

INTERNATIONAL SOCIETY FOR SOIL MECHANICS AND GEOTECHNICAL ENGINEERING



This paper was downloaded from the Online Library of the International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE). The library is available here:

<https://www.issmge.org/publications/online-library>

This is an open-access database that archives thousands of papers published under the Auspices of the ISSMGE and maintained by the Innovation and Development Committee of ISSMGE.

Sorption influence of chromium, cadmium, nickel and lead in monospecie and multispecie solution in a residual soil from Southern Brazil

Gláucia Carine dos Santos, Eduardo Pavan Korf & Karla Salvagni Heineck
Federal University of Rio Grande do Sul, Porto Alegre/Rio Grande do Sul, Brasil

Rafael de Souza Tímbola & Antonio Thomé
University of Passo Fundo, Passo Fundo/Rio Grande do Sul, Brasil



ABSTRACT

The presence of inorganic contaminants in soil has been the subject of many researches, especially when considering the risks that contaminants may cause in the quality of surface water and groundwater. Among these inorganic contaminants there are the toxic metals, which are present in various chemical forms that exhibit different physical and chemical behavior. The aim of this study is to evaluate the sorption influence of different toxic metals present in monospecie and multispecie solutions in a basalt residual soil from southern Brazil. The undeformed specimens were molded and column test were carried out. The tests were performed with solutions percolation containing 5 mg/L of toxic metals Cr^{3+} , Cd^{2+} , Ni^{2+} and Pb^{2+} , in monospecie and multispecie solution. The total metals concentration was 20 mg/L in multispecie solution. The specimens were divided into five layers and subjected to the 3050B-EPA method for metals extraction. It was possible to find the values of sorption present in each layer subjected to this method. The higher retention capacity in tests submitted to monospecie and multispecie solutions was observed for chromium and the lowest retention capacity was observed for cadmium in monospecie solution and nickel for the multispecies solution. The selectivity sequence for multispecie solution was: $\text{Cr} > \text{Cd} > \text{Pb} > \text{Ni}$.

RESUMEN

La presencia de contaminantes inorgánicos en el suelo ha sido objeto de mucha investigación, especialmente al considerar los riesgos que los contaminantes pueden causar en la calidad de las aguas superficiales y subterráneas. Entre estos contaminantes inorgánicos son los metales tóxicos, los cuales están presentes en diversas formas químicas que presentan diferentes comportamientos físicos y químicos. El objetivo de este estudio es evaluar la influencia de la sorción de diferentes metales tóxicos presentes en soluciones monospecie o multispecie en un suelo residual de basalto del sur de Brasil. Espécimen sin deformar fueron moldados y ensayo de la columna fue ejecutado. Los ensayos se realizaron con la percolación de soluciones que contienen 5 mg/L de los metales tóxicos Cr^{3+} , Cd^{2+} , Ni^{2+} e Pb^{2+} , en soluciones monospecie y multispecie. La concentración total de metales fue de 20 mg/L en la solución multispecie. Los especímenes fueron divididos en cinco capas y sometido al método 3050B-EPA para la extracción de los metales. Es posible encontrar los valores de la sorción en cada capa sometida a este método. La capacidad de retención más alta en los ensayos sometidos a soluciones monospecie y multispecie se observó para el cromo y la capacidad de retención más baja se observó para el cadmio en solución monoespecie y níquel para la solución multispecie. La secuencia de selectividad para solución multispecie fue: $\text{Cr} > \text{Cd} > \text{Pb} > \text{Ni}$.

1 INTRODUCTION

Soil is an important resource for subsistence and development of living beings. When the soil is contaminated may endanger the quality of food and the environment. Several ions or compounds of organic or inorganic nature can contaminate soil, surface water, groundwater or sediments. Among these contaminants are toxic metals, which receive special attention due to its high toxicity. The excess of the contaminant in the soil can overwhelm the capacity of retention (Sangui and Sasi, 2001) and may result in contaminant leaching.

The wide use of toxic metals in many applications such as in industry, agriculture and sanitation contributed to increase soil contamination, allowing the occurrence of contamination by different metal species simultaneously (Diels et al., 2002).

The migration of contaminants through the porous media occurs according to transport mechanisms that are associated with physical and biochemical processes. The interest in the diagnosis and assessment of metal species in the soil and how they relate became the target of numerous studies due to problems related to soil enrichment (Teixeira, 2008).

The mobility, activity and bioavailability depends on several factors such as pH, temperature, redox potential, competition with another metal, anions bonding, composition and ionic strength of soil solution (Pedrotti and Mello, 2009).

