

Regulating the mobility of Cd, Cu and Pb in an acid soil with amendments of phosphogypsum, sugar foam, and phosphoric rock

F. GARRIDO^a, V. ILLERA^a, C. G. CAMPBELL^{b*} & M. T. GARCÍA-GONZÁLEZ^a

^aCentro de Ciencias Medioambientales, Consejo Superior de Investigaciones Científicas, Serrano 115 dpdo, 28006 Madrid, Spain, and

^bLawrence Berkeley National Laboratory, Berkeley, CA, USA

Summary

When acid soil has been contaminated by metals as a result of industrial discharges, accidental spills, or acid mine drainage it may be desirable to retain the metals in the soil rather than allow them to leach away. We have investigated the potential of phosphogypsum (PG), sugar foam (SF), and phosphoric rock (PR) to regulate the availability and mobility of Pb, Cd and Cu. We have also identified changes in attenuation during incubation for 1 year and the effect of aging on metal speciation in amended soils. We studied miscible displacement in columns of undisturbed soil previously treated with solutions of the amendments and soluble metals and, subsequently, single and sequential chemical metal extractions. All amendments increased the soil's metal retention capacity. This, in turn, increased the amount of metal extractable by diethylenetriaminepentaacetic acid (DTPA). However, over time the amounts of DTPA-extractable metal decreased, particularly for Cu and Pb. Both Cu and Cd were held preferentially within the acetic acid-extractable fraction (operationally defined exchangeable fraction – EX fraction), whereas Pb was associated mainly with the hydroxylammonium-extractable fraction (operationally defined bound to Fe and Al hydroxides – OX fraction). Both Pb and Cu in the oxide and organic fractions increased in the PG- and SF-treated soils. In general, the distribution of metal did not change in the PR-treated columns after the incubation. Finally, scanning electron microscopy in back-scattered electron mode (SEM–BSE) showed the formation of Al-hydroxy polymers which provides the soils with additional cation sorption capacity. In the PG- and PR-treated columns, P and S were associated with these formations. The three metals were associated with the Al polymers, probably through direct coordination or the formation of ternary complexes with the inorganic ligands phosphate and sulphate.

Introduction

Throughout the last decade manufacturing industry, fertilizer application, sewage discharges and sludge disposal have resulted in the deposition and accumulation of trace metals in soils. In addition, accidents such as the mining spill at Aznalcóllar in Andalusia, southern Spain, in April 1998 or acid mine drainage can degrade our environment. Metal contaminants either accumulate in or leach from soils, polluting surface and subsurface water bodies. Options available for remediating metal-contaminated soils are numerous, but most often the contaminated soil is capped *in situ* or is excav-

ated and removed. These engineering techniques are expensive and too expensive or logistically impracticable in many instances; they are also invasive and can prevent the restoration of environmental equilibrium.

An alternative is to apply amendments to the soil. These *in situ* treatments take advantage of the soil's natural mechanisms for controlling the mobility and bioavailability of metals and reducing to some extent the toxicity of metals to humans and the environment. This approach, though not changing the concentrations in total, is an effective, more realistic, and cost-effective choice for industrial sites and surrounding rural land, dumping grounds, or highly contaminated soils (Vangronsveld & Cunningham, 1998).

The use of industrial by-products to help soils and sediments to retain metals has recently been studied. This approach reduces waste disposal by making industrial wastes useful. For instance, sterilized, finely crushed bonemeal has been

Correspondence: F. Garrido. E-mail: fernando.garrido@ccma.csic.es

*Present address: Environmental Protection Department, Lawrence Livermore National Laboratory, 7000 East Avenue, L-627, Livermore, CA 94550, USA.

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used as a source of apatite to minimize the release of metals from contaminated soils (Hodson *et al.*, 2000). The aluminosilicate beringite produced in the coal mine at Beringen (Belgium) has been used for similar purposes (Lombi *et al.*, 2003). Other by-products rich in iron and manganese oxides such as red mud (a residue of the alumina extraction industry) and steel shot have been successfully used to mitigate the mobility and plant uptake of metals (Mench *et al.*, 1994; Lombi *et al.*, 2002). Also, an iron oxide by-product, rich in poorly crystalline ferrihydrite, derived from the processing of TiO₂ pigment has proved effective in reducing the bioavailability of Zn to some crops (Chlopecka & Adriano, 1996) and the susceptibility of Pb to leaching (Berti & Cunningham, 1997). Many of these by-products are sparingly soluble and must be mixed with the contaminated material. This restricts their ability to immobilize metals in the soil or sediment below the depth of the mixing. The need thus remains to find materials that can be used at small concentrations, preserve soil structure, and are cheap and suitable for application on arable land for *in situ* remediation of polluted soils and to prevent metals from contaminating ground water. Although several amendments have been suggested for this purpose, little information can be found on their potential to increase the soil's ability to act as an environmental filter or to prevent further environmental damage after a spillage or other accident.

