# Remediation of As-Contaminated Soils in the Guadiamar River Basin (SW, Spain)

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**Abstract** In 1998, the pond containing the ore wastes from a pyrite mine in Aznalcóllar (SW, Spain) broke open, spilling some $36 \times 10^5$ m$^3$ of acidic waters and $9 \times 10^5$ m$^3$ of tailings containing high concentrations of As and heavy metals. The affected area was around 55 km$^2$ of predominantly agricultural soils. After the clean-up of the tailings, many remediation actions were undertaken and the use of blocking agents to immobilize the As was one of the most extended measure. The first experiment performed was to determine the most important soil components in As adsorption under acidic conditions. A second experiment was conducted to neutralize the acidity caused by the solution coming from the tailings undergoing oxidation; an adequate liming material (sugar-refinery scum) was selected and the application rates were established. After the remediation measures, the zone was monitored for three years. A detailed study in four experimental plots located in the most polluted sector was carried out to test the influence of iron oxides in the As immobilization. The use of red soils of the area (rich in free-iron oxides Fe$_d$) was established as an appropriate material in the remediation of the area.

**Keywords** arsenic · Aznalcóllar · iron oxides · red soils · remediation

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## 1 Introduction

Arsenic is of increasing concern in environmental studies due to its high toxicity. Ingesting food or water containing more than 0.01 mg l$^{-1}$ of inorganic arsenic is harmful to the body, while an inorganic arsenic content exceeding 60 mg l$^{-1}$ can be fatal (WHO, 1993). Arsenic has been demonstrated that to cause toxicity in plants or may accumulate in vegetal tissues and thereby enter the animal and human food chain.

Chemically, As exists as organic and inorganic species. It has two main oxidation states (+III and +V; Hossain, 2006), depending on the type and amounts of sorbents, pH, redox potential (Eh), and microbial activity (Yong & Mulligan, 2004). Inorganic compounds are the most frequent in soil due to their water solubility. The most thermodynamically stable species within the pH range 4.0–8.0 include $H_3AsO_3$ of As$^{III}$, and $HAsO_4^{2-}$ and $H_2AsO_4^{-}$ of As$^v$ (Smith, Naidu, & Alston, 1998).

Mine tailings and effluents usually contain high concentrations of As and are of concern as potential sources of environmental contamination; although groundwater contamination by naturally occurring As dissolution from minerals has been reported (Çolak, Gemici, & Tarcan, 2003). In mine tailings, arsenic occurs in various forms such as arsenopyrite, realgar, orpiment, and arsenates and is associated with iron oxy-hydroxides (Wang & Mulligan, 2006).

Arsenic in soil is usually found in association with iron, aluminium, and manganese hydroxides, clays, and mineral oxyanions (sulphates, phosphates and carbonates) which may serve as significant repositories of As due to their ubiquity in the environment (Foster, 2003). Iron hydroxides, such as goethite and ferrihydrite, are commonly found in soil and have been shown to be important in influencing the mobility behaviour of As (Foster, 2003; Jiang et al., 2005; Sun & Doner, 1996; Waychunas, Rea, Fuller, & Davis, 1993). Arsenic behaviour in soil is related to many factors. Microbial activity changes the oxidation state and in volatile As compounds by methylation, the former being of the process that leads to losses of this element in the superficial horizons (Dudas, 1987). In any case, these reactions depend both of the microorganism type as well as the As compound (NRCC, 1978).

The arsenic mobility in soils is low and under reducing conditions the concentration of dissolved As declines. The availability of this element in soils can increase under acidic conditions (mainly pH below 5), due to the greater solubility of the iron and aluminium compounds, which augment As toxicity (O'Neill, 1995). In general, its mobility is directly related to the total amount of As and inversely to time as well as the iron and aluminium content; also, under oxidation conditions, its bioavailability is strongly limited (Kabata-Pendias & Pendias, 2001).

On 25 April 1998 the holding pond of a pyrite mine in Aznalcóllar, SW, Spain, broke open, spilling $36 \times 10^5$ m$^3$ of acidic water and $9 \times 10^5$ m$^3$ of toxic tailings into the Guadiamar river basin, affecting approximately 55 km$^2$ (Simón et al., 1998, 1999; Vidal et al., 1999; Galán, González, & Fernández-Caliani, 2002). The disaster left sludge deposits between 1 cm and 1.5 m in depth in different parts of the affected area (Simón et al., 1999; López-Pamo et al., 1999).