The USEPA (The U.S. Environmental Protection Agency) has identified several toxic chemicals based on the adverse effects to human health and the environment and grouping them into categories. In the group of inorganic chemicals are included toxic metals such as Cr, Cd, Ni, Pb and Hg (USEPA, 2004).

According to the metals identified by the USEPA (2004), chromium, cadmium, nickel and lead were used in this research to evaluate the influence of competitiveness among the metals present in monospecie or multispecie solution in soil sorption, both prepared at pH 4.5.

2 MATERIALS AND METHODS

Soil samples were collected to 1.50 m depth in the experimental field of geotechnical engineering at the University of Passo Fundo - UPF. The physical and chemical properties of soil are presented in Table 1.

It was used the backpressure of 20kPa and confined pressure of 40kPa. The tests were conducted on a non-saturated form where contaminant solutions were percolated directly on the specimens in two times the void volumes: the first one is collected in the equipment output and the second void volume remains inside of the specimen.

The amount of contaminant solution leached in each specimen is presented in Table 2. The average tests duration was 30 minutes.

The specimens were sectioned into five layers with 2cm thick each one as it is shown in Figure 1.

Table 1. Physical and chemical properties of residual soil from Southern Brazil

Characteristics	Sample
Clay (%)	67
Silt (%)	5
Sand (%)	28
Liquidity limit (%)	53
Plasticity limit (%)	42
Plasticity index	11
G	2.67
Natural moisture (%)	34.62
Natural specific weight (kN/m ³)	16.30
Void index	1.19
Degree of saturation (%)	75.70
Porosity (%)	54
pH (H ₂ O)	5.00
Organic matter (%)	<0.80
CEC (cmol _e /dm ³)	12.50
Permeability (m/s)	1.39x10 ⁻⁵

The specimens were molded with 10cm long and 5cm in diameter. The specimen physical characteristics are

presented in Table 2. Monospecie and multispecie contaminant solutions were prepared with the metals chromium, cadmium, nickel and lead with 5mg/L concentration for each metal and pH 4.5.

Table 2. Physical characteristics of specimens.

Test	Metal	Mass (g)	Total Volume	Porosity (n)	Vv (cm ³)
1	Ni ²⁺	325.90	212.75	0.58	122.52
	Pb ²⁺	287.50	203.09	0.61	123.49
	Ni ²⁺	313.24	210.56	0.59	123.84
	Pb ²⁺	302.30	217.00	0.61	133.30
2	Cd ²⁺	281.91	193.45	0.60	115.40
	Cd ²⁺	307.71	208.39	0.59	123.19
	Pb ²⁺	330.41	216.85	0.58	125.38
	All	310.95	207.26	0.58	121.17
3	Cr ³⁺	302.20	206.68	0.60	122.98
	Ni ²⁺	321.61	221.92	0.60	132.88
	All	315.05	208.02	0.58	120.80
	Cd ²⁺	287.80	194.78	0.59	115.10
4	Cr ³⁺	310.28	200.54	0.57	114.63
	Cr ³⁺	321.43	211.08	0.58	122.09
	All	312.91	189.66	0.54	103.02
	All	312.91	189.66	0.54	103.02

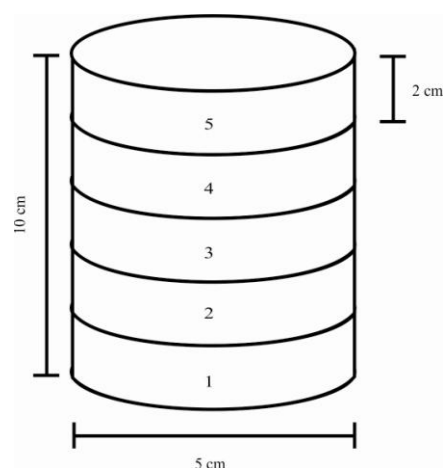


Figure 1 – Diagram of how was sectioned and identified of specimen layers

The layers were subjected to 3050B method (USEPA, 1996) for metals extraction and were analyzed by atomic spectrophotometer absorption method.

The tests were carried out using the column equipment that allows testing up to three samples simultaneously as shown in Figure 2.

