

# Remediation of the soils affected by a spill of pyritic tailings in Aznalcóllar (SW Spain)

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## INTRODUCTION

On 25 April 1998 the broken dam of the holding pond from the pyrite mine of Aznalcóllar (south-western Spain) spilled approximately 4 Hm<sup>3</sup> tailings and 2 Hm<sup>3</sup> of acid waters into the Agrio and Guadalimar rivers (Figure 1), affecting an area of 44 km<sup>2</sup>. Tailings penetrated the soils in a very heterogeneous way depending mainly on soil structure (Figure 2). The principal pollutants were Zn, Pb, Cu, As, Cd and Tl. The penetration of these metals in the soil was by solid phase (tailings) and solution phase (acid waters). Most of the Cu, Zn and Cd entered the soil by the solution phase of the spill, while the other elements penetrated as part of the solid phase (Simón *et al.*, 1999). Drying and consequent aeration of tailings produced an intense acidification when the sulphides oxidized to sulphates. This process increased quickly the pollution mainly in the first 10 cm due to the formation and precipitation of polymetallic sulphate salts. In this study we analyse the effectiveness of the remediation actions taken after the accident, based on soil properties and on the total, soluble and extractable with EDTA concentration of each metal.

## REMEDIATION ACTIONS

**First stage** (from the beginning of May to the end of November 1998):

Removal of the layer of tailings by mechanical and manual methods (Figure 3).

**Second stage** (from January to May 1999):

- Cleaning of soils in the place still polluted
- Liming with floating sugar refinery (Figure 4).
  - 40 T/ha in acid soils
  - 20 T/ha in carbonated soils



Figure 4. Liming after the second cleaning.

## RESULTS AND DISCUSSION

### FIRST SAMPLING

With the samples collected after the removal of tailings (first remediation action), and according to soil properties (0-50 cm), we assigned 5 different groups by a cluster analysis via k-means method (Table 1). Soil types 1 and 2 were acid, with little or no carbonate. Type 1 had loam texture while Type 2 was dominated by gravel and sand. The other types proved neutral or slightly alkaline and carbonated, differing also in texture (Type 3: clay loam, Type 4: loam, Type 5: silty clay). Total pollution of heavy metals in these five soil types is also shown in Table 1, indicating that As, Zn and, to a lesser extent Pb, were the most important pollutants that exceeded the Critical Level (CL) for natural parks in most of the soil types (CL of metals: As = 100 mg/kg, Zn = 1000 mg/kg, Cd = 15 mg/kg; Adriano *et al.*, 1987; Godin, 1983). Pb = 500 mg/kg; (Sheppard *et al.*, 1992). Tl = 5 mg/kg). In the same way, according to the affected surface, we established that for 98% of the total surface polluted by As, 80% by Zn, 36% by Pb and 13% in Cu, the other elements did not exceed the Critical Level indicated above.

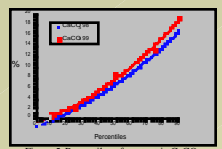


Figure 5. Percentiles of content in CaCO<sub>3</sub> (%) in all soils in the two years sampled

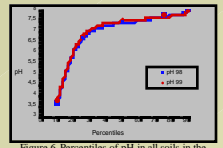


Figure 6. Percentiles of pH in all soils in the two years sampled

### SOLUBLE FORMS (0-10 cm)

In general, all the soluble metals studied changed to non-soluble forms. Soluble-in-water As and Zn were reduced considerably, only 15% and 25% of samples, respectively, exceeded the Critical Level, whereas this same level was exceeded in 1998 by the 60% and 50% of samples, respectively (Figures 11 and 12). According to soil type, this limit is exceeded mainly in acid soils. (CL: As = 0.035 mg/kg (Bohn *et al.*, 1985); Zn = 1 mg/kg (Ewers, 1991)). Less than 20% of samples were polluted in soluble Cu and Cd, mainly in acid soils. No pollution of soluble Pb appeared in any soil, due to the low solubility of this element.

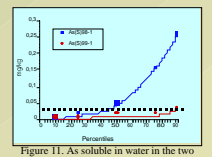


Figure 11. As soluble in water in the two sampling periods.

