Heavy metal pollution of soils affected by the Guadiamar toxic flood

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Total heavy metal concentrations were determined in soil samples of seven selected areas along the Guadiamar river valley affected by the toxic flood, after removal of the deposited sludge. Mean total concentrations of nine elements (As, Au, Bi, Cd, Cu, Pb, Sb, Tl and Zn) out of the 23 (As, Au, Ba, Be, Bi, Cd, Co, Cr, Cu, In, Mn, Mo, Ni, Pb, Sb, Sc, Sn, Th, Tl, U, V, Y and Zn) analysed were higher in sludge-covered soils than in unaffected soils. Mean values of total As, Au, Pb, Sb, Tl and Zn in sludge-affected soils were higher than the upper limits for normal soils world-wide. Mean concentrations of Bi, Cd and Cu were within these ranges, although some individual values exceeded the upper limits. In all sampling areas, severe heavy metal pollution was observed in the superficial layers (0−20 cm) of most of the affected soils, which decreased downward in the soil profile. Generally, in soils with more than 25% of clay, concentration of heavy metals below the 20-cm depth decreased to values close to those of the background level of the Guadiamar valley soils, while in coarser soils, heavy metal pollution penetrated below this depth, being noticeable down to a depth of at least 50−80 cm.

Keywords: Soil; Heavy metals; Pollution; Soil texture

1. Introduction

In the early hours of the 25th April 1998, a tailing-dam dike at Los Frailes open-pit pyrite mine (Aznalcóllar, 45 km west of Seville, Spain) was breached, allowing water and solids from the tailings pond to be discharged into the nearby Agrio river, a tributary of the Guadiamar river. Approximately 4.5 million cubic meters of slurry, composed of acidic water loaded with heavy metals and other toxic elements, finely divided metal sulphides (mainly pyrite), and materials used in the refining (floating) process, inundated both riverbanks of the Agrio and Guadiamar rivers and threatened the Doñana National Park, Europe's largest national park. Along 40 km, a strip of approximately 300 m wide on both sides of the rivers was covered by a layer (2–30 cm thick) of toxic black sludge (IGME, 1998). Approximately 4500 ha of agricultural land devoted to dry-land agriculture and fruit and olive tree orchards were affected by the pollution (Consejería de Medio Ambiente, 1998).

Dissolved and particulate heavy metals (from now on we use the term heavy metals to refer not only to those metals with density > 5 g cm^{-3}, but also to other trace and toxic elements) in the slurry can pollute the soil. Dissolved heavy metals react with soil components (clay minerals, iron, aluminium and manganese oxides, carbonates, and organic matter) and are retained through different sorption processes (Selim and Amacher, 1997). The retention, and therefore the depth of penetration, of the dissolved heavy metals depends on the soil properties (pH, redox potential, moisture content, bulk density, texture, and composition) (Adriano, 1986). At the same time, sludge rich in heavy metal sulphides can enter the soil through cracks and pores, increasing the total concentration of heavy metals in the soil. Sulphidic components of the sludge, exposed to atmospheric oxygen and moisture aided by bacteria (e.g. *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*), can undergo a series of oxidation and hydrolysis reactions producing sulphuric acid and soluble and mobile metal sulphates (Förstner and Wittmann, 1983). According to Williamson and Johnson (1981), the factors liable to affect soil acidification are the carbonate:pyrite (or metal sulphide) ratio of the soil and the reactivity of the sulphidic components (which is related to the crystal form and to the particle size of the minerals).

In order to start the remediation of the affected soils, rapid information was necessary on the extent of the pollution. This paper deals with the work carried out immediately after the flood to evaluate the degree and the penetration of the heavy-metal pollution in the profiles of the affected soils.

2. Experimental

2.1. Sampling areas and sites

Between the 8th and 15th of May 1998, soil samples were taken at different depths (0–5, 5–10, 10–15, 15–20, and 20–50 cm) at sampling sites in seven areas along the Guadiamar valley (Fig. 1), all of them on land devoted to extensive agriculture.

Sites S1–S4 are in the area named Finca Soberbina (4.5 km from the tailing-dam), on the left bank of the Guadiamar river opposite the confluence with the Agrio river. The soil is a piedmont of the calcareous Mio-Pleistocene massif of Aljarafe, and had alluvial influence until recent times, when the river formed a new meander and left its old bed. Today, this soil is outside the river's dynamic influence. Sites S2 and S4 are approximately 200 m from the river bed, in the area of land covered by the sludge, and S1 and S3 some 20 m from S2 and S3, respectively, outside the sludge-affected area.

Site D is on the right bank, 25 m from the Guadiamar river bed, close to the bridge of Las Doblas (12 km from the tailing-dam) on the trunk road N-431, on a soil covered with sludge. This soil is in the low-water river bed and received alluvial deposits during flash flood events.

Sites L1–L4 are on the right bank of the river at Cortijo los Lagares (15 km from the tailing-dam), at 40 (L1), 80 (L2) and 150 (L3) m from the water course on affected land, and at 180 m (L4) on unaffected soil. Sites L1 and L2 are in the floodplain of the river, and sites L3 and L4 are outside the dynamic influence of the river.

Sites PA1 and PA2 are 23 km from the tailing-dam, on the right bank of the river, 20 m from the river bed, on unaffected (PA1) and affected (PA2) soil. These sites are close to the old bridge (Puente de Aznalcázar) of the Aznalcázar-Pilas road.

