

## REMEDIATION OF Pb-CONTAMINATED SOILS IN THE GUADIAMAR RIVER BASIN (SW SPAIN)

J. AGUILAR\*, C. DORRONSORO, E. FERNÁNDEZ, J. FERNÁNDEZ, I. GARCÍA,  
F. MARTÍN and M. SIMÓN

*Departamento de Edafología y Química Agrícola, Facultad de Ciencias, Universidad de Granada,  
Granada, Spain*

*(\* author for correspondence, e-mail: aguilar@ugr.es, Fax: +34 958 244160)*

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**Abstract.** Soil remediation has been studied after a spill from a settling pond of a pyrite mine in Aznalcóllar (SW Spain). The affected area was approximately 55 km<sup>2</sup> and extended about 40 km from the spill. The Pb concentration in soils ranged from 35.8 to 3231.0 mg kg<sup>-1</sup>, with a mean value of 385.8 mg kg<sup>-1</sup>. The remediation techniques investigated included: manual and mechanical removal of the contaminated soil, mixing the upper part of the soils by ploughing, and addition of different amendment materials to reduce the Pb solubility, such as carbonates, zeolites, iron-rich soils, bentonites and yeasts. A combination of liming with iron-rich soils proved the most effective treatment.

**Keywords:** Guadiamar river, lead, soil contamination, soil remediation

### 1. Introduction

On 25 April 1998 the holding pond of a pyrite mine in Aznalcóllar, SW Spain (Figure 1), broke open, spilling  $36 \times 10^5$  m<sup>3</sup> of acidic water and  $9 \times 10^5$  m<sup>3</sup> of toxic tailings into the Guadiamar river basin, affecting approximately 55 km<sup>2</sup> (Simón *et al.*, 1998). The main affected soils, Fluvisols and Regosols (CSIC-IARA, 1998), were covered with a layer of tailings averaging 7 cm thick and containing high concentrations of Zn, Cu, Cd, As, Pb, Sb, Bi and Tl.

The soils were polluted in two stages. First, tailings and acidic waters covered and penetrated the soils; approximately 75% of the Pb contamination in the soil came from the tailings, whereas the remaining 25% was attributed to the acidic waters (Simón *et al.*, 1999). In the second stage, the oxidation of the pyrite tailings released high concentrations of Pb which entered the soil and increased Pb content in the uppermost 10 cm by two- to three-fold (Simón *et al.*, 2001). Four months after the spill, the tailings were removed from the upper part of the soils using heavy machinery. However, both the action of the machinery and the rainfall during this period caused the tailings to penetrate the soils, increasing pollution with a highly irregular distribution pattern.

Whereas the Pb content of uncontaminated soils of the area ranged from 22.0 to 74.6 mg kg<sup>-1</sup>, with a mean of 41.8 mg kg<sup>-1</sup>, (Simón *et al.*, 1999), the contaminated



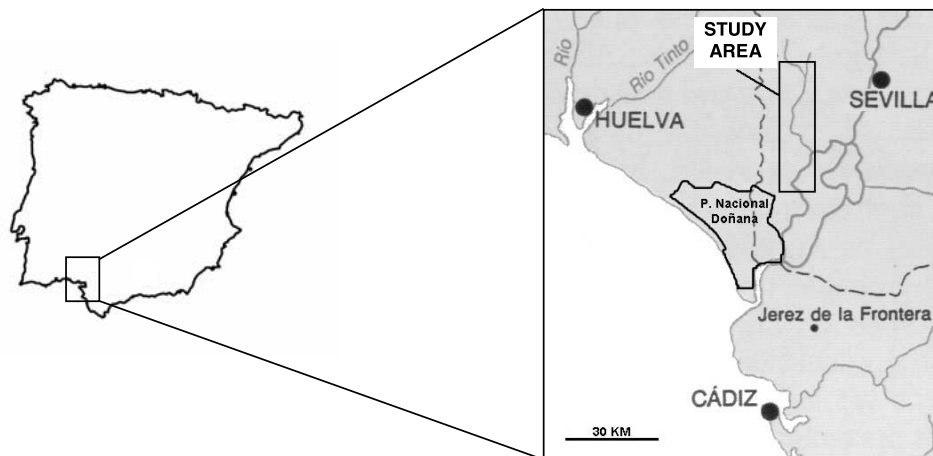


Figure 1. Location of the study area.

soils, after the removal of tailings (the first remediation measure), registered a mean Pb concentration of  $204.1 \text{ mg kg}^{-1}$  in the upper 50 cm, and  $385.8 \text{ mg kg}^{-1}$  ( $35.8\text{--}3231.0 \text{ mg kg}^{-1}$ ) in the uppermost 10 cm.

