Co²⁺ sorption capacity indicators of La Plata region's soils: insights and correlations with soil properties

M.L. Montes*

IFLP, Instituto de Física La Plata – CONICET CCT-La Plata, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina. Diagonal 113 y 64, 1900, La Plata, Argentina Fax: +542214840247 Email: Imontes@fisica.unlp.edu.ar Email: mlucianamontes@gmail.com *Corresponding author

M.A. Fernández

CETMIC – CONICET – CCT La Plata, CICBA. Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina. Camino Centenario y 506, 1897, M.B. Gonnet, La Plata, Argentina Email: mfernandez@cetmic.unlp.edu.ar

J. Brendlé and L. Michelin

Axe Matériaux à Porosité Contrôlée, Institut de Science des Matériaux, Institut de Recherche Jean-Baptiste Donnet, 3 bis rue A. Werner, Mulhouse Cedex, 68093, France Email: jocelyne.brendle@uha.fr Email: laure.michelin@uha.fr

M.A. Taylor

IFLP, Instituto de Física La Plata – CONICET CCT-La Plata, Facultad de Ingeniería Universidad Nacional de La Plata, Diagonal 113 y 64, 1900, La Plata, Argentina Email: taylor@fisica.unlp.edu.ar

2

R.M. Torres Sánchez

CETMIC – CONICET – CCT La Plata, CICBA, Camino Centenario y 506, 1897, M.B. Gonnet, La Plata, Argentina Email: rosa.torres@gmail.com

Abstract: Notwithstanding that the soil act as a pollutant sink, its Co sorption capacity presents still controversial results. Here, Co^{2+} sorption on soil samples from La Plata (Argentina) was analysed. Four sorption indicators were used: K_{dis} (estimated from the entire sorption isotherm), K_{FI} (estimated from the lineal part of the sorption isotherm), K_{dx} , (solid-solution distribution coefficient) and K_r , a dimensionless parameter recently developed. Pearson correlation coefficients between the parameters and soil properties were calculated. Significant and negative correlations with silt were obtained, whereas significant and positive correlations were established with clay and smectite content. Soil clay fractions were isolated and Co^{2+} sorption was evaluated, observing relatively high removal. The correlations with kaolinite, magnetite and Mn and Fe oxides showed debatable results: K_{dis} could be more sensitive than K_r to magnetite variations whereas K_r seems to be more sensitive to Mn changes. K_{FI} presented similar behaviour to K_r . The studied soils presented a high Co^{2+} sorption capacity, making them an effective barrier of this pollutant, avoiding its passage to groundwater and crops.

Keywords: cobalt sorption; soil/clay; isotherms; distribution coefficients; correlations; soil properties.

Reference to this paper should be made as follows: Montes, M.L., Fernández, M.A., Brendlé, J., Michelin, L., Taylor, M.A. and Torres Sánchez, R.M. (xxxx) ' Co^{2+} sorption capacity indicators of La Plata region's soils: insights and correlations with soil properties', *Int. J. Environment and Health*, Vol. x, No. x, pp.xxx–xxx.

Biographical notes: M.L. Montes received her PhD in Exact Sciences, Chemistry (La Plata National University). She is working as a Researcher at the National Council for Scientific and Technical Research (CONICET) of Argentina and as teacher at La Plata National University Physic Department. Her research is related to environmental radioactivity as well as the development of new technologies based on clay systems for water remediation, including heavy metals coming from nuclear industry. She has published around 10 papers in international journals peer review as well as two books and two book chapters as well as more than 30 congress presentations.

M.A. Fernández received her PhD in Biotechnology (Quilmes National University). Her research interest is related to the development of new technologies for water remediation including adsorption of heavy metals and agrochemicals. The related adsorbents studied were raw, thermal and mechanical treated clays and nano-clays as well as soils. She has published more than 20 papers in international journals peer review as well as two book chapters and more than 30 congress presentations. She is Adjoint Researcher belonging to National Council for Scientific and Technical Research (CONICET) of Argentine, carries out his research work at CETMIC and teaching work at the Univ. Nac. de La Plata.

J. Brendlé received her PhD in Chemistry (1996): Elaboration of pillared beidellites and heterostructures from beidellites synthesised in acidic and fluorinated medium and characterisation, Univ. Haute Alsace/Sci Institute of Mulhouse Materials. She is working as researcher on the development of phyllosilicates by hydrothermal, sol-gel, aerosol and microwaves and the preparation and characterisation of phyllosilicate-photopolymer composites, phyllosilicates-biopolymers, the study of their structure and the evaluation of their properties. Moreover, she is university Professor since 2003, University of Haute Alsace, Mulhouse. France. She has published more than 100 papers in international journals, directed several research projects and several PhD students.

L. Michelin is an Assistant Engineer in the Mulhouse Materials Science Institute (IS2M) since 2002. Her skills and expertise are the porous materials characterisation by X-ray diffraction and X-ray fluorescence.

