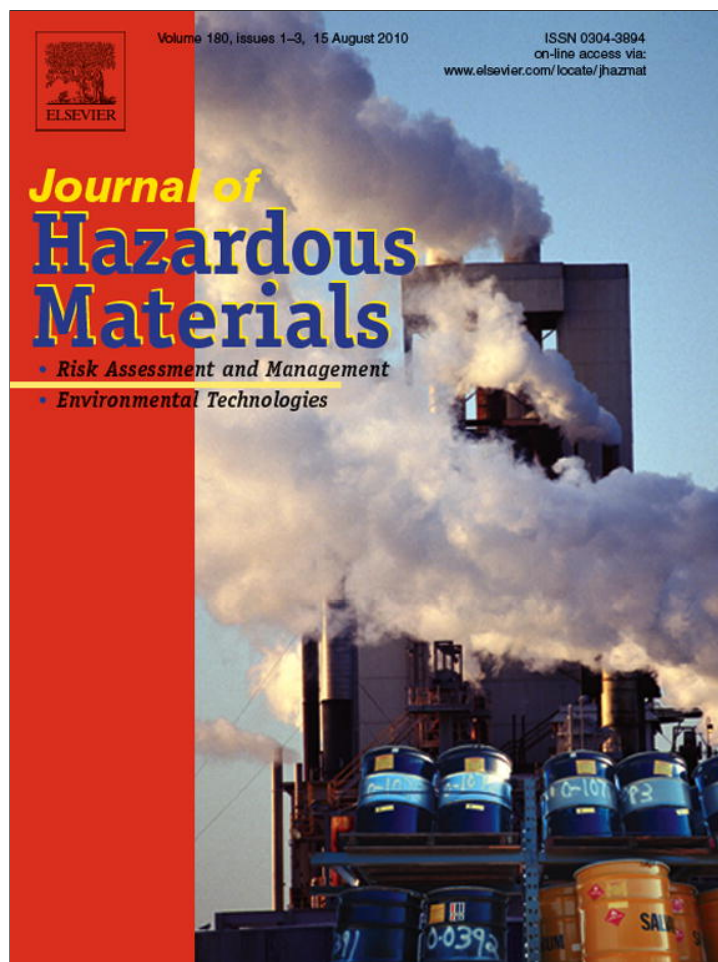


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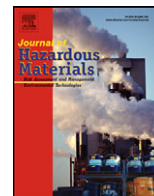
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Use of liming in the remediation of soils polluted by sulphide oxidation: A leaching-column study

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ABSTRACT

Pure CaCO₃ in ascending quantities was added to a soil to study the effect of liming after contamination by an acidic solution from the oxidation of pyrite tailings. The samples were placed in percolation columns, and soils and leachates were monitored. In the soil samples, the mineralogy, pH, CaCO₃, iron, and total content in Cu, Zn, As, Cd, and Pb were determined. The presence of CaCO₃ in the soils considerably limited their acidification, favouring the precipitation of Cu, Zn, and Cd, and promoting precipitation of iron and SO₄²⁻ ions in the form of iron hydroxysulphates and gypsum. The iron hydroxysulphates tended to retain the less mobile elements (As, and Pb) near the top of the soil. The more mobile elements (Zn, Cd and Cu) precipitated in deeper layers, directly related mainly to the CaCO₃ added and to pH. The CaCO₃ clearly did not reduce Zn and Cd toxicity effectively enough, given that the concentrations of both elements were above the toxic level in all leachates. The amounts of liming needs to be properly controlled, as excessively high pH limits As fixing, at the same time as the effectiveness of CaCO₃ is limited by coating precipitation, reducing its capacity to react with the acidic solution.

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1. Introduction

Soil can be considered an open system that exchanges matter and energy with the atmosphere, hydrosphere, lithosphere, and biosphere. Being one of the essential media in which most human activity takes place, soil is vital not only for its natural role in the environment but also for its use and management by humans. Therefore, it is fundamental to avoid soil degradation, including pollution, for its conservation for the future.