Sites A1–A3 are 25 km from the tailing-dam, on the right bank of the river, 50 (A1) and 100 (A3) m (on sludge-covered soils) and 120 m (A2) (on unaffected soil) from the river bed. This series of sites was designated to Aznalcázar because of the proximity of this village. Soils at PA1, PA2

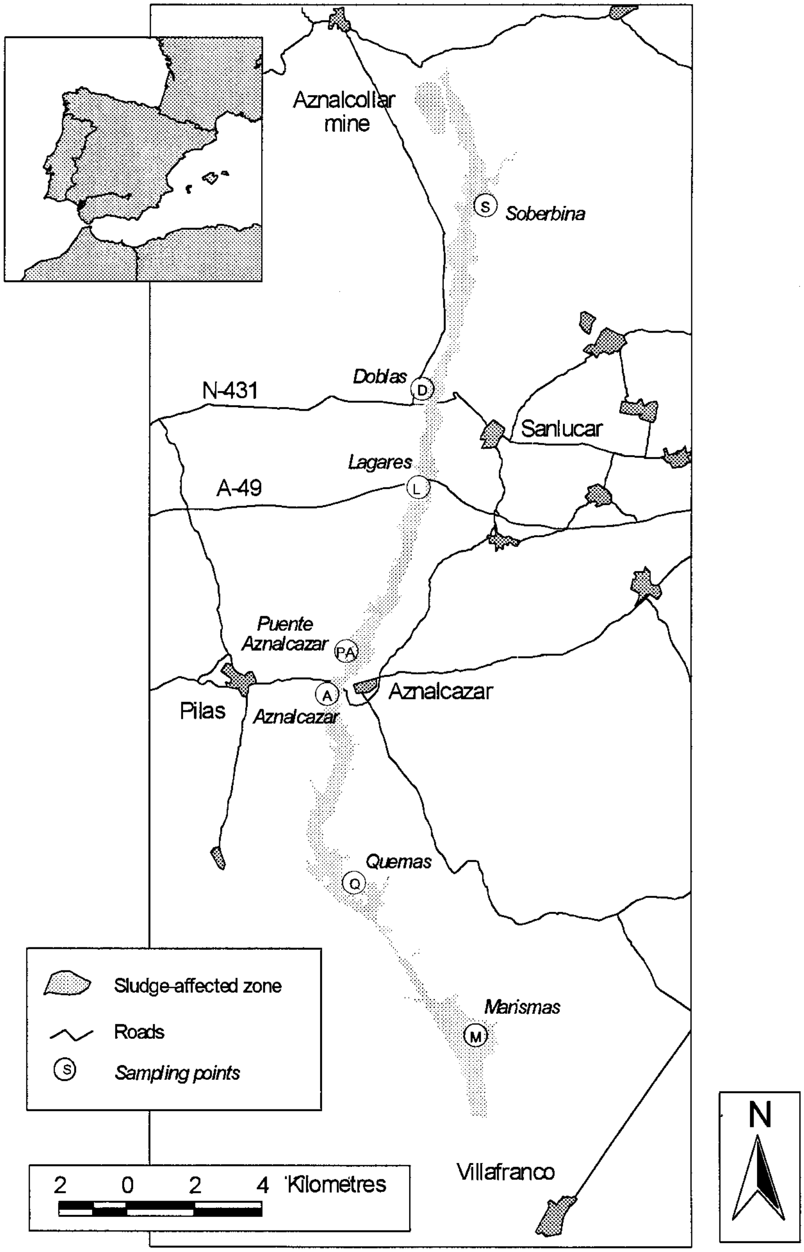

Fig. 1. The Guadiamar river. Extent of the affected zone and situation of the sampling areas. (Adapted from IGME, 1998.)

and A1 are in the floodplain of the river, subjected to river sedimentation, although sites PA1 and PA2 are today outside the river's influence because of the construction of a road. Soils at A2 and A3 are outside the dynamic influence of the river.

Site Q is on sludge-affected soil on the left bank of the river, 50 m from the river bed, at Cortijo de Quemas (30 km from the tailing-dam). Soils at this site are alluvial and are in the sedimentation meandering zone.

Sites M1–M3 (38 km from the tailing-dam) are on the marshes of the Guadalquivir river, across which the river flows in the last stretch of its course. This is a flat area liable to flash flooding. Here, the right bank of the river is protected with a levee to prevent flooding of the reclaimed saline soils on that bank. M1 is on the right bank, 20 m from the river, unaffected by the sludge, and M2 and M3 are located on the left bank, parallel to the river and 20 m from it, on sludge-covered land.

At sites S3, S4, A2, A3, L3 and L4, soil samples were also taken at a depth > 50 cm.

The soils were classified as Typic Xerofluvent (D, L1, L2, PA1, PA2, A1 and Q), Vertic Xerofluvent (M2 and M3), Typic Xerochrept (A2 and A3), Calcixerollic Xerochrept (S1–S4), Typic Haploxeralf (L3 and L4) and Aquic Haploxerert (M1) (Soil Survey Staff, 1994).

2.2. Soil sampling and analytical methods

Sampling of the affected soils was carried out by digging a pit 50 cm deep after removing the deposited sludge and cleaning the surface. Whenever possible, samples of soils unaffected by the sludge were also taken in a similar way at sites close to the affected spots. Samples of sludges were also taken at each site.

Soil and sludge samples were oven-dried (50°C) and crushed to pass through a 2-mm sieve, and then ground to < 60 μm. Soil samples (2 mm) were analysed for pH in saturated paste (Hesse, 1971), total carbonate content was determined by the manometric method (Demolon and Leroux, 1952), and size particle distribution by the hydrometer method (Gee and Bauder, 1979).

Heavy metal and other trace element contents (As, Au, Ba, Be, Bi, Cd, Co, Cr, Cu, In, Mn, Mo, Ni, Pb, Sb, Sc, Sn, Th, Tl, U, V, Y and Zn) in the soil (< 60 μm) and sludge samples were determined by ICP-MS after digesting the samples with a mixture of concentrated HNO_3 and HF to dryness and redissolving in 4% concentrated HNO_3. Total heavy metal concentrations were calculated on a dry weight basis. The accuracy and precision of the method were assessed by carrying out analyses of two BCR reference samples: CRM 141 (calcareous loam soil) and CRM 277 (estuarine sediment) (Colinet et al., 1983; Griepink and Muntau, 1988). Recoveries from CRM 141 ranged from 83 to 118%, with a relative standard deviation (R.S.D.) of 0.79–77%, being $< 10\%$ for 18 out of the 23 elements analysed. Recoveries from CRM 277 ranged from 81 to 107%, with R.S.D. of 0.54–21%, being $< 5\%$ for 19 out of the 23 analysed (Table 1).