M.A. Taylor is a Professor of the Engineering Faculty-UNLP. She is Researcher of CONICET – Argentina. She is Director of GISDRAMA group (Faculty of Exact Sciences, UNLP, IFLP, CCT-La Plata. She is co-author of more than 50 and 60 conferences presentations and co-authored a book chapter and two books. Her research interests are structural, electronic and magnetic properties of materials based on oxide; nanoscopic experimental techniques and ab initio calculus. Applied to impurities-oxide systems with potential technological interest. Environmental topics: characterisation of gamma ray emitters present in environmental samples (soils, milk, etc.). Clay-metal interaction in relation with environmental remediation problems. Theoretical and experimental approach. Modified clays-metal interactions; especially those including magnetic phases.

R.M. Torres Sánchez received her PhD in Natural Sciences. Currently, she is retired working with a contract as principal researcher at the National Council for Scientific and Technical Research (CONICET) of Argentine. Her research interests focus on the clays and soils characterisation, clays application in water and effluent treatments and as agrochemical adsorbents. She teaches several postgraduate courses, published more than 100 papers in international journals peer review, several book chapters, directed several research and technological projects and more than 10 PhD students.

1 Introduction

At present, the rapid industrial development of urban areas made necessary to determine the impacts of heavy metals pollution on environmental soil quality as well as human health (Cachada et al., 2012; Praveena et al., 2015). In particular, cobalt is a toxic heavy metal that can affect the environment and that also can provoke human health problems (Manohar et al., 2006). It is essential for both human and animal health but in relatively high concentrations it could cause health effects as vomits, heart and thyroid problems, paralysis, low blood pressure, lung irritations and bone defects among others, and harmful impact for crop production as well (Jalali and Majeri, 2016; Manohar et al., 2006).

It is known that soils are one of the ultimate sinks for pollutants discharged into the environment. Therefore, the knowledge of the interactions between them is crucial to

predict contaminants distribution and the potential transfer to animals, crops and the human alimentary chain.

Despite the great variety of industries that release cobalt into the environment and the potential risk to human health and environmental quality, controversial results about cobalt interactions with soils and soil components still remain, assigned mainly to the variations on the key components (organic matter, clays and Fe oxides) of the soils, coming from different world regions.

Regarding soils organic matter content, a significant role was found in Co^{2+} sorption for a sandy soil from Korea (Chon et al., 2012) and also in Scotland soils, with clay content between 10% and 30% (McLaren et al., 1986). Moreover, a significant high Co^{2+} sorption was obtained for a Japanese soil with 36% of clay and 17% of total carbon (Abd Elfattah and Wada, 1981), although the opposite statement was observed for Iran soils with clay range that included the previous (15.0 and 43.2%), presenting relatively lower organic matter content, between 0.7 and 3.5% (Jalali and Majeri, 2016). In addition, after analysing in situ 70 polluted soils in a Wales, Great Britain, industrial area, a weak but negative correlation between Co^{2+} concentration and organic matter content was determined (Davies, 1997).

Considering clay mineral content, a relatively high Co^{2+} sorption capacity was determined for Indian, US and Egypt soils (El-Sofany et al., 2009; Gutierrez and Fuentes, 1991; Rawat et al., 1996), but on Scotland and Iran soils it was stated that minerals probably had not a significant influence on Co^{2+} sorption (Jalali and Majeri, 2016; McLaren et al., 1986).

In relation to Fe oxides content, for Japanese soils it is highlighted the higher selectivity coefficient obtained for Fe oxides than those obtained for clays and organic matter (Abd Elfattah and Wada, 1981). Moreover, Co^{2+} bounds to Fe and Mn oxides and carbonates was observed for a Serbian soil composed principally by quartz, kyanite and muscovite (Smičiklas et al., 2015). In addition, a direct correlation between solid-solution distribution coefficient values and Mn and Fe oxide contents was reported for Amazonian soils (de Souza Braz et al., 2013). Conversely, low affinity between Co^{2+} and amorphous Fe oxides, goethite and haematite (Gunnarsson et al., 2000; Han, 2007) and non-significant correlation between Fe and Co^{2+} sorption for calcareous Iranian soils were reported (Jalali and Majeri, 2016).

Summing up, the results show that Co^{2+} interaction with soils and its main components is a complex process that can be influenced by the different combinations of soil composition.

The presence of cobalt and other heavy metals in sediments collected around the most important petrochemical pole of South America located in La Plata, Argentina, evidenced the generated pollution (Labunska et al., 2000). Thus, concern was originated about the ability of metals soil retention and the transfer of this pollution to groundwater, rivers and crops.

The aim of this study was to analyse the influence of soils and soil components from La Plata region, Argentina, on Co^{2+} sorption capacity. A deep characterisation of soils properties has been performed by a variety of techniques and three main distribution coefficients used in soil interaction studies were determined (distribution coefficient K_{dis} , the solid-solution distribution coefficient K_{dx} and the indicator of sorption capacity K_r) and the correlation between them was presented.

2 Materials and methods

2.1 Soil samples

In La Plata region (Figure 1), two principal geomorphological units are identified: the coastal and inland zones. Inland region is covered by loessic Pampean deposits and the soils are developed from wind and fluvial sediments whereas the coastal zone is covered by marine and fluvial deposits coming from La Plata River and the fluvial transport, with soils developed from sediments carried by marine ingressions (Hurtado et al., 2006). Soil samples were collected from six unperturbed soils: SP1, SP2 and SP5 (inland region) and SP3, SP4 and SP6 (coastal zone). Samples were collected from soil pits (0–50 cm depth) and three subsamples of each profile were selected: surface, medium deep and the deepest one; labelled with a, b and c letters, respectively, along with the soil profile number (i.e., 1a, 2c, etc.). The clay fraction of some medium depth soil samples (1b, 2b, 5b, 3b, 4b and 6b) was isolated using the methodology proposed by Carver (1971) and then they were dried at 90°C, crushed and sieved. These samples were labelled adding cl to the end of the soil sample name, i.e., 1bcl corresponds to the clay fraction of the 1b soil sample.