We have tested three amendments, phosphogypsum (PG), sugar foam (SF), and phosphoric rock (PR), applied to the soil in small concentrations, for their efficacy in fixing metals from aqueous solutions in undisturbed soil columns. Phosphogypsum is generated in the wet-acid production of phosphoric acid from rock phosphate; sugar foam is produced when beet juice is purified by flocculation of colloidal matter with a lime, Ca(OH)₂, solution followed by treatment with CO₂. Both by-products have proved to ameliorate subsoil acidity and the phytotoxicity of Al in the subsoil (Alcordero & Rechcigl, 1993; Illera *et al.*, 2004b). Additionally, phosphogypsum has been tested to reduce the aqueous concentrations of metals (Carbonell *et al.*, 1999) and promote the precipitation of anglesite-type minerals in the presence of lead (Illera *et al.*, 2004a). The addition of PG and SF to acidic soils induces the formation and retention of Al-hydroxy polymers (Toma & Saigusa, 1997; Illera *et al.*, 2004b) which could boost the retention capacity of the soils through the formation of ternary complexes (McBride, 1989). Ma & Rao (1997) showed that phosphate rock immobilizes Pb from aqueous solutions and soils through the precipitation of pyromorphite-like minerals. Traina & Laperche (1999) and McGowen *et al.* (2001) found that other sources of phosphate anions such as mineral apatite, synthetic hydroxyapatite and diammonium phosphate reduce solubility and bioavailability of metals through the formation of metal-phosphate minerals with varying effectiveness as a function of the metal, pH, and ligand concentration among other factors.

In a previous study (Illera *et al.*, 2004a) we showed in batch experiments that gypsum- and lime-rich industrial by-products

can reduce the concentrations of metals in solution, suggesting several retention mechanisms. We have since investigated the potential of phosphogypsum, sugar foam, and phosphoric rock to diminish the availability and mobility of the metals Pb, Cd and Cu and the effect of the amendments and aging on the metal speciation. We did so in hydrodynamic experimental conditions by miscible displacement studies in undisturbed soil columns and subsequent single and sequential chemical extraction procedures both immediately after the transport experiments and after 1 year of aging.

Materials and methods

Soil characteristics and sample collection

We did our experiments with a weathered acid soil, developed from formations of Pliocene-Quaternary age in a degraded area of central Spain, and classified as a Plinthic Palexerult. From a level area of the experimental site, 24 undisturbed columns of soil (8 cm diameter × 20 cm length) were taken from the Ap horizon on a uniform grid at 50-cm intervals. The moisture content (averaging a gravimetric water content of 0.20 ± 0.01) of the soil at the sampling time minimized compaction and disturbance. The columns were kept moist until their subsequent use on trays filled with bulk soil.

Samples of the Ap horizon were collected at various sampling points, air-dried, crushed, sieved through a 2-mm mesh, and bulked before general characterization. Table 1 summarizes the important physical, chemical and mineralogical properties. Soil pH was measured in deionized water (pH_w) and in 1 M KCl (pH_K) (in a 1:2.5 suspension), and organic carbon (OC) was determined by wet digestion (Walkley & Black, 1934). The exchangeable bases were extracted with 1 M NH₄OAc (pH 7) (Thomas, 1982), and the exchangeable aluminium (Al_K) was determined with 1 M KCl (Barnhisel & Bertsch, 1982). The effective capacity of the exchange complex (ECEC) was calculated as the sum of Al_K and the amounts of Ca, Mg, Na and K extracted by 1 M NH₄OAc at pH 7 (Shuman, 1990). The Al and Fe contents in the poorly crystalline and amorphous fraction (Al_{OX} and Fe_{OX}) were extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid solution at pH 3 (McKeague & Day, 1966). We separated the supernatants from each extraction by centrifuging and stored them in polyethylene containers at 4°C until analysis. Analyses were performed in triplicate. The Ca, Mg, K, Na and Al contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Perkin Elmer OPTIMA 4300 DV. The mineralogical compositions of the total (≤ 2 mm) and clay (≤ 2 μm) fractions were identified by X-ray powder diffraction on a Philips X'Pert diffractometer with graphite-monochromated Cu-Kα radiation. We obtained semi-quantitative estimates of the minerals from random powder and oriented aggregated patterns.

Table 1 Physical, chemical and mineralogical properties of the soil horizons

pH _w	pH _K	EC ^a /mS cm ⁻¹	OC ^b	Sand /g kg ⁻¹	Silt	Clay	Ca ²⁺	Mg ²⁺	Na ⁺ /cmol _c kg ⁻¹	K ⁺	Al ³⁺	Fraction ^c ≤ 2 mm				Fraction ^c ≤ 2 μm								
												ECEC ^c	Al _{ox} ^d /mg kg ⁻¹	Fe _{ox} ^d	Q	G	H	Ph	Q	G	H	Ph	V	I
5.0	4.1	0.03	22.4	675	250	75	0.32	0.08	0.04	0.09	1.26	1.79	841	480	74	4	3	19	12	6	6	8	11	57

^aEC, electrical conductivity.^bOC, organic carbon.^cECEC, sum of exchangeable Ca²⁺, Mg²⁺, K⁺, Na⁺ and Al³⁺.^dAl and Fe oxalate-extractable contents.^eSemi-quantitative composition in %: Q, quartz; G, goethite; H, haematite; Ph, phyllosilicates; V, vermiculite; I, illite; K, kaolinite.