2.3. Quantification of the soil pollution

The degree and the penetration of heavy metal pollution in the affected soils were measured and compared using the Pollution Load Index (PLI) of Tomlinson et al. (1980). This index is based on the values of the Concentration Factors (CF) of each metal in the soil. The CF is the ratio obtained by dividing the concentration of each metal in the soil ($C_{\text{heavy metal}}$) by the base line or background value (concentration in unpolluted soil, $C_{\text{background}}$)

$$\mathrm{CF}_i = \frac{C_{\text{heavy metal}}}{C_{\text{background}}}$$

In this paper, background values were estimated from the mean concentrations of the heavy metals in unaffected soils of the studied area.

For each sampling site, PLI at one determined soil depth may be calculated as the nth root of the product of the n CF:

$$\mathrm{PLI} = \sqrt[n]{(\mathrm{CF}_1 \times \mathrm{CF}_2 \times \ldots \times \mathrm{CF}_n)}$$

This index provides a simple, comparative means for assessing the level of heavy metal pollution. Values of $\mathrm{PLI} = 1$ indicate heavy metal loads close to the background level, and values above 1 indicate pollution.

2.4. Statistical analysis

When sets of data of total heavy metal concentrations in affected and unaffected soils were normally distributed, Student's t-test was used to detect differences between paired means. When the normality test failed, the Mann–Whitney

Table 1
Analysis of BCR reference samples[a]

Element	CRM-141					CRM-277				
	Certified (indicative)		Experimental			Certified (indicative)		Experimental		
	Mean	R.S.D.	Mean	R.S.D.	Recovery (%)	Mean	R.S.D.	Mean	R.S.D.	Recovery (%)
Mn	(547)	ND	530	0.79	97	(1600)	ND	1560	0.80	98
Be	ND	–	2.07	9.9	–	(1.6)	ND	1.81	21	113
Ba	ND	–	234	2.2	–	(324)	ND	300	0.81	93
Sc	ND	–	9.93	3.4	–	9.0	1.3	9.17	2.9	102
V	ND	–	87.7	1.8	–	(102)	ND	101	0.39	99
Cr	(75)	ND	72.7	3.1	97	192	3.6	172	1.1	90
Co	(9.2)	ND	10.9	4.2	118	(17)	ND	16.3	1.3	96
Ni	(30.9)	ND	33.8	4.8	109	43.4	3.7	45.3	1.4	104
Cu	32.6	4.3	34.3	5.5	106	101.7	1.6	105	0.79	103
Zn	81.3	4.6	83.4	2.9	103	547	2.2	585	0.69	107
Y	ND	–	18.1	1.6	–	ND	–	33.2	0.41	–
Mo	ND	–	0.56	7.7	–	(1.5)	ND	1.59	2.1	106
As	(8)	ND	7.68	1.1	–	47.3	3.4	42.8	1.4	90
Cd	0.36	27.8	0.30	12.4	83	11.9	3.4	11.6	1.3	97
In	ND	–	0.054	7.5	–	ND	–	0.32	11	–
Sb	ND	–	0.84	36	–	(4)	ND	3.25	6.5	81
Au	ND	–	0.37	77	–	ND	–	0.19	21	–
Sn	ND	–	2.03	15	–	ND	–	7.55	7.0	–
Bi	ND	–	0.58	11	–	ND	–	3.66	2.8	–
Tl	ND	–	0.55	2.5	–	ND	–	1.01	3.0	–
Pb	29.4	8.8	27.7	4.0	94	146	2.1	145	1.1	99
U	ND	–	1.55	2.0	–	(3)	ND	2.5	0.54	83
Th	ND	–	10.7	3.3	–	ND	–	8.92	4.6	–

[a] ND, not determined; R.S.D., relative standard deviation.

non-parametric test was used. A significance level of $P < 0.05$ was used throughout the study. The Sigmastat (1992) analysis program of the Jandel Corporation was used for the statistical analysis.

3. Results and discussion

3.1. Soil characteristics

Table 2 shows some characteristics of the soils. The pH of the unaffected soils ranged from 7.0 to 7.8, while the pH of the affected soils ranged from 5.8 to 7.8. Minima of the pH range of some samples of affected soils (S2, S4, L1, L2, A3, M2, and M3) were lower than those of the corresponding unaffected soils (S1, S2, A2, and M1). Generally, the lowest pH coincided with the lowest $CaCO_3$ contents. The lowest mean values of pH in the studied soils were found in the sample of Las Doblas (D), which had the lowest mean values of $CaCO_3$ and clay content.

3.2. Heavy metal contents of soils

Available data on the composition of the acidic water of the slurry (pH 5.5, As 0.27 mg l^{-1}, Cd 0.85 mg l^{-1}, Cr 0.039 mg l^{-1}, Cu 0.021 mg l^{-1}, Hg 0.008 mg l^{-1}, Mn 91 mg l^{-1}, Ni 1.1 mg l^{-1}, Pb 3.6 mg l^{-1}, Zn 462 mg l^{-1}) (Consejería de Medio Ambiente, 1998) indicated that soils affected by the flood received large amounts of dissolved heavy metals.

