Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. *77* (1) 119–129 (2012)
JSCS–4254

UDC 504.53.054+546.76:66.061.34:550.4+
550.8.013
Original scientific paper

Leaching of chromium from chromium contaminated soil – a speciation study and geochemical modelling

DARKO H. ANDJELKOVIĆ[1]*, TATJANA D. ANDJELKOVIĆ[2#], RUŽICA S. NIKOLIĆ[2], MILOVAN M. PURENOVIĆ[2], SRDJAN D. BLAGOJEVIĆ[3#], ALEKSANDAR LJ. BOJIĆ[2#] and MILICA M. RISTIĆ[1]

[1]*Water Works Association "Naissus", Kneginje Ljubice 1/I, 18000 Niš, Serbia,* [2]*Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia and* [3]*Faculty of Agriculture, University of Belgrade, Nemanjina 16, 11081 Belgrade, Serbia*

(Received 16 December 2010, revised 20 February 2011)

Abstract: The distribution of chromium between soil and leachate was monitored. The natural process of percolation of rainwater through soil was simulated under laboratory conditions and studied by column leaching extraction. Migration of chromium in soil is conditioned by the level of chromium soil contamination, the organic matter content in the soil and rainwater acidity. Chromium(III) and chromium(VI) were determined by a spectrophotometric method with diphenylcarbazide in acidic media. Comparing the results of chromium speciation in the leachate obtained by experimental model systems and geochemical modelling calculations using the Visual MINTEQ model, a correlation was observed regarding the influence of the tested parameters. Leachate solutions showed that the concentration of Cr depended on the organic matter content. The influences of pH and soil organic matter content were in compliance after their experimental and theoretical definition. The Stockholm humic model used to evaluate the leaching results corresponded rather well with the measured values.

Keywords: chromium; speciation; leaching; rainwater; soil organic content.

INTRODUCTION

Speciation analysis is a measurement process giving quantitative and qualitative data about the chemical forms of an element in a sample. It usually involves two phases: separation of the target element from the sample matrix and its determination. Differentiation of the forms of the element is realized between oxidation states, simple and coordinated ions, cationic, neutral and anionic forms, protonated and unprotonated, and monomeric and polymeric species.[1]

---

* Corresponding author. E-mail: darko.andjel@gmail.com

[#] Serbian Chemical Society member.

doi: 10.2298/JSC101216154A

Chromium speciation is important due to its wide usage in the metallurgic and chemical industries. Improper disposal, poor storage and leakage of chromium from waste discharge through soil can release chromium to the environment, causing contamination of groundwater and adverse biological and ecological effects.[2] Cr(VI) is a strong oxidizing agent and shows chronic toxic effects including carcinogenic property and it induces dermatitis. Occupational exposure to Cr(VI) compounds leads to a variety of clinical problems. A significant concentration of Cr(III) can cause adverse effects because its strong capability to coordinate various organic compounds results in inhibition of some metallo–enzyme systems.[3,4]

Chromium is present in the environment in the form of Cr(III) and Cr(VI). These two forms show different chemical, physico-chemical and biochemical properties. Cr(VI) species are more soluble, mobile and bioavailable than Cr(III) species. The presence of these two forms and their relative ratio is dependent on chemical and photochemical redox transformation, precipitation/dissolution and adsorption/desorption reactions.[5] Due of these differences in chemistry, biochemistry and physico–chemistry of Cr(III) and Cr(VI) species, the determination of the total Cr concentration in a variety of samples does not give the necessary information to evaluate the effects of the different species. The potential risk of chromium from soils is determined by its solid–solution partitioning rather than its content. The release of chromium to the aqueous phase depends on its affinity to bind to reactive surfaces in the soil matrix. Quantifying adsorption/desorption and precipitation/dissolution reactions is a critical aspect of predicting the chemical behaviour of chromium in soil. Many factors can influence the migration process, such as pH, dissolved and solid organic matter and soil characteristics,[6,7] *e.g.*, cation exchange capacity, clay content, and competition from other metal ions. In addition, the presence of soluble natural organic ligands in soil, such as fulvic acid (FA), may significantly influence metal adsorption through the formation of stable complexes.

