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Soil pollution by a pyrite mine spill in Spain: evolution in time

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"Capsule": *Remediation measures carried out after the Aznalcóllar pyrite mine spill were effective in the reduction of the pollution, although three years after the accident many areas are still polluted by As.*

Abstract

Soil pollution was studied after the spill of the Aznalcóllar pyrite mine between 1998 and 2001, analyzing As, Zn, Cd, Cu and Pb both in total concentrations as well as in soluble and bioavailable forms. The main remediation measures were: clean-up of the tailings and polluted soils, plus application of amendment materials (liming). The results indicate that, after three years, 50–70% of the acidic soils and 25–30% of the basic soils are still highly polluted in total arsenic. The limit of 0.04 mg kg^{-1} for water-soluble arsenic is exceeded in 15–20% of all soils. The EDTA-extractable arsenic (bioavailable) exceeds the limit of 2 mg kg^{-1} only in the acidic sectors. After clean-up, the homogenization of the upper 20–25 cm of the soils appears to be the most recommended measure in the reduction of pollution.

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Keywords: Pyrite; Soil pollution; Heavy metals; Solubility; Bioavailability

1. Introduction

On 25 April 1998, the walls of the pond containing the ore-processing residues from the pyrite mine located in Aznalcóllar (SE Spain) broke open, spilling into the Agrio and Guadiamar rivers approximately 36×10^5 m^3 of polluted waters (solution phase) and 9×10^5 m^3 of toxic tailings (solid phase) with high concentrations of sulfur, iron and other contaminating elements, affecting some 43 km^2 of farmlands. The main pollutants in the soils were Zn, Pb, Cu, As and Cd. Most of the Cu, Zn and Cd entered the soil as part of the solution phase, while the other elements penetrated mostly as part of the solid phase (Simón et al., 1999). As a consequence of the drying and aeration of the tailings, the sulfides oxidized to sulfates, the pH fell markedly because of the formation of sulfuric acid, and the pollutant solubilized (Alastuey et al., 1999; Simón et al., 2001). Water-soluble sulphates, Zn, Cd and Cu increased markedly (45% of the total Cu and 65% of the Zn and Cd were solubilized) and quickly (the highest values were reached 25 days after the spill). On the other hand, the increase in soluble As and Pb was less intense (less than 2.5% of the total content became soluble forms) and slower (the highest values were reached 40 days after the spill). Subsequent rains infiltrated the acidic and polluted waters into the soil, increasing the mean contents in Zn and Cu in the uppermost 10 cm by between 2- and 2.5-fold, in As and Pb by between 3- and 3.5-fold, and in Cd by 4.5-fold (Simón et al., 2001).

The first remediation action was the clean-up, i.e., removal of the tailings and the uppermost layer of the

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polluted soils (spring–summer 1998). In the second stage (spring–summer 1999) the most polluted sectors were cleaned again, followed by a liming of all the affected area with sugar-refinery scum and tilling of the soil. In the third stage (spring–summer 2000) the most polluted areas were cleaned once more, and organic matter plus iron-rich clayey materials were added to the soils, followed by tilling the upper 20–25 cm of the soils.

The objective of the present study was to characterize the pollution of the soils affected by the spill three years after the accident, both in the total content of the different pollutants as well as in the soluble and bioavailable forms, to show the evolution over time, and to evaluate the efficiency of the different remediation actions during this period.

2. Materials and methods

The study was based on a random systematic sampling, by dividing the affected area into a grid of squares 400 m per side, and selecting 100 georeferenced sampling points (GPS) uniformly distributed throughout the area. At each sampling point, soil samples were taken by mixing 250 g of soil from each corner and center of a square 10 m per side. Three samples at the depths of 0–10 cm, 10–30 cm, and 30–50 cm were taken at each sampling point. The first sampling was in 1998, just after the clean-up of the soils; the second sampling, in 1999, was made after the second stage of the remediation actions; and the third sampling, in 2001, was made after the third stage.