Heavy metals entering the soil in particulate form can be deduced from the analysis of the sludge samples. Table 3 shows mean heavy metal concentrations and ranges in the samples of sludges covering the affected soil, compared with

Table 2
Some characteristics of soils (0–50 cm)[a]

Sample	Longitude	Latitude	Prof. (cm)	pH	$CaCO_3$ (%)	Sand[b] (%)	Silt[c] (%)	Clay[d] (%)	Mean texture
Unaffected soils									
S1	W 06° 12′ 23″	N 37° 27′ 29″	0–50	7.7 (7.5–7.8)	16.7 (16.2–17.2)	8.7 (6.3–10.5)	49.0 (47.5–50.2)	42.4 (41.9–42.9)	Silty clay
S3	W 06° 12′ 25″	N 37° 27′ 29″	0–65	7.8 (7.7–7.8)	16.6 (16.0–17.4)	17.7 (15.4–21.0)	47.9 (47.6–48.1)	34.5 (33.7–35.7)	Silty clay loam
L4	W 06° 13′ 58″	N 37° 21′ 54″	0–45	7.4 (7.3–7.5)	< 1	19.3 (11.5–30.2)	48.5 (45.1–52.6)	23.0 (20.4–25.3)	Loam
PA1	W 06° 15′ 39″	N 37° 18′ 21″	0–50	7.4 (7.0–7.5)	< 1	25.3 (18.7–33.2)	38.5 (33.8–43.6)	36.2 (33.1–37.4)	Clay loam
A2	W 06° 15′ 58″	N 37° 18′ 10″	0–50	7.5 (7.0–7.6)	< 1	24.5 (22.2–27.7)	33.6 (31.7–35.5)	41.9 (41.2–42.6)	Clay
M1	W 06° 11′ 23″	N 37° 11′ 14″	0–50	7.4 (7.0–7.6)	6.8 (6.3–7.8)	4.2 (3.5–5.1)	48.5 (47.9–49.7)	47.3 (46.4–48.2)	Silty clay
Affected soils									
S2	W 06° 12′ 31″	N 37° 27′ 30″	0–50	7.6 (7.3–7.8)	17.1 (15.4–18.9)	9.7 (8.1–11.8)	44.6 (41.1–46.9)	45.8 (44.9–47.1)	Silty clay
S4	W 06° 12′ 31″	N 37° 27′ 30″	0–55	7.3 (7.1–7.5)	16.6 (15.7–21)	12.1 (9.2–47.3)	49.1 (47.3–52.3)	38.7 (36.3–41.3)	Silty clay loam
D	W 06° 13′ 51″	N 37° 23′ 00″	0–50	6.9 (6.3–7.2)	< 1	48.4 (31.5–86.3)	33.9 (9.1–46.0)	17.8 (5.5–23.2)	Loam
L1	W 06° 13′ 49″	N 37° 21′ 47″	0–50	7.4 (7.0–7.7)	14.0 (12.0–15.7)	20.2 (13.5–25.4)	49.2 (46.0–53.6)	30.6 (28.9–33.2)	Silty clay loam
L2	W 06° 13′ 51″	N 37° 21′ 51″	0–50	7.3 (7.0–7.6)	14.3 (12.9–16.6)	24.5 (12.5–37.8)	48.4 (42.2–52.8)	27.1 (24.8–30.3)	Clay loam
L3	W 06° 13′ 55″	N 37° 21′ 49″	0–45	7.4 (7.0–7.6)	4.6 (0.0–8.1)	23.6 (18.6–31.8)	44.5 (43.2–53.3)	27.0 (25.0–28.4)	Clay loam
PA2	W 06° 15′ 39″	N 37° 18′ 21″	0–50	7.6 (7.4–7.7)	15.0 (13.4–16.2)	3.3 (8.2–5.5)	41.4 (39.7–44.3)	55.4 (50.3–57.4)	Silty clay
A1	W 06° 15′ 58″	N 37° 18′ 10″	0–50	7.2 (7.0–7.5)	7.0 (6.1–7.5)	63.2 (44.1–78.0)	25.6 (22.2–34.2)	11.2 (8.3–15.4)	Sandy loam
A3	W 06° 15′ 58″	N 37° 18′ 10″	0–50	7.0 (6.3–7.3)	3.3 (< 1–8.2)	17.9 (14.5–21.2)	38.3 (34.7–41.9)	43.9 (43.6–44.2)	Clay
Q	W 06° 15′ 55″	N 37° 14′ 47″	0–40	7.2 (7.0–7.4)	6.8 (6.5–7.0)	37.9 (37.4–38.4)	35.9 (34.8–36.9)	26.3 (25.0–27.6)	Loam
M2	W 06° 11′ 10″	N 37° 11′ 15″	0–50	7.0 (5.8–7.5)	7.1 (0.0–9.7)	12.2 (6.6–23.2)	50.4 (43.4–60.4)	37.4 (31.4–44.0)	Silty clay loam
M3	W 06° 11′ 10″	N 37° 11′ 15″	0–50	7.5 (7.0–7.7)	12.0 (10.1–13.4)	20.2 (7.3–30.2)	54.6 (49.9–63.6)	25.4 (20.1–38.3)	Silt loam

[a] Mean value (range).
[b] 2–0.05 mm.
[c] 50–2 μm.
[d] < 2 μm.

Table 3
Mean concentration and range (mg kg^{-1}) of heavy metals in samples of sludge compared with normal ranges in soils

Element	Sludge		Normal soil range[a]
	Mean	Range	
As	2878	1028–4022	0.1–40
Au	0.55	0.25–0.90	0.01–0.02
Ba	564	324–742	10–3000
Be	0.75	0.12–2.24	0.01–40
Bi	61.8	25.2–78.8	0.1–13
Cd	25.1	15.1–36.4	0.01–2
Co	43.8	26.2–55.4	0.05–65
Cr	51.7	29.4–67.7	5–1500
Cu	1552	715–2035	2–250
In	2.19	0.00–2.88	0.7–3
Mn	647	393–954	20–10000
Mo	6.77	2.74–8.28	0.1–40
Ni	15.9	10.1–23.2	2–750
Pb	7888	3664–9692	2–300
Sb	669	269–797	0.2–10
Sc	4.66	2.33–9.63	0.5–55
Sn	14.7	3.02–22.6	1–200
Th	3.35	1.31–9.70	1–35
Tl	51.6	28.3–61.8	0.1–0.8
U	1.82	1.34–2.21	0.7–9
V	34.8	19.3–48.6	3–500
Y	6.38	2.55–15.3	10–250
Zn	7096	4424–10950	1–900

[a] Bowen (1979).

normal ranges in soils (Bowen, 1979). Only nine elements (As, Au, Bi, Cd, Cu, Pb, Sb, Tl and Zn) out of the 23 analysed in the sludge samples present higher concentrations than the upper limit of the normal ranges in soils. Therefore, a first assumption is that those elements could pollute the soils on which the sludge was deposited.

