

# Effects of industrial by-product amendments on As, Cd and Tl retention/release in an element-spiked acidic soil

Javier Aguilar-Carrillo <sup>a,\*</sup>, Laura Barrios <sup>b</sup>, Fernando Garrido <sup>a</sup>,  
María Teresa García-González <sup>a</sup>

<sup>a</sup> Instituto de Ciencias Agrarias, Centro de Ciencias Medioambientales, Consejo Superior de Investigaciones Científicas, Serrano 115 dpdo, 28006 Madrid, Spain

<sup>b</sup> Centro Técnico de Informática, Consejo Superior de Investigaciones Científicas, Pinar 19, 28006 Madrid, Spain

Received 5 October 2006; accepted 7 March 2007

Editorial handling by G. Filippelli

Available online 10 May 2007

## Abstract

To assess the efficiency of two by-products (phosphogypsum (PG) and sugar foam (SF), rich in gypsum and calcium carbonate, respectively) in the immobilization of three toxic elements (As, Cd and Tl) in an acidic soil, batch-scale sorption and desorption experiments were conducted after 18 months of *in situ* amendment application. The Langmuir isotherms applied for sorption studies showed that the estimated maximum sorption capacity of the elements was highest in the SF-treated samples. The amount of element retained and the percentage of extraction after TCLP tests indicated that those samples amended with sugar foam (SF and PG + SF) had the potential to immobilize As, Cd and Tl in an acidic soil with low sorptive capacity. In addition to sorption and desorption experiments, scanning electron microscopy in back-scattered electron mode (SEM-BSE) showed the formation of Al-hydroxy polymers which provides the soil with additional sorption capacity. The three target elements were associated with the Al-hydroxy polymers, probably through direct coordination or the formation of ternary complexes. By means of statistical analysis it has been found that sorption processes of As, Cd and Tl in this soil mainly depend on the treatment, whereas desorption is an element-dependent process.

© 2007 Elsevier Ltd. All rights reserved.

## 1. Introduction

Methods for remediation of metal-contaminated soils include techniques based on physical separation, stabilization, chemical treatment, phytoremediation and other combined strategies. Recently,

*in situ* metal stabilization by means of the addition of amendments is being regarded as a choice to alleviate soil degradation. This approach provides no actual reduction in toxic element concentrations, but it reduces the leaching potential through element immobilization. In recent years, there has been considerable interest in the use of industrial by-products to minimize metal solubility in the soil. Examples of soil amendments include beringite (Hamon et al., 2002), steel shot (Geebelen et al., 2002), red mud (Gray et al., 2006) and olive wastes

\* Corresponding author. Tel.: +34 91 745 25 00; fax: +34 91 564 08 00.

E-mail address: [javier.aguilar@ccma.csic.es](mailto:javier.aguilar@ccma.csic.es) (J. Aguilar-Carrillo).

(Díaz-Barrientos et al., 2003). Although field studies indicate the effectiveness of such *in situ* treatments, the mechanisms of metal sequestration and thus whether the fixation processes are permanent or reversible with time, are still unknown in many cases (Adriano et al., 2004). If *in situ* treatments only induce their effect through changes in soil pH, then presumably re-acidification of soil could restore metal bioavailability to the initial toxic level (Hamon et al., 2002). Instead, sequestration of metals in non-labile pools in the soil such as entrapment in clay lattices, surface complexation by covalent bonding and precipitation of stable solid phases should be considered as actual alternative techniques to reduce availability and offsite metal transport. Some examples of this induced immobilization were obtained by Illera et al. (2004a), who found that the formation of Al-hydroxy polymers and the precipitation of anglesite played an important role in the immobilization of metals, and by Cao et al. (2003), who reported effective immobilization of Pb through the formation of a pyromorphite-like minerals.

The contaminant processes generally release a combination of anionic and cationic toxic elements. This was the case in the mine tailings spill accident in Aznalcóllar (SW Spain) where massive amounts of acidic waters and mud containing cationic (Zn, Pb, Cd, Co, Hg, Tl and Cu) and anionic toxic elements (Se, As and Sb) were released (Simon et al., 1999). The soil contamination derived from events like this is difficult to control due to the different behaviours of the elements involved. However, while there exist several options to remove cationic toxic elements from the soil solution of contaminated soil, few detailed studies have focused on the remediation of polluted soils where both anionic and cationic species are available (Burgos et al., 2006).

The sorption of trace metals on oxides and oxy-hydroxides is one of the most important geochemical processes controlling the fate, transport, and bioavailability of metals in the soil environment (Sparks, 2005). The direct addition of these sorbent phases to the soil or their *in situ* formation in the soil through the addition of other amendments (precursors) could be a viable approach to reduce the mobility of Cd, Cu and Pb in soils (Illera et al., 2004b; Burgos et al., 2006). The addition of the by-products phosphogypsum (PG) and sugar foam (SF) induce the formation and retention of Al-hydroxy polymers (Toma and Saigusa, 1997; Garrido et al., 2003), which could boost

the toxic element retention capacity of the soils. Campbell et al. (2006) concluded that these industrial by-products could regulate the mobility of the Pb, Cd and Cu in an acidic soil. However, their effectiveness with other elements has not been investigated.

The high mobility and toxicity of As, Cd and Tl, their common joint presence and their different ionic nature justify their interest and selection for this study. Different researchers have reported the relationship between Al oxy-hydroxides and As (Arai et al., 2001; Garcia-Sanchez et al., 2002), Cd (Saha et al., 2002) and Tl (Martín et al., 2004), although the behaviour and fate of Tl in soils is not well known. Therefore, the objectives of this study are (i) to ascertain the feasibility of the application of two by-products (PG and SF) as soil amendments to improve the soil sorption capacity of As, Cd and Tl and (ii) to identify the treatment that produces the best global result (high sorption and low desorption) for the three elements jointly.

## 2. Materials and methods

### 2.1. By-products

Samples of phosphogypsum (PG) provided by the Spanish fertilizer industry Fertiberia, S.A., and sugar foam (SF) from the Spanish sugar producer Azucarera Ebro, S.L., were dried at 45 °C (phosphogypsum) or 105 °C (sugar foam) and digested by acid digestion and alkaline fusion (Hossner, 1996). The resulting solutions were analyzed for major and trace elements by ICP-AES, ICP-MS and ion chromatography. In addition, radiochemical activity in the PG samples was measured with a Canberra gamma-spectrometer equipped with a Ge detector. The chemical compositions of PG and SF are described in Illera et al. (2004b). Gypsum is the main component of PG. In addition to Ca and sulphate, it also has substantial amounts of P, Si and F. Sugar foam contains CaCO<sub>3</sub>, traces of CaO, and is rich in Mg, Si and organic matter. In addition, Ba, Cr, Cu, Ni and Zn are present at high concentrations. However, the heavy metal contents are much less than those established by the European Community (1986) for sewage sludge and constitute no environmental hazard at the rates normally used in agriculture. Finally, small concentrations of natural radionuclides, not dangerous for handling of the wastes, were found in the PG samples (Garrido et al., 2003).

2.2. Field application of the amendments

The experiments were performed with a weathered acidic soil, developed from Pliocene-Quaternary age formations in a degraded area of central Spain and classified as Plinthic Paleixerult (Soil Survey Staff, 1999) (Table 1). Twenty-four plots (4.5 m × 6 m) were randomly treated in triplicate with phosphogypsum and sugar foam as single (PG, SF) and joint amendments (PG + SF), leaving six untreated plots as controls. All the treatments were uniformly spread onto the entire surface of the plots in solid state. Each treatment was applied at two rates. Sugar foam was added at 0.17% (rate 1, SF<sub>1</sub>) and 1% (rate 2, SF<sub>2</sub>) w/w calculated on the basis of 25-cm soil depth and a bulk density of 1.3 g cm<sup>-3</sup>. These amendments involved the addition of 4.4 and 25.5 kg of Ca for each addition rate, respectively. The amount of PG applied onto the plots was calculated in order to add similar amounts of Ca as in the SF-treated plots. Thus, PG was applied at 0.21% (rate 1, PG<sub>1</sub>) and 1.15% w/w (rate 2, PG<sub>2</sub>), respectively. The PG+SF treatment applied at rate 1 ((PG + SF)<sub>1</sub>) involved the addition of double the amount of Ca to that applied in the single amendment at rate 1, meaning the addition of this joint amendment at 0.38% w/w. Lastly, at rate 2 ((PG + SF)<sub>2</sub>), PG + SF amendment was applied at 1.11% w/w so that the amount of Ca added was similar to that in the single treatments applied at the same rate.

Eighteen months after the amendment applications, four samples from each of the 24 plots (including those untreated) were collected from the Ap horizon (4–20 cm). The topmost 4 cm of the soil were discarded to avoid uncertainties due to the possible presence of any undissolved amendments particles. All the samples were air-dried, crushed and sieved through a 2-mm mesh. The mean pH and Al<sub>ox</sub> values are shown in Table 2.

