

# Long-term assessment of remediation treatments applied to an area affected by a mining spill

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## Abstract

This study evaluates the effectiveness of remediation treatments in the long-term (twenty years later) in one of the largest mine spills in the world, the Aznalcóllar accident. Soil recovery was carried out through the application of different rates of organic (compost and manure) and inorganic amendments (materials rich in iron oxides and calcium carbonate). The different amendment combinations were grouped in four treatments (T1 to T4) and applied in different sectors depending on the soil properties and the degree of initial pollution. To assess the degree of soil recovery, the physicochemical properties, the total, soluble and bioavailable concentrations of the main pollutants (Pb, As, Zn and Cu) were determined over time. The applied treatments increased the pH, CaCO<sub>3</sub> and organic carbon of the soils, reduced the EC and decreased the mobility of the pollutants, indicating that remediation treatments were efficient in the recovery of soils contaminated by potentially harmful elements. However, twenty years after the accident, total concentrations of Pb and As still exceed the intervention levels of the current regulations in certain areas. These areas are located in the sectors closest to the mine and where treatments T1 and T2 were applied; in these cases, the dose of organic amendment, materials rich in iron oxides and calcium carbonate were not effective enough, so the application of new treatments is recommended to complete the full recovery of the area.

## Keywords:

Amendments - Bioavailability - Potentially harmful elements - Remediation treatments - Soil recovery.

## 1. Introduction

Soil contamination by potentially harmful elements (PHEs) is a growing problem in the world. Heavy metals and associated elements released into the environment are persistent and their toxicity represents a serious threat to organisms exposed to high concentrations of such pollutants (Bernard and Oluranti, 2017). For the treatment of contaminated soils, one of the major current remediation techniques is the assisted natural remediation, which consists of improving the soil properties to favor the reestablishment of its main functions and promote the growth of vegetation (Adriano et al., 2004). In this sense, the application of organic and inorganic amendments to the contaminated soil favors its natural remediation, since it is based on the reduction of the mobility and bioavailability of the polluting elements (Xiong et al., 2015). In addition, the application of amendments favors the biological activity of the soil, promoting the implantation of bioremediation techniques such as phytostabilization, in which the mechanisms in the soil-microorganism-plant system are enhanced to speed up the recovery of contaminated areas (Bernard and Oluranti, 2017). Revegetation of areas affected by PHEs is a widely used alternative to reduce related environmental risks, but requires regular monitoring to control potential passive transmission of pollutants into the food chain

(Pardo et al., 2018). Therefore, assisted phytoremediation and the use of amendments are efficient, cost-effective and environmentally friendly methods for the recovery of contaminated soils (Wiszniewska et al., 2016). Medium-term studies based on the application of organic and inorganic amendments to an acidic soil contaminated with different PHEs, demonstrated the effectiveness of carbonated materials in increasing pH and reducing Cd, Cu and Zn concentrations in the soil solution (Xiong et al., 2015). Likewise, Pardo et al. (2018) evaluated the revegetation of an acidic soil contaminated with metals, after six years of incorporating lime amendments with and without compost, concluding that lime plus compost amendment was the best treatment to increase vegetation cover.

In this work, we evaluate the remediation of an area contaminated by the Aznalcóllar mine accident (Seville, Spain), twenty years after the spillage of tailings and acidic waters with high concentrations of heavy metals and other PHEs (Simón et al., 1999). Recovery actions initially focused on the removal of potentially toxic tailing and the highly contaminated topsoil, followed by assisted natural remediation based on the application of organic and inorganic amendments and on phytostabilization with native vegetation (Madejón et al., 2018). The recovery of the affected area was realised through the largest soil restoration program carried out to date in Spain, with the participation of the Administration, Universities and research institutions (CSIC), with an investment of 280 M \euro (OECD, 2004). The initial removal of the soils affected by the spill was performed depending on the particular characteristics of the terrain. In the northern part of the study area, the one closest to the mine, more than a meter of the original soil was removed, while in the rest of the areas only the top layer of soil, less than 30 cm, was affected (Martín Peinado, 2001).

