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## Soil pollution by oxidation of tailings from toxic spill of a pyrite mine

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### Abstract

On the 25th April 1998, toxic water and tailings from a pyrite mine of Aznalcóllar (southern Spain) spilled into the Agrio and Guadiamar River Basin affecting some 40 km<sup>2</sup>. In five sectors throughout the basin, we monitored the physical and chemical properties of the tailings as well as the degree of pollution in the soils on four different sampling dates: 5 May, 20 May, 4 June and 22 July 1998. The characteristics of the tailings deposited on the soils are shown to be related to distance from the spill. The oxidation rate of the tailings and the solubilization of the pollutant elements were more pronounced in the middle and lower sectors of the basin, where the particle size was finer, the sulfur content higher and the bulk density less. The increases in water-soluble sulfates, Zn, Cd and Cu were very rapid (the highest values being reached 25 days after the spill) and intense (reaching 45% of the total Cu, 65% of the total Zn and Cd). Meanwhile, the increases in water-soluble As, Bi, Sb, Pb and Tl were far lower (ranging between 0.002% of the total Tl and 2.5% of the total As) and less rapid in the case of As, Bi and Pb (the highest values for these elements being reached 40 days after the spill). These soluble elements infiltrated the soils with the rainwater, swiftly augmenting the soil pollution. Twenty-five days after the spill, when the rainfall ranged between 45 and 63 mm, the first 10-cm of the soils in the middle and lower sectors of the basin exceeded the maximum concentration permitted for agricultural soils in Zn, Cu and Tl. At 40 days after the spill, when the rainfall ranged between 60 and 89 mm, all the soils reached or exceeded the maximum permitted concentrations for As and Tl. Nevertheless, the pollutants tended to concentrate in the first 10 cm of the soils without seriously contaminating either the subsoil or the groundwaters. Consequently, a rapid removal of the tailings and the ploughing of the first 25–30 cm of the soils would be urgent measures to diminish pollutant concentration in the soils affected by the spill. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Pyrite mine; Tailings oxidation; Pollutant solubilization; Soil contamination

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## 1. Introduction

Pyrite mines have been worked for centuries in the province of Seville (southern Spain), especially in the Aznalcóllar mining district, on the eastern edge of the Iberian Pyrite Belt (Carvalho, 1976). The mineral phases consisted of different sulfides such as pyrite (83.1%), sphalerite (5.4%), galene (2.1%), chalcopyrite (1.4%) and arsenopyrite (0.9%), as well as minor amounts of bournonite, boulangerite, nuffieldite, jaskolskiite and numerous trace metals (Almodovar et al., 1998). On 25 April 1998, the walls of two contiguous ponds containing the ore-processing residues from the pyrite mine located in Aznalcóllar (Spain) broke open, and approximately  $36 \times 10^5$  m<sup>3</sup> of polluted water (solution phase) and  $9 \times 10^5$  m<sup>3</sup> of toxic tailings (solid phase) spilled into the Agrio and Guadiamar River Basin (Fig. 1). The toxic spill spread some 50 km downriver (the solid phase spread 37 km, and the solution phase the entire 50 km), affecting some 40 km<sup>2</sup> of farmland.

On 4 May (9 days after the spill), we studied seven sectors in the affected area, analysing tailings, polluted water, and contaminated as well as uncontaminated soils (Simón et al., 1999). The principal pollutants of the soils were: Zn, Pb, Cu, As, Sb, Bi, Cd and Tl. The range of total contamination of each element was extremely broad, as penetration of the tailings depended on the soil characteristics. Most of the Cu, Zn and Cd penetrated the soil in the solution phase of the spill, while the other elements penetrated mostly as part of the solid phase. Nevertheless, in these types of tailings, as a result of drying and, consequently, aeration, sulfides oxidize to sulfates, the pH falls markedly due to the formation of sulfuric acid, and the pollutants solubilize (Förstner and Wittmann, 1983). Therefore, with future rains, this acidic solution would infiltrate the soil and aggravate the soil-pollution problem.

In the present study, we continued to monitor the concentrations of the pollutants in the tailings and soils in five of the seven aforementioned sectors, to ascertain the oxidation rate of the tailings as well as the increase in soil contamination over time. Because the tailings were removed

from the surface of the soils, this monitoring ended on 22 July 1998 (88 days after the spill).

## 2. Methods

Five sectors were studied along the basins of the Agrio and Guadiamar Rivers: near the mine (MIN), at the point of the spill; Soberbina (SOB), at 5.5 km from the spill; Aznalcázar (AZN), at 21 km; Quema (QUE), at 29 km; and Pescante (PES), at 36 km (Fig. 1). In each sector, a square plot was laid out (25 × 25 m). At each corner and in the centre of the plot, samples were taken of tailings as well as of soil at 0–10 cm and at 10–30 cm in depth. All samples, categorized according to origin (tailings and the two soil depths), were air dried and screened (2 mm mesh size). Next, 250 g of each sample category from the five sampling points per plot were mixed and homogenized for laboratory analysis. Following this procedure, given that the five sectors had been sampled on 4 May 1998 (Simón et al., 1999), we continued sampling each plot on three different dates: 20 May (25 days after spill), 4 June (40 days after spill) and 22 July 1998 (88 days after spill). The soils of the plots were classified into four categories according to the World Reference Base For Soil Resource (FAO, ISRIC, ISSS, 1998): Calcaric Fluvisols (MIN and QUE), Eutric Arenic Fluvisol (SOB), Calcaric Regosol (AZN) and Calcaric Hiposalic Regosol (PES).

