

Assessment of the use of industrial by-products for induced reduction of As, and Se potential leachability in an acid soil

M.P. Rodríguez-Jordá, F. Garrido, M.T. García-González*

Instituto de Ciencias Agrarias, Centro de Ciencias Medioambientales, Consejo Superior de Investigaciones Científicas, Serrano 115-dup, 28006, Madrid, Spain

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ABSTRACT

Four industrial by-products (phosphogypsum, PG; red gypsum, RG; sugar foam, SF and ashes from the combustion of biomass, ACB) were evaluated as possible amendments for reducing the leachability and bioavailability of As and Se in a metalloid-spiked acidic soil. The treatments were applied as single, double and triple amendments and at two different rates. The effectiveness of the treatments was evaluated after a series of leaching experiments using a chelating agent (DTPA solution) or a weak acidification (acetic acid at pH 4.93). The most effective treatments (ACB and RG, both applied at high rate) were identified by means of Cluster Analysis using the leachability indexes. Different sorption mechanisms involved in the overall reduction of metalloid leachability were identified using scanning electron microscopy (SEM-BSE and SEM-EDS). In the ACB-treated samples, Se was found associated to organic matter aggregates and to Fe compounds. In the RG-treated samples, EDS analyses showed that As and Se were associated to Fe/Ti (hydr)oxides phases which are present not only in the by-product as maghemite and rutile, but also in the soil as hematite and goethite. In addition, the application of RG induced the formation of non-crystalline Al-hydroxy polymers with As and Se in their composition.

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1. Introduction

The use of conventional, engineering-type techniques to clean up metal-contaminated soils is typically invasive and expensive. The most ecologically friendly and economically viable method is *in situ* immobilization of metals and metalloids using abundant, inexpensive soil amendments [1] aiming at enhancing natural attenuation processes [2] such as (ad)sorption, precipitation, complexation and redox reactions [3] that reduce potential leachability and bioavailability of toxic elements.

Remediation of soils contaminated with several elements, and very often with combinations of anionic and cationic species, requires solutions effective for all target elements. The different properties of the contaminants restrict the choice of possible amendments in order to avoid, for example, large pH fluctuations and consequent mobilization of one or more of the elements. In addition, the presence of one contaminant (e.g. Cu or Pb) can decrease the stabilization efficiency of others (e.g. Zn) due to competition for sorption sites [4], while several contaminants of opposite charge can have a synergistic effect on each other. Thus, the diversity of contaminant species and the selective efficiency of the by-products for some elements, is promoting the search for new treatments applied in single or combined amendments. Very

often, the use of a combination of amendments can improve the single treatment efficiency of multi-element contaminated sites [4].

In recent years, there has been considerable interest in the use of some industrial by-products as amendments. This approach transforms wastes into useful commercial industrial co-products [5]. Various by-products have been tested as *in situ* fixing additives to remediate As contaminated soils. Examples include red mud [6], compost [7], lime [8], iron oxide coated cement [9], water treatment sludges [10], steel shot [11] and phosphogypsum and sugar foam [12,13]. However, only a few studies have focused on the fixation of Se species by amendments, such as gypsum [14,15] or lime [16]. Although As and Se coexist in some contaminated soils, like the affected by the mine tailings accident at Aznalcóllar (southern Spain) [17], or the surrounding coal ash disposal facilities [18,19], no studies are available on the addition of soil amendments to improve the leachability of both metalloids together. Taking into account these facts, the objectives of this work are: (i) to ascertain the feasibility of the application of four industrial by-products (phosphogypsum, PG; red gypsum, RG; sugar foam, SF and ashes from the combustion of biomass, ACB) as amendments for the immobilization of As and Se in a metalloid-spiked acidic soil under unsaturated conditions, (ii) to identify those treatments that are effective in reducing both potential mobility and bioavailability of the two elements, and (iii) to explore possible sorption mechanisms through which As and Se are retained in the soil matrix as a result of selected treatments.

* Corresponding author. Tel.: +34 91 745 25 00; fax: +34 91 564 08 00.
E-mail address: mtgg@ccma.csic.es (M.T. García-González).

