Arsenic Contamination in Soils Affected by a Pyrite-mine Spill (Aznalcóllar, SW Spain)

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Abstract On 1998, a settling pond of a pyrite mine in
Aznalcóllar (SW Spain) broke open, spilling some
3.6×10^6 m^3 of water and 0.9×10^6 m^3 of toxic tailings
into the Agrio and Guadiamar river basin 40 km
downstream, nearly to Doñana National Park. The
soils throughout the basin were studied for arsenic
pollution. Almost all the arsenic penetrated the soils
in the solid phase (tailings) in variable amounts,
mainly as a result of the different soil structure. The
chemical oxidation of the tailings was the main cause
of the pollution in these soils. A study of the
relationships between the main soil characteristics
and arsenic extracted with different reagents (water,
CaCl$_2$, acetic acid, oxalic–oxalate and EDTA) indi-
cates a direct relationship with the total arsenic
concentration. The highest amount of arsenic was
extracted by oxalic–oxalate (24%–36% of the total
arsenic), indicating the binding with the iron oxides.

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1 Introduction

Many studies on arsenic chemistry in contaminated
soils indicate that arsenic can accumulate because it is
only partially removed by leaching, methylation, and
erosion or because it is slightly taken up and
accumulated by plants. Different forms of arsenic
identified in soils can be divided into two main
groups: organic and inorganic compounds. Inorganic
compounds are the most frequent in soil due to their
water solubility.

Although information on the concentration and
nature of arsenic in the soil solution under field
conditions is scarce (Wenzel et al., 2001), many data
are available on the nature and solubility of arsenic
species under reducing conditions simulated in the
laboratory. These studies show that As^v species
predominate in soil solutions under moderate reducing
conditions, but As^{III} forms are more abundant when
the redox potential is below 500 mV (Masscheleyn,
Delaune, & Patrick, 1991). These authors also indicate
that a rise in pH, or a fall in As^v to As^{III}, boost the
concentration of arsenic in the solution, while arsenic
solubility under moderately reducing conditions is
controlled by the dissolution of iron hydroxides
(Marin, Masscheleyn, & Patrick, 1993). On the other
hand, it is well known that the arsenic concentration in
a soil solution is governed by the physical and

chemical properties of the soil, which influence adsorption–desorption processes. Arsenic has a high affinity for oxidic surfaces, and the reactivity of the oxides varies considerably with the pH, the charge density and the composition of the soil solution. The soil texture and the nature of the mineral constituents also affect adsorption processes (Hiltbold, Hajek, & Buchanan, 1974). Pierce and Moore (1980) demonstrated the specificity of the surface of iron hydroxides and the influence of pH in the arsenic adsorption.

In contrast to the abundant data on arsenic adsorption, little information is available on arsenic desorption in soils. In this sense, Carbonell, Burló, and Mataix (1996) discovered that the adsorption of As^{III} forms is a reversible process, whereas the adsorption of As^V is a hysteresial process.

Soils contaminated with arsenic are an immediate as well as a long-term hazard to the health of plants and animals, including humans (Smith, Naidu, & Alston, 1998). The sources of arsenic in soils are different; according to the rock type, Bhumble and Keefer (1994), point out that sedimentary rocks contain proportionally more arsenic (between 1.7 and 40 mg kg^{-1}) than do igneous rocks (between 1.5 and 3 mg kg^{-1}). Reports have described arsenic contamination by agricultural activities or industrial origin as sulphuric acid and arsenic pesticide manufacturing (Aurilio, Durant, Hemond, & Knox, 1995; Sadler, Olszowy, Shaw, Biltoft, & Connell, 1994); also, mining activities are a major source of arsenic concentration in soils.

On 25 April 1998, a settling pond of a pyrite mine in Aznalcóllar (SW Spain) broke open (Figure 1), spilling some 3.6×10^6 m^3 of water and 0.9×10^6 m^3 of toxic tailings into the basins of the Agrio and Guadiamar rivers (Aguilar et al., 2003; Simón et al., 1998). The toxic tailings spread approximately 40 km downstream, reaching the wetlands of the Doñana National Park (proclaimed world heritage by UNESCO in 1994). The total affected area was roughly 55 km^2; 2.9 km^2 were river courses, 12.3 km^2 eucalyptus forestation, 11.9 km^2 cereals and olive trees, 9.9 km^2 pastures, 5.4 km^2 rice fields, 4.9 km^2 marsh areas, 3.0 km^2 orchards, 2.2 km^2 cotton fields, 0.8 km^2 riverbank vegetation, 0.8 km^2 gravel beds, 0.5 km^2 meadows, and 0.4 km^2 vegetable crops (Aguilar, Dorronsoro, Galán, & Gómez, 1999; Simón et al., 1999).