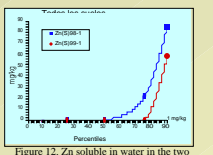


Figure 12. Zn soluble in water in the two sampling periods.

## CONCLUSIONS

- Liming was insufficient to raise the pH in acid soils and was not necessary to apply in carbonated soils.
- The total content of pollutants tended to decrease over time, although 80% of the surface is still polluted in As.
- Soluble-in-water forms also tended to decrease over time, indicating that they are changing to insoluble forms. Arsenic strongly reduced the concentration of this form one year later. In total, 55% of the surface was polluted by soluble Zn, and 25% to 30% by Cu and Cd soluble.
- EDTA-extracted forms also reduced over time, indicating a change to non-bioavailable forms, although in 1999 between 35% and 40% of the surface was still polluted in Zn and As.

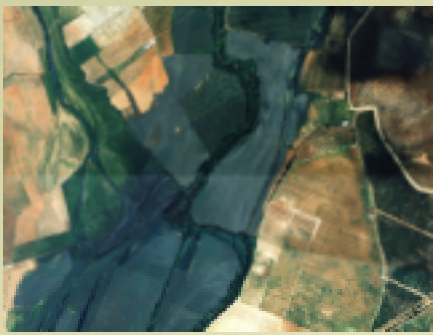


Figure 1. Aerial view of the spill in the central part of the area.

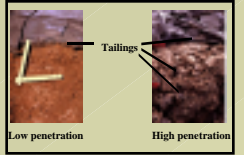


Figure 2. Tailings penetration depending on soil structure.



Figure 3. Aerial view of the same area of figure 1 after removal of tailings.

## MATERIAL AND METHODS

A systematic sampling of 100 points in a centred-square plot (400 x 400 m) was laid out in the affected area. Compound samples were taken mixing approximately 0.5 kg from the centre and corners of a square 10 m side. At each sampling point we collected at three different depths (0 - 10 cm, 10 - 30 cm and 30 - 50 cm). The **first sampling** was made in 1998, after the first and before the second stage of the remediation actions. A **second sampling** was conducted in 1999, after the second stage of the remediation actions, at the same sampling points. Total, soluble-in-water and extractable-with-EDTA (0.05 M) metals were measured by ICP-MS with a PE SCIEX ELAN-5000A spectrometer. Particle-size distribution was determined by the pipette method (Loveland and Whalley, 1991), pH was measured potentiometrically in a 1:2.5 soil:water suspension, and CaCO<sub>3</sub> equivalent was determined by the method of Bascom (1961). For the statistical analysis the StatView 4.02 program was used.

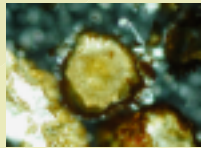
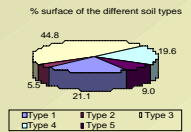


Figure 7. Coatings on carbonated grains.

	type 1		type 2		type 3		type 4		type 5	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
pH	4.9	1.9	6.7	1.8	7.7	0.4	7.7	0.7	8.1	0.3
CaCO <sub>3</sub> (%)	1.3	2.0	0.5	0.8	11.9	5.4	6.0	5.3	13.6	4.9
OC (%)	1.0	0.4	0.5	0.4	1.0	0.5	0.9	0.4	1.3	0.5
CEC (cmol kg <sup>-1</sup> )	14.8	6.4	7.0	2.3	17.9	5.4	12.8	4.6	22.9	4.9
Sand(%)	50.3	17.0	83.6	7.9	21.2	14.8	45.4	14.3	4.9	7.1
Coarse silt(%)	11.3	5.8	3.2	2.2	16.7	5.5	15.5	4.7	7.9	7.9
Fine silt(%)	19.2	10.4	6.5	4.1	31.0	9.2	19.3	8.2	39.8	10.9
Clay(%)	19.2	7.2	6.7	3.1	31.1	11.6	19.7	6.9	47.4	14.0
Gravel(%)	8.9	10.6	37.5	26.7	8.1	10.0	4.2	7.7	8.2	9.6
Cu (mg kg <sup>-1</sup> )	216.4	175.1	185.7	135.5	192.0	143.6	161.8	113.9	208.2	135.8
Zn (mg kg <sup>-1</sup> )	1097.2	941.9	621.6	661.3	1064.5	666.6	614.0	489.9	1375.3	598.3
As (mg kg <sup>-1</sup> )	274.6	250.5	143.3	142.7	190.2	266.0	168.4	158.1	114.9	208.0
Cd (mg kg <sup>-1</sup> )	3.6	3.2	1.9	2.2	3.4	2.2	2.0	1.8	4.3	1.8
Sb (mg kg <sup>-1</sup> )	46.7	41.5	26.1	20.0	31.2	47.0	15.3	21.5	13.8	26.0
Bi (mg kg <sup>-1</sup> )	4.1	3.4	2.2	2.2	3.4	4.6	1.9	2.3	2.0	3.0
Tl (mg kg <sup>-1</sup> )	4.9	4.4	2.2	2.7	3.3	4.1	1.7	2.3	2.0	2.6
Pb (mg kg <sup>-1</sup> )	642.8	541.4	361.2	343.0	512.5	692.5	241.2	330.2	274.5	489.8