Characteristics of the soil amendments

Samples of phosphogypsum (PG) from the Spanish fertilizer industry Fertiberia, S.A., sugar foam (SF) from the Spanish sugar producer Azucarera Ebro, S.L., and phosphoric rock (PR), a commercially available fertilizer, were digested by acid digestion and alkaline fusion (Hossner, 1996) after they had been dried at 45°C (phosphogypsum) or 105°C (sugar foam and phosphoric rock). The resulting solutions were analysed for elements by ICP–AES, ICP–MS, and ion chromatography. Calibration curves for elemental analyses were run before and after each sample series (20 samples including matrix-matched blanks and in-between calibration checks). The calibration solutions covered the range of the concentrations in the samples and were prepared in the same matrix as the extracting reagents from certified stock solutions. Sample blanks were analysed for correction of background effect on instrument response. Trace metal standards were used to assess instrument precision. We calculated metal concentrations in unknown solutions on the basis of the external calibration, averaging the concentrations from two repetitions for each experimental replicate. Limits of detection were calculated as three standard deviations of the instrument response from 10 repeated analyses of sample matrix-matched blank solutions. The detection limits showed that a concentration of a few $\mu\text{g l}^{-1}$ of the three metals could be analysed. In addition, radiochemical activity in the PG samples was measured with a Canberra gamma-spectrometer equipped with a Ge detector (Garrido *et al.*, 2003). The chemical composition of PG and SF can be found in Garrido *et al.* (2003). Details on the radionuclide content of PG can be found in El-Mrabet *et al.* (2003) and Al-Masri *et al.* (2004). The composition of PR is dominated by calcium phosphate in addition to significant amounts of sulphate anions.

Miscible displacement studies

Before the miscible displacement studies of the metals Cd, Cu and Pb, triplicate soil columns were treated with solutions of the amendments containing similar concentrations of Ca^{2+} (approximately 13 mg l^{-1}). We treated the soil columns with these solutions instead of using the solid amendments themselves to avoid uncertainties associated with the different solubilities of the three amendments and their undissolved phases and to equilibrate the amount of Ca^{2+} added as a result of the amendments. We obtained the amendment solutions by dissolving 3 g of the products per litre of deionized water during 48 hours at controlled room temperature ($24 \pm 2^\circ\text{C}$). Since these solutions had different concentration of Ca^{2+} , those of PG and PR were diluted as required to achieve a concentration of Ca^{2+} similar to that in the SF solution. No metals were detected in the three solutions, which suggests that the metals remained in the insoluble fraction after 48 hours of shaking. The resulting chemical compositions of the product solutions are

shown in Table 2. The soil columns were flushed with 4.51 (i.e. a volume equivalent to the mean annual rainfall at the experimental site) of the amendment solutions in triplicate in unsaturated conditions (averaging a volumetric water content of 0.34 ± 0.02) and steady flow (12 ml hour^{-1}). Triplicate control columns were irrigated in similar conditions with deionized water. Control and treated columns were kept at 10°C and approximately similar water content on a weight basis before they were used for subsequent studies on metal transport.

For these studies, the columns were irrigated at constant flow rate (12 ml hour^{-1}) with deionized water until a steady flow of water was achieved. Then, a 2-cm (i.e. 100 ml) pulse of a trimetal solution containing approximately 500 mg l^{-1} of Cd, Cu and Pb was applied to the surface of the columns. We believed this concentration to be necessary to have sufficient soluble metal to assure migration through the soil columns in a workable period of time and yet achieve the breakthrough. However, note that the approximate mass of metal input in these studies was 52 mg of each metal and that the average mass of soil contained in each column was $1468 \pm 70 \text{ g}$. Metal solutions were prepared from the Cl^- salts of the metals in deionized water. Theoretical calculations by MINTEQA2 (US Environmental Protection Agency, 1991) indicated that the solutions were not saturated with respect to the metal chlorides at the pH of the solution. Immediately after the pulse of metals had been applied, the leaching with deionized water resumed and the pulse was displaced through the columns of soil. Samples of effluent were collected with automatic fraction collectors and analysed for pH, electrical conductivity, Cl^- (measured by an ion-selective electrode), and Cd, Cu and Pb (by ICP–AES).

Incubation experiments

Another set of columns were used to evaluate changes in metal sorption with residence time. In total 12 soil columns (control and treated columns) were flushed with amendment solutions and deionized water in triplicate in conditions similar to those described above. Following the application of amendment, a 2-cm pulse of trimetal solution was introduced in the columns

Table 2 Chemical composition of the solutions of the by-products

	PG	SF	PR
pH	5.46	7.68	6.52
EC /mS cm^{-1}	88.1	116	140
Ca^{2+} /mg l^{-1}	11.8	13.2	14.9
Mg^{2+} /mg l^{-1}	ND	0.6	ND
Zn^{2+} /mg l^{-1}	0.24	0.08	0.08
F^- /mg l^{-1}	0.6	0	0.65
PO_4^{3-} /mg l^{-1}	0.51	1.31	34.6
SO_4^{2-} /mg l^{-1}	31.2	1.7	23.9

ND, not detected.

in the same hydrodynamic conditions as described above and leached with a similar amount of deionized water (approximately 2.6 l) at the same steady flow rate (12 ml hour⁻¹). The effluent from these leaching experiments was not collected. The columns were incubated on trays filled with bulk soil at room temperature for 1 year, and we maintained the same content of water in them by spraying the required amount of deionized water (determined by difference of weight) on the surfaces of the columns.