The present study examines the behaviour of arsenic in soils of different characteristics and the

Figure 1 Localization of the affected area and the seven sectors studied.
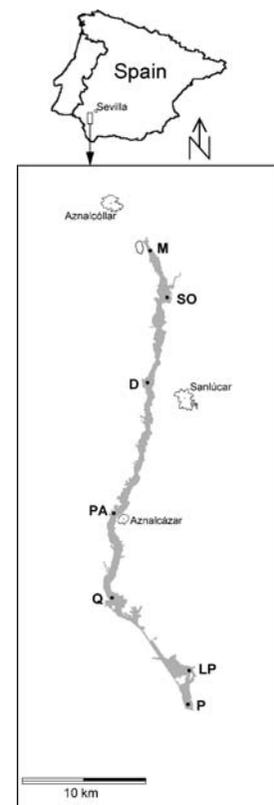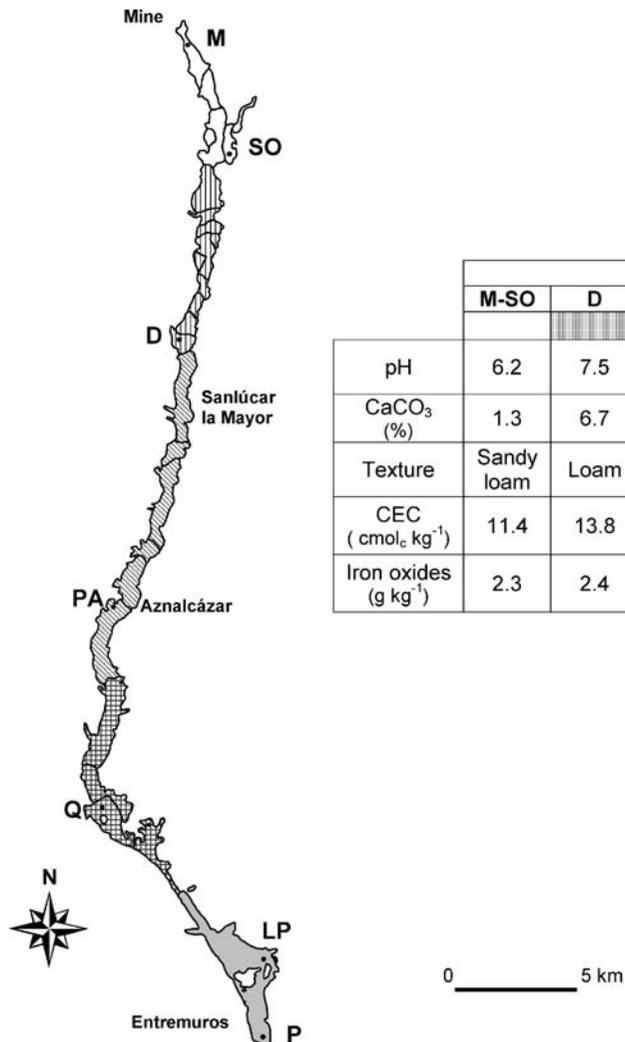
relationships between the different extraction reagents of arsenic and the soil properties.

2 Materials and Methods

Since this study has different objectives, the material used has also been varied. For the assessment of the initial pollution, seven sectors in the affected river basins were studied: near the Mine (M), Soberbina (SO), Puente de las Doblas (D), Aznalcázar (PA), Quema (Q), Los Pobres (LP) and Pescante (P) (Figure 1). These sectors were selected according to five parameters that key to the study of the Arsenic dynamics: pH, $CaCO_3$ content, texture, cation-exchange capacity, and iron oxide content (Figure 2).

As a means of establishing the arsenic contamination level in the basin, after the removal of the tailings covering the soils, a systematic sampling was made in the Guadiamar river basin, using a network (400× 400 m) and selecting 91 sampling points. At each sampling point, samples were taken at the centre and

Figure 2 Main soil properties of the sectors studied.

	Sectors				
	M-SO	**D**	**PA**	**Q**	**LP-P**
pH	6.2	7.5	7.9	8.0	8.1
$CaCO_3$ (%)	1.3	6.7	8.2	8.9	12.2
Texture	Sandy loam	Loam	Silty loam	Loam	Clay loam
CEC ($cmol_c\ kg^{-1}$)	11.4	13.8	16.7	14.2	23.1
Iron oxides ($g\ kg^{-1}$)	2.3	2.4	3.9	2.4	2.8

four corners of a square (10 m side), at 0–10, 10–30 and 30–50 cm in depth. The samples for the same depth were mixed and homogenized, finally obtaining three samples for each sampling point. Samples were also collected from uncontaminated soils in nearby areas unaffected by the spill.

In the study of the fractionation of arsenic forms and their relationships with the soil parameters that influence the immobilization processes, 91 sampling points were grouped in five different soil types according to the soil properties between 0 and 50 cm in depth, using a cluster analysis via the k-mean method, with significant differences ($P<0.05$). Soil types 1 and 2, located in the upper part of the basin, were slightly acidic, with little or no carbonate; type 1 had a loamy texture while type 2 was dominated by

sand and gravel. Soil types 3, 4 and 5 were predominantly neutral or slightly alkaline and with carbonate, the main differences between them being texture (type 3, clay loam; type 4, loam; type 5, silty clay).

Finally, for monitoring the effect of the tailing oxidation in the soil, a plot with the tailings covering the soil was preserved for 465 days.

The contaminated and uncontaminated soils studied were classified as Typic Xerofluvent (upper part of the basin) and Typic Xerorthent (middle and lower part of the basin) (Soil Survey Staff, 2003). Field descriptions of soils were based on procedures of the Soil Survey Staff (1951).

