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Leaching of Cd, Zn, Pb, and Cu in Packed and Undisturbed Columns of Soils Affected by the Spill from a Pyrite Mine in the South of Spain

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A study has been made of the leaching of Cd, Zn, Pb, and Cu in three representative soils within the zone affected by the spill from a pyrite mine in Aznalcollar (Sevilla, Spain) employing packed soil columns. According to the breakthrough and cumulative leaching curves, the relative mobilities of the different toxic elements in the columns are as follows: Cd> Zn> Cu> Pb. The effect of leaching on the distribution of metals as a function of depth using intact soil cores was also studied. The results showed that the soils themselves have a good capacity for immobilizing the soluble fraction of the elements from the spilled mud. This capacity varied as follows: clayey soil with a high carbonate content > clayey soil with a moderate carbonate content > sandy-clay loam soil with a low carbonate content. However, sandy soils with a low carbonate content could pose a risk to groundwater if initial contamination was high. These results could be considered during the evaluation of remedial technologies for the immobilization of soil metals.

KEY WORDS: heavy metals, leaching, contaminated soils, soil columns, soil cores, pyrite tailings.

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INTRODUCTION

A spill, containing potentially high contents of toxic metals, of pyrite-rich mud occurred on April 1998 as a result of the collapse of a tailings pond dam. This pond was located at the Aznalcollar pyrite mining site (Sevilla, southern Spain) at a distance of 50 km from the World Heritage site of the Doñana National Park. An area 40 km long and 0.5 km wide was covered by a 3- to 30-cm-thick layer of pyrite slurry, reaching the edges of the Doñana National Park. About 4500 h of crops, pasture lands, and woodlands were affected.

Analyses carried out immediately after the spill revealed high concentrations in heavy metals such as Cd, Zn, Cu, and Pb in the mud overlying the soils as well as the fact that some elements had reached high concentrations in the first 0 to 20 cm of the affected soils (Bravo, 1998). The incorporation of heavy metals into these soils occurred through percolation of the acid waters from the spill, by direct entry of solutions through cracks and fissures in the soil, and through washing of the deposited mud via occasional rains.

Between June and October of 1998, the mud deposited on the soils was removed mechanically. However, the soil considered to be clean continued to contain mud mixed with the soil that could still allow leaching of the toxic metals to deeper soil horizons.

It is generally known that soil may act as a sink for heavy metals, although it may also act as a potential site of metal remobilization, depending on the prevailing environmental conditions. The total content of heavy metals in polluted soils cannot be considered an index for the estimation of the potential risk to other environmental reservoirs because this depends on the soluble fraction of each of the elements. Historically, as an approximation of potential risk, different extraction procedures have been employed (Tessier *et al*., 1979; Beckett, 1989), but risk determination is considered more reliable, although more tedious, when carried out by means of soil leaching in packed columns (Korte *et al*., 1976; Tyler and McBride, 1982). On the other hand, the distribution of metals in the soil profile as a function of leaching can be studied, in an approximate way, in intact soil cores (columns or lysimeters) (Sheppard *et al*., 1987; Camobreco *et al*., 1996), which allow control of the water flow that is not possible in field studies.

A series of chemical and physicochemical processes are involved in the vertical leaching or mass flow of metals in the soil (Ross, 1994; Alloway, 1995). In turn, these depend on the chemical characteristics of each metal and on the soil parameters, such as pH, the carbonate content, free iron and aluminium oxide contents, and the nature and content of the clay and organic matter fractions (Davies, 1980; Adriano, 1986; McBride, 1994).

Regarding the problem due to the spill, after the emergency studies others were conducted on the impact of the spill on the soils (Simón *et al*., 1998), and also concerning the impact on air (Querol *et al*., 1999) and water quality (Manzano *et al*., 1999). Studies have also been carried out aimed at predicting the mobility of metals in soils affected by the spill (Vidal *et al*., 1999; Díaz-Barrientos *et al*., 1999). Vidal *et al*. (1999) made an estimation of long-term trace element mobility based on the forms extractable with CH_3-COOH and with C_aCl_2 and on the distribution coefficients, Kd, of a given metal in a given soil. Diaz-Barrientos *et al*. (1999) estimated the potentially mobilizable elements in the affected soils based on the forms extractable with CaCl2 and with EDTA. No studies have provided more realistic results about the mobility or leaching of heavy metals in the affected soils, such as investigations that involve the leaching with water of soil columns that simulate field leaching conditions with rainwater.