Particle-size distribution was determined by the pipette method after the elimination of organic matter with H<sub>2</sub>O<sub>2</sub> and dispersion with sodium hexametaphosphate (Loveland and Whalley, 1991). Bulk-density data were obtained using the clod method. The pH was measured potentiometrically in a 1:2.5 soil–water suspension. The total sulfur was analysed by dry combustion with a LECO instrument. A saturated extract of the tailings was prepared, and the sulfates were precipitated as BaSO<sub>4</sub>, following the guidelines of the US Salinity Laboratory Staff (1954). Samples of the tailings and soils, very finely ground (< 0.05 mm), were digested in strong acids (HNO<sub>3</sub> + HF + HCl). In each digested sample and saturated

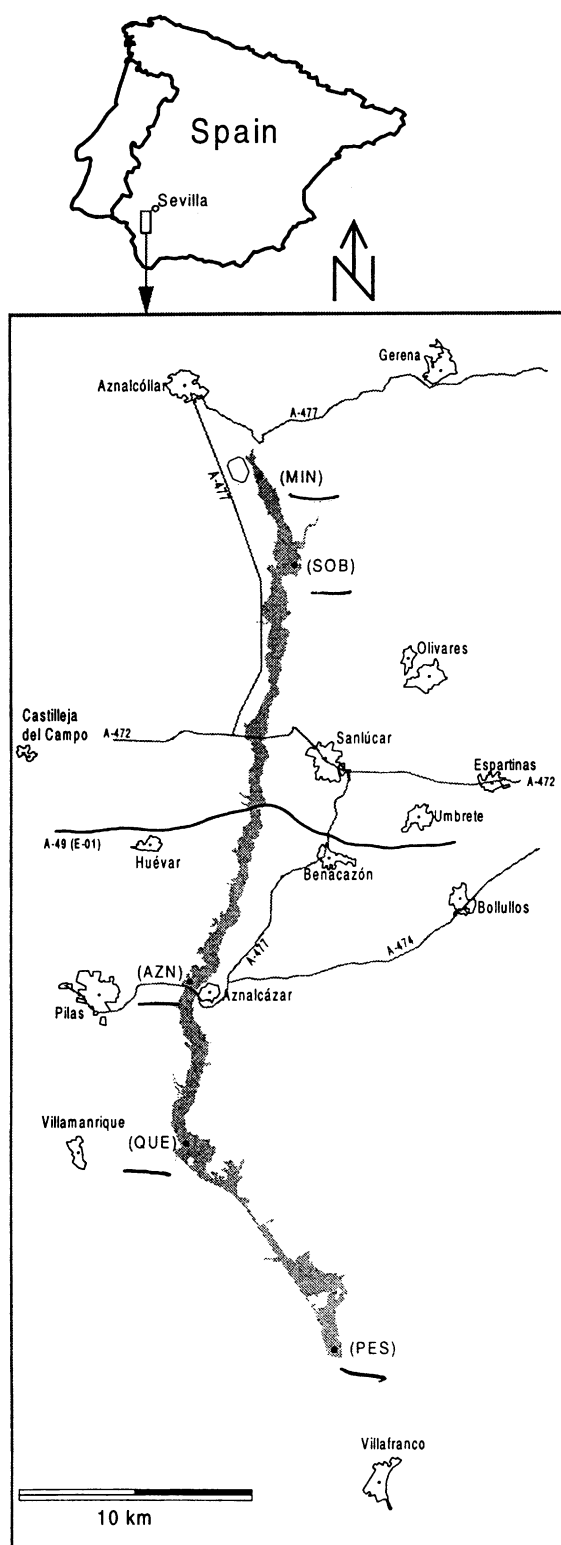


Fig. 1.

extract of the tailings, Cu, Zn, Cd, As, Pb, Sb, Bi and Tl content were measured by ICP-MS with a PE SCIEX ELAN-5000A spectrometer. The accuracy of the method was corroborated by analyses (six replicates) of a standard reference material: SRM 2711 (soil with moderately elevated trace element concentrations; Gills and Kane, 1993) (Table 1). For the statistical analysis, the StatView 4.02 program was used.

The climate of this area is typically Mediterranean (hot, dry summers; cold, wet winters; temperate autumns and springs with variable rainfall). The rainfall data from 4 May to 22 July 1998 (late spring–early summer) in the five sectors studied are shown in Table 3. The data for MIN and SOB were taken from the Aznalcóllar weather station (very close to the point of the spill), while the data for AZN, QUE and PES were taken from the Aznalcázar weather station (at 21 km from the spill).