2.3. Sorption isotherms experiments

Equilibrium sorption isotherms were carried out by adding 15 mL of 0.27, 0.57, 0.79, 1.14, 1.49, 2.05, 2.53 and 3.29 mM of either As or As + TI + Cd solutions to 3 g soil samples (n = 6) in 50-mL polypropylene centrifuge tubes. The source of the As, Cd and TI were the analytical-grade salts KH<sub>2</sub>AsO<sub>4</sub>, Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O and TiNO<sub>3</sub>, respectively. Theoretical calculations using Visual MINTEQ (Gustafsson, 2002) indicated that the initial solution was undersaturated with respect to

Table 1  
Some physical, chemical and mineralogical properties of the soil

pH <sup>a</sup>	OC <sup>b</sup>	Sand/ g kg <sup>-1</sup>	Silt/ g kg <sup>-1</sup>	Clay/ g kg <sup>-1</sup>	Ca <sup>2+e</sup> / cmol <sub>c</sub> kg <sup>-1</sup>	Mg <sup>2+</sup> / cmol <sub>c</sub> kg <sup>-1</sup>	Na <sup>+</sup> / cmol <sub>c</sub> kg <sup>-1</sup>	K <sup>+</sup> / cmol <sub>c</sub> kg <sup>-1</sup>	Al <sup>3+</sup> / cmol <sub>c</sub> kg <sup>-1</sup>	Al <sub>ox</sub> <sup>d</sup> / mg kg <sup>-1</sup>	Fe <sub>ox</sub> <sup>d</sup> / mg kg <sup>-1</sup>	Fraction <sup>e</sup> ≤ 2 mm			Fraction <sup>e</sup> ≤ 2 μm							
												Q	G	H	Ph	Q	G	H	Ph	V	I	K
5.45	33	700	250	50	1.60	0.10	0.07	0.07	1.91	4620	1701	74	4	3	19	12	6	6	76	8	11	57

Q = quartz, G = goethite, H = haematite, Ph = phyllosilicates, V = vermiculite, I = illite, K = kaolinite.

<sup>a</sup> pH in water (1:2.5).

<sup>b</sup> Organic carbon by wet digestion.

<sup>c</sup> Extracted with 1 M NH<sub>4</sub>AcO (Ca, Mg, Na, K) and 1 M KCl (Al).

<sup>d</sup> Extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid at pH 3.

<sup>e</sup> Relative % in sample and identified by X-ray powder diffraction.

Table 2

Mean values ( $n = 12$ ) and standard errors for the pH and  $Al_{ox}$  ( $mg\ kg^{-1}$ ) of the soil after 18 months of treatments applied

	Rate 1 <sup>a</sup>		Rate 2 <sup>b</sup>	
	pH	$Al_{ox}$	pH	$Al_{ox}$
C <sup>c</sup>	5.45 ± 0.04	4620 ± 140.6	5.45 ± 0.04	4620 ± 140.6
PG	5.29 ± 0.06	6650.6 ± 425.6	5.14 ± 0.05	6320.7 ± 342.6
SF	5.67 ± 0.13	7119.7 ± 372.6	7.21 ± 0.10	5931.6 ± 361.7
PG + SF	5.84 ± 0.11	6848.2 ± 362.0	6.14 ± 0.15	6136.4 ± 399.4

<sup>a</sup> Rate 1, dose with lowest calcium content.<sup>b</sup> Rate 2, dose with highest calcium content.<sup>c</sup> C, control; PG, phosphogypsum; SF, sugar foam.

each element salt and other possible solids. Soil suspensions were shaken on a rotary shaker (~40 rpm) for 24 h, centrifuged at 6640g for 10 min, and filtered through 0.45  $\mu m$  cellulose nitrate filters. The filtrates were acidified (pH  $\approx$  2) with 65%  $HNO_3$  and stored at 4 °C before the solutions were analyzed for total As (referred as As throughout the text), Cd and Tl by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Perkin Elmer OPTIMA 4300DV. The total amount of toxic element retained by the solid phase was obtained by the difference between the initial and remaining concentration in the supernatant. For all elemental determinations performed by ICP-AES, calibration curves were run before and after each sample series (20 samples including matrix-matched blanks and in-between calibration checks). The calibration solutions covered the range of concentration in the samples and were prepared in the same matrix as the extracting reagents from certified stock solutions. Sample blanks were analyzed for correction of background effect on instrument response. Trace metal standards were used to assess instrument precision. Metal concentrations were calculated in unknown solutions on the basis of the external calibration averaging the concentrations from two repetitions for each experimental replication. Limits of detection were calculated as three standard deviations of the instrument response from 10 repeated analyses of sample matrix-matched blank solutions. The detection limits showed that concentration of a few  $\mu g\ L^{-1}$  of the three elements could be analyzed.

The corresponding sorption isotherms were studied by fitting the Langmuir isotherm equation to the experimental data

$$S = \frac{Qk_L C}{1 + k_L C} \quad (1)$$

where  $S$  is the amount of element sorbed by the soil ( $mmol\ kg^{-1}$ ),  $C$  the equilibrium concentration in solution ( $mmol\ L^{-1}$ ),  $Q$  the maximum sorption ( $mmol\ kg^{-1}$ ) and  $k_L$  the bonding energy coefficient ( $mmol\ L^{-1}$ ) (Kinniburgh, 1986). The optimal parameter values were estimated by non-linear regression analysis, on the assumption of a constant relative error as the residuals revealed no systematic deviation. The goodness-of-fit for the isotherms equations was estimated by the coefficient of determination ( $R^2$ ), the confidence intervals (95%) of the estimated parameters, and the standard error of the estimate (SE).

#### 2.4. TCLP experiments

The treated and control soil samples after the interaction with highest element concentration solutions of the sorption isotherms were split into two subsamples. Each of them was subsequently used for the TCLP experiments. The EPA Toxicity Characteristic Leaching Procedure (USEPA, 1986) was used to determine the stability of the toxic elements retained in both treated and untreated soil samples. This method consists of two non sequential extractions of the elements using two solutions prepared from acetic acid at pH  $4.93 \pm 0.05$  (Fluid 1) and  $2.88 \pm 0.05$  (Fluid 2). The TCLP trials were performed by adding 20 mL of extracting solution (either fluid 1 or 2) to 1 g samples ( $n = 6$ ) in 50 mL polypropylene centrifuge tubes. The soil suspensions were shaken on a rotary shaker (~40 rpm) at a controlled room temperature ( $25\ ^\circ C \pm 1$ ) for 18 h. The suspensions were centrifuged at 6640g for 10 min and the supernatants were filtered through Whatman No. 5 filter papers, acidified (pH  $\approx$  2) with 65%  $HNO_3$ , and stored at 4 °C before the solutions were analyzed for As, Cd and Tl by ICP-AES.

## 2.5. Sorption–desorption interparametric statistical relationships

To examine the statistical significance of the differences found in the sorption and desorption parameters as a result of the treatments, a two-way analysis of variance (ANOVA), including treatment and element, was performed. The Bonferroni *post-hoc* test was used to establish statistical differences among the resulting pairs of the treatment and element combination. In addition, from a multivariate viewpoint, the relationships between equilibrium-based sorption (described by  $Q$  and  $M$  variables, where  $M$  is the mass of element retained per treatment) and desorption (characterized by  $F1$ ,  $F2$ ,  $Ex1$  and  $Ex2$  variables) parameters were assessed through an optimal scaling technique (Gifi, 1991) and it was interpreted through the Categorical Principal Components Analysis (CatPCA; SPSS, Inc., Chicago, IL). In this procedure, the experimental conditions (treatment and element) were identified in a new nominal variable (*trat\_elem*) with 21 levels or categories represented by two digits, the first one corresponding to the treatment (1–7) and the second to the element (1–3).

Considering that each experimental case can be reasonably represented by the centroid (an average weighted by membership values) and in order to separate the new *trat\_elem* variables into different groups, a  $K$ -means cluster analysis (CA), based on a Euclidean distance measure and inter-centroids linkage technique (non-parametric model) was used. The CA provides exploratory results and requires a subsequent stepwise discriminant analysis (DA). The DA is a supervised pattern recognition method that is designed to find one or more functions of quantitative measurements that can discriminate between previously established groups. All statistical analyses were done using the statistic package SPSS v. 14.0 (SPSS, Inc., Chicago, IL).

## 2.6. SEM 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 back-scattered electron mode (SEM-BSE). The samples obtained from the interaction between treated and untreated soil samples and solutions of the highest concentration of the elements were employed for this purpose. Samples were oven-dried

(50 °C) and embedded in low-viscosity acrylic resin (LR-White, medium grade). Blocks of resin-embedded samples were finely polished using a commercially available low-viscosity oil/water emulsion as a lubricant and subsequently observed on a DMS 940A-Zeiss microscope equipped with a 4-diode and BSE detector. Microprobe analysis and microprobe profiles were made with a Link Isis energy dispersive spectrometry (EDS) microanalytical system on the SEM. The following microscopy and analytical operating conditions were used: a take-off angle of 35°, an accelerating voltage of 15 kV, a working distance of 25 mm, and a specimen current of 1–5 nA.

