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Effect of phosphorus on the attenuation of lead and chromium transport in soils

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Abstract This study analyses the adsorption of Pb(II) and Cr(III) in soils. These metals are commonly found together in nature in urban wastes or industrial spillages, and the theoretical approach of the work was to evaluate the response of the soil to continuous Cr and Pb spillages to soil in terms of several physicochemical parameters. The influence of an anthropogenic input of phosphorus was evaluated. Continuous flow experiments were run in duplicates in acrylic columns (25 cm × 3.2 cm). The influent Cr(III) and Pb(II) solutions of 10 mg l^{-1} and 25 mg l^{-1} at pH 5 were pumped upward through the bottom of the columns to ensure saturation flow conditions. Also, successive experiments were run with the above concentrations of Cr(III) and Pb(II) and NaH$_2$PO$_4$, keeping metal to phosphorus ratio of 1:0, 1:0.1 and 1:1. Modelling parameters included Freundlich and Langmuir equations, together with the Two-site adsorption model using CXT-FIT code. Results obtained allowed concluding that Pb(II) adsorption presents a certain degree of irreversibility and the continued spillages over soil increment the fraction which is not easily desorbed. Cr(III) desorption was almost complete, evidencing its high mobility in nature. The presence of an anthropogenic input of phosphorus leads to a marked increase of both Pb(II) and Cr(III) adsorption in soils. Z-potential measurements allow to discard the electrostatic attraction of Cr(III) and Pb(II) with the surface charged soil as the dominant process of metal sorption. Instead, CheaqsPro simulation allows to identify PbH$_2$PO$_4^+$, PbHPO$_4$ (aq) and CrHPO$_4^+$ as the dominant species which regulate Cr(III) and Pb(II) transport in soils.

Keywords Isotherms · Zeta potential · Chromium · Lead · Phosphorus

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Introduction

Natural attenuation refers to the reduction in mass or concentration of a compound over time or distance, compared with that offered by other more active methods (USEPA 1999). It is expected that a solution leached through soils will be partially retained in the solid matrix, due to the pollution-neutralising capacity of the soils, either by mechanical retention or by sorption onto the soil matrix (Núñez-Delgado et al. 2002; López Periago et al. 2002; Devesa-Rey et al. 2010). Natural attenuation is gaining consideration as a remediation technique, which must be controlled by designing a legal framework for its application and detailed protocols (Declercq et al. 2012). The role of natural attenuation in restoration design and implementation must be analysed to gain insight into the potential benefits of natural restoration (Moore and Langner 2012).

The natural attenuation of soils contaminated with metals or metalloids is strongly conditioned by the nature of the metal. Common redox-sensitive processes, such as Cr(VI) to Cr(III), U(VI) reduction to (IV), or As(V) to As(III) (Fang et al. 2009; Quintelas et al. 2009a, b), may occur in the

environment under aerobic or anaerobic reductions. Where reduction of a metal to a lower redox state occurs, mobility and toxicity can be reduced, thus offering potential remediation applications (Gadd 2000). Also, acid/base-sensitive elements may be retained in soils by inducing their immobilisation, as suggested by Zhang et al. (2011), who employed controlled base addition to soils to sequester uranium.

This study analyses the adsorption of Pb(II) and Cr(III) in soils. These metals are commonly found together in nature in urban wastes or industrial spillages (Prechthai et al. 2008), and the theoretical approach of the work was to evaluate the response of the soil to continuous Cr and Pb spillages to soil in terms of several physicochemical parameters.

The present work is aimed at estimating the heavy metal adsorption capacity, evaluating the physicochemical parameters involved in metal retention and modelling their transport through flow experiments. Therefore, the following hypothesis will try to be answered: (1) heavy metal adsorption—desorption in soils is conditioned by physical constraints. If so, Z-potential may predict the heavy metal behaviour in soils; (2) Cr(III) and Pb(II) transport in soils may be adequately fitted to Langmuir and Freundlich, or two-site adsorption models, which afterwards may be employed to evaluate the adsorption—desorption behaviour of such metals in soil; and (3) The presence of a phosphorus input may alter the Cr and Pb profile by occluding the active sites of soils, or by complexation with metals.