Mean concentrations of As, Au, Bi, Cd, Cu, Pb, Sb, Tl and Zn in the 0–50-cm layer of affected soils were higher than in unaffected soils (Table 4). Mean concentrations of As, Au, Pb, Sb, Tl, and Zn in sludge-affected soils were also higher than the upper limits of the ranges of normal soils shown in Table 3 (Bowen, 1979). Mean concentration values of Bi, Cd and Cu in affected soils were within the ranges of normal soils, although some individual values of these elements exceeded the upper limit of those ranges. Available data in the literature show that many of the individual values of As, Cd, Cu, Pb and Zn concentration in affected soils (Table 4) can be considered toxic for plant growth (Ross, 1994; Singh and Steinnes, 1994).

Table 5 shows that mean heavy metal concentrations at different depths in the (0–50 cm) soil layer of affected soils were higher than the corresponding values in unaffected soils. Mean concentrations of heavy metals in unaffected soils were very similar throughout the profile, while in affected soils they tended to decrease with depth. In affected soils with textures from clay loam to silty clay loam, heavy metal concentrations below the 0–50-cm layer were similar to those in the corresponding unaffected soils. As an example, Fig. 2 shows the concentration trends of Zn, As and Tl in three profiles (0 to >100 cm) of affected soils of (S4, A3 and L3) compared with those in the corresponding unaffected soils (S3, A2 and L4).

To calculate the PLI values of each sampling site, the background values of the studied soils were estimated as mean concentration of As, Au, Bi, Cd, Cu, Pb, Sb, Tl and Zn in unaffected soils (Table 4). Background values of Cd, Cu, and Pb were very close to the median for normal soils (Bowen, 1979), but those of As, Bi, Sb, Tl and Zn, were respectively 3.2, 2.5, 1.8, 3.5, and 1.2 times higher than the median for normal soils. As mentioned above, concentration in unaffected soils were constant throughout the profile. However, mean values in the profiles (0–50 cm) tended to increase downstream, especially at the last sampling site (Marismas) (Fig. 3). The same has also been reported by IGME (1998). This increase is a consequence of flash flood events, to which the river-bank soils have frequently been subjected. Waters of the Guadiamar river are characterised by high heavy metal contents, which increase in flood events, due to the transport of heavy metal-rich solids precipitated upstream on the Agrio and Guadiamar river beds (Cabrera et al., 1984, 1987; Arambarri et al., 1996). For this reason, PLI mean values of unaffected soils increase downstream from 0.58 in Soberbina to 1.97 in Marismas (Fig. 3). Therefore, PLI underestimates or overestimates the heavy metal pollution level in upstream or downstream samples, respectively.

Generally, PLI values in sludge-affected soils

Table 4
Total concentration (mg kg^{-1}) of heavy metals in Guadiamar soils (0–50 cm) compared with values in normal soils and values considered toxic for plant growth

Element	Unaffected soils		Affected soils		Normal soils[a]	Concentration considered toxic[b]
	Mean	Range	Mean	Range	Median	Range
As	18.9	8.37–38.5	80.4	9.38–1684	6	20
Au	0.088	0.035–0.27	0.102	0.033–0.49	–	–
Ba	302	243–359	289	214–497	500	–
Be	1.91	1.36–2.56	1.55	0.55–3.67	0.3	–
Bi	0.49	0.24–1.17	1.80	0.31–33.4	0.2	–
Cd	0.33	0.12–1.06	1.69	0.12–22.0	0.35	3–8
Co	12.4	8.19–17.6	12.5	6.04–31.2	8	25–50
Cr	68.6	48.3–89.7	61.7	26.8–92.4	70	75–100
Cu	30.9	12.3–85.0	104	12.5–958	30	60–125
In	0.063	0.034–0.11	0.123	0.026–1.24	1	–
Mn	678	398–939	602	290–940	1000	1500–3000
Mo	0.53	0.33–0.99	0.69	0.25–3.79	1.2	–
Ni	26.9	19.0–36.1	22.9	8.04–39.0	50	100
Pb	38.2	19.5–86.3	234	25.3–4969	35	100–400
Sb	1.80	0.71–3.31	13.7	0.89–323	1	–
Sc	12.5	8.89–16.7	11.2	4.79–20.4	7	–
Sn	1.27	0.00–3.97	2.29	0.00–11.3	4	50
Th	11.1	8.75–18.8	9.88	5.39–14.7	9	–
Tl	0.70	0.37–2.77	2.11	0.40–30.3	0.2	–
U	1.65	1.42–2.26	1.65	1.07–2.21	2	–
V	94.4	69.4–120	84.9	36.2–120	90	–
Y	17.8	12.4–23.9	16.8	9.55–24.4	40	–
Zn	109	53.9–271	487	56.8–5283	90	70–400

[a] Bowen (1979).
[b] Ross (1994) and Singh and Steinnes (1994).