2. Materials and methods

2.1. Soil

An acidic soil developed from Pliocene-Quaternary aged formations and classified as Plinthic Paleixerult [20] was collected from an agricultural area in Cáceres (Spain). Air-dried samples from the Ap horizon were crushed and sieved through a 2 mm mesh prior to characterization and use in subsequent experiments. Table 1 summarizes the most important physical, chemical and mineralogical properties of the soil. Soil pH was measured in deionized water (pH_w) and in 1 M KCl (pH_k) (in a 1:2.5 suspension). Electrical conductivity (EC) was measured in a 1:5 suspension. Organic C (OC) was determined by wet digestion [21]. The exchangeable bases were extracted with 1 M NH_4OAc (at pH 7) [22]. The Al and Fe contents in the poorly crystalline and amorphous fraction of the soils (Al_{ox} , Fe_{ox}) were extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid solution at pH 3 [23]. The supernatants from each extraction were separated by centrifuging and stored in polyethylene containers at 4 °C until analysis. Analyses were performed in triplicate. The Ca, Mg, Na, K, Al and Fe were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Perkin-Elmer OPTIMA 4300DV. The mineralogical composition of the total (≤ 2 mm) and clay ($\leq 2 \mu\text{m}$) fractions of the soil was identified by X-ray powder diffraction (XRD) with a Philips X'Pert diffractometer using graphite-monochromated $\text{Cu-K}\alpha$ radiation. The XRD patterns were obtained from random powder mounts and various oriented aggregates of the clay fraction (air-dried, ethylene glycol-solvated, heated at 300 °C for 3 h, and heated at 500 °C for 3 h). Semi-quantitative estimates of the mineral contents were obtained from random powder and oriented aggregated patterns using the intensity factors given by Schultz [24].

2.2. Industrial by-products

Phosphogypsum (PG) is generated in the wet-acid production of phosphoric acid from rock phosphate in the industry of fertilizers. Red gypsum (RG) is a waste from the industrial production of titanium dioxide (TiO_2). Sugar foam (SF) is produced by the sugar manufacturing industry. Ashes from combustion of biomass (ACB) are originated in the cellulose production process.

Samples of PG, RG, SF and ACB supplied by the companies Fertiberia S.A., Tioxide Europe S.A., Azucarera Ebro S.A. and ENCE S.A., respectively, were dried at 45 °C (PG and RG) and 105 °C (SF and ACB) and digested by acid digestion and alkaline fusion [25]. The resulting solutions were analyzed for major and trace elements by ICP-AES, ICP-MS and ion chromatography. Organic C was determined by wet digestion [21]. The chemical composition of the by-products is shown in Table 2. Both gypsum-like wastes are rich in Ca and sulfate ions. In addition, because of its industrial origin from ilmenite (FeTiO_3), RG contains Fe and Ti. Regarding the trace elements, Ba, Cr and Cu are present at the largest concentrations among all elements analyzed in all by-products. In addition, RG and ACB are rich in Ni and Zn, and ACB also in Pb. However, the heavy metal contents are much less than those established by the European Community, Council Directive 86/278/EEC on the Use of Sewage Sludge in Agriculture [26] (Cd, 20–40 mg kg^{-1} ; Cu 1000–1750 mg kg^{-1} ; Ni 300–400 mg kg^{-1} ; Pb 750–1200 mg kg^{-1} ; Zn 2500–4000 mg kg^{-1}) and constitute no environmental hazard at the rates normally used in agriculture.

The mineralogical composition of the by-products was identified by X-ray diffraction from random powder patterns. Gypsum is the main component of PG and RG and is accompanied by small proportions of iron and titanium minerals in RG. An XRD study of the RG residue after dissolution of gypsum revealed the presence of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and rutile (TiO_2). SF consists mainly of

Table 1
Some physical, chemical and mineralogical properties of the Ap horizon.

pH_w	pH_k	EC^a (mS cm^{-1})	OC^b (g kg^{-1})	Sand (g kg^{-1})	Lime (g kg^{-1})	Clay (g kg^{-1})	Ca^{2+} ($\text{cmol}_c \text{ kg}^{-1}$)	Mg^{2+} ($\text{cmol}_c \text{ kg}^{-1}$)	Na^+ ($\text{cmol}_c \text{ kg}^{-1}$)	K^+ ($\text{cmol}_c \text{ kg}^{-1}$)	Al^{3+} ($\text{cmol}_c \text{ kg}^{-1}$)	Al_{ox}^c (mg kg^{-1})	Fe_{ox}^c (mg kg^{-1})	Fraction ^d $\leq 2 \mu\text{m}$									
														Q	G	H	Ph	I	K				
4.9	4.1	0.04	33	700	250	50	0.83	0.12	0.07	0.06	1.17	4772	1457	Q	G	H	Ph	I	K				
														84	tr	3	13	15	9	76	11	10	55

^a EC: electrical conductivity.

^b OC: organic carbon.

^c Al and Fe oxalate-extractable contents.

^d Semi-quantitative mineralogical composition (relative%): Q, quartz; G, goethite; H, hematite; Ph, phyllosilicates; V, vermiculite; I, illite; K, kaolinite; and tr, traces.

Table 2

Chemical composition of the by-products (SF, sugar foam; PG, phosphogypsum; RG, red gypsum; ACB, ashes from the combustion of biomass).