Figure 1 Sampling point locations. Dash line indicates the border between coastal and inland soils. SP1, SP2 and SP5 belong to the inland soils, whereas SP3, SP4 and SP6 to the coastal region (see online version for colours)



2.2 Soil samples characterisation

The textural and carbon content determinations for SP1–SP4 soils were previously published (Montes et al., 2013). SP5 and SP6 samples were characterised following the same procedure utilised for SP1–SP4 soils. The results are presented in Figure 2. Haematite content of all soil samples was previously reported (Montes et al., 2016).

2.2.1 Mineral content

Clay mineral content was determined from diffraction patterns (Mg- and glycol-saturated samples and annealed samples) according to Carver (1971). X-ray diffractograms were

obtained by a PANalytical, X'Pert PRO high-resolution diffractometer (CuK α radiation) from 3° to 32°, with a step mode collection of 0.02°, 0.02 s by step. The illite (I), smectite (Sm) and kaolinite (Ka) content were obtained by a semi-quantitative analysis (Foscolos et al., 1976).

2.2.2 Mn determination

 MnO_2 determinations were carried out by wavelength dispersive XRF using a Philips MagiX apparatus (PANalytical) on soil samples pellets. The pellets (200 mg) were prepared using 5 tn pressure. Uncertainties in the analysis were 5%.

Figure 2 Content for the indicated soils (a) Illite, smectite and kaolinite, (b) MnO₂ and (c) Ms value related with Magnetite. The table inset indicates the determined organic content (OC) and the clay, silt and sand percentages (data for 1, 2, 3 and 4 profiles were previously reported (Montes et al., 2013)



2.2.3 Saturation magnetisation

The saturation magnetisation (Ms) was obtained from the hysteresis loops measured by a VSM spectrometer LakeShore 7404 with external magnetic fields between -1.2 T and 1.2 T, after subtracting the paramagnetic contribution. Soil samples were supported in a diamagnetic sample holder with negligible magnetic response. In environmental samples, the Ms value was directly related to the type and concentration of the presence of magnetic minerals (Evans et al., 2003).

2.3 Sorption experiments

The Co^{2+} sorption experiments were performed during 24 h in batch conditions (25 mL) at 20°C, pH = 6 and soil/solution ratio 1 : 1, varying the initial Co^{2+} concentration Ci

(0.17, 0.34, 0.51, 0.68, 0.85, 1.02, 1.19, 1.44 and 1.70 mmol/L). Milli-Q water and CoCl₂.6H₂O (99%), supplied by Fluka-Sigma-Aldrich, was used to prepare the Co²⁺ solutions. All sorption experiments were done by duplicate. Co^{2+} sorption was also investigated on the clay fraction of selected soils, using Ci = 0.51 and 0.85 mmol/L and same conditions as indicated earlier.

After each sorption experiment, solid and liquid phases were isolated by centrifugation (15 min, 15,000 rpm). Supernatant was collected and properly stored for Co^{2+} concentration determination. Solid phase was dried at 90°C and kept into a desiccator for further analysis. Supernatants Co^{2+} concentration was determined by colorimetric method (Sandell, 1944) using a Hewlett-Packard 8453 UV-visible spectrophotometer ($\lambda = 620$ nm).

2.4 Data analysis

Several parameters are used for metal sorption studies on soils as the solid-solution distribution coefficients (K_{dx}), parameters extracted from sorption isotherms and a more recently developed parameter K_r .

The solid-solution distribution coefficient, K_{dx} (in L/g), for a specific metal concentration, is defined as:

$$K_{dx} = \frac{\left(C_i - C_e\right)V}{C_e m}$$
(1)

where C_i and C_e represent the Co²⁺ concentration in solution before and after sorption experiments and *m* and *V* the soil mass and the solution volume, respectively. *X* denotes the used metal initial concentration. This coefficient considers the net result of the several transfer processes between the metal and soil and it is useful to compare the sorption of a determinate cation on different soil samples under equal conditions (Vega et al., 2008).

The extracted parameters from the complete sorption isotherms and the recently developed parameter K_r (see here) are determined using the entire range of the used metal concentrations.

The Freundlich can be defined by the following equation:

$$\left(C_i - C_e\right) \frac{V}{m} = K_F C_e^{1/n} \tag{2}$$

Equation (2) allowed obtaining the K_F (mmol^{1-1/n} L^{1/n} g⁻¹) and *n* parameters and, complementary, the K_{Fl} parameter (L/g), if only the lineal part of the curve (lower concentrations, n = 1) is considered:

$$\left(C_{i} - C_{e}\right)\frac{V}{m} = K_{F1}C_{e} \tag{3}$$

The K_F parameter could introduce some interpretation problems owing to, depending on the used units, the achieved results can be contradictory. This is related to the presence of the *n* parameter in the unit change process. Therefore, instead of using K_F , here were used K_{FI} and K_{dis} (mmol^(n-1/n) L^(1-n+1/n)g⁻¹), defined as:

$$K_{dis} = K_F C^{n-1} \tag{4}$$

where the used Co^{2+} concentration was C = 0.017 mmol/L as previously proposed by Shaheen (2009).