Table 5
Mean concentrations (mg kg^{-1}) of heavy metals and values of PLI at different depths in affected and unaffected soils of the Guadiamar river valley

Depth	As	Au	Bi	Cd	Cu	Pb	Sb	Tl	Zn	PLI
Unaffected soils										
0–5	19.4	0.10	0.45	0.33	31.1	37.1	1.73	0.50	109	0.96
5–10	18.6	0.12	0.46	0.34	30.5	36.8	1.63	0.61	110	1.00
10–15	17.0	0.06	0.57	–	–	31.2	1.80	0.78	–	–
15–20	18	0.06	0.54	0.33	31.1	39.3	1.97	1.00	113	1.02
20–50	17.5	0.10	0.38	0.37	30.9	37.8	1.75	0.51	108	0.95
Affected soils										
0–5	106	0.10	2.26	3.07	108	352	20.9	2.96	965	5.39
5–10	172	0.13	3.64	2.57	137	510	31.8	3.92	678	6.73
10–15	31.9	0.07	0.87	0.84	69.0	88.6	4.14	1.28	248	1.89
15–20	37.2	0.11	1.09	0.95	81.1	102	4.75	1.46	272	2.26
20–50	38.1	0.10	0.91	1.02	100	86.5	4.25	1.05	263	2.11

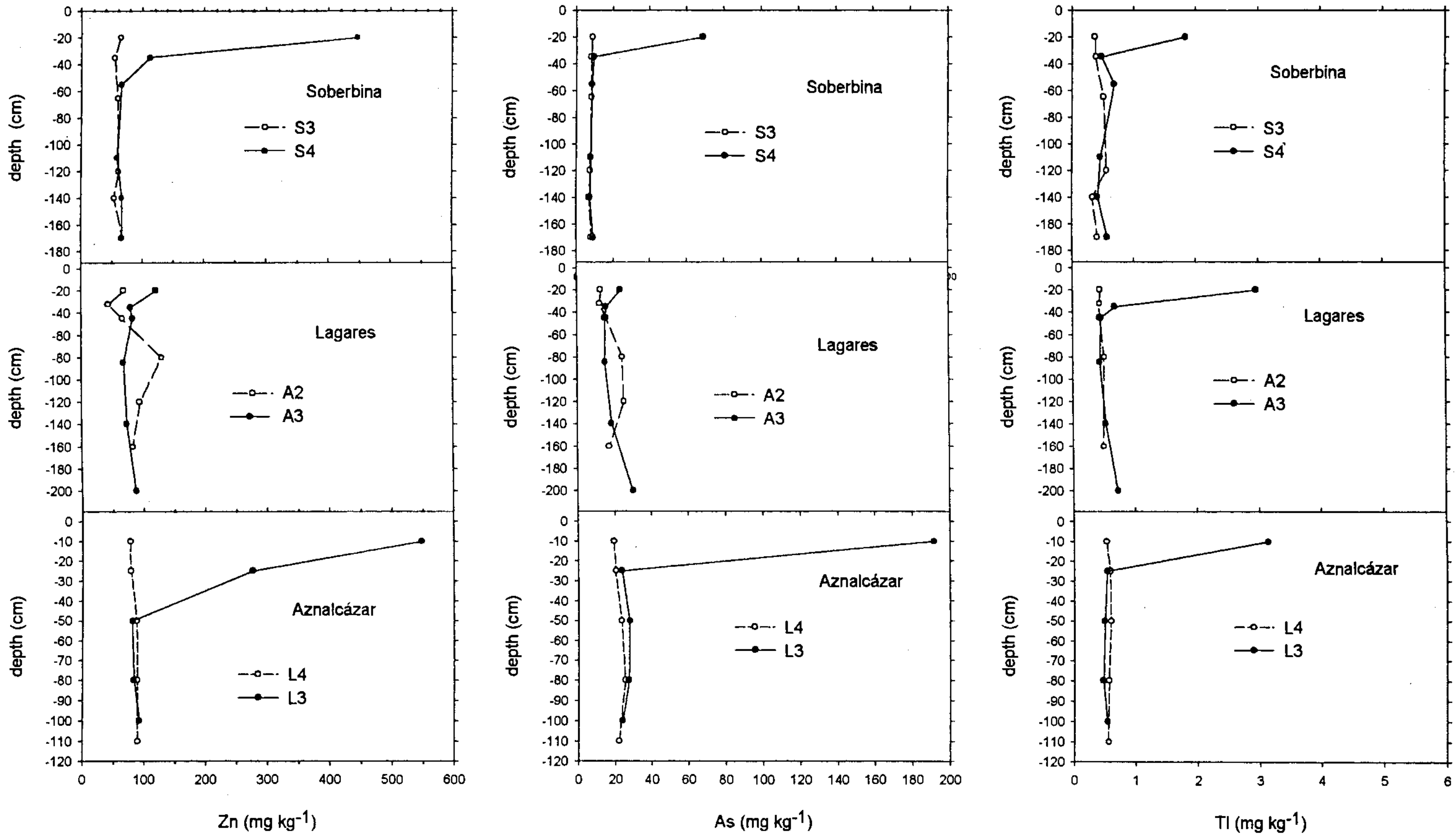

Fig. 2. Concentrations of Zn, As and Tl in soil profiles (0 to > 100 cm). Open points: unaffected soils. Solid points: sludge-affected soils.