In the present work we studied the leaching of Cd, Zn, Pb, and Cu in soils from the three areas with well-differentiated soil types of affected zone after removal of the muds using packed soil columns. The aim of these studies was, on the one hand, to determine the relative leaching of these elements from these specific soils, with an also specific pollution and, on the other, to determine the efficacy of the soils themselves at attenuating metal mobility as a function of their chemical and physicochemical properties. The mobility of the four elements was also studied in the affected soil cores with an aim to determining the distribution profile of the metals by simulating their leaching in the field by rainwater. These studies can provide data at this time in order to take decisions concerning the need for the immobilization of the metals and for the selection of remediation technologies of the soils.

Material and Methods

According to the cartographic study carried out by Clemente *et al*. (1998) in the zone affected (Figure 1), it is possible to distinguish three areas with well-differentiated types of soils: sandy-clay loam soils with a low carbonate content, clayed soils with a moderate carbonate content, and clayed soils with a high carbonate content (Clemente *et al*., 1998). In each of three areas, a sector was selected at the sites called: Doblas (soils D), Aznalcollar (soils A), and Soberbina (soils S). Samples of soils (0 to 20 cm) (D1, A1, and S1) and intact soil cores (D2, A2, and S2) after removing the mud were collected from these sectors. Samples (0 to 20 cm) were also taken from soils unaffected by the spill (D3, A3, and S3) in the same sectors. So that the selected soil samples were representative of each area, selection was made on the basis of the characteristics of the soil series taken and studied to perform the cartographic study of the zone (Clemente *et al*., 1998).

According to Clemente *et al*. (1998), the soils of these areas correspond to the following categories: Aquic Xerofluvents (D soils), Typic Haploxeralfs (A soils), and Calcic Haploxeralfs (S soils) (Soil Survey Staff, 1990). Table 1 shows selected characteristics of the samples.

The relative leaching of the elements was studied in 3 cm (i.d.) × 20 cm (length) glass columns packed with 100 g of soil (D1, A1, and S1) previously sieved through

