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Remediation measures and displacement of pollutants in soils affected by the spill of a pyrite mine

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ARTICLE DATA

ABSTRACT

The soils affected by the spill of a pyrite mine were analysed in 100 sampling points at three depths (0–10, 10–30, and 30–50 cm) in 1998 (after the tailings were removed), 1999 (after the cleaning of the highly contaminated areas), and 2004 (after the tilling of the upper 20–25 cm). The comparative study reveals that the removal of the tailings left a heterogeneous distribution pattern of the contaminants, with highly polluted spots alternating with less contaminated areas. The cleanup did not substantially lower the concentration in the highly polluted soils, and the spread of the pollutants increased the concentration in As and Pb in the uppermost 10 cm of 60% of the soils, while the Zn and Cd concentrations increased in only 30% of the soils. Given the high concentration of pollutants in the topsoil (especially As), the tilling of the upper 20–25 cm, despite reducing the average concentration of pollutants in the uppermost 10 cm, did not substantially lower the percentage of soils that exceeded the concentration of 40 mg As kg^{-1} dry soil and almost doubled the percentage of soils that surpassed this concentration between 10 and 30 cm. Meanwhile, the displacement of Zn and Cd within the soil supported the reduction in the percentage of soils that in the upper 10 cm exceeded the reference concentrations of these elements (900 mg Zn kg^{-1} dry soil and 2 mg Cd kg^{-1} dry soil), and the percentage of soils exceeding these concentrations between 10 and 50 cm in depth did not increase. Six years after the spill and at the end of all remediation measures, the intervention levels defined by the Environmental Agency of the Regional Government of Andalusia for natural parks were exceeded in the uppermost 10 cm in 35% of the soils.

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1. Introduction

The Iberian pyrite belt covers nearly 8000 km^2 in the southwestern corner of the Iberian Peninsula, including massive sulphide deposits of the mines Rio Tinto, Aljustrel, Neves Corvo, Tharsis, Sotiel, and Aznalcóllar (Spain). On 25 April 1998 the retention walls in a holding pond belonging to the Aznalcóllar mine broke open, spilling roughly 36×10^5 m^3 of polluted waters and 9×10^5 m^3 of toxic tailings into the Agrio and Guadiamar River basin. The total surface area affected by the toxic spill was approximately 45 km^2, forming a patch about 50 km long and 0.9 km wide (Fig. 1).

The infiltration of the acidic water and, especially the penetration of the tailings into the soils, considerably increased the concentration of pollutants in the affected soils. The penetration of the tailings was highly irregular, varying considerably from one sector to another according to the particle size and structure of each soil (Simón et al., 1999). The contamination therefore had highly irregular effects and the range of total contamination of the soils was very broad (López-Pamo et al., 1999).

As the tailings dried and aerated, complex processes (Stumm and Morgan, 1981; Nordstrom, 1982; Förstner and Wittmann, 1983) oxidized the sulphides to sulphates, lowering

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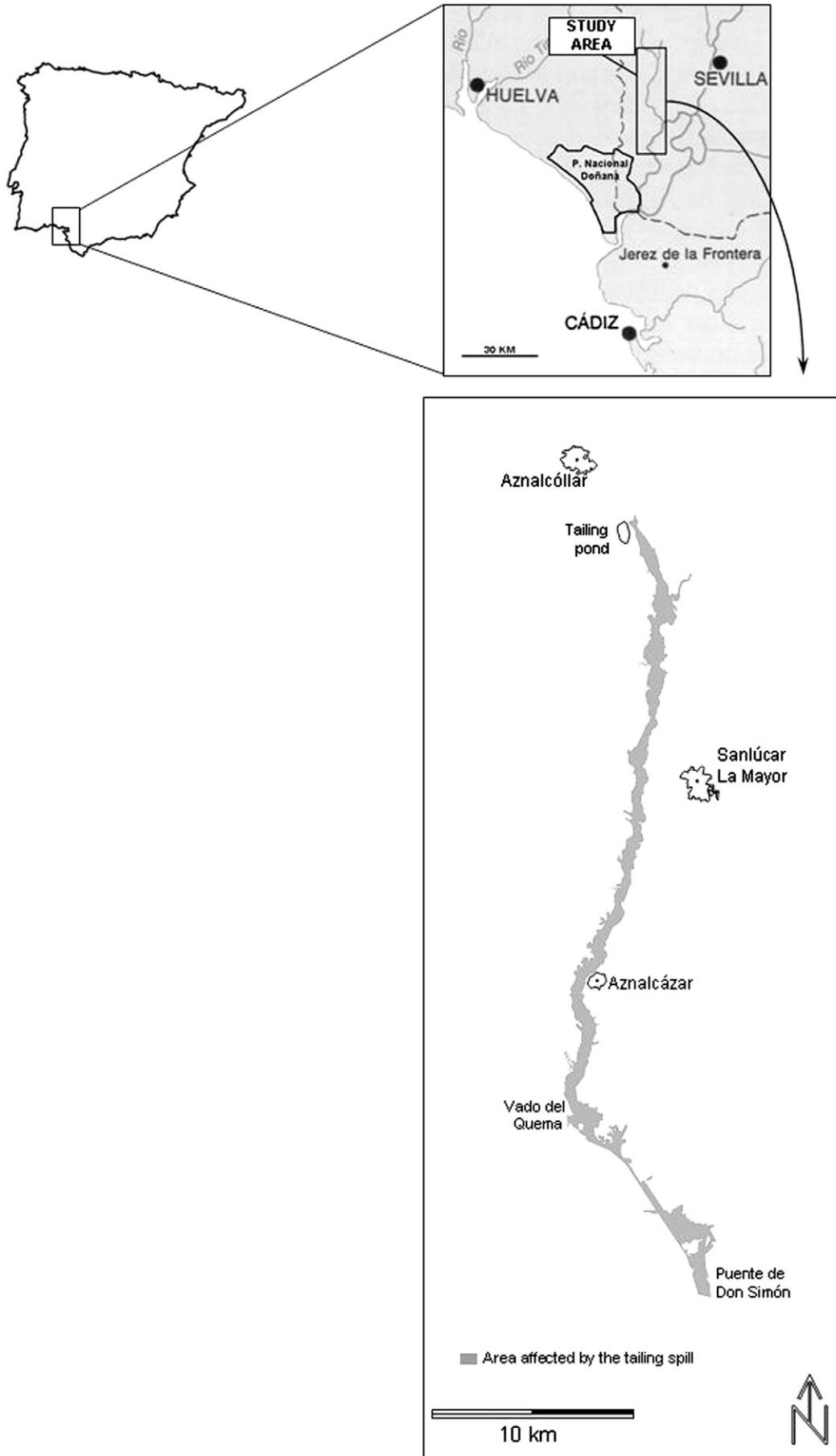
Fig. 1 – Map of the zone affected by the spill. Dark area represents tailings.

the pH and solubilizing part of the pollutants that had formerly remained insoluble. Subsequent rains dissolved the soluble salts formed, and the associated elements infiltrated the soil, raising the pollution level. Thus, in 3 months the concentration of the main pollutants (Zn, As, Cd, and Pb) multiplied 2.5-fold in the uppermost 10 cm of the same soils affected by the spill, without seriously contaminating either the subsoil or the groundwater (Simón et al., 2001). The increasing speed of the soil pollution underscored the urgency of removing the tailings.

In an extensive cleanup operation (May to December 1998) the tailings and a mean thickness of c. 10 cm of the uppermost part of the affected soils were removed by heavy machinery,

with cleanup efforts greater in the most contaminated areas (fundamentally, gravelly soils next to the mine and to the river). This rapid work (in eight months, 45 km^2 were cleaned) resulted in a deficient cleanup, as part of the tailings remained mixed with the soil and formed patches, while residual tailings appeared below 30 cm in depth. Cabrera (2000) reported a broad dispersion of the trace-element contents after the tailings were removed, and in many areas mean values of contaminants were higher than those found before the removal (Cabrera et al., 2005). Because of the heavy pollution of the soils after the cleanup, the most polluted areas (located mainly in the northern part) were cleaned again in spring–summer 1999, followed by a liming with sugar-refinery scum (4 kg m^{-2}) and superficial tilling

	1	2	3	4	5
pH	5.8	5.9	7.7	7.8	8.0
CaCO$_3$ (%)	< 2	< 1	≈ 10	5 – 10	> 10
Gravel (%)	< 10	> 35	< 10	< 10	< 10
Texture	Loam	Sandy loam	Clay loam	Loam	Silty clay
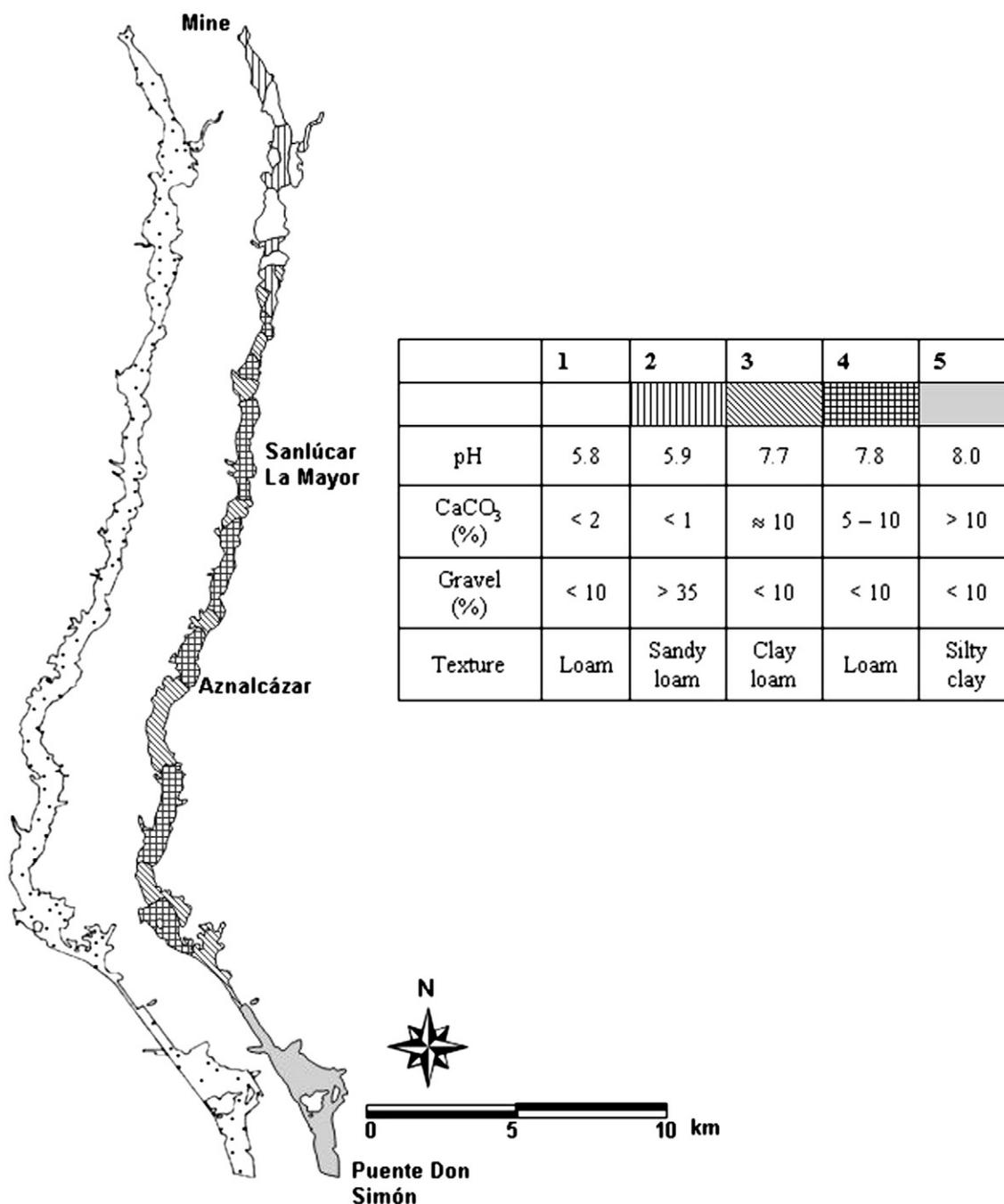
Fig. 2 – Sampling points, spatial distribution of the five zones and mean values of the soil properties.

