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# Pollution of Pb in Soils Affected by Pyrite Tailings: Influence of Soil Properties

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Additional information is available at the end of the chapter

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## 1. Introduction

Pb is considered one of the most common contaminant in the environment [1] and it is considered neither essential nor beneficial for plants or animals but highly toxic. Pb is one of the less mobile heavy metals so its compounds tend to accumulate in soils and sediments, and it is slightly affected by microbial degradation [2-4]. It has a strong affinity by the sulphur, so is frequently associated to sulphides, being the galena (PbS) the most frequent ore mineral. Pb has two stable oxidation states: Pb(II) and Pb(IV), but the most dominant species in nature is the plumbous one. Geochemically,  $Pb^{2+}$  can replace isomorphously  $K^+$  in silicate lattices or  $Ca^{2+}$  in carbonates and apatites, due to the similar ionic radius with these both elements [2].

In crustal rocks, the average Pb content is approximately  $16 \text{ mg kg}^{-1}$  [5]. In igneous rocks trend to increase from ultrabasic (gabbro  $1.9$ ) to acid (granite  $22.7$ ), meanwhile shales and mudstones have an average Pb content of  $23 \text{ mg kg}^{-1}$  and sandstones  $10 \text{ mg kg}^{-1}$ , being limestones and dolomites the rocks with higher average Pb content ( $71 \text{ mg kg}^{-1}$ ). The average concentration in uncontaminated soils is estimated to be  $40 \text{ mg kg}^{-1}$ , ranging from 2 to  $200 \text{ mg kg}^{-1}$  [6, 7].

On 25 April 1998, a breach in the dam of the holding pond of tailings from a pyrite mine in Aznalcóllar (S Spain) spilled around  $45 \times 10^5 \text{ m}^3$  of acidic waters and toxic tailings containing high concentrations of Zn, Cu, Cd, As, Pb, Sb, Bi and Tl into the Agrio and Guadiamar river basins, affecting around  $43 \text{ km}^2$  [8]. The soils were polluted in two stages [9]. First, the toxic water (liquid phase) and tailings (solid phase) covered the soils and penetrated in depth through macro and micropores; the acidic water had far lower heavy-metal content (Pb concentration ranging from  $2.05$  to  $2.60 \text{ mg dm}^{-3}$ ) than the tailings had (Pb concentration ranging from  $4352.3$  to  $9635.9 \text{ mg kg}^{-1}$ ). In the second stage, the oxidation of the pyrite tailings

causes sulphides to oxidize to sulphates, a marked fall in pH and a solubilization of heavy metals [10]. The lowest pH values were reached 25 days after the spill, and the total Pb concentration at 88 days doubled or tripled (depending the soil type) the initial value of contamination in the upper 10 cm of the soils [11].

The present study provides an evaluation of the contamination processes occurring just after the removal of the tailings and part of the upper soil, to assess the behaviour of the residual Pb concentrations in the affected area at this early stage. The aim of the present work is to analyse the mobility and availability of Pb in the initial steps of the contamination process, to obtain useful information in the planning of different strategies for future remediation activities in other affected areas based on a detailed study of the soil properties.

## 2. Material and methods

After the removal of the tailings, the basin was gridded into 91 sectors of 400 x 400 m, and in the centre of each sector a plot 10 x 10 m was laid out. In every plot, soils samples were taken at the four corners and centre of this plot, at depths of 0-10, 10-30 and 30-50 cm. For each depth, 250 g of soil from the five sampling points per plot were mixed and homogenized, providing three samples per plot, for a total of 273 soil samples for the entire basin. All the samples were air dried and screened to 2 mm, and the percentages of gravels (>2mm) and fine earth (<2mm) were determined. The laboratory analyses were made with the fine-earth fraction.

Particle-size distribution was measured by the pipette method after eliminating organic matter with H<sub>2</sub>O<sub>2</sub> and dispersion with sodium hexametaphosphate [12]. The pH was measured potentiometrically in a 1:2.5 soil:water suspension, as recommended by the International Society of Soil Science, in a CRISON Digit 501 instrument. The CaCO<sub>3</sub> equivalent was determined manometrically by the Barahona method [13]. Total carbon and total sulphur were measured by dry combustion with a LECO mod. SC-144DR instrument. Organic carbon was calculated as the difference between total carbon and inorganic carbon from CaCO<sub>3</sub>. The cation-exchange capacity (CEC) was determined with 1N Na-acetate at pH 8.2 [14], measuring the sodium in a METEOR NAK-II flame-photometer. The total concentration of iron (Fe<sub>t</sub>) 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. Amorphous and poorly crystallized iron (Fe<sub>o</sub>) and aluminium (Al<sub>o</sub>) oxides were extracted with oxalic-oxalate [15] and measured by atomic-absorption spectroscopy.