After the removal of the contaminated soils, different organic and inorganic amendments were used for the recovery of the soils. The application of the amendments depends on the soil properties and the residual concentration of contaminants. Initially, materials rich in  $\text{CaCO}_3$ , such as waste of sugar factory and cellulose pulp ash, were applied throughout the affected area, the doses applied in acidic soils (first 15 km from the mine) ranged between 60 and 90 t ha<sup>-1</sup> and were fixed in 20 t ha<sup>-1</sup> in basic soils (rest of the affected area). Subsequently, organic matter amendments were also applied throughout the whole area. Finally, in the most affected areas, clay materials rich in iron oxides were applied to favor the immobilization of arsenic, since it was considered one of the most persistent pollutant (Aguilar et al., 2004a, Madejón et al., 2018). The intensive remediation treatments ended three years after the accident, when the area modified its agricultural use and the Guadiamar Green Corridor (GGC) was implemented in 2003 as a Protected Landscape area, where agriculture, grazing, fishing or hunting were banned (CMA, 2003).

Over time, systematic samplings have been performed in the entire affected area to assess the degree of recovery in the zone, which has been generally considered as positive (Simón et al., 1999, Simón et al., 2001, Aguilar et al., 2004a, Simón et al., 2008). However, in recent years the presence of residual contamination has been detected in certain sectors of the GGC, which were initially identified through field observation, due to the presence of patches where no vegetation grows and a potential risk of dispersion of pollutants was detected (Martín et al., 2015, Romero-Freire et al., 2016a). In this sense, the objective of this work is to evaluate the evolution of the treatments and doses applied to the soils in the different sectors and how these treatments have developed twenty years after the accident. Changes in the physicochemical properties of soils, in total, soluble and bioavailable concentrations of the main pollutants (Pb, As, Zn and Cu) and the potential toxicity in the affected area are also evaluated.

## 2. Material and methods

### 2.1. Study area

The study area includes the Guadiamar Green Corridor (GGC), affected by the toxic spill from the Aznalcóllar mine (Seville, Spain), this area is characterized by a smooth topography associated with the Guadiamar river basin (Figure 1). The affected area was around 4600 ha and was characterized by its agricultural use before the accident, where the main soil groups found were Fluvisols and Regosols, according to WRB (IUSS, 2015) or Entisols, according to SSS (2014). In all cases, these are soils with poorly developed profiles, relatively high fertility and anthropogenic influence, with grazing and fruit and cereal crops predominating

(Cabrera et al., 1999, Martín Peinado, 2001). The climate of the area is conditioned by its location within the Guadalquivir Depression and the influence of the Mediterranean climate. The annual average temperature is 17.7° C (with average temperatures in the coldest months higher than 10°C) and the average annual precipitation is 612.7 mm. The annual insolation is greater than 2800 hours year<sup>-1</sup>, so the potential evapotranspiration values are higher than those of precipitation in more than 6 months a year (Martín Peinado, 2001). According to the classification of Rivas Martínez (1987), the climate is Mediterranean with drought in the summer season. Regarding the edaphic profile, the temperature regime is Thermic and the humidity regime is Xeric (USDA, 1999).

## 2.2. Soil sampling

The study is based on a systematic sampling made twenty years after the accident, throughout the whole affected area, including 84 georeferenced homogeneous plots (10 x 10 m) randomly distributed. Four samples of the surface layer (0 to 10 cm) were taken in each plot, which were mixed and homogenized in field in order to obtain a representative sample (composite sample) from each 100 m<sup>2</sup> plot. In this study, the data of the initial sampling from 1998, carried out the same year as the accident and before the application of any remediation action, were analyzed (Simón et al., 1999); and data from the sampling realised in 2004, once the recovery actions of the affected area have been completed, were also considered (Simón et al., 2005a), to compare the long-term recovery evolution.