of the soils (5–10 cm in depth) throughout the area affected by the spill. In spring–summer 2000, organic matter (2 kg m^{-2}) plus iron-rich clayey materials (2 kg m^{-2}) were added, followed by tilling of the upper 20–25 cm of the soils; subsequently, the tilling at the same depth was repeated in most of the affected area in 2002 and 2003. Nevertheless, after all the remediation measures, high metal concentration could be detected in the first 10 cm of the soils 4 years after the Aznalcóllar spill (Aguilar et al., 2004), with a 'hot spot' distribution of highly contaminated spots within other less severely polluted, and a strong displacement of Zn and Cd in vertical profiles (Kraus and Wiegand, 2006).

In May 2000 (15 months after the cleanup), Simón et al. (2005) studied the hydrological properties of the soils affected by the spill and the chemical composition of the liquid and solid phases of the run-off water, revealing that the final infiltration rate of the neutral-alkaline soils was clearly higher (28.9 mm h^{-1}) than that of the acidic soils (7.9 mm h^{-1}) where superficial crusts were formed; meanwhile, in both soil types, the liquid and solid phases of the run-off waters displayed high concentrations in pollutants.

The dimensions of the affected area, the proximity to the Doñana National Park and the potential toxicity of the elements involved, recommended the continuous monitoring of the area. In the present work, the pollutant concentration at three depths in 100 georeferenced sampling points taken in 2004, were compared with the samples taken after each remediation measure at the same locations, in order to estimate the displacement of the pollutants into the soil, the spread of the pollutants in the landscape, and the effectiveness of the remediation actions in the reduction of the soil-pollution levels 6 years after the spill.

1.1.　Study area

The study area is located in the Agrio and Guadiamar river valleys (SW Spain), in a strip (0.9 km wide and approximately 40 km long) from the tailings pond of the Aznalcóllar mine to the Puente Don Simón (Fig. 1). The climate of the area is typically Mediterranean (hot, dry summer; cold, wet winter; temperate autumns and springs with variable rainfall), with a mean annual rainfall of 613 mm, a mean temperature of 17.7 °C, and a potential evapotranspiration of 900 mm (data taken from 21 weather stations near the spill, over 27 years). In the study period, the mean annual rainfall in the weather station of Aznalcázar was 590 mm, and the mean monthly rainfall in March, October, and November were >90 mm. High-intensity rainfall episodes >30 mm h^{-1} were registered in 2001 (11-January, 7-March, and 5-November), in 2002 (7-May and 19-November), in 2003 (26 and 27 March), and in 2004 (2-May); meanwhile, high-intensity rainfall episodes >55 mm h^{-1} were registered in 2002 (16-September) and 2003 (6-December). Flash floods are also common but unpredictable in the area (Gallart et al., 1999).

2.　　Materials and methods

2.1.　Soil sampling

The contaminated area was monitored with a sampling network established on a grid of 400×400 m. The intersections and the centres, 400 in total, were correlatively numbered, and a number between 1 and 400 was raffled; starting from this number, one of each of the four numbers was selected, thus establishing 100 sampling points (Fig. 2) which were georeferenced by Global Positioning System (GPS) with a precision of <1 m in 95% of the acquisition time. At each sampling point a square plot was laid out (10×10 m) and samples were taken from the four corners and centre of each plot at depths of 0–10 cm, 10–30 cm, and 30–50 cm, and the 5 samples taken at each depth were pooled. In this way, after each cleanup and remediation action (autumn–winter of 1998, 1999, and 2004) a sampling of the selected points was taken.

For an estimate of the spatial variability of soil properties a geostatistical method (kriging) was used (Goovaerts, 1998). The kriging grid and the maps were calculated using the Surfer software, and five zones in relation to the soil properties were differentiated (Fig. 2). Zone 1 (with 13 sampling points) and 2 (with 11 sampling points), located in the upper part of the area, had acidic soils with little or no CaCO$_3$ and were differentiated by texture. Zone 1 had loam while Zone 2 had sandy–loam with high gravel content (>35%). The soils in Zone 3 (with 22 sampling points), 4 (with 39 sampling points) and 5 (with 15 sampling points) were neutral or slightly alkaline, with a CaCO$_3$ content higher than 5%. Textures differed markedly, with clay–loam in Zone 3, loam in Zone 4, and silty–clay in Zone 5.

2.2.　　Laboratory analysis

All soil samples were air-dried and sieved to 2 mm, whereupon the percentages of gravels (>2 mm) and fine earth (<2 mm) were calculated. In the fine earth, the particle-size distribution was determined by the pipette method after the removal of organic matter with H$_2$O$_2$ and dispersion with sodium hexametaphosphate (Loveland and Whalley, 1991). The pH was measured potentiometrically in a 1:2.5 soil–water suspension, and the calcium carbonate content was determined by a manometric method (Williams, 1948).

The fine earth, very finely ground (<0.05 mm), was digested in strong acids (HNO$_3$+HF+HCl). In each digested sample Zn, As, Cd and Pb were measured by inductively coupled plasma mass spectrometry (ICP-MS) with a PerkinElmer SCIEX ELAN-5000A spectrometer. The accuracy of the method (Table 1) was corroborated by analyses (six replicates) of Standard Reference Material 2711 (soil with moderately elevated trace elements concentrations; Gills and Kane, 1993).

Table 1 – Analysis of standard reference material 2711				
Element	Certified		Experimental	
	Mean	SD	Mean	SD
As	105	8	99.8	1.7
Pb	1162	31	1201	15
Zn	350.4	4.8	352.1	2.5
Cd	41.70	0.25	40.1	0.8
SD, standard deviation.				

3. Results

3.1. Concentration of the pollutants in the first 50 cm of the soils

The concentration of pollutants in the uppermost 50 cm of the soils (C_{50}) was estimated from the equation:

$$C_{50} = \frac{(C_1P_1 + C_2P_2 + C_3P_3)}{50}. \tag{1}$$

Where C_1, C_2, and C_3 are the concentrations of the pollutants of the samples taken between 0–10 cm, 10–30 cm, and 30–50 cm in depth, respectively, and P_1, P_2, and P_3 are the respective thicknesses of each sample in cm.

The box-and-whisker plots of the data distribution (Fig. 3) indicate that the less mobile elements (As and Pb) reached higher concentrations in the acidic soils (Zones 1 and 2), where 88% surpassed 40 mg As kg^{-1} dry soil (upper value in natural soils; Bowen, 1979) during the three sample years; meanwhile,

the most mobile elements (Zn and Cd) reached higher concentrations in the basic soils (Zones 3, 4, and 5), where 25% exceeded 2 mg Cd kg^{-1} dry soil (upper value in natural soils; Bowen, 1979) in 1998, and 20% continued to exceed this concentration in 1999 and 2004. In general, the pollutant concentrations were similar on the different sampling dates, and the mean concentrations did not significantly differ. Nevertheless, in 1999, compared with 1998, the upper extreme, upper quartile, and median values fell more sharply in the acidic soils than in the basic ones; meanwhile in 2004, compared with 1999, the differences in the five-number summaries of the data distribution (upper extreme, upper quartile, median, lower quartile, and lower extreme values) were minor in all soils.

3.2. Concentration of the pollutants in the uppermost 10 cm of the soils

In relation to 1998, the mean concentration of the pollutants decreased in 1999 between 19% and 30%, and in 2004 between 24% and 30% compared to that of 1999 (Table 2). The mean
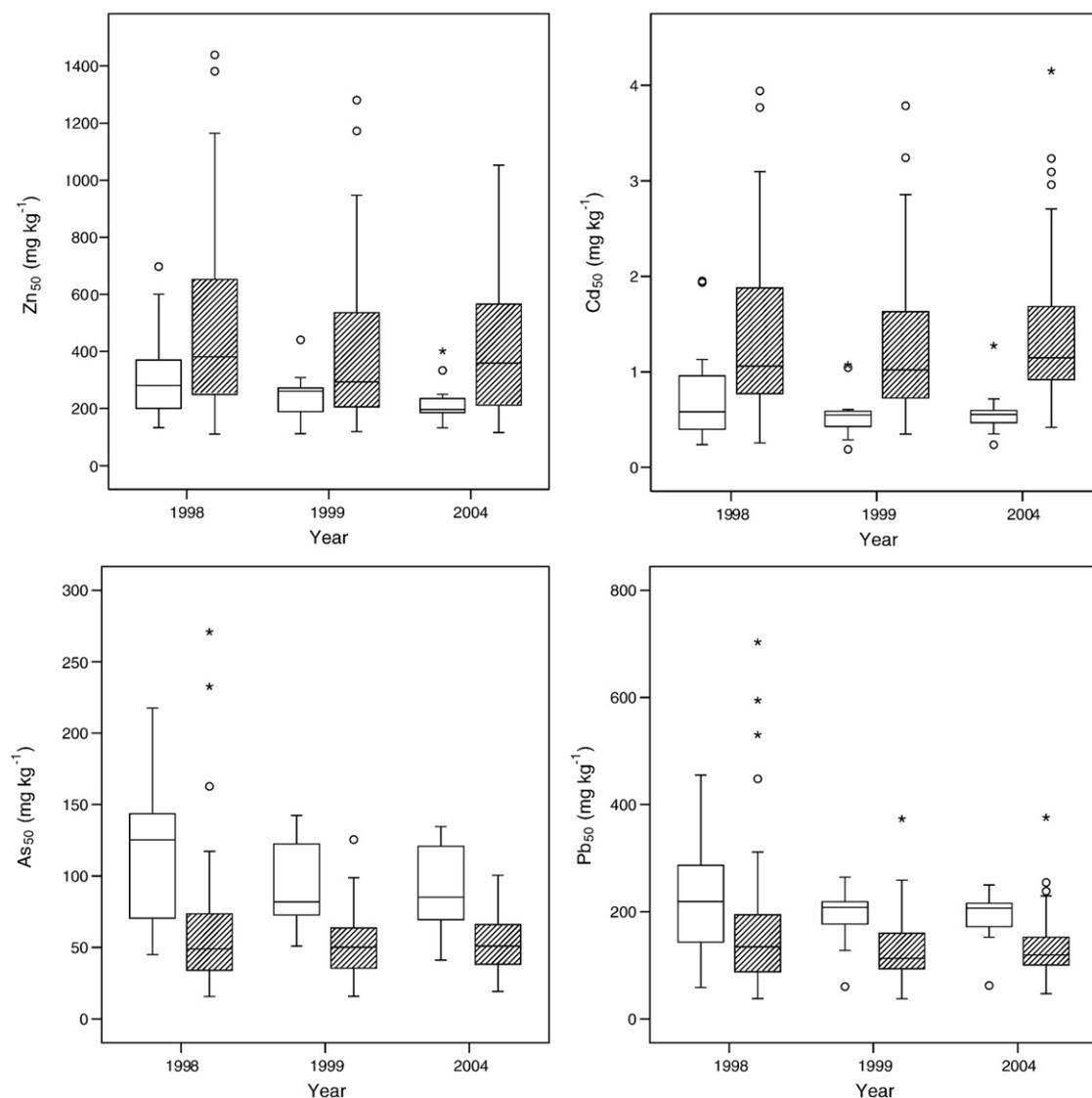
Fig. 3 – Box-and-whisker plots for the pollutant concentration between 0 and 50 cm in depth in the acidic (□) and basic (▨) soils sampled in 1998, 1999, and 2004.

