addition of distilled water; and the other two spiked at two different concentration levels using heavy metal nitrate salts in aqueous solution: low level (Tt1) (3 mg kg⁻¹ of Cd + 140 mg kg⁻¹ of Cu + 300 mg kg⁻¹ of Pb + 300 mg kg⁻¹ of Zn) or high level (Tt2) (20 mg kg⁻¹ of Cd + 875 mg kg⁻¹ of Cu + 600 mg kg⁻¹ of Pb + 2000 mg kg⁻¹ of Zn), within the limits proposed by the current European legislation (Directive 86/278/EEC).

Each soil sample and the corresponding 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 de-ionised water in cycles of about two weeks, in order to favour the metal redistribution processes within the soil matrix. These processes play a key role for determining metal (bio)availability in soils (McLaughlin, 2001). At the end of the equilibration period (12 months), duplicates were randomly removed from each un-spiked and metal-spiked soil sample in order to extract the metals by means of one-step extraction methods and for the bioassay experiments.

Different extraction solutions were used to assess mobile and potentially mobile metal fractions (Gupta et al., 1996). The mobile fraction was estimated with 0.01 M CaCl₂, 1 M MgCl₂, 0.1 M NaNO₃, and 1 M NH₄NO₃-methods; and the potentially mobile fraction was estimated with 5 mM DTPA, 0.05 M EDTA, 0.5 M HNO₃, 0.11 M HAc, 10 mM LMWOA (a mixture of low-molecular-weight organic acids) and 1 M NH₄Ac-methods (de Santiago-Martín et al., 2013b).

We selected two varieties of *L. sativa* L. (romaine and iceberg) for the bioassay experiments. For each variety, un-spiked and metal-spiked soil sample duplicates were placed in pots (1.5 kg per pot; 18 cm diameter × 15 cm high) and fertilised with 55.55 ml of Hoagland solution. The differences in nitrogen supply between the levels due to the application of metals as nitrate salts were adjusted by adding KNO₃. Three lettuces were planted per pot. Plants were grown in a growth chamber under controlled conditions: air temperature 20 °C and 12 h light per day. Pots were placed in saucers to prevent cross-contamination from drainage water and watered daily up to 60% of field capacity for one month.

2.3. Analytical methods

All chemicals were obtained from analytic-grade reagents from 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-ionised type I water.

Table 1
Physicochemical and mineralogical parameters of the un-spiked soil samples.

Soil sample	pH	Carbonate fraction		Organic fraction				Oxide fraction		Particle-size distribution				CEC	Total content			<2 mm		
		ECC	g kg ⁻¹	TOC	LPI	LPII	RP	Cry-Fe	Am-Fe	CS	FS	Silt	Clay		cmolc kg ⁻¹	Cu	Pb	Zn	Calcite	Dolomite
H1	8.2	106	18	10	18	72	13.4	0.8	159	590	78	172	6.9	12.0	25.5	52.9	++	tr		
H2	8.1	125	18	10	24	66	11.7	0.5	23	592	215	170	10.6	10.0	23.8	63.3	++	tr		
H3	8.4	118	15	20	25	54	11.1	0.6	95	605	146	154	8.9	10.8	24.4	62.0	+	tr		
M1	8.1	32	12	13	15	71	11.4	0.7	45	459	168	328	19.1	10.1	24.0	62.1	tr	nd		
M2	8.2	27	12	9	17	74	12.2	0.7	99	386	172	344	20.4	13.2	21.1	70.7	tr	tr		
M3	8.1	148	12	40	12	48	8.5	0.2	114	569	124	193	8.7	12.1	55.8	62.7	+++	+		
M4	8.7	117	10	18	24	57	8.0	0.2	166	567	129	139	5.6	15.0	23.7	74.9	+	tr		
L1	8.2	9	8	25	23	52	7.2	0.4	245	560	70	124	10.0	7.0	25.4	45.2	nd	nd		
L2	8.1	100	8	14	11	75	10.3	0.3	112	462	167	259	13.3	8.5	21.5	55.1	++	nd		
L3	8.4	190	6	17	14	69	8.1	0.2	111	603	126	161	7.1	8.0	14.0	54.7	+++	++		

ECC = equivalent CaCO₃; TOC = total organic C; LPI = labile pool I; LPII = labile pool II; RP = recalcitrant pool; Cry-Fe = crystalline Fe oxides; Am-Fe = amorphous Fe oxides; CS = coarse sand; FS = fine sand; CEC = cation exchange capacity. The total Cd content was in all cases lower than the quantification limit (<0.2 mg l⁻¹). Number of '+' is proportional to abundance: (++++) most abundant, (+) least abundant, (tr) trace, and (nd) not detected.

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