This study is based on assessing the evolution of the treatments applied to the soils in the different sectors of the affected area. In general, the affected area can be divided into four sectors (Table 1) according to the applied treatments (Aguilar et al., 2004a). In all cases, organic amendments (Org) were applied in order to restore fertility and promote biological activity after the impact, since the removal of the upperpart of the soils eliminated the most fertile layer of them. Organic amendments were applied more or less homogeneously in all sectors: in the most affected area (first 15 km downstream from the mine) 20 t ha<sup>-1</sup> of compost from different sources was applied, in the middle zone (between 15 and 30 km downstream) 20 t ha<sup>-1</sup> of manure were applied, and in the lowest area (last 10 km of the affected area) 15 t ha<sup>-1</sup> of manure were applied. The second most used amendment was a material rich in calcium carbonate (Cal), in order to neutralize the acidity generated by the oxidation of the residual tailing that was mixed with the soil matrix during the cleaning actions, to promote the immobilization of the contaminants. The most used carbonated amendment was the waste coming from the sugar beet industry, applied in different doses according to the affected area: on the first 15 km downstream from the mine, an average of 40 t ha<sup>-1</sup> was initially applied and the following year liming was repeated in variable doses (20, 30 or 50 t ha<sup>-1</sup>), giving a total dose for this sector between 60 and 90 t ha<sup>-1</sup>. In the rest of the affected area, the carbonate amendment was applied with a dose of 20 t ha<sup>-1</sup> and was not repeated the following year. In Table 1, for the Cal amendment, the value 1 corresponds to the application of 20 t ha<sup>-1</sup> and the value 2 to the applied doses higher than 20 t ha<sup>-1</sup>. Finally, the last applied amendment consisted of red soils rich in Fe oxides (Arc), which were applied to reduce the mobility of arsenic, considered one of the most potentially dangerous elements remaining after cleaning work (Aguilar et al., 2004b). The doses applied were heterogeneous and dependent on the residual arsenic concentrations in the soils, so they varied between 320 and 960 t ha<sup>-1</sup>. In Table 1, for the Arc amendment, the value 0 is for the sectors where this amendment was not applied and the value 1 for those where it was applied.

The combination of the amendments and applied doses defines a total of four treatments: T1 corresponds to areas where organic and iron oxides-rich amendments were used, and more than 20 t ha<sup>-1</sup> of carbonate-rich amendment were applied, T2 corresponds to areas where organic amendment and more than 20 t ha<sup>-1</sup> of carbonate-rich amendment were applied, but no iron oxides-rich amendment was used, T3 includes areas where organic and iron oxides-rich amendments were used, and less than 20 t ha<sup>-1</sup> of carbonate-rich amendment were applied, and T4 includes areas where organic amendment and less than 20 t ha<sup>-1</sup> of carbonate-rich amendment were applied, but no iron oxides-rich amendment was used (Figure 1).

## 2.3. Analytical methods

All soil samples were air-dried and sieved (<2 mm) before analyses, which were performed using standardized

methods (MAPA, 1994). The particle size characterization was determined by the Robinson's pipette method (USDA, 1972). The pH was measured potentiometrically in a 1:2.5 soil:water suspension and the electrical conductivity (EC) in saturated paste extract. The calcium carbonate content ( $\text{CaCO}_3$ ) was determined by the volumetric gas method (Barahona, 1984) and the organic carbon by the acid oxidation method (Tyurin, 1951), both parameters after fine grinding ( $<0.05$  mm) of the sample.