Another parameter used to analyse metal sorption in soil is the K_r indicator (Vega et al., 2008). To obtain the parameter, two plots must be constructed and fitted by a lineal model:

 C_e vs. C_i , obtaining K_{rl} as the slope of the obtained straight line

 $C_i - C_e$ vs. C_i , being K_{r2} the slope of the fitted curve

Then, the obtained fittings must be compared; K_r will be equal to K_{rl} if the coefficient of determination in the first fitting is better than that obtained in the second fit process. Contrarily, K_r is equal to $1 - K_{r2}$. This parameter is useful when Langmuir and Freundlich equations are not adequate to fit sorption isotherms (Vega et al., 2008), as it frequently occurs with soil samples. In cases where the Langmuir and Freundlich models can be used, K_r is an extra used parameter than can also provide complementary information.

Finally, once obtained the above-mentioned parameters, the correlations between the K values (soil sorption capacity) and soil properties were assessed by the Pearson correlation coefficients, considering 95% of confidence level.

3 Results and discussion

3.1 Samples characterisation

The organic carbon content (OC), resumed in table inset Figure 2, decreases with soil depth, contrarily to the clay content behaviour. Different textural classes were determined for the soils (Montes et al., 2013) whereas haematite content resulted, in general, lower for coastal than inland soils (Montes et al., 2016).

The illite, smectite and kaolinite content of soil samples (Figure 2(a)) indicated significant variations among mineral content in the different evaluated profiles. Illite and smectite were the major minerals for inland and coastal zone soils, respectively, whereas kaolinite was the minor mineral in both regions. MnO_2 content did not exceed 1% in none of the soil profiles (Figure 2(b)), being 0.7% the highest concentration, attained in the coastal region.

Soils from inland area presented higher Ms values than those from coastal zone (Figure 2(c)). The only two components present in the studied soils with ferrimagnetic or ferromagnetic behaviour were haematite and magnetite with Ms = 0.4 and $92 \text{ mAm}^2/\text{kg}$, respectively (Montes et al., 2012). The relatively lower Ms value of haematite with respect to magnetite allowed to associate directly the Ms value with magnetite content.

3.2 Cobalt sorption: effect of soil properties

Table 1 summarises n, K_{dis} , K_{FI} and K_r values. An example of K_{dx} distribution coefficient obtained for Co²⁺ initial concentration = 1.19 mmol/L, $K_{dI.19}$ (L/g) was also added. As it can be seen from Table 1, K_{dis} varied from 2.8 mmol^(n-1/n) L^(1-n+1/n)g to 10.2 mmol^(n-1/n) L^(1-n+1/n)g⁻¹, K_{FI} between 2.6 and 5.4 L/g, $K_{dI.19}$ from 3.29 L/g to 4.06 L/g and K_r from 0.741 to 0.780.

Table 1 $n, K_{dis}, K_{d1.19}$ and K_r obtained values

	2				2	
	$(\text{mmol}^{(n-1/n)}L^{(1-n+1/n)}/g)$	и	K_{FI} (L/g) $K_{dI.19}$ (L/g)	K_r	$(\text{mmol}^{K_{dis}}_{l^{(n-1/n)}L^{(1-n+1/n)}/g})$	$n = K_{FI}$ (L/g) $K_{dI,Ig}$ (L/g) K_r
la	5.8 ± 0.2	1.23 ± 0.02	3.5 ± 0.2 3.51 ± 0.05 0.	743 ± 0.008 3a	9.4 ± 0.6	1.33 ± 0.05 4.4 ± 0.2 3.98 ± 0.09 0.778 ± 0.008
1b	4.3 ± 0.2	1.11 ± 0.02	3.3 ± 0.1 3.50 ± 0.05 0.	770 ± 0.008 3b	10.2 ± 0.2	$1.52 \pm 0.03 \ 5.4 \pm 0.3 \ 4.06 \pm 0.09 \ 0.761 \pm 0.007$
lc	4.5 ± 0.1	1.08 ± 0.02	3.7 ± 0.2 3.71 ± 0.06 0.	773 ± 0.008 3c	6.1 ± 0.2	$1.19\pm0.03\ 5.0\pm0.2\ 4.03\pm0.09\ 0.776\pm0.008$
2a	2.8 ± 0.2	1.03 ± 0.05	2.6 ± 0.2 3.29 ± 0.05 0.	741 ± 0.009 4a	5.4 ± 0.2	$1.17\pm0.04\ \ 3.5\pm0.2\ \ 3.57\pm0.08\ \ 0.767\pm0.06$
2b	4.7 ± 0.1	1.10 ± 0.04	3.1 ± 0.2 3.48 ± 0.05 0.	769 ± 0.007 4b	7.2 ± 0.5	$1.26 \pm 0.06 \ 4.8 \pm 0.3 \ 4.24 \pm 0.09 \ 0.777 \pm 0.005$
2c	5.3 ± 0.1	1.19 ± 0.04	3.5 ± 0.2 3.50 ± 0.05 0.	757 ± 0.009 4c	6.3 ± 0.2	$1.20 \pm 0.04 \ 4.4 \pm 0.2 \ 4.31 \pm 0.09 \ 0.777 \pm 0.006$
5a	6.1 ± 0.2	1.08 ± 0.03	3.5 ± 01 3.75 ± 0.07 0.	773 ± 0.008 6a	3.9 ± 0.4	$1.05 \pm 0.05 \ \ 3.0 \pm 0.2 \ \ 3.33 \pm 0.07 \ \ 0.764 \pm 0.005$
5b	6.5 ± 0.4	1.21 ± 0.04	3.9 ± 0.1 3.70 ± 0.06 0.	764 ± 0.008 6b	7.7 ± 0.3	$1.30 \pm 0.04 \ 4.3 \pm 0.1 \ 3.82 \pm 0.08 \ 0.774 \pm 0.008$
5с	9.9 ± 1.0	1.30 ± 0.02	3.9 ± 0.2 3.91 ± 0.07 0.	770 ± 0.006 6c	5.6 ± 0.1	$1.25 \pm 0.05 \ 4.2 \pm 0.2 \ 4.05 \pm 0.09 \ 0.780 \pm 0.007$