Solid-phase analysis

Following the end of the miscible displacement studies and aging experiments, all columns were dismantled and the soil in them sectioned at intervals of approximately 4 cm. The portions obtained at 0–4, 8–12 and 16–20 cm from the surface were air-dried, crushed and sieved through a 2-mm mesh for subsequent analysis of metal in the solid phase and determination of pH. We estimated the availability of the metals that remained in the soil in duplicate 10-g subsamples with a mixture of 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M CaCl₂, and 0.1 M triethanolamine adjusted to pH 7.3 (Lindsay & Norvell, 1978) (Cd_{DTPA}, Cu_{DTPA} and Pb_{DTPA}). In addition, we fractionated the metals in the solid phase in the following sequence (Quevauviller *et al.*, 1994).

- 1 Water-soluble, exchangeable, weakly bound metal fractions extracted with 0.11 M acetic acid (EX, step 1).
- 2 Metal bound to Fe and Mn (hydr)oxide fraction, extracted with 0.1 M hydroxylammonium chloride (OX, step 2).
- 3 Metal bound to organic matter based on 30% hydrogen peroxide oxidation and 1 M ammonium acetate extraction (ORG, step 3).

In addition, we determined the pseudototal metal content (Cd_{Ptot}, Cu_{Ptot} and Pb_{Ptot}) of the subsamples by digestion in aqua regia (3:1 by volume 12 M HCl and 14 M HNO₃) as described by Vercoutere *et al.* (1995). All extracts and digests were stored in polyethylene tubes at 4°C for analysis, and metal concentrations were determined by ICP–AES. We followed the same quality control system as described above.

Scanning electron microscopy

Our aim was to infer possible mechanisms involved in retention of Cd, Cu and Pb and the differences in their distribution arising from the different treatments by means of scanning electron microscopy in the backscattered electron mode (SEM–BSE). Samples from the 0–4-cm depth sections of all the columns were oven-dried (50°C) and embedded in low-viscosity acrylic resin (LR-White, medium grade). The blocks of resin-embedded samples were finely polished, coated with carbon and subsequently observed with a DMS 940 A-Zeiss microscope equipped with a four-diode BSE detector. Point analyses and microprobe profiles were made with a Link ISIS energy dispersive spectrometry (EDS) microanalytical system

on the SEM with the following operating conditions: take-off angle of 35°; accelerating voltage of 15 kV; working distance of 25 mm; specimen current of 1–5 nA.

Statistical analyses

We made our experiments based on a full factorial statistical design (treatment and time) done at two times with repeated measurements. For each depth, a two-way analysis of variance (treatment, time) was done to identify interactions among the factors. For each depth and time, the differences as a result of the treatment were studied by analysis of variance (treatment). The effect of incubation time was assessed by a *t*-test (time) for each treatment and depth.

Results and discussion

Effects of amendments on metal retention

The addition of the amendments significantly increased the Cd, Cu and Pb retention capacity of the soil as measured by the pseudototal metal content at 0–4 cm (Table 3). However, differences in pseudototal content of metal at 8–12 cm and 16–20 cm among amended and control columns were small and generally not significant. The retention of Cd is enhanced by SF treatment in particular (Cd_{Ptot} at 0–4 cm was more than 3 times greater than in the control). As a result, Cd_{Ptot} at 8–12 cm and 16–20 cm were significantly less than those found in the control, as well as the PG- and PR-treated columns. On the other hand, the SF treatment increased Cu and Pb retention at a similar ratio at 0–4 cm (approximately 1.4 and 1.3 times greater) although, at 8–12 cm and 16–20 cm, Pb_{Ptot} were greater than Cu_{Ptot}.

Both PG and PR increased Cd retention, and no differences were found between these treatments at any depth. In contrast to what might be expected, PR increased Cd retention at 0–4 cm (1.6 times greater than in the control) more than Pb and Cu retention (approximately 1.4 times greater than the control). The effect of the PG treatment relative to the control was similar for the three metals, and their retention at 0–4 cm was increased by approximately a factor of 1.4 in comparison with the control.

Amendment effect on soil pH

The soil pH at 0–4 cm depth measured after the miscible displacement varied as a function of the amendments (Table 4). Even at the small rate of the amendment applied, and as described elsewhere (Alcordero & Rechcigl, 1993; Illera *et al.*, 2004b), the pH of the soil surface of the columns treated with PG decreased slightly, whereas the SF treatment significantly increased the pH. However, as a result of the 1-year incubation, the soil became more acid in the uppermost part of the columns where the accumulation of metals was greatest

Table 3 Effect of treatments on pseudototal content and solid-phase metal speciation in mg kg⁻¹