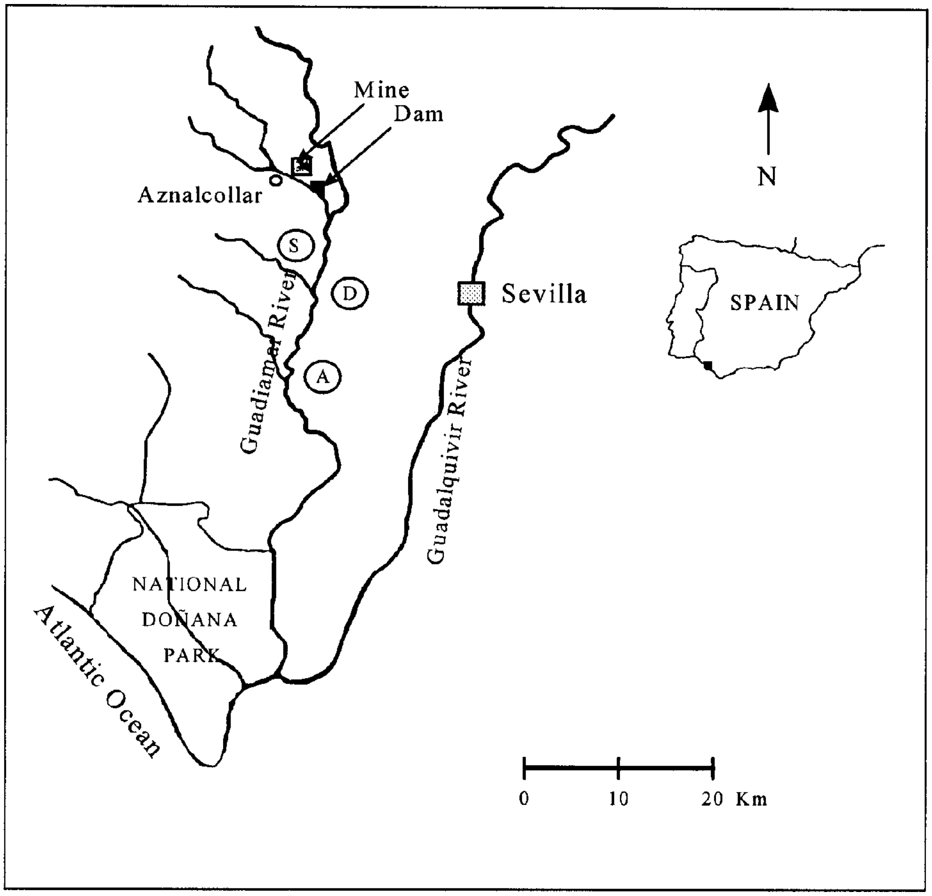

FIGURE 1

Location of soil samples.

a 4-mm screen. For a uniform packing, small increments of soil were added to the column held in firm contact with a vortex-type mixer. To prevent some breakthrough of soil particles, a glass wool bed was placed in the bottom of the column (Weber *et al*., 1986). The columns were leached with 400 mL (560 mm) of tapwater under a saturated flow regime, collecting successive 25-mL leach fractions in which the concentrations of Cd, Zn, Pb, and Cu were measured. The pH of the water used for leaching was 7.5, this being similar to that of the rainwater (pH 7.1). The pH of the leachates ranged between 7.2 and 7.7 for soil D, 7.2 and 7.6 for soil A, and 7.5 and 7.8 for soil S. To study the effect of leaching on the distribution of the metals at depth, the intact soil cores (9 cm (i.d.) × 40 cm [length] steel tubes) were washed with 40 mL of tap-water every day up to a total volume of 1200 mL (200 mm). Leached fractions were collected every day and analyzed for all metals that appeared at significant concentrations in the leachates (detection limit 20 μg L-1). At the end of the leaching, the soil cores were cut into 5-cm segments. All experiments were carried out in duplicate.

TABLE 1
Selected Soil Characteristics

Soil	pH	Carbonates %	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Free Fe_2O_3(%)	Free Al_2O_3 (%)	Clay mineralogy*
D1	6.6	1.02	1.58	54.8	10.9	34.3	2.52	0.45	I,K,S
D3	7.3	9.78	1.42	44.2	9.3	46.5	1.26	0.25	
A1	6.6	0.20	2.97	34.0	17.8	48.1	1.88	0.56	I,K,S
A3	7.5	4.09	1.26	42.3	14.9	42.8	1.50	0.53	
S1	7.2	6.59	2.33	25.4	18.8	55.9	1.76	0.61	I,K,S
S3	7.5	6.64	1.42	29.5	18.9	51.7	1.37	0.57	

[a] I, illite; K, kaolinite; S, smectite.

To determine the total content of the different metals in the polluted and unpolluted soils (0 to 20 cm) and in each segment of the soil cores, 1 g of finely powdered sample (< 0.75 mm) was dissolved in 7.5 mL of HCl and 2.5 mL HNO_3, using a CEM microwave oven, model MDS-2000, and brought up to a volume of 25 mL with distilled water.

Heavy metals were determined by atomic flame spectrophotometry using a Varian-1475 instrument coupled to a GTA-95 graphite furnace (Varian). Standard solutions containing the same matrix as the samples were made up at appropriate concentrations for each element. Analyses were performed according to the recommendations given in the Varian Manual for Analytical Methods (Rothery, 1982). Analytical accuracy in the determinations of the total contents of the elements was checked with BCR reference materials: CRM 141 (calcareous loam soil) (Colinet *et al*., 1983) and CRC 320 (river sediment) (Griepink and Muntau, 1988) (Table 2). The precision of the method was assessed by performing the experiments 10 times for a single soil sample. The relative standard deviation (RSD) for total content determinations of elements was between 5 and 10%.