	SF (g kg ⁻¹)	PG (g kg ⁻¹)	RG (g kg ⁻¹)	ACB (g kg ⁻¹)
Al ₂ O ₃	13.4	14.8	8.3	60.1
CaO	424	305	248	171
Fe ₃ O ₄	5.3	0.2	128	16.3
K ₂ O	3.0	0.1	0.2	32.0
MgO	18.6	0.1	8.2	30.0
MnO	0.3	<0.1	3.8	6.3
Na ₂ O	0.9	31.7	0.7	15.4
P ₂ O ₅	14.6	69.0	0.8	11.9
SiO ₂	30.8	17.9	4.9	353
TiO ₂	0.3	0.2	60.2	20.2
F ⁻	<0.1	3.3	<0.03	<0.1
SO ₄ ²⁻	81.4	534	425	36.9
LOI ^a	464	221	205	252
OC ^b	49	1	-	37
	SF (mg kg ⁻¹)	PG (mg kg ⁻¹)	RG (mg kg ⁻¹)	ACB (mg kg ⁻¹)
As	<2.5	<2.5	10.3	7.08
B	<2.5	<2.5	6.4	<2.5
Ba	53.3	112	13.9	396
Be	<0.4	<0.4	<2.4	1.31
Cd	<0.4	2.9	<2.4	<0.4
Co	0.9	<0.4	12.1	5.3
Cr	13.5	8.7	95.2	36.9
Cu	12.0	5.2	17.1	45.8
Mo	<0.4	1.9	5.4	8.68
Ni	5.19	2.9	61.7	177
Pb	3.05	2.2	28.1	79.0
Se	<2.5	<2.5	<2.4	<2.5
Zn	19.3	7.3	388	204

^a LOI: loss on ignition (45–1000 °C).^b OC: organic carbon and -: not detected.

calcium carbonate (CaCO₃) and traces of calcium oxide (CaO). ACB contains SiO₂, a small proportion of calcium carbonate and traces of calcium oxide.

2.3. Contamination procedure

Air-dried and sieved (≤ 2 mm) soil samples were homogeneously packed to a bulk density of 1.25 g cm⁻³ into seven PVC columns, 8.2-cm diameter and 25-cm length. The mass of packed soil (1278 g per column) was calculated considering further experimental needs. The inner walls of the columns were previously spread with a film of soft Vaseline to avoid preferential flow along the wall of the columns. The columns were irrigated at a constant flow rate of 100 ml h⁻¹ with 0.05 M NaNO₃ until a steady flow was achieved in water unsaturated conditions. Previous equilibrium sorption isotherms experiments were done in order to estimate the soil maximum sorption capacity of As and Se. According to this information, a front of a bioelemental solution (totalizing 9.5 L of solution per column) containing 500 mg L⁻¹ of As and Se (from analytical-grade salts KH₂AsO₄ and Na₂O₄Se, respectively) was applied to the surface of the columns at the same constant flow rate. Once the columns were contaminated, they were dismantled, and the topmost 3 cm was discarded to avoid uncertainties due to the possible presence of precipitates in the surface. The rest of the soil was oven-dried (50 °C) and thoroughly homogenized.

2.4. Incubation procedure

Portions of 210-g contaminated soil samples were evenly blended with the industrial by-products as single (SF, PG, RG, ACB), double (SF + PG, SF + RG, SG + ACB, PG + ACB, RG + ACB), and triple treatments (PG + SF + ACB, RG + SF + ACB). The whole incubation procedure was performed in two successive steps; the first one involved the single treatment experiments and the subsequent one,

both the double and triple treatment ones. Consequently, two additional portions were maintained untreated as a control. A control column (C₁) was used for the group of columns with single treatments and another control column (C₂) for the group of double and triple treatments. Each treatment was applied at two rates. The single SF treatment was added at 0.5% (rate 1, SF₁) and 1% (rate 2, SF₂) w/w, which involved the addition of 0.42 and 0.84 g of Ca for each addition rate, respectively. In the treatments of PG, RG, PG + SF, RG + SF, SG + ACB, PG + ACB, RG + ACB, PG + SF + ACB, RG + SF + ACB the amount of by-product was calculated to add similar amounts of Ca as in the SF treatment.

All these soil samples (treated and control) were uniformly re-packed to a bulk density of 1.25 g cm⁻³ in 4.4-cm-diameter and 15-cm-length columns and maintained at room temperature (25 °C \pm 2) and field capacity by adding 60 ml of deionized water to the surface of the columns every two days. The incubation period of six weeks totalized a volume of 900 mm, equivalent to the average annual rainfall of the experimental site. After this period, the columns were then dismantled and samples of them were homogenized and oven-dried (50 °C). Acidity of the samples was measured in deionized water (pH_w) in a 1:2.5 suspension. Lastly, the samples were digested in a mixture of concentrated HNO₃ and HCl [27] and the resulting diluted solutions were analyzed for total As and Se using ICP-AES on a Perkin-Elmer OPTIMA 4300DV instrument. These element concentration values were subsequently used to calculate the leachability indexes as explained below.