The *n* values, related with the sorption sites heterogeneity, ranged from 1 to 1.52. This parameter was positively correlated with the clay and smectite content (Table 2), i.e., the inhomogeneous sorption sites for Co^{2+} sorption in soils could be associated to the presence of smectite in the samples, in agreement with results reported for different montmorillonite samples (Hashemian et al., 2015; Ma et al., 2011; Shawabkeh et al., 2007).

Pearson correlation coefficients between distribution coefficients (K_{dis} , K_{Fl} , K_r , $K_{d0.5l}$, $K_{d0.85}$, $K_{d1.19}$, $K_{d1.44}$ and $K_{d1.70}$) and soil properties are shown in Table 2. Organic carbon, sand, illite and haematite contents did not present significant correlation with any of the distribution coefficients evaluated and, consequently, they were not included in Table 2.

	-			-		-		
	Clay	Silt	Sm	Ka	Ms	Fe	Mn	
	Paran	neters depend	ing on the en	tire/partial c	concentration	range		
Ν	$0.52_{0.03}$	$-0.47_{0.04}$	$0.50_{0.04}$	ns	ns	ns	ns	
K_{dis}	0.59 _{0.01}	$-0.54_{0.02}$	$0.51_{0.03}$	ns	ns	ns	$0.67_{0.003}$	
K_{Fl}	$0.76_{0.0003}$	$-0.75_{0.0004}$	$0.73_{0.0005}$	$0.57_{0.02}$	$-0.63_{0.005}$	$0.63_{0.007}$	$0.65_{0.005}$	
K_r	$0.53_{0.02}$	$-0.54_{0.02}$	$0.53_{0.02}$	$0.47_{0.049}$	$-0.50_{0.03}$	$0.51_{0.03}$	ns	
Parameters depending on the specific concentration								
K _{ds0.51}	$0.71_{0.001}$	$-0.71_{0.001}$	$0.72_{0.0008}$	ns	ns	$0.51_{0.03}$	$0.64_{0.006}$	
K _{ds0.85}	$0.57_{0.01}$	$-0.51_{0.03}$	$0.53_{0.02}$	ns	ns	ns	$0.64_{0.005}$	
K _{ds1.19}	$0.81_{0.00004}$	$-0.75_{0.0003}$	$0.78_{0.0002}$	$0.68_{0.002}$	$-0.63_{0.005}$	$0.65_{0.004}$	$0.49_{0.04}$	
K _{ds1.44}	$0.67_{0.002}$	$-0.55_{0.02}$	$0.55_{0.02}$	$0.61_{0.006}$	$-0.50_{0.04}$	ns	ns	
K _{ds1.70}	$0.64_{0.004}$	$-0.63_{0.005}$	$0.66_{0.003}$	$0.64_{0.004}$	$-0.64_{0.004}$	$0.54_{0.03}$	ns	

Table 2Pearson correlation coefficients between soil properties and n, K_{dis}, k_{dx} and K_{r} ;
ns: no significant correlation. Subscripts indicate the correlation significance

The absence of correlation between Co^{2+} sorption and OC content was in agreement with results obtained for soils with OC values below 26 g/kg (Anderson and Christensen, 1988; de Souza Braz et al., 2013; Jalali and Majeri, 2016; Rawat et al., 1996).

For sand content, the absence of correlation with Co^{2+} sorption was expected owing to the deedless of sand fraction.

The significance and correlation type (positive or negative) obtained between the sorption capacity indicators and clay, silt and smectite were similar. However, differences in the correlation significances were obtained for kaolinite, saturation magnetisation and Mn and Fe content, depending on the observed sorption parameter.

Focused on K_{dx} coefficients, it seems that kaolinite affects significantly and positively the Co²⁺ sorption on soils for C_i equal or higher than 1.19 mmol/L, being not significant for the lower Co²⁺ concentrations. In addition, K_{FI} and K_r also revealed a significant correlation, contrary to the obtained results with K_{dis} . Therefore, it seems to indicate that K_{FI} and K_r parameters are more sensitive to kaolinite amount changes than K_{dis} coefficient. The significant correlations between kaolinite and K_{dx} for the highest Co²⁺ concentrations could be indicating that kaolinite presence becomes important for relatively high Co²⁺ concentration, probably owing to the smectite sorption sites, which has a higher efficiency for Co^{2+} sorption than kaolinite (Bhattacharyya and Gupta, 2008), which were already saturated.