Soil is considered polluted when its buffer capacity for one or several substances is exceeded and, therefore, becomes the focus of problems for other elements in the ecosystem [1]. In this case, the biogeochemical soil equilibrium is altered, and abnormal quantities of some elements trigger changes in the physical–chemical–biological soil properties, generating a toxicological risk to the environment. The trace-element concentration in soil should be related to the parent-material composition (geochemical background) and to soil processes. Human activity may increase the content of some elements in the soil to potentially polluting concentrations. Anthropogenic inputs, such as fertilizers and pesticides [2,3], residual sludge [4,5], or urban solid wastes, mining activities [6,7], and atmospheric transport–deposition [8,9] are the

main sources of increased trace-element concentrations which can exceed toxic levels in the soil.

The risks that these elements pose to ground-water quality and the ecosystem depend on their availability and mobility through the soil profile. In turn, the availability and mobility of heavy metals depend on (i) chemical properties such as soil pH and redox potential, which affect chemical speciation and solubility [10], (ii) solute–solute interactions such as metal complexation with either organic or inorganic species [11], (iii) soil-surface characteristics and metal–soil interactions, affecting sorption reactions [12], and (iv) physical soil properties affecting water movement [13]. Metal-complexation reactions and metal–soil interactions are, in turn, affected by pH and redox conditions, further affecting metal solubility [14].

Many mechanisms for the recuperation of polluted soils by physical, chemical, and biological treatments have been studied [15]. Chemical immobilization mechanisms are based on increased adsorption of the metal, formation of insoluble metallic compounds, precipitation, and redox reactions. Reduced mobility of the pollutant reduces the risk of surface and groundwater pollution, and improves soil properties. In this way, column studies have frequently been used to provide information about element release and transport in soil, chemistry of soil and leachates, and for kinetics and mass-balance studies [13,16–19]. This type of study is suitable for analysing the pollution process and assessing the influence of remediation measurements.

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Table 1
Mean values (M) and standard deviation (SD) of pH, CaCO₃ content, chroma, and free (Fed) and amorphous (Feo) iron forms in the soils after the contamination process.

Sample	pH M (SD)	%CaCO ₃ M (SD)	Chroma M (SD)	%Fed M (SD)	%Feo M (SD)
SB0	2.7 (0.1)	0.00 (0.00)	3 (0.0)	0.86 (0.17)	0.46 (0.25)
SB2	3.1 (0.4)	0.77 (0.05)	5.5 (1.0)	1.41 (0.27)	1.02 (0.18)
SB4	4.5 (1.3)	1.23 (0.69)	5.5 (0.5)	1.50 (0.25)	1.18 (0.42)
SB6	5.2 (1.2)	2.02 (1.25)	6.5 (1.5)	1.77 (0.50)	1.34 (0.67)
SB8	5.8 (0.6)	3.20 (1.89)	6.5 (1.5)	1.62 (0.59)	1.49 (0.68)
SB10	6.1 (0.9)	4.49 (2.33)	6.5 (1.5)	1.54 (0.77)	1.52 (1.03)

The aim of this paper is to examine the changes that take place in the chemistry of a soil artificially polluted with a solution coming from the oxidation of pyrite tailings. The selected soil has a low neutralization power and was analysed after the addition of increasing amounts of calcium carbonate to evaluate their effect on the retention of contaminants by the soil, and to assess the composition and toxicity of leachates. The results can contribute to the knowledge of the effect of liming in the remediation of polluted soils by acidic solutions from sulphide mining-related activities.