The objectives of this investigation were to study the distribution of chromium between soil and soil leachate. The natural percolation of rainwater through the soil was simulated under laboratory conditions and studied by column leaching extraction. Migration of chromium in the soil is conditioned by the level of chromium soil contamination, the organic matter content of the soil and the acidity of rainwater.

Comparing the results of speciation of chromium in soil and infiltration water obtained by experimental model systems and geochemical modelling calculations using the Visual MINTEQ model, a correlation was observed regarding the influence of the tested parameters.

Visual MINTEQ includes three different models for calculating cation binding to humics: *i*) the Gaussian dissolved organic matter (DOM) model,[8] *ii*) the

Stockholm humic model (SHM),[9] which can be used for both aqueous speciation and solid–solution partitioning, and *iii*) the non-ideal competitive adsorption-Donnan (NICA-Donnan) model,[10] which is available only for aqueous speciation. Each of these models show considerable complexity caused by the extreme heterogeneity of the humic binding sites, the variable stoichiometry of metal–humic binding reactions and the presence of electrostatic interactions.

This study focused on the Stockholm humic model (SHM),[9] which was created to provide a more realistic assessment of metal–humic complexation than had been possible using the Gaussian DOM model in MINTEQ. The SHM is related to more mechanistic models and the NICA-Donnan model, although it is also different in some respects, *i.e.*, in the electrostatic model.

EXPERIMENTAL

Soil sampling, properties and soil column set up

Two soil types were used in this study: *i*) grass-covered and well-drained urban green-field soil and *ii*) organic substrate for horticultural container growing. A 10-cm depth of park soil (situated within the city centre of Niš, Serbia) was collected immediately beneath the upper zone, in which plant remains were dominant. The soils were air dried and passed through a 60 mesh sieve. Selected physico-chemical soil properties, *i.e*., pH, electrical conductivity (EC) and organic matter content, are given in Table I. The electric conductivity and pH were measured in water suspensions. The soil content of organic matter was determined on finely ground samples by the wet combustion method based on bichromate reduction.[11]

TABLE I. Characteristics of the employed soil and rainwater

Characteristic	Urban soil	Organic substrate	Rainwater	Acid rainwater
pH	8.6	8.3	5.7	3.2
Electrical conductivity, μS cm^{-1}	113.0	677.0	26.7	270.0
Organic matter, %	1.76	15.77	–	–

Glass columns, 20 cm in length with an internal diameter of 2 cm were used in this study. The bottom of each column contained a porous glass frit. Soil (30 g) was carefully packed with gently tapping on the sides of the column to ensure good contact between the materials without making air compartments.

Chromium leaching and determination

Four different treatments were included in the study. In all treatments, artificial rainwater was added to the columns. The chemical composition of the artificial rainwater was similar to that of average rainwater in urban areas (SO_4 – S 0.8 mg L^{-1}, Cl 0.5 mg L^{-1}, NO_3 – N 0.4 mg L^{-1}, NH_4 – N 0.3 mg L^{-1}, Na 0.2 mg L^{-1}, K 0.03 mg L^{-1}, Mg 0.03 mg L^{-1}, pH 5.0). The acid rainwater was obtained by acidification of rainwater with H_2SO_4 to pH 3.5. Before starting the leaching, de-ionized water was added to the columns to bring the soil to field water capacity. 40 mL of inflow solution was added slowly (2 h) as droplets to the top of the columns. The total volume of rainwater corresponded to 734 mm, the average total annual precipitation in the region of Serbia. The pH value and EC of the rainwaters are given in Table I.

The urban soil and organic substrates were polluted with potassium dichromate. Considering the fact that the average chromium content of urban soil is 40–80 mg Cr kg^{-1} soil,[12] the applied Cr amount was 2.4 mg Cr per 30 g of soil.