The total concentration of contaminants (Pb, As, Zn and Cu) was analyzed by X-ray fluorescence (XRF), using the finely ground sample, with a NITON XL3t-980 GOLDD+ portable analyser (Niton, Billerica, USA). The precision and accuracy of the contaminating elements was made from measurement (6 replicates) of a certified reference material (CRM 052-050 RT-Corporation Limited, Salisbury, United Kingdom), obtaining the following results (*certified* vs. measured, mean values in  $\text{mg kg}^{-1}$  and standard error in brackets): Pb: 82.6 (4.0) vs 92.6 (4.8), As: 14.6 (2.9) vs 15.5 (3.9), Zn: 89.0 (4.0) vs 94.4 (6.2), Cu: 44.2 (6.9) vs 48.5 (8.0). In all cases, the measured values were within the confidence interval of the certified value.

The concentrations of water soluble contaminants were determined in a 1:5 suspension (soil:water) according to Sposito et al. (1982), and the bioavailable forms were extracted with 0.05 M EDTA at pH 7.0 according to Quevauviller et al. (1998); in both cases, the extracted elements were measured by inductively coupled plasma mass spectrometry (ICP-MS), with a Perkin Elmer SCIEX ELAN-5000A spectrometer (Waltham, MA, USA). The precision of the method was corroborated by analysis (6 replicates) of a standard reference material (SRM 2711), obtaining the following results (*certified* vs. measured, mean values in  $\text{mg kg}^{-1}$  and standard error in parentheses): Pb: 1162.0 (31.0) vs 1138.1 (11.0), As: 105.0 (8.0) vs 102.4 (1.1), Zn: 350.4 (4.8) vs 350.3 (3.4), Cu: 114.0 (2.0) vs 115.0 (1.6). For all target elements, the measured values were within the confidence interval of the certified value.

#### 2.4. Statistical analysis

The data obtained were analysed to check its normal distribution using the Kolmogorov-Smirnov test, and the homogeneity of variance was also analysed using the Levene test. After fulfilling both assumptions, the data were analyzed using the parametric mean comparison test (ANOVA), considering the study periods (years) and the types of amendments (Org., Cal. and Arc.) as independent variables. Subsequently, the Tukey post hoc test determined the significant differences ( $p < 0.05$ ) between the different independent variables considered. All statistical analyzes were carried out using SPSS software v.20.0 (SPSS Inc., USA).

To show the mean values of the concentrations of soluble and bioavailable contaminants in the different sampling periods, radial charts were constructed with Excel, the scale was determined independently for each item. The area obtained for each element was measured with Adobe Acrobat 9.0 (Adobe Systems Incorporated, USA) and the sum of the areas obtained for each treatment and each year was calculated. Finally, the soil remediation index (RA) was calculated according to Xiong et al. (2015), who define this index as the relationship between the surface of each polygon in each sampling period and the surface of the initial polygon (1998), therefore considering RA equal to 1 for the year 1998.

### 3. Results

#### 3.1. Soil properties

Soil granulometric analysis was compared between the soils sampled at the beginning of the accident (1998) and twenty years later (2018), to check whether the removal of the surface layer of the soils (Aguilar et al., 2004b) generated differences in the textural class. We found no significant textural differences between the soils sampled just after the accident and twenty years later (Table 2), thus, the soils on which T1, T2 and T3 treatments were applied have a more coarse texture ("Loam" component), while the soils where T4 treatment was applied have a finer particle size ("Silty-clay" component).

Twenty years after the accident and with the application of remediation treatments, the pH, electrical conductivity, calcium carbonate and organic carbon content significantly changed in relation to the initial soil values and depending on the applied treatment (Table 3). The soils where the treatments were applied, were divided in two different sectors (Aguilar et al., 2004a), one including moderately acidic soils, with loam

to sandy loam textures and low  $\text{CaCO}_3$  content, located in the first third of the area affected by the spill (first 15 km downstream from the mine) and coinciding with the soils where T1 and T2 treatments were applied, and a second sector of neutral or slightly alkaline soils, with clay component textures and a high content of  $\text{CaCO}_3$ , located in the following two thirds of the affected area (from the end of the moderately acidic soil sector to the end of the affected area) and coinciding with the soils where T3 and T4 treatments were applied.

