Steps in soil pollution by the toxic spill of a pyrite mine (Aznalcóllar, Spain)

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Introduction

On 25 April 1998, the walls of two contiguous ponds containing the ore-processing residues from a pyrite mine located in Aznalcóllar (southwestern Spain) broke open (Figure 1), and toxic water and tailings were spilled into the Agrio and Guadiamar River basin, affecting some 40 km^2. The tailings spread in a down-river direction and stopped at 40 km from the point of the spill. The polluted water continued some 10 km more and reached the Guadalquivir River, affecting the National Park of Doñana (proclaimed by UNESCO in 1994 as part of World Heritage). Nevertheless, a retention dam was rapidly constructed, minimizing the damage of the toxic wastes in the wildlife reserve.

The aim of this work is to describe the steps in soil pollution over time.

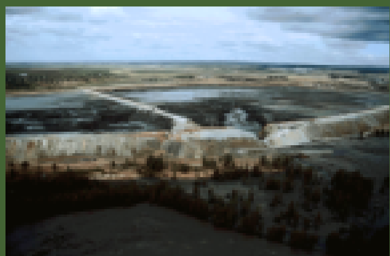

Figure 1. Breaking of the walls of the ponds and toxic spill in the Guadiamar basin.

Sectors	pH	$CaCO_3$ (%)	Organic Carbon (%)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Fe (%)	Structure type/size/grade	SDI
M (T)	50	00	050	00	96	729	17.5	-	pl/ vc /3	9
M (0-10)	76	29	050	123	39.6	220	261	129	sbk/ c/ 2	10
M (10-30)	79	25	043	96	513	166	225	115	sbk/ vc /1	3
SO (T)	44	00	030	00	96	759	145	-	pl/ vc /3	9
SO (0-10)	73	03	080	08	680	185	127	089	sg /- / 0	0
SO (10-30)	74	00	065	12	712	166	110	100	sg /- / 0	0
D (T)	49	00	021	00	20	89.0	90	-	pl/ vc /3	9
D (0-10)	76	186	093	29.7	225	214	264	096	sbk/ m/ 2	14
D (10-30)	74	19.6	061	428	161	222	189	112	sbk/ m/ 2	14
A (T)	48	00	023	00	06	830	164	-	pl/ vc /3	9
A (0-10)	77	148	165	00	19	525	456	081	abk/ vc /1	3
A (10-30)	78	146	134	00	17	548	435	092	m/ - /0	0
Q (T)	43	00	022	00	12	819	169	-	pl/ vc /3	9
Q (0-10)	79	9.4	136	00	219	37.7	404	115	sbk/ m/ 1	7
Q (10-30)	81	70	092	00	19.4	451	355	144	sbk/ c/ 1	5
P (T)	51	00	022	00	18	815	167	-	pl/ vc /3	9
P (0-10)	72	143	102	21	77	27.1	631	110	abk/ f /3	30
P (10-30)	78	147	061	19	63	282	636	118	abk/ vc /1	3
LP (T)	49	00	024	00	14	822	164	-	pl/ vc /3	9
LP (0-10)	78	153	098	69	11	29.7	623	084	abk/ vc /1	3
LP (10-30)	78	155	046	58	09	310	623	088	m/ - /0	0

M= Mine, SO= Soberbina, D=Puente de las Doblas, A= Aznalcázar, Q=Quema, P=Pescante and LP= Los Pobres.
Structure type: pl= platy, abk=angular blocky, sbk= subangular blocky, m=masive, sg= single grain
Structure size: f= fine, m= medium, c= coarse, vc= very coarse.
Structure grade: 0=structureless, 1= weak, 2= moderate, 3= strong.

Table 1. Analytical data, structure and structure-development index (SDI) of the tailings (T) and contaminated soils (0-10 and 10-30 cm in depth) by sectors.

Materials and methods

On 4 May 1998, nine days after the spill, seven sectors in the affected area were studied along the basins of the Agrio and Guadiamar Rivers, analysing tailings, polluted water and contaminated as well as uncontaminated soils: near the mine (M), at the point of the spill; Soberbina (SO), at 5.5 km from the spill; Puente de las Doblas (D), at 12 km; Aznalcázar (A), at 21 km; Quema (Q), at 29 km; Los Pobres (LP), at 34 km and Pescante (P), at 36 km (Figure 2). In each sector, a square plot was laid out (25 m x 25 m). At each corner and in the centre of the plot, samples were taken of tailings as well as of the soil at 0-10 cm and at 10-30 cm in depth. In order to monitor the contamination over time, each plot was sampled on 3 more dates: 20 May, 4 June and 22 July 1998. However, in two sectors (D and LP), the tailings were removed before 4 June. In Quema, two plots with tailings (250 m^2) were left untouched for scientific study and an additional sample was taken on 19 July 1999 (450 days after the spill). Field descriptions of the soils were based on procedures of the Soil Survey Staff (1951). In all soils, physical, chemical and physico-chemical properties were determined (Table 1): particle-size, pH, bulk density, electric conductivity, total carbon, organic carbon, equivalent carbonate content, cation-exchange capacity (CEC), exchangeable bases, total iron (Fe_t), iron oxides (Fe_d), iron-oxide amorphous forms (Fe_o) and total sulphur. A saturated extract of the tailings was prepared and the sulphates were precipitated as $BaSO_4$. Samples of the tailings and soils, very finely ground (< 0.05), were digested in strong acids (HNO_3 + HF + HCl). In each digested sample and saturated extract of the tailings, Cu, Zn, Cd, As, Pb, Sb, Bi and Tl content were measured. To provide a quantitative assessment of the soil structure, a structural-development index (SDI) was formulated, using the equation: SDI= Size x Grade, where values of the grade are given in Table 1, and the size of the structure take the following values: fine=10, medium=7, coarse=5, very coarse=3.