Clean-up operations began almost immediately, and on November 1998 the tailings were almost completely removed with heavy machinery, and the acidic waters had been treated and discharged (Aguilar et al., 2003). Arsenic was one of the major components of the toxic tailings, with a mean concentration of 4,953 mg kg$^{-1}$ (López-Pamo et al., 1999). The correlation between total As and sulphur strongly suggest that As was present in the tailings as arsenopyrite (FeAsS) and that oxidation of the tailings would release iron and As (Simón et al., 2001).

After the clean-up of the basin, almost 70% of the polluted surface area exceeded the permitted level of total As for agricultural soils (Aguilar et al., 2003), whereas 62% exceeded the level of As extracted by distilled water and 35% exceeded the level of As extracted by EDTA (Aguilar et al., 2004). These results show clearly that a remediation process was completely necessary; the monitoring and final result of this process is the objective of the present work.

## 2 Materials and Methods

This study was conducted in the area affected by the spill of the pyrite mine in Aznalcóllar (SW, Spain) in 1998 (Figure 1). After the clean-up of the tailings and the upper part of the contaminated soils, to quantify the As retention by different soil components, we selected soils from the area with different properties: organic matter (OM), clay, cation-exchange capacity (CEC), free-iron (Fe$_d$), pH and CaCO$_3$ (Table I). A pollutant solution was prepared by adding 1,000 cm$^3$ of H$_2$O$_2$ (15%) to 10 g of tailings (Urrutia, García-Rodeja, & Macías, 1992). This pollutant solution was extremely acidic (pH 1.7), with high concentrations of sulphates (5,472 mg dm$^{-3}$), iron (2,663 mg dm$^{-3}$) and arsenic (61.4 mg dm$^{-3}$). Afterwards, 25 ml of this pollutant solution were added to 2.5 g of each soil sample, and the mixture was shaken for three days. The As retained by the soils was determined as the difference between their concentration in the two solutions.

The first remediation measure was the liming. To select the most appropriate material and the application rate, we made neutralization tests in laboratory. Increasing amounts of different carbonate materials (cellulose ash, sugar-refinery scum, sewage sludge, pure CaCO$_3$) were applied to a contaminated soil (from the area) mixed with the tested materials in increasing proportions, until approaching soil pH 6.5.
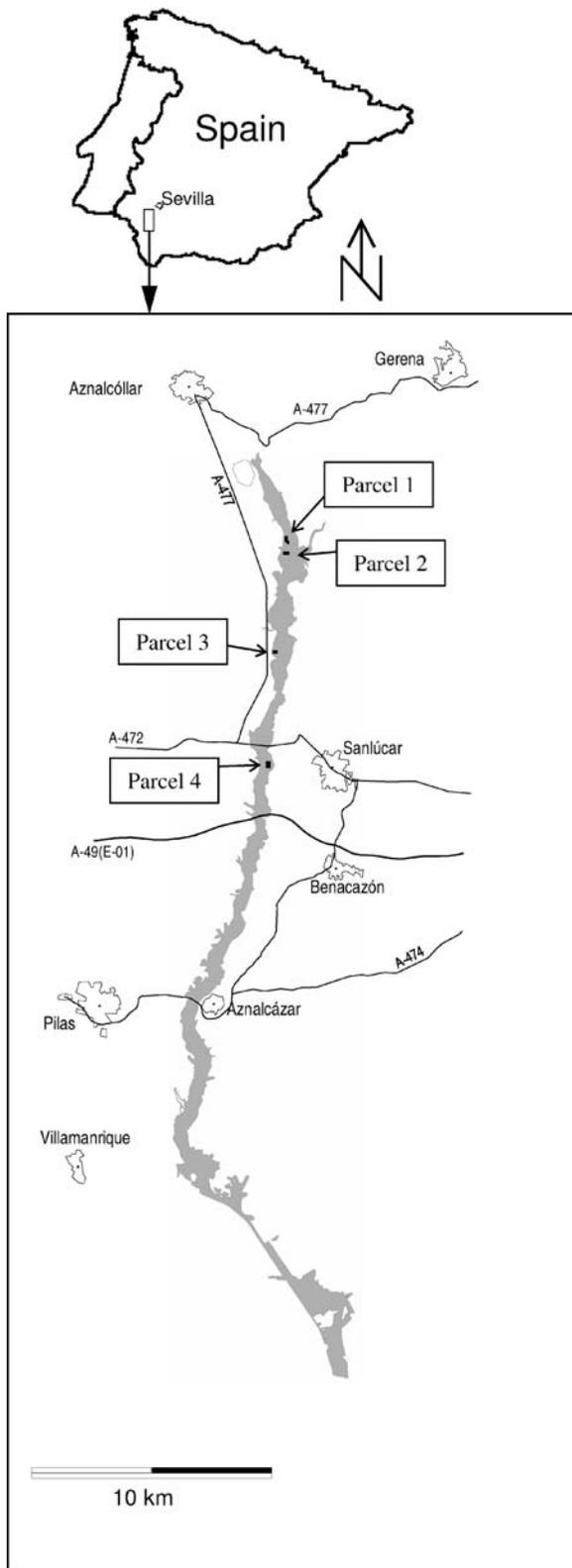
Figure 1 Location of the study area.