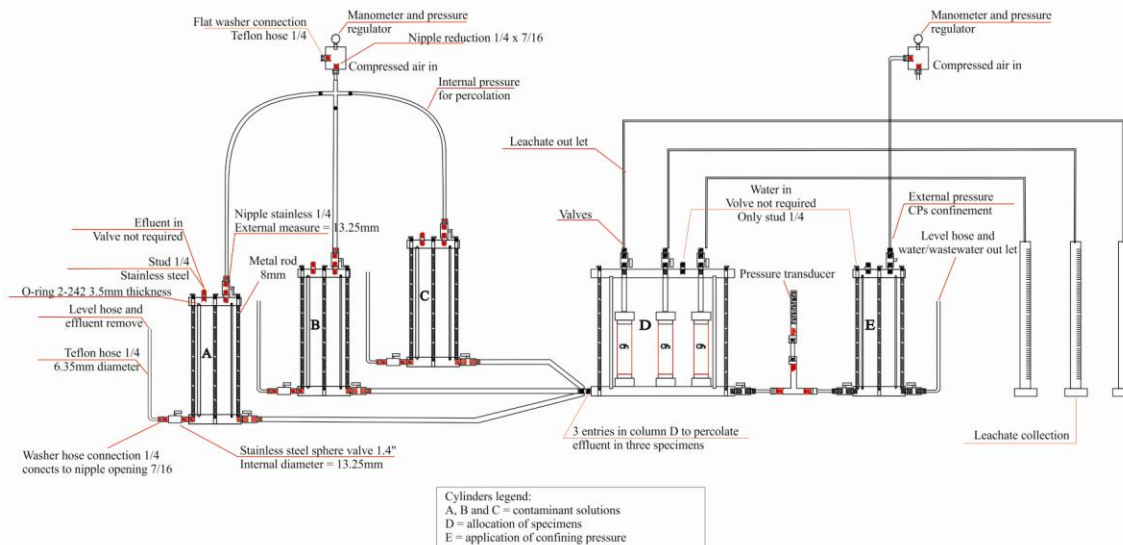


Figure 2 –Column equipment used in the research.

3 RESULTS AND DISCUSSION

The average of results obtained for the natural soil by the 3050B method extraction (USEPA, 1996) is presented in Table 3.

Table 3. Experimental results of sorption to natural soil.

Sorption (mg/kg)	Cr	Cd	Ni	Pb
Monospecie solution	62.50	0	27.80	33.80
Multispecie solution	50.10	0	26.60	30.60

The values in Table 3 for monospecie or multispecie solution of metals are shown separately because the natural soil samples were submitted to both curves in atomic absorption equipment. Analyzing the obtained results for determination of monospecie and multispecie solution to natural soil it is possible to observe differences in sorption values and the values with multispecie solution is lower than with monospecie solution. The difference found for chromium was about 19%. The cadmium metal did not show difference in the different solutions. For nickel and lead the difference was around 4% and 9%, respectively.

In Table 4 are presented the average results of the 3050B extraction method (USEPA, 1996) for samples subjected to leaching with monospecie and multispecie solution with chrome, in three repeats, R_1 , R_2 and R_3 , with the value of natural soil discounted.

Analyzing the results in Table 4 can be observed that there are decreases in sorption values to multispecie solution when compared with results from monospecie solution. When the average results of first layer of both solutions are compared, there is a difference of around 16% and when comparing the results of last layer the difference is around 19%.

Table 4. Experimental results to chromium sorption in monospecie and multispecie solution.

Layer	Sorption* R_1	Sorption* R_2	Sorption* R_3	$\bar{X}$	Standard deviation
Monospecie solution					
1	23.30	56.20	51.30	53.70	3.46
2	12.90	48.00	48.00	48.00	0
3	10.30	43.20	43.20	43.20	0
4	7.67	42.00	41.50	41.70	0.354
5	5.07	30.90	41.50	36.20	7.50
Multispecie solution					
1	18.50	43.60	45.80	44.70	1.53
2	5.30	41.10	45.70	43.40	3.25
3	4.976	30.70	44.00	37.30	9.40
4	3.92	29.70	40.60	35.10	7.75
5	0	22.60	35.90	29.20	9.43

It can be observed in Table 4 that there is a decreasing behavior when the solution moving from one layer to another. This happened in tests with monospecie or multispecie solutions.

Table 5 shows the average results from 3050B extraction method (USEPA, 1996) for samples subjected to leaching on monospecie and multispecie solution with cadmium metal.

Analyzing the results in Table 5 it can be observed that there is an increase on sorption values in tests submitted to multispecie solution when compared with results obtained with monospecie solution. When the results of the first layer of both solutions are compared, the difference is approximately 24% and when comparing the last layer values the difference is around 28%. The results in Table 5 also show decreasing sorption behavior when solution moving from one layer to another in monospecie or multispecie solution.

Table 5. Experimental results to cadmium sorption in monospecie and multispecie solution.