Soil samples were air-dried and sieved to 2 mm to estimate the gravel content. Soil analyses were made with the <2 mm fraction. Sulphate was determined in

the saturation extract (water-soluble sulphate) by ion chromatography in a Dionex-120 chromatograph. Particle-size distribution was determined by the pipette method after elimination of organic matter with H_2O_2 and dispersion with sodium hexametaphosphate (Loveland & Whalley, 1991). The pH was measured potentiometrically in a 1:2.5 soil:water suspension. The $CaCO_3$ equivalent was determined by the method of Bascomb (1961). Total carbon was analysed by dry combustion with a LECO SC-144DR instrument. Organic carbon (OC) was determined by the difference between total carbon and inorganic carbon from $CaCO_3$. The cation-exchange capacity (CEC) was determined with 1 N Na-acetate at pH 8.2, measuring the sodium in a METEOR NAK-II flame-photometer. The total concentration of iron (Fe_T) was measured by X-ray fluorescence in a Philips PW-1404 instrument, from a disc of soil and lithium tetraborate in a ratio of 0.6:5.5. Poorly crystallized iron oxides (Fe_O) were extracted with ammonium oxalate (Schwertmann & Taylor, 1977), and measured by atomic absorption spectroscopy.

Samples of the tailings and soils, finely ground (<0.05 mm), were digested in strong acids (HNO_3 + HF) and the arsenic determined by ICP-MS in a Perkin Elmer Elan 5000 instrument. A Multi-element Calibration Standard 4 (Perkin-Elmer) was used with Rh as the internal standard. The detection limit for arsenic in soils measured by this technique was 0.01 μg l⁻¹. 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 & Kane, 1993). For arsenic, the mean certified value was

105.0 mg kg⁻¹ with a standard deviation of 8.0; the mean experimental value was 102.4 mg kg⁻¹ with a standard deviation of 1.1. For the fractionation of the arsenic forms, extractions were conducted with acetic acid (As_A) (Ure, Quevauviller, Muntau, & Griepink, 1993), calcium chloride (As_C) (Novozamsky, Lexmond, & Houba, 1993), EDTA (As_{EDTA}) (Quevauviller et al., 1998), ammonium oxalate (As_O) (Schwertmann & Taylor, 1977) and distilled water (As_W) from a saturation extract of soil.

3 Results and Discussion

3.1 Initial pollution

Table I shows the results for the arsenic content in waters, tailings, and affected as well as unaffected soils nine days after the spill. It can be seen that the arsenic content in water decreased from the mine to the lower part of the basin (where the water stopped), whereas the arsenic content in tailings increased from the Mine to Pilas-Aznalcázar (middle part of the spill), and from there it decreased up to the limit where the tailing reached. The fact that some elements (Sn, Bi) were no found in the contaminated water, indicated the amount of tailings that penetrated the soil, Simón et al. (1999) estimated that around 95% of the arsenic concentration came from the direct input of tailings into the soil, while only 5% was due to the infiltration of polluted waters. In any case, the pollution was very heterogeneous, with values in affected soils similar to those of unaffected ones (close to 600 mg kg⁻¹). This unevenness was owed in

Table I Arsenic content in waters, tailings and soils (contaminated (CS) and uncontaminated (UCS) by the spill), nine days after the spill

Sector	Water (μg dm⁻³)	Tailings (mg kg⁻¹)	CS (0–10 cm) (mg kg⁻¹)	UCS (0–10 cm) (mg kg⁻¹)
M	4.30	1,437.0	29.0	17.5
SO	3.64	2,426.0	20.1	15.8
D	3.16	3,884.0	60.1	8.0
PA	2.66	4,122.6	24.6	8.5
Q	2.14	3,834.2	46.3	11.5
P	1.89	3,766.0	598.2	26.0
LP	1.74	2,291.7	73.8	11.2
Max	4.30	4,122.6	598.2	26.0
Min	1.74	1,473.0	20.1	8.0
Mean	2.79	3,113.5	121.7	14.1
SD	1.34	1,066.4	198.2	3.5

Max Maximum, *Min* minimum, *SD* standard deviation
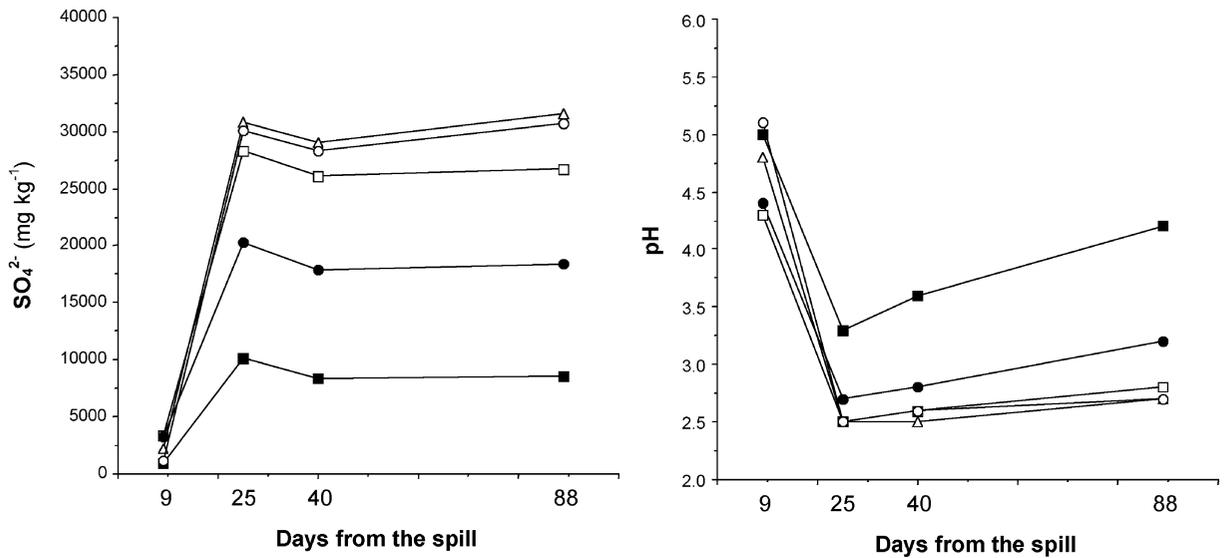
Figure 3 Variation in time of the sulphates and pH in the tailing solution (Sectors: ■ M, • SO, △ PA, □ Q, ○ P).