Table 2 – Mean, standard deviation (SD) and variation coefficient (VC) of the total concentration of pollutants in soils between 0 and 10 cm in depth in the sampling of 1998, 1999, and 2004

	1998				1999				2004			
	Zn	Cd	As	Pb	Zn	Cd	As	Pb	Zn	Cd	As	Pb
Mean	918a	2.7a	156a	440a	675b	2.1b	126ab	305ab	487c	1.6c	89b	224b
SD	618	2.0	198	511	346	1.1	76	163	248	0.8	49	112
VC	0.67	0.74	1.27	1.16	0.51	0.52	0.60	0.53	0.51	0.50	0.55	0.50

For each pollutant, values of the mean followed by the same letter do not differ significantly according to the Scheffé test ($p < 0.05$).

concentration of Zn and Cd differed significantly in 1999 and 2004, while the mean concentrations of As and Pb differed significantly only in 2004 with respect to 1998. Similarly, the variation coefficient also declined over time.

The box-and-whisker plots of the data distribution (Fig. 4) reveal that in 1999, compared to 1998, in the acidic soils the upper extreme and upper quartile values fell, while the lower extreme and lower quartile values rose. In the basic soils, fundamentally the outliers (values higher than the upper extreme) decreased in the case of As and Pb and, in the case of Zn and Cd, the five-number summaries of the data distribution decreased. In 2004, in relation to 1999, all soils declined in the five-number summaries of the data distribution of the four pollutants. In 2004 some 90% of the soils exceeded $40 \, \mathrm{mg \, As \, kg^{-1}}$
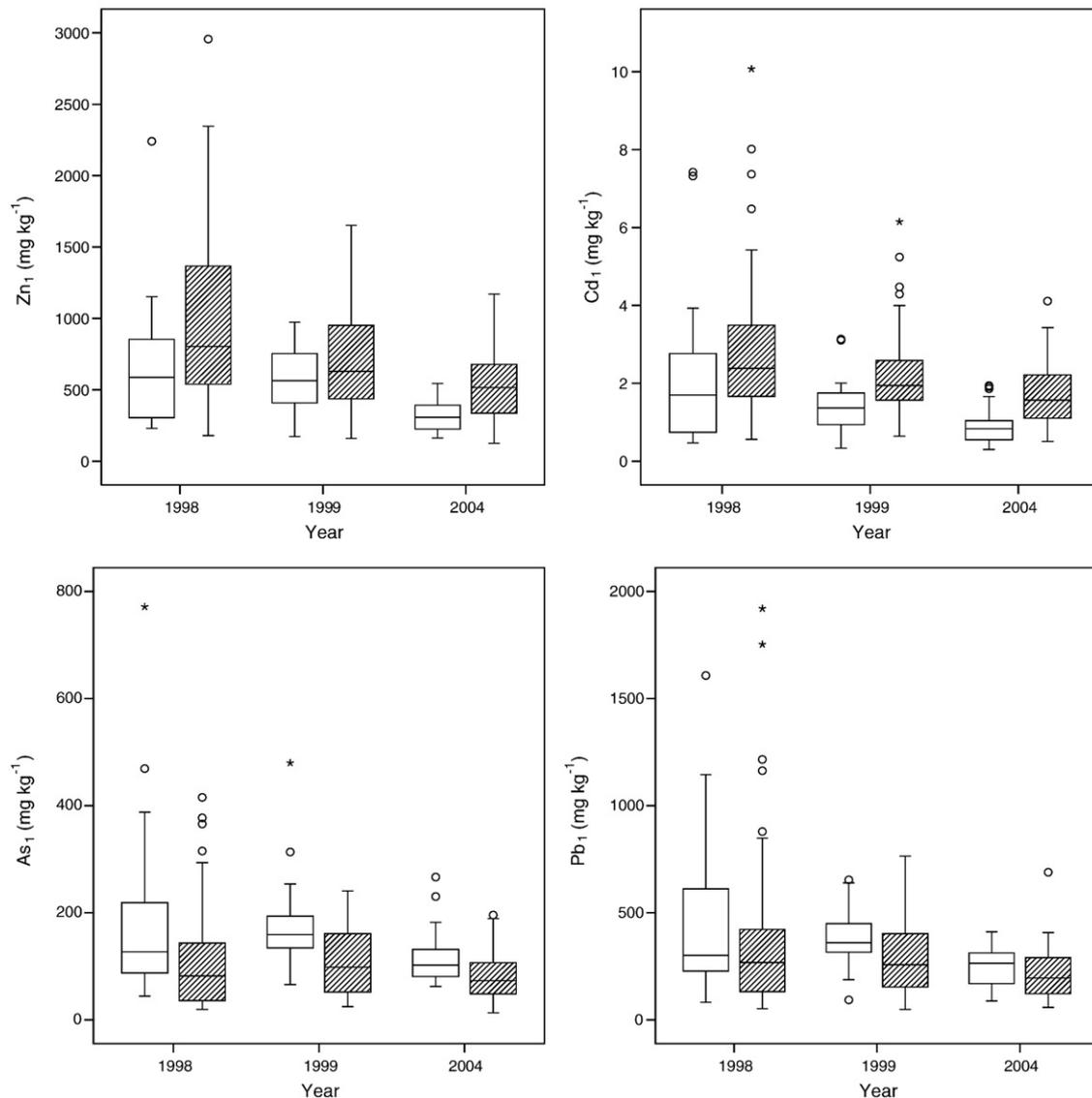
Fig. 4 – Box-and-whisker plots for the pollutants between 0 and 10 cm in the acidic (□) and basic (▨) soils sampled in 1998, 1999, and 2004.
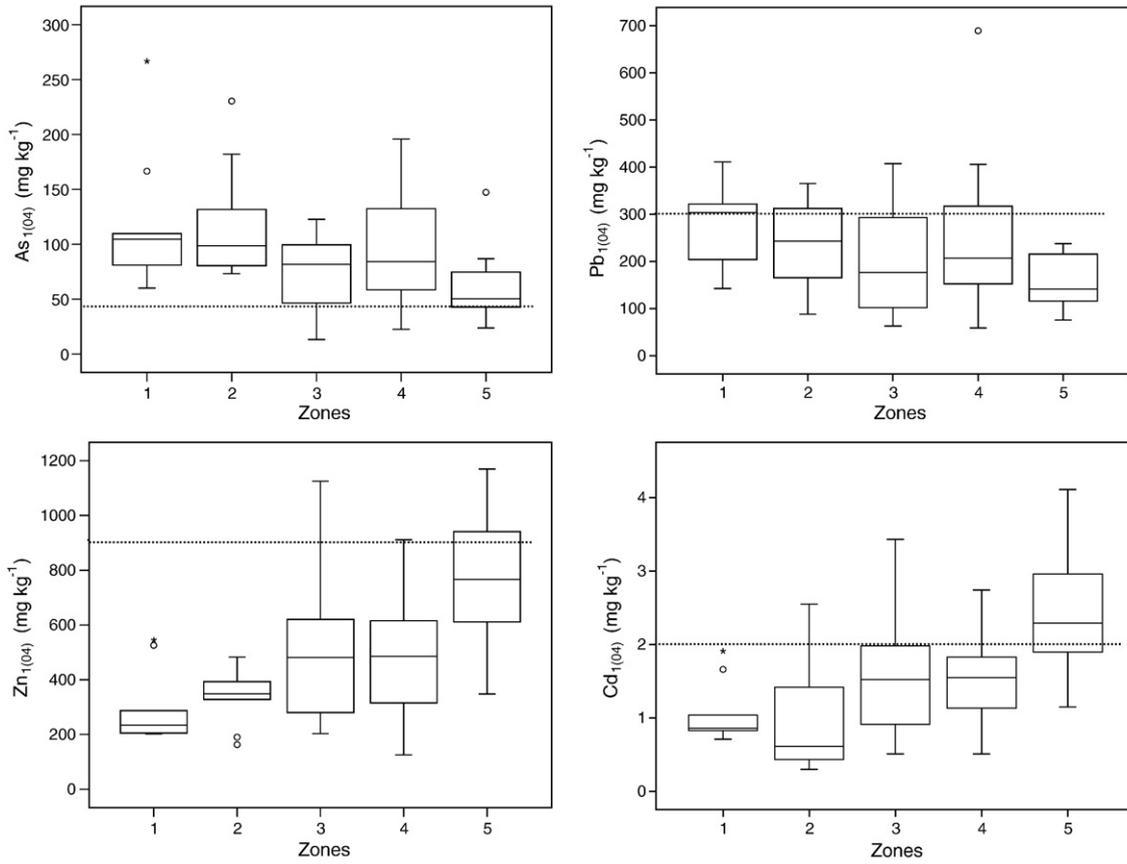
Fig. 5 – Box-and-whisker plots for pollutants concentrations by zones between 0 and 10 cm in depth in 2004 (dotted lines: normal range in soils).