The pH values of the soils did not significantly increase after the application of the treatments 6 years after the accident (2004), while these differences were significant at 20 years in the soils where the T2, T3 and T4 were applied. In all cases, the mean pH values are above 7, reaching values higher than 8 in the case of T3 and T4; anyway, soils with treatments T1 and T2 presented values significantly lower than soils with treatments T3 and T4 both at the beginning (1998) and twenty years after the accident.

Electrical conductivity (EC) is a parameter closely related to this type of soil contamination, since the oxidation of the sulphides in the residual tailings that were mixed with the soils after the initial cleaning actions, generated soluble salts (mainly sulphates) that increased this parameter in the soil (Simon et al., 2001). The different treatments applied were effective in reducing the EC in all cases, the differences being significant 6 years after the accident and remaining constant over time.

The application of organic amendments was also widespread throughout the area affected by the spill. In this sense, the OC content increased in the soils after the application of all treatments, although these increases were statistically significant only in the last sampling period (2018).

### 3.2. Total concentration of pollutants in soils

Soil contamination was initially very high, due to the entry of tailings and acidic waters into the soil matrix (Simon et al., 1999). In 1998 there were no official regulatory levels to declare a soil as contaminated in Spain, so the evaluation of potential contamination in the area was made based on the current proposal of the Regional Government of Andalusia (CMA, 1999). In this proposal, the intervention levels for agricultural soils were set at: Pb:  $350 \text{ mg kg}^{-1}$  (soils with  $\text{pH} < 7$ ) and  $500 \text{ mg kg}^{-1}$  (soils with  $\text{pH} > 7$ ), As:  $50 \text{ mg kg}^{-1}$ , Zn:  $600 \text{ mg kg}^{-1}$  (soils with  $\text{pH} < 7$ ) and  $1000 \text{ mg kg}^{-1}$  (soils with  $\text{pH} > 7$ ), and Cu:  $300 \text{ mg kg}^{-1}$  (soils with  $\text{pH} < 7$ ) and  $500 \text{ mg kg}^{-1}$  (soils with  $\text{pH} > 7$ ). In this sense, just after the accident, the mean values of the different pollutants in the soils revealed an intense initial contamination (Table 4), since the intervention levels for As were exceeded in all the affected sectors, while that for Pb and Zn were exceeded in soils where T1 and T2 treatments were applied. The mean values for Cu did not exceed the intervention levels in any sector, although they did occasionally exceed in certain soils on which the T1 treatment was applied.

The subsequent removal of tailings and soils significantly reduced the total concentration of potentially contaminating elements in the soils, although subsequent studies indicated that this cleaning left a heterogeneous contamination pattern distributed throughout the affected area (Aguilar et al., 2004a). If we compare the initial concentrations with those analyzed 20 years after the accident, we observe that for Pb, As, and Cu there has been a significant decrease in the soils of treatments T3 and T4, but not in soils where T1 and T2 treatments were applied. Zn has been the element whose mean values have decreased in all sectors, these differences being significant 6 years after the accident. Our data confirm the decrease in mean concentrations in most of the restored area (soils with T3 and T4 treatments), although potentially dangerous concentrations of Pb and As were detected in some soils located in the first third of the area affected by the spill (soils with T1 and T2 treatments). Our results are in agreement with those reported by Martin et al. (2015), in areas randomly distributed close to the mine.