Afterwards, the tailings present in the same contaminated soil were oxidized with $H_2O_2$ (5 g soil+ 100 ml $H_2O_2$ at 15%), and neutralized with increasing amounts of the selected material (sugar-refinery scum), to calculate the application rate in the remediation action of the soils of the area.

To select the most appropriate material in the arsenic retention, we designed a field experiment in reduced plots (5×4 m) in the most polluted area (high part of the basin, Vicario sector), testing different materials for the immobilization of this element: iron oxides (Fe), zeolites (Z), benthonites (B) and yeasts (Y), preserving three plots untreated as reference. The application rates were: 10 ton $ha^{-1}$ for Fe; 20 ton $ha^{-1}$ for Z; 10 ton $ha^{-1}$ for B; and 2.5 ton $ha^{-1}$ for Y. We collected five samples from each plot before the application of the different materials and we repeated the sampling six months later. In all samples the soluble As was determined in a saturation extract of soil and water.

The soils selected to apply in the remediation measurement were red soils next to the affected area (Aljarafe, Seville; Mudarra, 1988). They were selected for the As blockage by their content in free-iron ($Fe_d$), ranging from 2.26% to 6.31% with a mean value of 4.39 (Table II). Thus, the treatment of these soils in the remediation actions involves high spatial variability because of the differences in free-iron content.

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). Free-iron oxides ($Fe_d$) were extracted with citrate–dithionite (Holmgren, 1967) and measured by atomic absorption spectroscopy in a Perkin Elmer 305B instrument.

Samples of treated soils, finely ground (< 0.05 mm), were digested in strong acids ($HNO_3$+HF) and the total As (AsT) was determined by inductively coupled plasma–mass spectrometry (ICP–MS) in a Perkin Elmer Elan 5000 instrument. 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 As forms, extractions were made with EDTA (AsEDTA) (Quevauviller et al.,

**Table I** Characteristics of the different soils treated with the pollutant solution coming from the tailing oxidation

| Soil | OM (%) | Clay (%) | CEC (cmol$_c$kg$^{-1}$) | Fe$_d$ (%) | pH | CaCO$_3$ (%) |
|------|--------|----------|-------------------------|------------|-----|--------------|
| 1 | 4.5 | 13 | 12 | 1.0 | 7.5 | 0 |
| 2 | 1.5 | 13 | 5 | 2.2 | 5.0 | 0 |
| 3 | 2.0 | 12 | 6 | 1.5 | 7.5 | 0 |
| 4 | 0.8 | 50 | 14 | 3.0 | 7.0 | 0 |
| 5 | 0.4 | 5 | 3 | 0.6 | 8.5 | 0 |
| 6 | 0.5 | 5 | 3 | 0.4 | 8.5 | 18 |

*OM* Organic matter; *CEC* cation-exchange capacity; *Fe$_d$* iron extracted with dithionite–citrate.

1998) and with distilled water (AsS) in a soil–water saturation extract, to estimate As mobility. To determine the speciation of As forms in soils, we used the method of Gómez Ariza, Sánchez Rodas, and Giraldez (1998).

Finally, to monitor the As concentration in soils after the remediation, we selected four parcels in the most polluted sector of the affected area, the one with slightly acidic soils with little carbonate content (Figure 1). The parcels had an area of between 4 and 11 ha and, in all cases, the samples were taken in a systematic sampling with 50 m separation each sample. In parcel 1 (the smallest one), 16 samples were collected; in parcel 2, 42 samples; in parcel 3, 40 samples; and in parcel 4 (the largest one), 64 samples were collected. Each sample was constituted by the mixing of five subsamples (centre and four corners of a square 10 m side); and two depths were collected: 0–30 and 30–50 cm, to monitoring the As mobility in depth.

