Distribution of As and Zn in Soils Affected by the Spill of a Pyrite Mine and Effectiveness of the Remediation Measures

M. Simón · M. Díez · I. García · F. Martín

Abstract The concentrations of As and Zn in 100 georeferenced soils uniformly distributed throughout the area affected by the spill from the Aznalcóllar mine (April 1998) were analysed at three depths (0–10, 10–30, and 30–50 cm) and on four dates (autumn–winter 1998, 1999, 2001, and 2004). For an estimate of the geochemical background, 30 unaffected soils near the edge of the spill were also analysed at the same depths. The soils were contaminated before the spill and, the accident seriously increased the concentration of As and Zn in the first 10 cm of almost all the affected soils. After the enormous efforts of cleaning up the tailings, around 45% of the soils had a concentration higher than 100 mg As kg^{-1} dry soil, and some 35% had a concentration higher than 1,000 mg Zn kg^{-1} dry soil. Both As and Zn penetrated between 10 and 30 cm in 25% and 45% of the soils, respectively, but reached 30 cm in only 12% of the soils. The remediation actions, especially the tilling and homogenisation of the uppermost 25 cm of the all soils, caused the As and Zn concentrations to decline in the soils, but this change was not very effective from the standpoint of pollution. Thus, 6 years after the spill, the uppermost 10 cm of 30% of the soils continued to have an As concentration higher than 100 mg As kg^{-1}, while the Zn concentration diminished considerably on the surface due to its greater mobility, accumulating between 10 and 30 cm in depth, where 20% of the soils continued to register more than 1,000 mg Zn kg^{-1} dry soil.

Keywords Pyrite mine · Soil pollution · Arsenic and Zinc · Cumulative frequency · Remediation

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1 Introduction

The Iberian pyrite belt covers nearly 8,000 km^2 in the south-western corner of the Iberian Peninsula. This area, which includes massive sulphide deposits of the Rio Tinto, Aljustrel, Neves Corvo, Tharsis, Sotiel, and Aznalcóllar mines, is considered to be one of the largest metal reserves in Western Europe. The mineral phase consists of different sulphides (Schermerhorn 1982; Almodovar et al. 1998): pyrite (83.1%), sphalerite (5.4%), galena (2.1%), chalcopyrite (1.4%), arsenopyrite (0.9%) and non-productive materials (7.1%).

The Aznalcóllar mining district, on the eastern edge of the Iberian pyrite belt (Seville province, southern Spain), has been exploited for centuries. The studies of Cabrera et al. (1984, 1987) and Ramos et al. (1994)