### 3. Results and discussion

#### 3.1. Tailings

##### 3.1.1. Physical characteristics and chemical composition

The data from the 4th May 1998, the sampling date on which the tailings were still relatively moist and had not yet undergone major oxidation, were taken as the reference to estimate the original characteristics of the tailings. According to these data, the particle sizes of the tailings (Table 2) proved to be related to distance from the spill (Table 4), the fine-silt augmenting ( $P < 0.1$ ) and the coarse-silt ( $P < 0.1$ ) as well as the sand ( $P < 0.05$ ) fractions diminishing. These relationships did not present a higher statistical significance level, because beyond AZN (at 21 km from the spill), the particle size tended to remain relatively constant. The clay fraction was not related to

Fig. 1. Map of the zone affected by the spill. Dark area represents tailings. The situation of the five study sectors is indicated in parentheses.

Table 1  
Analysis of standard reference material 2711<sup>a</sup>

Element	Certified		Experimental	
	Mean	S.D.	Mean	S.D.
As	105.0	8.0	102.4	1.1
Cd	41.7	0.25	40.8	0.27
Cu	114.0	2.0	115.0	1.6
Pb	1162.0	31.0	1138.1	11.0
Tl	2.47	0.15	2.57	0.08
Zn	350.4	4.8	350.3	3.4
Bi	ND	–	2.66	0.17
Sb	ND	–	21.0	0.18

<sup>a</sup>ND, not determined; S.D., standard deviation.

distance from the spill, whereas the fine silt content of the tailings proved to be negatively related

Table 2  
Particle size, bulk density and sulfur content of the tailings on different dates of 1998 by sectors

Sector/ Date	(%)				Bulk density (g cm <sup>-3</sup> )	Sulfur (g kg <sup>-1</sup> )
	Sand (2–00.5 mm)	Coarse silt (0.05–0.02 mm)	Fine silt (0.02–0.002 mm)	Clay ( < 0.002 mm)		
<i>Mine</i>						
4 May	9.6	46.3	26.6	17.5	2.51	275.2
20 May	11.3	47.5	24.3	16.9	2.56	274.8
4 June	13.2	49.4	23.6	13.8	2.49	274.5
22 July	13.6	48.9	23.1	14.4	2.48	274.4
<i>Soberbina</i>						
4 May	9.6	17.2	58.7	14.5	2.33	353.1
20 May	12.3	18.3	57.2	12.2	2.37	352.5
4 June	13.4	19.6	56.1	10.9	2.29	352.2
22 July	13.7	19.8	55.9	10.6	2.28	352.1
<i>Aznalcázar</i>						
4 May	0.6	9.5	73.5	16.4	2.19	382.1
20 May	3.8	9.6	71.2	15.4	2.24	380.7
4 June	4.3	10.4	70.4	14.9	2.18	380.2
22 July	4.5	10.5	70.3	14.7	2.18	380.4
<i>Quema</i>						
4 May	1.2	10.6	71.3	16.9	2.08	380.8
20 May	3.9	11.3	70.8	14.0	2.13	379.3
4 June	4.3	11.7	70.4	13.6	2.10	378.9
22 July	4.6	12.1	69.9	13.4	2.11	379.0
<i>Pescante</i>						
4 May	1.8	8.9	72.6	16.7	1.96	382.4
20 May	3.9	9.1	72.1	14.9	2.03	381.8
4 June	4.7	10.2	70.6	14.5	1.95	381.5
22 July	5.1	10.0	70.8	14.1	1.94	381.3

to the bulk density ( $P < 0.05$ ), and positively to the sulfur content ( $P < 0.01$ ).

The pollutant contents differed in behaviour according to the element (Table 3). Thus, the content in As, Bi, Tl and Pb showed a positive relationship ( $P < 0.01$ ) with the fine-silt and S contents of the tailings (Table 4). Also, Sb was positively related to these parameters, although with lower significance ( $P < 0.1$ ). The Cu content tended to increase with higher fine-silt and S content, but without statistical significance. Meanwhile, Zn and Cd, with minor, uneven variation over the distance of the spill, were not related to any of the parameters of the tailings nor with any of the other contaminants. This lack of relationship could be explained by the fact that

Table 3  
Rainfall, ratio between sulfur as soluble sulfate and total sulfur ( $S_s:S_t$ ), and concentration of pollutants in the tailings on different dates of 1998 by sectors<sup>a</sup>