Table 1. Soil properties and total concentration exceeding the Critical Level.

Table 1. Soil properties (0-50 cm) and principal pollutant (0-10 cm) of the different soil types

### TOTAL POLLUTION (0-10 cm)

Pollution decreased or remained the same in the soils with respect to 1998, the decrease being more evident in the most polluted soils (second cleaning effect). As and Zn concentrations fell only in soils having more than 150 mg/kg and 600 mg/kg respectively, exceeding the CL in 50% of samples for As and 25% for Zn (Figures 8 and 9). The Pb concentrations diminished only in soils having more than 400 mg/kg, while the 15% of samples exceeded the CL (Figure 10). Meanwhile, Cu, Cd and Tl did not exceed the CL in any soil considered.

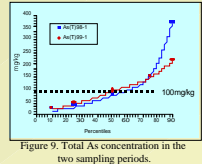


Figure 9. Total As concentration in the two sampling periods.

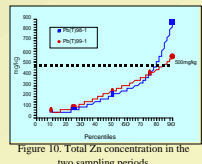


Figure 10. Total Zn concentration in the two sampling periods.

### EDTA-EXTRACTABLE FORMS (0-10 cm)

There was a reduction of EDTA extractable forms in all the soils studied. As and Zn extractable with EDTA reduced considerably, with only 20% and less than 25% of samples, respectively, exceeding the Critical Level, whereas this same level was exceeded in 1998 by the 60% and 55% of samples, respectively (Figures 13 and 14). In relation to Zn, this CL was indeed exceeded in carbonated soils, while 50% of samples of acid and sandy soils remained polluted. (CL: As = 2 mg/kg; Zn = 150 mg/kg). There are no data available for CL of Pb extractable with EDTA. This form of Cd indicates that less than 20% of the samples were polluted, while there was no pollution in Cu extractable with EDTA.

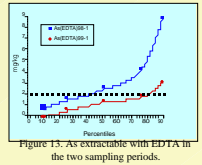


Figure 13. As extractable with EDTA in the two sampling periods.

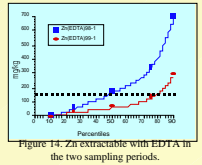


Figure 14. Zn extractable with EDTA in the two sampling periods.

### AREAL DISTRIBUTION OF POLLUTANTS IN SOILS

The areal distribution was made using the algorithm of the least Euclidean distance with the software Surfer 7.0., defining intervals of pollution levels and calculating the area of each one on the resulting maps. Figure 15, shows the percentage of surface exceeding the CL for total, soluble-in-water and extractable-with-EDTA forms of pollutants in soils sampled in 1998 and 1999.

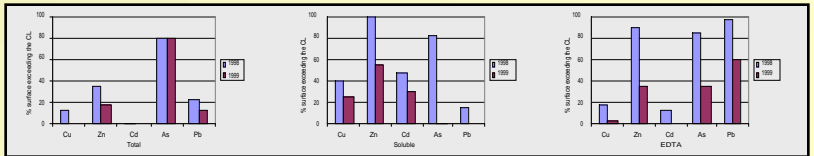


Figure 15. Percentage of surface exceeding the CL of the different forms studied in the two sampling periods.