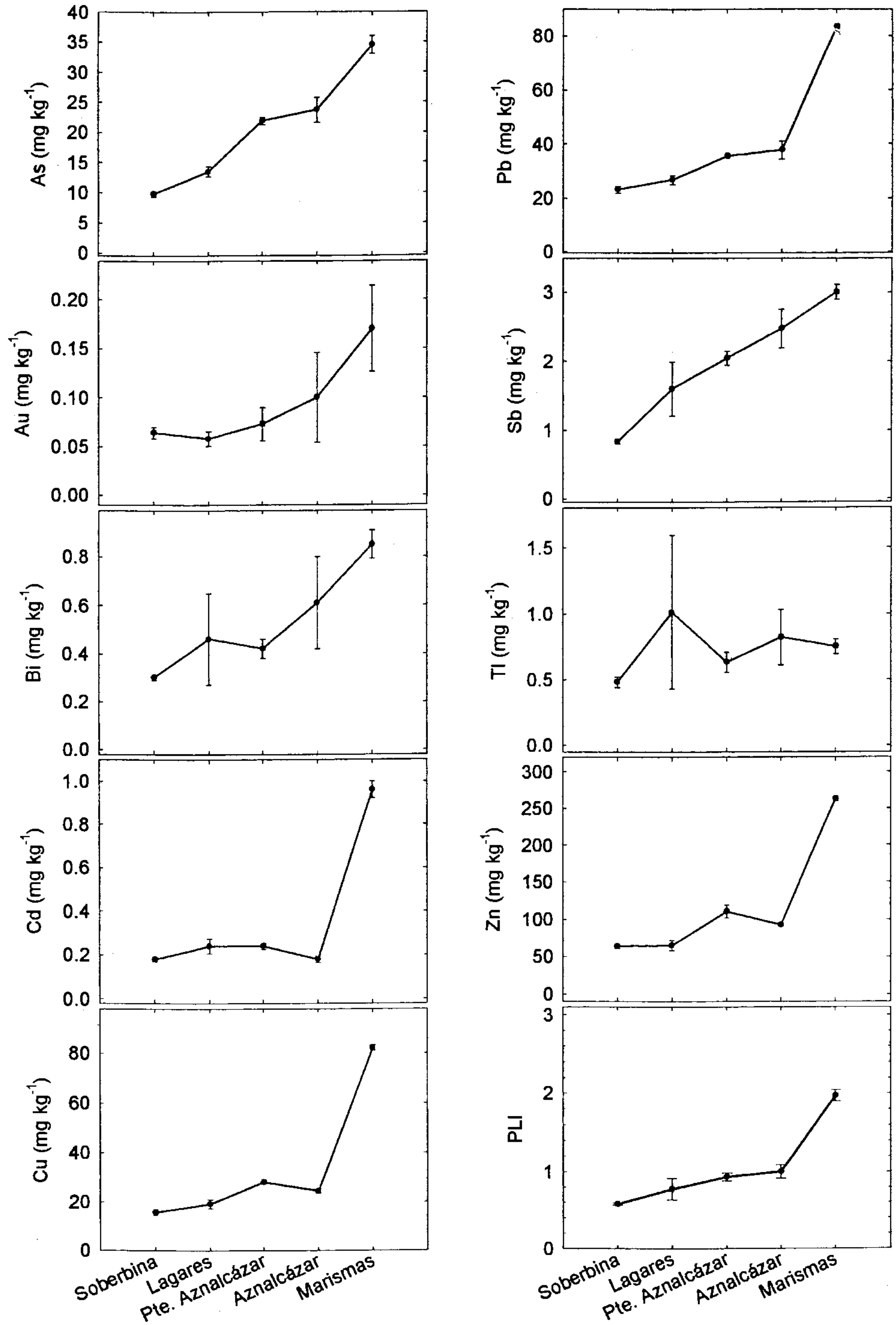

Fig. 3. Mean values of heavy metal and Pollution Load Index (PLI) in the soil profiles (0–50 cm) of unaffected soils along the Guadiamar River. Vertical bars are standard errors (S.E.).

decrease downward in the profile (Fig. 4). In most of these soils, PLI values are very high in the superficial layers, indicating severe heavy metal pollution. In soils S2, S4, L1–L3, PA2, A3 and M2, the PLI values below the 10–20-cm layer tended to reach the characteristic values of unaffected soils. However, in soil D between 10 and 50 cm, and in soil A1 between 20 and 80 cm, the PLI values still indicate heavy metal pollution. A completely different pattern was found in soil M3, in which the superficial layer was less contaminated than the deepest layer.

The clay content of soils S2, S4, L1–L3, PA2, A3, and M2 (open points) was higher than 25%, while most of the points belonging to soils D, A1, and M3 (solid points) are below 25% of clay (Fig. 5). The first group comprises soils in which heavy metals did not penetrate below 20 cm (Fig. 4), while the second group includes soils in which values of PLI below 20 cm indicate heavy metal