Samples of air-dried soils, ground to < 0.05 mm, were digested in open flasks by strong acids (HNO<sub>3</sub>:HF in a ratio 2:3) at 160 °C till dry, and 100 ml HNO<sub>3</sub> at 4% were added. In the digested samples, total Pb (Pb<sub>t</sub>) was measured by ICP-MS with a PE SCIEX-ELAN 5000A spectrometer. A multi-element calibration standard 4 (Perkin-Elmer) was used with Rh as the internal standard. The detection limit for Pb was 0.001 µg L<sup>-1</sup>, and 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 [16]). For Pb, the mean certified value was

1162.0 mg kg<sup>-1</sup> with a standard deviation of 31.0; the mean experimental value was 1138.1 mg kg<sup>-1</sup> with a standard deviation of 11.0.

Soluble Pb (Pb<sub>l<sub>w</sub></sub>) was measured in the extract from a saturated soil paste. Pb extracted by calcium chloride 0.01 M (Pb<sub>c</sub>) using the method [17], Pb extractable by acetic acid 0.43 M (Pb<sub>a</sub>) following [18], and Pb extractable by oxalic-oxalate pH 3 (Pb<sub>o</sub>) as in [15]. For the EDTA 0.05 M extractable fraction (Pb<sub>e</sub>) method [19] were followed. The Pb of all the extracts was measured by ICP-MS.

For the statistical analysis, the SPSS 15.0 program was used. The areal distribution of the contamination was established by the algorithm of the least Euclidean, using the software Surfer 7.0.

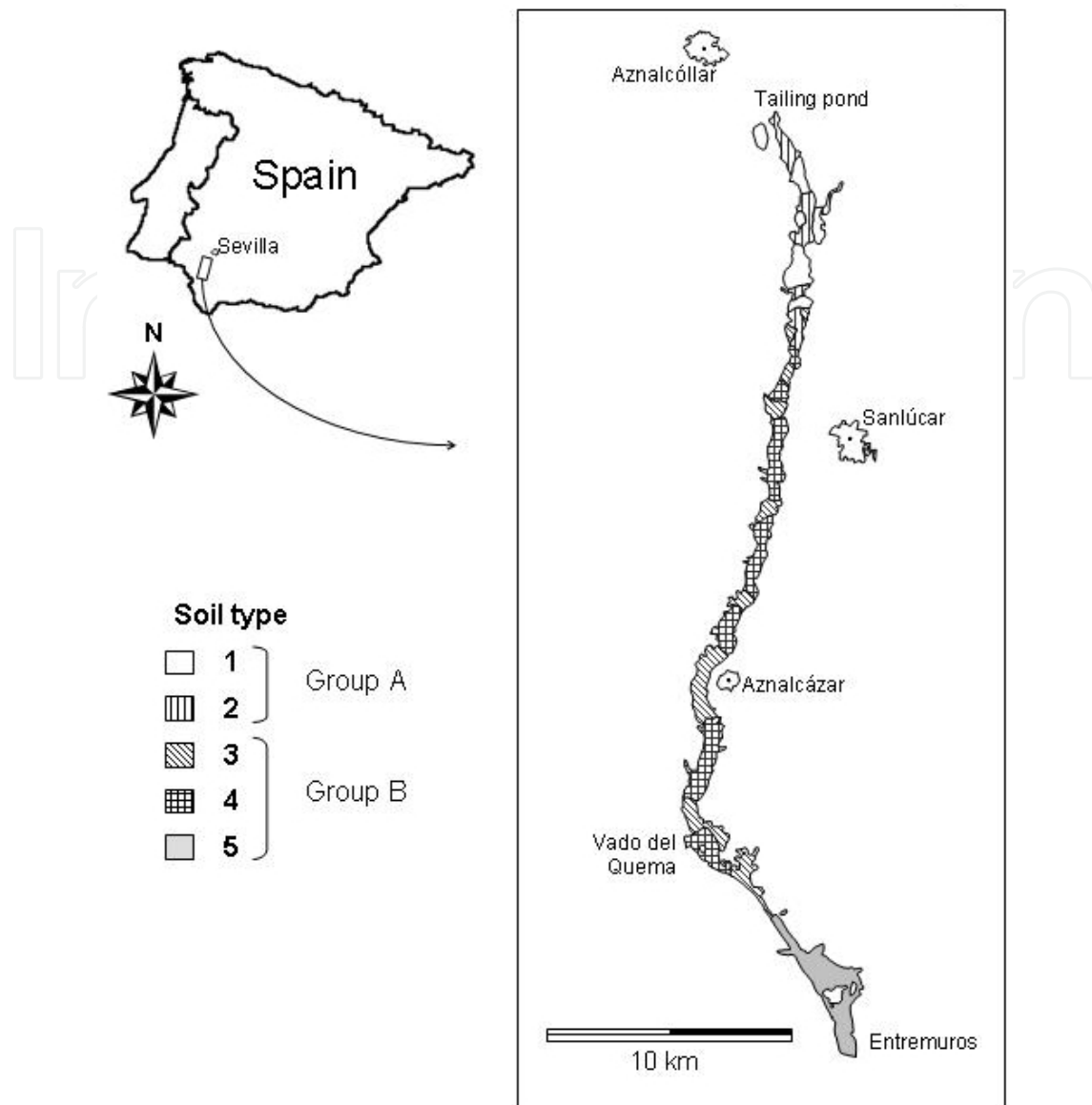
The climate of this area is typically Mediterranean (hot, dry summers; cold, wet winters; temperate autumns and springs with variable rainfall). The mean annual rainfall of 613 mm, the mean temperature of 17.7 °C, and the potential evapotranspiration of 900 mm (taken from 7 weather stations near the spill, over 27 years). The affected soils were Typic Xerofluvents and Typic Xerothents [20] developed on alluvial deposits coming from the erosion of sedimentary and metamorphic materials of the Agrio and Guadiamar River basin, mainly gravels, sands, silts and clays from the Miocene and Plio-Quaternary.