The aim of the present work is to assess the pollution of soils in the Guadiamar river basin and seek remediation measures appropriate to local conditions (Mediterranean climate in flood-plain soils).

## 2. Materials and Methods

The study area is located on the Guadiamar river flood plain affected by the spill (Figure 1). The mean annual temperature is  $17.7 \text{ }^\circ\text{C}$ , the mean annual precipitation exceeds slightly 600 mm, and the potential evapotranspiration values reach 900 mm. Thus, the temperature regime is thermic and the moisture regime xeric (USDA, 1999).

The total contamination was studied with a sampling network established on a grid of  $400 \times 400 \text{ m}$  covering the affected area. At each intersection and in the centre of each cell, a square ( $10 \times 10 \text{ m}$ ) was sampled (4 corners and centre pooled) at three depths: 0–10, 10–30 and 30–50 cm.

Two laboratory experiments and one field experiment were performed to analyse the possible remediation measures.

- (1) *Neutralization tests*: In the laboratory, increasing amounts of carbonate materials (cellulose ash, sugar-refinery scum, sewage sludge, pure  $\text{CaCO}_3$ ) were added to a contaminated soil of the area, until approaching soil pH 7. Afterwards, the tailings from the same contaminated soil were oxidized with  $\text{H}_2\text{O}_2$

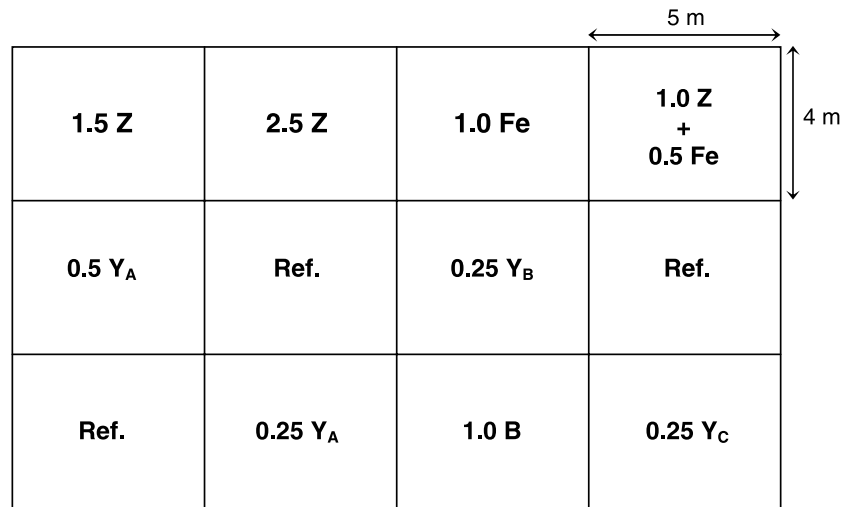


Figure 2. Application scheme of the field experiment (amendment materials: Fe = iron oxides, Z = zeolites, B = bentonites, Y = yeasts type A, B and C; the number accompanying the symbol indicates the application rate in  $\text{kg m}^{-2}$ ; Ref. = reference plots, untreated).

(5 g soil + 100 mL  $\text{H}_2\text{O}_2$  at 15%), and neutralized with increasing amounts of cellulose ash.

- (2) *Soil-properties test*: In the laboratory, soil properties were evaluated with respect to Pb retention. Different soil samples (2 replicates) were selected as characteristic of a given soil property: pH,  $\text{CaCO}_3$ , organic matter (OM), clay, free-iron ( $\text{Fe}_d$ ). A pollutant solution was prepared by adding 1000  $\text{cm}^3$  of  $\text{H}_2\text{O}_2$  (15%) to 10 g of tailings from the area (Urrutia *et al.*, 1992). 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. Pb retention by soils was determined as the difference between the Pb concentration in the initial pollutant solution and the final soil-sample solution.
- (3) *Field experiment*: In one of the most polluted sectors (Vicario), test plots of  $4 \times 5$  m were treated with different amounts of various amendment materials: iron oxides (Fe), zeolite (Z), bentonite (B) and yeasts (Y). The application scheme appears in Figure 2. In each plot, samples (collected from 5 sampling points) were taken on three different dates in 1999 (29 March, 17 May and 29 September) and total, water-soluble and EDTA-extractable Pb were analysed.