RESULTS AND DISCUSSION

Table 3 shows the total contents of Cd, Zn, Pb, and Cu in the mud deposited on the soils, top soils affected by the spill, unaffected top soils, and top layers (3 cm) of intact cores. The contents of the four heavy metals in the muds are high. These metals are found in the pyrite muds in the form of sulfides: Zn as sphalerite (ZnS), Cu as chalcopyrite (CuFeS2), Pb as galena (PbS), and Cd as isomorphic substitutions in the sulfides (Sierra, 1984). According to the range of critical concentrations proposed by Kabata-Pendias and Pendias (1992), and based on values considered to be critical by different investigators, the three unaffected soils have a previous degree of contamination in Cd and soil D3 is also contaminated by Zn and Cu. Of these three soils, D3, in general, is the most polluted. Such high previous pollution in these soils is not surprising because they are from the area of influence of the mine, which has been exploited, with sporadic interruptions, for many years.

TABLE 2
Total Contents of Elements (μg g^{-1}) for BCR Certified Reference Materials

Element	CRM 141		CRM 320	
	Reference value	Found value	Reference value	Found value
Cd	0.36 ± 0.11	0.38 ± 0.05	0.53 ± 0.04	0.49 ± 0.06
Zn	81.3 ± 6.35	77.4 ± 5.31	142 ± 4.72	131 ± 11.5
Pb	29.4 ± 4.66	31.4 ± 2.43	42.3 ± 1.89	42.1 ± 3.45
Cu	32.6 ± 2.51	28.3 ± 1.74	44.1 ± 1.73	40.8 ± 2.73

TABLE 3
Total Metal Contents (µg g^{-1}) in the Mud, in Affected and Nonaffected Soils (0 to 20 cm) and in the Top Layer (3 cm) of Intact Soil Cores

Sample	Cd	Zn	Pb	Cu
Mud	50	7933	7002	1880
Soil D1	6.0	829	359	218
Soil D3	3.0	147	89.8	198
Soil D2	19.1	4999	4900	1306
Soil A1	6.9	869	785	156
Soil A3	3.3	40.9	37.8	12.8
Soil A2	2.4	700	980	252
Soil S1	5.0	341	239	56.5
Soil S3	3.5	44.1	43.1	13.4
Soil S2	4.9	1130	250	153

Note: D1, A1, S1 = packed column soils.
D3, A3, S3 = nonaffected soils.
D2, A2, S2 = top layer (3 cm) of intact soil cores.

The high background of heavy metals in this area has already been discussed by other authors (Ramos *et al*., 1994; Arambarri, 1998).

The three soils affected by the spill can be considered to be polluted by all the elements studied. According to the Dutch guide for the assessment of polluted soils (Alloway, 1995), they can be classified as type C, meaning that they require remediation. This is the case for Zn and Cu in soils A1 and D1 and for Pb in soil A1.

Figure 2 shows the leaching curves of Cd, Zn, Pb, and Cu in packed columns of mud and of soils (0 to 20 cm) affected by the spill. Data are presented in the plots as heavy metal concentration (breakthrough curves) and cumulative amounts (cumulative curves) in the leachates (percent of total amount in the column) vs. leachate volume. Table 4 shows the ratios of metals leached to the total contents of the columns as a percentage.

The percolation curves for the different metals in the mud column suggest a rapid leaching of the soluble fraction of all the metals per 110 mL of leachate. The fractions of Zn and Cu leached are high, representing 56.5 and 38.2% of the total. The fraction of Cd leached is lower, representing 21.6% of the total, whereas Pb is immobile (0.22%).