part to soil properties, mainly structure, which affected the penetration of the tailings in the soil (Simón et al., 1999).

3.2 Oxidative pollution

In the pyrite tailings, as a result of drying and aeration, sulphides oxidize to sulphates (Nordstrom, 1982), the pH falls markedly due to the formation of sulphuric acid (Stumm & Morgan, 1981) and the formerly insoluble pollutants partly solubilize.

During the days following the spill, this oxidation became evident, the sulphates increased rapidly in the tailings solution, this being accompanied by a sharp fall in pH (Figure 3). The concentration of soluble arsenic, measured in a water extract of tailings, was also found to vary over time (Figure 4). Thus, although nine days after the spill no soluble arsenic was detected, values sharply increased over time. In this way, most of this solubilization occurred between 25 and 40 days from the spill (increasing more than fivefold the water-soluble arsenic in soil in relation to the previous period), when the oxidation
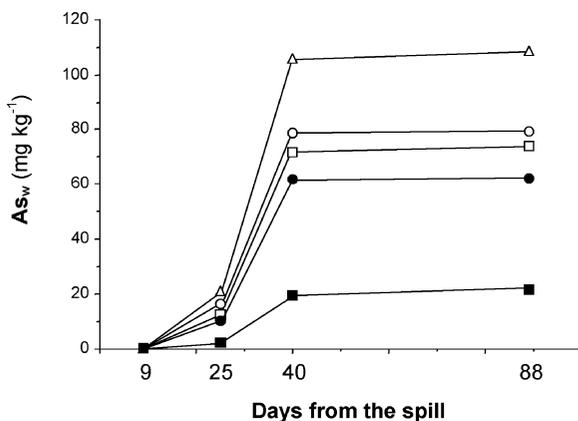
Figure 4 Variation in time of the water-soluble arsenic concentration in the tailings (Sectors: ■ M, • SO, △ PA, □ Q, ○ P).
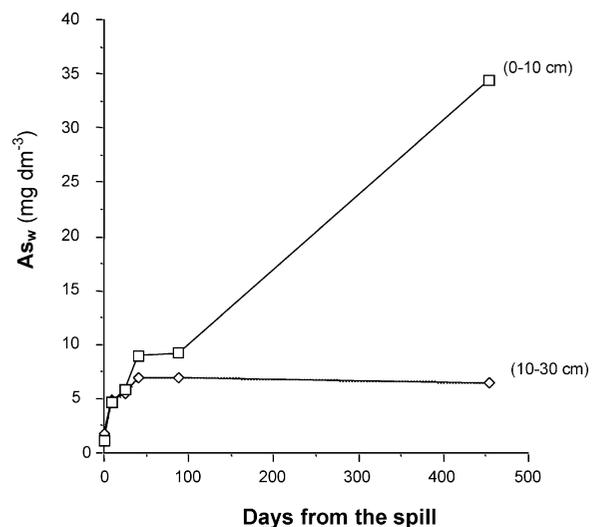
Figure 5 Variation in time of the water-soluble arsenic concentration (mean values of all sectors) in the soil at 0–10 cm and 10–30 cm depth.

and solubilization of the sulphides bonding to arsenic in the tailings were highest and a rainfall period occurred. At 88 days from the spill, the oxidative pollution was negligible. Figure 5 reflects the increase in water-soluble arsenic in the soils due to the oxidative pollution, and it can be seen that at 456 days after the spill, the arsenic concentration continued rising considerably over time in the surface samplings (0–10 cm) but without increasing the pollution in the samples at 10–30 cm in depth.

3.3 Arsenic content in the soils after the removal of the surface layer of tailings

The above results clearly demonstrated the need for immediate removal of the tailings and the upper layer of polluted soils, this being accomplished in four months. To test the effectiveness of the cleanup work after the removal of the tailings, the total arsenic

content was determined, as well as arsenic extracted with distilled water (As_W), $CaCl_2$ (As_C), acetic acid (As_A), oxalic–oxalate (As_O) and EDTA (As_{EDTA}). Finally, we studied the relationship between the arsenic content and the soil properties that mainly influence its immobilization (iron oxides, clay, calcium carbonate, pH).