dry soil, and 53% doubled this concentration, especially in the acidic soils (Zones 1 and 2) in which more than 70% exceeded the concentration of 80 mg As kg^{-1} dry soil (Fig. 5). More than 30% of the basic soils (Zones 3, 4, and 5) surpassed the limit values of 2 mg Cd kg^{-1} dry soil, especially those with the finest texture (Zone 5), in which these values were exceeded by more than 70%
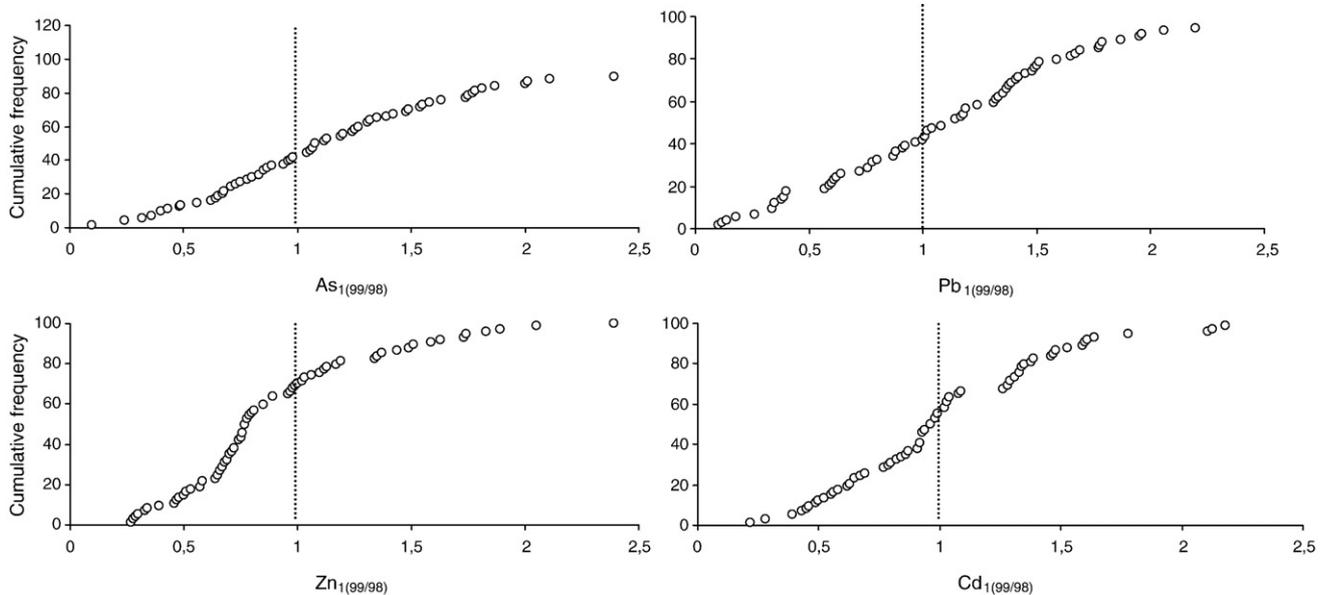
Fig. 6 – Cumulative frequency distribution for the ratio of the pollutants concentrations in 0–10 cm in depth between 1999 and 1998.
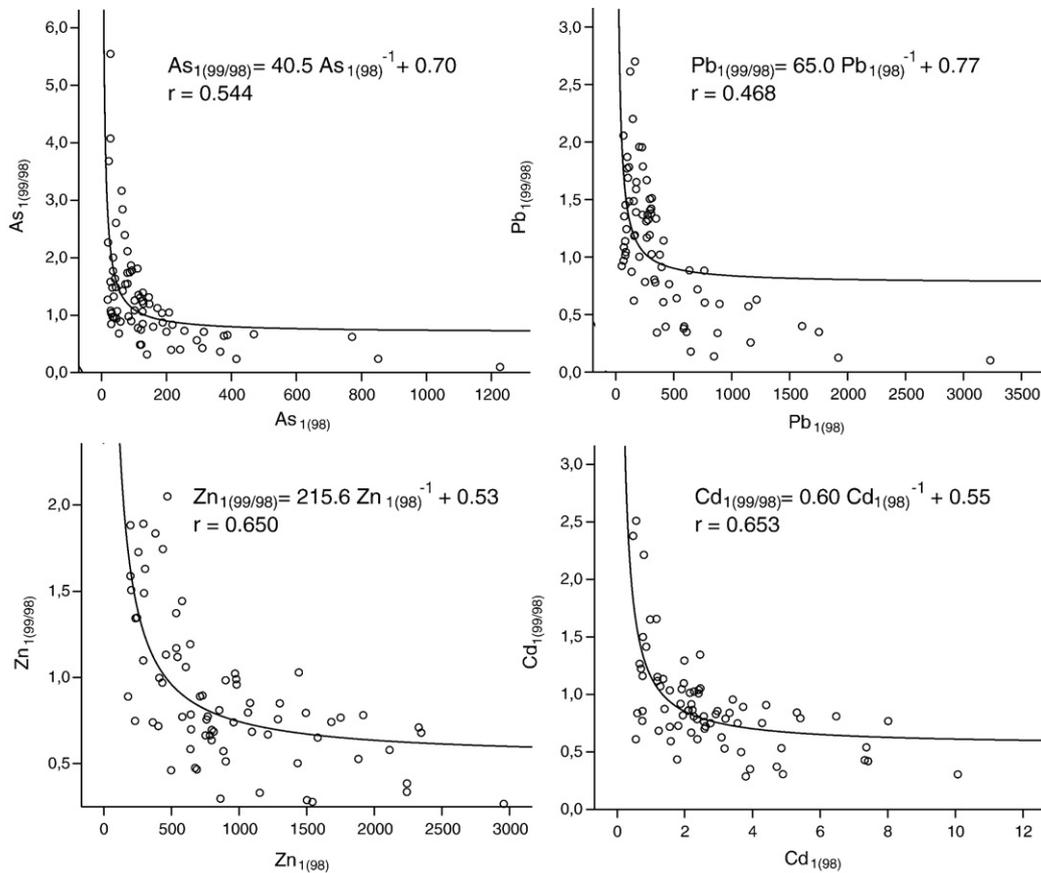
Fig. 7 – Relationship between $C_{1(99/98)}$ and $C_{1(98)}$ in the uppermost 10 cm of the soils.

of the soils; meanwhile, the concentration of 300 mg Pb kg^{-1} dry soil (upper value in natural soils; Bowen, 1979) was surpassed in 25% of the soils studied.

The ratio of the concentration of each pollutant between 1999 and 1998 ($C_{1(99/98)}$) indicates that the ratios $As_{1(99/98)}$ and $Pb_{1(99/98)}$ were greater than one in almost 60% of the soils

sampled, while the ratios for $Zn_{1(99/98)}$ and $Cd_{1(99/98)}$ were higher than one in only 30% and 40%, respectively (Fig. 6). In addition, these ratios were significant ($P<0.001$) and inversely related to the total concentration of the pollutant in 1998 ($C_{1(98)}$) (Fig. 7). Meanwhile, the ratios of the concentrations of all the contaminants between 2004 and 1999 ($C_{1(04/99)}$) were greater than
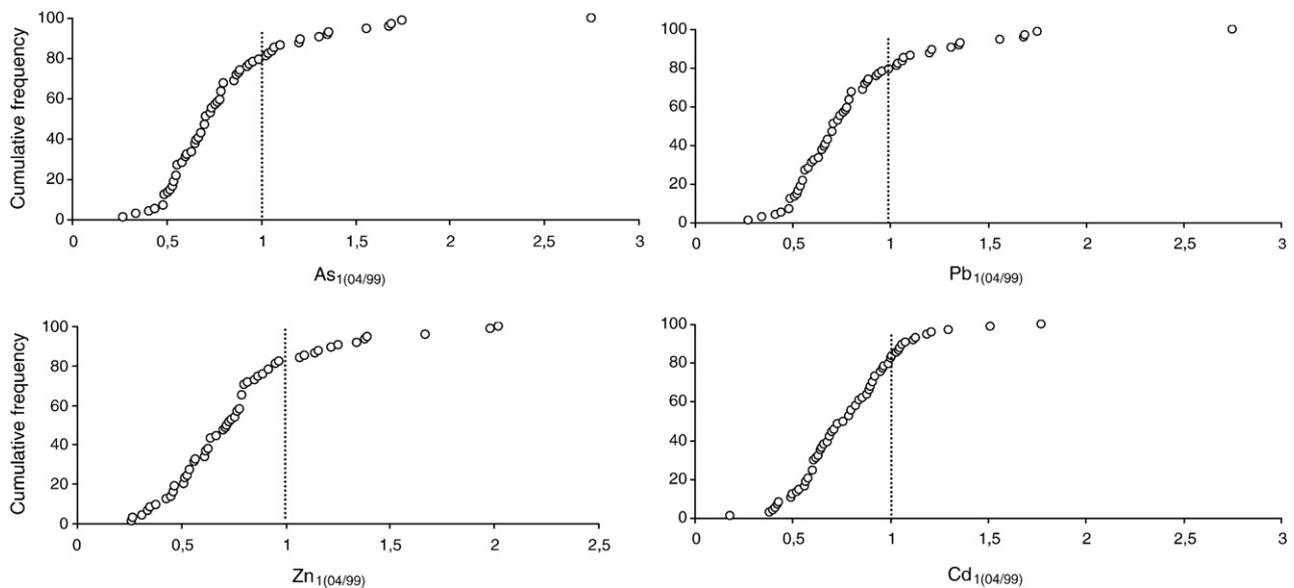
Fig. 8 – Cumulative frequency distribution for the ratio of the pollutants concentrations in 0–10 cm in depth between 2004 and 1999.

Table 3 – Mean and standard deviation (SD) of the ratios $C_{1(99/98)}$ and $C_{1(04/99)}$ between 0 and 10 cm in depth

	$Zn_{1(99/98)}$	$Zn_{1(04/99)}$	$As_{1(99/98)}$	$As_{1(04/99)}$	$Pb_{1(99/98)}$	$Pb_{1(04/99)}$	$Cd_{1(99/98)}$	$Cd_{1(04/99)}$
Mean	0.90	0.79	1.29	0.78	1.10	0.83	0.91	0.79
SD	0.42	0.37	0.91	0.31	0.58	0.42	0.42	0.23

one in approximately 20% of the soils (Fig. 8), and both the mean and the standard deviation of these ratios were clearly lower than those of the ratios $C_{1(99/98)}$ (Table 3). In addition, except in the case of Cd, the ratios $C_{1(04/99)}$ were also significant ($P<0.001$) and inversely related to the total concentrations of the pollutants in 1999 ($C_{1(99)}$) through the following equations:

$$As_{1(04/99)} = 20.6\ As_{1(99)}^{-1} + 0.57 \qquad r = 0.467 \tag{2}$$

$$Pb_{1(04/99)} = 69.5\ Pb_{1(99)}^{-1} + 0.50 \qquad r = 0.581 \tag{3}$$

$$Zn_{1(04/99)} = 160.8\ Zn_{1(99)}^{-1} + 0.48 \qquad r = 0.476. \tag{4}$$

3.3. Pollution between 10 and 30 cm in depth

Between 10 and 30 cm in depth, the mean concentration of the pollutants decreased in 1999 compared to 1998 between 6% and 18%, while in 2004 compared to 1999 the concentrations of Zn and Cd increased between 22% and 27% and those of As and Pb increased between 41% and 48%, respectively (Table 4). The mean concentration of Zn and Cd did not differ significantly between years, whereas the mean concentrations of As and Pb differed significantly only in 2004 in relation to 1999. Similarly, the variation coefficient declined over time.