All samples were air-dried and sieved to 2 mm, the percentage of gravels (>2 mm) and fine earth (<2 mm) was calculated. All laboratory analyses were performed with the fine earth fraction. Texture was determined by the pipette method (Loveland and Whalley, 1991). The pH was measured in a soil:water suspension of 1:2.5. The calcium carbonate content was determined by the method of Bascomb (1961). Total carbon and sulfur were analyzed by dry combustion at 1100 °C in a LECO-SC32 instrument. Organic carbon was calculated as the difference between the total carbon and the inorganic coming from the $CaCO_3$. Cation-exchange capacity was determined with sodium acetate 1 N at pH 8.2. The pollutant elements were analyzed, after very fine grinding and digestion in strong acids, by ICP-MS in a PE SCIEX ELAN-5000A spectrometer. Water-soluble forms of the pollutant elements were determined in the extract of the saturated paste, before acidification with HNO_3, and bioavailable forms were extracted with EDTA 0.05 M at pH 7.0 according to Quevauviller et al. (1998); in both cases, the elements were also measured by ICP-MS.

3. Results

3.1. Properties of the affected soils

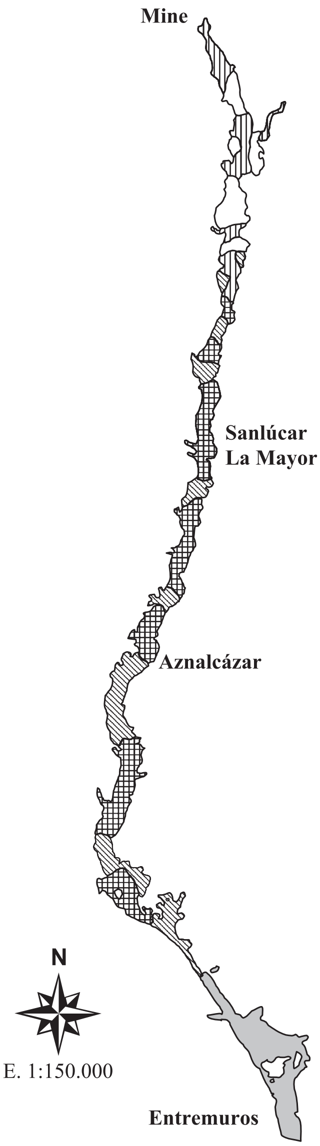
A hierarchical model type Cluster (by the square Euclidean distance method), made with all the soil properties, resulted in the division of the area into five sectors (Fig. 1). In each one, the soil properties proved relatively homogeneous but each sector differed significantly from the others; in all cases, the differences of these properties with depth were not significant, indicating low development of the soils. Sectors 1 and 2, located in the upper part of the area, had acidic soils, with little or no $CaCO_3$ and were differentiated by texture, loam in sector 1, and sandy-loam with a high gravel content in sector 2. The soils in sectors 3, 4 and 5 were neutral or slightly alkaline, with a $CaCO_3$ content higher than 5%; the main differences also being texture: clay-loam in sector 3, loam in sector 4, and silty-clay in sector 5.

The $CaCO_3$ content in the uppermost 10 cm of the soils slightly increased in 1999 as a consequence of the addition of the liming material (sugar-refinery scum), otherwise, pH did not change significantly in relation to 1998 (Fig. 2). Otherwise, in 2001, the $CaCO_3$ content showed a clear reduction in most cases; meanwhile, soil pH clearly increased, especially in most acidic soils, resulting in pH values higher than 6 in all cases.

3.2. Soil pollution

From the clean-up of the soils to the end of our study, in general, the total content of the different pollutant elements declined over time (Fig. 3). Considering that, the different pollutants concentrated mainly in the uppermost 10 cm, without significantly affecting the subsoil or groundwater (Simón et al., 1999, 2001, 2002; Dorronsoro et al., 2002). As a result of the different remediation measures, in 2001 the total content in Cu, Zn, Cd and Pb in the uppermost 10 cm of the soils did not exceed the permitted levels for natural areas (500 mg kg^{-1} for Cu, 1000 mg kg^{-1} for Pb and Zn, and 15 mg kg^{-1} for Cd; Aguilar et al., 1999) in almost all the soils sampled. These measures were less effective in reducing the total As content, although the concentrations fell in the most polluted areas (especially between 1998 and 1999). Subsequently, the concentrations remained nearly constant and with high values (more than 55% of the samples in 2001 exceeded the permitted level of 100 mg kg^{-1} for natural areas (Aguilar et al., 1999).