The percolation curves of Cd in the three soils (Figure 2) display an initial elution maximum. The concentration of this maximum and the concentrations successively leached decrease in the following order: soil D1 > soil A1 > soil S1. The total amount leached ranges between 3.01% for soil D1 to 0.05% for soil S1. The percolation curves for soils D1 and A1 show a constant decrease in the height of the tail, which is revealed as an increase in the concavity of the cumulative curve. This indicates that although the leaching of Cd potentially leachable with water has not finished with the volume of water used in the experiment, it would

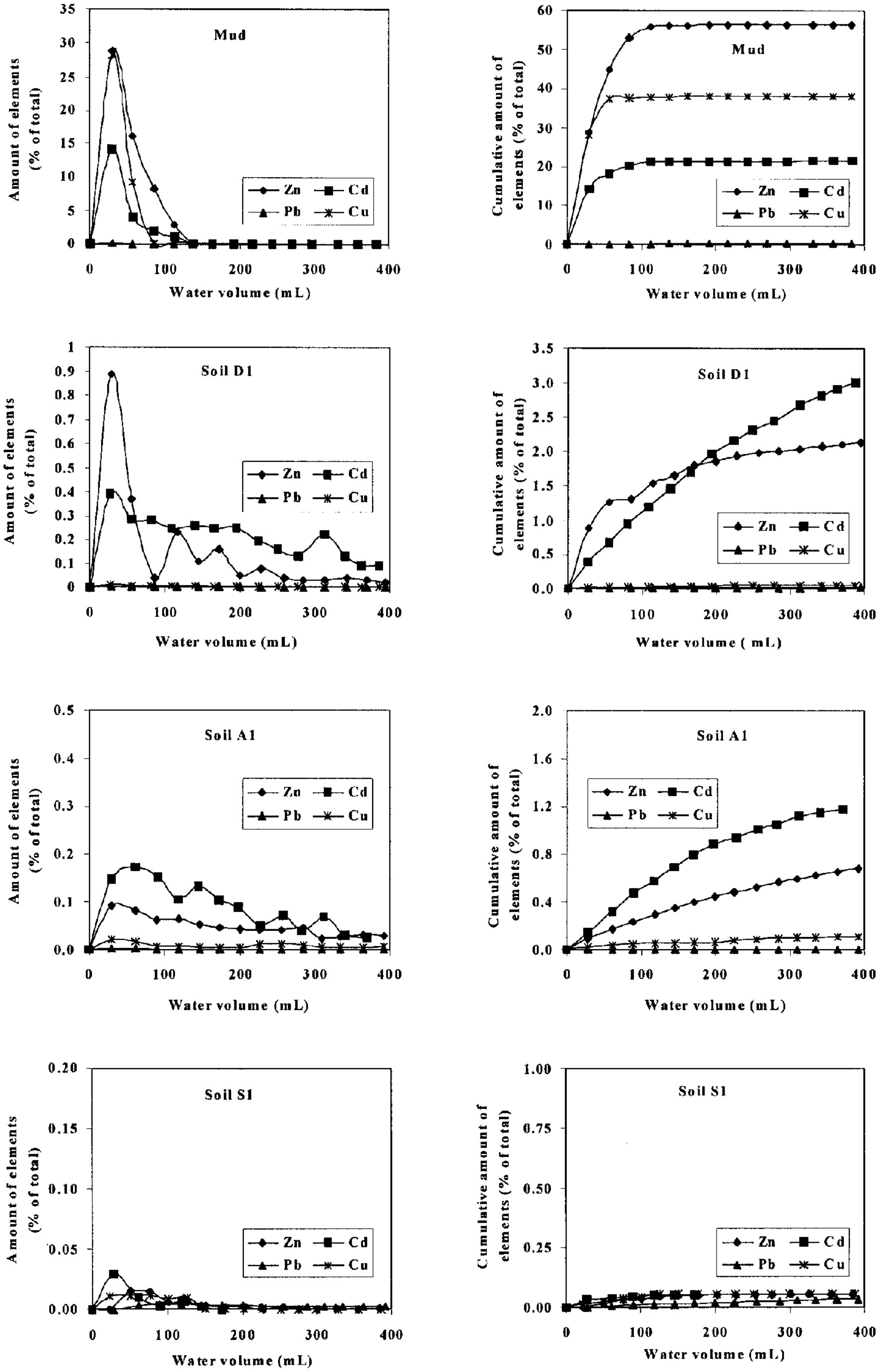

FIGURE 2

Breakthrough and cumulative curves of metal leaching in columns of mud and of affected soils.