# 3 Results and Discussion

Given the amounts of As and the characteristic of the basin (an alluvial plain with topographical differences below 2 m from the top to the bottom of the area), and the climatic conditions of a Mediterranean type, in which the potential evapotranspiration (PET = 900 mm) clearly exceeds precipitation (600 mm). The only remediation measures applicable after the clean-up of the tailings and the upper part of the polluted soils were: (1) additional clean-up; (2) dilution of the contamination; (3) encouragement of immobilization.

## 3.1 Additional clean-up

A second clean-up was necessary, especially in the higher part of the basin, primarily because the first clean-up, performed by the Boliden-Apirsa, was clearly uncompleted. After the second effort, by the Environmental Council of the Andalusian Regional Government, we found a substantial reduction in the pollution level, although the upper part was still polluted. We conducted an additional clean-up in an experimental plot located in the Soberbina area (5 km from the tailing pond). Before the clean-up, the As in the uppermost 10 cm had a mean value of 435 mg kg$^{-1}$ and afterwards 302.8 mg kg$^{-1}$. To remove more soil would have been unadvisable, as it would discourage or even hamper the implementation of the vegetation for the construction of a green corridor proposed by the regional government.

## 3.2 Dilution of the contamination

The tilling involved the mechanical mixing of the upper 25 cm of the soil. According to the contamination level of As at depths of 0–10 cm (157.3 mg kg$^{-1}$) and 10–30 (63.4 mg kg$^{-1}$), we could predict the result if the upper 25 cm were mixed. The As would reduce its contamination level by some 17%, this would be beneficial but not completely adequate (Figure 2). Despite all the efforts, the pollution persisted, not only because of the very large quantities of pollutants that had entered the soil, but also because the pollution took on a mosaic pattern (Figure 3), and also because of the dynamic of the clean-up, which took place under wet conditions and the use of heavy machinery mixed the tailings deep into the soil

**Table II** Adsorption of arsenates (mg l$^{-1}$) by six different red soils (RS) next to the area

| Soil | Fe$_d$ (%) | As (0.1) | As (1) | As (10) | As (50) |
|------|-----------|----------|--------|---------|---------|
| | | Arsenates adsorbed (mg l$^{-1}$) | | | |
| RS1 | 2.26 | 0.1 | 1 | 7.25 | 7.26 |
| RS2 | 3.26 | 0.1 | 1 | 10 | 10.90 |
| RS3 | 3.86 | 0.1 | 1 | 10 | 12.94 |
| RS4 | 4.64 | 0.1 | 1 | 10 | 15.60 |
| RS5 | 6.01 | 0.1 | 1 | 10 | 20.15 |
| RS6 | 6.31 | 0.1 | 1 | 10 | 21.15 |

*Fe$_d$* iron extracted with dithionite–citrate; *As (N)N* = mg l$^{-1}$ of added arsenates.

**Figure 2** As concentration in the three depth sampled. *r.l.* reference level (20 mg kg$^{-1}$), *i.l.* intervention level for agricultural soils (50 mg kg$^{-1}$; Aguilar, Dorronsoro, Galán, & Gomez-Ariza, 1999).
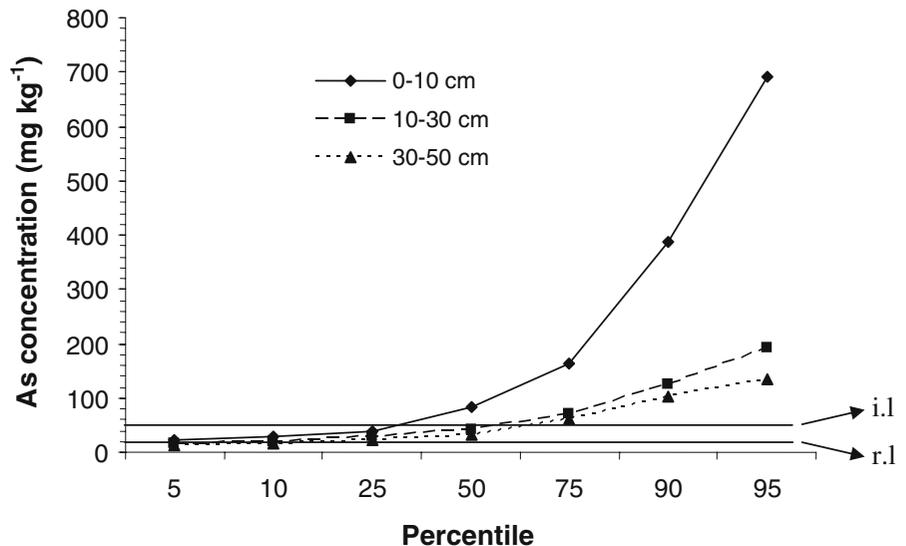


profile. Consequently, for the remaining pollution, the only plausible measure was blockage.