2.5. Leaching experiments

From each incubated column, six 20-g sub samples were taken and re-packed in small columns for subsequent estimation of potential mobility and availability of the elements as a result of the treatments through a series of leaching experiments. Element bioavailability was assessed by leaching one set of triplicate

columns at constant flow rate with 100 ml of DTPA solution (0.005 M diethylenetriaminepentaacetic acid, 0.01 M CaCl_2 and 0.1 M triethanolamine) adjusted to pH 7.3 [28]. A similar second set was used to evaluate the potential mobility of the anions following the same leaching procedure with 100 ml of an acetic acid solution at pH 4.93 (AA). The column total effluents were acidified with HNO_3 (pH \approx 2) and analyzed for total As and Se by ICP-AES. The percentage of element concentration recovered after each leaching procedure was calculated with respect to the total concentration contained in the samples before these leaching experiments were executed, *i.e.* right after the incubation procedure. Both AA- and DTPA-leachability indexes for the anions (As^{AA} , Se^{AA} for identifying potential mobility and As^{DTPA} , Se^{DTPA} for metal bioavailability) were computed for each replicated column. In order to compare the whole set of treatments, all leachability indexes were normalized with respect to the mean leachability indexes obtained in the corresponding control columns.

2.6. Scanning electron microscopy observations

Possible mechanisms involved in the sorption of the toxic elements in the soil matrix and differences due to the application of the amendments were investigated using scanning electron microscopy in the backscattered electron mode (SEM-BSE). Contaminated and amended samples were oven-dried (50 °C) and embedded in a low-viscosity acrylic resin (LR-Whyte, medium grade). Blocks of the resin-embedded samples were polished using a commercially available low-viscosity oil/water emulsion as lubricant and subsequently observed under a DMS 940A Zeiss microscope equipped with BSE detector. Semi-quantitative elemental analyses, using point analyses, were done by energy dispersive spectrometry (EDS) with a Link Isis microanalytical system on the SEM.

2.7. Statistical analysis

The statistical differences in the leachability of each anion as a result of the treatments were assessed by one-way analysis of variance (ANOVA) and the Bonferroni *post-hoc* pair-tests. These analyses were done using the AA- and DTPA-normalized leachability indexes of both anions. According to these results, and as explained below, one variable, As^{AA} , was not taken into account for subsequent analysis aimed at identifying the optimum treatment and application rate (dose) to reduce the extractability of the two anions.

On the other hand, a K-means Cluster Analysis (CA) was used to find those groups of treatment conditions (treat \times dose) showing similar responses with respect to the variables As^{DTPA} , Se^{DTPA} and Se^{AA} . The different treat \times dose experimental conditions considered were projected over a 2-dimension plot to identify those treat \times dose clusters that operates reducing both AA and DTPA leachability for Se and DTPA leachability for As (optimum treat \times dose). All statistical analyses were done using the statistic package SPSS v. 17.0 (SPSS, Inc., Chicago, IL).

3. Results and discussion

3.1. Effect of treatments on metalloids leachability

The leachability indexes for the amended samples vary in function of the type of extractant, the element and the treatment (Table 3). Effective treatments for reducing anions extractability are identified by values less than one.

The As^{AA} leachability indexes for all treated samples are higher than the unit. This could indicate that the mechanisms of retention, induced as a result of treatments, are not very resistant to the

acidification. In addition, the possible new solid phases and non-crystalline Al-hydroxy polymers (formed after the application of the amendments) could be dissolved at the slightly acid pH of the AA solution, promoting As release in spite of the strong bonding between arsenate O atoms and functional groups of Al-OH polymers. Thus, the As^{AA} variable was not considered further.

In general, the application of the amendments at high rate (rate 2) produced lower leachability indexes than when applied at low rate (rate 1) (Table 3). The most effective treatments for reducing As^{DTPA} were ACB_2 , $(\text{RG} + \text{ACB})_2$ and SF_2 , with leachability indexes of 0.60, 0.71 and 0.75, respectively. In the case of Se, the lowest leachability indexes after the extraction with DTPA were obtained as a result of the addition of ACB, PG and RG treatments, all of them at high rate. In the extraction with AA these treatments showed to be effective (Table 3). In the $(\text{PG} + \text{SF} + \text{ACB})_1$ -treated samples the extraction of Se also decreased, with a normalized leachability index of 0.91.

3.2. Identification of the most effective treatments

The normalized leachability indexes upon the different treat \times dose experimental conditions were projected over a 2-dimension plot to identify those treat \times dose that operate reducing both AA and DTPA leachability for Se and DTPA leachability for As. A K-means Cluster Analysis was used to find those groups of treatment conditions (treat \times dose) showing similar responses with respect to these variables. Based on these results, CA divided all treatments into four clusters as it is shown in Fig. 1. Optimum treatments for reducing the extraction of As and Se are those located approximately within the bottom left-hand quadrant on the cluster plots, where the leachability indexes are less than one. The treatments that are included in these relative positions on both plots were defined as effective treatments for reducing bioavailability of As and Se and potential mobility of Se. These treatments were ACB_2 and RG_2 .