### 3. Results and discussion

We assigned five different soil types, according to the soil properties between 0 and 50 cm in depth, with significant differences ( $p < 0.05$ ) by a cluster analysis via the k-mean method (Table 1). Soil types 1 and 2 (hereafter Group A), located in the upper part of the basin, were acidic, with little or no carbonate; type 1 had a loam texture while type 2 was dominated by gravel and sand. Soil types 3, 4 and 5 (hereafter Group B) were predominantly neutral or slightly alkaline and carbonated, the main differences between them being texture (type 3, clay loam; type 4, loam; and type 5, silty clay).

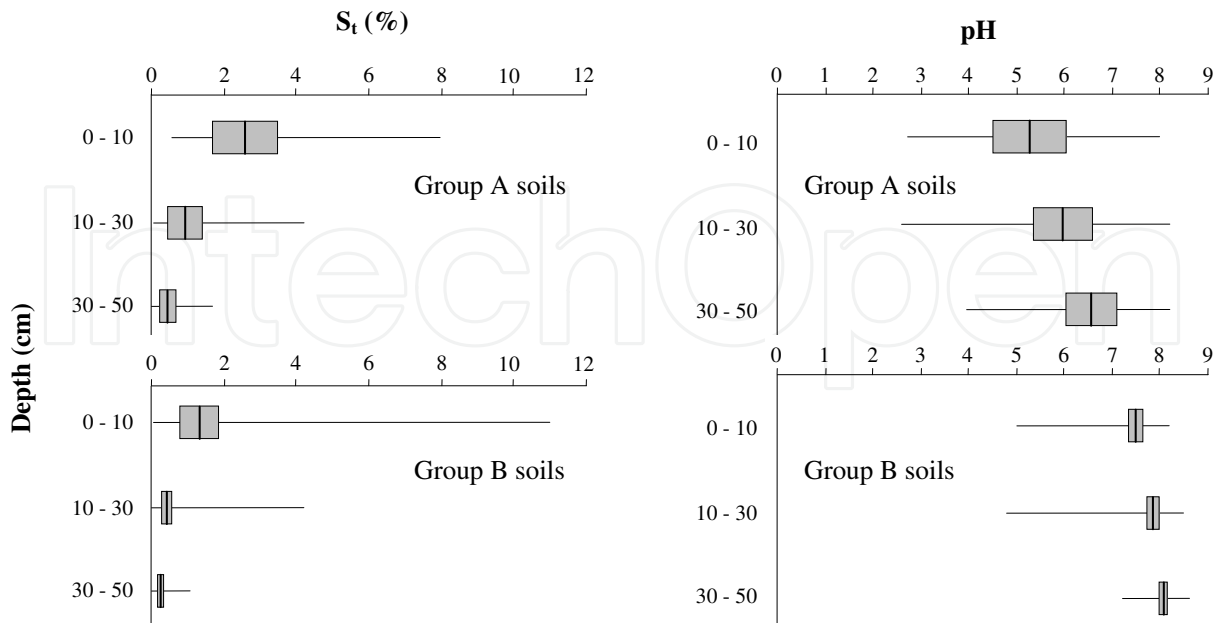
Soil type	n	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	pH	CaCO <sub>3</sub> (%)	OC (%)	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )
1	36	5.2 (3.5)	50.7 (18.4)	30.8 (14.1)	18.5 (6.9)	5.8 (1.9)	1.7 (3.5)	1.0 (0.4)	15.5 (5.8)
2	33	37.2 (24.5)	76.2 (17.1)	13.6 (9.3)	10.2 (8.6)	5.9 (1.8)	0.8 (1.7)	0.4 (0.3)	7.7 (3.7)
3	63	6.9 (9.4)	19.6 (11.2)	49.4 (9.7)	31.0 (11.2)	7.7 (0.5)	10.0 (5.0)	1.1 (0.5)	18.1 (5.2)
4	87	4.8 (8.5)	48.8 (12.6)	32.5 (9.4)	18.7 (6.0)	7.8 (0.7)	6.9 (6.3)	0.9 (0.4)	12.1 (4.2)
5	54	8.2 (9.6)	4.9 (7.1)	47.7 (11.2)	47.4 (14.0)	8.0 (0.3)	13.6 (4.9)	1.3 (0.5)	22.9 (4.9)