TABLE 4
Amount of the Metals Leached as Percentages of Total Contents of Packed Columns[a]

Metal	Mud	Soil D1	Soil A1	Soil S1
Cd	21.6	3.01	1.18	0.05
Zn	56.6	2.13	0.69	0.06
Pb	0.22	0.02	0.01	0.03
Cu	38.2	0.06	0.11	0.06

[a] Leaching with 400 mL of tapwater.

tend to finish with a moderate increase in the flow of water. Based on the leaching curves obtained for soil S1, all the potentially leachable Cd of the column has passed to the leachates under the experimental conditions.

Variations in metals leached, from the different soils, are consistent with the variations in the carbonate and clay content, which together with the pH are the principal controls in the adsorption and mobility of Cd in soils (Korte *et al*., 1976; Sánchez-Camazano and Sánchez-Martín, 1993). These characteristics also govern the distribution of this element in the profile of natural soils (Sánchez-Camazano *et al*., 1994; Hargital, 1995; Sánchez-Camazano *et al*., 1998).

The leaching and cumulative curves of Zn in the soils (Figure 2) are very similar to those of Cd and the amounts leached vary in the same order: soil D1 > soil A1 > soil S1. The percentage of the total of the column leached is slightly lower than that of Cd in soils D1 and A1 and similar in soil S1. This kind of behavior is in agreement with results showing that Zn is less mobile than Cd (Tyler and McBride, 1982; Hickey and Kittrick, 1984). Increased mobilization of this element in soil D1 may be related to the lower contents of organic matter and clay in this soil, as these fractions are the dominant controls of Zn adsorption in soils.

Considered to be the least mobile heavy element in soils (Adriano, 1986; McBride, 1994), Pb is almost completely immobilized in all three soils, the amounts leached always being lower than 0.05% of the total of the column (Table 4). Although the soils differ in their organic matter content, and although there are differences in the contents of free oxides and carbonates, the amounts of these components and their joint action seem to be sufficient for the element to become immobilized in all three soils.

Cu shows low mobility in the three polluted soils, only 0.06 to 0.11% of the total of the column is leached (Table 4). According to percolation curves, amounts of Cu leached are slightly higher than those of Pb. As is known, copper and lead are the least mobile heavy metals (McBride, 1994), and Cu is strongly adsorbed by all the colloidal components of the soil, such as oxides of iron and aluminium, clays, and organic matter. The amounts of these components in the three soils studied here seem to be sufficient for the complete immobilization of this element.

According to these results, the following conclusions may be drawn. The relative leaching of the elements studied in the polluted soils calculated from the percentages leached in the soil columns are as follows: Cd > Zn > Cu > Pb. The polluted soils themselves have a good capacity to immobilize the soluble fraction of the elements from the mud incorporated into the soil if one takes into account the higher percentages of these elements that are leached from the mud columns (Table 4). In general, this capacity varies as follows: clay-rich soil with a high carbonate content > clay-rich soil with a moderate carbonate content > sandy-clay loam soil with a low carbonate content.

The order of mobility of the metals is in accordance with that reported by Vidal *et al*. (1999) in a study about the prediction of metal mobility in soils affected by this toxic spill based on their desorption in different reagents, such as CaCl2, EDTA, and CH3-COOH. However, Diaz-Barrientos *et al*. (1999) found a higher mobility for Pb and Zn than Cu in soils affected by the spill based on the extraction of metals with CaCl2 and EDTA.

In studies on the leaching of these metals added to three packed soil columns and eluted with a CaCl2 solution, Tyler and McBride (1982) also showed that the mobility of the metals in the soils tended to follow the order of Cu<<Zn<Cd and the lowest mobility was observed in a fine-loamy soil with a relatively high pH. Along the same line, Camobreco *et al*. (1996) found a mobility order of Cd>Zn>>Cu>Pb when they studied the leaching of these metals added to packed and undisturbed soil columns.