3.3.1 Total Arsenic Concentration

Total arsenic, S, iron (Fe_T) and iron extracted with oxalic–oxalate (Fe_O) in the five soil types, sampled at 91 points are shown in Table II. In the overall profile (0–50 cm), the soils with the highest concentrations in total arsenic were slightly acidic with a loamy texture (Type 1), their mean values approaching 100 mg kg^{-1}, while those less affected were clayey soils at the end of the basin (Type 5), followed by the sandy carbonate (Type 4). In the uppermost 10 cm of the

Table II Mean values of total arsenic (As), total sulphur (S), total iron (Fe_T) and iron extracted with oxalic–oxalate (Fe_O) in relation to the soil type and depth

Soil types	Depth (cm)	As Mean (mg kg^{-1})	SD	Sig	S Mean (%)	SD	Sig	Fe_T Mean (%)	SD	Sig	Fe_O Mean (g kg^{-1})	SD	Sig
1	0–10	256.38	237.95	0.002	3.07	2.31	0.001	8.93	2.93	0.026	3.36	1.53	0.013
	10–30	74.44	78.93		1.00	1.26		6.86	1.60		2.03	1.33	
	30–50	43.39	29.88		0.40	0.56		6.86	0.70		1.82	0.84	
	0–50	98.41	170.62		1.47	1.90		7.55	2.13		2.40	1.40	
2	0–10	180.74	187.87	0.031	2.08	1.87	0.018	9.11	4.81	0.206	2.62	1.00	0.028
	10–30	58.26	47.94		0.82	0.52		7.24	2.27		1.90	0.71	
	30–50	58.77	63.47		0.48	0.49		6.41	1.70		1.52	0.79	
	0–50	82.96	124.90		1.16	1.35		7.64	3.38		2.03	0.94	
3	0–10	209.46	292.36	0.015	2.17	2.94	0.005	6.88	3.06	0.413	2.71	1.29	0.187
	10–30	75.05	120.17		0.58	0.93		6.06	1.37		2.07	1.48	
	30–50	52.15	31.08		0.31	0.37		6.18	1.01		1.89	1.27	
	0–50	92.77	193.48		0.98	1.89		6.35	1.97		2.21	1.38	
4	0–10	90.12	90.72	0.039	0.94	1.03	0.002	5.85	2.15	0.512	2.59	1.92	0.672
	10–30	63.15	52.46		0.41	0.37		5.96	2.26		2.74	2.13	
	30–50	45.51	36.03		0.31	0.29		5.32	1.91		2.26	1.82	
	0–50	61.49	66.08		0.56	0.71		5.72	2.11		2.53	1.95	
5	0–10	114.86	208.05	0.090	1.04	2.09	0.128	6.91	1.96	0.540	2.04	0.96	0.526
	10–30	40.84	28.10		0.21	0.21		6.62	1.42		2.16	1.21	
	30–50	29.58	17.38		0.13	0.20		6.23	0.94		1.68	1.15	
	0–50	51.14	126.36		0.46	1.26		6.60	1.49		1.97	1.10	
Mean	0–10	157.33	211.04	<0.001	1.67	2.13	<0.001	7.10	3.08	<0.001	2.63	1.51	0.164
	10–30	63.43	73.85		0.54	0.73		6.36	1.87		2.29	1.62	
	30–50	47.18	39.93		0.32	0.38		6.04	1.49		1.92	1.36	
	0–50	75.71	139.44		0.84	1.44		6.50	2.29		2.84	1.53	

SD Standard deviation, *Sig* degree of significance in depths

affected soils, the mean concentration was 157.3 mg kg^{-1}, with a maximum value of 1,226.8 mg kg^{-1}.

The pollution exceeded the permitted value for agricultural soils (50 mg kg^{-1}) (Aguilar et al., 1999) in 82% of the overall surface area affected by the tailings, 96% in the acidic zone (soil types 1 and 2), and 76.8% in the carbonate zone (soil types 3, 4 and 5). Meanwhile, 53% of the affected soils surpassed the limit of 100 mg kg^{-1} maximum permitted for Natural Park in Andalusia (Aguilar et al., 1999). In all cases, the total arsenic decreased sharply in depth, without serious groundwater contamination (CSIC, 1998).

The analysis of bivariate correlations between the total arsenic (As$_T$) and the properties of the uppermost 10 cm of the soils indicates that the arsenic was positively and significantly related to the total iron content (Fe$_T$), amorphous iron oxides (Fe$_O$), and sulphur. The correlation between the total arsenic and sulphur reveals a close relationship that can be quantified by the following equation:

$$As_T \left(mg\ kg^{-1} \right) = 20.03 + 8.10\,S \left(g\ kg^{-1} \right)$$

$$(P < 0.05)$$

3.3.2 Arsenic Fractionation

While the total arsenic values may be a valid reference for legislative reasons, they are not a reliable index for the mobility and bioavailability of arsenic in soils (Fedotov, Fitz, Wennrich, Morgenstern, & Wenzel, 2005). Therefore, in Table III, we show soluble arsenic (As$_W$) and values for arsenic extractable by CaCl$_2$ (As$_C$), acetic acid (As$_A$), oxalic–oxalate (As$_O$) and EDTA (As$_{EDTA}$), which indicate the potential pollution of this element.