3.3. Induced sorption mechanisms of metalloids after ACB and RG treatments: SEM observations

Among all the by-products applied, only ACB_2 and RG_2 were effective treatments in reducing the extractability of As and Se. Different sorption mechanisms may be involved in the overall reduction of metalloid leachability shown after these treatments.

SEM-BSE study of the ACB_2 -treated samples showed the presence of Se associated with organic matter aggregates (Fig. 2). The organic matter present in the ACB by-product (6.4%) could increase the sorption of Se in the samples according to Singh et al. [29] who showed the complexing role of organic matter on Se and Levesque [30] who indicated that Se was presumably bound to organometallic complexes. However, As was not found associated with organic matter. This result agrees with the findings of Fitz and Wenzel [31] and Waltham and Eick [32], who concluded that there is no evidence of organic matter contribution to the sorption of significant amounts of As in soils.

ACB_2 -treated samples also showed considerable amounts of Se associated to Fe (hydr)oxides identified in the mineralogical composition of the soil (Fig. 3). It is important to note that As was not related to the presence of these compounds. This observation agrees with the findings of Redman et al. [33] who demonstrated that organic matter can compete with As for sorption sites and displace both As(V) and As(III) from iron oxides.

Although not confirmed in this work, other mechanisms might have been involved in the reduction of As leachability. At the pH of ACB_2 -treated samples (6.6, Table 4), As adsorption could be enhanced by the presence of calcium through the formation of stable Ca-As precipitates with different solubility, such as

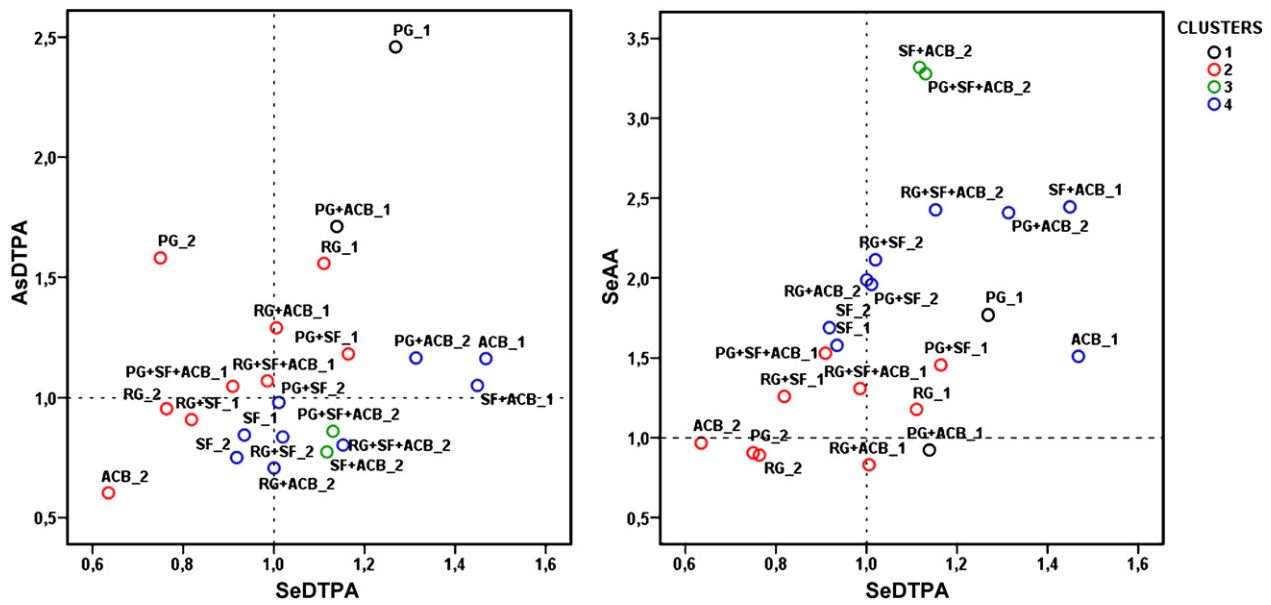


Fig. 1. K-means Cluster Analysis (CA). As^{DTPA} , Se^{DTPA} , leachability indexes for As and Se after the DTPA extraction. Se^{AA} , leachability index for Se after the AA extraction.