Figure 3 shows the distribution profiles of Cd, Zn, Pb, and Cu in the intact soil cores after being leached with 1200 mL of water (200 mm) under nonsaturated flow conditions. Although the D2, A2, and S2 soil cores were taken in the same zones and in the same sectors as soils D1, A1, and S1, owing to the low degree of uniformity in the distribution of the residual muds after their removal the contents of Cd, Zn, Cu, and Pb in the surface horizon of the soil cores (before leaching) do not correspond exactly to those of soils D1, A1, and S1 (Table 3). Contamination by the four elements of the D2 soil core in the top layer is especially high.

The distribution profile of the four elements in the three soil cores is similar, a decreasing accumulation in the first segments that reaches a greater or lesser depth, depending on the metal and the soil. This accumulation is in all cases followed by a homogeneous distribution in the remaining segments of the column. In the three soils, the accumulation of Cd and Zn occurs down to 13 cm and that of Cu and Pb down to 8 cm.

Table 5 shows the total amounts of the four elements leached in the contaminated soil cores expressed in μg m^{-2}. These amounts are expressed in absolute form, extrapolating from the surface of the column to a surface of 1 m^2 because the aim was to simulate leaching in the field with a view to knowing the distribution of the elements in the soil profile and the magnitude of leaching from the three soils**.** Cd, Zn, and Cu were detected in the leachates of cores A2 and S2, but Pb was not detected in them, whereas in the leachates of core D2 all four elements were

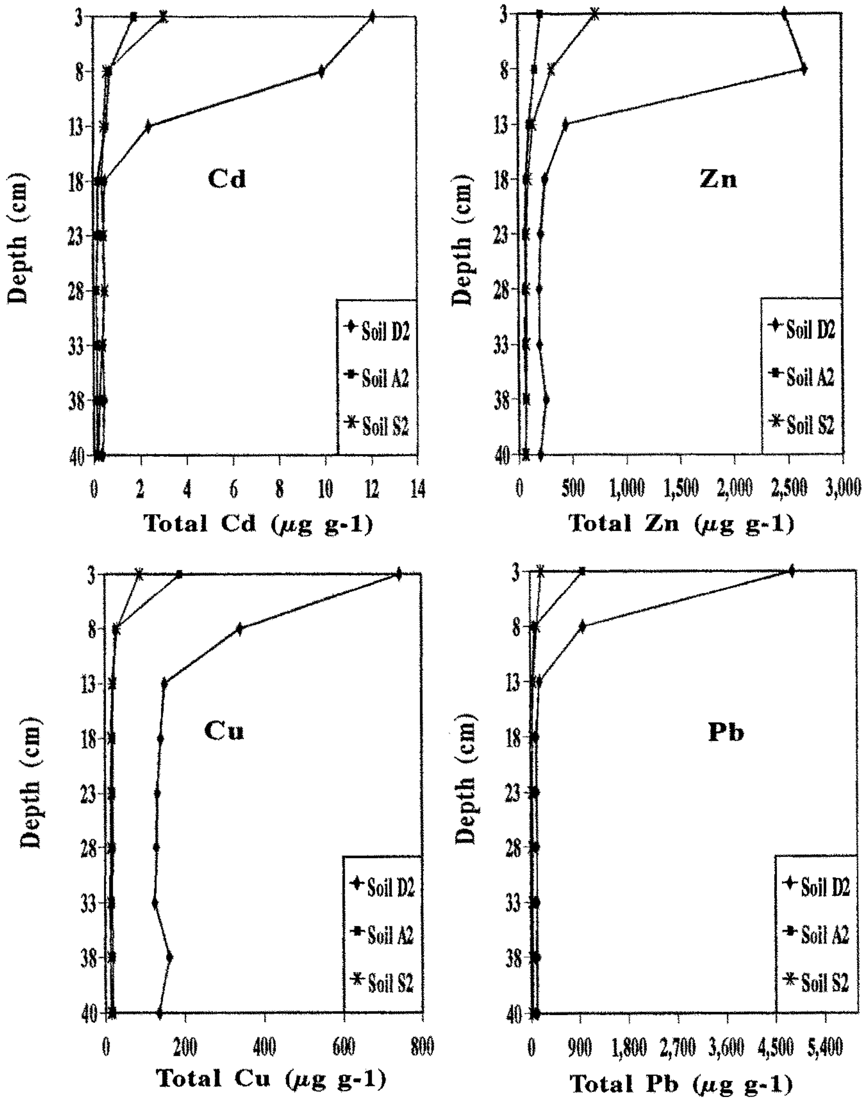

FIGURE 3

Vertical distribution profile of metals in the intact soil cores after washing.