Materials and methods

Study area and sampling

The soils selected were sampled at Póvoa de Varzim (Oporto, Portugal), a small village located in the North of Portugal ($41°25'15.58''$N and $8°45'58.27''$O) (Fig. 1). This area presents mild temperatures throughout the year with a mean value of 13.8 °C, whereas the annual rainfall varies between 1,200 and 1,400 mm. The land use is predominantly agricultural, with a significant percentage allocated to vineyards of the commercially known as *Green Wine*. Soils samples were collected from the O-horizon and A-horizon (0–30 cm) at 4 to 6 sites and combined to obtain a unique sample representative of the study area. Samples were stored in plastic bags and, once in the laboratory, they were air dried and sieved using 2 mm mesh sieve.

Methods

Soil characterization

Particle size distribution was determined as per Guitián and Carballas (1976). Carbonate content was determined by

Fig. 1 Identification of sampling location, with indication of the soil type of the area

titration with HCl and measurement of CO_2 released in a Scheibler calcimeter. Cationic exchange capacity was quantified using ammonium acetate at pH 7 (Hendershot et al. 1993). The metal concentrations in soil were determined by flame atomic absorption spectrometry (Varian SpectraAA 220FS), after microwave (CEM MDS2000) digestion with a mixture of acids ($HF:HNO_3:HCl$, 1:5:5). Soil pH was determined with 1:1 soil/water suspension. Total organic carbon (TOC) was determined by oxidation with a mixture of $K_2Cr_2O_7$ and H_2SO_4 and titration with Mohr Salt (Guitián and Carballas 1976). Amorphous Fe (Fe_{ox}) and Mn (Mn_{ox}) oxides were extracted in oxalic acid–ammonium oxalate (Schwertmann 1964).

Electro kinetic measurements

Z-potential was determined by electrokinetic measurements using a microelectrophoretic apparatus (Zetasizer Nano ZS ZEN3600) by shaking 1 g of soil sample with 10 ml of $CaCl_2$ 0.01 M. After 1 h, samples were adjusted at the desired pH in the range 3–7 with HCl and NaOH in

triplicate, performing between 25 and 30 replicates of each series.

Batch experiments

Batch experiments with Cr and Pb were performed by soil to single-metal solutions in 1:10 ratios. The concentrations for both metals varied from about 50–200 mg l^{-1}. Suspensions were agitated in an orbital mixer at 20 °C and 100 rpm at different intervals up to 48 h. Supernatants were acidified with HNO$_3$ to pH 2, stored at 4 °C and analysed by flame atomic absorption spectrometry (Varian SpectraAA 220FS). The amount of metal adsorbed on the soil was fitted to Freundlich or Langmuir, by applying the following equations:

$$S_e = k_F C_e^n \tag{1}$$

$$S_e = \frac{(S_{max} C_e b)}{1 + bC_e} \tag{2}$$

where S_e is the mass of metal adsorbed per mass of soil (mg kg^{-1}), in equilibrium with the concentration of the metal in the liquid phase, C_e (mg l^{-1}); k_F is the Freundlich constant ($L^{1/n}$ mg$^{(1-1/n)}$ kg^{-1}); n is the metal (mg kg^{-1}) and b is the Langmuir equilibrium constant (l mg^{-1}).

Column experiments

Continuous flow experiments were run in duplicates in acrylic columns (25 cm × 3.2 cm). Soil samples were conveniently packed inside the column with a slight vibration and progressively saturated with deionized water to prevent air entrapment. The influent Cr(III) and Pb(II) solutions of 10 mg·l^{-1} and 25 mg l^{-1} at pH 5 were pumped upward through the bottom of the columns to ensure saturation flow conditions (Papelis 1999). Also, successive experiments were run with the above concentrations of Cr(III) and Pb(II) and NaH$_2$PO$_4$, keeping metal to phosphorus ratio of 1:0, 1:0.1 and 1:1. Effluent samples were collected at the top of the columns, filtered by 0.45 μm, acidified and stored at 4 °C until analyses by atomic absorption (Varian SpectraAA 220FS). Breakthrough curves were fitted by two-site adsorption parameter model (TSM) using CXTFIT code (Toride et al. 1995).

Previously to the flow tests with Cr(III) and Pb(II), a flow experiment using CaCl$_2$ (0.01 M) as a tracer was conducted to evaluate independently the average pore water velocity (v) and the dispersion coefficient (D), by measuring the conductivity of the effluents and fitting the breakthrough curve with the CXTFIT code to the equilibrium convection—dispersion equation (CDE). These two parameters were kept constant for the fitting of Cr(III) and Pb(II) breakthrough curves.