## 3. Results and discussion

### 3.1. Sorption experiments

#### 3.1.1. Arsenic, Cd and Tl isotherms

The sorption of As, Cd and Tl on both the control and amended soil samples was adequately described by the Langmuir equation (Fig. 1) with values of coefficient of determination ( $R^2$ ) higher than 0.95, 0.95 and 0.97 for As, Cd and Tl, respectively (Table 3). The goodness-of-fit of the three elements agree with other studies for As (Goh and Lim, 2004), Cd (Illera et al., 2004a) and Tl (Jacobson et al., 2005), although these authors used other element concentration ranges. In those soil samples treated with SF (SF<sub>1</sub>, SF<sub>2</sub>, (PG + SF)<sub>1</sub> and (PG + SF)<sub>2</sub>), the resulting sorption isotherms for Cd were H-type ones (Giles et al., 1974), indicating a high affinity for the sorbents (Table 3).

In the control soil samples, the estimated maximum sorption capacity ( $Q$ ) and the bonding energy coefficient ( $k_L$ ) for As were greater than those for Cd and Tl. The addition of the amendments to the soil produced changes in  $Q$  and  $k_L$  values depending on the element and by-product used (Table 3). While the addition of single PG to the soil produced a minor effect on As, Cd and Tl sorption, the SF-treated samples showed the greatest increase in the sorption of the three elements. In all cases, the estimated maximum sorption capacity at rate 2 was higher than that at rate 1, especially in the sorption of As in the SF-treated samples. Similarly, Bothe and Brown (1999a) proved that the addition of lime to As-containing wastes is beneficial to reduce the mobility of dissolved As. On the other hand, the application of PG<sub>2</sub> decreased the soil sorption capacity of As. Genc-Fuhrman et al. (2005) showed

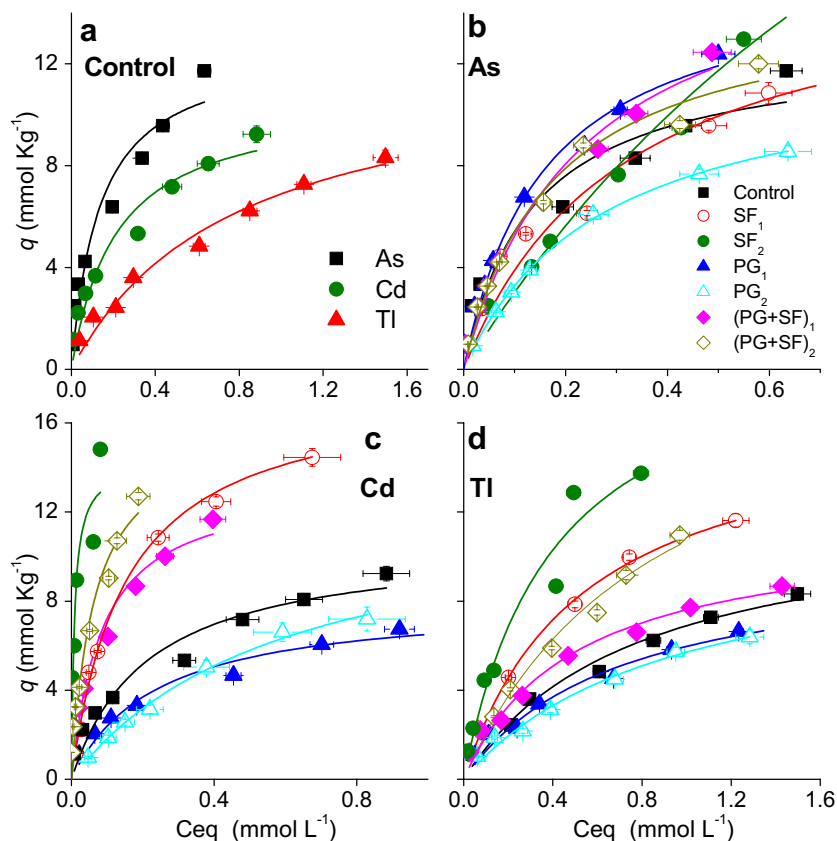


Fig. 1. Sorption isotherm experiments for As, Cd and Tl using trielemental mixed solutions. (a) Comparison among the toxic elements in control samples. (b)–(d) Comparison among treatments for each element. Solid curves depict results of curve-fitting with the Langmuir equation. Error bars denote standard errors ( $n = 6$ ).

minor competition between  $\text{SO}_4$ , as well as  $\text{PO}_4$ , and  $\text{AsO}_4$  anions for sorption on red mud. However, other authors have described competing sorption processes between these anions in goethite (O'Reilly et al., 2001), alumina (Xu et al., 1988) and in mine pit lakes (Eary, 1999). This competitive sorption between  $\text{SO}_4$  and  $\text{AsO}_4$  ions could lead As anions to be sorbed on more specific sorption positions, as suggested in a previous work (Aguilar-Carrillo et al., 2006).

On the other hand, in all cases,  $Q_{\text{Tl}}$  was lower than that of As and Cd. The result of the presence of  $\text{K}^+$  coming from the chemical source of As used in this study ( $\text{KH}_2\text{AsO}_4$ ) as well as from the SF by-product itself should also be considered. Jacobson et al. (2005) found that  $\text{K}^+$  effectively competes with  $\text{Tl}^+$  for the same sorption sites in soil minerals due to their similar ionic radii (1.51 Å and 1.59 Å, respectively). Additionally, other cations (e.g.,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , etc.) showing stronger affinity than  $\text{Tl}^+$ , could easily displace it from non-specific sorp-

tion sites of the clay minerals. This would result in a decrease of the number of available soil sorption sites and, in turn, a decrease of the soil sorption capacity for Tl (Yang et al., 2005). This could be particularly true in the PG-treated samples in which the resulting pH values were lower than in control ones (Table 2) and matched up with a reduction of the sorption capacity for Tl (Table 3).

### 3.1.2. Effect of Cd and Tl on As sorption

To study the effect of the presence of Cd and Tl on As retention, sorption experiments with As and As + Tl + Cd initial solutions in control and amended soil samples were performed (Table 4).

In the control soil samples, the presence of Cd and Tl cations produced a significant increase in the maximum sorption capacity ( $Q$ ) and bonding energy coefficient ( $k_L$ ) of As compared to those for As in mono-elemental solutions (Table 4). On the other hand, previous isotherm experiments including As + Tl solutions (data not shown) showed no

Table 3  
Mean values ( $n = 6$ ) of Langmuir constants for As, Cd and Tl sorption in amended and unamended soil samples

		Equilibrium parameters				
Treatment <sup>a</sup>		$Q^b$	SE <sup>c</sup>	$k_L^d$	SE	$R^{2e}$
		/mmol kg <sup>-1</sup>		/L mmol <sup>-1</sup>		
As	C	12.55	1.46	5.59	2.63	0.95
	PG <sub>1</sub>	14.33	1.23	7.77	1.73	0.98
	SF <sub>1</sub>	19.72	1.87	3.74	0.87	0.96
	(PG + SF) <sub>1</sub>	16.34	2.22	5.10	1.60	0.97
	PG <sub>2</sub>	11.77	0.79	6.10	0.65	0.99
	SF <sub>2</sub>	30.77	3.99	1.17	0.41	0.98
	(PG + SF) <sub>2</sub>	13.76	1.33	6.60	1.27	0.98
	PSE <sup>f</sup>	0.69		0.87		
Cd	C	10.55	1.25	5.43	0.53	0.96
	PG <sub>1</sub>	8.35	0.43	4.39	0.67	0.97
	SF <sub>1</sub>	17.90	1.27	N.F. <sup>g</sup>	N.F.	0.99
	(PG + SF) <sub>1</sub>	13.48	1.65	N.F.	N.F.	0.96
	PG <sub>2</sub>	14.61	1.54	2.50	0.50	0.99
	SF <sub>2</sub>	19.41	2.09	N.F.	N.F.	0.95
	(PG + SF) <sub>2</sub>	15.93	1.94	N.F.	N.F.	0.96
	PSE	0.82				
Tl	C	11.94	1.38	1.32	0.37	0.98
	PG <sub>1</sub>	10.32	1.27	1.46	0.39	0.97
	SF <sub>1</sub>	16.10	0.90	1.87	0.24	0.99
	(PG + SF) <sub>1</sub>	11.33	1.15	1.91	0.52	0.98
	PG <sub>2</sub>	11.71	2.14	1.09	0.34	0.98
	SF <sub>2</sub>	20.83	2.13	2.81	0.60	0.97
	(PG + SF) <sub>2</sub>	14.82	2.07	2.01	0.52	0.98
	PSE	0.75		0.37		

<sup>a</sup> C, control; PG<sub>1</sub>, phosphogypsum at rate 1; SF<sub>2</sub>, sugar foam at rate 2.

<sup>b</sup>  $Q$ , maximum sorption parameter from Eq. (1).

<sup>c</sup> SE, standard error of estimation.

<sup>d</sup>  $k_L$ , bonding energy coefficient from Eq. (1).

<sup>e</sup> Significant at  $p \leq 0.05$ .