Leaching was monitored after treatment of soil and organic substrate (polluted and unpolluted) with rainwater and acid rainwater. All treatments were conducted in triplicate for both soils and both rainwater types in 3 columns.

The leachate was collected in 10 mL portions. After centrifugation of the leachate portions, the pH, EC and chromium contents were determined. pH and EC were determined using HACH SensIon 3 pH-meter and HACH SensIon 5 conductometer. The most common method for determining Cr(VI) in aqueous solutions is based on the reaction of diphenylcarbazide with Cr(VI) at a pH of 1.0±0.3. As stated by many researchers, diphenylcarbazide has a very sensitive colour reaction with Cr(VI) in acid solution.[13-15] Chromium(III) was analyzed spectrophotometrically with diphenylcarbazide after oxidation with persulphate using a Lovibond multidirect colorimeter.

Modelling of chromium solubility

Equilibrium modelling of the metal concentrations in the leachates was performed using the Stockholm humic model (SHM). The parameterisation of the model uses the total concentrations of each component and the stability constants of species formed at equilibrium to set up a series of simultaneous mole balance and mass law equations, which are solved to give the equilibrium concentration of each species. The SHM was implemented in Visual MINTEQ, ver. 3.0 (www.lwr. kth.se/english/ourSoftware/Vminteq/index.htm).[9,16,17]

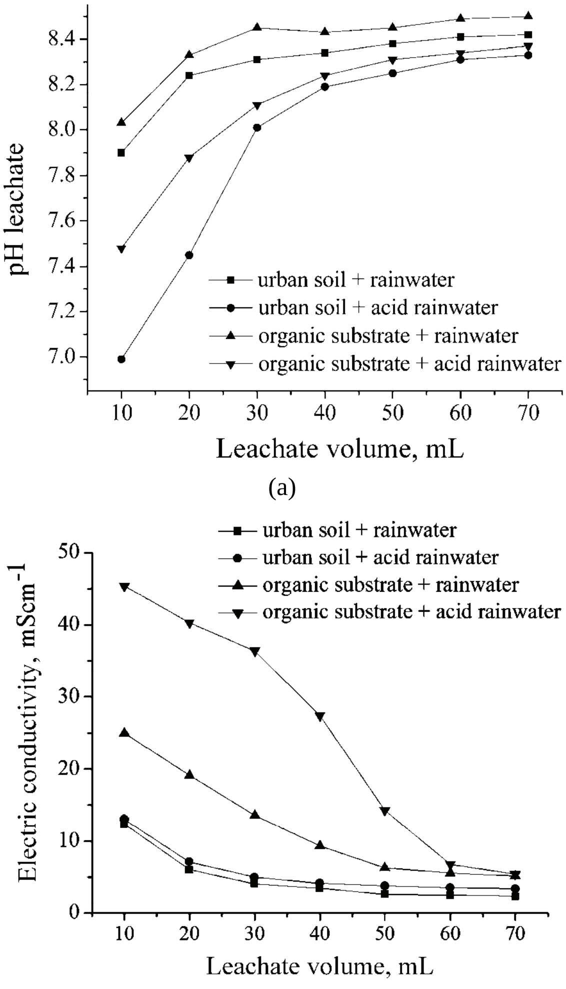
RESULTS AND DISCUSSION

There are several soil characteristics, such as soil pH, electrical conductivity and organic matter content, which are important for defining processes in soil. The urban soil used in the present study was a highly alkaline soil[18] and, due to the organic matter content (1.76 %), is considered as a soil with a low organic matter content[19] (Table I). The organic substrate for horticultural container growing had a similar pH value but with a characteristically high organic matter content (15.77 %).

During leaching with rainwater and acid rainwater, there was a significant change in pH and EC of the leachate at the start of the treatment, while subsequently all the values converged to a similar pH and EC level (Fig. 1).