		Time 0					Time 1 (1 year)					
		Depth /cm	Control	PG	SF	PR	SE ^a	Control	PG	SF	PR	SE
Cd	EX	0-4	33.4	46.2	124.8	62.4	5.7	43.4	54.0	137.3	70.3	5.0
		8-12	17.2	21.5	6.5	18.1	1.8	10.6	11.5	2.5	13.2	1.6
		16-20	5.2	7.7	0.3	6.6	1.5	4.32	3.3	1.1	4.4	1.4
	OX	0-4	13.9	22.0	44.1	20.8	1.5	29.0	28.6	67.8	21.9	4.9
		8-12	8.8	9.7	1.8	11.2	1.1	10.4	7.9	3.1	11.9	2.0
		16-20	2.3	4.2	0.1	2.8	0.9	3.9	3.9	0.7	2.9	1.3
	ORG	0-4	2.0	2.2	4.5	1.5	0.7	3.2	2.9	8.2	3.4	0.5
		8-12	3.1	2.9	0.4	2.2	0.6	2.6	4.0	1.4	2.4	1.0
		16-20	1.2	1.9	ND	0.4	0.5	0.9	1.0	0.4	1.3	0.2
Ptot	0-4	56.6	78.4	188.5	90.6	4.2	63.9	80.0	210.8	103.6	3.9	
	8-12	29.3	30.2	7.7	37.7	3.7	31.2	25.3	8.9	31.5	4.3	
	16-20	9.2	13.1	0.2	9.2	2.3	8.5	11.7	1.3	10.0	1.5	
Cu	EX	0-4	76.3	93.9	103.7	119.6	8.8	73.9	83.0	126.6	115.9	7.9
		8-12	0.5	0.3	0.7	0.7	0.3	0.5	1.9	0.7	0.7	0.2
		16-20	0.1	0.1	0.2	0.2	0.1	0.3	0.4	0.3	0.5	0.2
	OX	0-4	30.3	38.8	39.2	46.9	3.2	38.3	51.1	65.9	42.1	3.7
		8-12	0.4	0.2	0.5	ND	0.4	ND	0.2	0.3	ND	0.2
		16-20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	ORG	0-4	33.5	36.5	41.1	39.5	2.1	52.3	64.0	82.8	46.7	7.7
		8-12	3.9	2.6	3.1	4.8	1.1	5.8	3.4	4.5	2.8	1.1
		16-20	2.6	1.8	1.5	2.8	0.9	2.9	2.2	2.6	2.2	0.5
Ptot	0-4	191.1	242.6	270.5	266.6	10.8	206.0	237.3	281.8	267.6	20.5	
	8-12	6.6	5.9	15.1	9.1	1.9	9.6	8.6	10.5	8.8	1.6	
	16-20	5.4	3.8	4.8	5.6	1.5	7.8	7.8	7.1	6.3	1.1	
Pb	EX	0-4	44.5	65.5	47.6	75.6	3.7	40.4	53.0	50.6	73.0	4.6
		8-12	0.6	0.6	0.5	0.4	0.2	0.3	0.4	0.3	0.7	0.1
		16-20	0.4	0.3	0.3	0.3	0.1	0.1	0.1	0.2	0.3	0.1
	OX	0-4	105.5	130.6	126.6	149.0	4.4	130.0	155.6	167.2	156.0	6.1
		8-12	4.8	5.3	5.4	4.8	0.9	6.4	4.1	5.4	5.6	1.2
		16-20	3.3	3.0	2.9	1.4	0.8	2.3	1.9	2.0	3.7	0.7
	ORG	0-4	43.8	55.2	50.4	58.2	3.2	50.8	76.4	78.9	57.7	3.1
		8-12	6.4	6.9	6.6	7.0	1.2	10.4	17.3	18.5	11.1	2.3
		16-20	4.5	5.8	5.4	5.2	0.7	5.9	5.2	8.0	6.0	1.0
Ptot	0-4	214.2	293.5	269.4	304.5	4.1	228.2	301.0	300.7	295.3	5.6	
	8-12	30.7	21.9	34.5	31.4	2.7	30.4	30.1	27.0	34.7	5.2	
	16-20	19.7	19.2	20.1	21.2	1.2	21.9	21.3	19.9	24.7	2.3	

^aPooled standard errors.

ND, not detected.

Table 4 Effect of treatments on soil pH at time 0 and 1 year after (time 1)

		Time 0					Time 1 (1 year)					
		Depth /cm	Control	PG	SF	PR	SE ^a	Control	PG	SF	PR	SE
		0-4	5.25	5.05	5.34	4.92	0.13	4.66	4.67	4.99	4.83	0.13
		8-12	4.96	4.92	4.99	4.96	0.08	4.81	4.84	4.81	4.86	0.13
		16-20	4.90	4.80	4.94	4.86	0.10	4.76	4.74	4.72	4.78	0.14

^aPooled standard errors.

(0–4 cm); this affected significantly the control, and the PG- and SF-treated columns, and it altered the tendency of the soil to become more acid with depth as we found in the soil columns immediately after the miscible displacement except in the SF-treated columns.