<sup>f</sup> PSE, pooled standard error ( $p \leq 0.05$ ).

<sup>g</sup> N.F., not fitted.

significant effect on the  $Q$  and  $k_L$  values for As. Therefore, it seems that Cd was responsible for the increment of As retention through distinct pro-

cesses on the basis of the similar ionic radii of Ca<sup>2+</sup> (0.99 Å) and Cd<sup>2+</sup> (0.97 Å): (1) the formation of Al-OH polymeric new solid phases through two mechanisms: (i) Al<sup>3+</sup> exchanged by Ca<sup>2+</sup> previously displaced to the solution as a concomitant process of the sorption of Cd<sup>2+</sup> on solid surfaces – mainly reprecipitated carbonates – and (ii) Al<sup>3+</sup> directly exchanged by Cd<sup>2+</sup>. In both cases, the released Al<sup>3+</sup> hydrolyzes leading to the formation of Al-OH polymers, with high As sorption capacity; (2) the formation of ternary complexes resulting from the cooperative sorption of AsO<sub>4</sub> anions (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, H<sub>2</sub>AsO<sub>4</sub><sup>2-</sup>) and cations such as Ca<sup>2+</sup> or Cd<sup>2+</sup> on soil surfaces. Although the identification of such processes requires the use of advanced spectroscopic analytical techniques, McBride (1999) described similar processes with phosphate and other divalent elements on Fe and Al hydroxide surfaces; (3) the formation of an amorphous Cd-arsenate new phase due to the exchange reaction in Ca-type arsenates such as the Cd analogue of the sainfeldite (Ca<sub>5</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub> · 4H<sub>2</sub>O) obtained by Johnson et al. (2003). All these processes would also explain the significant increase of Cd uptake in the SF-treated samples as compared to the control ones (Table 3).

In the PG-treated samples, the  $k_L$  values for As significantly increased when both Cd and Tl were present (Table 4). However, in the single SF-treated samples this bonding energy decreased. This suggests that the occurrence of Cd and Tl in soil samples amended with single SF led to weaker retention mechanisms of As than those in the PG-treated samples. However, the amount of As sorbed in the soil was greater in SF-treated samples than in the PG-treated ones. Therefore, the mechanisms of As retention are different depending on the amendment employed. While retention of As in the presence of PG may be affected by the competitive

Table 4  
Effect of Cd and Tl simultaneous presence on Langmuir sorption parameters of As ( $n = 6$ ) in a concentration range of the three elements from 0.27 to 3.29 mM for both As- and (As + Cd + Tl) isotherms

		C <sup>a</sup>	PG <sub>1</sub>	SF <sub>1</sub>	(PG + SF) <sub>1</sub>	PG <sub>2</sub>	SF <sub>2</sub>	(PG + SF) <sub>2</sub>
		/mmol kg <sup>-1</sup>						
$Q$	As <sub>(As)</sub>	10.58	11.55	13.46	14.13	11.85	13.24	14.47
	As <sub>(As+Tl+Cd)</sub>	12.55	14.33	19.72	16.34	11.77	30.77	13.76
	PSE <sup>b</sup>	0.30	0.45	0.66	1.25	0.87	0.49	0.82
		/L mmol <sup>-1</sup>						
$k_L$	As <sub>(As)</sub>	2.03	2.80	1.01	3.62	3.77	2.48	2.85
	As <sub>(As+Tl+Cd)</sub>	5.59	7.77	0.47	4.56	6.10	1.17	6.60
	PSE	0.95	0.70	0.72	0.58	0.71	0.18	0.53

<sup>a</sup> C, control; PG<sub>1</sub>, phosphogypsum at rate 1; SF<sub>2</sub>, sugar foam at rate 2.

<sup>b</sup> PSE, pooled standard error ( $p \leq 0.05$ ).

sorption of  $\text{SO}_4$  and  $\text{AsO}_4$  anions, the retention of As in SF-treated samples seems to be linked to both Cd and Tl through different mechanisms such as those mentioned above.

### 3.2. Desorption experiments

The TCLP test provides information on the potential leachability of elements in soils under moderately (F1, pH 4.93) or strongly (F2, pH 2.88) acid conditions. The results of the test were expressed in two different ways: (1) in terms of the amount of element ( $\text{mg kg}^{-1}$ ) that remains within the soil matrix after the extraction procedure; (2) as the percentage of the mass of element extracted (Ex1 and Ex2 after reactions with fluid 1 and fluid 2, respectively) relative to the total mass sorbed on the soil samples (computed from the sorption isotherm experiments), thus, taking into account the different sorption capacity of the control and amended soil samples.

In all cases, the amount of As, Cd and Tl retained after the extraction at pH 4.93 (F1) was greater than that retained under more acidic conditions (Table 5). Arsenic was the element with lowest extraction percentage for both F1 and F2 extractions. The maximum immobilization efficiency of As was found after the  $\text{SF}_2$  treatment which yielded Ex1 and Ex2 values of 21% and 32%, respectively. Also, the amount of Cd retained in the soil was  $\sim 3$  ( $\text{SF}_1$ ) and  $\sim 4.5$  ( $\text{SF}_2$ ) times greater than that in the control after the F2 extraction. The masses of Tl retained upon the  $\text{SF}_1$  and  $\text{SF}_2$  treatments followed a similar trend, and were significantly higher than that in the control sample after the F1 and F2 extractions. The overall reduction in the leachability of the elements in the SF-treated samples might be the result of their retention through specific sorption reactions on the surface of carbonate solid phases or Al-hydroxy polymers. Once trace elements are specifically sorbed on the Al-OH polymers 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 (Bradl, 2004; Gray et al., 2006).

Furthermore, the extractability of Tl was also lower in these treated samples than in the control ones. Common to Cd and Tl, the mass of element retained in the  $(\text{PG} + \text{SF})_2$ -treated samples was significantly higher than in control ones, and the

Table 5

Mean amount ( $\text{mg kg}^{-1}$ ,  $n = 6$ ) of As, Cd and Tl retained by the soil after TCLP extraction, in parenthesis calculated as percentage of initial amount

		Fluid 1 <sup>a</sup>	Fluid 2 <sup>b</sup>
As	C <sup>c</sup>	616.2 (27.9)	481.7 (43.7)
	$\text{PG}_1$	686.7 (26.6)	540.6 (42.2)
	$\text{SF}_1$	670.3 (39.6)	628.8 (43.4)
	$(\text{PG} + \text{SF})_1$	644.5 (31.1)	566.8 (39.4)
	$\text{PG}_2$	555.1 (35.0)	450.3 (47.2)
	$\text{SF}_2$	836.6 (21.3)	723.4 (32.0)
	$(\text{PG} + \text{SF})_2$	604.1 (33.9)	510.1 (44.2)
	PSE <sup>d</sup>	35.8	46.3
Cd	C	568.4 (45.7)	156.2 (85.2)
	$\text{PG}_1$	262 (67.7)	27.3 (98.1)
	$\text{SF}_1$	995.5 (38.6)	457.4 (71.8)
	$(\text{PG} + \text{SF})_1$	558.0 (57.5)	157.4 (87.7)
	$\text{PG}_2$	666.5 (36.8)	264.9 (66.9)
	$\text{SF}_2$	1123.1 (42.6)	706.9 (63.9)
	$(\text{PG} + \text{SF})_2$	762.3 (46.0)	374.0 (73.4)
	PSE	94.5	89.8
Tl	C	693.2 (59.1)	374.3 (78.8)
	$\text{PG}_1$	441.4 (70.7)	129.0 (92.0)
	$\text{SF}_1$	1164.6 (50.6)	622.4 (73.6)
	$(\text{PG} + \text{SF})_1$	456.8 (74.8)	172.9 (90.0)
	$\text{PG}_2$	731.3 (60.5)	418.3 (78.2)
	$\text{SF}_2$	1191.3 (58.2)	879.1 (69.1)
	$(\text{PG} + \text{SF})_2$	940.9 (56.4)	714.4 (66.6)
	PSE	117.8	137.5

<sup>a</sup> Fluid 1, TCLP extraction under moderately acid conditions (pH 4.93).

<sup>b</sup> Fluid 2, TCLP extraction under strongly acid conditions (pH 2.88).

<sup>c</sup> C, control;  $\text{PG}_1$ , phosphogypsum at rate 1;  $\text{SF}_2$ , sugar foam at rate 2.

<sup>d</sup> PSE, pooled standard error ( $p \leq 0.05$ ).

extractability of these elements decreased under both extracting conditions. In general, the addition of SF in single ( $\text{SF}_1$ ,  $\text{SF}_2$ ) or combined ( $(\text{PG} + \text{SF})_2$ ) amendments produced a significant increased of the amount of As, Cd and Tl that remains within the soil after both TCLP extractions (F1 and F2 solutions) (Table 5). This demonstrates the potential of the amendments as fixing agents for *in situ* immobilization of these mobile toxic elements in acidic soils.