The two-site adsorption model can occur instantaneously (equilibrium) or be time dependent (first-order kinetic). Two-site non-equilibrium results from kinetic limitations during sorption (Brusseau and Rao 1989). Only sorbing solutes experience chemical non-equilibrium. Sorption is considered to occur in two domains, one allowing "instantaneous" sorption and one where sorption is rate-limited (Simpson and Bowman 2009). The behaviour of a non-sorbing tracer, as CaCl$_2$ used in this study to characterize the hydraulic conditions, is accurately described by an equilibrium model (Altare et al. 2007). On their turn, sorbing substances were characterized by a non-equilibrium transport model. The optimization program CXTFIT version 2.1 was used in this work under flux-type boundary conditions as described by Kreft and Zuber (1978), to predict solute transport. This code adjusts the following dimensionless form of the two-site non-equilibrium model to the breakthrough curves in order to estimate the transport and sorption parameters:

$$(1 - \beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \tag{3}$$

Where the dimensionless parameters are defined as follows:

$$C_1 = \frac{C}{C_0} \tag{4}$$

$$C_2 = \frac{S_2}{[(1 - F)k_L C_0]} \tag{5}$$

$$T = \frac{vt}{L} \tag{6}$$

$$R = 1 + \frac{\rho k_L}{\theta} \tag{7}$$

$$\beta = \frac{(\theta + F\rho k_L)}{(\theta + \rho k_L)} \tag{8}$$

$$\omega = \frac{\alpha(1 - \beta)RL}{v} \tag{9}$$

were C_1 and C_2 are the relative concentration of chromium and lead in equilibrium (1) and kinetic (2) sites scales to the input concentration C_0; T is the dimensionless time; L is the column length; R is the retardation factor (−); β is the fraction of instantaneous sorption (−); ω is the Damkohler number (−), which represents the ratio of hydrodynamic residence time to characteristic sorption time; k_L is the linear isotherm sorption coefficient; P is the dimensionless time (pore volumes); D is the dispersion coefficient (L^2 T^{-1}); v is the average linear pore water velocity (L T^{-1}); x is the distance (L); ρ is the medium's bulk density (M L^{-3}); θ is the volumetric water content (−).

Simulation of Pb:P and Cr:P species was performed using the CheaqsPro computer speciation program.

CheaqsPro is an equilibrium speciation model used to describe the influence of competing processes or reactions on the overall behaviour of pollutants.

Results and discussion

General description

The general properties of the samples used in this study are summarised in Table 1. The samples analysed showed textures with a predominance of the sandy fraction (78.21 %), with pH of 6.2, CEC of 9.87 $cmol_{(c)}$ kg^{-1} and negligible carbonate concentration. The main binding agents of soil were characterized. The clay fraction was low in the soil (1.76 %) and, in turn, organic matter also showed a low value of 2.9 %.

Adsorption experiments

The two-site adsorption model was fitted to the flow experiments. Previously, the breakthrough (BTC) curve of the non-reactive tracer ($CaCl_2$) was fitted by using the CXTFIT code (Table 3). The two-site adsorption model satisfactorily describes the solute transport through the column soil, showing an acceptable fit in all the experiments ($0.80 \leq r^2 \leq 0.92$). Slightly lower fits were observed in the batch experiments when applying

Freundlich ($0.70 \leq r^2 \leq 0.89$) and Langmuir ($0.75 \leq r^2 \leq 0.89$) equations, although they were considered properly fitted for discussion.