Sector/ Date	Rainfall (mm)	$S_s:S_t$ ×100	(mg kg <sup>-1</sup> )							
			Zn	Cu	Cd	Pb	As	Sb	Bi	Tl
<i>Mine</i>										
4 May	0.0	0.1	8063.4	1875.3	28.6	5753.0	2072.9	588.1	40.5	49.4
20 May	45.6	1.2	7890.3	1796.2	26.2	5783.6	2149.4	610.5	43.4	48.5
4 June	15.2	1.0	7714.7	1770.6	25.8	5768.5	2105.5	591.1	43.5	48.3
22 July	0.0	1.0	7703.6	1768.9	25.4	5779.4	2109.8	593.4	43.4	48.4
<i>Soberbina</i>										
4 May	0.0	0.3	6793.9	1870.1	27.4	7601.8	2877.5	696.5	72.0	57.1
20 May	45.6	1.9	5771.6	1558.1	20.5	7666.1	3090.1	704.7	72.5	54.6
4 June	15.2	1.7	5052.3	1441.1	18.8	7592.1	2876.6	693.7	72.3	54.0
22 July	0.0	1.7	5061.3	1452.2	18.8	7608.4	2884.9	702.9	72.3	54.1
<i>Aznalcázar</i>										
4 May	0.0	0.1	7792.6	2149.4	36.8	9584.0	4122.6	824.8	86.6	65.6
20 May	63.1	2.7	6670.4	1779.1	29.9	9630.3	4293.4	840.8	89.6	62.4
4 June	25.6	2.5	6011.4	1718.3	22.3	9580.6	4039.7	835.8	88.7	62.9
22 July	0.0	2.8	5996.2	1722.0	22.2	9575.4	4040.5	826.3	88.3	62.3
<i>Quema</i>										
4 May	0.0	0.3	6922.6	2009.1	29.8	9507.3	3859.6	786.2	80.9	61.5
20 May	63.1	2.5	5331.9	1523.0	17.6	9534.1	3924.9	803.0	84.8	56.4
4 June	25.6	2.3	4745.7	1467.4	14.1	9479.6	3774.7	795.7	83.0	55.9
22 July	0.0	2.3	4753.8	1461.9	14.5	9474.3	3779.6	796.8	82.5	55.8
<i>Pescante</i>										
4 May	0.0	0.1	7183.5	2175.9	29.6	9635.9	3749.0	957.9	76.4	59.2
20 May	63.1	2.6	6206.7	1821.1	21.7	9711.1	3873.5	998.9	77.6	54.0
4 June	25.6	2.5	5586.3	1730.4	16.1	9650.0	3645.7	986.3	76.4	55.4
22 July	0.0	2.7	5591.1	1727.8	16.5	9646.7	3635.1	989.7	75.9	55.6

<sup>a</sup>The rainfall data for 4 May refer to the period between the spill and the first sampling, and the rest of the dates refer to the period between samplings.

part of the Zn, Cd and Cu in the tailings precipitated (presumably as hydroxides) from the solution phase of the spill, in which their concentration was relatively high (Simón et al., 1999).

### 3.1.2. Oxidation and solubilization of the pollutants

In these types of tailings, as a result of drying and, consequently, aeration, sulfides oxidize to sulfates (Nordstrom, 1982), the pH falls markedly due to the formation of sulfuric acid (Stumm and Morgan, 1981) and the formerly insoluble pollutants partly solubilize (Rogowski et al., 1977; Caruccio and Geidel, 1978). Because the sulfates that form remain soluble in the acidic solu-

tion, the oxidation rate can be estimated from the ratio between sulfur as soluble sulfate ( $S_s$ ) in the saturation extracts and total sulfur ( $S_t$ ) of the tailings. Given that on the 4th May 1998, the tailings remained relatively moist and their oxidation rate (Table 3) was more strongly related to moisture than to other characteristics (Simón et al., 1999), the differences in the oxidation rate of the tailings was estimated from the relationship  $S_s/S_t$  for the sampling on 20 May 1998, when the tailings had reached relatively uniform dryness. This oxidation rate clearly increased with the distance from spill (Table 3), maintaining a positive relationship with the fine-silt and total-sulfur

Table 4

Correlation matrix including distance from spill in km (DFS), particle size in % (sand, coarse silt [CS], fine silt [FS] and clay), bulk density (BD), sulfur concentration ( $\text{g kg}^{-1}$ ) and trace-element concentrations ( $\text{mg kg}^{-1}$ ) of the tailings sampled on 4 May 1998, and oxidation rate ( $S_s:S_t$ ) on 20 May 1998<sup>a</sup>

	DFS	Sand	CS	FS	Clay	BD	Sulfur	Zn
DFS	1.00							
Sand	-0.89**	1.00						
CS	-0.79*	0.76	1.00					
FS	0.83*	-0.82*	-0.99***	1.00				
Clay	0.21	-0.31	0.36	-0.28	1.00			
BD	-0.98***	0.84*	0.87*	-0.88**	-0.04	1.00		
Sulfur	0.83*	-0.81*	-0.99***	1.00***	-0.29	-0.89**	1.00	
Zn	-0.36	0.09	0.61	-0.55	0.63	0.50	-0.57	1.00
Cu	0.85*	-0.89*	-0.69	0.75	0.25	-0.81*	0.73	0.05
Cd	0.30	-0.67	-0.39	0.46	0.19	-0.24	0.43	0.44
Pb	0.91**	-0.92**	-0.95**	0.98***	-0.06	-0.93**	0.97***	-0.42
As	0.85*	-0.94**	-0.92**	0.96***	-0.03	-0.85*	-0.95***	-0.32
Sb	0.92*	-0.81*	-0.84*	0.86*	0.01	-0.95**	0.85*	-0.34
Bi	0.72	-0.78	-0.98***	0.98***	-0.35	-0.77	0.98***	-0.52
Tl	0.67	-0.84*	-0.90**	0.93**	-0.21	-0.70	0.92**	-0.30
$S_s:S_t$	0.88**	-0.91**	-0.95**	0.98***	-0.09	-0.90**	0.97***	-0.37
	Cu	Cd	Pb	As	Sb	Bi	Tl	$S_s:S_t$
DFS								
Sand								
CS								
FS								
Clay								
BD								
Sulfur								
Zn								
Cu	1.00							
Cd	0.66	1.00						
Pb	0.84*	0.52	1.00					
As	0.84*	0.65	0.99**	1.00				
Sb	0.91**	0.36	0.90**	0.84*	1.00			
Bi	0.67	0.53	0.94**	0.95**	0.75	1.00		
Tl	0.72	0.72	0.92**	0.96***	0.70	0.97***	1.00	
$S_s:S_t$	0.86*	0.58	0.99***	0.99***	0.89**	0.95**	0.94**	1.00

<sup>a</sup>Significance levels: \* $P < 0.1$ ; \*\* $P < 0.05$ ; \*\*\* $P < 0.01$ .

contents in the tailings ( $P < 0.01$ ), and negative one with the sand, coarse-silt and bulk density ( $P < 0.05$ ; Table 4).