Thus, three years after the spill, and after the remediation actions were taken, the soils still have a high degree of pollution in As. The distribution of the pollution differs according to the sector (Fig. 4). Sectors 1 and 2 (acidic and noncarbonate) are the most polluted in As; almost 70% of the soils in sector 1 and 45% of



	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
O.C. (%)	≈ 1	< 0.5	≈ 1	≈ 1	1 – 2
C.E.C. ($cmol_c\ kg^{-1}$)	15 - 20	< 10	15 - 20	10 - 15	> 20

Fig. 1. Spatial distribution of the five sectors and mean values of the main soil properties (O.C.: organic carbon; C.E.C.: cation-exchange capacity).

the soils in sector 2 exceed 100 mg kg^{-1}. On the other hand, neutral–alkaline sectors have clearly lower levels of pollution; 20% of the soils in sectors 3 and 4, and 10% of soils in sector 5 exceed the permitted level of 100 mg kg^{-1}.

3.3. Concentration of soluble and bioavailable elements

In this type of pollution, it is not as important to know the total concentration of the pollutant elements as to understand the form in which they are present in

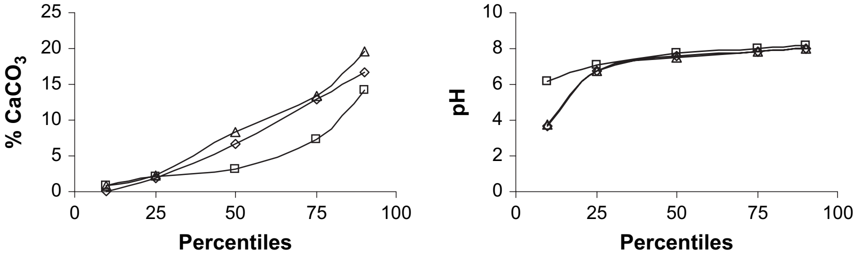


Fig. 2. Percentiles of the $CaCO_3$ content and pH of the uppermost 10 cm of the soils in the three sampling periods (◇: 1998; △: 1999; □: 2001).

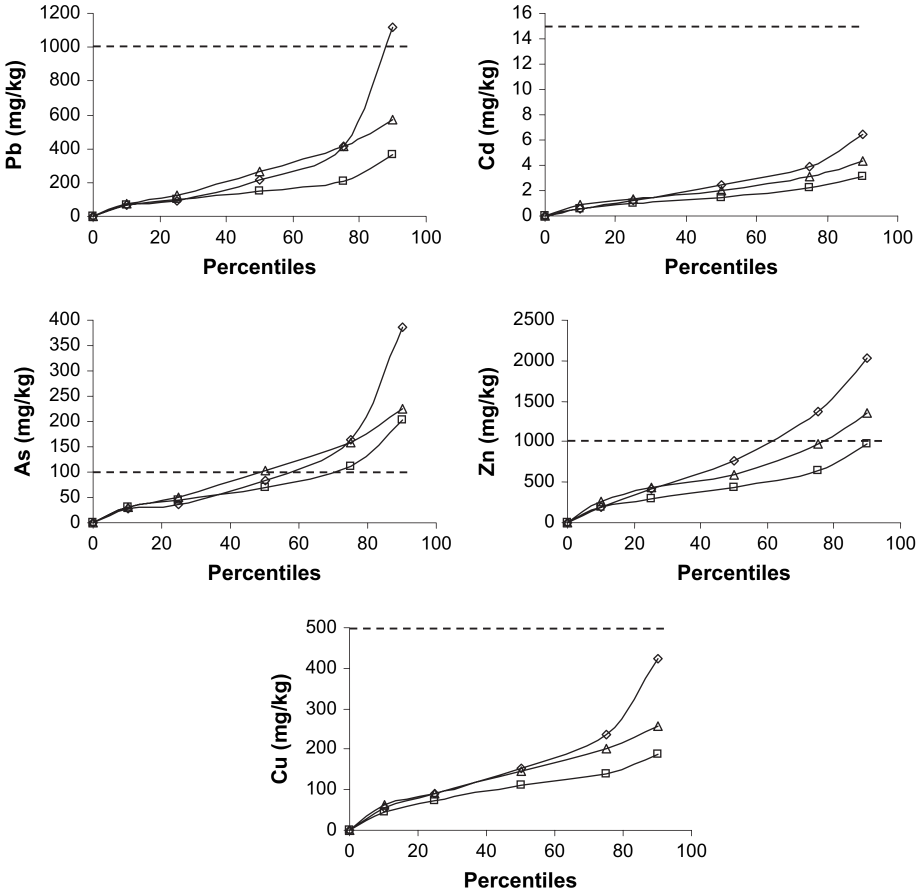


Fig. 3. Percentiles of the total Pb, Cd, As, Zn and Cu content in the uppermost 10 cm of all soils in the three sampling periods (◇: 1998; △: 1999; □: 2001; discontinuous line = permitted levels for natural parks and forestry areas, Aguilar et al., 1999).