### 3.3. Sorption–desorption interparametric relationships

#### 3.3.1. Sorption processes

Overall, the two-principal components model explained 94% of the total variance. The first component (CatPC1), considered as the desorption

component, was represented by *F1* and *F2* variables and explained 77% of the total variance (Fig. 2a). The second component (CatPC2), regarded as the sorption one, was represented by *Q* and *M* variables, and explained 17% of the total variance. The component loadings plot (Fig. 2a) shows that sorption variables (*Q* and *M* vectors) appear together and close to the *trat\_elem* vector. The same trend is observed in the case of desorption variables (*F1* and *F2* vectors). Thus, sorption and desorption transformed variables are plotted in the same direction, indicating high correlation coefficients between *trat\_elem* and the variables *F1* ( $\rho_{F1} = 0.971$ ), *F2* ( $\rho_{F2} = 0.938$ ), *M* ( $\rho_M = 0.926$ ) and *Q* ( $\rho_Q = 0.926$ ) as can be seen in Fig. 2a, i.e. the smaller the angle of the vectors, the higher the correlation between the involved variables.

The order in which the model has transformed the *trat\_elem* variable is especially relevant. In Fig. 2b, the *trat\_elem* values are depicted in a two-dimensional plot and arranged depending on the sorption–desorption features. In addition, to better understand the results of this analytical procedure, two dummy axes are plotted: a sorption related one, synthesized by the *Q* vector, and another desorption related axis, synthesized by the *Ex2* and *F2* vectors. The arrangement of the *trat\_elem* values depended on the treatment type suggesting that sorption phenomena of the three elements mainly depend on the treatment. As can be seen, in agreement with the sorption data previously discussed (Table 3), the *trat\_elem* values corresponding

to those treatments where sugar foam was present (SF and SF + PG) were located on the right side of the sorption axis (Fig. 2b; in blue), i.e. on the highest sorption zone. The addition of SF to acid soils enhances the formation and retention of Al–OH polymers as a result of Ca–Al exchange reactions (Toma and Saigusa, 1997; Garrido et al., 2003) (Table 2) and increases the pH dependent negative surface charge of the soil. On the other hand, these new Al solid phases, along with the Fe oxyhydroxides and carbonates, play a pivotal role in the sorption of trace elements and provide the soil with a large sorption capacity for As (Goldberg, 2002). This may be due to direct complexation (inner-sphere monodentate–bidentate complexes) (Goldberg and Johnston, 2001) on the reactive surface of the Al–OH polymers. However, the retention of As through coprecipitation (Waychunas et al., 1993) and/or entrapment (Arai and Sparks, 2002) should be considered as well. Also, Lombi et al. (2004) hypothesized that the addition of lime to the soil increases the amount of As sorbed by carbonates. In the present samples, since the topmost 4 cm of the soil were discarded, the presence of carbonates may be due to the reprecipitation phenomena of clay- and fine-silt-size new carbonate particles. These carbonates would be formed by the lateral redistribution and/or upward movement of carbonate-rich pore water driven by evaporation (Bui et al., 1990). Thus, As could be sorbed on these secondary carbonates. Also, Ca coming from lime could form Ca arsenates with different solubility

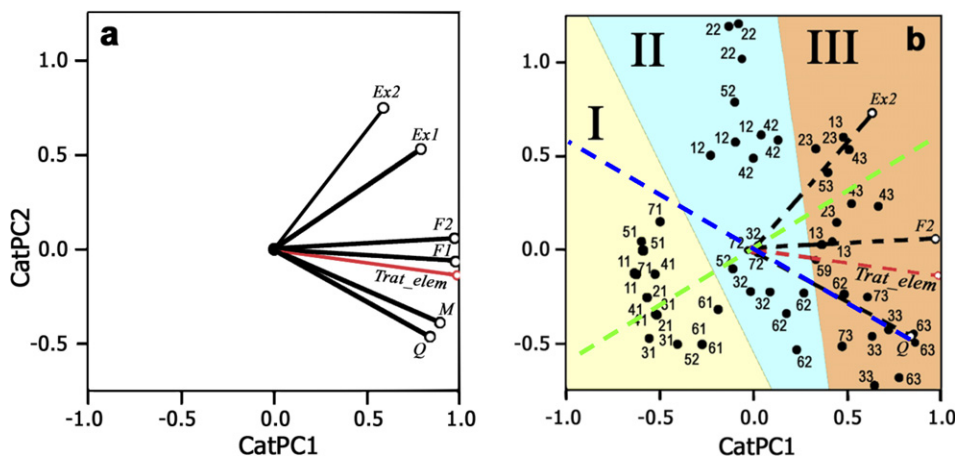


Fig. 2. Biplot of component loadings from the CatPCA showing (a) the relationship between sorption and desorption variables and (b) the projection of the *trat\_elem* variables including sorption (blue) and desorption (green) dummy axes. First digit indicates the treatment (1, C; 2, PG<sub>1</sub>; 3, SF<sub>1</sub>; 4, (PG + SF)<sub>1</sub>; 5, PG<sub>2</sub>; 6, SF<sub>2</sub>; 7, (PG+SF)<sub>2</sub>). Second digit indicates the element (1, As; 2, Cd; 3, Tl).

( $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$  or  $\text{Ca}_5\text{H}_2(\text{AsO})_4 \cdot 9\text{H}_2\text{O}$ ) which are the predominant species in the pH range of this study (pH 5–7) (Bothe and Brown, 1999b).

The role of Al- and Fe-oxides in the retention of Tl and Cd has also been reported by Martin and Kaplan (1998). The sorption of Tl by amorphous Al-oxides might have been responsible for the higher Tl retention in neutral-alkaline soils (Martín et al., 2004). Also, an increase in pH (pH > 6.5) facilitates the sorption of Tl on soil oxides (Lin and Nriagu, 1998). Other mechanisms resulting from Van der Waals interactions, such as those reported by Sposito (1989) for the sorption of Cd on Al-OH polymers in a kaolinitic soil, cannot be disregarded. Besides the sorption of Cd on the highly reactive Al-OH polymer phases,  $\text{Cd}^{2+}$  released to the soil solution could also undergo a fast exchange reaction with  $\text{Ca}^{2+}$  at the hydrated surface of reprecipitated carbonate particles followed by a slow recrystallization of  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$  to form an ideal  $\text{Ca}_{1-x}\text{Cd}_x\text{CO}_3$  solid phase on the surface of these particles (McBride, 1999). Thus, the increased Cd retention as a result of the SF treatments may be due to sorption and/or coprecipitation reactions at the surfaces of calcite and Fe and Al oxy-hydroxides. Therefore, several mechanisms such as adsorption, cluster formation, homogeneous and/or heterogeneous solid solution or a combination of these processes may be involved (Widerlund et al., 2005).

### 3.3.2. Desorption processes

Three different areas can be observed (Fig. 2b) along the direction of the dummy desorption axis (represented by the F2 vector). Within each area, the *trat\_elem* values were clearly arranged according to the elements and there are differences relative to the treatments, i.e. homogeneity in zone I and dispersion in zones II and III (especially with 22, 23 and 43 variables corresponding to Cd in  $\text{PG}_1$ -treated samples and, Tl in  $\text{PG}_1$ - and  $(\text{PG} + \text{SF})_1$ -treated samples, respectively). Therefore, zones I, II and III correspond to the As, Cd and Tl elements, respectively. The As *trat\_elem* group values are placed on the left side of the desorption axis (Fig. 2b; in green), indicating lesser As desorption tendency. This could be related to the preferential intraparticle diffusion of arsenate ( $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ ) into the Al-OH polymers lattice when SF is applied to this acidic soil (Aguilar-Carrillo et al., 2006). This might also be linked with the shared charge (i.e. valence of central atom divided by the number of bonded O

atoms) of the arsenate oxyanion (1.25). McBride (1999) ranked different oxyanions depending on their shared charge and reported that the smaller the shared charge, the greater effective negative charge residing on each O atom, and the stronger is the metal-oxyanion ionic bond, where the metal is  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . Therefore, the low extractability of As may be due to the strong bonding between arsenate O atoms and functional groups of Al-OH polymers. This result should be considered carefully since Ghosh et al. (2006) showed that TCLP significantly underestimates the leaching potential of As under certain conditions.

Along this desorption axis (Fig. 2b; in green), Cd and Tl appear at the centre and on the right side, respectively, showing higher desorption tendency than As (Table 5). In the case of Cd, the high sorption capacity of the SF-treated samples (Fig. 2b; 32 and 62), yielding H-type isotherms (Fig. 1), does not result in a relative lesser desorption tendency. This is due to the fact that the new solid phases likely formed in the presence of  $\text{CaCO}_3$  ( $\text{CdCO}_3$  (otavite) and/or  $(\text{Ca,Cd})\text{CO}_3$  solid solution) are unstable under the pH of the extracting solutions.

Thallium was the element with highest extraction percentage after the reaction with F1 and F2 solutions in most of the treatments (Table 5). This is in agreement with the low  $k_L$  values obtained (Table 3), suggesting its retention by means of weak bonds between Tl and the soil sorbent phases. This is reasonable since Tl derived from anthropogenic sources tends to be sorbed on the surface of the soil minerals on easily exchangeable sites (Kaplan and Mattigod, 1998). In addition, Yang et al. (2005) studied the distribution of Tl in soil profiles close to a pyrite slag pile and also found that in the 15 cm top soil, Tl was mainly associated with the exchangeable phase.