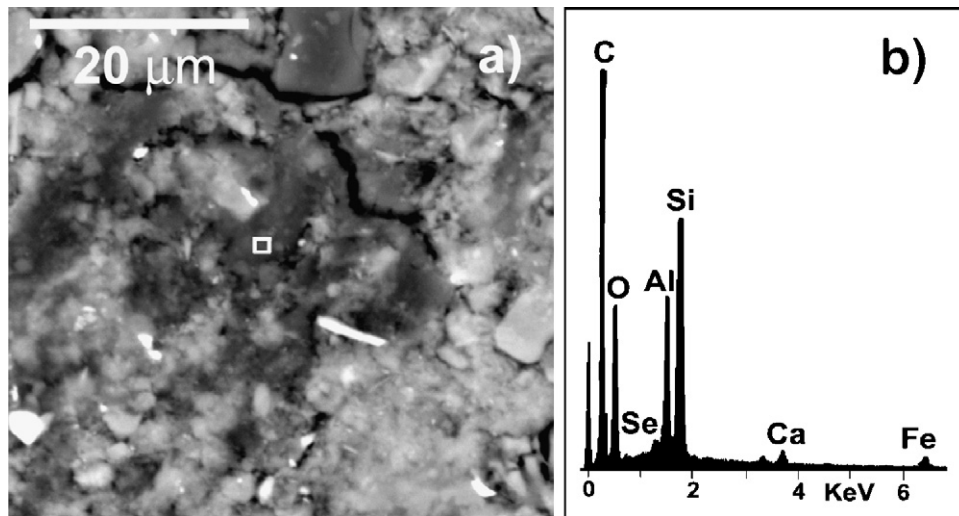


Fig. 2. (a) SEM-BSE image of organic matter aggregates in an ACB_2 -treated soil sample. (b) The corresponding EDS X-ray spectrum showing the presence of Se. A small square shows the analyzed zone.

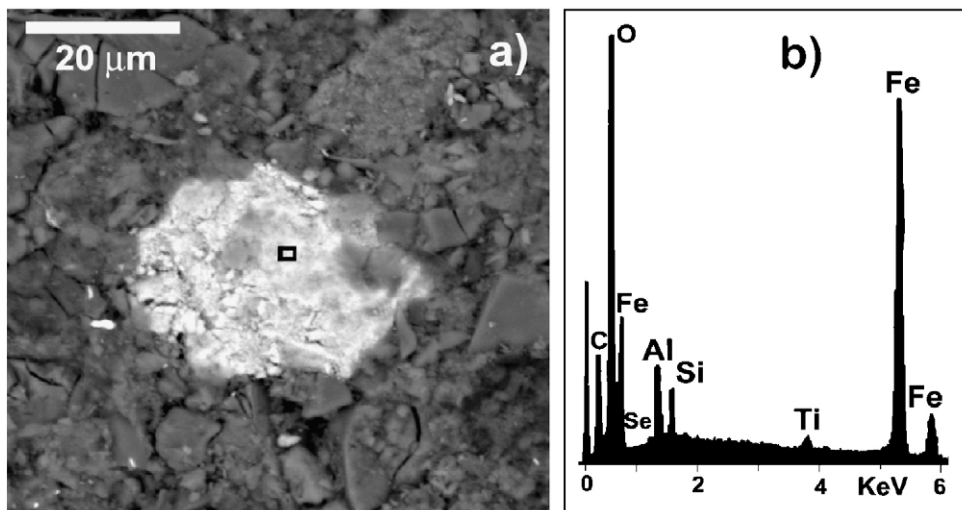


Fig. 3. (a) SEM-BSE image of Fe compounds in an ACB_2 -treated soil sample. (b) The corresponding EDS X-ray spectrum showing the presence of Se. A small square shows the analyzed zone.

Table 3
DTPA and AA-leachability indexes for As and Se ($n=3$).

Treatments	Rate												
	Rate ^a	PG ^b	RG	SF	ACB	PG + SF	RG + SF	PG + ACB	RG + ACB	SF + ACB	PG + SF + ACB	RG + SF + ACB	PSE ^c
As ^{DTPA} ^d	1	2.46	1.56	0.84	1.16	1.18	0.91	1.71	1.29	1.05	1.05	1.07	0.06
As ^{AA} ^e	1	4.96	2.85	4.69	2.05	3.69	2.89	3.64	2.96	4.75	3.72	4.36	0.29
As ^{DTPA}	2	1.58	0.95	0.75	0.60	0.98	0.84	1.17	0.71	0.77	0.86	0.80	0.06
As ^{AA}	2	4.63	2.13	5.01	2.67	6.05	4.07	5.90	3.44	4.39	5.01	4.33	0.29
Se ^{DTPA}	1	1.27	1.11	0.93	1.47	1.16	0.82	1.14	1.01	1.45	0.91	0.99	0.08
Se ^{AA}	1	1.77	1.18	1.58	1.51	1.46	1.26	0.92	0.83	2.44	1.53	1.31	0.16
Se ^{DTPA}	2	0.75	0.76	0.92	0.64	1.01	1.02	1.31	1.00	1.12	1.13	1.15	0.08
Se ^{AA}	2	0.91	0.89	1.69	0.97	1.96	2.11	2.41	1.98	3.32	3.28	2.43	0.16

^a Rate 1 = 0.5%; rate 2 = 1%.^b PG: phosphogypsum; RG: red gypsum; SF: sugar foam; and ACB: ashes from the combustion of biomass.^c PSE: pooled standard error ($P \leq 0.05$).^d As^{DTPA}, Se^{DTPA}, leachability indexes for As and Se after the DTPA extraction.^e As^{AA}, Se^{AA}, leachability indexes for As and Se after the Acid Acetic extraction.**Table 4**
 pH_w values for the contaminated soil-by-products mixtures after incubation.