3.3 Encouragement of immobilization

To analyse the soil parameters involved in the fixation and retention of As, and to choose the most appropriate soil material for the remediation actions, we performed a laboratory experiment with six soils of different properties (Table I), adding a pollutant solution (rich in As and Fe) coming from the oxidation of the tailings (the As and Fe precipitation was estimated as the percentage between the concentration added in the pollutant solution and the concentration measured in soil after the experiment).



**Figure 3** Heterogeneous contamination (*mosaic pattern*) affecting vegetation recovery.

The results (Figure 4) highlight that As had a variable solubility depending on the soil properties. Soils 6 (carbonated), 4 (rich in iron and clay) and 1 (rich in organic matter) were more effective in As precipitation than the others.

According to the former data, the first measure recommended to immobilize the As was liming. The amount of liming material depends on the CaCO$_3$ content to be added to increase the pH near the neutrality. We made an estimate by a neutralizing experiment in a soil with pH 4.0 mixed with different liming materials (pure CaCO$_3$, sewage sludge, sugar-refinery scum and cellulose ashes). Neutralization curves indicated that soil pH rose in proportion to the carbonate content of the liming, and the soil reached a pH of 6.5 at 10,000 kg ha$^{-1}$ for pure CaCO$_3$ and 18,000 kg ha$^{-1}$ for sugar-refinery scum, while for cellulose ashes and sludge, the soil reached a pH of 6.5 at around 13,000 kg ha$^{-1}$ (Figure 5a).

In any case, all our soils contain variable amounts of pyritic sulphur, which oxidizes, intensifying acidification and increasing the need for liming. Thus, we calculated the oxidation pH of the soil previously tested (after reaction with H$_2$O$_2$), finding a value of 2.0 for the same soil. In this case, the liming necessary to reach a pH of 6.5 (the most effective to fix As) was around 110,000 kg ha$^{-1}$ (using cellulose ashes; Figure 5b), this being around 8-fold greater than the initial amount estimated. This implies that liming of about 20,000 kg ha$^{-1}$ would be insufficient to neutralize the majority of the acidic

soils and to fix most of the As present, so many soils would require this operation to be repeated five or six times to avoid abrupt changes in pH that could alter soil fauna and the recovery process.

The use of sugar-refinery scum was recommended for the following reasons: (a) it is less expensive than other materials (it is an industrial waste); (b) its action it is not as aggressive as that of pure $CaCO_3$, so that pH rises gradually; (c) the content in organic matter in these scum (15%–20%) is particularly beneficial because much of the topsoil was removed together with the tailings.

The Environmental Council of the Regional Government of Andalusia decided to lime using 50 tons ha$^{-1}$ in the upper, 30 tons ha$^{-1}$ in the middle and 20 tons ha$^{-1}$ in the lower part of the affected basin.