In the overall profile (upper 50 cm of soil), the highest concentrations of As$_W$ were found in the carbonate soils (types 3 and 4), and those of As$_C$ in the carbonate soils with clayey texture (types 3 and 5). On the other hand, the slightly acidic soils (types 1 and 2) contained the highest concentrations of As$_{EDTA}$, due possibly to the dissolution from surfaces of iron oxides, whereas, in the case of As$_O$, the highest values were registered for slightly acidic soils with a loamy texture (type 1). However, As$_A$ showed no significant differences between soil types. When the soil pH < 4.5, the mean value of arsenic extracted with EDTA was fourfold greater than at higher pH values. Thus, strongly acidic pH values facilitate the

Table III Mean values (mg kg^{-1}) of the different extracted forms of arsenic

| Soil types	Depth (cm)	As$_W$	As$_C$	As$_A$	As$_O$	As$_{EDTA}$
1	0–10	0.120	0.951	8.492	111.605	18.893
	10–30	0.036	0.771	3.411	26.123	2.890
	30–50	0.101	0.810	2.379	20.479	2.328
	0–50	0.079	0.823	4.014	40.962	5.866
2	0–10	0.054	0.860	5.693	54.734	8.973
	10–30	0.042	0.813	2.394	22.604	5.164
	30–50	0.043	0.771	1.635	18.632	6.856
	0–50	0.045	0.806	2.750	27.441	6.603
3	0–10	0.150	8.121	6.024	52.062	3.414
	10–30	0.082	1.044	3.238	19.275	2.346
	30–50	0.134	1.172	3.440	19.009	2.205
	0–50	0.116	2.511	3.876	25.726	2.503
4	0–10	0.229	0.440	4.349	33.014	2.278
	10–30	0.163	0.498	2.809	21.185	2.309
	30–50	0.113	0.480	3.269	16.102	2.274
	0–50	0.156	0.479	3.301	21.518	2.289
5	0–10	0.067	1.168	4.669	41.204	2.452
	10–30	0.073	1.127	3.954	18.722	1.988
	30–50	0.085	1.458	3.448	14.744	1.632
	0–50	0.077	1.268	3.895	21.627	1.938

As$_W$ Water-soluble, *As$_C$* extracted with CaCl$_2$, *As$_A$* with acetic acid, *As$_O$* with oxalic–oxalate, *As$_{EDTA}$* with EDTA

mobilization of these arsenic forms. The buffering role of $CaCO_3$ is clear, since the soils with content above 2.5% had threefold less arsenic extracted by EDTA than did soils with little or no carbonate content. In relation to the distribution in depth, the concentrations of As_W and As_C were quite uniform in all soil types, meanwhile the other forms (As_A, As_O and As_{EDTA}) tended to concentrate in the surface.

We have also analysed the soil properties that could be involved in the mobility of the arsenic. The most important properties in connection with the possible mobilization or immobilization of arsenic are: pH, $CaCO_3$ content, fine-silt + clay content, or-

ganic carbon, and Fe_O content (Hartley, Edwards, & Lepp, 2004). Figure 6 indicates the average contents of each of the above properties in the five soil types considered and at the three depths studied (0–10, 10–30 and 30–50 cm). This graph displays the rise in pH throughout the basin with the only exception of soil types 1 and 2, because in the former the carbonate content is low and the texture is finer. On the other hand, the pH increases in all cases with the depth of the profile.

The carbonate content varies very little with depth and very markedly with the soil type, in relation to the parent material of the soil. Fine-silt + clay decreases
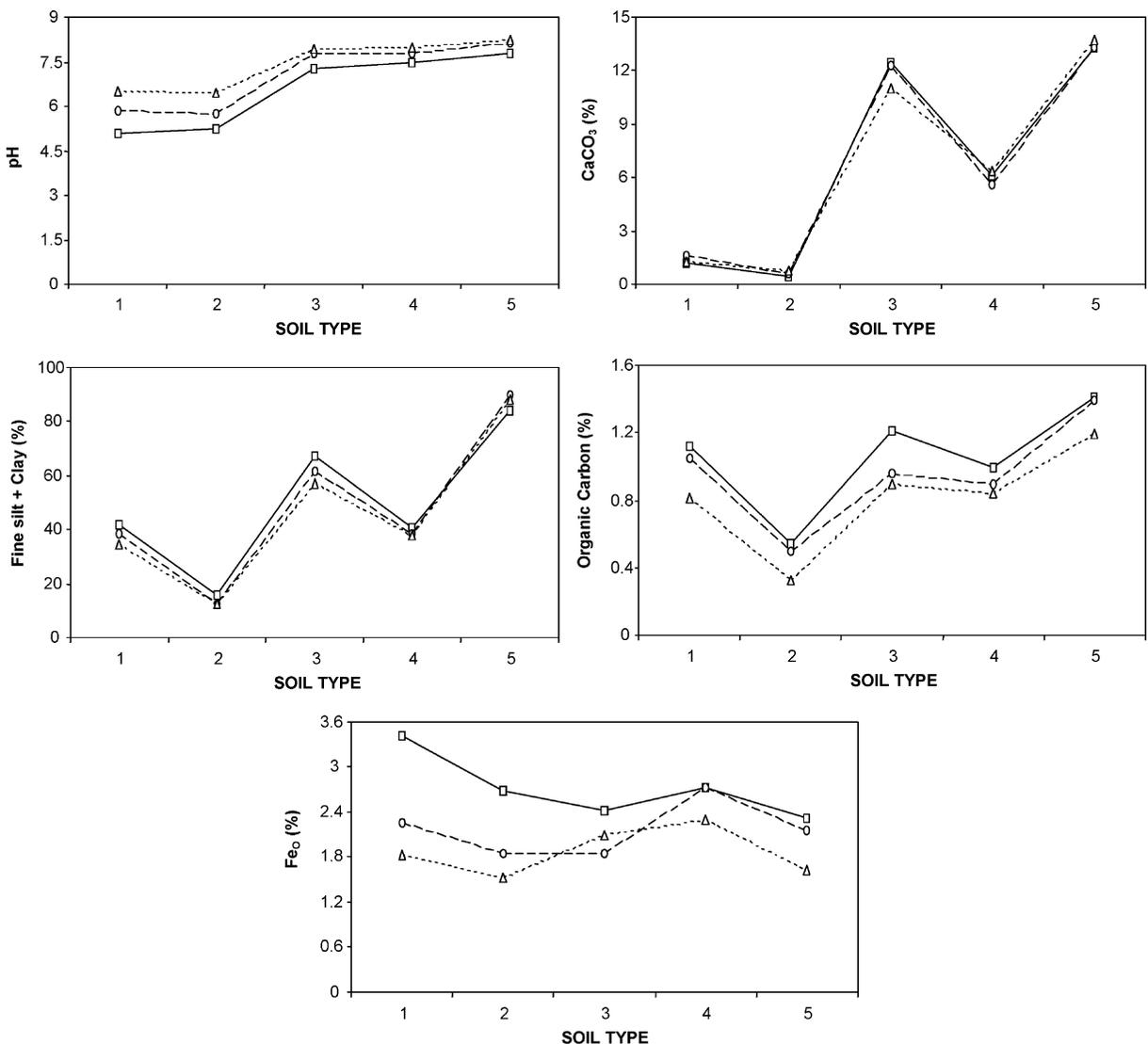
Figure 6 Main soil properties of the five soil types in depth (□ 0–10 cm, ○ 10–30 cm, ▵ 30–50 cm).