indicated that the soils of the Agrio and Guadiamar River basin, affected by this mining district, had abnormally high contents in Cu, Cd, Zn and Pb, with a tendency to increase over the years. This contamination appears to have originated from the periodic discharges of acidic and metal-rich waters into the Guadiamar River from the mining companies of Aznalcóllar working for decades, and by the use of these waters by local farmers. On 25th April 1998, the retention walls broke open in a holding pond belonging to the Aznalcóllar mine. Approximately 36×10^5 m^3 of polluted waters and 9×10^5 m^3 of toxic tailings were spilled into the Agrio and Guadiamar River basin. The total surface area affected by the toxic spill was approximately 45 km^2, forming a patch of about 50 km in length and 0.9 km in 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. Due to the fact that 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 range of total contamination of the soils was very broad (Cabrera et al. 1999; López-Pamo et al. 1999), although, only in the sectors where the penetration of the tailings was relatively higher, did As and Zn exceed 50 and 1,000 mg kg^{-1}, respectively. Nevertheless, as the tailings dried and aerated, complex processes (Stumm and Morgan 1981; Nordstrom 1982; Förstner and Wittmann 1983) oxidised the sulphides to sulphates, lowering the pH and solubilising part of the pollutants that had formerly remained insoluble. Subsequent rains dissolved the soluble salts formed, which then infiltrated the soil and thereby, raised the pollution level. These processes were very fast; in 10 days, the content in soluble SO_4^{2-} multiplied 10-fold in the driest tailings in relation to the wettest, and in 3 months, the concentration of most of the pollutants multiplied 2.5-fold in the first 10 cm of the soils (Simón et al. 2001). This speed underscores the urgency of removing the tailings from the soil surfaces in these types of spills. In an extensive cleanup operation (May to December 1998), the tailings and the upper part of the soils were removed by heavy machinery. This rapid work (in 8 months, 45 km^2 were cleaned) resulted in a deficient cleanup, as part of the tailings remained mixed with the soil and residual tailings appeared
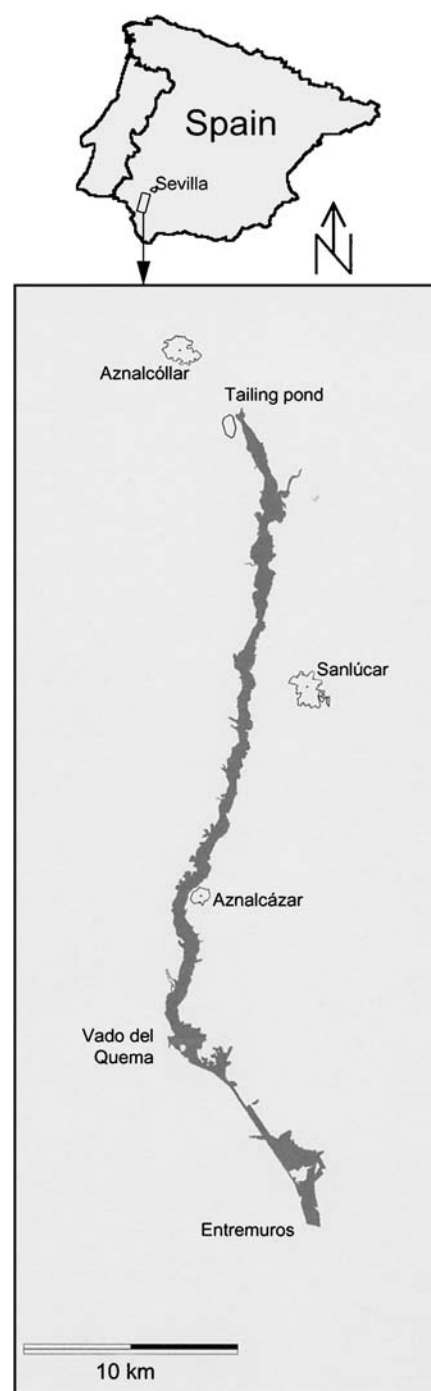

Fig. 1 Situation and morphology of the area affected by the toxic spill

below 30 cm in depth. Because of the high pollution of the soils after the tailings were removed, the most polluted sectors were cleaned again in spring–summer 1999, followed by a liming with sugar-refinery scum

(4 kg m^{-2}) and superficial tilling of the soils (5–10 cm in depth). In spring–summer 2000, organic matter (2 kg m^{-2}) and iron-rich clayey materials (2 kg m^{-2}) were added, followed by tilling the upper 20–25 cm of the soils. The tilling of the upper 20–25 cm was repeated, although not in a generalised way, in 2002 and 2003. In any case, high metal concentrations were detected in the soils 4 years after the Aznalcóllar spill (Aguilar et al. 2004; Kraus and Wiegand 2006).

In the present study, Zn and As concentrations in soils affected by the spill, sampled after each cleanup and remediation action, were compared with unaffected soils in order to estimate the pollution level of the soils before the spill, the increase in the soil pollution by the spill, the distribution of the pollutants within the soils, and the effectiveness of the remediation actions in the reduction of the soil pollution levels 6 years after the spill.

2 Materials and Methods

The contaminated area was monitored with a sampling network established on a 400×400 m grid. The intersections and the centres, 400 in total, were correlatively numbered and a number between 1 and 400 was drawn at random. Starting from the number assigned, one of each four was selected, thus appointing 100 sampling points which were georeferenced by Global Positioning System (GPS). At each sampling point, a square plot was laid out (10×10 m) and samples were taken from the four corners and from the centre of each plot at depths of 0–10, 10–30, and 30–50 cm, and the five samples taken at each depth were pooled. In this way, after each cleanup and remediation action, a sampling was made (autumn–winter of 1998, 1999, 2001 and 2004). In addition, 30 non-irrigated and unaffected soils near the border of the spill, and uniformly distributed throughout the area, were also sampled at the same depths.