First experiments were conducted by pumping solutions of 25 mg l^{-1} of Cr(III) and Pb(II) through independent column soils. Both metals showed similar profiles through the columns, showing well-defined BTCs (Figs. 2, 3). Cr(III) showed less affinity by the active sites of the soil and it was less retained than Pb(II). Desorption of Cr(III) was also observed, thus showing a high degree of reversibility, although the left-skewed curve indicates that
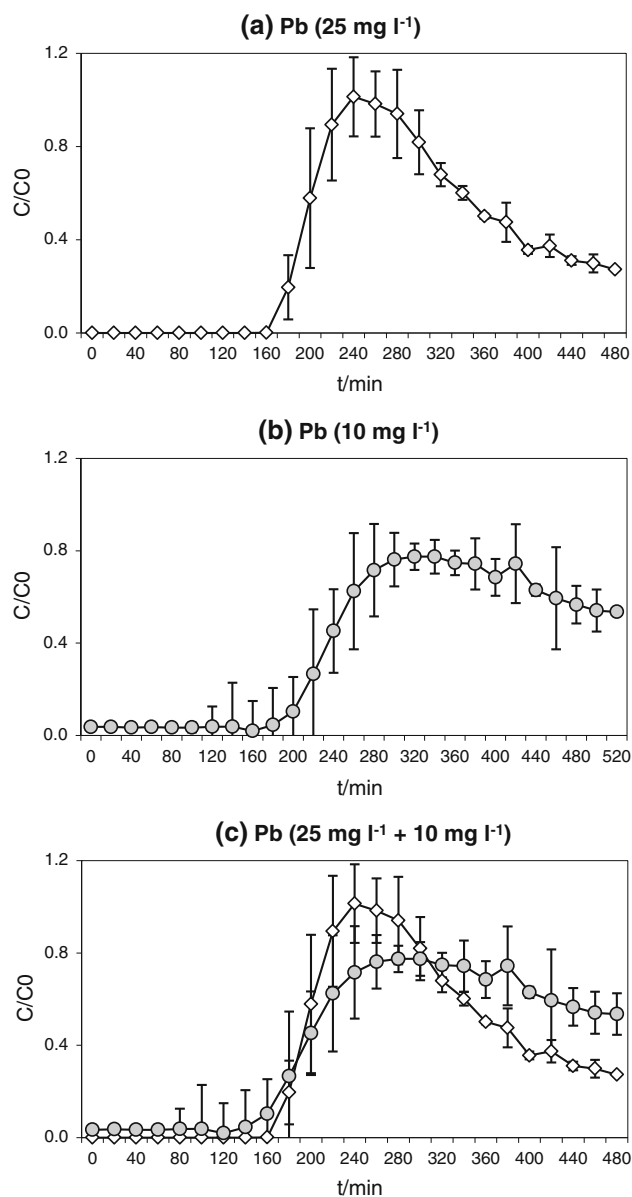
Table 1 Chemical and physical properties of soil sample taken from Póvoa de Varzim (Portugal)

Soil properties	
Granulometry (%)	
Clay	1.76
Silt	20.03
Sand	78.21
pH (H_2O)	6.2
pH (KCl)	5.6
Cationic exchange capacity ($cmol_c$ kg^{-1})	9.87
Total organic matter (%)	2.9
Metal concentrations	
Fe (%)	2.61
Mn (mg kg^{-1})	612
Pb (mg kg^{-1})	4.7
Cr (mg kg^{-1})	39.7
Fe_{ox} (%)	0.9
Mn_{ox} (mg kg^{-1})	42
Carbonate content	
$CaCO_3$ (mg kg^{-1})	n.d.
Apparent density[a]	
ρ_b (kg m^{-3})	2,119

[a] Disturbed sample; *nd* not detected

Fig. 2 Experimental and fitted BTCs with the two-site model (TSM), for soil columns contaminated with different lead influents: **a** $C_0 = 25$ mg l^{-1}; **b** $C_0 = 10$ mg l^{-1}; **c** comparison of both concentrations

(a) Cr (25 mg l⁻¹)

(b) Cr (10 mg l⁻¹)

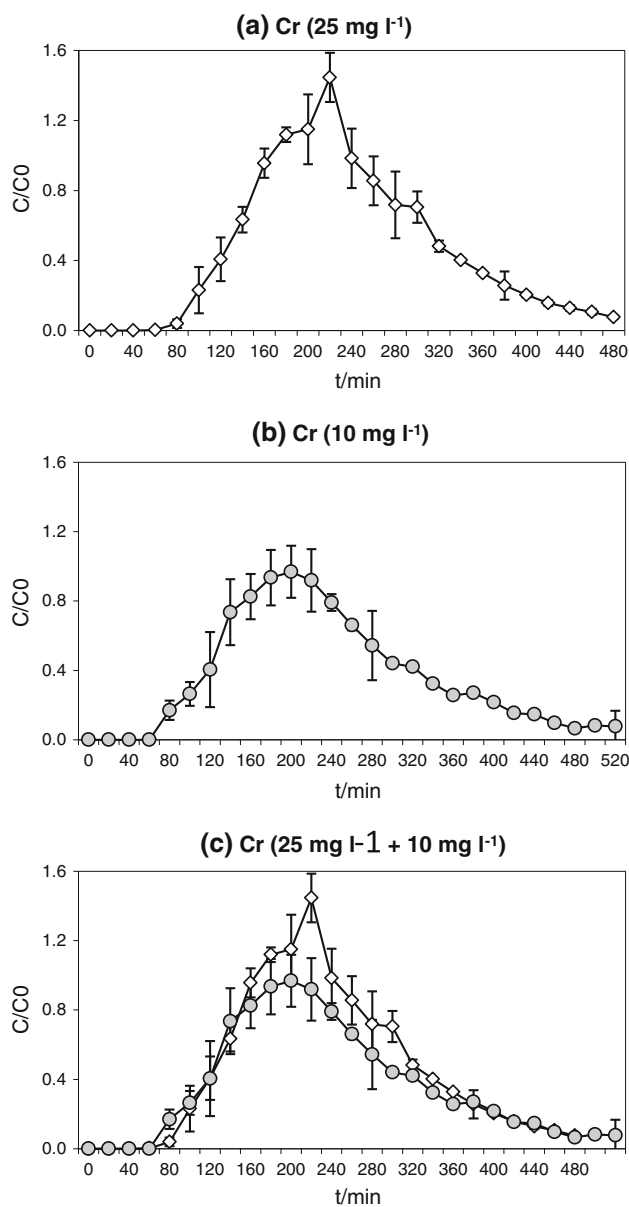## (c) Cr (25 mg l-1 + 10 mg l⁻¹)