The obtained correlations between Ms and the evaluated K parameters followed the same behaviour than those found for kaolinite amount, although the sign of the correlations was negative. Then, it seems that for a C_i value higher than 1.19 mmol/L, the magnetite content affected negatively the Co²⁺ sorption on the studied soils.

Concerning the Mn oxide amount, despite the determined low content, K_{dx} showed a significant and positive correlation for Co^{2+} concentration values lower than 1.19 mmol/L, whereas K_r did not reveal any kind of correlation. Moreover, it seems that K_{FI} and K_{dis} are more sensitive to disclose changes in Mn concentration than K_r , contrarily to that indicated for kaolinite contents.

Regarding Fe content, debatable correlation results were observed (Table 2). Again, K_r , K_{FI} and K_{dis} did not indicate the same tendency; in this case, Fe content and K_r and K_{FI} correlation resulted significant and positive, whereas the correlation with K_{dis} resulted not significant. In addition, K_{dx} did not present a defined behaviour with the Co²⁺ concentration. Therefore, not conclusive observation can be done for Fe amounts influence on Co²⁺ sorption for La Plata region soils.

Pearson correlation coefficients between silt fraction and K_{dis} , K_{FI} , K_r and K_{dx} were significant and negative, indicating that this fraction influenced negatively the Co²⁺ sorption. This behaviour could be assigned to the aggregation of silt fraction by organic matter, producing a decrease of the reactive surface sites for Co²⁺ sorption.

The significant correlation between the evaluated *K* parameters and smectite content and the no significant correlations with illite concentrations can be understood considering the sorption studies of Co^{2+} on these different clay minerals. In general, when comparing Freundlich and Langmuir parameters, it could be concluded that the retention capacity of Co^{2+} by smectite was larger than for illite clays (Kubilay et al., 2007; Ozsoy and Bekbolet, 2018).

The Pearson coefficients determined between the K coefficients and clay content of La Plata soils were significant and positive, in agreement with results from Denmark (Anderson and Christensen, 1988) and Indian soils (Rawat et al., 1996) and corroborated by the higher K_d values obtained when clay content, in soil contaminated with radionuclides, increases (Gil-García et al., 2009).

	0.51 m	mol/L	0.85 mmol/L		
Sample	Sorption (%)	As/Acl	Sorption (%)	As/Acl	
1bcl	90 ± 1	0.90 ± 0.03	88 ± 1	0.90 ± 0.03	
2bcl	79 ± 1	1.00 ± 0.03	84 ± 1	0.93 ± 0.03	
5bcl	82 ± 1	1.00 ± 0.03	79 ± 1	1.00 ± 0.03	
3bcl	84 ± 1	1.04 ± 0.03	86 ± 1	0.97 ± 0.03	
4bcl	86 ± 1	0.99 ± 0.03	87 ± 1	0.91 ± 0.03	
6bcl	79 ± 1	1.01 ± 0.03	81 ± 1	1.03 ± 0.03	

Table 3Co2+ sorption percentage for indicated clay fractions, and relation of sorption
percentage from bulk soil and clay fraction (As/Acl)

To go deeper on the later K correlations, several clay fractions of some medium depth soil samples were used as Co^{2+} sorbents and the results of the sorption experiments are

indicated in Table 3, where As/Acl represents the rate between sorption percentage on soils and clay fraction.

The obtained As/Acl values (Table 3) were lower or equal to 1, which means that these clay fractions played a main role in Co^{2+} sorption on the evaluated soils. This behaviour also pointed out that organic carbon and sand fraction did not participate significantly in the Co^{2+} sorption, which support correlation results discussed previously.

4 Conclusions

The Co²⁺ sorption on 18 soils (belonging to six unperturbed soils from La Plata region) with different characteristics was investigated. The influence of soil parameters on Co²⁺ sorption was analysed by the Pearson correlation coefficient between four sorption indicator parameters (K_{dis} , K_{Fl} , K_{dx} and K_r) and the principal soil properties.

The analysed coefficients showed no correlation with organic carbon, sand, illite and haematite content of soils. Debatable correlations with kaolinite, magnetite and Mn and Fe oxides contents were determined. The results seem to indicate that K_{FI} and K_r were more sensitive than K_{dis} to kaolinite and magnetite changes, whereas K_{FI} and K_{dis} seem to be more sensitive to manganese oxides variations than K_r .

A significant correlation between clay, silt and smectite content and K_{dis} , K_{Fl} , K_{dx} and K_r was established. Silt fraction seems to affect negatively Co²⁺ sorption, whereas clay and smectite content seems to affect it positively.

Regarding clay, the Co^{2+} sorption percentage determined in clay fraction of some soils resulted equal or higher than the sorption percentage observed in the corresponding soil samples, supporting the previously determined correlation. The positive correlation with smectite content reveals its importance on Co^{2+} sorption as reported for sorption Co^{2+} experiments on this mineral alone. This also supports the no correlation observed with illite (mineral with a lower Co^{2+} sorption efficiency than smectite) and the positive correlation determined for K_{dx} and kaolinite for relatively high Co^{2+} concentrations, where, possibly, the smectite sorption sites were already saturated. These results indicate that the higher the smectite content, the better the soil Co^{2+} sorption capacity.