All soil samples were air-dried and sieved to 2 mm, and the percentage of gravels (>2 mm) and fine earth (<2 mm) was calculated. The fine earth, very finely ground (<0.05 mm), was digested in strong acids (HNO$_3$+HF+HCl). Since Zn and As were the principal pollutant elements of the soils (Alastuey et al. 1999; Cabrera et al. 1999; López-Pamo et al. 1999; Simón et al. 1999), these elements were measured in each digested sample 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 SRM2711 (Gills and Kane 1993).

In an effort to minimise the influence of the outliers (Reimann et al. 2004), the Zn and As geochemical background ranges were calculated from unaffected soils by the median ± twice the median absolute deviation (MAD), defined as the median of the absolute deviations from the median of all data (Md ± 2MAD; Tukey 1977). For the discrimination of the different homogeneous populations in the dataset of each sampling, in close approximation to the Lepeltier method (Lepeltier 1969), cumulative frequency distribution (CFD) were used, establishing the limits of each population from bends of the slope in the curves (Bauer and Bor 1995).

3 Results and Discussion

3.1 Unaffected Soils

The concentration of Zn and As in the soils which were unaffected by the spill did not significantly differ in depth. In addition, the cumulative frequency distribution (CFD) of the data did not markedly depart from ideal Gaussian (normal) curve, with similar mean and median values and low skewness (Table 2). Consequently, the data without transformation of all samples were used to establish the As and Zn natural background ranges of the area from Tukey's method, for which the upper limits were 25.3 mg As kg^{-1} dry soil and 101.4 mg Zn kg^{-1} dry soil, respectively.

3.2 Pollution of the Soils Prior to the Spill

Given that, prior to the removal of the tailings, the soils were not significantly affected under the first

Table 1 Analysis of standard reference material 2711

Element	Certified		Experimental	
	Mean	SD	Mean	SD
As	105.0	8.0	99.8	1.7
Zn	350.4	4.8	352.1	2.5

SD, standard deviation

Table 2 Statistical parameters of the Zn and As concentrations in uncontaminated soils and range of the geochemical background

	Zn (mg kg^{-1})	As (mg kg^{-1})
Minimum	35.1	8.3
Maximum	152.6	29.4
Mean	76.1	17.7
Median	76.9	18.3
Sdev	27.8	5.5
skewness	0.216	0.155
Md ± 2MAD	52.6–101.4	13.3–25.3

10 cm (Dorronsoro et al. 2002; Simón et al. 2002), with the exception of a few sectors in which the tailings had penetrated to depth through structural cracks in the first step of pollution (Simón et al. 1999), the geochemical background and the CFD of As and Zn between 10–30 cm and 30–50 cm were used to estimate the degree of pollution before the spill and, consequently, to calculate the effect of the spill in the total pollution level of the soils.

Thus, the CFD of As and Zn between 30 and 50 cm (Fig. 2) shows two clearly different populations of data (solid line). The inflection point (threshold point) between the two populations was identified as the end data point for which population 1 showed a skewness which was closest to 0 (Fleischhauer and Korte 1990). Population 1 (≈90% of the soils) had a relatively uniform slope, and according to Bauer and Bor (1995), would represent the "background" dataset and, consequently, the range of As and Zn concentrations in soils before the spill. Nevertheless, the upper limit of this collective data is higher than the upper limit of the natural background estimated from the unaffected soils. Therefore, population 1 can be divided into two sectors (broken line): the first one, with As and Zn concentrations below the upper limit of the geochemical background (Table 2), the presumably

non-polluted soil group (≈33% in the case of As, and 23% in the case of Zn); and the second one, with As and Zn concentrations above the upper limit of the natural background, the presumably contaminated soil group prior to the spill (≈67% in the case of As, and 77% in the case of Zn). The higher concentration of Zn in the acidic waters coming from the mine (Simón et al. 1999), together with the higher mobility of the Zn and deeper infiltration into the soil (Vidal et al. 1999; Simón et al. 2002; Galán et al. 2002), explain the higher percentage below the first 30 cm of contaminated soils in Zn than in As before the spill.