Fig. 3 Experimental and fitted BTCs with the two-site model (TSM) for soil columns contaminated with different chromium influents: **a** $C_0 = 25$ mg l^{-1}; **b** $C_0 = 10$ mg l^{-1}; **c** comparison of both concentrations

(a) Pb (25 mg l⁻¹)

(b) Cr (25 mg l⁻¹)

Fig. 4 Empirical isotherms for the sorption of Pb and Cr by soils in the absence of presence of phosphorus at various Metal:Phosphorus ratios. *White squares* represent experiments carried out without phosphorus (1:0 Metal:P ratio); experiments carried in presence of phosphorus are drawn with *grey triangles* (1:0.1 Metal:P ratio) and *white diamonds* (1:1 Meta:P ratio)

adsorption occurs faster, whereas desorption takes more time. Instead, Pb(II) showed a lower degree of reversibility, as indicates the right tail of the BTC. So, at the time where Cr(III) desorption was almost complete (480 min), there was still 27 % of the initial Pb(II) remaining in the soil. Higher reversibility in Cr(III) when compared with Pb(II) was also observed by Dong et al. (2009) at pH 5, which found that higher mobility in the soil/groundwater system is expected for Cr(III), due to the limited amount adsorbed by soil.
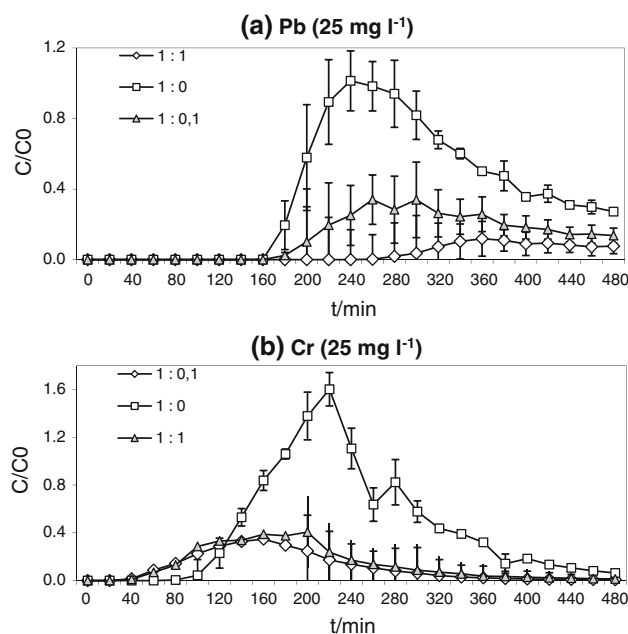
Next, 10 mg l^{-1} of Cr(III) and Pb(II) were pumped through the same soil columns, to simulate the effect of repetitive spillages over soils, of different intensities. As in the previous experiment, Cr(III) showed a left-skewed curve with a subsequent desorption phase, which was almost complete. In the case of Pb(II), desorption was even lower, when compared with the first experiment, with the 66 % of the initial Pb(II) being still adsorbed at the end of the experiment. Fitting parameters were coherent with the experiments assayed, with the highest retardation factor (R) observed at the highest concentration level and correlated also with the valence of the ions, as predicted the diffuse double layer theory (Rose et al. 2009). Freundlich and Langmuir constants—k_F and S_{max}—were higher with the highest concentrations, both for Cr(III) and Pb(II).