with depth in the soil types 1, 2, 3 and 4, and increases in soil type 5 (common in marshland).

The OC content followed the same trend as fine-silt + clay in the five soil types, naturally decreasing with the depth of the profile.

The Fe_O had the highest contents near the mine, closely related to the amount of tailings deposited, part of which were not possible to remove and were mixed with the soil in the clean up activity.

The results from the principal-components analysis between the soil properties and the different extractions of arsenic (Table IV), indicate that around 75% of the variance is explained by four components. The first relates the stronger extractants (acetic acid (As_A), ammonium oxalate (As_O) and EDTA (As_{EDTA})) with the total contamination, represented by the total arsenic (As_T) and total sulphur (S_T). The second component groups the main soil properties (calcium carbonate, fine silt and clay, organic carbon, and cation-exchange capacity). The third component indicates the inverse relationship between the iron extracted with ammonium oxalate (Fe_O) and pH; meanwhile, the last component relates the water-soluble arsenic (As_W) and the arsenic extracted with calcium chloride (As_C), also in an inverse way.

In this first statistical approach, we found a strong influence of the pollution on the different extracted forms but could not identify any relationship between soil properties. Therefore, we performed several correlation and regression analyses grouping the samples according to the five soil types previously used.

3.3.2.1 Water-soluble arsenic (As_W) In the acidic soils (Types 1 and 2), the As_W was related to the total concentrations of As_T, although the soluble concentrations were very low.

$$As_w\left(mg\ kg^{-1}\right) = 0.00025\ As_T\left(mg\ kg^{-1}\right)$$

$$(P < 0.01)$$

At the same time, given that the As_T would be directly related to acidity (higher pollution, lower pH), the As_W was inversely and linearly related to pH:

$$As_w\left(mg\ kg^{-1}\right) = 0.24 - 0.03\ pH \qquad (P < 0.05)$$

This reveals that for each unit of pH rising in these soils, the concentrations of soluble arsenic declined 0.03 mg. In this case, the critical concentration of 0.04 mg kg^{-1} of arsenic in soil solution (Bohn, McNeal, & O'Connor, 1985) would be reached below pH 6.7.

In the basic soils (Types 3, 4 and 5), the As_W content was higher than in the acidic soils, and the relationship with As_T can be expressed with the following equation:

$$As_w\left(mg\ kg^{-1}\right) = 0.00078\ As_T\left(mg\ kg^{-1}\right)$$

$$(P < 0.001)$$

This reflects that for each gram of total arsenic present in alkaline soils, almost 0.8 mg was dissolved in water, around threefold more than in acidic soils.

The relationship with pH in these alkaline soils also differed from that of acidic ones, as As_W decreased some 0.3 mg per unit of increase in pH (10-fold more than in acidic soils).

$$As_w\left(mg\ kg^{-1}\right) = 2.39 - 0.30\ pH \qquad (P < 0.001)$$

In this case, when the pH of alkaline soils reached 7.8, the concentration of total arsenic would be enough to reach the critical arsenic concentration (0.04 mg kg^{-1}) in soil solution.