soil, especially regarding solubility and bioavailability, because they can spread within the soil and through the landscape as well as be absorbed by organisms (animals and plants) in the surrounding environment. To study the mobility of these elements in the area, we considered the maximum permitted levels in soils (mg kg^{-1}) for water-soluble forms presented in Table 1.

In relation to As, the main pollutant in soils (as mentioned above) solubility decreased markedly between 1998 and 1999 (Fig. 5), indicating a quick change of this element to precipitated forms; otherwise, this precipitation did not progress over time, given that soluble As underwent no significant changes between 1999 and 2001; indeed, it appears to have increased in the most polluted sectors (Fig. 5). In 2001, 19% of the acidic soils (sectors 1 and 2) exceeded the critical level of 0.04 mg kg^{-1} (Bohn et al., 1985), this value falling to 10% in the case of the neutral–alkaline sectors (no samples in sector 5 exceeded the critical level for soluble As).

None of the other pollutant elements exceeded the critical levels for total concentrations in 2001, but the soluble concentrations differed. The critical levels for

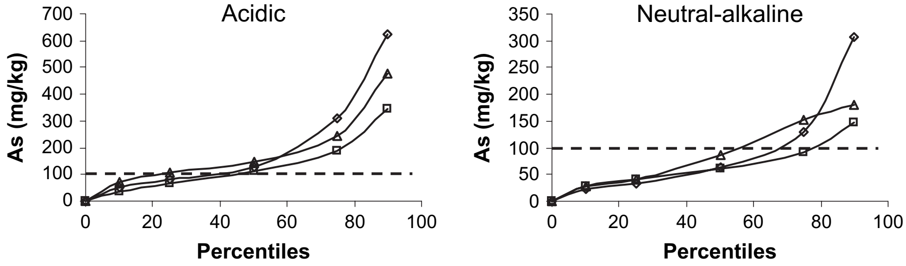


Fig. 4. Percentiles of the total As content in the uppermost 10 cm of acidic sectors soils (1 and 2), and basic sectors soils (3, 4 and 5) in the three sampling periods (◇: 1998; △: 1999; □: 2001; discontinuous line = permitted levels for natural parks and forestry areas, Aguilar et al., 1999).

Table 1
Maximum permitted levels (mg kg^{-1}) for the water-soluble forms of the elements considered

Element	Permitted levels (mg kg^{-1})	Authors
Cd	0.03	Ewers, 1991
Zn	0.5	Ewers, 1991
Cu	0.7	Ewers, 1991
Pb	1.0	Ewers, 1991
As	0.04	Bohn et al., 1985

water-soluble forms were exceeded by Cu, Zn and Cd; although the elements that still had solubility problems in 2001 were As, because of its slight but worrisome increase in relation to the preceding years, and Zn, because it seriously affected almost 30% of the acidic soils (Table 2).

In the case of the two most problematic elements for water-soluble forms (As and Zn), bioavailable forms (extracted with EDTA) were analyzed for mobility (Fig. 6). The EDTA-extracted arsenic [As(EDTA)], like water-soluble arsenic, decreased sharply in 1999 in relation to 1998, indicating a quick change of As to non-bioavailable forms. In the acidic soils (sectors 1 and 2), this process appeared to end, as no significant differences appeared between 1999 and 2001; nevertheless, in neutral–alkaline sectors, this precipitation in non-bioavailable forms continued decreasing over time. Thus, in 2001, 40% of the soils in sector 2 and 30% of the soils in sector 1 exceeded the value of 2 mg kg^{-1} for the EDTA-extracted As; meanwhile in none of the neutral–alkaline soils (sectors 3, 4 and 5) was this level exceeded.