Field descriptions of soils were based on the Soil Survey Staff (1951). Particle-size distribution was determined by the pipette method after elimination of organic matter with  $\text{H}_2\text{O}_2$  and dispersion with sodium hexametaphosphate (Loveland and Whalley, 1991). The pH was measured potentiometrically in a 1:2.5 soil:water suspension. The  $\text{CaCO}_3$  equivalent was determined by the method of Bascomb (1961). Total carbon was analysed by dry combustion with a LECO SC-144DR instrument,

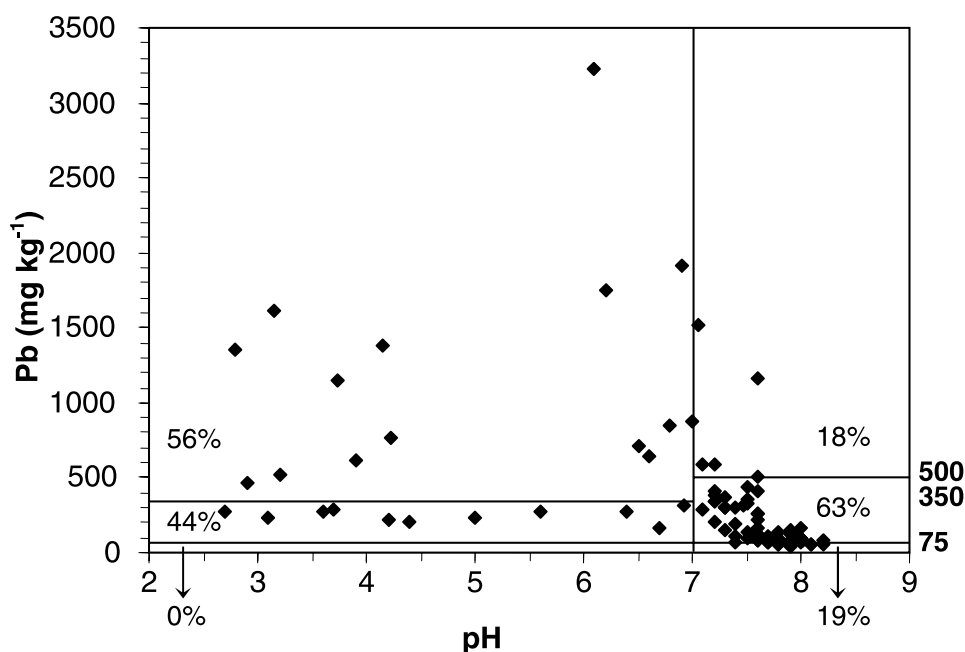


Figure 3. Total Pb concentration and percentage of soil samples exceeding permitted levels for agricultural soils ( $350 \text{ mg kg}^{-1}$  for  $\text{pH} < 7$  and  $500 \text{ mg kg}^{-1}$  for  $\text{pH} > 7$ ) and the uncontaminated soils of the area ( $>75 \text{ mg kg}^{-1}$ ) after the removal of the tailings.

and organic carbon (OC) estimated as the difference between total carbon and inorganic carbon from  $\text{CaCO}_3$ . Free-iron oxides ( $\text{Fe}_d$ ) were extracted with citrate dithionite (Holmgren, 1967) and measured by atomic absorption spectroscopy in a Perkin Elmer 305B instrument. Soil samples, finely ground ( $<0.05 \text{ mm}$ ), were digested in strong acids ( $\text{HNO}_3 + \text{HF}$ ) and the Pb was determined by ICP-MS with a Perkin Elmer Sciex-Elan 5000A spectrometer.

For the speciation of Pb forms, extractions were made with EDTA (Quevauviller *et al.*, 1998) to estimate the bioavailable Pb (Sposito *et al.*, 1982), and with distilled water in a soil-water saturation extract to estimate the soluble Pb.