Seventeen years after the accident, the Regional Government of Andalusia published the Generic Reference Levels (GRL) to declare a soil as potentially contaminated (BOJA, 2015). In the case of the studied contaminants, the values established for the protection of human health were as follows:  $275 \text{ mg kg}^{-1}$  for Pb,  $36 \text{ mg kg}^{-1}$  for As,  $10000 \text{ mg kg}^{-1}$  for Zn and  $595 \text{ mg kg}^{-1}$  for Cu. According to these values, the total mean concentrations of Zn and Cu throughout the GGC twenty years after the accident do not exceed the GRL in any of the sectors. The total concentrations of Pb exceed the GRL in 13.1% of all analysed soils,

with strong differences between treatments: 35.7% of the areas where T1 was applied, 40% where T2 was applied, 5.4% of soils with T4 and was not exceeded in any case within the area where T3 was applied. As is considered the element with the highest risk of potential contamination, since 69% of the soils analysed exceed the GRL, with differences in percentages between treatments: 86% of the soils where T1 was applied, 90% where T2 was applied, 61% where T3 was applied and 62% where T4 was applied.

### 3.3. Solubility and availability of contaminants in soils

In studies involving contamination of inorganic elements, besides to analyse the total concentration, it is essential to evaluate the solubility and bioavailability of pollutants in soils. These forms are directly related to the risk of dispersal of pollutants within the soil and throughout the rest of the ecosystem, as well as the risk of toxicity when absorbed by organisms, both animals and plants (Kim et al., 2015). In our case, we have analysed the concentrations of elements soluble in water, as the fraction with the highest risk of dispersion in the shortest term, and the concentrations of elements extractable with EDTA, as the potentially bioavailable fraction in the medium-long term (Quevauviller et al., 1998). EDTA tends to extract soluble, exchangeable and weakly adsorbed elements from the soil (Schramel et al., 2000, Alvarez et al., 2006), and at pH 7.0 it can also dissolve elements that are bound to humic substances in the soil. Due to the high stability of the complexes, EDTA could also dissolve elements that are present in the soil, such as water-insoluble carbonates (Yotova et al., 2018).

The heterogeneity of the contamination in our study area, described in the previous section, makes that the total concentration of the pollutants shows great variability; therefore, to evaluate the evolution of the mobility of the pollutants after the application of the different treatments in a comparative way, we have calculated the relative percentages of soluble (S) and bioavailable (E) fractions in relation to the total concentrations (Table 5).

The water soluble and potentially bioavailable forms present differences depending on the element considered and the treatment applied. In the case of Pb, after the application of treatments (2004), the solubility and bioavailability significantly decrease in all cases, and it remains low over time, however, 20 years after the accident, the soils where T3 and T4 treatments were applied have higher relative concentrations of soluble and bioavailable Pb than where T1 and T2 treatments were applied. However, although the total concentration of Pb is lower in T3 and T4 (Table 4), the soluble and bioavailable concentrations are not lower than in T1 and T2.

Arsenic shows a different behavior, since its relative solubility in water does not decrease over time for treatments T1 and T2, while an increase in treatments T3 and T4 is observed twenty years after the accident, furthermore, as with Pb, T3 and T4 treatments show a higher relative solubility of As in relation to T1 and T2 treatments. The bioavailability of As significantly decreases in all cases after the applied treatments and remains low over time; however, T3 and T4 treatments show a higher bioavailability of As in relation to T1 and T2 treatments in relative terms, considering that the total As concentration in T3 and T4 is significantly lower than in T1 and T2.

The solubility and relative bioavailability of Zn are significantly reduced after the application of treatments and this reduction continues until 2018. In 2004 it is observed that the relative solubility of Zn in soils where T1 and T2 treatments were applied was higher than where T3 and T4 were applied, although the opposite occurs with the total concentrations (Table 4). Therefore, the remediation measures were more effective in the case of Zn in the most distant sector from the mine, where although liming was less intense, the carbonated character of the soils influenced in the reduction of its solubility.

Cu does not significantly reduce its relative solubility over time, and an increase in T4 treatment is observed 20 years after the accident. There are no significant differences in the relative solubility of Cu between the different treatments, which is related to the low mobility of this element in soils. Cu does not reduce its relative bioavailability after the application of treatments (2004), although it does significantly decrease in the long term (2018), it is also observed that the relative bioavailability of Cu is higher in soils where T3 and T4 treatments were applied than where T1 and T2 were applied.