The comparison of the CFD of As and Zn at 10–30 cm and 30–50 cm (Fig. 2) shows that, up to 75 percentile in the case of As and up to 55 percentile in the case of Zn, both curves were very closely parallel to each other, although the curves at 10–30 cm were consistently above the curves for 30–50 cm. These results indicate that, before the spill, the As and Zn concentrations tended to increase towards the soil surface, so that, at 10–30 cm in depth, the soils with As and Zn concentrations above the upper limit of the natural background (dotted line) peaked at 81% in the case of As (14% more than at 30–50 cm), and at 89% in the case of Zn (12% more than at 30–50 cm). Consequently, given that this pollution tended to increase towards the soil surface, it can be deduced that in the first 10 cm, most of the soils affected by the accident were already contaminated prior to the spill.

3.3 Pollution of the Soils by the Spill

The second part of the CFD between 30 cm and 50 cm (Fig. 2), characterised by an abrupt change in the slope (population 2), indicates that about 10% of the soils roughly increased the concentration in As and Zn. This sudden increase would represent the

Fig. 2 Cumulative frequency distribution of As and Zn between 10–30 cm (*open circles*) and 30–50 cm (*closed circles*) of the soils sampled on 1998, immediately after clean-up of the tailings
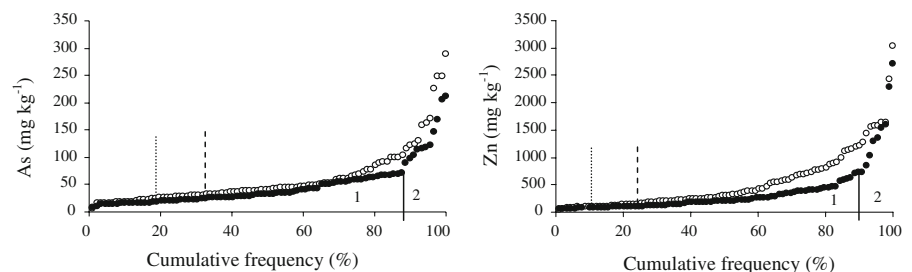
polluted soils (Bauer and Bor 1995) and, therefore, the contamination from the accident. As the pollutants dissolved from the oxidation of the tailings did not penetrate below 30 cm in depth, this contamination would be mainly determined by the initial penetration of the tailings as well as by the mixing of the tailings below the first 30 cm during the cleanup.

On the other hand, the divergence of the two CFD (10–30 cm and 30–50 cm; Fig. 2) must also have originated from the spill. Consequently, since the CFD values of As tended to diverge from the 75% percentile and those of Zn from the 55% percentile at 10–30 cm in depth, around 25% of the soils in the case of As and 45% in the case of Zn were found to be affected by the spill (more than 2-fold and almost 4-fold, respectively, of those affected at 30–50 cm). In this case, the higher proportion of soils contaminated by Zn than by As would not be due to the penetration of tailings (which would have increased the concentration of both elements equally) but rather to higher mobility and deeper infiltration of the Zn dissolved in the liquid phase, which must have penetrated beyond the first 10 cm in many soils, accumulating between 10 and 30 cm and raising the percentage of soils contaminated at this depth.

The CFD in the first 10 cm of the contaminated soils (Fig. 3) revealed that only 10% of the sampled soils in the case of As, and 2% in the case of Zn, had concentrations lower than the upper limit of the background (dotted line); meanwhile, the other 90% and 98%, respectively, presented different degrees of pollution. The CFD of As between 0 and 10 cm tended to diverge from the CFD at greater depths starting at 45 percentile (broken line), while the CFD values of Zn diverged from 10 percentile on, indicating that, in the uppermost 10 cm, the spill

boosted the As concentration in 55% of the soils and that of Zn in 90% of the soils (around twice of the soils that increased these concentrations at 10–30 cm). In the most contaminated soils, the clear separation of the CFD of As at 0–10 cm from those at greater depths indicates that the As tended to concentrate mainly in the first 10 cm of the soils. This confirms the relatively low mobility of this element. On the contrary, the CFD of Zn at the different depths tended to approach those of the most contaminated soils, implying that Zn tended to distribute itself more homogeneously in the first 50 cm of the soils (even in the same soils, the maximum Zn concentration was found in the subsoil) and verifying the higher mobility and infiltration rate into the soils. This agrees with the results of Galán et al. (2002). On the other hand, the bend of the CFD of Zn at 0–10 cm in depth was far less marked than that of the CFD of As, apparently indicating that the Zn contamination on the soil surfaces was much more generalised than that of As. This may be because the liquid phase of the spill (with high Zn concentration; Simón et al. 1999) contaminated the affected area in a more homogeneous way than the solid phase (where As was concentrated).