Acknowledgements

The authors acknowledge Project I191-Univ. Nacional de La Plata, Fondo Argentino Sectorial (FONARSEC) FSNano-008/2010 and PIP112 201201 00691 Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for financial support. Thanks to the NANOPYMES program (Ministerio de Ciencia, Tecnología e Innovación Productiva (MINCyT)-European Union (EU), EuropeAid/132184/D/SUP/AR) and M. Ceolín for helping discussions.

References

Abd Elfattah, A. and Wada, K. (1981) 'Adsorption of lead, copper, zinc, cobalt, and cadmium by soils that differ in cation-exchange materials', *J. Soil Sci.*, Vol. 32, pp.271–283, https://doi. org/10.1111/j.1365-2389.1981.tb01706.x

- Anderson, P.R. and Christensen, T.H. (1988) 'Distribution coefficients of Cd, Co, Ni, and Zn in soils', *J. Soil Sci.*, Vol. 39, pp.15–22, https://doi.org/10.1111/j.1365-2389.1988.tb01190.x
- Bhattacharyya, K.G. and Gupta, S.S. (2008) 'Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review', Adv. Colloid Interface Sci., Vol. 140, pp.114–131, https://doi.org/10.1016/j.cis.2007.12.008
- Cachada, A., Pereira, M.E., Ferreira da Silva, E. and Duarte, A.C. (2012) 'Sources of potentially toxic elements and organic pollutants in an urban area subjected to an industrial impact', *Environ. Monit. Assess.*, Vol. 184, pp.15–32, https://doi.org/10.1007/s10661-011-1943-8
- Carver, R.E. (1971) Procedures in Sedimentary Petrology, Wiley-Interscience.
- Chon, J.K., Lee, K-J. and Yun, J-I. (2012) 'Sorption of cobalt(II) on soil: effects of birnessite and humic acid', J. Radioanal. Nucl. Chem., Vol. 293, pp.511–517, https://doi.org/10.1007/ s10967-012-1806-y
- Davies, B.E. (1997) 'Heavy metal contaminated soils in an old industrial area of Wales, Great Britain: source identification through statistical data interpretation', *Water. Air. Soil Pollut.*, Vol. 94, pp.85–98, https://doi.org/10.1007/BF02407095
- de Souza Braz, A.M., Fernandes, A.R., Ferreira, J.R. and Alleoni, L.R.F. (2013) 'Prediction of the distribution coefficients of metals in Amazonian soils', *Ecotoxicol. Environ. Saf.*, Vol. 95, pp.212–220, https://doi.org/10.1016/j.ecoenv.2013.05.007
- El-Sofany, E.A., Zaki, A.A. and Mekhamer, H.S. (2009) 'Kinetics and thermodynamics studies for the removal of Co2+ and Cs+ from aqueous solution by sand and clay soils', *Radiochim. Acta*, Vol. 97, https://doi.org/10.1524/ract.2009.1573
- Evans, M.E., Heller, F., Heller, F.C. and Evans, M. (2003) *Environmental Magnetism: Principles* and Applications of Enviromagnetics, Academic Press.
- Foscolos, A.E., Powell, T.G. and Gunther, P.R. (1976) 'The use of clay minerals and inorganic and organic geochemical indicators for evaluating the degree of diagenesis and oil generating potential of shales', *Geochim. Cosmochim. Acta*, Vol. 40, pp.953–966, https://doi.org/ 10.1016/0016-7037(76)90144-7
- Gil-García, C., Tagami, K., Uchida, S., Rigol, A. and Vidal, M. (2009) 'New best estimates for radionuclide solid–liquid distribution coefficients in soils. Part 3: miscellany of radionuclides (Cd, Co, Ni, Zn, I, Se, Sb, Pu, Am, and others)', *J. Environ. Radioact.*, Vol. 100, pp.704–715, https://doi.org/10.1016/j.jenvrad.2008.12.001
- Gunnarsson, M., Jakobsson, A-M., Ekberg, S., Albinsson, Y. and Ahlberg, E. (2000) 'Sorption studies of Cobalt(II) on colloidal hematite using potentiometry and radioactive tracer technique', J. Colloid Interface Sci., Vol. 231, pp.326–336, https://doi.org/10.1006/ jcis.2000.7149
- Gutierrez, M. and Fuentes, H.R. (1991) 'Competitive adsorption of cesium, cobalt and strontium in conditioned clayey soil suspensions', *J. Environ. Radioact.*, Vol. 13, pp.271–282, https://doi. org/10.1016/0265-931X(91)90001-V
- Han, F.X. (2007) Biogeochemistry of Trace Elements in Arid Environments, Environmental Pollution, Springer, Netherlands.
- Hashemian, S., Saffari, H. and Ragabion, S. (2015) 'Adsorption of Cobalt(II) from aqueous solutions by Fe3O4/bentonite nanocomposite', *Water. Air. Soil Pollut.*, Vol. 226, https://doi.org/10.1007/s11270-014-2212-6
- Hurtado, M., Gimenéz, J.E. and Cabral, M.G. (2006) 'Análisis Ambiental del Partido de La Plata', *Aportes al Ordenamiento Territorial*, Vol. 134.
- Jalali, M. and Majeri, M. (2016) 'Cobalt sorption-desorption behavior of calcareous soils from some Iranian soils', *Chem. Erde – Geochem.*, Vol. 76, pp.95–102, https://doi.org/10.1016/ j.chemer.2015.11.004
- Kubilay, Ş., Gürkan, R., Savran, A. and Şahan, T. (2007) 'Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite', *Adsorption*, Vol. 13, pp.41–51, https://doi.org/10.1007/s10450-007-9003-y