In the first 70 mL of the leachate, the amount chromium leached was less than 2 % of the total chromium added to the soil for the treatments with polluted soil (PS) and polluted organic substrate (POS) (Table II). The obtained results for PS indicate that more chromium was leached with acid rainwater (2.01 %) than with rainwater (1.44 %). Acid rainwater, which frequently precipitates in urban areas, can control chromium accumulation in the soil profile, enhance the downward movement of chromium to the groundwater and the bioavailability for plant uptake.

However, in the case of soil rich in organic matter (POS), the acidity of the rainwater decreased the amount of leached chromium. Only 0.29 % of the total chromium applied to the soil is leached by acid rainwater. This decrease is probably due to the retention of some of the chromium by the soil in the form of insoluble $Cr(OH)_3$, which is adsorbed on the surface of the soil.[12] The insoluble $Cr(OH)_3$ was formed by the reduction of Cr(VI) that was enhanced by the high content of organic matter and the increased acidity of system.[12] This was confirmed by the fact that only a minor quantity of chromium was detected in the leachate and that only Cr(VI) species were detected in the leachate. On the other hand, in the case of low acidity, more chromium was leached (0.63 %) than with acid rainwater, because in the acidic pH range, chromium appears only as soluble Cr(III) species, generated by reduction of Cr(VI). This was also confirmed by the fact that only Cr(III) species were detected in the leachate.



(a)

(b)

Fig. 1. a) pH and b) electrical conductivity of the leachate during the leaching of polluted soil and organic substrate.

TABLE II. Ratio of leached chromium to total added Cr in the soil column (%)

Sample	Rainwater	Acid rainwater
Polluted soil (PS)	1.44	2.01
Polluted organic substrate (POS)	0.63	0.29

Humic substances (HS), that mostly comprise soil organic matter, are very important components that control the adsorption of heavy metals by soil. Humic substances are heterogeneous in nature and are considered as polydisperse mixtures of natural organic polyelectrolytes containing a large number of different functional groups. The ability of HS to form stable complexes with polyvalent cations is attributed to their high content of oxygen-containing functional groups, including carboxyl, phenol, hydroxyl, enol and carbonyl structures of various types.[20,21]

If this highly complex natural ligand strongly complexes with Cr in solution, the presence of this ligand in the soluble form has the potential to reduce sorption to soil and increase leaching. The results presented in Table II shows that the humic ligand mixture in POS sorbed to the soil and increased the amount of ternary soil–ligand–chromium complexes, facilitating the chromium retention in soil column, and leading to decreased mobility.[22–25] Thus, in the treatment set with POS and acid rainwater, the decrease of chromium in leachate was 10 times more compared to the soil with the low organic matter content – PS (0.29 comparing to 2.01 %). This confirms the influence of organic matter on the retention of chromium by soil.

The speciation diagram of Cr(III) as a function of pH, calculated by the speciation software MINTEQ, is shown in Fig. 2a. The dominant species of Cr(III) for pH < 4.5 are $Cr^{3+}_{(aq)}$ and $Cr(OH)^{2+}$. For pH > 4.5, mainly insoluble $Cr(OH)_3$ is formed. Soluble polyhydroxyl species, such as $Cr(OH)_4^{-}$, $Cr_2(OH)_2^{4+}$, $Cr_3O_4(OH)_4^{3-}$, $Cr_4(OH)_4^{5+}$, $Cr_2O_2(OH)_4^{2-}$ and others, appear at highly alkaline values.[26,27]

The speciation diagram of Cr(III) *vs*. pH in the presence of soil organic matter, as defined by the Stockholm humic model (SHM), is presented in Fig. 2b. The SHM was created to provide a more realistic assessment of metal–humic complexation than the Gaussian dissolved organic matter model in MINTEQ. The SHM allows metals binding to humic to be described either as monodentate or as bidentate ligand. As humic substances may occur both in the dissolved and solid phases, cation binding was considered both for dissolved and solid-phase humic substances. This model is based on the following: dissolved fulvic acid ($FA_{(aq)}$) and its value of 0.048 g L^{-1} represents the concentration of 'active' dissolved organic matter in the system. The humic substances in the solid phase are assumed to be a mixture of humic and fulvic acid and the relative proportions of these were set to $FA_{(s)}$ 0.845 g L^{-1} and $HA_{(s)}$ 1.457 g L^{-1}. To accelerate the cal-