Pb(II) irreversibility was also observed by Strawn and Sparks (2000), who found that Pb behaviour in soils is mainly controlled by organic matter, corroborated by ageing experiments until 32 days. Barbosa and Hvitved-Jacobsen (1999) found both for Cr and Pb an increased desorption rate at pH 2, when compared with neutral pH. This must be considered an important limitation for *onsite* remediation procedures, which cannot be carried out under such acidic pH values. Taking into account that natural spillages use to exceed the natural attenuation of soils (Hellerich et al. 2008), enhanced recovery strategies onsite must be developed.

Table 2 Parameters for two-site adsorption, Freundlich and Langmuir equations fitted to the empirical isotherms for sorption of Cr or Pb by soils in the presence or absence of a source of phosphorus

C_0 (mg l^{-1})	P:metal ratio	Physical parameters ($R = 1$)			Two-site adsorption				Freundlich			Langmuir		
		D	v	r^2	R	β	ω	r^2	k_F	n	r^2	S_{max}	b	r^2
25 (Cr)	0:1	53.18	30.09	0.91	2.31	0.02	0.17	0.81	303	1.09	0.78	64.54	0.04	0.83
25 (Pb)	0:1	60.77	22.36	0.92	1.11	$0.1 \cdot 10^{-3}$	0.13	0.80	202	1.46	0.89	49.63	0.02	0.76
10 (Cr)	0:1	23.14	12.28	0.96	1.44	$0.1 \cdot 10^{-3}$	0.01	0.87	10.72	0.81	0.70	30.03	0.03	0.89
10 (Pb)	0:1	22.14	12.11	0.98	1.87	$0.1 \cdot 10^{-3}$	0.02	0.92	2.72	1.33	0.84	25.03	0.02	0.75
25 (Cr)	0.1:1	46.65	22.37	0.92	100	$5.5 \cdot 10^{-3}$	0.31	0.86	471	1.03	0.82	79.34	0.05	0.88
25 (Pb)	0.1:1	44.60	19.51	0.98	29.37	$0.1 \cdot 10^{-3}$	0.35	0.82	281	1.86	0.79	67.98	0.04	0.87
25 (Cr)	1:1	58.60	24.44	0.94	100	0.013	0.34	0.84	505	1.82	0.81	86.09	0.04	0.79
25 (Pb)	1:1	37.56	16.44	0.96	39.66	$1.3 \cdot 10^{-4}$	2.39	0.80	391	1.79	0.85	79.31	0.03	0.78

There are also shown physical parameters obtained by fitting the equilibrium CDE to the BTC of CaCl$_2$ tracer

Effect of phosphorus on the adsorption

In the second series of experiments, increasing mole Cr:P and Pb:P ratios were assayed (Fig. 4). The profiles in the presence of phosphorus were similar than those obtained individually with Cr(III) or Pb(II). So, adsorption reversibility was almost complete for all chromium assays, whereas lead recovery was again incomplete. The lowest mole Cr:P or Pb:P ratios (1:0.1) did not significantly affect the Cr adsorption onto soils. However, mole Cr:P ratio of 1:1 significantly reduced the Cr adsorption onto soil. The effect of phosphorus on Pb(II) sorption was even more marked, and the final Pb(II) concentrations were reduced up to 13 % of its initial concentrations. In the same sense, Pérez-Novo et al. (2009) found that the sorption of copper on soils was increased significantly by treatment with phosphate. This fact was tentatively explained by Summer (1999) who argued that soil colloids as present particularly high affinity for phosphorus.

Fitting parameters varied according to the different experiments (Table 2). So, the retardation factor (R) and the mass transfer coefficient (ω) showed the highest values in the presence of phosphate, where the distribution of metals towards the soil is enhanced. Also Freundlich and Langmuir factors evidenced the favoured metallic sorption under these conditions. From k_F and S_{max} can be deduced that Freundlich fits better to the soil adsorption model than Langmuir. This fact was also observed by Quintelas et al. (2009a, b) for Cr adsorption on soils, which suggested that chromium binding does not occur as a monolayer on the soil surface. On its turn, Vázquez et al. (2006) suggested that the disagreement with the Langmuir model might be due to the heterogeneity of the sorbent surface with resulting in adsorption energy.
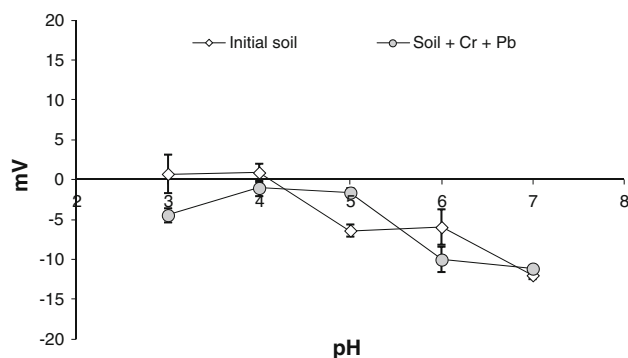