Amendment effect on metal DTPA-extractability

Although DTPA-extractable Cd, Cu and Pb contents increased significantly as a result of the treatments (Table 5), the fractions of metals retained in available forms differ little as functions of either the treatment or metal species at 0–4 cm, averaging $56 \pm 9\%$. The proportion of Cd_{DTPA} was similar at all depths in both the control and treated columns (0.58 ± 0.12). However, both Cu_{DTPA} and Pb_{DTPA} proportions at 8–12 cm and 16–20 cm (averaging 0.12 ± 0.01 and 0.05 ± 0.01 for Cu and Pb, respectively) were substantially less than at 0–4 cm (0.34 ± 0.05). Although this result should be treated with caution at the small concentrations found at those depths, this tendency suggests that when the concentrations are small the metals tend to be retained largely in non-exchangeable forms (McBride, 1989).

Amendment effect on solid-phase metal speciation

Our results suggest that the distributions of the three metals in both the untreated and treated columns depend on the metal, depth and treatment. In the untreated columns, 59% and 40% of the pseudototal contents of Cd and Cu, respectively, at 0–4 cm are in the EX fraction (Table 3). This accords with the results of other studies (Veeresh *et al.*, 2003). However, whereas at 0–4 cm Cu was retained in similar proportions (17%) in the OX and ORG fractions, Cd_{OX} accounted for 24% of its pseudototal content and Cd_{ORG} was the least of all the fractions at any depth. This result does not exclude Cd

bonding on organic matter at sites with small activation energies that could count as Cd_{EX} .

The distribution of Pb at 0–4 cm was different from that of Cd and Cu; half of $Pb_{P_{TOT}}$ was associated with the OX fraction, and both Pb_{EX} and Pb_{ORG} each accounted for 20%. Theory suggests that Cu exhibits stronger affinity than Pb does for organic matter at pH 5 (McBride, 1989); however, in our case, both the absolute Pb_{ORG} and its proportion to the $Pb_{P_{TOT}}$ were greater than for Cu. On the other hand, soft non-transition metals such as Pb^{2+} exhibit greater affinity for Fe and Al hydroxides over Cd^{2+} , a harder borderline transition metal (McBride, 1989), and the preference for Pb^{2+} to be retained in oxide-bound forms also accords with other studies (Dollar *et al.*, 2001). However, although chemisorbed Pb^{2+} is unlikely to exchange with cations with no specific affinity for the oxide, it is partly reversible if the pH changes (McBride, 1989), and so it exchanges in the second step of the extraction procedure when the solution is made more acid (pH 2, Fe and Mn (hydr)oxide fraction).

The formation of Al-hydroxy polymers by hydrolysis of the Al^{3+} exchanged by Ca^{2+} (Toma & Saigusa, 1997; Garrido *et al.*, 2003) and their retention on organic and inorganic soil particles was the commonest feature developed in the soil matrix as a result of all treatments (Figure 1). Also, the addition of sulphate and phosphate anions modifies the chemical and mineralogical characteristics of soils with variable charge, enhancing their metal sorption capacity (Harter & Naidu, 2001). In the PG- and SF-treated samples (Figure 1a–d), the three metals, along with S (Figure 1a,b), were associated with the Al-hydroxy polymers, a result also seen in the corresponding EDS X-ray spectra (Figure 1b,d). This could indicate the formation of metal–ligand ternary surface complexes (McBride, 1989), although the identification of such processes requires advanced spectroscopic analytical techniques. Similar formations of Al-hydroxy polymers were found in the PR-treated samples (Figure 1e). However, in this case, we found no associated Pb (Figure 1f)

Table 5 Effect of treatments on metal DTPA-extractability in $mg\ kg^{-1}$

Depth /cm	Time 0					Time 1 (1 year)					
	Control	PG	SF	PR	SE ^a	Control	PG	SF	PR	SE	
Cd	0–4	29.0	37.2	138.8	70.0	14.1	46.7	33.6	113.5	49.0	8.0
	8–12	16.4	20.1	2.2	21.5	1.6	11.1	8.4	1.8	8.0	0.7
	16–20	5.1	8.3	0.3	5.9	2.3	3.4	4.7	0.4	3.6	0.5
Cu	0–4	98.2	119.3	144.1	156.1	13.0	78.7	79.9	119.2	94.4	5.7
	8–12	1.7	0.7	1.2	0.7	0.2	1.0	1.1	1.3	1.1	0.2
	16–20	0.3	0.1	0.8	0.6	0.2	0.8	0.9	1.0	0.8	0.1
Pb	0–4	109.4	143.3	131.8	178.7	17.6	75.8	73.0	96.6	94.0	10.1
	8–12	1.7	1.8	1.9	1.7	0.3	1.5	1.3	1.4	1.4	0.2
	16–20	1.5	1.4	1.2	1.2	0.2	1.0	1.1	1.2	1.1	0.1

^aPooled standard errors.