These results indicate that the desorption process of As, Cd and Tl, regardless of whether the soil samples are treated or not, is an element-dependent process, i.e. the influence of the treatment on the desorption processes was not as significant as the chemical nature of the elements.

### 3.3.3. Overall sorption–desorption behaviour patterns

The projection of the *trat\_elem* centroids on the sorption–desorption variables representation (Fig. 3) confirmed the conclusions obtained in the previous section but additional information could be extracted from it. Within each element separately, the *trat\_elem* centroid values corresponding

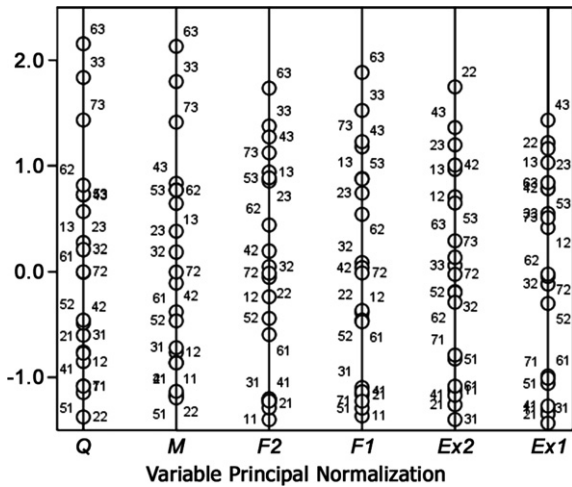


Fig. 3. Projection of the *trat\_elem* centroids on sorption and desorption variables. First digit indicates the treatment (1, C; 2, PG<sub>1</sub>; 3, SF<sub>1</sub>; 4, (PG + SF)<sub>1</sub>; 5, PG<sub>2</sub>; 6, SF<sub>2</sub>; 7, (PG + SF)<sub>2</sub>). Second digit indicates the element (1, As; 2, Cd; 3, Tl).

to those samples amended with SF<sub>2</sub> (61, 62 and 63, for As, Cd and Tl, respectively) showed greater values than expected considering all the treatments. This indicates that SF by-product is, within the amendments tested in this study, an extraordinary amendment to reduce the mobility of these three toxic elements in the soil.

Due to the reduction of the number of objects to classify and attending to the different possibilities for group conformation, the cluster analysis (CA) showed three groups of objects. In addition, based on the three previously established groups, two discriminant functions were generated through stepwise discriminant analysis (DA). For each function, higher absolute values of pooled within-group correlation coefficients are related to greater capacity to discriminate between cases. As can be seen in Table 6, *F2* ( $r = 0.953$ ) and *Q* ( $r = 0.857$ ) were the independent variables with largest absolute size of correlation within functions 1 and 2, respectively. This indicated that the combination of both *F2* (desorption) and *Q* (sorption) variables was the best possible one to classify the data into three different behaviour groups (Fig. 4). The first group (Fig. 4a) exclusively included objects corresponding to As element and it is characterized by low-medium sorption and low desorption. It is relevant that As presents practically the same desorption tendency irrespective of the applied treatment. A second group (Fig. 4b) included all the objects corresponding to Cd and Tl elements, except those where Tl

Table 6  
Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions

	Function	
	1	2
<i>F2</i>	0.953 <sup>b</sup>	0.304
<i>F1</i> <sup>a</sup>	0.796 <sup>b</sup>	0.405
Ex1 <sup>a</sup>	0.472 <sup>b</sup>	-0.063
<i>Q</i>	0.516	0.857 <sup>b</sup>
<i>M</i> <sup>a</sup>	0.608	0.653 <sup>b</sup>
Ex2 <sup>a</sup>	0.322	-0.532 <sup>b</sup>

<sup>a</sup> Variable not used in the analysis.

<sup>b</sup> Largest absolute correlation between each variable and any discriminant function.

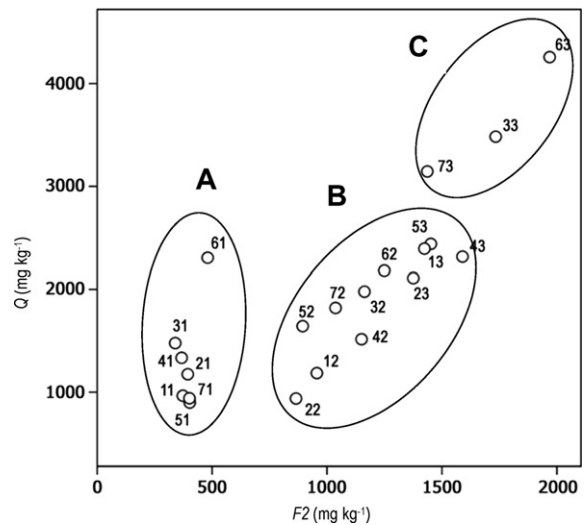


Fig. 4. Distribution of the *trat\_elem* centroids based on the combination of both *F2* (desorption) and *Q* (sorption) variables that was the best possible to classify the data in three different behaviour groups A, B and C. First digit indicates the treatment (1, C; 2, PG<sub>1</sub>; 3, SF<sub>1</sub>; 4, (PG+SF)<sub>1</sub>; 5, PG<sub>2</sub>; 6, SF<sub>2</sub>; 7, (PG + SF)<sub>2</sub>). Second digit indicates the element (1, As; 2, Cd; 3, Tl).

and SF appeared together. This second group is characterized by a low-medium sorption and medium-high desorption. In addition, this group presents a linear correlation between *F2* and *Q* variables, indicating that higher sorption values correspond to higher desorption ones. Therefore, the percentage of extraction (Table 5) should be considered as an indicator to assess the potential leachability of toxic elements in contaminated soils. Finally, a third group (Fig. 4c) characterized by the highest sorption and highest desorption, included objects corresponding to the Tl when SF was present, except the object related to Tl in the (SF + PG)<sub>1</sub>-

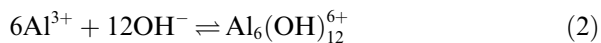
treated sample. This confirms that the presence of SF produced a significant enhancement in the Tl sorption (Fig. 4, Table 3).

### 3.4. SEM observations

Regardless of the treatment, SEM-BSE analysis confirmed the formation of non-crystalline Al-hydroxy polymers frequently associated with particles mainly composed of phyllosilicates and organic matter. However, not all the treatments increased the retention capacity of As, Cd and Tl to a similar extent. Therefore, and based on sorption data, the SEM discussion is focused on SF<sub>2</sub>-treated samples, which showed the overall highest sorption capacity for the three elements.

In the SF<sub>2</sub>-treated samples (Fig. 5), the three toxic elements were found associated with these Al-hydroxy polymers, irrespective of whether the elements were added in monoelemental (As, Fig. 5a and b) or trielemental (As + Cd + Tl, Fig. 5c and d) solutions. During the polymerization

of Al, arsenate anions may be incorporated in the Al amorphous structure, leading to the formation of new Al hydroxide layers/clusters entrapping As sorption complexes within the structure (Arai and Sparks, 2002). In addition, Al<sup>3+</sup> ions rapidly coalesced to form 6-member ring-form polynuclear ions (May and Nordstrom, 1991)



which would slowly associate with other anions (such As) to form amorphous metastable hydroxy-aluminum-anion solids. EDS X-ray spectra showed large amounts of As associated with massive formations of Al amorphous polymers (Fig. 5b and d). Similar results were found by Garcia-Sanchez et al. (2002), who demonstrated that the large As sorption capacity of Al-hydroxy was due to their large specific surface area and the low degree of crystallinity. This agrees with previous studies showing a strong correlation between As- and Al-oxalate extractable (Tao et al., 2006), indicating the importance of As fixation on amorphous Al phases in soils. In addition, the