2. Materials and methods

2.1. Soil and pollutant solution

The experiment was carried out using the surface horizon (Ap) of a soil (SB) classified as Haplic Cambisol (Eutric) [20], which developed over sedimentary materials in the fluvial terrace of the Guadiamar river in the locality of Soberbina in the Province of Seville (Spain). The sample was air-dried at 20 °C to constant weight, then ground and sieved (2-mm mesh), prior to preparing the soil column. This soil sample has a moderately low buffer capacity. The main properties are pH close to neutral (7.6), cation-exchange capacity (CEC) 16.3 cmol (+) kg⁻¹, base saturation about 70%, organic-carbon content below 3 g kg⁻¹, sandy loam texture, low gravel content (7%), no carbonate, and 10YR 5/3 colour. The soil background concentrations of Pb, Cu, Zn, As, and Cd were 32.0, 32.2, 44.6, 10.5, and 0.14 mg kg⁻¹ respectively. The major element concentrations (%) were: 36.5 Si, 5.17 Al, 2.39 Fe, 0.85 Ca, 0.37 Mg, 0.63 Na, and 1.21 K.

A pollutant solution (PS) was prepared by adding 1000 cm³ of H₂O₂ (15%) to 10 g of pyrite tailings and after 3 days the solution was removed, the pH measured (1.8), and the sediment discarded. The element concentration in the PS (mg dm⁻³) was: SO₄ 15078, Fe 4360, Al 290, Ca 9.6, Mg 222, Zn 718, As 135, Cu 136, Pb 3.6, and Cd 2.6.

2.2. Column study

Six samples were prepared for the column study, one with the original sample (SB0) and the other with increasing amounts of CaCO₃ (2, 4, 6, 8, and 10%), labelled SB2, SB4, SB6, SB8, SB10, respectively. All samples were inserted in 10-cm-long glass columns with an inner diameter of 3.5 cm narrowing towards the bottom to an inner diameter of 0.4 cm. The bottoms of the columns were filled with fibreglass to keep the soil in. All soil columns were 5 cm high. The top of the column was covered with a 2-cm layer of fibreglass to facilitate uniform flow.

Afterwards, 50 cm³ of PS were added to each column with a 10 cm³ h⁻¹ flow in the dark to inhibit algal growth [21]. This addition was repeated three times every 5 days. The pH of the leachates collected after each addition was measured, and the solutions were immediately vacuum-filtered through 0.45-μm-pore cellulose filters into PyrexTM flasks previously washed with acid, and stored at <4 °C until analysed.

Once the contamination process was completed, the column was laid out horizontally, and cut into 0–1, 1–2, 2–3, 3–4, and 4–5-cm sections. These subsamples were then air-dried, stored in plastic bags, homogenized by shaking, weighed, and prepared for further analyses.

2.3. Analytical methods

Analyses were made with the <2-mm fraction. In the original and amended soil samples, pH was measured potentiometrically in a 1:2.5 soil:water suspension. In the fraction finer than 50 μm (silt and clay) particle-size distribution was analysed by the pipette method [22], and in the fraction between 50 μm and 2 mm (sand), by sieving. Calcium carbonate content was measured by the Williams method [23]. Sample colour was determined using Munsell soil-colour charts. Free-iron (Fe_d) and -aluminium (Al_d) oxides were extracted with citrate dithionite [24] and poorly crystallized iron (Fe_o) and aluminium (Al_o) oxides were extracted with ammonium oxalate [25]. Both were measured in a VARIAN SpectraAA 220FS atomic absorption spectrometer.

Samples of the very finely ground soils (<0.05 mm), were digested in strong acids (HNO₃ + HF), and in each digested sample, Cu, Zn, Cd, As, and Pb concentrations were measured by ICP-MS with a PE SCIEX ELAN-5000A spectrometer. The accuracy of the method was corroborated by analyses (6 replicates) of a Standard Reference Material: SRM 2711 [26]. The total concentrations of major elements (Si_T, Al_T, Fe_T, Ca_T, Mg_T, Na_T, K_T, S_T) were determined after preparing soil pellets with lithium tetraborate 0.6:5.5, by X-ray fluorescence in a Philips PW-1404 spectrometer. The mineralogical composition of the samples was studied using a PW-1710 X-ray diffractometer with Cu Kα radiation. The PS and leachates obtained during the experiment were immediately analysed. The pH was measured potentiometrically. The Cu, Zn, Cd, As and Pb concentrations were measured by ICP-MS with a PE SCIEX ELAN-5000A spectrometer.