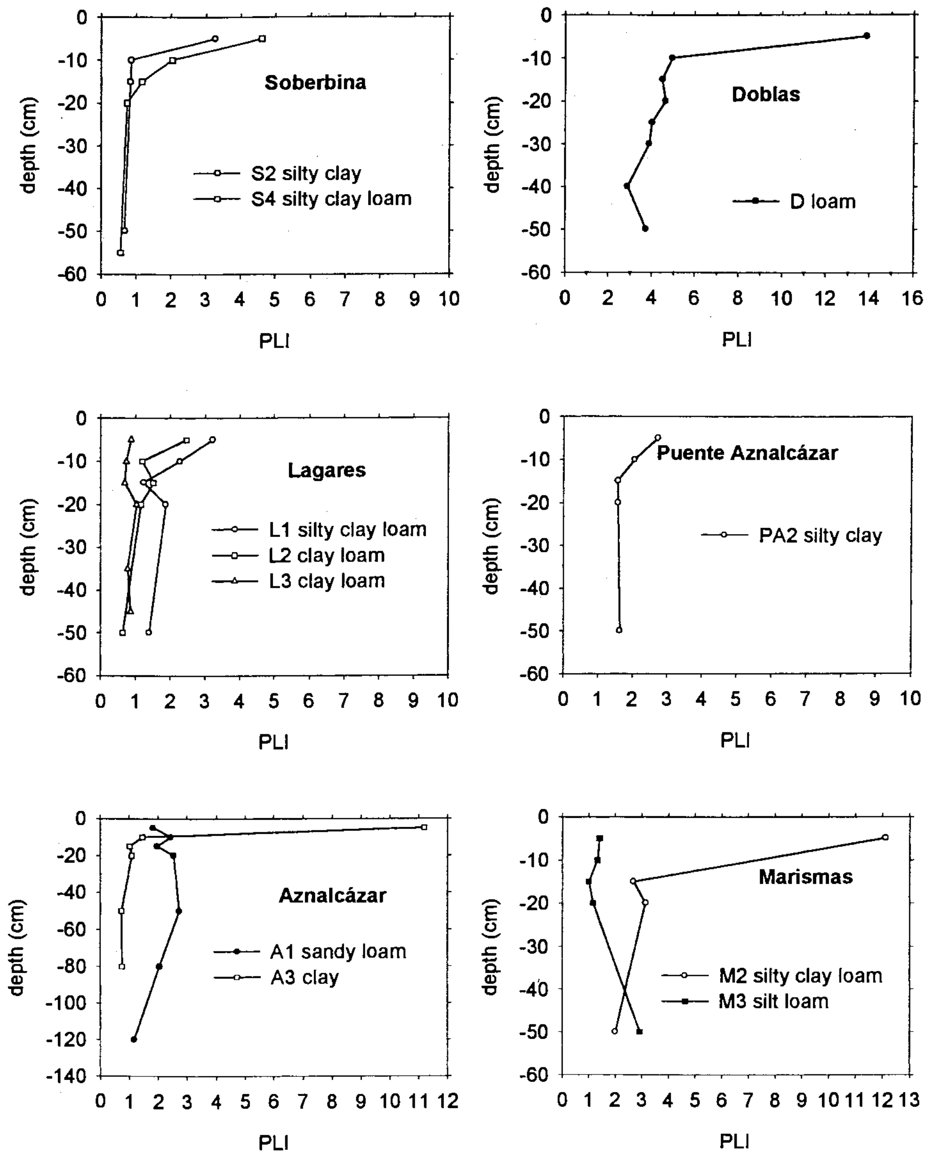

Fig. 4. Values of the Pollution Load Index (PLI) throughout the soil profile in sludge-affected soils.

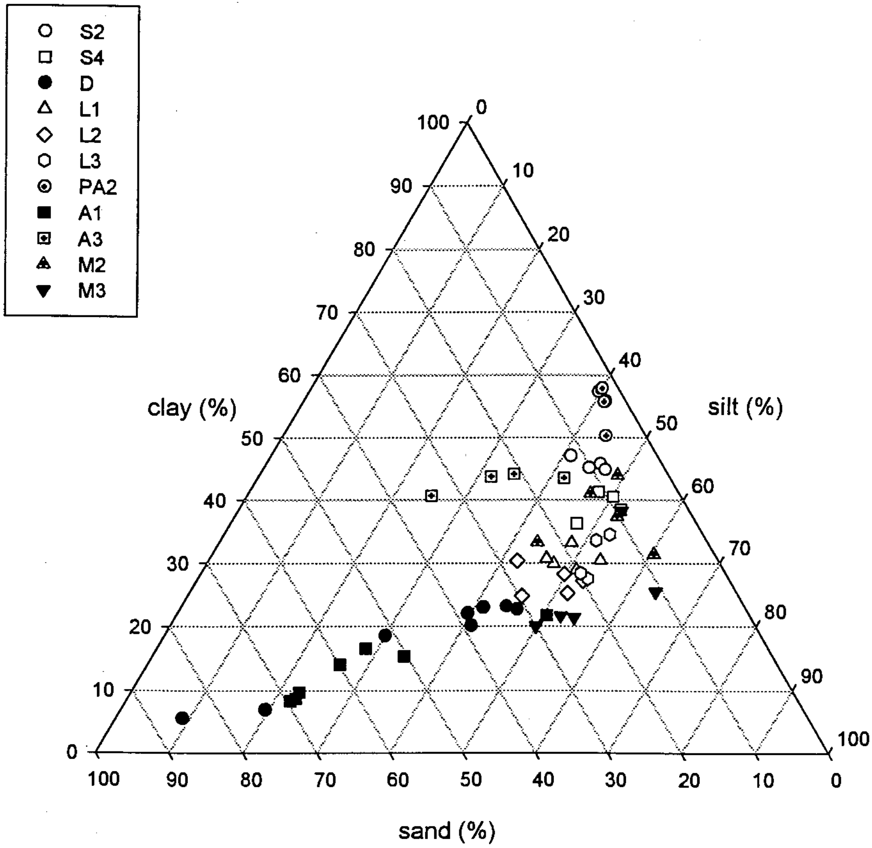

Fig. 5. Textural characteristics of sludge-affected soil samples. Open points: soils in which heavy metal pollution did not penetrate below a 20-cm depth. Solid points: soils in which heavy metal pollution penetrated below a 20-cm depth.

pollution. Therefore, it seems that in soils with more than 25% of clay, heavy metals did not penetrate below 20 cm. In soil M3, in which the PLI value in the 20–50-cm layer is higher than in the 0–20-cm layer, the clay content of the superficial layers (0–15 cm) ranges from 20.1 to 25.5%, while it is 25.5% at 15–20 cm, and 38.3% at 20–50 cm (see the only two solid points in the area of open points in Fig. 5). These textural characteristics could explain the different behaviour of soil M3 regarding the penetration of heavy metals in the soil profile. It seems that in this soil, sorption of dissolved heavy metals in the slurry was the main mechanism of metal retention in the soil. Dissolved heavy metals were preferentially retained in the deeper layer, richer in clay, which is normally composed of the more reactive components of the soils.

4. Conclusions

The results of this study show that at all sampling sites, severe heavy metal pollution was observed in the superficial soil layers (0–20 cm) of most of the sludge-affected soils, and that heavy metal pollution decreased downward in the soil profile. Generally, in soils with more than 25% of clay, concentration of heavy metals below the 20-cm depth decreased to values close to those of the background level of the Guadiamar valley soils. In coarser soils, heavy metal pollution penetrated below this depth, being noticeable down to at least 50–80 cm.

This study shows a wide range of degrees of pollution and penetration of heavy metals in the Guadiamar river-bank soils affected by the toxic flood. Although from this study it was impossible to make a general recommendation for the remediation of these soils, an immediate suggestion for the 'cleaning' of the soils was to remove the layer of deposited sludge, together with the first 0–20-cm layer of the soil. With this soil management, most of the finer-textured soils would have levels of polluting elements close to the background level of the area. A later deep ploughing (20 cm) would mix the soil within the ploughed depth, distributing and diluting pollutants throughout this depth. In coarser-textured soils, in which pollutants penetrated deeper, the solution would be the application of amendments (e.g. lime, iron, aluminium and manganese oxides, zeolites) to increase immobilisation of the pollutants, preventing leaching to ground water and uptake by plants. In any case, a programme of monitoring the bioavailability of pollutants in 'cleaned' soils would be an important tool to provide a warning of pollutant transfer between components of the air–water–soil–plant–animal system.

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