TABLE 5
Total Amounts of the Metals Leached in the Soil Cores[a] Expressed in $\mu g\ m^{-2}$

Metal	Soil D2	Soil A2	Soil S2
Cd	593	58.2	17.3
Zn	144716	9799	10083
Cu	2501	192	676
Pb[b]	9234	<100	<100

[a] Leaching with 1200 mL of tapwater.

[b] Detection limit in the leachates 20 $\mu g\ L^{-1}$.

detected. The amounts of the four elements leached in core D2 were always higher than those leached in cores A2 and S2 and can be considered moderately high.

The increase in the leaching of metals in core D2, especially for Cu and Pb, with respect to the leaching that occurs in the packed soil column must first be due to the greater degree of pollution of core soil (Table 3). Additionally, this increase suggests the possible existence of preferential flow paths in the core, because it occurs in the nonsaturated leaching regimen and not in the packed column, where leaching could be favored by the saturated flow regimen. The preferential flow paths could be due to specific structure of the core and also to the changes in soil humidity due to the intermittent washing. Camobreco *et al*. (1996) have also reported for a soil, longer leaching of the same metals studied in this work in cores than in packed columns. These authors also attribute this leaching increase as due to preferencial flow paths in the cores.

The leaching of metals in the intact cores of soils affected simulates the fate of metals in the real scenary in each soil type, and it gives rise to results on the distribution of the elements that corroborate that the polluted soils themselves have a good capacity to immobilize the soluble fraction of the elements from the mud. However, under conditions of abundant rain, the soils of type D2 (sandy, with a low carbonate content and a high level of pollution) do pose some risk with respect to the contamination of underground waters if one considers the total amount of metals potentially leachable below 40 cm of soil (Table 5).

These results reflect the leaching of the elements in the three types of soil that were taken immediately after the spilled mud had been removed. In these soils, a slight decrease in pH was observed with respect to adjacent soils unaffected by the spill (Table 1). This decrease is due to the acid nature of the spill and to the leaching and later hydrolysis of soluble sulfates arising from the oxidation of pyrite (Simón *et al*., 1998). This is a frequent process and, in view of its environmental importance, has been studied in depth in zones of residues and tailings from pyrite mines (Lowson, 1982; Kelly, 1988; Allan, 1995; McGregor *et al*., 1998). An increase in the content of free iron oxides due to the hydrolysis of iron sulfate was also observed (Table 1). However, as later a progressive oxidation of the sulfides incorporated as such into the soils continues to be observed (M. Simón, 1999, personal communication), the soils must be undergoing acidification (M. Simón, 2000, personal communication), which can promote the leaching of certain elements. This latter phenomenon could mainly affect elements that are adsorbed as exchange cations by soil colloids (Kabata-Pendias and Pendias, 1992), such as Cd and Zn, which could change from being moderately mobile in soils similar to D1 with a pH of 6 to highly mobile if the soils were to reach pH values below this. The decrease in pH would also affect Cu and Pb (McBride, 1994), which would change from being almost immobile to being moderately mobile.

The increase in the mobility of toxic metals due to acidification of the soil will demand the application of remediation techniques. It will be necessary to select physicochemical technologies to immobilize the elements. In this sense, already established methods for the physicochemical immobilization of heavy metals, such as those based on the addition to polluted soils (Adriano *et al*., 1998) of limestone, clay minerals, zeolites, hydroxyapatite, Fe oxides, and organic materials are currently being tested in soils from zone (A. García-Sánchez, 2001, personal communication) with a view to selecting the most appropriate technique.

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