	Rate 1 ^a	Rate 2
CONTROL ₁ ^b		5.81
CONTROL ₂ ^c		6.02
PG ^d	5.05	4.55
RG	5.17	4.93
SF	6.52	7.60
ACB	6.21	6.59
PG + SF	5.93	6.35
RG + SF	5.84	6.66
PG + ACB	5.47	5.85
RG + ACB	5.45	6.04
SF + ACB	6.49	8.05
PG + SF + ACB	6.20	7.30
RG + SF + ACB	6.32	7.31

^a Rate 1 = 0.5%; rate 2 = 1%.^b Untreated contaminated soil; control for the single treatments.^c Untreated contaminated soil; control for the double and triple treatments.^d PG: phosphogypsum; RG: red gypsum; SF: sugar foam; and ACB: ashes from the combustion of biomass.

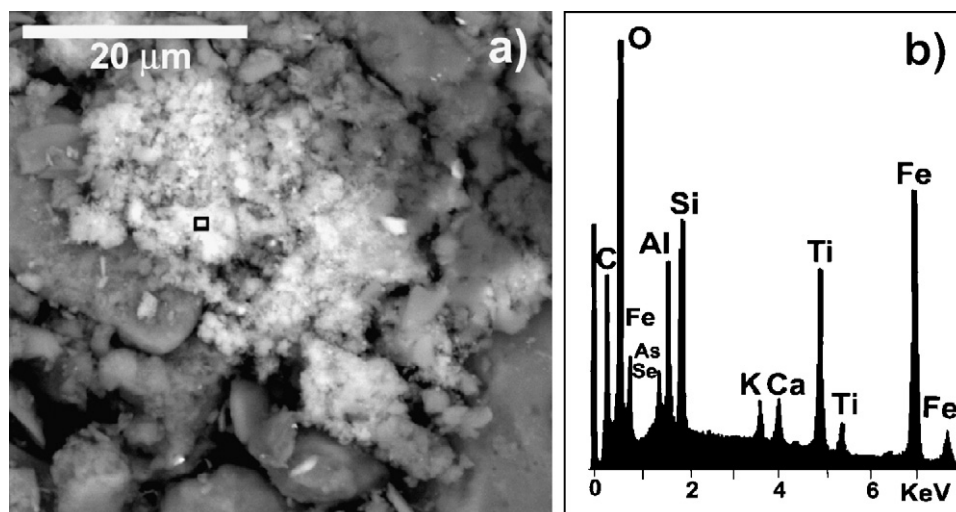
farmacolite-type minerals ($\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$) [34]. However, neither SEM nor XRD analyses of the ACB₂-amended samples proved the presence of these compounds. On the other hand, the adsorption of calcium (present in a considerable amount in the ACB by-product) could produce positive charged mineral surfaces, which would favor the adsorption of As species according with the observations

of Jia and Demopoulos [35] in samples of ferrihydrite treated with gypsum. Our SEM results did not confirm these observations.

SEM-BSE study of the RG₂-treated samples showed that Se was found associated to Fe/Ti (hydr)oxide phases which are present not only in the by-product as maghemite and rutile, but also in the soil as hematite and goethite (Fig. 4). At the pH of these amended samples (4.9, Table 4), the Se predominant specie was selenite (Se^{4+}) [36] which is adsorbed, more strongly than selenate, on the surfaces of iron oxy-hydroxides forming outer sphere complexes [37]. Maghemite in the RG by-product could play an important role in the sorption of Se as suggested by Peak and Sparks [38] in other Fe samples.

EDS X-ray spectra of the RG₂-treated samples (Fig. 4) showed considerable amounts of As included in the Fe/Ti phases. Maghemite and rutile, components of the RG by-product, can act as relevant sorbents for As in agreement with the findings of Hartley et al. [8] who demonstrated that maghemite increases the adsorption of As, and O'Reilly et al. [39] and Pena et al. [40] who found that arsenate can be sorbed onto micron-sized particles of rutile, being this mineral effective for As removal. Other mechanisms that cannot be disregarded for reducing As mobility could be the formation of an amorphous iron arsenate ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) [41,42] or the retention through ligand exchange of the As species for OH_2 and OH^- in the coordination spheres of surface structural Fe atoms [43].

Other SEM-BSE observations on RG₂-treated samples confirmed the formation of non-crystalline Al-hydroxy polymers containing

**Fig. 4.** (a) SEM-BSE image of Fe/Ti phases in a RG₂-treated soil sample. (b) The corresponding EDS X-ray spectrum showing the presence of As and Se. A small square shows the analyzed zone.