Therefore, although almost all the soils presented a certain degree of contamination before the spill, the accident seriously raised the concentration of As and Zn in the affected soils. Thus, after the enormous efforts of cleaning up the tailings, in around 45% of the soils, As exceeded the concentration of 100 mg/kg between 0 and 10 cm; meanwhile, 35% of the soils exceeded the Zn concentration of 1,000 mg/kg. This contamination penetrated to 10–30 cm in 25% of the soils in the case of As, and 45% in the case of Zn, while in only 10% of the soils, this contamination penetrated more than 30 cm in depth.

Fig. 3 Cumulative frequency distribution and limits of each population of As and Zn concentrations of the first 10 cm of the soils sampled on 1998 (*open squares*), in relation to those between 10–30 cm (*open circles*) and 30–50 cm (*closed circles*)
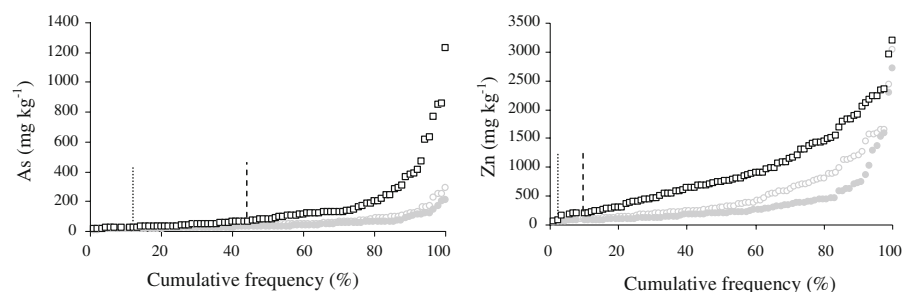
3.4 Effectiveness of the Remediation Actions

The comparison of the CFD values of As and Zn between 0 and 10 cm in depth on the different sampling dates (Fig. 4) indicates that the cleanup and remediation actions progressively decreased the concentration of pollutant elements in the soils. Thus, the repetition of the cleanup in spring–summer 1999 for the most contaminated soils clearly decreased (roughly in 20% of all the analysed soils) the As concentration in the uppermost 10 cm (mean concentration ≈273 mg kg^{-1}) in relation to 1998 (mean concentration ≈472 mg kg^{-1}), but did not lower the percentage of soils that exceeded 100 mg As kg^{-1} dry soil, this continuing to be around 45% of the total analysed soils. On the contrary, the tilling and homogenisation of the uppermost 25 cm of all soils in spring–summer 2000 generally lowered the As concentration in the uppermost 10 cm of the soils, lowering this concentration in 75% of the soils sampled in 2001 with respect to those sampled in 1999, at the same time as the soils that exceeded the concentration of 100 mg As kg^{-1} dry soil fell around 30%. Nevertheless, the effectiveness of this remediation measure was less patent in the most contaminated soils (approximation of the CFD of 1999 and 2001), this presumably being

due to the greater surface compaction of these soils (Simón et al. 2005) which hampered the working and mixing of the first 25 cm of soil. The repetition of the tilling in 2002 and 2003 improved the homogenisation of the uppermost 25 cm of the most contaminated soils, and a sharper decline in the As concentration in the uppermost 10 cm of the soils sampled in 2004. Nevertheless, the percentage of soils that exceeded 100 mg As kg^{-1} dry soil remained at 30%.

The CFD of the Zn (Fig. 4) presented a similar behaviour to that of As, although the fall in the Zn concentration was more accentuated and generalised. Thus, in 1999, more than 60% of the soils lowered the Zn concentration between 0 and 10 cm with respect to 1998, otherwise only 20% lowered the As values. Meanwhile, in 2001, practically all the soils declined with regard to the Zn concentration in the uppermost 10 cm, and 75% declined in the case of As. Therefore, the decrease of the Zn concentration in the uppermost 10 cm of the soil must have involved processes other than those determining the fall in the As concentration, such as a more intense leaching and infiltration to a greater depth, as demonstrated above. Thus, the remediation measures, together with the leaching, progressively diminished the percentage of soils that exceeded the concentration of 1,000 mg Zn kg^{-1} dry