The box-and-whisker plots of the data distribution (Fig. 9) reveal that values in 1999 compared to 1998 diminished mainly in the upper extreme and upper quartile values, while in 2004, in relation to 1999, the five-number summaries of the data distribution increased. For this increase, more than 75% of the soils exceeded the concentration of 40 mg As kg^{-1} dry soil in 2004, especially the acidic soils of Zone 2, in which more than 90% exceeded this concentration and 45% doubled this value. Meanwhile, some 12% of the basic soils exceeded concentrations of 900 mg Zn kg^{-1} dry soil and 25% the concentration of 2 mg Cd kg^{-1} dry soil, especially in Zone 5, where these concentrations were exceeded in the 30% and 70% of the soils, respectively (Fig. 10).

The ratios of the concentrations between 1999 and 1998 of As ($As_{2(99/98)}$) and Pb ($Pb_{2(99/98)}$) were greater than one in approximately 15% of the soils, those of Zn ($Zn_{2(99/98)}$) in 20%, and those of Cd ($Cd_{2(99/98)}$) in 30%. Meanwhile, the ratios of the concentrations of all the pollutants between 2004 and 1999 ($C_{2(04/99)}$) were greater than one in almost all the soils (Fig. 11). In addition, the

concentrations of the pollutants between 10 and 30 cm in depth in 2004 ($C_{2(04)}$) were linearly and significantly related ($P<0.001$) to the concentrations between 0 and 10 cm in 1999 ($C_{1(99)}$) by the following equations:

$$As_{2(04)} = 33.62 + 0.271\ As_{1(99)} \qquad r = 0.605 \tag{5}$$

$$Pb_{2(04)} = 53.67 + 0.376\ Pb_{1(99)} \qquad r = 0.812 \tag{6}$$

$$Zn_{2(04)} = 12.81 + 0.639\ Zn_{1(99)} \qquad r = 0.785 \tag{7}$$

$$Cd_{2(04)} = 0.177 + 0.617\ Cd_{1(99)} \qquad r = 0.767. \tag{8}$$

3.4. Pollution between 30 and 50 cm in depth

The mean concentration as well as the standard deviation and variation coefficient of the pollutants between 30 and 50 cm hardly changed on the different sampling dates, and the differences between mean values were not significant (Table 5).

The box-and-whisker plots of the data distribution (Fig. 12) show slight variation in the five-number summaries of the data distribution, with marginal increases in the upper extreme, upper quartile and mean values of Zn in 2004 and of Cd in 1999 and 2004. In the three sampling years, around 3% exceeded the concentration of 900 mg Zn kg^{-1} dry soil, 8% exceeded the concentration of 2 mg Cd kg^{-1} dry soil, and around 30% exceeded the concentration of 40 mg As kg^{-1} dry soil (Fig. 13).

While the concentration ratios of As and Pb between 2004 and 1999 ($As_{3(04/99)}$ and $Pb_{3(04/99)}$, respectively) were close to 1.0 (1 ± 0.15), the ratios of Zn and Cd ($Zn_{3(04/99)}$ and $Cd_{3(04/99)}$, respectively) exceeded 1.20, especially in the case of Cd, in which more than 50% of the samples surpassed this value (Fig. 14). In addition, the concentrations of the contaminants in 2004 ($C_{3(04)}$) were related linearly and significantly ($P<0.001$) to those of 1999 ($C_{3(99)}$) through the following equations:

$$As_{3(04)} = 0.949\ As_{3(99)} + 0.778 \qquad r = 0.994 \tag{9}$$

$$Pb_{3(04)} = 0.943\ Pb_{3(99)} + 0.071 \qquad r = 0.995 \tag{10}$$

$$Zn_{3(04)} = 1.062\ Zn_{3(99)} + 7.754 \qquad r = 0.994 \tag{11}$$

$$Cd_{3(04)} = 1.096\ Cd_{3(99)} + 0.119 \qquad r = 0.984 \tag{12}$$

In all these equations, the slopes of the straightlines were close to 1.0, but slightly lower than 1.0 in the case of the less

Table 4 – Mean, standard deviation (SD), and variation coefficient (VC) of the total concentration of pollutants in soils between 10 and 30 cm in depth in the sampling of 1998, 1999, and 2004

	1998				1999				2004			
	Zn	Cd	As	Pb	Zn	Cd	As	Pb	Zn	Cd	As	Pb
Mean	431a	1.2a	59ab	133ab	365a	1.1a	48a	114a	445a	1.4a	68b	168b
SD	345	0.9	45	92	283	0.8	29	63	280	0.9	34	75
VC	0.80	0.75	0.76	0.69	0.78	0.72	0.60	0.55	0.63	0.64	0.50	0.45

For each pollutant, values of the mean followed by the same letter do not differ significantly according to the Scheffé test ($p<0.05$).
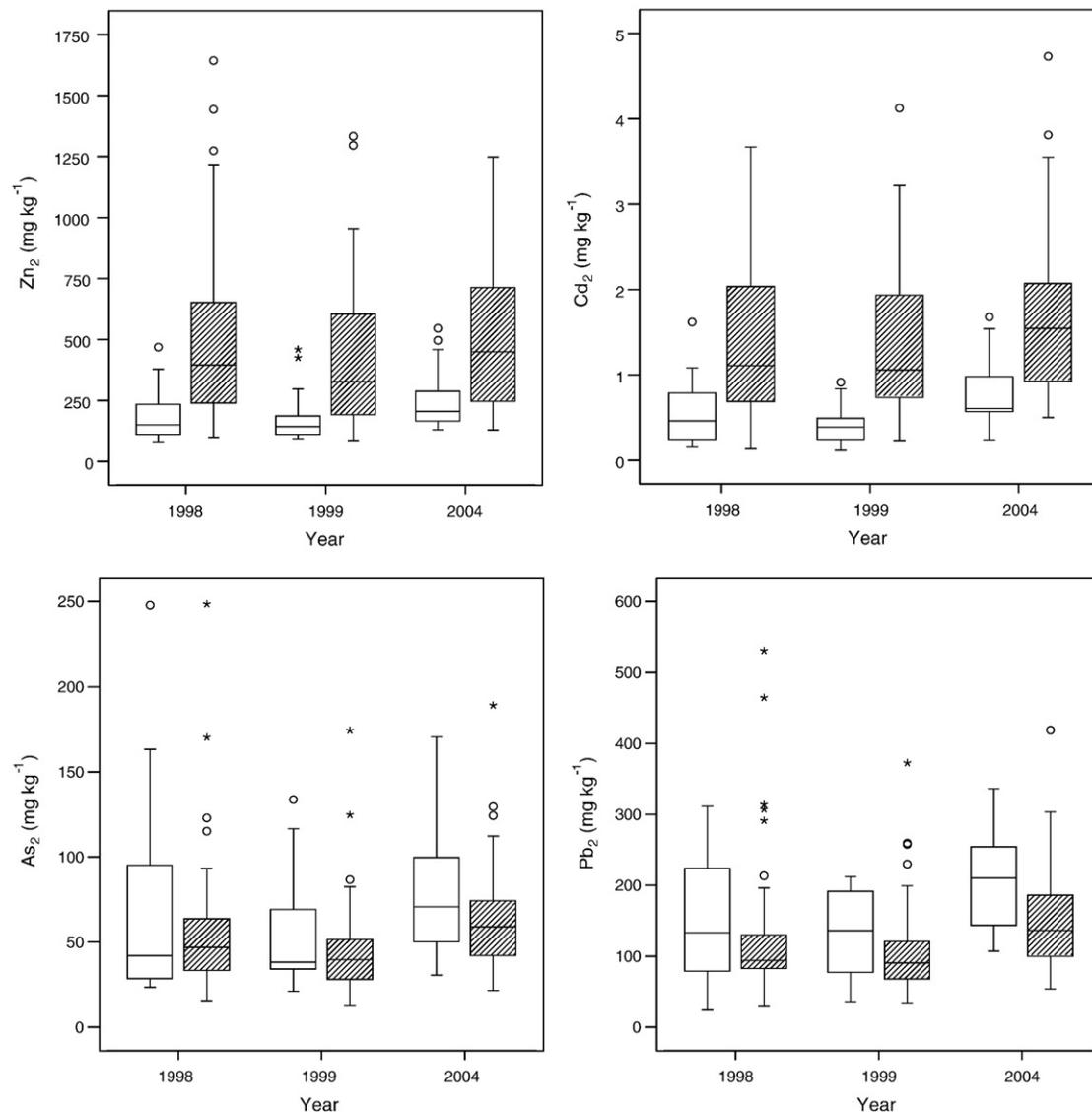
Fig. 9 – Box-and-whiskers plots for the pollutants concentration between 10 and 30 cm in depth in the acidic (□) and basic soils (▨) sampled in 1998, 1999 and 2004.

mobile elements, As and Pb, and slightly higher for the more mobile elements, Zn and Cd.

4.   Discussion

The remediation measures did not significantly change the mean concentration of the pollutants in the upper 50 cm of the soils. Nevertheless, the cleanup and the addition of amendments in spring–summer 1999 (hereafter *cleanup-99*), decreased the pollutant concentration more abruptly in the highly polluted soils of Zones 1 and 2 (Fig. 3). This could be attributed to the fact that *cleanup-99* was more intense in zones that remained more polluted after the removal of the tailings. The amendments and the tilling of the upper 20–25 cm of soil between the years 2000 and 2003 (hereafter *tilling-00*), given that they did not involve the removal of the

pollutants, hardly changed the concentration of the pollutants in the upper 50 cm of the soil in 2004.