In all the sectors, this oxidation process was very rapid, reaching the highest concentration of sulfates and lowest pH values on 20th May (25 days after spill; Fig. 2). After the 20th May, the sulfate content stopped rising, indicating a slowing of the oxidation rate, and in fact this content fell between the 20th May and 4 June, implying a greater loss of sulfate ions by leaching than those formed by oxidation during this period. This pattern of concentration in sulfate ions was paral-

leled by that of water-soluble Zn, Cu and Cd (Fig. 2), with the solubilization on the 20th May reaching between roughly 20% (sector MIN) and 65% (sectors AZN, QUE and PES) of the total Zn and Cd present in the tailings, and between approximately 8% (sector MIN) and 45% (sectors AZN, QUE and PES) of the total Cu. This reflects a swift and intense oxidation of sulfides bonded to these elements (such as sphalerite or chalcocopyrite). In addition, the marked fall in the pH values must also have prompted the solubilization of the hydroxides of these elements precipitated from the solution phase of the spill.

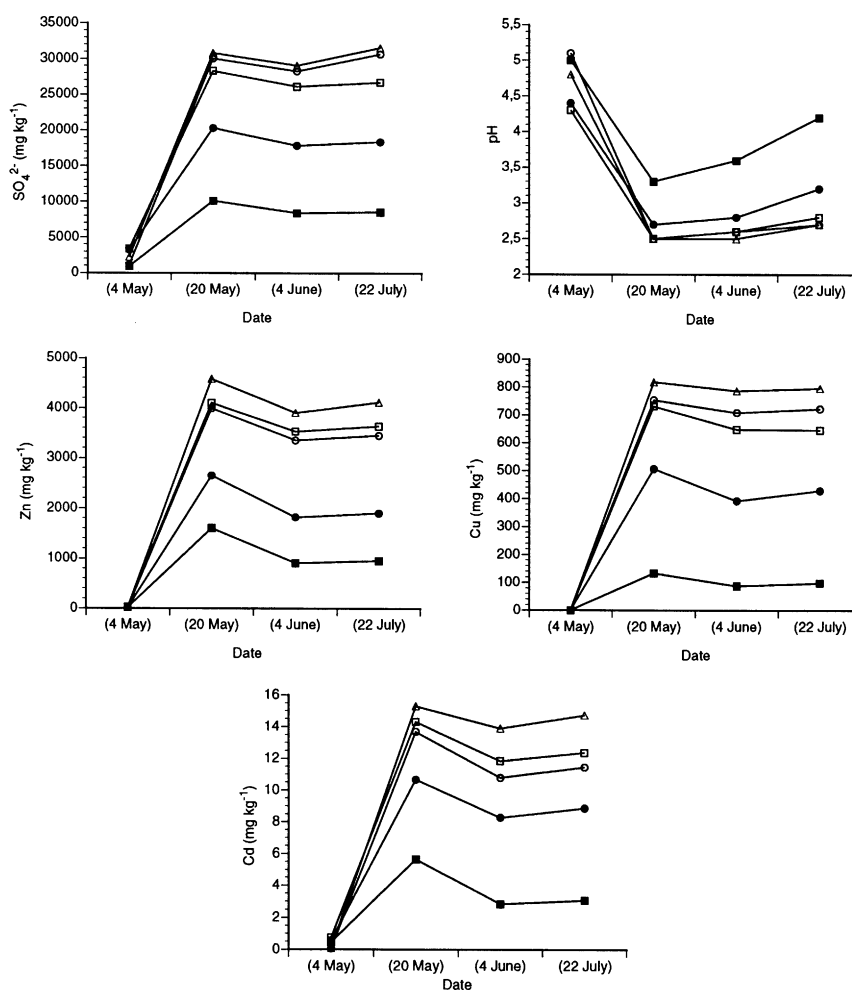


Fig. 2. The pH and water-soluble sulfates, Zn, Cu and Cd in the tailings of different dates of 1998 by sectors: ■ MIN; ● SOB; △ AZN; □ QUE; ○ PES.

Nevertheless, other sulfurs present in the tailings, such as arsenopyrite, galene or jaskolskiite oxidated more slowly and less intensely, as reflected by the fact that the greatest concentration values of soluble As, Pb and Bi in the tailings were reached on 4 June (40 days after spill; Fig. 3) and that these values represent only a minor fraction with respect to the total (the highest values being approx. 2.5% for As, 2.0% for Bi, 0.4% for Sb and 0.1% for Pb). Soluble Tl showed a singular distribution. On 4 May, values were highest, but clearly differed between sectors according to the drying and oxidation rates of the

tailings (Simón et al., 1999). On 20 May, values dropped abruptly in all the tailings and remained very low until the end of the monitoring period. This trend appears to indicate that the solubilized Tl rapidly leached by rains did not accumulate in the tailings.