3. Results

3.1. Effect of pollutant solution on soil properties

The first changes observed in the soil columns after the addition of the PS were in the colour. Only the original soil (SB0) remained the same colour as before contamination. The chroma increased with the calcium carbonate content in all the other samples up to 8 (10YR 5/8, yellowish brown) in the topmost centimetres of samples SB6, SB8, and SB10.

The mean pH in the samples (Table 1) increased directly with the calcium carbonate content and depth. In both the original soil (SB0) and SB2, the pH decreased to below 3.7, whereas in the SB4 pH remained below 4 in the top 2 cm and increased to above 5 at the bottom. In the other samples, the pH increased progressively, although in no case was the pH of the original soil (pH 7.6) reached (Fig. 1).

Acidification caused partial dissolution of the carbonates (Table 1), and no effect was detected in any soil at any depth. The

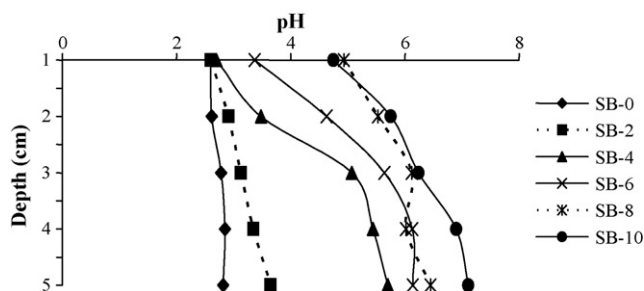


Fig. 1. Variation in depth of soil pH with the different soil columns.

raising of the pH by calcium carbonate caused the Fe in the PS to precipitate into amorphous oxide forms (Fe_0), which were dominant in all samples and especially in SB8 and SB10.

With regard to the mineralogy, the reaction between the $CaCO_3$ content and the PS caused significant changes in the main species. Neof ormation of gypsum was observed in all amended samples, increasing in amount with larger additions, with up to 10% gypsum in the samples SB8 and SB10 (Table 2). The neof ormation of jarosite was also detected in all carbonate samples, although in trace amounts. All neof ormed minerals tended to concentrate at the soil-column surface.

3.2. Distribution of polluting elements in the soil

After addition of the PS, the mean concentration of polluting elements sharply increased over the original soil (Table 3). This increment was greater with larger amounts of $CaCO_3$ in the soil. The differences in distribution of the elements in depth were less pronounced in the non-carbonate soil (SB0), whilst in the carbonate soils the elements tended to concentrate at the surface and to a greater extent with $CaCO_3$ concentration.

Two different behaviours were noted depending on the distribution of the polluting elements in the soil. On one hand, the less mobile elements such as As (Fig. 2a) and Pb accumulated mainly in the upper 2 cm, and their concentration in depth tended to approximate the original soil. Precipitation of As in the uppermost 1 cm of the soil increased with the sample $CaCO_3$ content. On the other hand, the more mobile elements such as Zn (Fig. 2b), Cu, and Cd tended to accumulate in the deeper layers or to leach partially from the soil when $CaCO_3$ increases, although the precipitation of these elements in the top 2 cm was not directly related to the increase in $CaCO_3$ content.

3.3. Properties of leachates

The pH of the leachates tended to decrease with the amount of PS added (Fig. 3). The acidification of the non-carbonate samples (SB0) ranged from 2.26 to 1.89 with the addition of 50 and 200 ml of PS, respectively. Neutralization of most of the H^+ added occurred in sample SB2 when 50 ml of PS was added, but the same occurred in sample SB4 when 100 ml of PS was added, whereas neutraliza-