- Labunska, I., Brigden, K., Stringer, R., Johnston, P., Santillo, D. and Ashton, J. (2000) 'Organic pollutants and heavy metals found in sediments and water samples associated with the petrochemical complex in La Plata district, Argentina', *Stop Pollution*, Vol. 7.
- Ma, B., Oh, S., Shin, W.S. and Choi, S-J. (2011) 'Removal of Co2+, Sr2+ and Cs+ from aqueous solution by phosphate-modified montmorillonite (PMM)', *Desalination*, Vol. 276, pp.336–346, https://doi.org/10.1016/j.desal.2011.03.072
- Manohar, D.M., Noeline, B.F. and Anirudhan, T.S. (2006) 'Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase', *Appl. Clay Sci.*, Vol. 31, pp.194–206, https://doi.org/10.1016/j.clay.2005.08.008
- McLaren, R.G., Lawson, D.M. and Swift, R.S. (1986) 'Sorption and desorption of cobalt by soils and soil components', J. Soil Sci., Vol. 37, pp.413–426, https://doi.org/10.1111/j.1365-2389.1986.tb00374.x
- Montes, M.L., Mercader, R.C., Taylor, M.A., Runco, J. and Desimoni, J. (2012) 'Assessment of natural radioactivity levels and their relationship with soil characteristics in undisturbed soils of the northeast of Buenos Aires province, Argentina', J. Environ. Radioact., Vol. 105, pp.30–39, https://doi.org/10.1016/j.jenvrad.2011.09.014
- Montes, M.L., Rivas, P.C., Taylor, M.A. and Mercader, R.C. (2016) 'Approximate total Fe content determined by Mössbauer spectrometry: Application to determine the correlation between gamma-ray-emitter activities and total content of Fe phases in soils of the Province of Buenos Aires, Argentina', J. Environ. Radioact., Vols. 162–163, pp.113–117, https://doi.org/ 10.1016/j.jenvrad.2016.05.016
- Montes, M.L., Silva, L.M.S., Sá, C.S.A., Runco, J., Taylor, M.A. and Desimoni, J. (2013) 'Inventories and concentration profiles of 137Cs in undisturbed soils in the northeast of Buenos Aires Province, Argentina', J. Environ. Radioact., Vol. 116, pp.133–140, https://doi.org/10.1016/j.jenvrad.2012.10.003
- Ozsoy, O. and Bekbolet, M. (2018) 'Surface interactions of Cs+ and Co2+ with bentonite', Environ. Sci. Pollut. Res., Vol. 25, pp.3020–3029, https://doi.org/10.1007/s11356-015-4103-9
- Praveena, S.M., Yuswir, N.S., Aris, A.Z. and Hashim, Z. (2015) 'Contamination assessment and potential human health risks of heavy metals in Klang urban soils: a preliminary study', *Environ. Earth Sci.*, Vol. 73, pp.8155–8165, https://doi.org/10.1007/s12665-014-3974-2
- Rawat, J.P., Umar Iraqi, S.M. and Singh, R.P. (1996) 'Sorption equilibria of cobalt(II) on two types of Indian soils – the natural ion exchangers', *Colloids Surf. Physicochem. Eng. Asp.*, Vol. 117, pp.183–188, https://doi.org/10.1016/0927-7757(96)03700-4
- Shaheen, S.M. (2009) 'Sorption and lability of cadmium and lead in different soils from Egypt and Greece', *Geoderma*, Vol. 153, pp.61–68, https://doi.org/10.1016/j.geoderma.2009.07.017
- Shawabkeh, R.A., Al-Khashman, O.A., Al-Omari, H.S. and Shawabkeh, A.F. (2007) 'Cobalt and zinc removal from aqueous solution by chemically treated bentonite', *The Environmentalist*, Vol. 27, pp.357–363, https://doi.org/10.1007/s10669-007-9048-1
- Smičiklas, I., Dimović, S., Jović, M., Milenković, A. and Šljivić-Ivanović, M. (2015) 'Evaluation study of cobalt(II) and strontium(II) sorption-desorption behavior for selection of soil remediation technology', *Int. J. Environ. Sci. Technol.*, Vol. 12, pp.3853–3862, https://doi.org/ 10.1007/s13762-015-0817-y
- Vega, F.A., Covelo, E.F. and Andrade, M.L. (2008) 'A versatile parameter for comparing the capacities of soils for sorption and retention of heavy metals dumped individually or together: results for cadmium, copper and lead in twenty soil horizons', J. Colloid Interface Sci., Vol. 327, pp.275–286, https://doi.org/10.1016/j.jcis.2008.08.027