### 3.2. Soil pollution

The total concentrations of S, Zn, Cu, Cd and Tl in the tailings of all the sectors progressively diminished over time (Table 3). The less soluble elements such as As, Pb, Sb and Bi, although

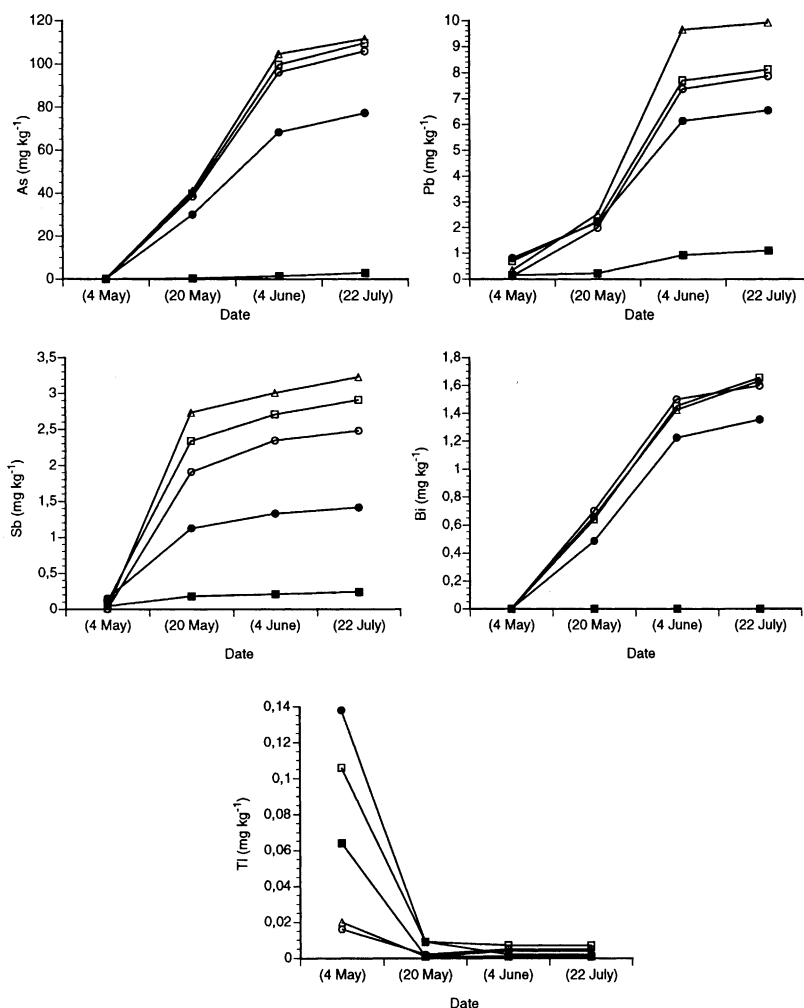


Fig. 3. Water-soluble As, Pb, Bi, Sb and Tl in the tailings different dates of 1998 by sectors: ■ MIN; ● SOB; △ AZN; □ QUE; ○ PES.

increasing in concentration on 20 May (apparently owing to a greater leaching of the more soluble elements), also decreased afterwards; i.e. the elements solubilized during the oxidation and acidification of the tailings leached with the rain-water, accumulating in the underlying soil and thereby exacerbating the soil pollution.

### 3.2.1. From 0 to 10 cm in depth

Given that between 25 April (date of the spill) and 4 May (date of the first sampling) no rain fell (Table 3), the concentration in the different pollutants of the soils sampled on 4 May would be

attributable only to the soil concentrations prior to the spill (background) and the amount that penetrated the soil from the solution and solid phases of the toxic spill (initial pollution). These concentrations were highly variable (Table 5) because the range of the initial pollution was extremely broad, as the penetration of the solid phase depended on the soil characteristics; values being especially high in PES, where the amount of tailings that penetrated the soil reached 150 g kg<sup>-1</sup> (Simón et al., 1999). On the contrary, the increase of these elements in the soils sampling on 20 May or later, can be ascribed to the oxida-



Table 5

Total concentration ( $\text{mg kg}^{-1}$ ) of pollutant elements between 0 and 10 cm in depth of the contaminated soils sampled on 4 May and 22 July 1998 by sectors