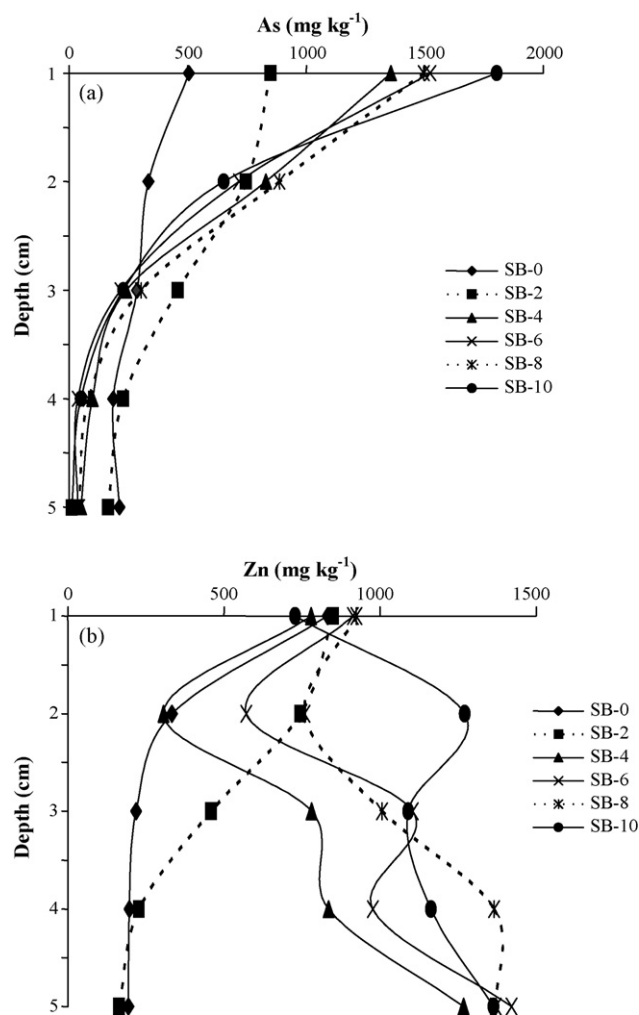


Fig. 2. Distribution of As and Zn in depth in the different soil columns.

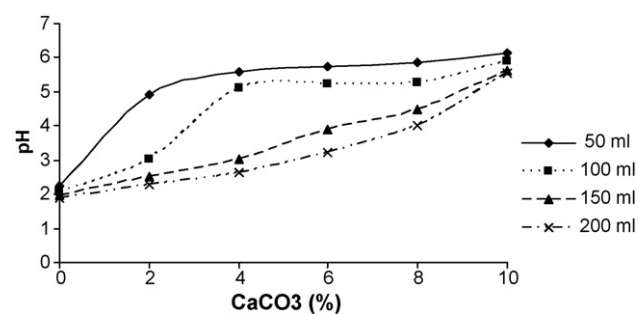


Fig. 3. Variation in pH of leachates at different dose and soil columns.

Table 2
Mineralogical composition (%), in the soils after the contamination process.

Muestra	Quartz	Feldspars	Phyllosilicates	Calcite	Gypsum	Jarosite
SB0	80	10	10	–	–	–
SB2	75	10	10	–	Tr	Tr
SB4	75	10	5	tr	5	Tr
SB6	75	10	5	tr	5	Tr
SB8	65	10	5	5	10	Tr
SB10	65	10	5	5	10	Tr

Table 3
Mean concentration (mg kg⁻¹) of contaminant elements in the original soil (SB) and in the contaminated soils.