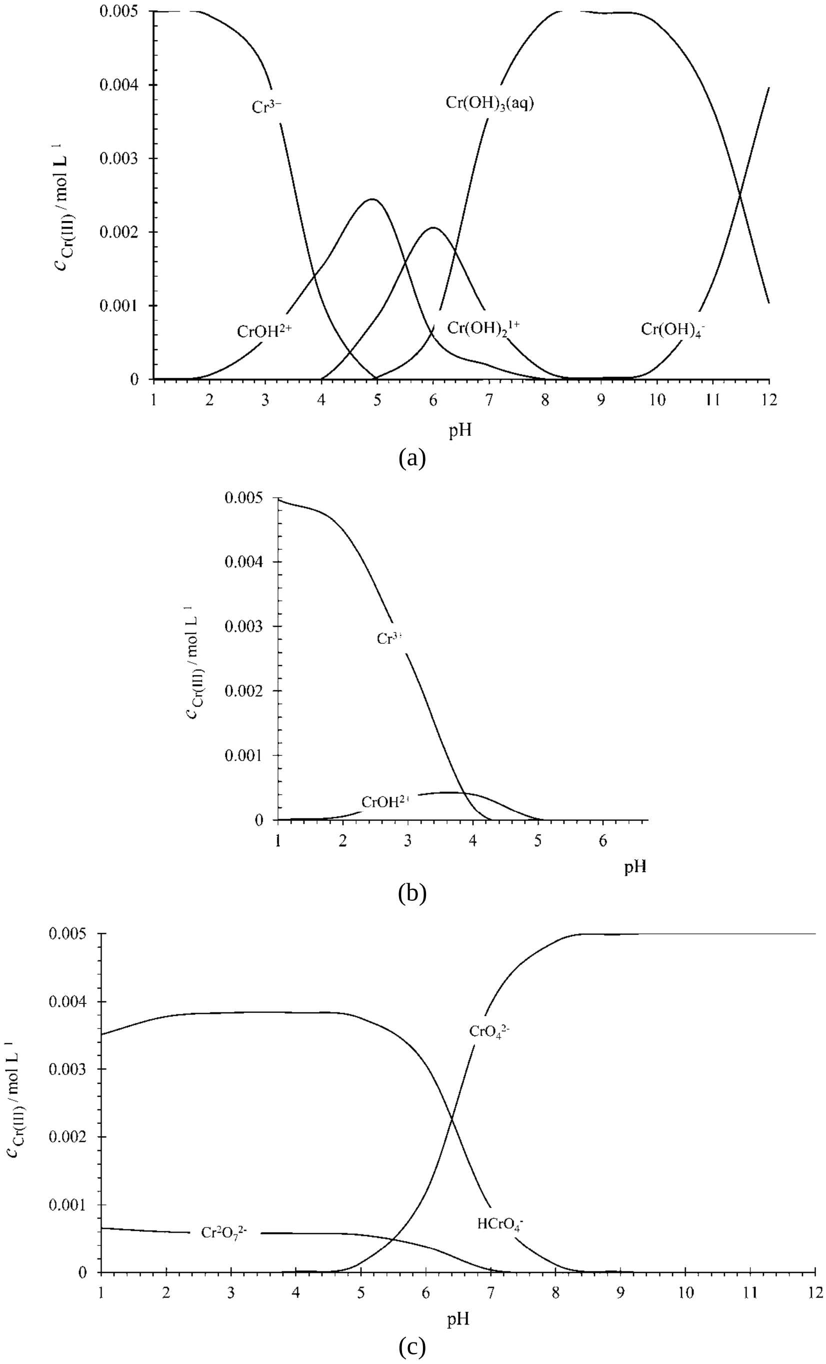
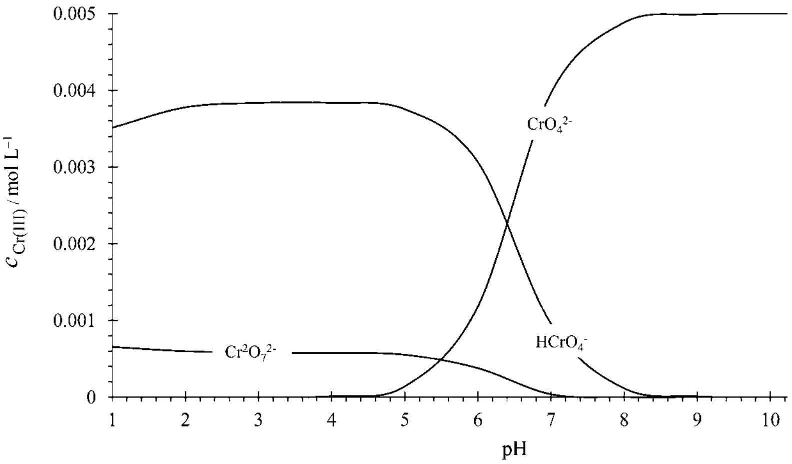