The EDTA-extracted zinc [Zn(EDTA)] exceeds the level of 150 mg kg^{-1} in 25% of the soils in sector 1, in 35% of soils in sector 2, and in 50% of soils in sector 5. The higher bioavailability of Zn in soils of sector 5 (silty-clay texture and high cation-exchange capacity) could be due to the preferential adsorption of Zn by the negative electric charges in soil, thereby maintaining bioavailability for soil organisms.

4. Discussion

According to the soil properties, the changes in $CaCO_3$ content and pH are related to the addition of liming material and to the oxidation of the tailings remaining in soil. The acidic solution that formed as a consequence of the oxidation of the residual tailings in the soil was neutralized by the $CaCO_3$ (both added by liming and that originally present in soil), resulting in a clear $CaCO_3$ reduction in 2001. This decrease in relation to 1998 and 1999 indicates that the amounts added by liming were insufficient to neutralize the acidity generated by the oxidation process, causing the weathering of a portion of the original carbonates. Thus, soil pH clearly increased in 2001, especially in most acidic soils. In view of the inadequacy of the liming, the factor responsible for this increase could be mainly the homogenization of the upper 20–25 cm of the soils, given that the pollution and acidification mainly affected the first 10 cm (Simón et al., 2001).

In relation to the total concentration of the pollutants, the reduction observed in the three sampled periods, could be caused by the clean-up actions, including the tilling and homogenization of the upper 20–25 cm and, to a lesser extent, to the dilution effect of the different amendment materials added to the soils

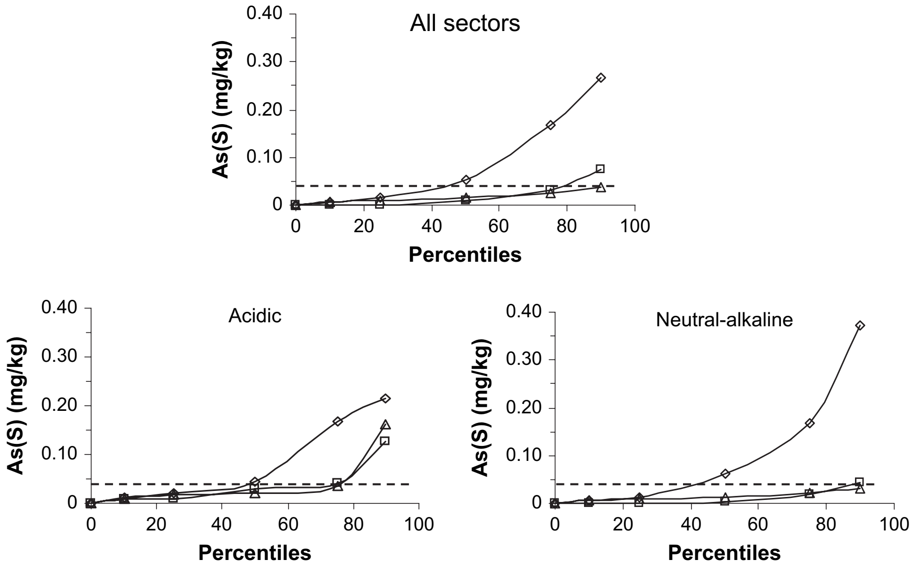


Fig. 5. Percentiles of the water-soluble arsenic [As(S)] in the uppermost 10 cm of all soils of acidic sectors (1 and 2) and basic sectors (3, 4 and 5) in the three sampling periods (◇: 1998; △: 1999; □: 2001; discontinuous line = permitted level, Bohn et al., 1985).

Table 2
Affected surface (%) exceeding the maximum permitted levels for water-soluble forms (Table 1), in acidic soils (sectors 1 and 2) and neutral–alkaline soils (sectors 3, 4 and 5) in the three periods considered

Element	Acidic soils			Neutral–alkaline soils		
	1998	1999	2001	1998	1999	2001
Cd	62	48	13	26	1	3
Zn	96	81	28	70	13	7
Cu	48	48	13	12	3	1
Pb	0	0	0	13	0	0
As	58	15	19	53	6	10

(sugar-refinery scum, organic matter, and clayey materials). The high concentration in total As reached in the initial stages of pollution (exceeding 4-fold the permitted level of 100 mg kg^{-1}), resulted in the high degree of pollution in total As in many areas at the end of the sampling period.