After clean-up and liming actions, we monitored the evolution of the soils throughout the basin in 1999, 2000 and 2001. The results (Figure 6) reflect that the soluble concentrations sharply diminished from 1999 to 2000 as a consequence of the applied treatment, whereas the decline in 2001 was almost negligible; possibly due to the formation of a contaminant coating covering the carbonates grains that impeded their dissolution (Figure 7) or due to insufficient amount of $CaCO_3$ used. In any case regular ploughing of the soil to break the coatings on $CaCO_3$ particles, and to improve the liming reaction, was also necessary.
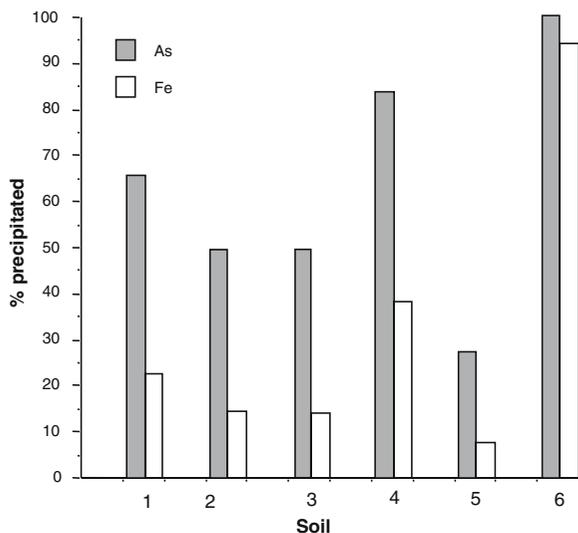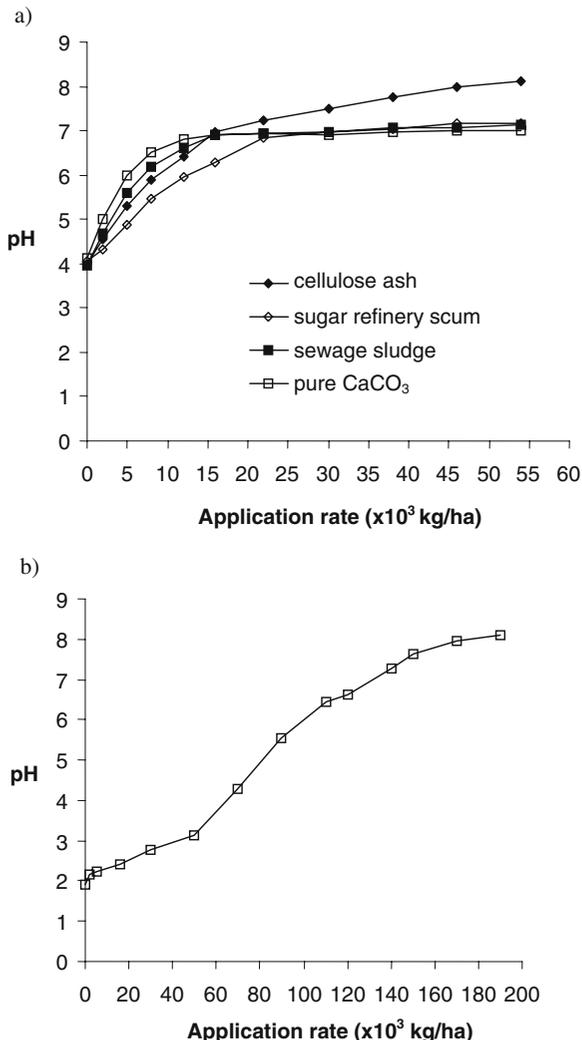
**Figure 5** (a) Neutralization curves of a polluted soil using different liming materials. (b) Neutralization curve with cellulose ash, after oxidation of sulphides in the same polluted soil as in (a).

Even with the application of the 110,000 kg ha$^{-1}$ of sugar-refinery scum required to neutralize the effects of the pyritic sulphur mixed with the soils, free As would persist in variable concentrations, so the As retention was hardly induced by this carbonated substance. Therefore, for the As fixation, we designed several experiments at Vicario area, located in the upper part of the basin. We laid out several plots (5×4 m) to which we applied several blocking agents: iron oxides (Fe), zeolites (Z), benthonites (B) and yeasts (Y); three plots were left as control. The As concentration in the different plots before the treatment and the quantities of soluble As in
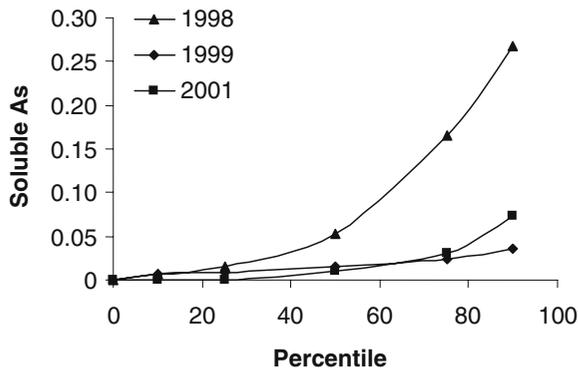
**Figure 4** As and Fe precipitation in the different soils in Table I.

Figure 6 As soluble concentration in the three periods sampled.



Figure 8 As soluble concentrations in the different plots treated with different materials. (*Z* zeolite; *B* benthonite; *Fe* iron oxides; *Y* yeast; *Ref* reference [untreated]).