Fig. 5 Z-potentials of the contaminated and uncontaminated soils at various pH values. *Vertical bars* indicate standard deviations

Effect of pH on surface charge and speciation of Cr:P and Pb:P species

One possible explanation for the increased retention of Cr(III) and Pb(II) in the presence of phosphorus was given by Pérez-Novo et al. (2009) who argued that sorbed phosphate may add negative charges to the surfaces of sorbent particles and thereby tends to increase their affinity for ions. So, in order to evaluate the variations in the surface charge as a result of metal inoculation, electrochemical interactions between the metals and the soil surface were evaluated by means of Z-potentials. Measurements were carried out in two series, comparing soils before and after inoculation with Cr(III) and Pb(II). The Z-potentials of both series increasingly showed negative values as pH increased (Fig. 5), thus indicating the existence of variable charges in the soil surface. However, no significant changes were observed in Z-potentials between contaminated and uncontaminated soils, thus suggesting that Cr(III) and Pb(II) sorption onto soil is the result of chemical

Table 3 Results of Cr and Pb speciation (%) in the absence or presence of phosphate by simulation with CheaqsPro software

pH	P	%	Cr	%	Cr–P (1:0.1)	%	Cr–P (1:1)	%	Pb	%	Pb–P (1:0.1)	%	Pb–P (1:1)	%
3	$H_2PO_4^-$	90.64	$Cr_4(OH)_6^{6+}$	99.84	$Cr_4(OH)_6^{6+}$	99.31	$Cr_4(OH)_6^{6+}$	93.35	Pb^{2+}	99.92	Pb^{2+}	90.35	$PbH_2PO_4^+$	74.10
	H_3PO_4(aq)	9.33	$Cr(OH)_2^{2+}$	0.14	$CrHPO_4^+$	0.53	$CrHPO_4^+$	6.47	$Pb_2(OH)^{3+}$	0.08	$PbH_2PO_4^+$	9.56	Pb^{2+}	25.74
			Cr^{3+}	0.01									$PbHPO_4$ (aq)	0.15
4	$H_2PO_4^-$	98.82	$Cr_4(OH)_6^{6+}$	99.95	$Cr_4(OH)_6^{6+}$	99.71	$Cr_4(OH)_6^{6+}$	95.35	Pb^{2+}	99.19	Pb^{2+}	89.68	$PbH_2PO_4^+$	73.82
	H_3PO_4 (aq)	1.02	$Cr(OH)_2^{2+}$	0.04	$CrHPO_4^+$	0.24	$CrHPO_4^+$	4.57	$Pb_2(OH)^{3+}$	0.78	$PbH_2PO_4^+$	9.40	Pb^{2+}	24.65
											$PbHPO_4$ (aq)	0.23	$PbHPO_4$ (aq)	1.47
5	$H_2PO_4^-$	98.33	$Cr_4(OH)_6^{6+}$	99.97	$Cr_4(OH)_6^{6+}$	99.89	$Cr_4(OH)_6^{6+}$	96.32	Pb^{2+}	76.94	Pb^{2+}	72.00	$Pb_4(OH)_4^{4+}$	63.60
	HPO_4^{2-}	1.57	$Cr(OH)_2^+$	0.01	$CrHPO_4^+$	0.08	$CrHPO_4^+$	2.98	$Pb_4(OH)_4^{4+}$	18.14	$Pb_4(OH)_4^{4+}$	13.92	Pb^{2+}	23.17
	H_3PO_4 (aq)	0.10	$Cr(OH)_2^{2+}$	0.01					$Pb_2(OH)^{3+}$	4.66	$PbH_2PO_4^+$	7.72	$PbHPO_4$ (aq)	12.50
											$PbHPO_4$ (aq)	1.90		
6	$H_2PO_4^-$	86.93	$Cr_4(OH)_6^{6+}$	99.95	$Cr_4(OH)_6^{6+}$	99.92	$Cr_4(OH)_6^{6+}$	98.99	$Pb_4(OH)_4^{4+}$	67.74	$Pb_4(OH)_4^{4+}$	64.66	$PbHPO_4$ (aq)	46.65
	HPO_4^{2-}	13.06	$Cr(OH)_2^+$	0.05	$Cr(OH)_2^+$	0.05	$CrHPO_4^+$	0.85	$Pb_6(OH)_8^{4+}$	19.97	$Pb_6(OH)_8^{4+}$	14.35	$PbH_2PO_4^+$	23.79
	H_3PO_4 (aq)	0.01			$CrHPO_4^+$	0.03	$Cr(OH)_2^+$	0.16	Pb^{2+}	10.69	$PbHPO_4$ (aq)	6.31	$Pb_4(OH)_4^{4+}$	20.36
											$PbH_2PO_4^+$	2.64		
7	$H_2PO_4^-$	48.41	$Cr_4(OH)_6^{6+}$	99.84	$Cr_4(OH)_6^{6+}$	99.80	$Cr_4(OH)_6^{6+}$	99.06	$Pb_6(OH)_8^{4+}$	83.70	$Pb_6(OH)_8^{4+}$	77.83	$PbHPO_4$ (aq)	51.22
	HPO_4^{2-}	51.59	$Cr(OH)_2^+$	0.15	$Cr(OH)_2^+$	0.17	$Cr(OH)_2^+$	0.56	$Pb_4(OH)_4^{4+}$	14.87	$Pb_4(OH)_4^{4+}$	14.75	$Pb_6(OH)_8^{4+}$	35.20
			$Cr(OH)_3$ (aq)	0.02	$CrHPO_4^+$	0.01	$CrHPO_4^+$	0.30	Pb^{2+}	0.73	$PbHPO_4$ (aq)	5.77	$Pb_4(OH)_4^{4+}$	10.08
											$PbH_2PO_4^+$	0.26	$PbH_2PO_4^+$	2.41