Fig. 2. Concentration of chromium species (mol L^{-1}) at different pH values, calculated by Visual MINTEQ in the presence of a) Cr(III), b) Cr(III) and organic matter and c) Cr(VI).



(d)

Fig. 2. (Continued) Concentration of chromium species (mol L^{-1}) at different pH values, calculated by Visual MINTEQ in the presence of d) Cr(VI) and organic matter.

culations, solid-phase HA (humic acid) and solid-phase FA are normally bulked together as one component. Using such a defined humic model, the equilibrium chemistry of a soil suspension with 2.5 g L^{-1} of active humic substances, of which 62 % is HA and 38 % FA, was simulated. 48 mg L^{-1} FA was dissolved (equivalent to 24 mg L^{-1} dissolved organic carbon (DOC) if the entire DOC is assumed to be FA). The soil was suspended with SO_4 – S 0.8 mg L^{-1}, Cl 0.5 mg L^{-1}, NO_3^- – N 0.4 mg L^{-1}, NH_4 – N 0.3 mg L^{-1}, Na 0.2 mg L^{-1}, K 0.03 mg L^{-1} and Mg 0.03 mg L^{-1}. In this problem, the total concentrations of K, Mg and Na constitute the sum of the dissolved + complexed ions. The equilibrium constants of the chromium species and the model parameters for soil FA and soil HA defined in Visual MINTEQ are given in Table III.

TABLE III. Model parameters and equilibrium constants defined in Visual MINTEQ for the system Cr(III), Cr(VI) and soil organic matter

Sample	Proton dissociating groups (mmol g^{-1})	Site density (sites nm^{-2})	ΔpK_A (strong acid groups)	ΔpK_B (weak acid groups)
Soil FA	7.02	1.2	3.48	2.49
Soil HA	5.33	1.2	3.03	3.03
Equilibrium constants				
$Cr(OH)_2^+ + 2H^+ \leftrightarrow Cr^{3+} + H_2O$			log K = 9.84	
$2Cr(OH)_2^+ + 2H^+ \leftrightarrow Cr_2(OH)_2^{4+} + 2H_2O$			log K = 14.68	
$3Cr(OH)_2^+ + 2H^+ \leftrightarrow Cr_3(OH)_4^{5+} + 2H_2O$			log K = 18.77	

TABLE III. Continued

Equilibrium constants	
$CrO_4^{2-} + 2H^+ \leftrightarrow H_2CrO_4$	log K = 6.31
$CrO_4^- + H^+ \leftrightarrow HCrO_4^-$	log K = 6.51
$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$	log K = 14.56
$Cr(OH)_2^+ + H^+ \leftrightarrow CrOH^{2+} + H_2O$	log K = 6.27

The distribution of chromium between dissolved, sorbed and precipitated phases for Cr(III) and organic matter and Cr(VI) and organic matter, calculated by Visual MINTEQ, are presented in Table IV. Under the leaching conditions, 99 % of Cr(III) is sorbed (Table IV), which confirms the experimentally observed trend. Chromium(III) was not detected in the leachate of the organic substrate when acid rainwater was used, due to its sorption on organic matter (Fig. 2b).