**Table 1.** Mean and (standard deviation) of the particle size, pH, CaCO<sub>3</sub>, organic-carbon (OC) content, and cation exchange capacity (CEC) in the different soil types (n = number of samples in each soil type).



**Figure 1.** Location of the study area, including the distribution of the different soil types analysed in Table 1. Group A include non-carbonate soils and Group B consist of carbonate soils.

As mentioned above, these soils were quite homogeneous in depth, so the variation in the soil properties with the depth were not significant in the cases of texture, calcium-carbonate content, organic-carbon content and cation-exchange capacity. Nevertheless, total sulphur content ( $S_t$ ), related to the contamination, registered its highest values in the upper 10 cm in all soil types, with values declining progressively and significantly ( $p < 0.001$ ) in depth (Fig. 1). The difference in  $S_t$  between the first 10 cm and the interval 10-30 cm was greater in Group A soils than in Group B. In addition, the contamination also affected the pH increasing the acidity towards the soil surface, and with significant differences in depth. In the Group B soils, where differences between depths were less pronounced for the presence of  $\text{CaCO}_3$ , the pH remained higher, rarely falling below 6.0 (Fig. 1).



**Figure 2.** Total sulphur content ( $S_t$ ) and pH in the two soil groups (horizontal lines range from minimum to maximum values; boxes show the confidence interval at 95% for the mean; vertical lines mark the mean values).