Fig. 4 Cumulative frequency distribution of As and Zn concentrations of the first 10 cm of the soils sampled on 1998 (*open circles*), 1999 (*open squares*), 2001 (*open triangles*), and 2004 (*closed triangles*)
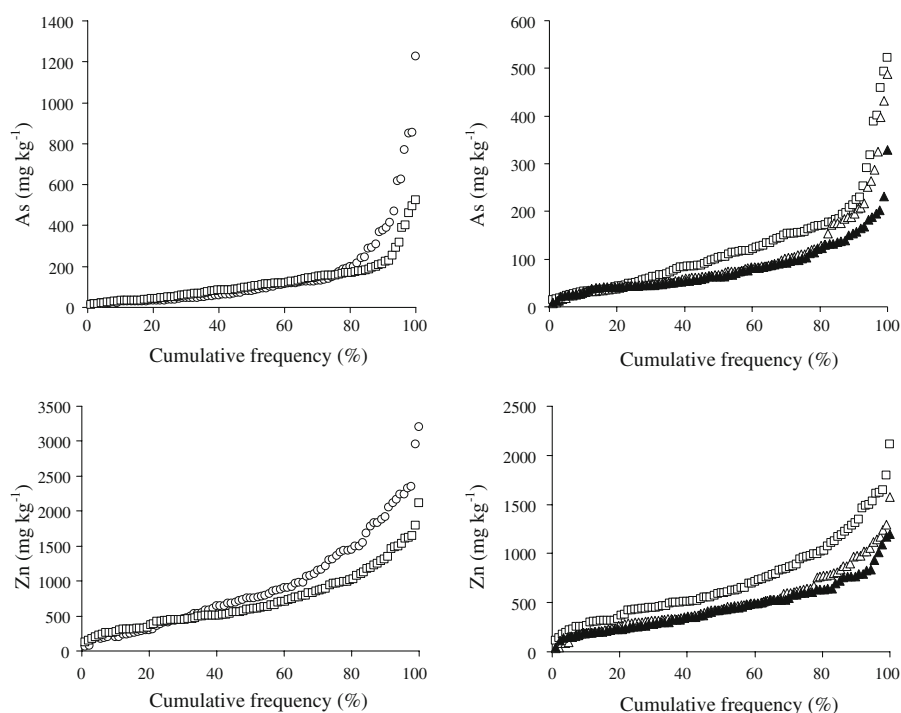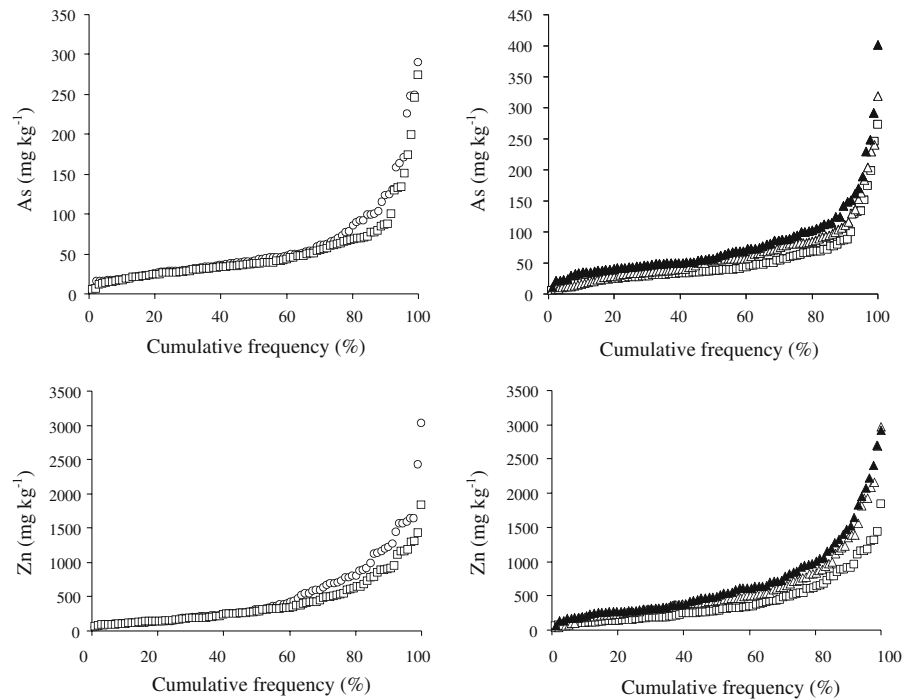
Fig. 5 Cumulative frequency distribution of As and Zn concentrations between 10–30 cm of the soils sampled on 1998 (*open circles*), 1999 (*open squares*), 2001 (*open triangles*), and 2004 (*closed triangles*)


soil in the uppermost 10 cm of the soil from 35% in 1998 to only 5% in 2004.