### 3. Results and Discussion

After the analysis of the pyrite spill, limits for Pb pollution in agricultural soils were posed, taking into account the existing legislation in other countries (GRER, 1996; Kloke *et al.*, 1994; Sheppard *et al.*, 1992; Adriano *et al.*, 1997):  $350 \text{ mg kg}^{-1}$  in soils with  $\text{pH} < 7$  and  $500 \text{ mg kg}^{-1}$  for soils with  $\text{pH} \geq 7$  (Aguilar *et al.*, 1999). After the tailings were removed, 56% of the acidic soils and 18% of the basic soils had Pb concentrations exceeding these levels (Figure 3). The remaining 44% of the acidic soils and 63% of the basic soils surpassed the highest value of the

TABLE I

Percentage of soil samples in the Guadiamar river basin exceeding permitted levels after the removal of tailings

	Natural Park use <sup>a</sup>	Agricultural use		
	Total Pb	Total Pb <sup>b</sup>	Soluble Pb <sup>c</sup>	EDTA Pb <sup>d</sup>
% Soil samples above intervention level	15	26	10	25

<sup>a</sup> 1000 mg kg<sup>-1</sup>.

<sup>b</sup> 350 mg kg<sup>-1</sup> for pH < 7 and 500 mg kg<sup>-1</sup> for pH > 7.

<sup>c</sup> 1 mg kg<sup>-1</sup>.

<sup>d</sup> 100 mg kg<sup>-1</sup>.

uncontaminated soils of the area (75 mg kg<sup>-1</sup>). Based on these results, the Regional Government of Andalusia (Spain) prohibited the agricultural use of these soils.

In the case of soluble Pb, the maximum permitted level, 1 mg kg<sup>-1</sup> (Ewers, 1991), was exceeded in 10% of the soils of the area. For EDTA-extractable Pb, we set a maximum level of 100 mg kg<sup>-1</sup> (extrapolated from the limits for total Pb), 25% of the total area surpassing this value. These values (summarized in Table I) clearly indicate the need of soil remediation throughout the basin.

The following remediation measures were considered most appropriate: (a) Cleanup, i.e., further soil removal and reduction of pollution concentration by tilling; (b) Pb immobilization by liming and adding other amendment materials.

For the cleanup, soils were removed to approximately 10 cm in the acidic area and tilled to a depth of 25 cm, thereby reducing the mean Pb concentration in the remaining uppermost 10 cm from 526.4 to 398.6 mg kg<sup>-1</sup>. However, despite the substantial reduction, the Pb content remained too high for agricultural use in large parts of the affected area.

As no further cleanup was feasible, remediation focused on the immobilization of Pb. For this, the soil parameters related to the fixation and retention of Pb were analysed. Experiments were conducted using soil horizons containing different contents in OM, clay, CaCO<sub>3</sub>, pH and Fe<sub>d</sub> (Table II). A solution from the oxidation of tailings (Pb concentration 3.20 mg dm<sup>-3</sup>, pH 1.65) were added to each sample. The results (Figure 4) show that Pb was retained in large quantities in all the soil samples, but more effectively in carbonate soils (95–98%), followed by iron-rich and clayey soils (75–82%). The soils with the lowest pH and without carbonates showed the least Pb retention (8–25%). According to these results, the most important soil property in Pb retention in all the soils is CaCO<sub>3</sub>, and therefore the first recommended measure to immobilize this metal is liming.

The amount of liming would depend on the CaCO<sub>3</sub> content, as well as on the pH and pyritic sulphur content of the soils to be treated. Therefore, different neutralization curves resulted for a contaminated soil from the area (pH 4.0) by the

TABLE II  
 Characteristics of the soil horizons treated with the pollutant solution prepared from the tailings oxidation

Soil	O.M. (%)	Clay (%)	CEC ( $\text{cmol}_c \text{ kg}^{-1}$ )	Fed (%)	pH	CaCO <sub>3</sub> (%)
11	5.20	13.3	10.23	1.08	7.56	0.0
12	4.24	13.2	8.03	1.18	7.41	0.0
21	1.59	13.0	5.00	2.50	5.72	0.0
22	1.93	13.3	5.49	2.15	4.86	0.0
31	2.83	8.2	5.48	1.70	7.25	0.0
32	1.69	19.7	7.30	1.37	7.86	0.0
41	0.69	33.1	7.30	2.47	7.20	0.0
42	0.79	57.6	13.50	3.63	7.09	0.0
51	0.45	5.5	2.56	0.74	8.86	0.0
52	0.55	5.1	2.56	0.55	8.60	0.0
61	0.55	5.2	2.56	0.32	9.04	22.0
62	0.46	5.9	2.19	0.39	8.68	16.0