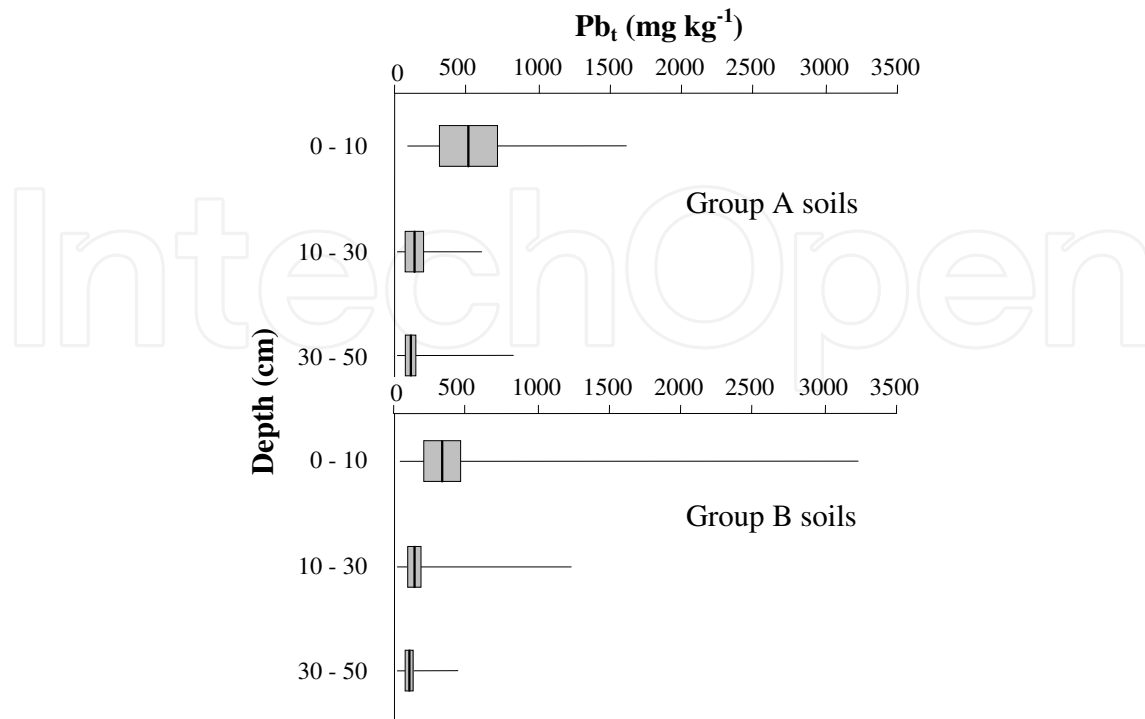
*Total Pb content*

In uncontaminated soils next to the affected area the concentrations of the total Pb ( $Pb_t$ ) were between 22.0 and 74.6 mg kg<sup>-1</sup>, with a mean value of 41.8 mg kg<sup>-1</sup> [9]. Meanwhile, in contaminated soils, the mean Pb content in the uppermost 10 cm was 385.8 mg kg<sup>-1</sup>, ranging between 35.8 and 3231.0 mg kg<sup>-1</sup>. This mean value significantly declined with depth in all soil types (Fig. 2), with a distribution similar to that of  $S_t$  (Fig.1). Consequently, in all soils, a highly significant linear relationship ( $p < 0.001$ ) was found between  $Pb_t$  and  $S_t$  (Table 2).

		$Pb_t$	
variable	value	std. Error	P value
	<b><math>r^2 = 0.832</math></b>		< 0.001
Intercept	27.58	10.95	0.012
$S_t$	22.45	0.65	< 0.001

**Table 2.** Multivariable regression model of the  $Pb_t$  (mg kg<sup>-1</sup>) and  $S_t$  (g kg<sup>-1</sup>) in all soils.

In addition, the  $Pb_t$  concentration in the 10-30 cm layer did not significantly differ from that of the 30-50 cm layer, and had values higher than unaffected soils (doubled or tripled the mean value for uncontaminated soils), which could be associated with a previous contamination in the area [21].



**Figure 3.** Total Pb content ( $Pb_t$ ) in the two soil (horizontal lines range from minimum to maximum values; boxes show the confidence interval at 95% for the mean; vertical lines mark the mean values).

In any case, the pH range as well as the  $S_t$  and  $Pb_t$  values in the upper 10 cm of the soils were very broad, indicating a highly heterogeneous contamination, as previously reported in [9]. To quantify the degree of  $Pb_t$  pollution, we used the intervention levels proposed by the Andalusian Regional Government (350 and 500 mg kg<sup>-1</sup> for agricultural soils with pH < 7 and > 7, respectively; and 1000 mg kg<sup>-1</sup> for natural parks). The soil use in the area was mainly for agriculture and grazing and, according to these levels, 15.0% of the area proved to be uncontaminated, with values below the reference level for the area (< 75 mg kg<sup>-1</sup>), 23.7% was contaminated for agricultural use, and 10.6% was seriously contaminated (> 1000 mg kg<sup>-1</sup>). The remaining 50.7% had anomalous values (above the reference level and below the intervention levels).

#### *Pb extractions*

To assess the speciation of Pb in the polluted soils, selective extractions using reagents with different strengths were used, although most of them are not specific to a given soil phase [22], they provide useful information in relation to mobility and availability of the pollutant element. The average concentration and standard deviation of the different extracted forms of Pb are shown in Table 3.