Sample	Pb		Cu		Zn		As		Cd	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
SB	32.0	2.9	32.3	1.6	44.6	3.4	10.5	1.1	0.14	0.03
SB0	47.3	10.3	107.9	56.4	355.0	272.9	305.3	126.4	1.30	1.09
SB2	42.6	8.9	210.4	77.2	462.3	233.7	489.3	304.2	1.81	0.88
SB4	43.9	9.4	285.6	89.7	793.9	340.6	515.5	564.2	3.48	1.61
SB6	44.2	12.0	389.9	125.8	997.6	308.4	506.1	633.0	4.47	1.61
SB8	43.8	11.2	394.6	127.1	1085.2	273.6	562.2	621.3	4.99	1.67
S10	44.1	16.0	508.1	176.6	1123.5	244.5	549.4	745.7	5.21	1.62

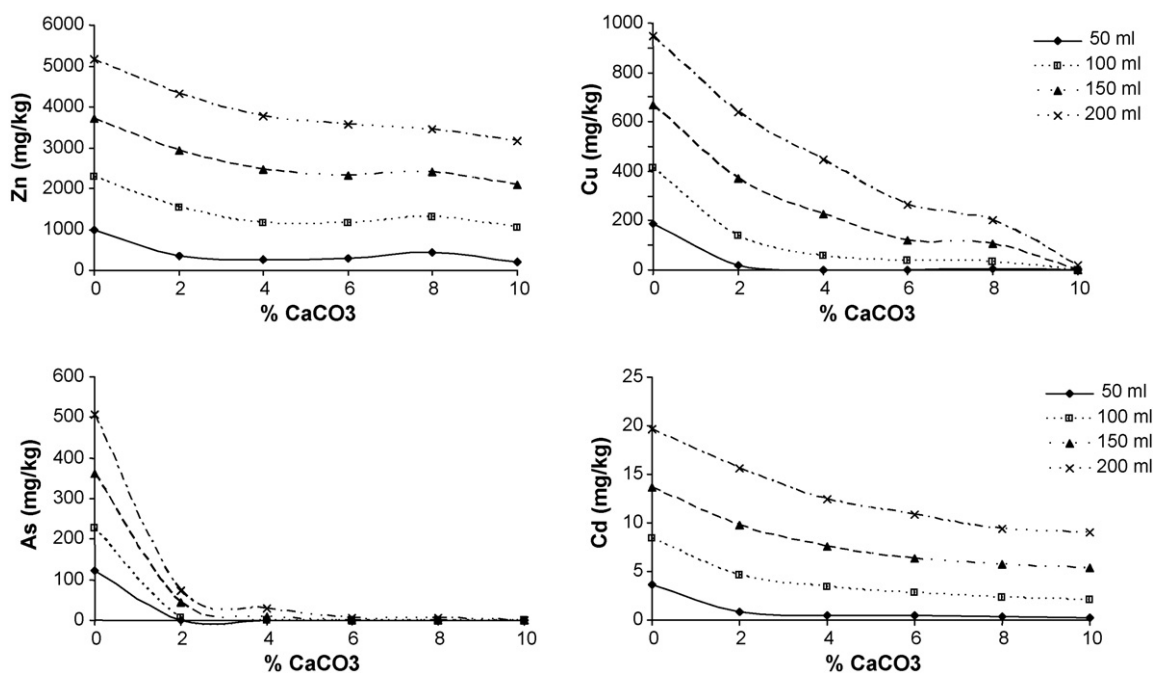


Fig. 4. Concentration in pollutant elements in leachates at different dose and soil columns.

tion occurred in sample SB10 only when larger amounts of PS were added.

Depending on the concentration of the polluting element in the different leachates (Fig. 4), the concentration in the solutions was observed to increase directly with the amount of PS added, and inversely with the amount of CaCO₃ in the samples. Behaviour differed depending on the element. Zn and Cd were leached in all the samples, even in SB10, with less pronounced differences in leachate concentration with increasing amounts of CaCO₃. Cu was moderately leached in the solutions, with stronger differences in concentration with increasing amounts of CaCO₃. Leaching of Cu in the SB10 samples was absent or minimal in all cases. As was leached to a lesser extent, mainly in samples SB0 and SB2. Leaching sharply decreased with the amount of CaCO₃ in the soil, and there was no lixiviation of As in the SB10 samples, even with the addition of 200 ml of PS.