Layer	Sorption* R ₁	Sorption* R ₂	Sorption* R ₃	$\bar{X}$	Standard deviation
Monospecie solution					
1	8.20	8.53	3.76	6.83	2.66
2	4.19	4.19	3.83	4.07	0.21
3	3.13	2.78	4.76	3.56	1.06
4	2.47	2.64	3.00	2.70	0.27
5	2.31	2.16	1.79	2.09	0.27
Multispecie solution					
1	9.18	8.85	14.30*	9.01	0.23
2	4.72	8.13	12.30*	6.42	2.41
3	3.81	3.64	12.20*	3.72	0.12
4	2.78	1.66	12.10*	2.22	0.79
5	1.94	1.06	11.60*	1.50	0.62

The table 6 presents the average results from the 3050B extraction method (USEPA, 1996) for samples subjected to leaching with monospecie and multispecie solution with nickel metal.

Table 6. Experimental result for nickel sorption in monospecie and multispecie solution.

Layer	Sorption* R ₁	Sorption* R ₂	Sorption* R ₃	$\bar{X}$	Standard deviation
Monospecie solution					
1	0*	0*	10.90*	-	-
2	0*	0*	0.64*	-	-
3	0*	0*	0*	-	-
4	0*	0*	0*	-	-
5	0*	0*	0*	-	-
Multispecie solution					
1	0.89*	6.49	6.09	6.29	0.28
2	0*	6.44	4.43	5.43	1.42
3	0*	1.47	1.64	1.55	0.12
4	0*	1.89	1.62	1.75	0.19
5	0*	0	0.09	0.045	0.06

* problems in results were not presented.

The results presented in Table 6 showed decreasing sorption value when the liquid moving from one layer to another. It was not possible to make comparison between monospecie and multispecie sorption results due to problems presented on the tests.

Table 7 shows the average results obtained by the 3050B extraction method (USEPA, 1996) for samples subjected to leaching with monospecie and multispecie solution with lead metal.

Table 7. Experimental results to lead sorption in monospecie and multispecie solution.

Layer	Sorption* R ₁	Sorption* R ₂	Sorption* R ₃	$\bar{X}$	Standard deviation
Monospecie solution					
1	2.40	17.10	2.34*	9.75	10.40
2	7.48	7.58	0*	7.53	0.071
3	6.15	4.83	0*	5.49	0.933
4	2.32	3.75	0*	3.03	1.01
5	0.98	3.74	0*	2.36	1.95
Multispecie solution					
1	4.15	16.90	0*	10.50	8.99
2	1.35	2.07	0*	1.71	0.51
3	2.07	0	0*	1.03	1.46
4	3.25	4.61	0*	3.93	0.96
5	0	2.07	0*	1.03	1.46

* problems in results were not presented.

Most results presented in Table 7 shows decreasing sorption value when the contaminant moving from one layer to another, as happened to the other metals analyzed. Comparing the tests averages values it can be observed an increase in the amount of sorption in the first layer of the multispecie test when compared with results obtained with the monospecie solution. The difference was approximately 7%. Comparing the last layer of both solutions, the result with monospecie solution presents the highest value of sorption, which the difference was approximately 56%.

The results for chromium metal (monospecie and multispecie solutions) have indicated that was the metal with highest sorption over the other metals. This behavior was observed also by Oliveira and Mattiazzo (2001) that attributed the immobility of chromium due its presence in the trivalent form (Cr^{3+}). In this case it could have been precipitated as hydroxides of generics in alkaline or slightly acid and have been complexed with the poorly soluble and organic molecules adsorbed on the surface of minerals.

According to Moreira (2004), the competition between the metals affects the magnitude of sorption of all them. The behavior observed by Moreira (2004) was also observed in almost all tests carried out in this work, except only for cadmium metal, which showed an increase in the sorption. To Moreira (2004), the affinity sequence found in most non-competitive system was $\text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$ and competitive system, the most common sequence was $\text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$. Observing these results, we can compare that to the cadmium and nickel metals had identical behavior in the test carried out. The sequence obtained for the tests submitted to monospecie metal solution could not be compared due to the problems presented by nickel metal.

To Demuelenaere (2004) carried out column test and indicated that as the contaminant is being percolated through the column, the concentration decreases in the first layer. The concentration is higher and the trend is going decreasing until the specimen last layer, which agrees with the results of this work.

Lafuente et al. (2008) have studied some sorption metals in soil. It was observed that Cr and Pb showed higher affinity to the soil than Cd. The same behaviors

were also observed by Xiong et al. (2005) and Zhang and Zheng (2007). This was also observed in the results of this work through the sequence of selectivity obtained for the monospecie test. For the multispecie test, Pb had lower soil sorption than Cd.