Table IV Principal-components analysis between the different extractions of arsenic and the main soil properties

| | Principal components | | | |
	Comp. 1	Comp. 2	Comp. 3	Comp. 4
As_W				−0.776
As_C				0.672
As_A	0.868			
As_O	0.942			
As_{EDTA}	0.645			
As_T	0.898			
pH			−0.585	
CaCO$_3$		0.622		
F. silt + clay		0.905		
OC		0.699		
CEC		0.882		
Fe_O			0.861	
S_T	0.908			
Cumulative variance (%)	31.1	51.9	64.4	75.1

F. silt Fine silt, *OC* organic carbon, *CEC* cation-exchange capacity, *S$_T$* total sulphur

3.3.2.2 Arsenic extractable with CaCl₂ (As_C) In the acidic soils, as in the case of As_W, As_C was directly related to As_T.

$$As_C\left(mg\ kg^{-1}\right) = 0.003\ As_T\left(mg\ kg^{-1}\right)$$

$$(P < 0.001)$$

There was a significant relationship between As_C and As_W, indicating that roughly 8% of the As_C was water soluble.

$$As_C\left(mg\ kg^{-1}\right) = 12.723\ As_W\left(mg\ kg^{-1}\right)$$

$$(P < 0.01)$$

The As_C in the alkaline soils, as the As_W, was also higher than in the acidic soils. Thus, when As_C is related to As_T, the following regression equation results:

$$As_C\left(mg\ kg^{-1}\right) = 0.034\ As_T\left(mg\ kg^{-1}\right)$$

$$(P < 0.001)$$

This indicates that, for each 50 mg kg^{-1} of As_T present in the basic soils, 1.7 mg kg^{-1} were extracted with calcium chloride, roughly 11-fold more than in the acidic soils. This confirms that in the alkaline soils the toxic levels of easily bioavailable arsenic were reached at a much lower As_T concentration than in acidic soils.

In contrast to acidic soils, alkaline soils showed no significant relationship between the As_C and As_W. In addition, there was no significant relationship between As_C and the cation-exchange capacity (CEC) or related parameters (organic matter and clay) both in acidic soils as well as in alkaline ones.

3.3.2.3 Arsenic extractable with acetic acid (As_A) This extraction had no relationship with any soil property, and was related only to the total pollution and therefore with the concentrations of As_T, significant differences appearing between the acidic and basic soils. The linear regression equations were:

Acidic soils $As_A\left(mg\ kg^{-1}\right) = 0.030\ As_T\left(mg\ kg^{-1}\right)$ $\quad(P < 0.001)$
Basic soils $As_A\left(mg\ kg^{-1}\right) = 0.017\ As_T\left(mg\ kg^{-1}\right)$ $\quad(P < 0.001)$

This indicates that in the acidic soils the concentrations of arsenic extractable with acetic acid was around 3% of the total arsenic, while in the alkaline soils these concentrations were only 1.7%.

3.3.2.4 Arsenic extractable with EDTA (As_EDTA) In all the soils, As_{EDTA} proved to be lineally related to As_T, with significant differences between acidic and alkaline soils, indicating that EDTA extracted almost sevenfold more arsenic in acidic than in basic soils.

Acidic soils $As_{EDTA}\left(mg\ kg^{-1}\right) = 0.068\ As_T\left(mg\ kg^{-1}\right)$ $\quad(P < 0.001)$
Basic soils $As_{EDTA}\left(mg\ kg^{-1}\right) = 0.010\ As_T\left(mg\ kg^{-1}\right)$ $\quad(P < 0.001)$

arsenic occurred with acetic acid, As_{EDTA} was unrelated to any other soil property.

3.3.2.5 Arsenic extractable with oxalic–oxalate (As_O) The arsenic extracted with oxalic–oxalate was related to As_T, with significant differences between acidic and alkaline soils. The linear regression equations were:

Acidic soils $As_O\left(mg\ kg^{-1}\right) = 0.359\ As_T\left(mg\ kg^{-1}\right)$ $\quad(P < 0.001)$
Basic soils $As_O\left(mg\ kg^{-1}\right) = 0.235\ As_T\left(mg\ kg^{-1}\right)$ $\quad(P < 0.001)$

This signifies that oxalic–oxalate extracted approximately 1.5-fold more arsenic in acidic (36%) than in alkaline soils (24%) (far higher than those extracted by other reagent); so the formation of amorphous iron oxides is considered the most important process in the retention of arsenic in this type of soils.

The correlation matrix between arsenic extracted with oxalic–oxalate (As_O) and the most important soil properties related to the retention of elements (clay, organic carbon (OC), cation exchange capacity (CEC), calcium carbonate, and amorphous iron oxi-hydroxides (Fe_O), indicated no other significant ($P<0.01$) correlation than the one with Fe_O. The differences between slightly acidic and basic soils were also significant, being the correlation coefficient of 0.863 and 0.667 respectively; indicating a better relation in the retention of arsenic by iron oxi-hydroxides in the slightly acidic soils than in the basic ones.

4 Conclusions

In the pollution of soils affected by the pyrite-mine spill in Aznalcóllar (SW Spain), the chemical oxidation of the tailings was the main reason of the pollution in these soils. The total arsenic concentration exceeded the value of 50 mg kg^{-1} in 82% of the affected area. The study of the relationships between the main soil properties and arsenic extracted with different reagents (water, CaCl₂,

acetic acid, oxalic–oxalate and EDTA) indicates a direct relationship to the total concentration of arsenic in all cases. The highest amount of arsenic was extracted by oxalic–oxalate (24%–36% of the total arsenic), indicating the preferential retention by amorphous phases of iron oxi-hydroxides.

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