4. Discussion

When PS enters the soil, CaCO₃ partly dissolves, releasing large amounts of Ca²⁺ ions that react with the sulphates in the solution, and precipitating gypsum. At the same time, the dissolution process reduces the H⁺ concentration in the soil solution (two mols of H⁺ for each mol of CaCO₃ dissolved), increasing the pH and oxidation of Fe²⁺ to Fe³⁺; which also reacts with the SO₄²⁻ ions in the PS precipitating iron hydroxysulphates like jarosite.

In this case, considering that the pH of water in equilibrium with CaCO₃ is around 8.3 [10], after the contamination process, some of this carbonate remains in soils with over 2% calcium carbonate, but the pH remains acidic. This is attributed to the formation of a coating of iron hydroxysulphates and gypsum covering the CaCO₃ particles, and impeding reaction with the acidic solution. This process has also been reported by other authors [27,28].

Principal-component analysis including some soil properties and trace-element concentrations (Table 4) indicates that three fac-

Table 4
Principal-component analysis of some soil properties and trace-element concentrations (CaCO₃ content, iron and aluminium forms are expressed in %; trace-element concentrations are expressed in mg kg⁻¹).

	Factor 1	Factor 2	Factor 3
pH		0.802	0.496
CaCO ₃		0.817	
Fe _d	0.898		
Fe _o	0.932		
Al _d		0.747	
Al _o			0.841
Cu		0.538	0.785
Zn		0.850	
As	0.923		
Cd		0.895	
Pb	0.806		
Chroma	0.777		
Accum. var. (%)	41.7	77.2	85.8

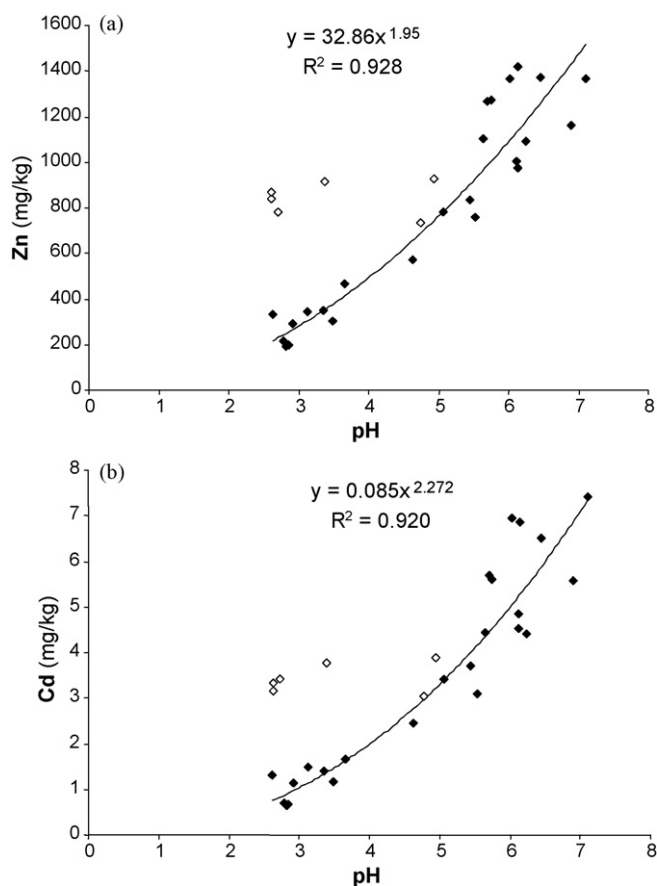


Fig. 5. Regression plots between Zn (a) and Cd (b) in soil and pH (unfilled point correspond to samples of the first centimetre of the column).

tors explain 85.8% of the variance. The first factor, explaining 41.7% of the variance, includes iron oxides, chroma, As and Pb concentrations, showing that these elements behave in a similar manner and are related to iron oxides and, therefore, to the reddening from the increase in chroma. The second factor, explaining 35.5% of the variance, includes pH, calcium carbonate content, Al_d , Zn, Cd and, to a lesser extent, the Cu concentrations, indicating that the precipitation of these elements is strongly related to the presence of calcium carbonate and a higher pH. The third factor, explaining 8.6% of the variance, relates amorphous aluminium forms (Al_o) to Cu and, although less so, to pH, showing that the precipitation of Cu in this soil was related mainly to aluminium oxides and pH.