4.1.   Concentration of pollutants in the uppermost 10 cm of the soils

In 1999, the lowering of the mean pollutant concentration in the uppermost 10 cm of the soils cannot be attributed exclusively to the *cleanup-99*. The increase in 1999 of the pollutant concentrations in the less contaminated acidic soils (increase of the lower extreme and lower quartile; Fig. 4), together with the inverse relationship in all the soils between $C_{1(99/98)}$ and $C_{1(98)}$ (Fig. 7), indicate the spread of the pollutants. This spread could be due to contaminated run-off waters (rainfall intensities higher than the final infiltration rate of the soils are frequent in the affected area), or to superficial tilling of the soils. In addition, the greater mobility and the deeper
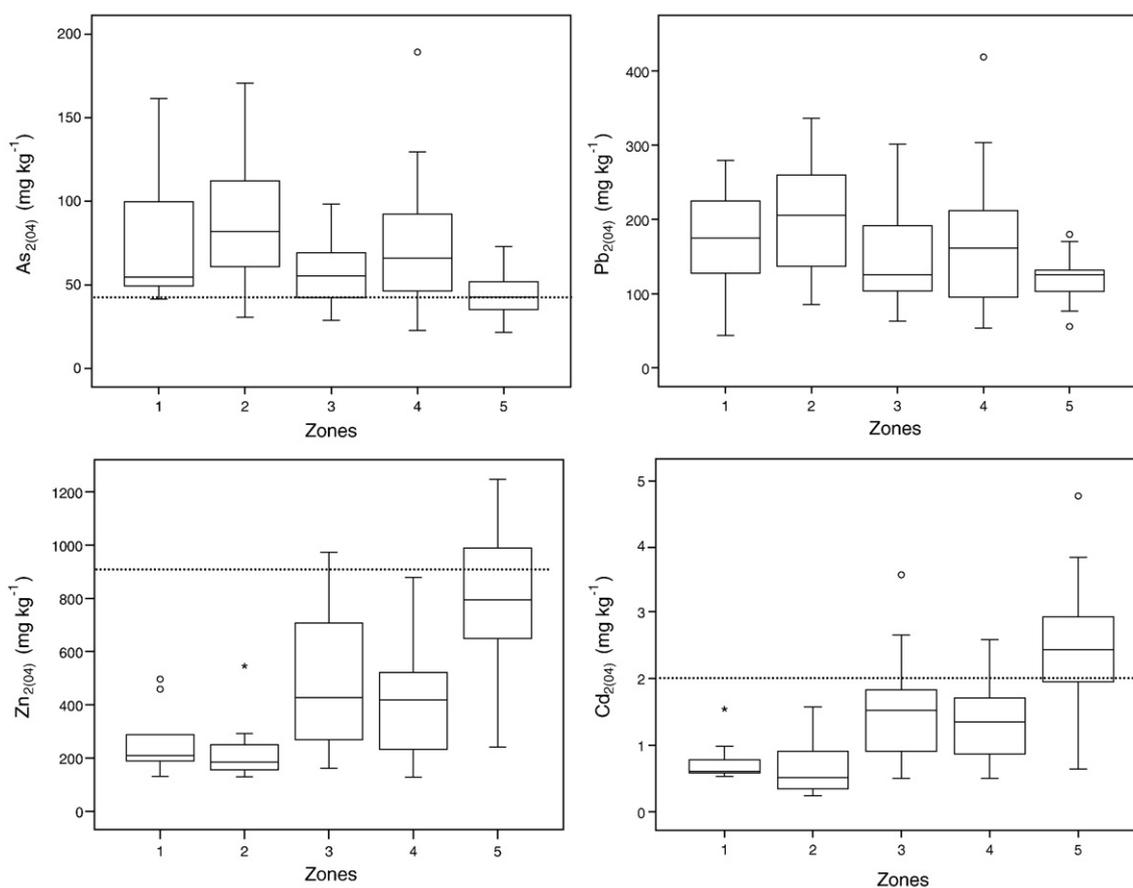
Fig. 10 – Box-and-whisker plots for pollutant concentrations by zones between 10 and 30 cm in depth in 2004 (dotted lines: normal range in soils).
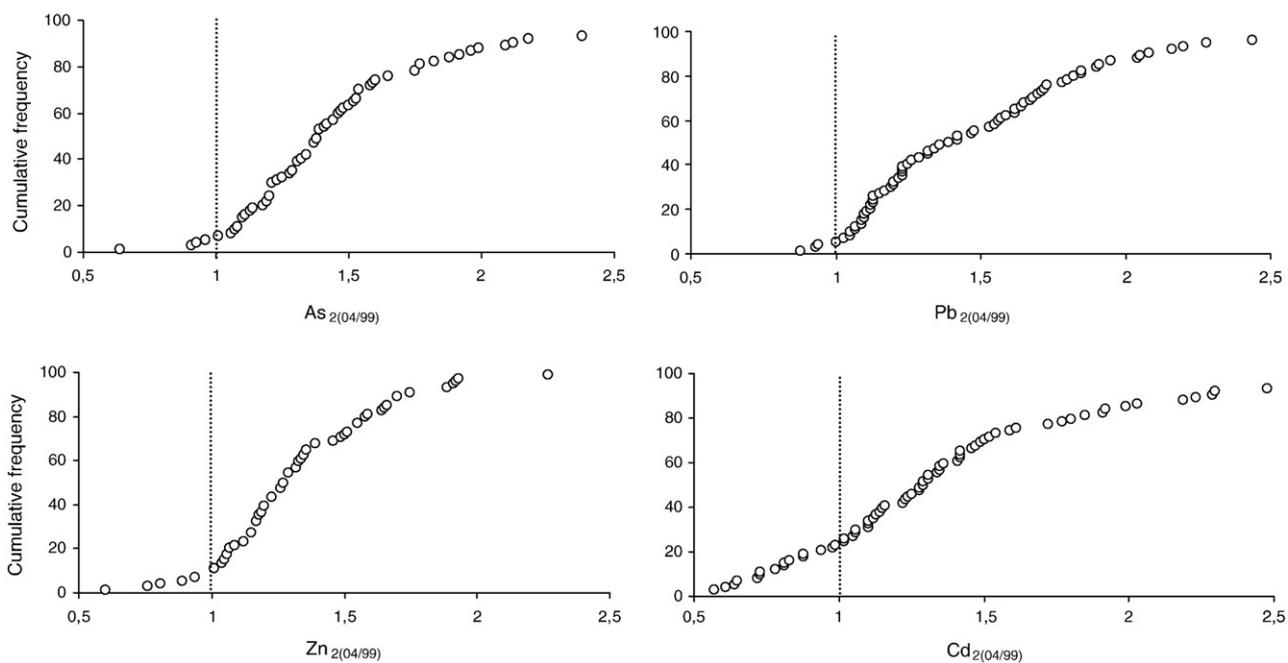
Fig. 11 – Cumulative frequency distribution for the ratio of the pollutant concentrations at 10–30 cm in depth between 2004 and 1999.

Table 5 – Mean, standard deviation (SD), and variation coefficient (VC) of the total concentration of pollutants in soils between 30 and 50 cm in depth in the sampling of 1998, 1999, and 2004

	1998				1999				2004			
	Zn	Cd	As	Pb	Zn	Cd	As	Pb	Zn	Cd	As	Pb
Mean	267a	0.8a	37a	88a	254a	0.8a	37a	88a	277a	1.0a	36a	83a
SD	251	0.7	20	46	243	0.7	20	45	260	0.8	19	42
VC	0.94	0.88	0.54	0.52	0.96	0.88	0.54	0.51	0.94	0.80	0.54	0.51

For each pollutant, values of the mean followed by the same letter did not differ significantly according to the Scheffé test ($p < 0.05$).

infiltration in the soil of Zn and Cd in relation to As and Pb (Galán et al., 2002; Kraus and Wiegand, 2006), could have been responsible for the lower proportion of soils in which the ratios $Zn_{1(99/98)}$ and $Cd_{1(99/98)}$ were greater than 1.0 (Fig. 6), as well as the general decline in the concentrations of Zn and Cd in the uppermost 10 cm of the soils in 1999 compared to 1998 (Fig. 4). It may also explain why differences in mean pollutant concentrations between 1998 and 1999 were significant only in the case of Zn and Cd (Table 2).