Sector/ Date	$(\text{mg kg}^{-1})$							
	Zn	Cu	Cd	Pb	As	Sb	Bi	Tl
<i>Mine</i>								
4 May	144.6	33.8	0.4	64.6	29.0	5.7	0.5	0.6
22 July	374.2	61.4	2.7	156.2	50.2	8.8	1.0	1.0
<i>Soberbina</i>								
4 May	160.2	82.4	0.5	60.0	20.1	4.2	0.5	0.5
22 July	430.7	166.4	2.2	196.1	82.5	10.1	1.9	1.1
<i>Aznalcázar</i>								
4 May	633.6	64.8	2.1	97.9	24.6	3.8	0.6	1.0
22 July	1652.7	235.9	7.1	335.2	139.1	13.3	3.3	3.3
<i>Quema</i>								
4 May	562.6	191.3	2.3	135.3	46.3	8.3	1.0	1.0
22 July	1322.9	330.4	6.9	351.0	118.1	12.8	2.9	2.2
<i>Pescante</i>								
4 May	1449.1	419.8	5.9	1785.5	598.2	146.6	12.3	9.4
22 July	2093.4	542.0	10.7	2002.5	676.0	154.9	14.7	10.8

tion of the tailings, solubilization of the pollutants in the rainwater and infiltration into the soils (oxidative pollution). Thus, the rate of oxidative pollution of each element (OPi) on a given date can be calculated by the difference in the concentrations between the first soil sampling (on 4th May) and any subsequent one.

The oxidative pollution of the soils between 0 and 10 cm in depth augmented with time (Fig. 4), and by 22nd July 1998, had more than doubled the overall concentration of the pollutants in the first 10 cm of the soils, except in PES where the initial pollution was very heavy (Table 5). The majority of this contamination in Zn, Cd, Cu, Sb and Tl (65–90%) occurred between the 4th and 20th May (Fig. 4), the period in which the strongest oxidation and solubilization of the sulfides bonded to these elements in the tailings took place. During this period, the rainfall ranged from 45 mm (in the sectors closest to the spill) to 63 mm (in the sectors farthest from the spill). Meanwhile, most of this contamination in As, Pb

and Bi (70–90%) occurred between the 20th May and 4th June (Fig. 4), when the oxidation and solubilization of the sulfides bonded to these elements in the tailings were highest and the total rainfall from the date of the spill reached between 60 and 89 mm (in the sectors closest and farthest from the spill, respectively). Between the 4th June and 22nd July, the oxidative pollution increased very little in the absence of rainfall.

As a result of this intense oxidative pollution, on the 22nd July 1998 (88 days after spill) the first 10 cm of the soils of MIN, SOB, AZN and QUE reached or exceeded the maximum concentration permitted for agricultural soils of As ( $50 \text{ mg kg}^{-1}$ ; NMHPPE, 1991, in Alloway, 1995) and Tl ( $1 \text{ mg kg}^{-1}$ ; Kabata Pendias and Pendias, 1992). The soils of AZN and QUE exceeded the maximum permitted concentrations in Zn and Cu ( $720$  and  $190 \text{ mg kg}^{-1}$ , respectively; NMHPPE, 1991, in Alloway, 1995; Van Den Berg et al., 1993). In the soils nearest the spill (MIN and SOB), where the initial pollution and subsequent oxidation and