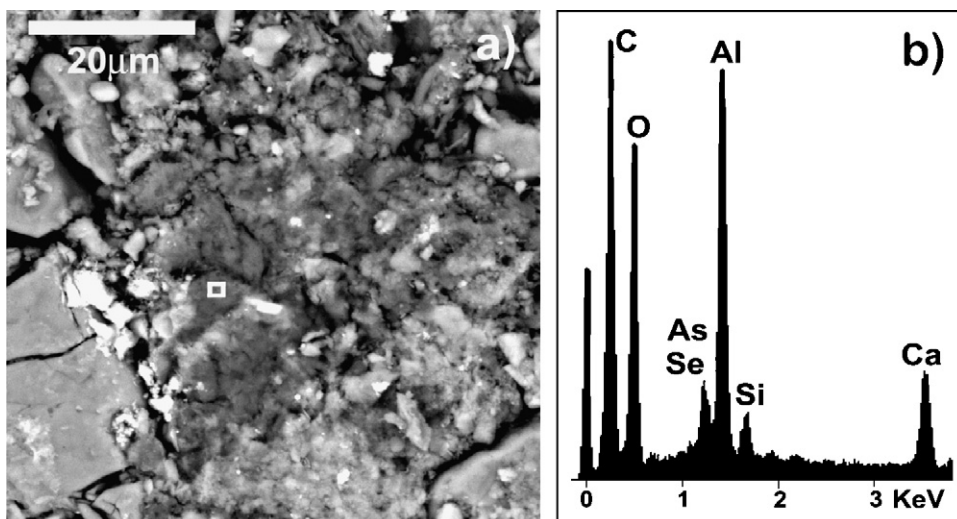


Fig. 5. (a) SEM-BSE image of a massive formation of Al-hydroxy polymers in a RG₂-treated soil sample. (b) The corresponding EDS X-ray spectrum including Ca, As and Se. A small square shows the analyzed zone.

a significant amount of As and Se. Sizable amounts of Ca were also frequently present in these compounds (Fig. 5). The application of gypsum-rich amendments to acidic soils could produce the formation of non-crystalline Al-hydroxy polymers [44] with high As sorption capacity [13]. During the polymerization of Al, arsenate and selenate anions may be incorporated in the amorphous structure of the Al-hydroxy polymers, leading to the formation of new Al hydroxide layers/clusters entrapping As and Se sorption complexes within the structure [45]. Once trace elements are specifically sorbed on the Al–OH polymer surfaces, they may become irreversible fixed as a result of several mechanisms, including migration of element into micropores on the surface of the oxide, solid state diffusion of ions into the crystal lattice of the oxides, or perhaps occlusion of elements [46,47].

Apart from these evidences, the presence of SO_4^{2-} in the RG₂-treated samples could reduce the leachability of Se, as reported by Mikkelsen et al. [48] who detected that the Se concentration of forage crops decreased after application of SO_4^{2-} fertilizers. In the case of As the effect of the presence of considerable amounts of SO_4^{2-} could cause a decrease in the adsorption of As considering that As competes with sulfate for sorption/coprecipitation sites [41]. This competitive sorption between sulfate and arsenate ions for the sorption sites could lead As anions towards more specific sorption positions [49].

The fact that our SEM observations never showed As associated to the phyllosilicates, did not allow us to conclude about other possible As retention mechanisms, such as the formation of ternary complexes resulting from the cooperative sorption of AsO_4 anions (H_2AsO_4^- , $\text{H}_2\text{AsO}_4^{2-}$) and cations such as Ca^{2+} on clay mineral surfaces.

4. Conclusions

The present study evaluates the potential use of four industrial by-products (phosphogypsum; red gypsum; sugar foam and ashes from the combustion of biomass), applied at two different rates in single and combined amendments, to reduce the mobility and availability of As and Se in an element-spiked acidic soil. Of all the amendments applied, ACB and RG, both at high rate, were selected as the most effective treatments to reduce the leachability of both toxic elements. However, the retention mechanisms induced in the soils treated with these amendments are not resistant to severe acidification.

SEM-BSE analysis of the ACB-treated samples showed the presence of Se associated with organic matter aggregates. The large amount of organic matter contained in the ACB by-product played a complexing role on Se. In addition, this toxic element was found included in the Fe (hydr)oxides identified in the mineralogical composition of the soil.

In the case of the RG-treated samples, EDS analyses showed that As and Se were associated to Fe/Ti phases which are present not only in the by-product as maghemite and rutile, but also in the soil as hematite and goethite. In addition, the application of the RG by-product induced the formation and retention in the soil of non-crystalline Al-hydroxy polymers including As and Se in their chemical composition.

The results of this study suggest that the industrial by-products red gypsum and ashes from the combustion of biomass are useful amendments for soils containing both As and Se. These findings also increase the number of toxic elements that can be immobilized in contaminated soils.

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