The percentages of the soluble and bioavailable concentrations of Pb, As, Zn and Cu have been represented in the form of radial graphs (Figure 2), to estimate the effects of each treatment on the studied elements, the smaller the polygon, the lower the risk of potential toxicity (Xiong et al., 2015).

From the data in Figure 2, the soil remediation index (RA) was calculated according to Xiong et al. (2015), who define it as the relationship between the surface of each polygon and the surface of the initial polygon (1998), therefore considering RA equal to 1 for the year 1998. In this sense, the lower the value of RA, the greater it will be the reduction of the soluble or bioavailable forms and, therefore, greater efficiency has been in the recovery treatments. The results of the calculation of RA are shown in Table 6

## 4. Discussion

### 4.1. Soil properties

The  $\text{CaCO}_3$  content is closely related to the increase of pH in soil and it is associated with the generalized application of carbonate amendments throughout the area affected by the spill (Aguilar et al., 2004a). However, the variations in the  $\text{CaCO}_3$  content are not very significant, both between the different treatments applied and between the years considered. In treatments T1 and T2, higher doses of carbonate material were applied in relation to treatments T3 and T4, but in the case of the former, the soils on which they were applied had a lower initial content of carbonates and a higher degree of residual contamination, which caused a partial dissolution of  $\text{CaCO}_3$  that buffered the pH of the soils (Simon et al., 2005a). In the case of the T3 and T4 treatments, there are also no significant differences in the carbonate content of the soils over time, since liming was carried out at lower doses and only during the first year, since these soils were originally carbonated and had less residual contamination, anyway, no significant increase was observed because a partial dissolution of calcium carbonates occurred (Simon et al., 2008).

The reduction of the EC has been considered as a general indicator of the degree of recovery in the area (Garcia-Carmona et al., 2017). However, the soils in which T1 and T2 treatments were applied have higher mean EC values than in the other treatments (Table 3), which is related to the presence of residual contamination in these areas (Martin et al., 2015).

The application of organic amendments during the restoration actions recovered the soil OC values before the accident, so the differences between 1998 (before the removal of the contaminated soils and the upper part of the soils) and 2004 samplings (after completion of remediation measures) are not significant. The evolution over time has favored the growth of vegetation on all the GGC soils (Pastor-Jauregui et al., 2020), which has promoted the contribution of organic matter to the soils and has produced a significant increase in the OC content observed twenty years later.

### 4.2. Total concentration of pollutants in soils

These differences between sectors may be due to the joint influence of soil properties and applied treatments. The T1 and T2 treatments contributed with large amounts of carbonates to soils that received a higher concentration of pollutants, but had poor properties to cope with contamination (moderately acidic pH, low or no calcium carbonate content and sandy textures), so the dynamic of the pollutants in these soils was influenced by a high mobility in the soil matrix which, together with the high evapotranspiration of the area, caused the precipitation of the pollutants in the first centimeters of the soils, which is where liming was effective (Simon et al., 2005a). However, the soils on which T3 and T4 treatments were applied, in addition to receiving a lower load of contaminants, had better properties (basic pH, carbonates and fine textures), which allowed the contaminants to penetrate to a lesser extent in the soils and, in the cases where they entered in depth, the precipitation in the soil matrix prevented its capillary rise and its concentration on the soil surface, favoring the dilution effect of the contamination (Martin et al., 2008).

These data show that twenty years after the accident, and after the remediation measures were completed, there are still potentially contaminated soils in the GGC according to current legislation. However, the clean and application of amendments to these soils were effective in most of the GGC, promoting the immobilization of potentially harmful elements, the restoration of essential soil functions and the growth

of vegetation, although the full recovery in some of the soils located closest to the mine is still needed (Pastor-Jauregui et al., 2020).