The effect of these remediation actions was clearly weaker below the first 10 cm. Thus, between 10 and 30 cm in depth (Fig. 5), the repetition of the cleanup in the most polluted sectors in spring–summer 1999, although the As and Zn concentrations declined, was less effective (CFD of As and Zn of 1998 and 1999 remain closer). Meanwhile, as expected, the tilling and homogenisation of the uppermost 25 cm increased the As and Zn concentrations between 10 and 30 cm in depth (CFD of 2004 higher than the previously sampled CFD values), and the soils that exceeded concentrations of 100 mg As kg^{-1} dry soil and 1,000 mg Zn kg^{-1} dry soil at this depth increased

from roughly 10% in 1999 to 20% in 2004. Nevertheless, because of the higher mobility and infiltration rate into the soils of Zn in relation to As, it would be expected that between 10 and 30 cm in depth, the Zn concentrations would rise more than those of As (the CFD of Zn in 1999 and 2004 should be more separate than those of As), but this is not appreciable in Fig. 5. This appears to indicate that the leaching of Zn from the uppermost 10 cm of the soils did not concentrate only at 10–30 cm, but rather tended to be distributed at a greater depth, as reflected by the fact that CFD of Zn at 30–50 cm in 2004 (Fig. 6) was higher than the CFD of previous samplings, while the level of CFD for As of the different samplings tended to become superimposed.

Fig. 6 Cumulative frequency distribution of As and Zn concentrations between 30–50 cm of the soils sampled on 1999 (*open squares*), 2001 (*open triangles*), and 2004 (*closed triangles*)
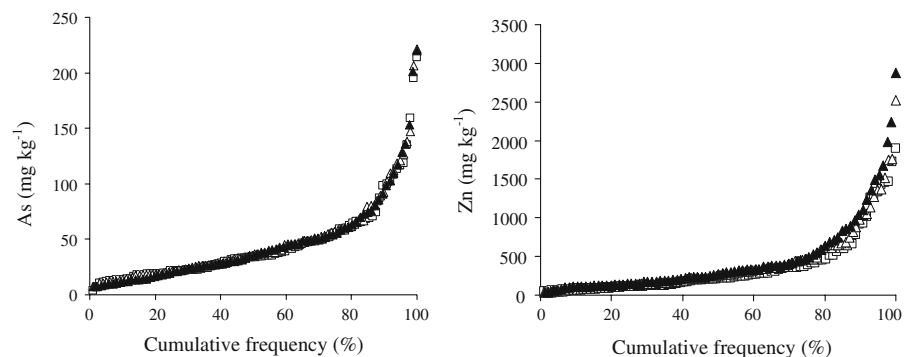
Consequently, because of the narrow difference between the upper limit of the background of As (25.3 mg kg^{-1}) and the maximum permitted level for agricultural soils (50 mg kg^{-1}), notably less than in the case of Zn (101.3 mg kg^{-1} and 1,000 mg kg^{-1}, respectively), and of the higher mobility and infiltration rate into the soils of Zn in relation to As, the main difference in the soil pollution of the two elements was their risk. Thus, in 2004, although the remediation measurements decreased the As concentrations, the percentage of soils exceeding the maximum permitted level for agricultural soils was around 65% of the total soils analysed, and around 30% of the soils had even doubled the maximum permitted of As (100 mg kg^{-1}); meanwhile, only 20% of soils exceeded the maximum permitted level for Zn (1,000 mg/kg). Consequently, 6 years after the spill, despite the many remediation actions, most of the soils still had excessively high, and hence, potentially toxic, As concentrations.

4 Conclusion

The cumulative frequency distribution curves of the pollutant elements in the landscape as well as at different soil depths constitute a reliable statistical tool for estimating the steps and levels of pollution, the relative mobility of the elements, and the effectiveness of the remediation measures in contaminated soils.

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