each of the plots as well as their evolution over time are presented in Figure 8. The treatments with the best results correspond to the plots treated with iron oxides, in which the soluble arsenic is reduced by more than 40% in relation to the initial value of the same soil before treatment. We also found a close relationship between the amounts of Fe and As precipitated by the soils, signifying that both elements are closely connected by the following regression equation:

$$As\left(mg\ kg^{-1}\right) = -350.0 + 138.9\ \log\ Fe\left(g\ kg^{-1}\right)$$

$$r^2 = 0.970;\ P < 0.001$$

indicating that for each gram of iron, 67 mg of As is precipitated in these soils.
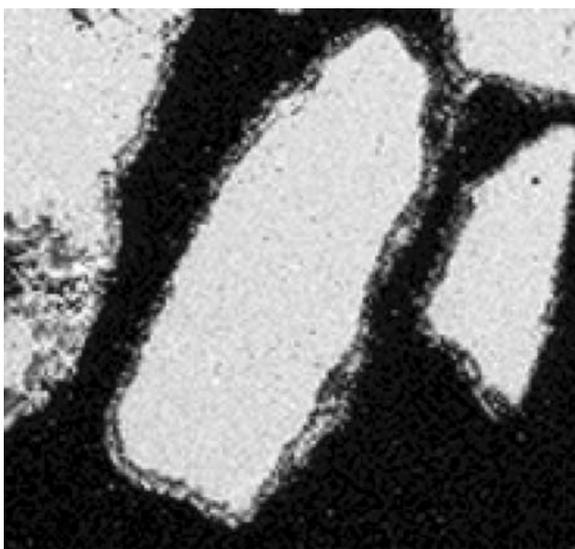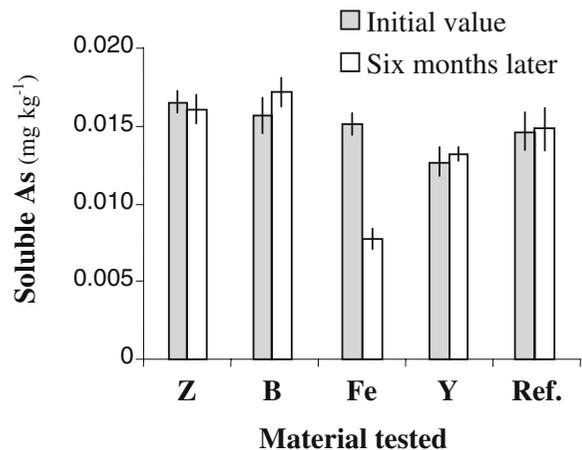


Figure 7 Coating on a calcite grain.

Given the As contamination of the area (Aguilar et al., 2004), and the data from the laboratory experiment, the recommended doses are shown in Table III. Therefore, for As retention in the affected area, the Regional Government of Andalusia added 250 ton ha$^{-1}$ in the most polluted sectors (upper part), 150 ton ha$^{-1}$ in the medium polluted (middle part) and 50 ton ha$^{-1}$ in the less polluted sectors (bottom part). Because of the very heterogeneous contamination pattern (mosaic), the application rates were excessive in some cases and insufficient in others.

According to the results and the bibliographic data, the most effective materials in the specific adsorption of As are iron oxyhydroxides, especially the amorphous ones or those with a low degree of crystallization (Pierce & Moore, 1980). In this way, for the application in the recovery of the area, the most appropriate materials selected were red soils rich in iron, and located next to the affected area (Aljarafe, Seville), with concentrations in free-iron oxides between 2.26% and 6.31% (Mudarra, 1988).

To determine the capacity of As adsorption, we first determined the form of this element in the soils using the method of Gómez Ariza et al. (1998), with the result that 99.87% was in arsenate form and only 0.13% in arsenite form.

To monitor the As contamination after this treatment, we undertook a more exhaustive study in four plots located in the most polluted sector (Figure 1). The results (Table IV) indicate a high variability in the distribution and evolution of the

**Table III** Recommended amounts of red soils to be added according to the As concentration in polluted soils

| As concentration (mg kg$^{-1}$) | Amount of red soils (Tm ha$^{-1}$) |
|---|---|
| < 50 | No addition |
| 50–100 | 120 |
| 100–150 | 180 |
| 150–200 | 240 |
| 200–250 | 300 |
| > 250 | Additional clean-up |

contamination and a bad distribution of the application of liming and red soils. The effect of the liming in the upper part of the soils (0–30 cm) increased the carbonates significantly ($P < 0.05$) in the parcels 1, 2 and 3, although the $CaCO_3$ content remained lower than 3% in all cases. This increase in carbonates significantly raised the pH only in the upper part of the soils in parcels 1 and 2; in parcel 3, the most polluted one, the increase in carbonates was not related to a rise in pH, probably due to the influence of the oxidation and acidification processes occurring more intensely in these soils. In parcel 4 the soils were carbonate, and the liming significantly increased neither the $CaCO_3$ content nor the pH. In some cases, despite the acidic pH of the soil (pH < 5), we found a $CaCO_3$ content of between 1% and 2%, an therefore the presence of these carbonates must be accompanied by the formation of coatings sealing off the carbonate grains inhibiting them from the dissolution (Barnhisel, Powell, Akin, & Ebelhar, 1982; Ziemkiewicz, Skousen, Brant, Sterner, & Lovett, 1997).