#### 4.3. Solubility and availability of contaminants in soils

The behavior observed in Pb could be related to the higher vegetation development where T3 and T4 treatments were applied and the affinity of the organic matter to form organic complexes with Pb easily extracted with EDTA (Sierra et al., 2019). In the case of As, it does not form stable complexes with EDTA (Přibil, 1982), which could explain the low values of bioavailability extracted. Arsenic is a low mobility element and its availability depends on soil properties such as Fe oxides, pH, calcium carbonate, clay content, cation exchange capacity and organic matter content (Martín et al., 2012, Romero-Freire et al., 2014).

The influence of carbonates and pH on the solubility of Zn is widely reported in the literature (Kraus and Wiegand, 2006, Madejón et al., 2006, Clemente et al., 2008, Romero-Freire et al., 2016b), where the decrease in the solubility of Zn is directly related to the increase in pH. Regarding the decrease in the bioavailability of Zn, the effect of liming on the soils of the area is recognized as a very effective measure according to Simón et al. (2005b), and, according to our data, remains over time.

Cu mobility is strongly related to pH, increasing its solubility in acidic soil conditions (García et al., 2009). Rocco et al. (2018), reported that the absorption by plants was positively related to the bioavailability of potentially harmful elements in the soil, presenting Zn greater mobility with respect to Cu. Moreover, Cu is strongly retained by the soil, is less mobile and less sensitive to changes in soil pH compared to Zn, with relative adsorption at pH values below 5. For this metal, the content of organic matter and iron oxides are the most significant parameters that govern their adsorption processes in soils (García-Carmona et al., 2019).

The influence of climate in our study area is also a key factor to be considered; in this sense, Liu et al. (2020) indicate that high temperatures accelerate the transformation of soluble fractions of potentially harmful elements, contributing to the increase in mobility of heavy metals. In acidic soils, solubility increases because the degradation of particulate organic carbon and the dissolution of Fe-Mn particles are accelerated (Zhang et al., 2014).

The results of the calculation of RA (Table 6), show a positive evolution in all treatments, since the values are below 1 in all cases. In the case of the solubility of the studied elements, the reduction is very strong after the application of the remediation treatments (2004), although this reduction is maintained over time in the case of T1 and T2 treatments, but increases in T3 and T4 treatments. This increase in soluble forms were mainly observed for Pb and As, which in these soils seem to be related to the competing effects between these elements and the soil organic matter content (Sierra et al., 2019). In the case of bioavailability, the reduction is greater for all treatments applied and this reduction strongly increases over time, indicating a general reduction in the availability of potentially harmful elements throughout the study area regardless of the treatments applied. However, the presence of residual contamination and the specific evolution in some sectors (Pastor-Jauregui et al., 2020), makes it necessary to monitor the whole area and to apply remediation measures in those sectors where a potential risk for toxicity is detected.

## 5. Conclusions

Our results indicate that the combination of organic and inorganic amendments used represents an efficient method to recover soils contaminated by heavy metals and arsenic. The different doses used mainly increased the pH, CaCO<sub>3</sub> and organic carbon content of the soils, reduced the EC and decreased the solubility and bioavailability of the contaminants. The effect of the different treatments became very evident 6 years after the accident, and the positive evolution over time has produced a homogenization of soil recovery in all sectors. Nevertheless, treatments T1 and T2 were applied in doses that were not sufficient to improve the properties of these soils at the same rate as in the other treatments, mainly due to the higher degree of the initial contamination received and the worse properties of the soils where these treatments were applied. Moreover, in certain sectors where T1 and T2 treatments were applied, total concentrations of Pb and

As have been detected exceeding the intervention levels of the current regulations, indicating the presence of potentially contaminated soils. Additional treatments with higher doses of organic amendment, iron-rich material and calcium carbonate amendments are recommended to complete the full recovery of these residual areas.

## 6. References

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