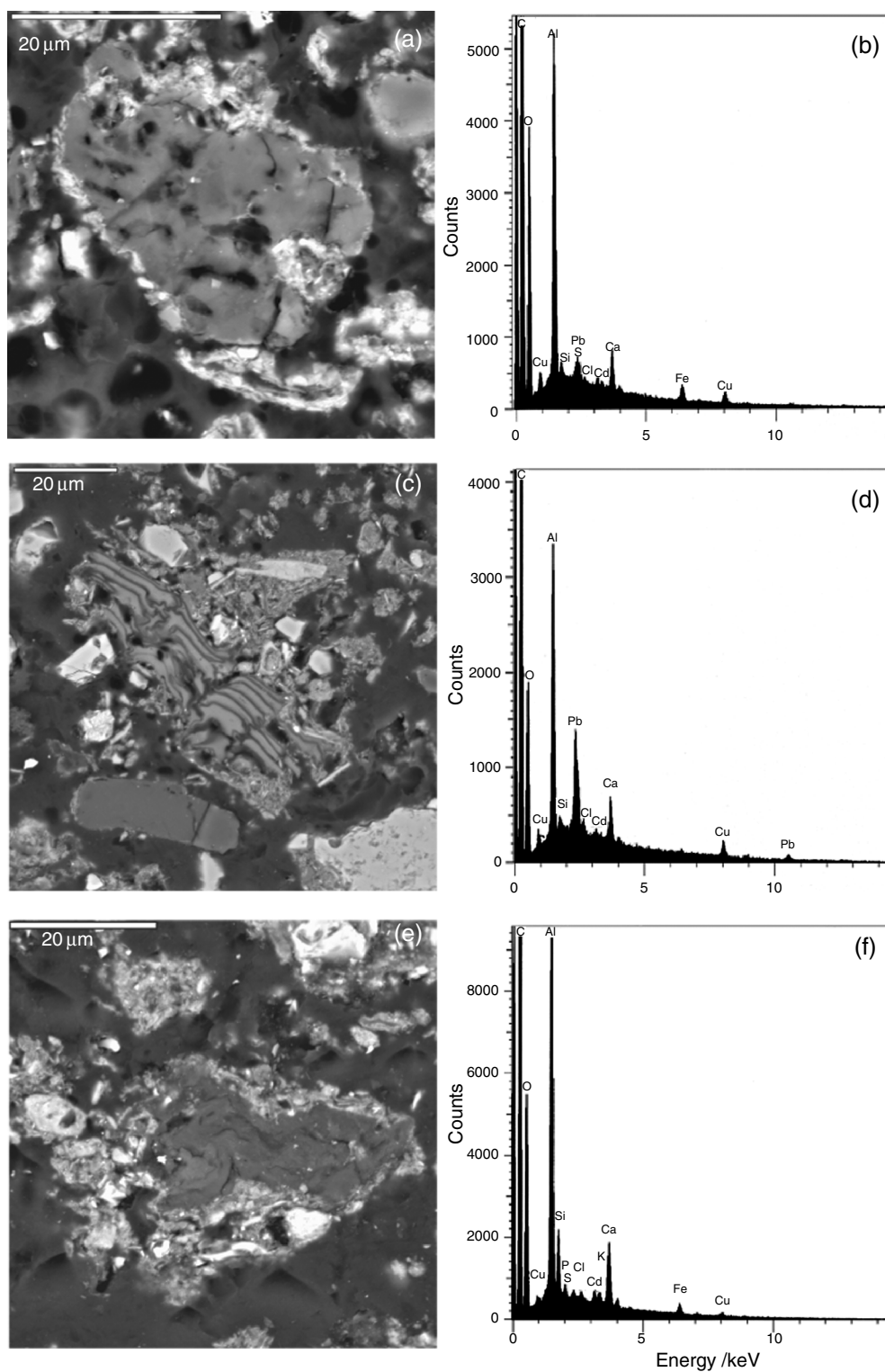


Figure 1 SEM–BSE images of massive formations of Al polymers in (a) PG-treated columns and (b) the corresponding EDS X-ray spectrum showing the presence of S and Pb, Cd and Cu metals; (c) in SF-treated columns and (d) EDS X-ray spectrum showing the presence of the three metals; (e) in PR-treated columns and (f) EDS X-ray spectrum including Pb, Cd and Cu.

although a sizeable amount of P was detected. This might indicate that retention of Pb within the PR-treated soil is controlled by the formation of both pyromorphite- and anglesite-type minerals that were not found by SEM-BSE nor detected by X-ray diffraction analyses.

In the treated columns, the EX and OX fractions of Cd and Cu increased significantly at 0–4 cm. However, despite these differences in absolute concentrations, both ratios Cd_{EX}/Cd_{Ptot} and Cu_{EX}/Cu_{Ptot} were similar in the control and treated columns, averaging 0.63 ± 0.04 and 0.41 ± 0.02 at 0–4 cm, respectively. On the other hand, while minor concentrations of Cd_{ORG} were measured at all depths, sizeable concentrations of Cu_{ORG} at 8–12 cm and 16–20 cm in all columns suggest that stable soluble complexes of organic matter and Cu that enhance Cu mobility might not be affected by the type of amendment. Last, the distribution of Cd_{EX} with depth in all columns was similar to that of Cd_{DTPA} , and the average difference between the two values was about 10% (excluding the SF-treated columns at 8–12 cm). Instead, Cu_{EX} concentrations were less than Cu_{DTPA} in both the untreated and treated columns. However, the sum of Cu_{EX} and Cu_{ORG} was remarkably similar to Cu_{DTPA} at 0–4 cm, especially in the SF- and PR-treated columns. This finding agrees with the affinity sequence of divalent metal ions in which Cu^{2+} shows the strongest relative preference for soil organic matter, and therefore tends to form more stable covalent bonds (McBride, 1989) not affected by mild extractants such as dilute acetic acid (EX fraction, step 1).