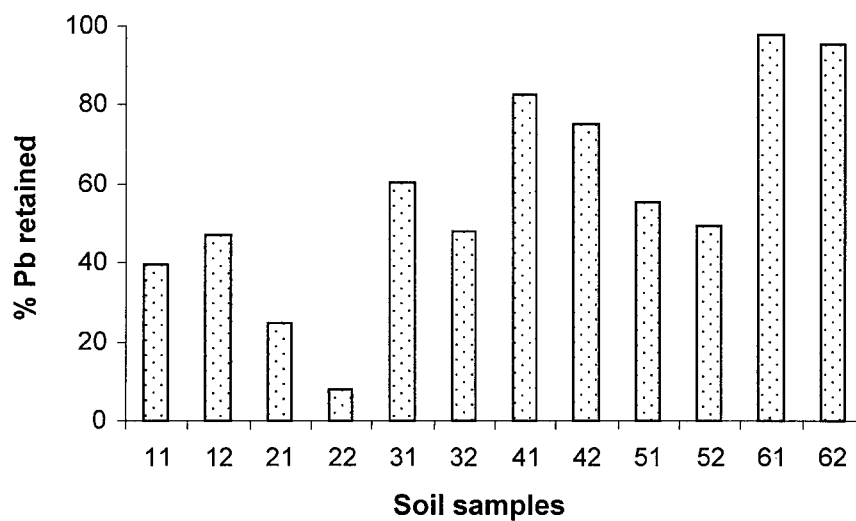


Figure 4. Percentage of retained Pb in the different soil samples of Table II.

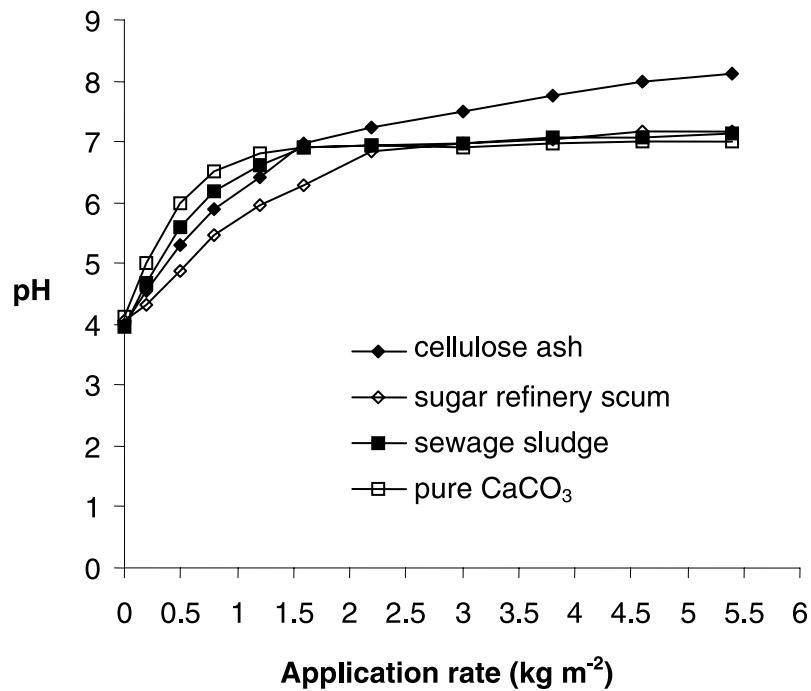


Figure 5. Neutralization curves of an affected soil (pH 4) by the addition of increasing amounts of carbonate materials.

addition of different carbonate amendment materials (pure CaCO<sub>3</sub>, sewage sludge, sugar-refinery scum, and cellulose ash). The soil pH increased proportionally to the carbonate in the amendment material. Soil neutralization was achieved at application rates of 1.2 kg m<sup>-2</sup> (pure CaCO<sub>3</sub>) to 2.2 kg m<sup>-2</sup> (sugar-refinery scum). For cellulose ash and sewage sludge, the neutralization was reached at roughly 1.6 kg m<sup>-2</sup> (Figure 5).