In general, water extracted forms constitute the soluble fraction [23, 24]; forms extracted with CaCl<sub>2</sub> is considered the exchangeable fraction [25, 26]; forms extracted with acetic acid is

Soil type	Depth (cm)	Pb <sub>e</sub>		Pb <sub>a</sub>		Pb <sub>o</sub>		Pb <sub>c</sub>		Pb <sub>w</sub>	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	0-10	149.29	155.50	41.16	49.52	17.92	28.14	4.00	5.94	0.32	0.24
	10-30	29.74	54.56	21.30	48.65	7.21	8.83	0.86	2.72	0.30	0.57
	30-50	13.39	17.94	7.80	10.59	4.12	5.47	0.70	1.92	0.40	0.63
2	0-10	117.96	137.29	43.48	63.77	5.61	12.60	7.74	15.42	0.39	0.35
	10-30	25.61	22.38	9.21	9.89	4.35	6.12	1.31	1.52	0.29	0.33
	30-50	19.58	28.56	18.79	32.71	4.61	4.13	1.47	3.69	0.21	0.20
3	0-10	83.00	68.52	31.59	28.93	5.36	23.32	0.49	0.49	0.58	0.98
	10-30	31.79	22.31	9.88	6.66	0.79	1.63	0.20	0.36	0.45	0.78
	30-50	29.53	20.67	8.66	9.79	1.49	5.36	0.73	1.27	0.69	1.49
4	0-10	55.21	68.16	20.29	38.82	2.11	3.23	1.61	5.46	0.74	1.32
	10-30	37.39	69.96	8.87	14.87	4.55	9.14	1.18	3.46	0.65	1.45
	30-50	26.55	27.98	7.11	9.91	4.01	8.41	0.48	0.60	1.10	2.05
5	0-10	37.86	35.56	11.56	13.09	5.65	13.49	0.80	0.76	0.17	0.50
	10-30	20.58	13.32	4.61	2.35	3.41	5.80	0.89	0.99	0.11	0.11
	30-50	15.94	14.61	4.20	3.21	2.21	4.47	0.83	0.80	0.14	0.20

**Table 3.** Mean content (mg kg<sup>-1</sup>) and standard deviation (SD) in the five soil types for Pb extracted with EDTA (Pb<sub>e</sub>), acetic acid (Pb<sub>a</sub>), oxalic-oxalate (Pb<sub>o</sub>), calcium chloride (Pb<sub>c</sub>) and water (Pb<sub>w</sub>).

used as the bio-available fraction associated with carbonates and also specifically adsorbed by oxides as well as organic matter [25, 27-29]; forms extracted with EDTA is also considered to be the bio-available fraction associated with carbonates, inorganic precipitates, amorphous oxides and organic matter [24, 27-30]; and the forms extracted with oxalic oxalate is held on, or occluded in, amorphous or poorly crystallized iron, aluminium or manganese oxides [22, 31].

The reagent that extracted the highest concentrations of Pb was EDTA (around 20 - 25 % of the total Pb), indicating that a very high proportion of the Pb forms inorganic precipitates easily complexed by this reagent, but not dissolved by acetic acid or oxalic-oxalate. When all soils were pooled, the Pb extracted with EDTA (Pb<sub>e</sub>) was related to total Pb (Pb<sub>t</sub>), sulphates (SO<sub>4</sub><sup>2-</sup>), and amorphous iron oxides (Fe<sub>o</sub>) with highly significant (p < 0.001) relationship (Table 4). Therefore, apart from the relation with the total contamination (Pb<sub>t</sub>), we can suppose that the main forms in which Pb is retained in the soils could be iron oxy-hydroxysulphates. The presence of iron compounds promote the sorption of Pb in the soil [32]; and these results are consistent with the obtained by [33] in alluvium contaminated by metal in an adjacent mining area (Tinto river basin). These authors pointed that the highest amounts of Pb of all contaminant metal-bearing minerals in the area were characterised by Fe oxy-hydroxysulphate minerals.



	value	<b>Pb<sub>e</sub></b> std. Error	P value	VIF <sup>a</sup>
<i>All soils</i>	<b>r<sup>2</sup> = 0.726</b>		< 0.001	
Pb <sub>t</sub>	0.121	0.008	< 0.001	1.689
SO <sub>4</sub> <sup>2-</sup>	0.014	0.002	< 0.001	1.552
Fe <sub>o</sub>	0.003	0.001	0.019	1.736
Group A soils	<b>r<sup>2</sup> = 0.867</b>	<b>Pb<sub>e</sub></b>	< 0.001	
Pb <sub>t</sub>	0.207	0.017	< 0.001	1.966
SO <sub>4</sub> <sup>2-</sup>	0.008	0.003	0.004	1.966
Group B soils	<b>r<sup>2</sup> = 0.651</b>	<b>Pb<sub>e</sub></b>	< 0.001	
Pb <sub>t</sub>	0.100	0.008	< 0.001	1.416
Fe <sub>o</sub>	0.006	0.001	< 0.001	1.416

<sup>a</sup> The variance inflation factor (VIF) is the reciprocal of tolerance. Values next to 1 indicate the independent variables have no redundant information.