The solubility of the As in these soils, does not appear to be related to soil pH, but rather with the precipitation and crystallization of the iron oxides, which are the main constituents in the adsorption of the As in solution of this polluted area (Dorronsoro et al., 2002; Simón et al., 2002). In this sense, the stability of the compounds formed under these conditions appears to be affected over time (increasing the concentration of water-soluble As), so the addition of iron-rich amendments to this type of pollution, should be studied in more detail (Martín, 2001). More studies are being carried out to correlate the adsorption and bioavailability of these elements by the main soil components of these soils. At the same time, further sampling is being realized in 2004 to continue the monitoring of the main elements that continue to be problematic after the end of the extensive remediation measures in 2001.

5. Conclusions

According to our data, three years after the Aznalcóllar pyrite mine spill (SE Spain), between 50 and 70% of the acidic soils without carbonates of the northern part of the area, and between 25 and 30% of the neutral–alkaline soils with carbonates of the mid to southern part of the affected area, still revealed a high degree of pollution in total As. Only in the soils of sector 5, located at the end of the spill, did the serious pollution in As not exceed the 10% of the samples analyzed. Although the solubility and bioavailability of As decreased over time, 2001 marked a slight increase in relation to the preceding year. Between 15 and 20% of the soils in all sectors, with the exception of sector 5, exceeded the level of 0.04 mg kg^{-1} in soluble As, and between 30 and 40% of the soils in sectors 1 and 2 the level of 2 mg kg^{-1} in EDTA-extractable As. The other elements, although not exceeding the critical levels in total concentrations in 2001, the maximum permitted levels were exceeded for soluble and bioavailable forms in certain areas, especially in the acidic sectors at the northern part of the area. In the case of bioavailable Zn, 50% of the soils in sector 5 exceed the level established for this element. According to these results, the homogenization of the upper 20–25 cm of the soils appears to be the most recommended measure in the reduction of the pollution. Also, the application of amendment materials (liming, organic matter, iron-rich

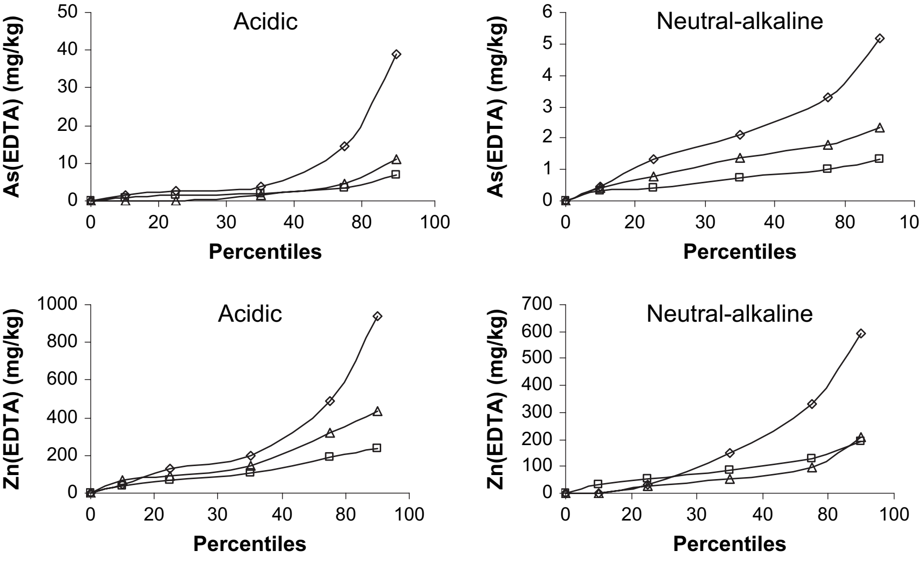


Fig. 6. Percentiles of the EDTA-extracted arsenic [As(EDTA)] and EDTA-extracted zinc [Zn(EDTA)] in the uppermost 10 cm of acidic sector soils (1 and 2) and basic sector soils (3, 4 and 5) in the three sampling periods.

clayey materials) is essential in the reduction of the concentrations of the soluble and bioavailable forms of the pollutant elements. New studies are being carried out in 2004 to continue monitoring the evolution of the main pollutant elements, and to correlate their mobile forms with the main soil properties.

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