In all cases, pyritic sulphur remained in the soils at a mean concentration of 1.65%, ranging between 0.01 to 10.92%. The progressive oxidation of this sulphur would cause acidification and thereby require a higher rate of liming. To simulate this situation, we induced the total oxidation of sulphur in the soil sample by adding H<sub>2</sub>O<sub>2</sub>, whereupon the liming needed to reach neutrality approached 12 kg m<sup>-2</sup> in the case of cellulose ash (roughly 8-fold the initial rate). This result implies that about 2 kg m<sup>-2</sup> of amendment material, the initial rate applied in many affected areas, would be insufficient to neutralize the potential acidity generated by the oxidation of sulphur in the acidic soils. Therefore, in many soils this treatment should be repeated 6 or 7 times in order to reach stable neutralization (Figure 6).

According to these results, and given that the materials tested had similar neutralization capacities, the use of sugar-refinery scum is recommended for the following reasons: (1) low cost; (2) gradual change in pH for more efficient Pb stabilization; (3) restoration of organic matter lost during the cleanup.

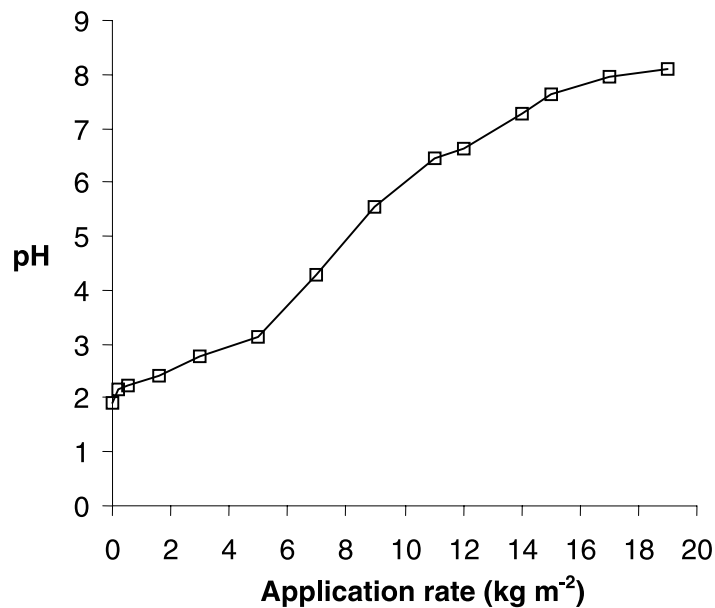


Figure 6. Neutralization curve after total oxidation of sulphur in the same soil sample of Figure 5, by increasing amounts of cellulose ash.

Even with the application of  $16 \text{ kg m}^{-2}$  of sugar-refinery scum, certain amounts of Pb would still remain in free forms. One year later, 10% of the samples treated at this rate had values of soluble Pb higher than  $0.5 \text{ mg kg}^{-1}$ , while 25% of the same samples had values of EDTA-extractable Pb higher than  $100 \text{ mg kg}^{-1}$ .

For the identification of other compounds that retain Pb, 12 test plots were laid out in the Vicario sector (northern part of the basin), where the soils have no calcium carbonate. Different amounts of iron, zeolite, bentonite and different types of yeast were added to the plots, without using liming materials. The soils of these plots were analysed for total Pb before treatment (3 March 1999; Figure 7) and also for soluble Pb three times afterwards (29 March, 17 May and 29 September 1999). The results for the soluble Pb (Figure 8) reflect the great spatial variability of the contamination and reveal that the most effective reduction resulted with zeolites, iron, and the mixture of iron and zeolites. Because of the proximity of red soils in Aljarafé area (calic Rhodoxeralf), with high amounts of free iron oxides and clays, these materials were selected as the best agents in the Pb-remediation treatments of the affected area.

#### 4. Conclusion

The cleanup and tilling of the soils affected by the toxic spill from the pyrite mine in Aznalcóllar (S Spain) were insufficient measures in many sectors to reduce the