**Table 4.** Multivariable Regression Model of the Pb<sub>e</sub> (mg kg<sup>-1</sup>), Pb<sub>t</sub> (mg kg<sup>-1</sup>), SO<sub>4</sub><sup>2-</sup> (mg kg<sup>-1</sup>) and Fe<sub>o</sub> (g kg<sup>-1</sup>) in the different soil groups.

Nevertheless, when the soils were separated into acidic (Group A) and neutral alkaline (Group B), the former correlated significantly Pb<sub>e</sub> with Pb<sub>t</sub> and SO<sub>4</sub><sup>2-</sup>, meanwhile the latter correlated Pb<sub>e</sub> with Pb<sub>t</sub> and Fe<sub>o</sub> (Table 4), indicating that the soil properties of each group are essential in the forms of Pb retention. In the case of acid soils, the relationship between Pb<sub>e</sub> and SO<sub>4</sub><sup>2-</sup> is significant, but the one with the Fe<sub>o</sub> disappear. In these soils, the pH is maintained in acidic values, so the iron released from the pyrite oxidation (Fe<sup>2+</sup>) is mobile, being able to rise and accumulate in the soil surface by the effect of the semi-arid climate of the area. This process occurs under Mediterranean climatic conditions, where the precipitation are lower than the evapotranspiration and the predominant upward movement of the soil solutions generate the formation of hard surface crusts, of scarce mm thickness and high iron concentration, observed by us in the acid soils of the affected area [34]. According to this behaviour, the Pb retention in acid soils seems to be related mainly to the precipitation as Pb sulphate (PbSO<sub>4</sub>); this retention has been already reported as the main process in the Pb immobilization from acid mine waters [35].

In the case of basic soils, the relationship between Pb<sub>e</sub> and Fe<sub>o</sub> is statistically significant, but the one with the SO<sub>4</sub><sup>2-</sup> disappears. In these soils, the presence of calcium carbonate produce the releasing of Ca<sup>2+</sup> by the acidification caused by the oxidation of sulphides, and the precipitation of gypsum (CaSO<sub>4</sub> 2H<sub>2</sub>O) is dominant. These reactions could be responsible in the disappearance of the statistical relation between Pb<sub>e</sub> and sulphates, but solubility of

gypsum allows to maintain certain amounts of soluble sulphates ( $1.51 \cdot 10^{-2}$  M, at 25 °C), so the formation of other types of sulphates is possible, being the presence of jarosite  $[KFe_3(SO_4)_2(OH)_6]$  common in this type of contamination [36]. In addition, the basic values of the pH encourage the precipitation of iron oxy-hydroxydes, but the Pb retention by poorly crystalized iron oxides in our basic soils, seems to be less important than the one produced by iron oxy-hydroxysulphates [37]. In fact, the concentration of Pb extracted by oxalic-oxalate ( $Pb_o$ ) is very low (between 1 and 3% of the total Pb). According to these results, we suppose that the main Pb-bearing mineral in basic soils should be plumbojarosite  $[PbFe_6(SO_4)_4(OH)_{12}]$ . The formation of this mineral has also been described in others sulphide mine contamination of the area [33, 38].