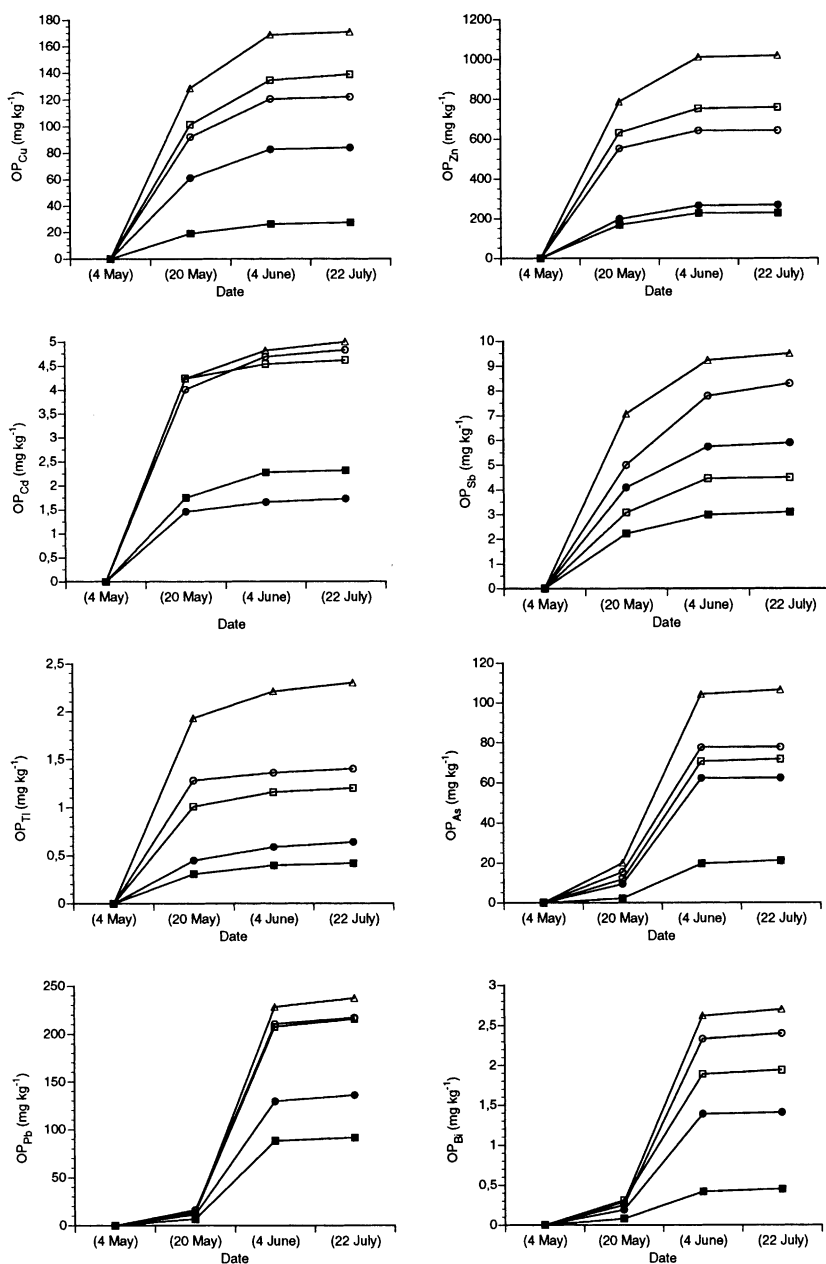


Fig. 4. Oxidative pollution for each element (OP<sub>i</sub>) in the soils between 0 and 10 cm in depth on different dates of 1998 by sectors: ■ MIN; ● SOB; △ AZN; □ QUE; ○ PES.

solubilization rates of the tailings were lower, the increases in the Zn and Cu content were weaker and the above-mentioned toxicity limits were not reached. Meanwhile, the soil concentration in Cd, Pb, Bi and Sb was considerably raised by the

oxidative pollution, but in no sector, except PES, did Cd and Pb exceed the maximum level allowed for agricultural soils (12 and 530 mg kg<sup>-1</sup>, respectively; NMHPPE, 1991, in Alloway, 1995; Van Den Berg et al., 1993). In PES, this maximum was

Table 6  
Oxidative pollution in the soils from 0 to 10 cm and 10 to 30 cm in depth on 22 July 1998 by sectors

Sectors (depth cm)	(mg kg <sup>-1</sup> )							
	Cu	Zn	Cd	As	Pb	Sb	Bi	Tl
MIN (0–10 cm)	27.6	229.6	2.32	21.2	91.6	3.1	0.45	0.42
MIN (10–30 cm)	5.7	28.8	0.27	5.2	18.1	1.1	0.15	0.03
SOB (0–10 cm)	84.0	270.5	1.73	62.4	136.1	5.9	1.41	0.64
SOB (10–30 cm)	11.2	37.1	0.20	17.9	21.3	2.9	0.57	0.03
AZN (0–10 cm)	171.1	1019.1	5.00	106.5	237.3	9.5	2.70	2.30
AZN (10–30 cm)	20.2	125.8	0.74	24.5	43.1	3.8	1.09	0.06
QUE (0–10 cm)	139.1	760.3	4.62	71.8	215.7	4.5	1.94	1.20
QUE (10–30 cm)	18.9	119.7	0.63	20.8	39.9	1.8	0.81	0.07
PES (0–10 cm)	122.2	644.3	4.83	77.8	217.0	8.3	2.40	1.40
PES (10–30 cm)	14.6	109.8	0.70	15.4	32.8	3.3	0.80	0.08

surpassed by the initial pollution in all elements, except in Cd. For Bi and Sb, no reference levels are available.

### 3.2.2. From 10 to 30 cm in depth

The oxidative pollution on the 22nd July 1998 from 10 to 30 cm in depth was considerably less than that of the first 10 cm of the soils (Table 6), averaging 95% less in Tl, 80–85% less in Cd, Zn, Cu and Pb, and 70–80% less in As. In all sectors, the concentrations in the different pollutants were far lower than the maximum permitted for agricultural soils. Consequently, the pollutants tended to remain in the first 10 cm of the soils without seriously contaminating either the subsoil or the groundwater.

## 4. Conclusions

The characteristics of the tailings deposited on the soils proved to be related to distance from the spill, the fine-silt fraction and the sulfur, As, Pb, Bi, Tl and Sb content increasing considerably and the bulk-density decreasing. The Zn, Cd and Cu content were not related to distance from the spill. The oxidation rate of the tailings, acidification and solubilization of the pollutants clearly increased with the distance from the spill. In each sector, the water-soluble sulfates, Zn, Cd and Cu increased very rapidly and intensely. Meanwhile, the increases in water-soluble As, Bi, Sb, Pb and Tl were far lower and less rapid in the case of As, Bi and Pb.

The pollutants solubilized during the oxidation and acidification of the tailings leached with the rainwater, intensifying the soil pollution with time. As a result of this oxidative pollution, 25 days after the spill, the first 10 cm of the soils in the middle and lower sectors of the basin exceeded the maximum concentration permitted for agricultural soils of Zn, Cu and Tl; meanwhile, 40 days after spill, all the soils reached or exceeded the maximum permitted concentrations in As and Tl. Consequently, a rapid removal of the tailings is essential and should begin in the middle and lower sector of the basin. The oxidative pollution from 10 to 30 cm in depth was considerably less than that of the first 10 cm of the soils and the concentrations in the different pollutants were far lower than the maximum permitted for agricultural soils. Therefore, after the removal of the tailings, the first 25–30 cm of the soils could be homogenized by ploughing as a means of reducing the overall concentration of pollutants.

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