Because the pollutants were concentrated mainly in the topsoil (Simón et al., 2002; Kraus and Wiegand, 2006), the mixing of the upper 20–25 cm during the *tilling-00* must have been responsible for the decreased mean concentration of the pollutants in the uppermost 10 cm of the soils in 2004 in relation to 1999. The reduction in the five-number summaries of the data distribution of Zn, Cd, As, and Pb (Fig. 4), show that this decrease was more generalized and affected a greater proportion of soils than during the *cleanup-99*. Similar to what
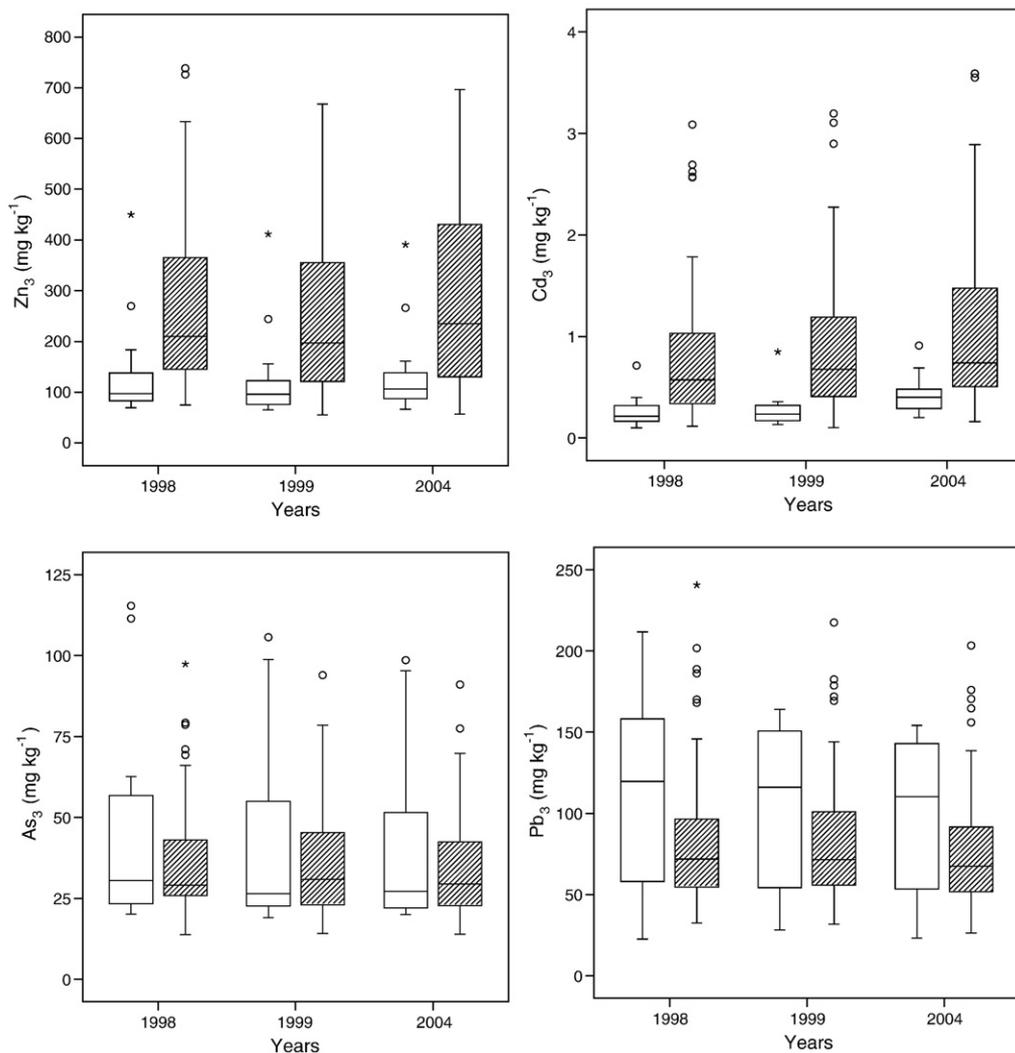
Fig. 12 – Box-and-whisker plots for the pollutants concentration between 30 and 50 cm in depth in the acidic (□) and basic (▨) soils sampled in 1998, 1999, and 2004.
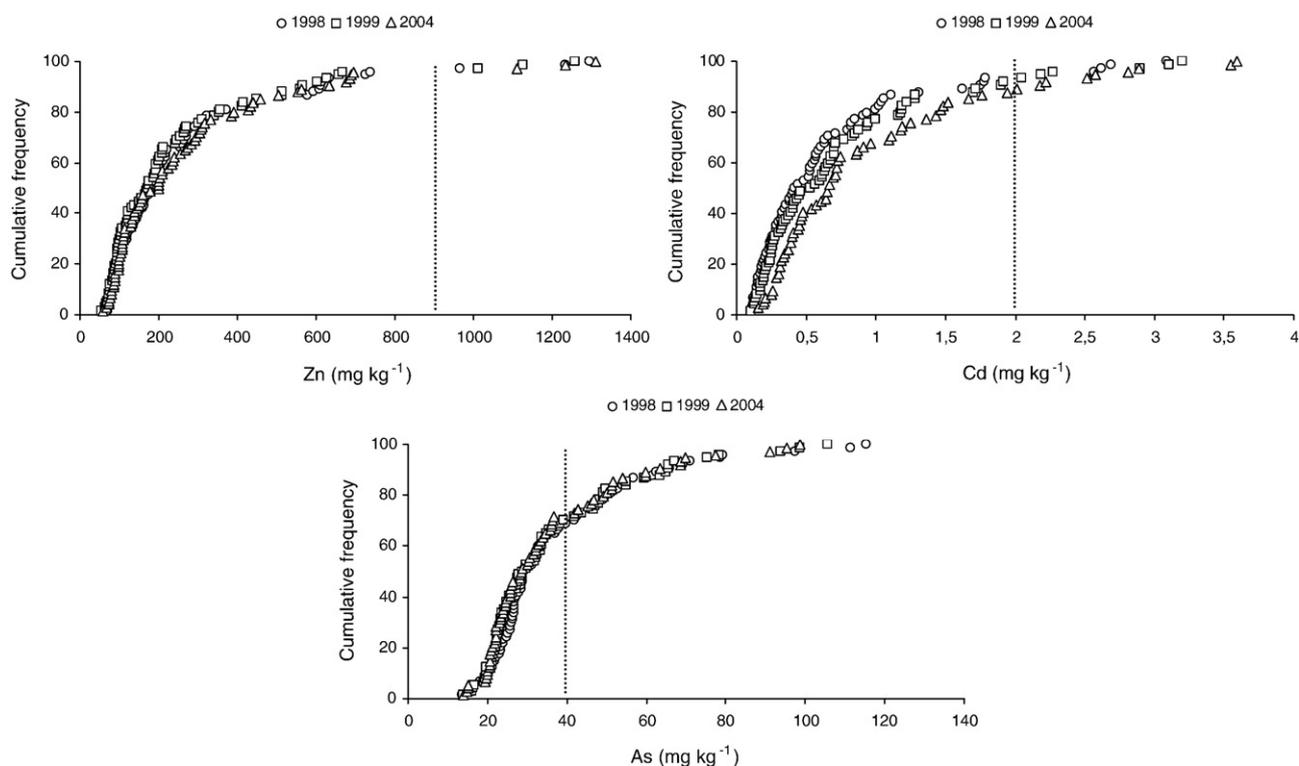
Fig. 13 – Cumulative frequency distribution of the Zn, Cd, and As concentration between 30 and 50 cm in depth in the three sample years.

occurred between 1998 and 1999, the run-off water between 1999 and 2004, together with the tilling of the upper 25 cm of the soil, must have spread the pollutants. Infiltration water appears to have mobilized the Zn and Cd within the soil, as demonstrated by the inverse relationships (except in the case of Cd) between $C_{1(04/99)}$ and $C_{1(99)}$ (Eqs. (5)–(7)), while Zn and Cd were the only elements with significant differences in the mean concentrations between the three sampling years (Table 2). The spread and mobilization of the pollutants into the soils must have been even more intense between 1999 and

2004 as a consequence of the greater time that elapsed (4 years); nevertheless, the tilling of the soils in this period must have been responsible for the alteration observed in the results. Thus, with tilling deeper than the uppermost 10 cm, part of the pollutants accumulated beneath the first 10 cm, so that the $C_{1(04/99)}$ ratios were greater than 1 in only 20% of the soils (Fig. 8) and clearly lower that the $C_{1(99/98)}$ ratios (Table 3). In addition, the mixing of the upper 20–25 cm of the soils caused the $C_{1(04/99)}$ ratios, both of the minor mobile elements (As and Pb) as well as the more mobile ones (Zn and Cd), to be greater than 1 in a similar percentage of soils (Fig. 8). The ratios of the concentrations of Cd between 2004 and 1999 (Cd$_{1(04/99)}$) were not inversely related to the Cd concentrations in 1999 (Cd$_{1(99)}$), which could be due to the more intense leaching of Cd that would infiltrate below the depth affected by the tilling (20–25 cm). Galán et al. (2002) reported that in some soil profiles the maximum Cd concentration was found in the subsoil.

4.2. Concentration of the contaminants between 10 and 30 cm in depth

If it is taken into account that the pollutant concentration tends to decline with depth, the lowering of the pollutant concentration in 1999 in relation to 1998 (Fig. 9) could be attributed to the fact that, when the first few centimetres of highly polluted soils were removed during the *cleanup-99*, the depth at which the samples were taken in 1999 increased with regard to those that were taken in 1998, by a distance equivalent to the thickness of the soil removed. For example, if the first 10 cm of soil were removed, the depth of 10–30 cm after the *cleanup-99* would

Fig. 14 – Box-and-whisker plots for the ratio of the pollutant concentrations at 30 to 50 cm in depth between 2004 and 1999 (C$_{3(04/99)}$).

correspond to the depth of 20–40 cm before the cleanup. Also, this cleanup, as during the removal of the tailings, could have embedded part of the pollutants below the uppermost 10 cm, thereby explaining why the ratios $As_{2(99/98)}$ and $Pb_{2(99/98)}$ were greater than one in 15% of the soils. This embedding, together with a greater leaching of the most mobile elements from the uppermost 10 cm and their precipitation between 10 and 30 cm, would explain why the ratios $Zn_{2(99/98)}$ and $Cd_{2(99/98)}$ were greater than one in a higher percentage of soils (20% in the case of Zn and 30% in the case of Cd).

The *tilling-00* in 2004 sharply raised the pollutant concentration between 10 and 30 cm in depth in most of the soils

(ratios $C_{2(04/99)}$ greater than one in 80% of the soils; Fig. 11). The idea that this increase was due to the effect of mixing by the tilling is confirmed by the linear relationship between $C_{2(04)}$ and $C_{1(99)}$ (Eqs. (5)–(8)), while the fact that the slopes of Eqs. (5) and (6) are lower than the slopes of Eqs. (7) and (8) indicates that part of the increase in Zn and Cd between 10 and 30 cm must have been caused by displacement from the uppermost 10 cm. Nevertheless, given that the less mobile elements tended to concentrate in the uppermost 10 cm of the soil by precipitation or co-precipitation processes (Simón et al., 2005), the increase provoked by the tilling in the pollutant concentration between 10 and 30 cm was greater in the case of As and Pb than in the case of Zn and Cd (Table 4). In fact, only the differences in mean As and Pb concentrations between 1999 and 2004 were significant.

4.3.   Pollutant concentrations at 30–50 cm in depth

Given that the remediation measures mainly affected the upper 25 cm of the soils, the concentration of the pollutants between 30 and 50 cm of depth hardly changed between the different dates of sampling, and the slopes of the regressions that relate the pollutant concentrations between 1999 and 2004 (Eqs. (9)–(12)) were very close to 1.0. Nevertheless, the fact that these slopes were greater in the case of Zn and Cd,
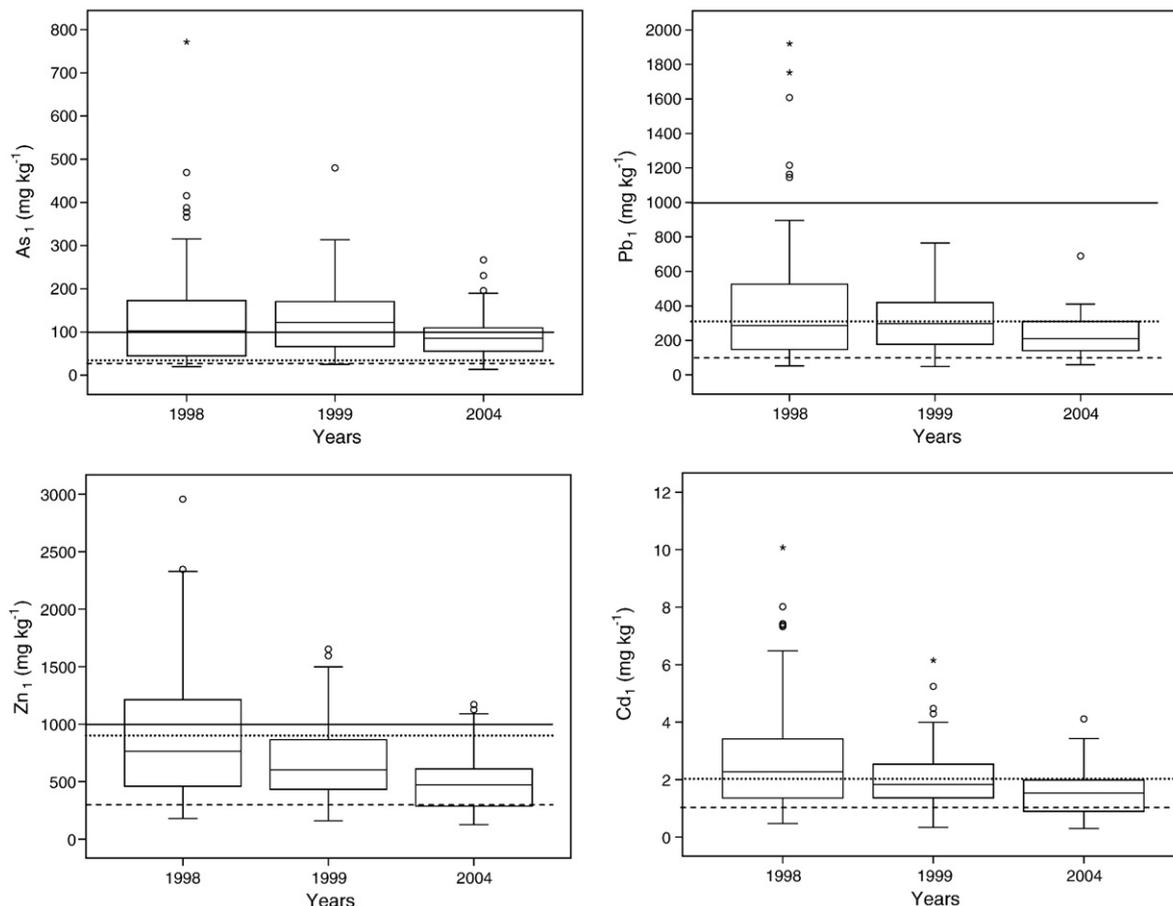
Fig. 15 – Box-and-whisker plots for pollutant concentrations between 0 and 10 cm in depth in 1998, 1999, and 2004 (••••••: normal range in soils; - -: uncontaminated soils in the area; —: intervention levels; Table 6.

together with the fact that the ratios $Zn_{3(04/99)}$ and $Cd_{3(04/99)}$ were clearly greater than the ratios $As_{3(04/99)}$ and $Pb_{3(04/99)}$ (Fig. 14), confirms that the displacements of the more mobile elements reached the depth of 30–50 cm. The $Cd_{3(04/99)}$ ratios are clearly greater than those of $Zn_{3(04/99)}$, indicating that the displacement of Cd was greater than that of Zn, and attributable to the lower specific adsorption of Cd as a consequence of its lower ability to form hydroxy complexes (Brummer, 1986). These results agree with those of Kraus and Wiegand (2006), who reported peak concentrations of Zn and Cd at depths of 10–30 cm and 30–50 cm, respectively, in 2002 in a soil covered with tailings.