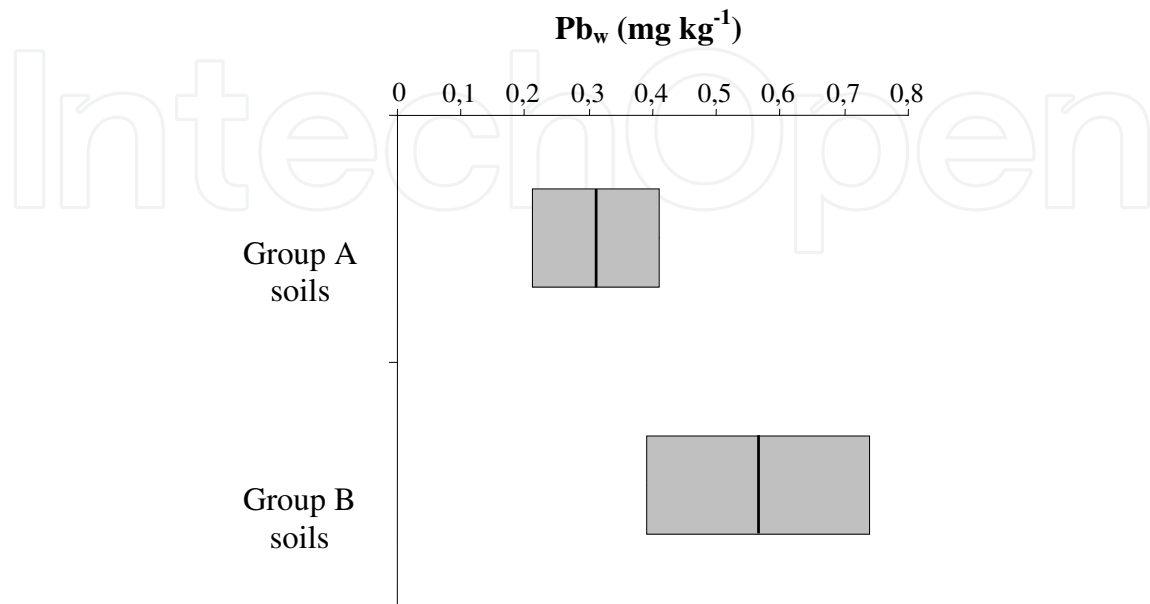
The Pb extracted with calcium chloride ( $Pb_c$ ) in Group A soils was significantly related only to the percentage of clay fraction (Table 5). This implies that, in acid soils, a little fraction of Pb is retained by the clay fraction as easily exchangeable forms. On the contrary, in Group B soils, the  $Pb_c$  was nor significantly related to any of the properties studied, but only to the Pb soluble in water ( $Pb_w$ ). In addition, if we compare the amounts of  $Pb_c$  to the amounts of  $Pb_w$  in basic soils, we note that there are no statistical differences between the two forms.

		$Pb_c$	
<i>Group A soils</i>	value	std. Error	P value
	<b><math>r^2 = 0.836</math></b>		0.011
Intercept	0.807	0.066	0.029
clay	0.058	0.013	0.011
		<b><math>Pb_w</math></b>	
<i>Group B soils</i>			
	<b><math>r^2 = 0.871</math></b>		< 0.001
Intercept	1.304	0.122	< 0.001
clay	- 0.024	0.004	< 0.001

**Table 5.** Multivariable Regression Model of the  $Pb_c$  ( $mg\ kg^{-1}$ ) and clay (%) in acid soils (Group A); and  $Pb_w$  ( $mg\ kg^{-1}$ ) and clay (%) basic soils (Group B).

Soluble in water Pb ( $Pb_w$ ) was not significantly related to any of the soil properties in Group A soils, while in Group B soils,  $Pb_w$  proved to be negatively and significantly related to the clay fraction (Table 5), implying the retention of the soluble Pb forms by this soil fraction. This decrease in availability of Pb in relation to clay content is in agreement with the described by [39], although the type of clay should be studied in more detail [40]; in this way, high illite content has been described as an efficient mineral in the adsorption of Pb in soils [41]. Finally, we found that the concentrations of  $Pb_w$  was generally higher in basic soils in relation to the acid ones (Fig. 3), being this difference between groups statistically significant ( $p < 0.05$ ). This finding contradicts the usual increase in Pb solubility in acidic conditions [42, 43]. Therefore,

this variation could be related to the apparent solubility and stability of the iron oxy-hydroxides precipitated at different values of pH [44, 45], but more detailed studies are carrying out to verify this point.



**Figure 4.** Soluble Pb content ( $Pb_w$ ) in the two Group of soils (A: acid, B: basic). (boxes show the confidence interval at 95% for the mean; vertical lines mark the mean values).

#### 4. Conclusions

The mobility and solubility of Pb in the contaminated soils of this study is mainly controlled by the soil properties and ageing (oxidation) of the pyrite tailings. Regardless of the soil type, the Pb accumulates mainly in the top of the soils without contaminating the subsoil or groundwater. The climatic conditions (semi-arid Mediterranean climate) produce the upward movement of the soil solutions, which cause the formation of surface crusts but only in acidic soils (where the iron and contaminants remain soluble in higher proportion). The main Pb-bearing mineral in acid soils should be Pb-sulphates, and in basic ones should be iron hydroxysulphates (mainly plumbojarosite). The amounts of Pb retained by iron oxyhydroxides are very little in all soil types. The soluble Pb is significantly higher in basic soils than in acid ones, which contradict the normal behaviour of this contaminant in soils. According to the obtained results, more detailed studies in relation to the solubility and stability of the different phases precipitated at the early stages of the contamination are required, to improve the applications in the future of adequate remediation measurements in similar affected areas.

## Author details

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