The majority of Pb in all treatments was found associated with the OX fraction. At 0–4 cm, Pb_{OX} concentration increased significantly as a result of all treatments. However, this increment was significantly greater in the PR-treated columns than in the PG- and SF-treated ones, resulting in the greatest Pb_{OX}/Pb_{Ptot} ratio of the treated columns. This might indicate the formation of pyromorphite-like (Cao *et al.*, 2003) and anglesite-type (Illera *et al.*, 2004a) minerals, in this last case as a result of the amount of sulphate anions in the PR solution. However, the addition of PG and SF to soils induces the formation of Al polymers, including sulphate and phosphate anions in their composition, providing the soils with additional cation sorption capacity, probably through the formation of ternary complexes (McBride, 1989). At 0–4 cm, Pb_{EX} was significantly greater in the PG- and PR-treated columns than in the untreated and SF-treated ones. Last, Pb_{ORG} at 0–4 cm significantly increased as a result of the treatments, but the ratio Pb_{ORG}/Pb_{Ptot} was similar in all cases. The substantial amounts of Pb_{ORG} at greater depths could result from the formation of soluble complexes of organic matter and Pb increasing mobility of Pb.

Incubation effect on solid-phase metal extractability

After 1 year of incubation, the pseudototal content of the three metals did not vary significantly within each depth and treat-

ment. However, DTPA-extractability generally decreased, and differences as a result of the treatments were minor (Table 5). In addition, the proportion of DTPA-extractable metal to the pseudototal content decreased at 0–4 cm, averaging $41 \pm 12\%$. However, at 0–4 cm the incubation induced a greater reduction of both Cu_{DTPA} and Pb_{DTPA} and their proportion to the pseudototal content (averaging $37 \pm 3\%$ and $31 \pm 4\%$, respectively) than those for Cd.

In general, incubation did not produce significant changes in the EX fraction of the metal content in the untreated and treated columns (Table 3). Instead, the amounts of the three metals associated to the OX and ORG fractions increased significantly in the untreated, PG- and SF-treated columns (except for the case of the Cd_{ORG} fraction). However, the decrease in Pb_{DTPA} was not confirmed by the sequential extraction scheme in the PR-treated columns as no significant change was detected in its solid-phase distribution. These results contrast with what has been described in incubation experiments of lead-contaminated soils and hydroxyapatite mixtures resulting in changes of soil Pb to more stable forms due to the formation of chloropyromorphite minerals (Ryan *et al.*, 2001). In fact, whereas the greatest amounts of Pb_{OX} and Pb_{ORG} were found in the PR-treated columns at time 0, after incubation, the amount of Pb_{OX} was similar in all treated columns, and Pb_{ORG} was significantly greater in the PG- and SF-treated columns than in the PR-treated ones.

The decreases in the amounts of metal extractable in DTPA and the changes in solid-phase associations along with decreases in pH at 0–4 cm (Table 4) might be the result of the change of labile sorption mechanisms, such as the conversion of outer-sphere into inner-sphere complexes, with or without simultaneous hydrolysis and subsequent release of proton (Benjamin & Leckie, 1981), on to the surface of the Al-hydroxy polymers generated as a result of the amendments (Figure 1). Additional possibilities after the incubation of the untreated and treated columns include slow diffusion across surfaces and in micropores and neof ormation of precipitates (Scheidegger & Sparks, 1996).

Conclusions

We have shown the potential of industrial by-products as soil amendments to mitigate environmental impacts and to provide insight into the mechanisms by which metals are immobilized. As a result of the amendments the pseudototal content of Cd, Cu and Pb in the top 4 cm of the soil increased significantly. The sugar foam was the most effective treatment in immobilizing Cd, whereas the increase in both Cu and Pb sorption was similar in all treatments. In general, Cd tended to be held in more available and mobile forms than did Cu and Pb, for all three amendments. Whereas Cd and Cu were retained mainly in the exchangeable fraction, most of the Pb was found associated to the Fe and Al oxyhydroxide fraction. The distribution of this fraction of the metals relative to their pseudototal

content in the soil matrix did not change as a result of the treatments. With time, however, there were significant changes in availability and potential mobility of the metals. After 1 year of incubation the fractions of the three metals bound to Fe and Al oxyhydroxides and that of Cu and Pb bound to the organic fraction increased in the soil treated with phosphogypsum and sugar foam. In the soil treated with phosphate rock, incubation produced no change.

These results indicate that both lime-rich and gypsum-rich industrial by-products could regulate the mobility of Cd, Cu and Pb in acid soils. Greater metal retention appears to be obtained with longer residence times for the metal and by-products to interact, as we saw after the 1 year of incubation. The extent of this effect of residence time could depend on the treatment and soils, but it should be considered by those who apply these by-products to control mobility or to reduce the potential toxicity of metals.

The formation of Al-hydroxy polymers on to organic and inorganic particles and the addition of ligands such as sulphate and phosphate anions in the amendments enhanced the metal sorption capacity of the soil. The structure, relative importance and long-term stability of this sorption phenomenon in the overall sorption capacity of the treated soils remains unknown.

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