Based on the principal-component analysis relationships, multiple-regression analyses were performed to select the most significant parameters related to the precipitation of the polluting elements. Precipitated As in the soil was thus found to be significantly ($p < 0.001$) and directly related to amorphous iron forms (Fe_o) and inversely related to pH by the following multiple regression:

$$As (mg\ kg^{-1}) = 398.58 + 649.18Fe_o(\%) - 146.46pH \quad r^2 = 0.828$$

The correlation between Zn and Cd in soil and pH indicates that these elements behave differently in the uppermost centimetre. In this case, the amount of these elements precipitated was constant regardless of the soil pH (Fig. 5). This first centimetre received the initial impact of the PS and the reactions occurring in this part of the soil led to a constant concentration of these elements regardless of the amount of $CaCO_3$ added or raise the pH. The mean precipitation of Zn was around $800\ mg\ kg^{-1}$, and the mean precipitation of Cd was around $3.5\ mg\ kg^{-1}$ in all samples. The concentrations of Zn and Cd precipitated in soil are significantly ($p < 0.001$) and

directly related to the $CaCO_3$ content, but inversely related to the H^+ concentration in the pollutant solution (PSH^+) by the following multiple regressions:

$$Zn (mg\ kg^{-1}) = 504.9 + 213.4CaCO_3 (mol\ kg^{-1}) - 951.6PSH^+ (mol\ kg^{-1}) \quad r^2 = 0.836$$

$$Cd (mg\ kg^{-1}) = 2.04 + 1.06CaCO_3 (mol\ kg^{-1}) - 3.86PSH^+ (mol\ kg^{-1}) \quad r^2 = 0.908$$

Therefore, $CaCO_3$ tended to increase Zn and Cd precipitation in soil, whereas the H^+ added in the pollution process tended to decrease it. Zn and Cd precipitation decreased at $1\ mol\ H^+ kg^{-1}$ dry soil, whereas increased at $1\ mol\ CaCO_3 kg^{-1}$ dry soil. Considering that the highest pH was 6.1, and that the lowest Zn and Cd values in the pollutant solution were 718.4 and $2.57\ mg\ kg^{-1}$, respectively, the toxic levels of $1.2\ mg\ Zn\ dm^{-3}$ and $0.07\ mg\ Cd\ dm^{-3}$ [29] were exceeded in all leachates. Therefore, although $CaCO_3$ stimulates precipitation of Zn and Cd in the soil, this precipitation was insufficient to lower Zn and Cd below toxic levels.

5. Conclusions

After the addition of the pollutant solution from oxidation of pyrite tailings, the changes found in the soil columns were related to colour (yellowish brown), pH (strong acidification, decreasing from 7.6 to below 4), partial dissolution of calcium carbonate added, precipitation of iron (mainly in amorphous forms), and neof ormation of minerals (gypsum and jarosite).

The distribution of the polluting elements was strongly related to the soil properties and the behaviour of the element. The less mobile elements (As, Pb) precipitated in the top 2 cm of the soil, as well as the retention of these elements was related to iron precipitation and, in the case of As, retention was directly related to amorphous iron forms and inversely related to pH. The more mobile elements (Zn, Cd and Cu) precipitated in deeper layers, directly related mainly to the $CaCO_3$ added and to pH. The $CaCO_3$ did not reduce Zn and Cd toxicity effectively enough, as demonstrated by toxic concentrations of both elements in the leachates of all soils. Therefore, liming must be properly controlled, as excessively high pH can limit As fixing and, at the same time, the effectiveness of $CaCO_3$ can be limited by the precipitation of gypsum and iron hydroxysulphates on their surface, reducing their capacity to react with the acidic solution.

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