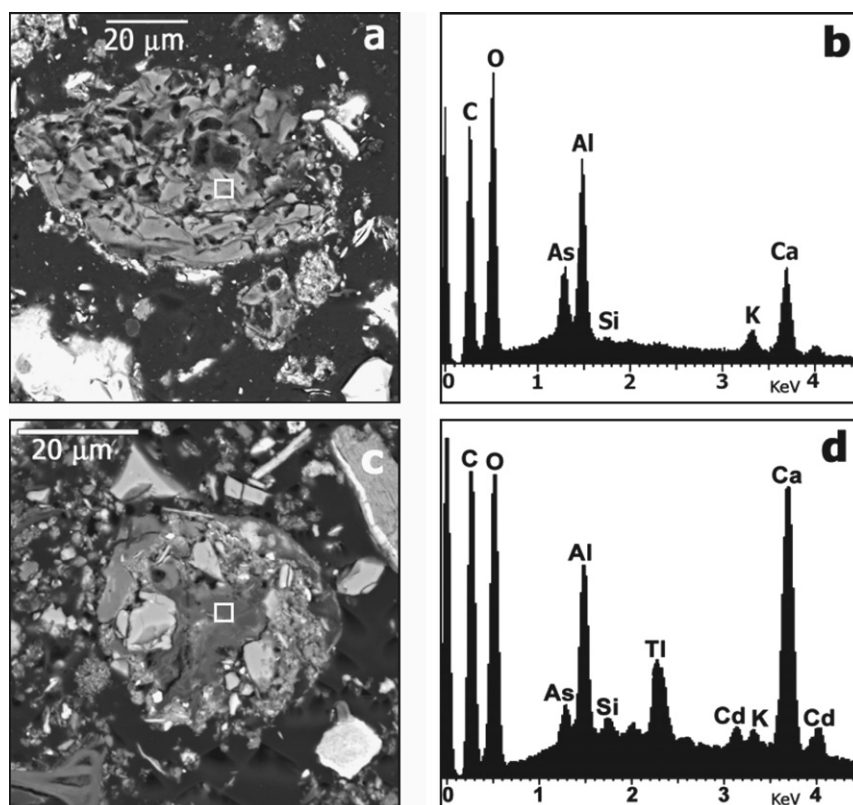


Fig. 5. SEM-BSE images showing massive formations of Al-hydroxy polymers in SF<sub>2</sub>-treated soil samples after interaction with (a) monoelemental As solution and (b) the corresponding EDS X-ray spectrum showing the presence of Ca and As; (c) with trielemental As + Cd + Tl solution and (d) EDS X-ray spectrum including Ca and the three elements.

formation of these Al amorphous polymers provided the soil with additional cation (Cd and Tl) sorption capacity, probably through the formation of ternary complexes. Garrido et al. (2006) found similar trends in the sorption of Cd, Cu and Pb on Al-hydroxy polymers, including  $\text{SO}_4$  and  $\text{PO}_4$  anions in their composition. The physical As entrapment caused by Al clusters could also explain the lower TCLP-extractability of As than that of Cd and Tl, specially in  $\text{SF}_2$ -treated samples.

Sizeable amounts of Ca were also frequently associated with As, Cd and Tl in the chemical composition of the Al-hydroxy polymers (Fig. 5b and d). It is widely known that As and Ca may form different mixed Ca arsenates. At the pH range of the  $\text{SF}_2$ -treated samples, the most probable species are  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$  and/or  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$  (Bothe and Brown, 1999b). This result confirms that an excess of lime favours trapping As through the formation of some form of Ca arsenate. Benzaazoua et al. (2004) found arsenate compounds containing Ca, located around macropores as amorphous phases. It is possible that this type of process also occurs when Cd substitutes Ca explaining the presence of both elements in some EDS spectra (Fig. 5d). In this case, Cd would be solubilized to the same extent as As in the extraction processes. The results from the TCLP tests showed higher extractability of Cd than that of As (Table 5). This suggests that Cd could be sorbed in a more soluble phase, i.e. Cd-rich phase on the  $\text{CaCO}_3$  surface and, to a lesser extent, as Cd-arsenate, since discrete particles of Cd-carbonates were not specifically identified in the EDS analyses. Besides all these possible sorption mechanisms, the sorption of Cd on Al-hydroxy polymers that have been reported by other researchers (Lothenbach et al., 1999) should also be considered. Massive formations of Al-hydroxy polymers containing Cd as well as Ca and As, were observed (Fig. 5c and d). Kretzschmar and Schafer (2005) suggested that specific adsorption of  $\text{PO}_4$  and other anions could also add negative charge to the surfaces of Fe- and Al-oxide colloids. Therefore, the formations observed in Fig. 5 could contain ternary complexes including Cd, Al hydroxides and arsenates. The chemistry of Tl is not well known and there are only a few studies based on the geochemical behaviour of Tl in soils (Yang et al., 2005). Thallium was similarly found associated to the amorphous Al-hydroxy polymers (Fig. 5d). This is consistent with previous studies (Martín et al., 2004) suggesting that both Fe and Al amorphous

oxides are the principal soil components in the sorption of Tl.

#### 4. Conclusions

The efficiency of PG and SF treatments in reducing the potential leachability of As, Cd and Tl in an element-spiked acidic soil was different depending on the treatment and element type although, the sorption patterns of the three elements were mainly influenced by the treatments and the desorption ones depended on the element nature. However, the results from the current study indicate that the application of SF reduces the mobility of the three elements and that the amount of the elements retained was greatest at high  $\text{CaCO}_3$  application rate, especially in the case of As. This might be due to either an enhanced formation of Al-hydroxy polymers or reprecipitation of new carbonate solid phases or both. The low sorption capacity of As in PG-treated samples could be due to a competitive sorption between  $\text{SO}_4$  and  $\text{AsO}_4$  anions, leading to  $\text{AsO}_4$  anions toward more specific sorption sites. In addition, the presence of Cd might favour As retention through different processes such as indirect formation of Al-hydroxy polymers as a consequence of exchange reactions between  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , the formation of element-ligand ternary complexes, or formation of amorphous Cd-arsenates. On the other hand, As was the element with the lowest percentage of extraction followed by Cd and Tl. The addition of sugar foam as single (SF) or combined (PG + SF) amendment also reduced significantly the leachability of the three elements, especially when SF and PG + SF were at highest rate.

The combination of the maximum sorption capacity ( $Q$ ) and the mass of element retained after TCLP extraction at pH 2.9 ( $F_2$ ) was found the best possible one to classify the overall sorption/desorption pattern of the elements and treatments in three different groups: (1) characterized by a low-medium sorption and a low desorption behaviour; (2) characterized by a low-medium sorption and medium-high desorption behaviour; (3) characterized by the highest sorption and highest desorption behaviour.

By means of SEM-EDX analysis the retention of As, Cd and Tl on Al-hydroxy polymers has been observed irrespective of if they were added in mono-elemental (As) or trielemental (As + Cd + Tl) toxic solutions. In addition, sizeable amounts of Ca were also frequently associated with As, Cd and Tl in the chemical composition of these Al-hydroxy polymers.

## Acknowledgments

This work was supported by the Spanish Ministry of Science and Technology, within the framework of the research project AGL2005-07017-C03-03. Ferti-beria S.A. and Azucarera Ebro S.A. are gratefully acknowledged for supplying us with samples of phosphogypsum and sugar foam, respectively.