Results and discussion

First Step

- Toxic water and tailings penetrated the soils (Figure 3).
- The principal pollutants were Zn, Pb, Cu, As, Sb, Bi, Cd, and Tl (Simón *et al.*, 1999).
- Because the water from the toxic spill contained no Bi, the total Bi contamination of the soils must have come from the tailings.
- The quantity of tailings that penetrated the soil in each sector (Z) can be calculated by the equation: Z (g kg^{-1}) = (CS_{Bi} - UCS_{Bi}) 10^3/ T_{Bi}, where T_{Bi} is the Bi concentration in the tailings and CS_{Bi} and UCS_{Bi} are the Bi concentration in the contaminated and uncontaminated soils, respectively, all expressed in mg kg^{-1} (Figure 3).
- The range of the total contamination of each element was extremely broad, as penetration of the tailings depended on soil characteristics (Figure 4).
- 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.
- The quantity of tailings that penetrated each soil generally decreased with depth.
- The pollution tended to acidify the soils, although this trend was not strongly evident apparently due to the buffering effect of the $CaCO_3$ in most of the soils.

Figure 3. Penetration of the toxic water and tailings into the soils at the beginning of the spill.

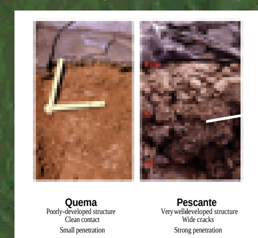

Figure 4. Penetration of the tailings according to the soil characteristics.

Figure 5. Detail of a soil aggregate.

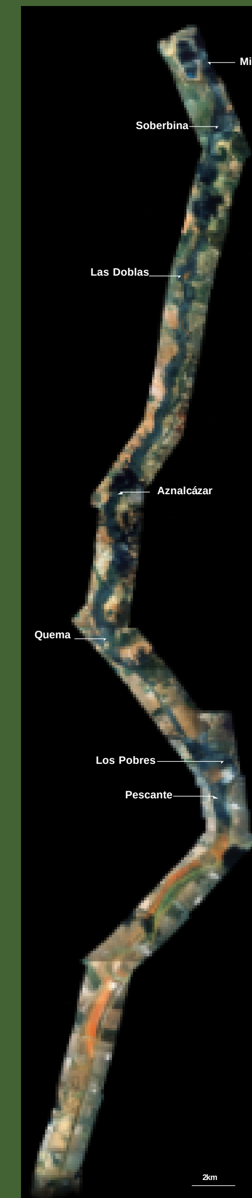

Figure 2. Map of the zone affected by the spill, showing the situation of the seven study sectors.

Second Step

- Drying and consequent aeration of the tailings that remained on the surface of the the soils rapidly oxidized sulphides to sulphates, lowered the pH and solubilized part of the formely insoluble pollutants (Fig.7).
- These processes were more pronounced in the middle and lower sectors of the basin, where the particle size was finer, the sulphur content higher and the bulk density less.
- The soluble elements infiltrated the soils with the rainwater, swiftly augmenting the soil pollution (Figure 6).
- Given that no rain fell for a long time after the spill, the solubilized elements remained in the solution phase of the tailings and, with evaporation, rose by capillary action to the surface, forming a white salty crust (Figure 8).
- The mobility rates of the elements in the tailings increased with time and those in the soils diminished.
- The pollutants tended to concentrate in the first 10 cm of the soils without seriously contaminating the groundwaters, at least in the carbonate soils.
- The total concentration of each element was directly related to the square root of the time elapsed after the spill (Figure 9).
- This results underscore the urgency of removing the tailings from the soil surfaces.

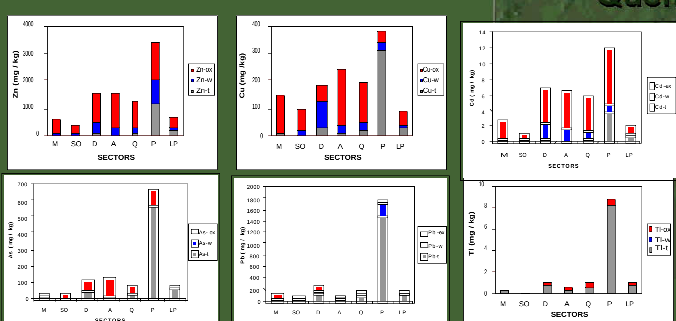

Figure 5. Contamination in the seven study sectors (0-10 cm) due to the tailings (t), the polluted water (w) and the oxidation process (ox) on 22 July.

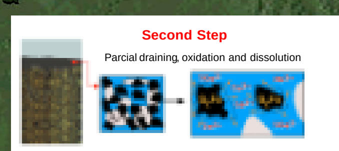

Figure 7. Partial soiubilization of the formely insoluble pollutants.

Figure 8. White salty crust formed three weeks after the spill.

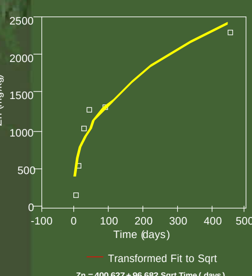

Figure 9. Relation between the concentration of Zn and the square root of the time elapsed after the spill.

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