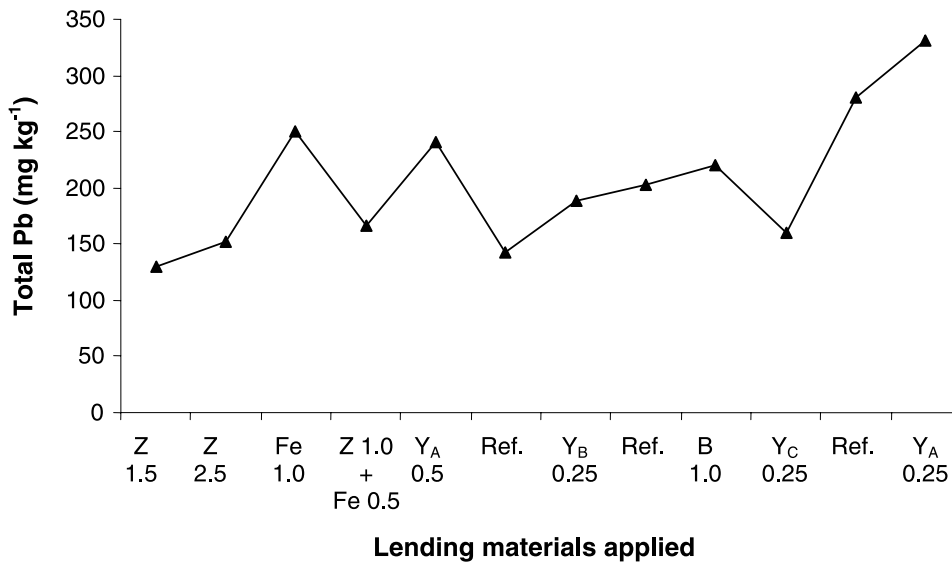


Figure 7. Total Pb concentrations (mg kg<sup>-1</sup>) in the experimental plots before the treatments (3 March 1999). (amendment materials: Fe = iron oxides, Z = zeolites, B = bentonites, Y = yeasts type A, B and C; the number accompanying the symbol indicates the application rate in kg m<sup>-2</sup>; Ref. = reference plot, untreated).

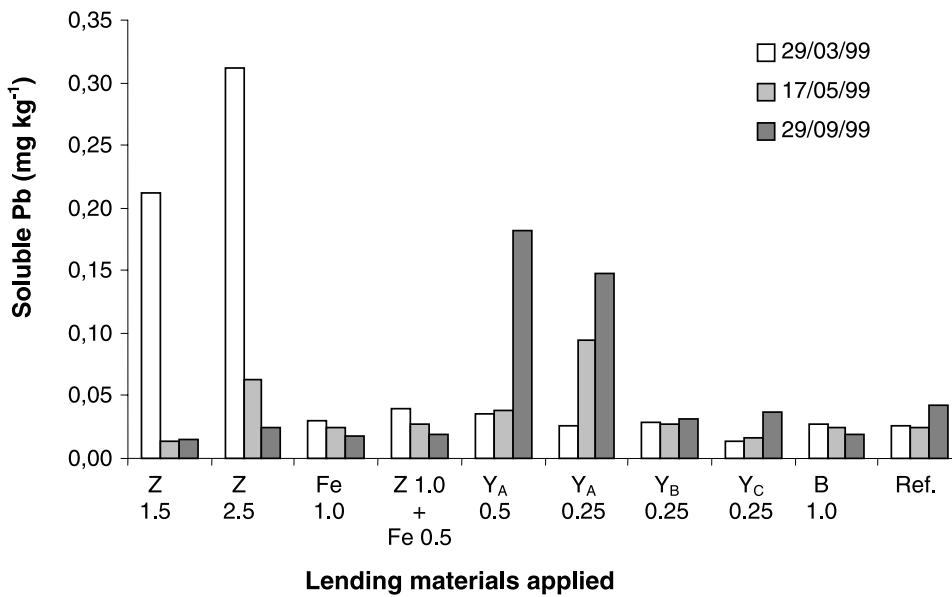


Figure 8. Soluble Pb (mg kg<sup>-1</sup>) in the experimental plots in the three sampling dates (amendment materials: Fe = iron oxides, Z = zeolites, B = bentonites, Y = yeasts type A, B and C; the number accompanying the symbol indicates the application rate in kg m<sup>-2</sup>; Ref. = reference plots, untreated).

Pb concentration to below the permitted limits for agricultural soils. According to our results, the most important soil property in Pb retention was CaCO<sub>3</sub> content. The initial application rate of 2 kg m<sup>-2</sup> of carbonate amendment material (sugar-refinery scum) would be insufficient to neutralize the sulphur remaining in soil. Therefore, this treatment should be repeated 6 or 7 times in order to reach stable neutralization. The experiments to identify the other compounds indicate that free-iron oxides, supplied by the red soils of the Aljarafe area, were the most effective in the Pb retention.

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