Contin et al. (2007), in study about toxic metals, observed that the sequence of metal fixation in soil was: Cu>Cd>Zn>Pb, and have no sorption to Ni. In this work was obtained: Cr>Cd>Pb>Ni.

4 CONCLUSION

According to the proposed objectives, the results found and the conditions under which this work was conducted, some conclusions were obtained:

The higher retention capacity of metals in the soil under study was observed in the tests submitted to monospecie and multispecie solution with chromium metal.

The lowest retention capacity of metals in the tests submitted to monospecie contaminant solution was observed for the cadmium metal and in the multispecies tests by nickel metal.

The chromium and lead metals showed a decrease in their ability to hold in tests submitted to multispecie contaminant solution while the cadmium metal showed retention capacity increased.

The sequence of selectivity shown for the test subject to monospecie contaminant solution was: Cr>Pb>Cd and to multispecie test: Cr>Cd>Pb>Ni.

The sequence of selectivity changed when presented in monospecie and multispecie test, indicating a preference for cadmium retention when it was present in multispecie solution.

5 REFERENCES

- Contin, M.; Mondini, C.; Leita, L.; Nobili, M. 2007. *Enhanced soil toxic metal fixation in iron (hydr)oxides by redox cycles*. Geoderma, v. 140, p. 164-175, 2007.
- Demuelenaere, R.G.A. *Caracterização de propriedades de transporte de metais pesados em solos residuais do Rio de Janeiro*. 2004. Dissertação (Mestrado em Engenharia Civil) - Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brasil.
- Diels, L.; Van Der Lelie, N.; Bastiaens, L. 2002. *New developments in treatment of heavy metal contaminated soils*. Re/Views in Environmental Science & Bio/Technology, v.1, p.75-82.
- Lafuente, A.L.; González, C.; Quintana, J.R.; Vázquez, A.; Romero, A. 2008. *Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region*. Geoderma, v. 145, p.238-244.
- Moreira, C.S. *Adsorção competitiva de cádmio, cobre, níquel e zinco em solos*. 2004. Dissertação (Mestrado em Agronomia) - Universidade de São Paulo, Piracicaba, Brasil.
- Oliveira, F.C.; Mattiazzo, M.E. 2001. *Mobilidade de metais pesados em um latossolo amarelo distrófico tratado com lodo de esgoto e cultivado com cana-de-açúcar*. Scientia Agrícola, v.58, p.807-812.
- Pedrotti, A., Mello Júnior, A.V. 2009. *Avanços em ciência do solo: a física do solo na produção agrícola e qualidade ambiental*, UFS, Aracajú, Brasil.
- Plassard, F., Winiarski, T.; Petit-Ramel, M. *Retention and distribution of three heavy metals in a carbonated soil: comparison between batch and unsaturated column studies*. 2000. Journal of Contaminant Hydrology, v.42, p.99-111.
- Sangui, R.; Sasi, K.S. 2001. *Pesticides and heavy metals in agricultural soil of Kanpur, India*. Bulletin of Environmental Contamination and Toxicology. v.67, p.446-454.
- Teixeira, R.S. *Caracterização e avaliação da contaminação do solo laterítico da área do depósito de resíduos sólidos urbanos de Londrina por metais pesados*. 2008. Tese (Doutorado em Engenharia Civil) - Universidade Federal de Santa Catarina, Florianópolis, 2008.
- Usepa - U.S. ENVIRONMENTAL PROTECTION AGENCY. *Cleaning up the Nation's waste sites: markets and technology trends*. September, 2004.
- Usepa - U.S. ENVIRONMENTAL PROTECTION AGENCY. *Method 3050B: Acid digestion of sediments, sludges, and soils*. December, 1996. Disponível em: <<http://www.epa.gov/SW-846/pdfs/3050b.pdf>>. Acesso em 02. Mar. 2008.
- Xiong, X.; Stagnitti, F.; Turoczy, N.; Allinson, G.; Li, P.; Nieber, J.; Steenhuis, T.S.; Parlange, J.Y.; LeBlanc, M.; Ziogas, A.K.; Ferreira, A.J. D.; Keizer, J.J. *Competitive sorption of metals in water repellent soils: implications for irrigation recycled water*. 2005. Australian Journal of Soil Research, v.43, p.351-356.
- Zhang, M.; Zheng, S. *Competitive Adsorption of Cd, Cu, Hg and Pb by Agricultural Soils of the Changjiang and Zhujiang Deltas in China*. 2007. Journal of Zhejiang University SCIENCE A, v.8, Nov, p.1808-1815.