## References

- Adriano, D.C., Wenzel, W.W., Vangronsveld, J., Bolan, N.S., 2004. Role of assisted natural remediation in environmental cleanup. *Geoderma* 122, 121–142.
- Aguilar-Carrillo, J., Garrido, F., Barrios, L., Garcia-Gonzalez, M.T., 2006. Sorption of As, Cd and Tl as influenced by industrial by-products applied to an acidic soil: Equilibrium and kinetic experiments. *Chemosphere* 65, 2377–2387.
- Arai, Y., Sparks, D.L., 2002. Residence time effects on arsenate surface speciation at the aluminum oxide–water interface. *Soil Sci.* 167, 303–314.
- Arai, Y., Elzinga, E.J., Sparks, D.L., 2001. X-ray absorption spectroscopic investigation of arsenite and arsenate adsorption at the aluminum oxide–water interface. *J. Colloid Interface Sci.* 235, 80–88.
- Benzaazoua, M., Marion, P., Picquet, I., Bussiere, B., 2004. The use of pastefill as a solidification and stabilization process for the control of acid mine drainage. *Miner. Eng.* 17, 233–243.
- Bothe, J.V., Brown, P.W., 1999a. Arsenic immobilization by calcium arsenate formation. *J. Hazard Mater.* 33, 3806–3811.
- Bothe, J.V., Brown, P.W., 1999b. The stabilities of calcium arsenates at  $23 \pm 1$  °C. *J. Hazard Mater.* 69, 197–207.
- Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. *J. Colloid Interface Sci.* 277, 1–18.
- Bui, E.N., Loeppert, R.H., Wilding, L.P., 1990. Carbonate Phases in Calcareous Soils of the Western United-States. *Soil Sci. Soc. Am. J.* 54, 39–45.
- Burgos, P., Madejon, E., Perez-de-Mora, A., Cabrera, F., 2006. Spatial variability of the chemical characteristics of a trace-element-contaminated soil before and after remediation. *Geoderma* 130, 157–175.
- Campbell, C.G., Garrido, F., Illera, V., Garcia-Gonzalez, M.T., 2006. Transport of Cd, Cu and Pb in an acid soil amended with phosphogypsum, sugar foam and phosphoric rock. *Appl. Geochem.* 21, 1030–1043.
- Cao, R.X., Ma, L.Q., Chen, M., Singh, S.P., Harris, W.G., 2003. Phosphate-induced metal immobilization in a contaminated site. *Environ. Pollut.* 122, 19–28.
- Díaz-Barrientos, E., Madrid, L., Maqueda, C., Morillo, E., Ruiz-Cortes, E., Basallote, E., Carrillo, M., 2003. Copper and zinc retention by an organically amended soil. *Chemosphere* 50, 911–917.
- Eary, L.E., 1999. Geochemical and equilibrium trends in mine pit lakes. *Appl. Geochem.* 14, 963–987.
- European Community, 1986. Council directive 86/278/EEC on the use of sewage sludge in agriculture, L181, pp. 6–12.
- García-Sánchez, A., Álvarez-Ayuso, E., Rodríguez-Martín, F., 2002. Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils. *Clay Miner.* 37, 187–194.
- Garrido, F., Illera, V., Vizcayno, C., García-González, M.T., 2003. Evaluation of industrial by-products as soil acidity amendments: chemical and mineralogical implications. *Eur. J. Soil Sci.* 54, 411–422.
- Garrido, F., Illera, V., Campbell, C.G., García-González, M.T., 2006. Regulating the mobility of Cd, Cu and Pb in an acid soil with amendments of phosphogypsum, sugar foam, and phosphoric rock. *Eur. J. Soil Sci.* 57, 95–105.
- Geebelen, W., Vangronsveld, J., Adriano, D.C., Carleer, R., Clijsters, H., 2002. Amendment-induced immobilization of lead in a lead-spiked soil: evidence from phytotoxicity studies. *Water Air Soil Poll.* 140, 261–277.
- Genc-Fuhrman, H., Bregnhøj, H., McConchie, D., 2005. Arsenate removal from water using sand-red mud columns. *Water Res.* 39, 2944–2954.
- Ghosh, A., Saez, A.E., Ela, W., 2006. Effect of pH, competitive anions and NOM on the leaching of arsenic from solid residuals. *Sci. Total Environ.* 363, 46–59.
- Gifi, A., 1991. *Nonlinear Multivariate Analysis*. John Wiley & Sons Ltd., Chichester, England.
- Giles, C.H., D'Silva, A.P., Easton, I.A., 1974. A general treatment and classification of the solute adsorption isotherm. II. Experimental interpretation. *J. Colloid Interface Sci.* 47, 766–778.
- Goh, K.-H., Lim, T.-T., 2004. Geochemistry of inorganic arsenic and selenium in a tropical soil: effect of reaction time, pH, and competitive anions on arsenic and selenium adsorption. *Chemosphere* 55, 849–859.
- Goldberg, S., 2002. Competitive Adsorption of Arsenate and Arsenite on Oxides and Clay Minerals. *Soil Sci. Soc. Am. J.* 66, 413–421.
- Goldberg, S., Johnston, C.T., 2001. Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *J. Colloid Interf. Sci.* 234, 204–216.
- Gray, C.W., Dunham, S.J., Dennis, P.G., Zhao, F.J., McGrath, S.P., 2006. Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environ. Pollut.* 142, 530–539.
- Gustafsson, J.P., 2002. Visual minteq ver. 2.30, KTH, Stockholm, Sweden.
- Hamon, R.E., McLaughlin, M.J., Cozens, G., 2002. Mechanisms of attenuation of metal availability in in situ remediation treatments. *Environ. Sci. Technol.* 36, 3991–3996.
- Hossner, L.R., 1996. Dissolution for total elemental analysis. In: Sparks, D.L. (Ed.), *Methods of Soil Analysis: Part 3, Chemical Methods*. American Society of Agronomy, Madison, WI, pp. 49–64.
- Illera, V., Garrido, F., Serrano, S., García-González, M.T., 2004a. Immobilization of the heavy metals Cd, Cu, and Pb in an acid soil amended with gypsum- and lime-rich industrial by-products. *Eur. J. Soil Sci.* 55, 135–145.
- Illera, V., Garrido, F., Vizcayno, C., García-González, M.T., 2004b. Field application of industrial by products as Al toxicity amendments: chemical and mineralogical implications. *Eur. J. Soil Sci.* 55, 681–692.
- Jacobson, A.R., McBride, M.B., Baveye, P., Steenhuis, T.S., 2005. Environmental factors determining the trace-level sorption of silver and thallium to soils. *Sci. Total Environ.* 345, 191–205.
- Johnson, C.D., Skakle, J.M.S., Johnston, M.G., Feldman, J., Macphee, D.E., 2003. Hydrothermal synthesis, crystal struc-

- ture and aqueous stability of two cadmium arsenate phases,  $\text{CdNH}_4(\text{HAsO}_4)\text{OH}$  and  $\text{Cd}_5\text{H}_2(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ . *J. Mater. Chem.* 13, 1429–1432.
- Kaplan, D.I., Mattigod, S.V., 1998. Aqueous geochemistry of thallium. In: Nriagu, J.O. (Ed.), *Thallium in the Environment*. John Wiley & Sons, New York, pp. 15–29.
- Kinniburgh, D.G., 1986. General purpose adsorption isotherms. *Environ. Sci. Technol.* 20, 895–904.
- Kretzschmar, R., Schafer, T., 2005. Metal retention and transport on colloidal particles in the environment. *Elements* 1, 205–210.
- Lin, T.-S., Nriagu, J.O., 1998. Speciation of thallium in natural waters. In: Nriagu, J.O. (Ed.), *Thallium in the Environment*. John Wiley & Sons, Inc., New York, pp. 31–43.
- Lombi, E., Hamon, R.E., Wieshammer, G., McLaughlin, M.J., McGrath, S.P., 2004. Assessment of the use of industrial by-products to remediate a copper- and arsenic-contaminated soil. *J. Environ. Qual.* 33, 902–910.
- Lothenbach, B., Furrer, G., Schärli, H., Schulz, R., 1999. Immobilization of zinc and cadmium by montmorillonite compounds: Effects of aging and subsequent acidification. *Environ. Sci. Technol.* 33, 2945–2952.
- Martín, F., García, I., Dorronsoro, C., Simón, M., Aguilar, J., Ortiz, I., Fernández, E., Fernández, J., 2004. Thallium behavior in soils polluted by pyrite tailings (Aznalcollar, Spain). *Soil Sedim. Contamin.* 13, 25–36.
- Martin, H.W., Kaplan, D.I., 1998. Temporal changes in cadmium, thallium, and vanadium mobility in soil and phyto-availability under field conditions. *Water Air Soil Poll.* 101, 399–410.
- May, H.M., Nordstrom, D.K., 1991. Assessing the solubilities and reaction kinetics of aluminous minerals in soils. In: Ulrich, B., Sumner, M.E. (Eds.), *Soil Acidity*. Springer-Verlag, Berlin Heidelberg, pp. 125–148.
- McBride, M.B., 1999. Chemisorption and precipitation reactions. In: Sumner, M.E. (Ed.), *Handbook of Soil Science*. CRC Press, Boca Raton, pp. B265–B302.
- O'Reilly, S.E., Strawn, D.G., Sparks, D.L., 2001. Residence time effects on arsenate adsorption/desorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* 65, 67–77.
- Saha, U.K., Taniguchi, S., Sakurai, K., 2002. Simultaneous adsorption of cadmium, zinc, and lead on hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes. *Soil Sci. Soc. Am. J.* 66, 117–128.
- Simon, M., Ortiz, I., García, I., Fernández, E., Fernández, J., Dorronsoro, C., Aguilar, J., 1999. Pollution of soils by the toxic spill of a pyrite mine (Aznalcollar, Spain). *Sci. Total Environ.* 242, 105–115.
- Sparks, D.L., 2005. Toxic metals in the environment: The role of surfaces. *Elements* 1, 193–197.
- Sposito, G., 1989. *The Chemistry of Soils*. Oxford University Press, New York.
- Staff, S.S., 1999. *A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. US Government Printing Office, Washington, DC.
- Tao, Y., Zhang, S., Jian, W., Yuan, C., Shan, X.-Q., 2006. Effects of oxalate and phosphate on the release of arsenic from contaminated soils and arsenic accumulation in wheat. *Chemosphere* 65, 1281–1287.
- Toma, M., Saigusa, M., 1997. Effects of phosphogypsum on amelioration of strongly acid nonallophanic andosols. *Plant Soil* 192, 49–55.
- USEPA, 1986. *Test Methods for Evaluating Solid Wastes*. US Government Printing Office, Washington, DC.
- Waychunas, G.A., Rea, B.A., Fuller, C.C., Davis, J.A., 1993. Surface-Chemistry of Ferrihydrite: Part 1. EXAFS Studies of the Geometry of Coprecipitated and Adsorbed Arsenate. *Geochim. Cosmochim. Acta* 57, 2251–2269.
- Widerlund, A., Shcherbakova, E., Carlsson, E., Holmstrom, H., Ohlander, B., 2005. Laboratory study of calcite-gypsum sludge-water interactions in a flooded tailings impoundment at the Kristineberg Zn–Cu mine, northern Sweden. *Appl. Geochem.* 20, 973–987.
- Xu, H., Allard, B., Grimvall, A., 1988. Influence of pH and Organic-Substance on the Adsorption of As(V) on Geologic Materials. *Water Air Soil Poll.* 40, 293–305.
- Yang, C., Chen, Y., Peng, P.A., Li, C., Chang, X., Xie, C., 2005. Distribution of natural and anthropogenic thallium in the soils in an industrial pyrite slag disposing area. *Sci. Total Environ.* 341, 159–172.