4.4.   Effectiveness of the remediation measures

If the range of the uncontaminated soils (Table 6) is taken as a reference, the remediation measures were ineffective in the case of As and Pb (Fig. 15), given that the percentage of the soils that surpassed the upper values in the first 10 cm does not decrease (≈90% of the soils exceeded the concentration of 38.5 mg As kg^{-1} dry soil and 86.3 mg Pb kg^{-1} dry soil in 1998, 1999, and 2004); meanwhile, in the case of Zn and Cd the measures were somewhat more effective (85% of the soils exceeded the concentration of 271 mg Zn kg^{-1} dry soil and 1.1 mg Cd kg^{-1} dry soil in 1998 and 1999, and 75% in 2004). Nevertheless, if the normal range in soils (Bowen, 1979) is taken as a reference, the remediation measures can be considered to have been effective in the case of Zn (30% of the soils exceeded a concentration of 900 mg Zn kg^{-1} dry soil in 1998, 22% in 1999, and 9% in 2004); somewhat less effective in

the cases of Cd (59% of the soils exceeded a concentration of 2 mg Cd kg^{-1} dry soil in 1998, 40% in 1999, and 25% in 2004), and Pb (45% of the soils exceeded a concentration of 300 mg Pb kg^{-1} dry soil in 1998 and 1999, and 25% in 2004); and ineffective in the case of As (≈85% of the soils exceeded a concentration of 40 mg As kg^{-1} dry soil in 1998, 1999, and 2004). Consequently, the remediation measures were ineffective in reducing considerably the concentration of the pollutants, although, except in the case of As, the concentration of pollutant in many soils fell, compared with the normal range in soils.

According to these results, the effectiveness of the remediation measures could be related to the concentration of each contaminant in the uppermost 10 cm of the soils (C_1) after the pollution in relation to the maximum value considered (MV_c: defined as the upper values of the normal range in soils, Table 6), and also related to the movement of each element both in the landscape as well as within the soil. The higher the ratio between the concentration in the topsoil of each pollutant in 1998 ($C_{1(98)}$) and the MV_c, the less effective the remediation measures were. If the upper values of the natural range are considered as MV_c, the ratios $As_{1(98)}/MV_{As}$ (Fig. 16) were very high (>2.0 in the 60% of the soils), and even increased in 1999 (>2.0 in 70% of the soils), so that the cleanup-99 did not substantially reduce the As concentration in the topsoil, and the run-off and the tilling spread the As. Given that the ratios $As_{1(99)}/MV_{As}$ were higher than 2.0 in 70% of the soils, the tilling-00 did not decrease the percentage of soils in which the concentration of 40 mg As kg^{-1} dry soil was exceeded. Therefore, the remediation measures were not effective in the case of As. In the cases of Zn and Cd, the
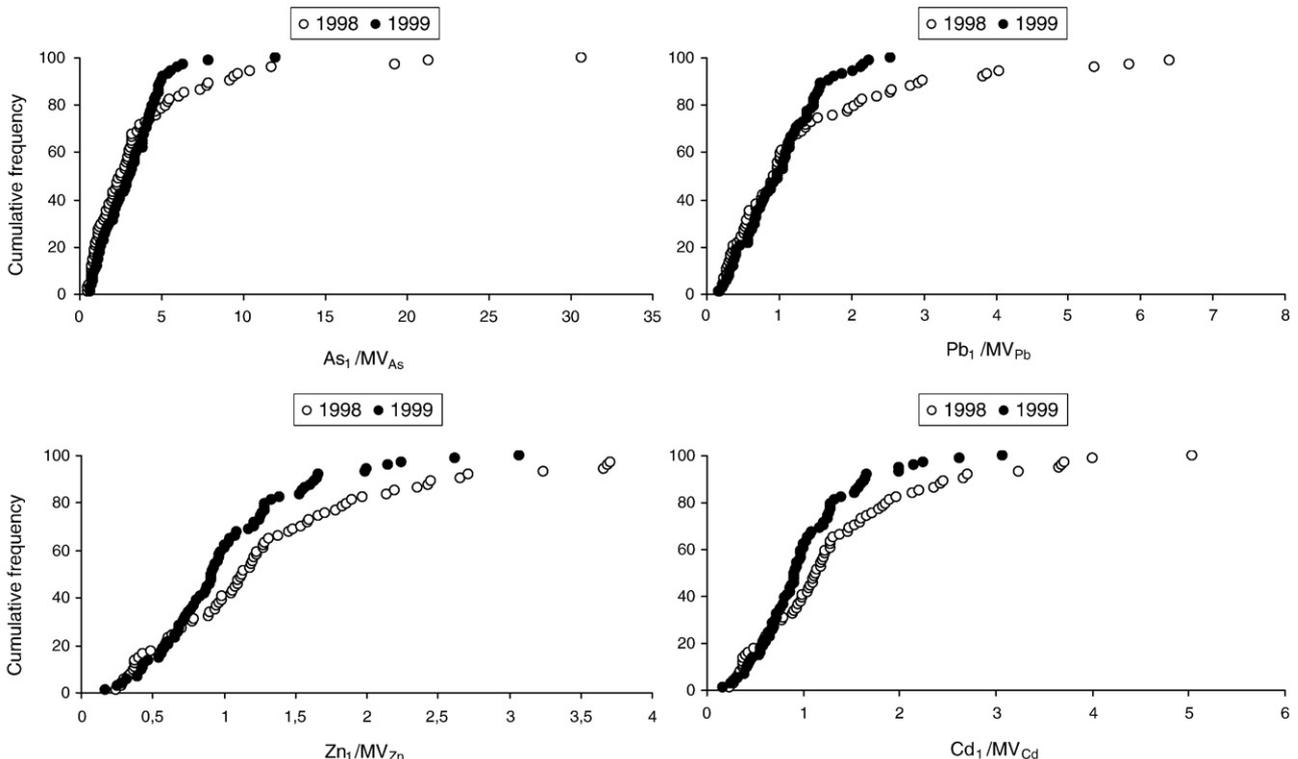
Fig. 16 – Cumulative frequency distribution for the ratios between pollutant concentrations at 0–10 cm in depth (C_1) and upper values of the normal range in soils (MV_c).

lower $Zn_{1(98)}/MV_{Zn}$ and $Cd_{1(98)}/MV_{Cd}$ ratios and the greater mobility and displacement below the upper 10 cm of the soils, made the *cleaning-99* and *tilling-00* more effective than in the case of As, reducing considerably the soils that surpassed the MV_c values in 2004 (Fig. 16). In addition, although the movement within the soil increased the Zn and Cd concentrations below the uppermost 10 cm, it did not boost the percentage of soils that exceeded the limit values. Therefore, in the three sampling years, around 10% of the soils exceeded the concentration of 900 mg Zn kg^{-1} dry soil and 18% the concentration of 2 mg Cd kg^{-1} dry soil between 10 and 30 cm in depth, and approximately 4% and 8%, respectively, exceeded these concentrations between 30 and 50 cm in depth (Fig. 15). Finally, the ratios $Pb_{1(98)}/MV_{Pb}$ were also low (>2.0 in 20% of the soils), and decreased in 1999 ($Pb_{1(99)}/MV_{Pb}$>2.0 in only 7% of the soils) (Fig. 16), so the *cleaning-99* lowered the Pb concentration to below the MV_{Pb} value in most of the most heavily polluted areas. The spread of Pb was not sufficient to increase the concentration to above this value, the *tilling-00* lowered the percentage of soils in which the concentration of 300 mg Pb kg^{-1} dry soil was exceeded, and the effectiveness of the remediation measures was similar to that of the Cd (Fig. 15).

In agreement with the above, if the MV_c is raised, the ratio $C_1:MV_c$ tends to diminish and therefore it would increase the effectiveness of the remediation measures. Thus, if we take as a reference the intervention levels for the affected zone (Table 6), defined by the Environmental Agency of the Regional Government of Andalusia (EARGA) for natural parks (Llamas et al., 2000), the effectiveness of the remediation measures is higher. In 2004 no soil exceeded the limit values for Pb and Cd, only 4% exceeded the limit value for Zn and 32% exceeded the limit value for As. A special case is Cd, as the limit value of 15 mg kg^{-1} is above the Cd concentration reached in the polluted soils in any of the sampling years, and above normative limit values of most countries. Therefore, we recommend that this limit be reviewed, particularly taking into account the high mobility and toxicity of Cd. In any case, even using the limit values of the EARGA, 6 years after the accident, in about 35% of the soils the intervention level of at least one pollutant was exceeded.

5.   Conclusions

In these types of spills, in which the distribution of the pollutants in the landscape is irregular, with heavily polluted spots alternating with less contaminated ones, the cleanup of the more contaminated areas should be rapid and sufficiently intense so that the concentrations of the pollutants in the topsoil do not strongly exceed the maximum values (concentration≤2-fold MV_c). The presence of these strongly polluted spots and the spread of the pollutants could increase the percentage of polluted soils (concentration>MV_c). Although the tilling of the upper 20–25 cm generally tends to diminish the pollutant concentration in the topsoil, it is not effective in reducing the percentage of the polluted soils when the concentration of the pollutant in the uppermost 10 cm of the soil exceeds the MV_c by 2-fold. Nevertheless, highly mobile elements (Zn and Cd) are moved through the soil by infiltration waters precipitating in depth, reducing their concentration in the topsoil and helping to improve the results of remediation measurements.

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