According to the total contamination, we find that the As concentration increased in the upper part of the soil, with higher and statistically different values ($P < 0.05$) in parcels 2, 3 and 4. The most contaminated was parcel 3, in which the values between 0 and 30 cm were double those between 30 and 50 cm, and the mean concentration was around 92 mg kg$^{-1}$. Parcel 1 was the least contaminated, with similar values on the surface and in depth, and also similar to the values in depth of the other parcels, reflecting that the clean-up actions were effective only in this parcel in relation to the other.

The As extractable with EDTA and the soluble As registered higher concentrations in surface samples than in depth. In the case of EDTA, these differences were significant in all the parcels, whereas for soluble As the increase was significant in all parcels with the exception of parcel 4. In this way, we found that the increase in carbonates in the surface samples were not related to the decrease of the As mobility; in fact, the concentration of the mobile forms of As was higher in the surface samples than in depth. Moreover, parcel 2 had the lowest and significant values ($P < 0.05$) of As extracted with EDTA and soluble As. According to the toxic level in the soil solution of 0.04 mg kg$^{-1}$ (Bohn, McNeal, & O'Connor, 1985), in parcels 1, 3 and 4 this level was surpassed in more than 90% of the surface samples, meanwhile in parcel 2 this level was only exceeded in 50% of the samples. These differences may be related to pH, according to Simón et al. (2005), as the most effective pH in the reduction of As mobility should be around 6.4. Parcel 2 had a

**Table IV** Some soil properties and As concentration (total: AsT; extracted with EDTA: AsEDTA; soluble in water: AsS) in the four parcels studied

| Parcel | Depth | pH | CaCO$_3$ (%) | AsT (mg kg$^{-1}$) | AsEDTA (mg kg$^{-1}$) | AsS (mg kg$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 1 | 7.35[a] (0.11) | 2.80[a] (0.63) | 50.80 (9.75) | 1.66[a] (0.21) | 0.14[c] (0.01) |
|   | 2 | 6.66[b] (0.27) | 0.50[b] (0.27) | 47.41 (8.38) | 1.09[b] (0.11) | 0.11[d] (0.01) |
| 2 | 1 | 6.32[a] (0.23) | 1.64[a] (0.39) | 64.60[a] (7.51) | 0.85[a] (0.09) | 0.05[c] (0.01) |
|   | 2 | 5.18[b] (0.29) | 0.62[b] (0.11) | 44.42[b] (6.05) | 0.55[b] (0.08) | 0.03[d] (0.01) |
| 3 | 1 | 6.09 (0.23) | 0.66[a] (0.13) | 91.96[a] (7.03) | 1.67[a] (0.16) | 0.12[c] (0.01) |
|   | 2 | 6.01 (0.25) | 0.28[b] (0.06) | 44.45[b] (3.59) | 0.73[b] (0.09) | 0.08[d] (0.02) |
| 4 | 1 | 7.69 (0.06) | 9.14 (1.62) | 71.58[a] (5.52) | 1.50[a] (0.15) | 0.12 (0.01) |
|   | 2 | 7.66 (0.08) | 8.66 (1.80) | 53.39[b] (4.81) | 1.01[b] (0.11) | 0.11 (0.02) |

Depth 1 = 0–30 cm; 2 = 30–50 cm.

Significant differences in depth: [a, b] = $P < 0.05$; [c, d] = $P < 0.1$.

Mean values, standard error in brackets.

mean value of 6.32, and, when the pH was over this value, the mobility increases (Jones, Inskeep, & Neuman, 1997). However, this effect of pH on As mobility was observed because the retention of this element by the iron oxides was not important because the amounts applied of iron-rich materials (red soils) were insufficient.

## 4 Conclusion

The results indicate that after the many remediation actions in the area, the contamination level of As, mainly the soluble fraction, remains very high in many sectors of the affected area. On the basis of the different experiments conducted, the treatments applied in the remediation of the area were the appropriate ones, but the heterogeneity in the distribution of the materials on the soil surface (mainly carbonate and iron rich soils), the absence of tilling repetition over time (to destroy the coatings on the carbonate grains) and the insufficient amounts used in several areas, have not produced the expected results. Consequently, long-term monitoring of the pollution would be advisable.

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