pH 5, used in this study, was shaded in grey

interactions with P species, more than a mere electrostatic attraction of metal ions by soil particles.

Simulation of the Cr:P and Pb:P species formed were carried out using CheaqsPro software for Windows. The results of CheaqsPro simulation for pH 5 evidence the formation of Cr:P and Pb:P species with greater affinity than Cr or Pb for the sorbent surfaces of the soil (Table 3). With regard to Cr:P species, no significant different species appear independently of the Cr:P ratio, being $CrHPO_4^+$ the major product, with up to a 2.98 % at pH 5. Instead, markedly differences would be observed in the treatment of Cr(III) with phosphate at pH 2, where $CrHPO_4^+$ reaches de 6.47 % in the 1:1 ratio.

Pb(II) at pH 5 showed differences between 1:0.1 and 1:1 of Pb:P ratios. The behaviour of Pb(II) at the 1:0.1 (Pb:P) ratio seems to be regulated by the formation of $PbH_2PO_4^+$ (7.72 %) and $PbHPO_4$ (aq) (1.90 %) species. In the case of 1:1 (Pb:P) ratio, its behaviour seems to be controlled by the formation of $PbHPO_4$ (aq) (12.50 %) species. The application of a P source gradually decreases the Pb(II) in solution at pH 5, which confirms the observations made in the BTCs (Fig. 3). Again, as in the Cr:P ratios, acidic pH would mark differences between 1:0.1 and 1:1 ratios, as at pH 3 $PbH_2PO_4^+$ is the major species, accounting with a 74.10 %. However, such acidic pH would cause dissolution of lattices, thus producing such the opposite effect by releasing Cr(III) of soil.

Conclusions

This study evaluates the adsorption–desorption of lead and chromium in soils and the effect of phosphorus inputs on the breakthrough curves. The two-site adsorption model satisfactorily describes the mobility of lead and chromium in soils showing that, in the soils evaluated, chromium was less retained than lead. Lead desorption showed a lower degree of reversibility when compared with chromium. The increase in phosphorus concentration resulted in the higher adsorption of chromium and lead. CheaqsPro simulation allows identifying $PbH_2PO_4^+$, $PbHPO_4$ (aq), and $CrHPO_4^+$ as the dominant species which regulate Cr(III) and Pb(II) transport in soils.

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