TABLE IV. Equilibrium mass distribution of chromium between dissolved, sorbed and precipitated phases calculated by Visual MINTEQ for systems: Cr(III) and organic matter and Cr(VI) and organic matter

Sample	Dominant species	Dissolved, %	Sorbed, %	Precipitated, %
Cr(III) + organic matter	$Cr(OH)_2^{1+}$	0.966	99.034	0.0
Cr(VI) + organic matter	CrO_4^{2-}	100	0	0.0

The chromium speciation when the soil has a low organic matter content is shown in Fig. 2c. The dominate chromium(VI) ionic species are $HCrO_4^-$ and $Cr_2O_7^{2-}$ for pH < 6.5. On increasing the pH, the concentration of $HCrO_4^-$ decreases rapidly and at pH 8 approaches zero. For pH > 6.5, CrO_4^{2-} is preferably observed. Under highly alkaline conditions, Cr(VI) exists only in the form of CrO_4^{2-}.

It is apparent comparing to Fig 2d that the presence of organic matter does not affect the Cr(VI) concentration in infiltration water. Leaching of soil with high or low organic matter content, the concentration of Cr(VI), in the form of $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}, is the same. This is probably due to the fact that no interaction occurs between the negatively charged ionic species and the negatively charged active functional groups of the organic matter, which leads to leaching of chromium and its migration to the groundwater. The results in Table IV show also that no chromium is sorbed or precipitated, leading to its total dissolution and possible downward movement to the groundwater or plant uptake.

CONCLUSIONS

This study demonstrated that the extent of chromium transport in soil columns depends on the mobility of the organic matter–metal complexes and that this mobility is governed by a variety of factors: the extent of soil pollution by chromium, the chromium valence state, soil organic matter content and acidity of the rainwater.

Chromium leaching was monitored for urban soil and an organic substrate for horticultural container growing with and without chromium pollution by treating with rainwater. The leachate solutions from all treatments showed that the concentration of Cr was strongly influenced by the organic matter content. This is explained by the increased metal sorption onto the organic matter of soil. Increasing the rain acidity resulted in the presence of not only Cr(VI), but also Cr(III) in the leachate. Considering that the soil was artificially polluted with chromium(VI) by addition of $K_2Cr_2O_7^{2-}$ to the soil, the Cr(VI) was reduced to Cr(III) only when the acidity of the rain was increased, because dichromate reduction by electron donor soil components, such as soil organic matter (humic substances), is realised with the consumption of H^+.

The experimentally and theoretically determined influences of pH and soil organic matter content are in agreement. The Stockholm humic model was used to evaluate the leaching results, and the obtained theoretical values corresponded rather well with the measured ones

ИЗВОД

ИЗЛУЖИВАЊЕ ХРОМА ИЗ ХРОМОМ ЗАГАЂЕНОГ ЗЕМЉИШТА – СПЕЦИЈАЦИОНА АНАЛИЗА И ГЕОХЕМИЈСКО МОДЕЛОВАЊЕ

ДАРКО Х. АНЂЕЛКОВИЋ[1], ТАТЈАНА Д. АНДЈЕЛКОВИЋ[2], РУЖИЦА С. НИКОЛИЋ[2], МИЛОВАН М. ПУРЕНОВИЋ[2], СРДЈАН Д. БЛАГОЈЕВИЋ[3], АЛЕКСАНДАР Љ. БОЈИЋ[2] и МИЛИЦА М. РИСТИЋ[1]

[1]*ЈКП „Naissus“, Кнегиње Љубице 1/I, 18000 Ниш,* [2]*Природно–математички факултет, Универзитет у Нишу,Вишеградска 33, 18000 Ниш и* [3]*Пољопривредни факултет, Универзитет у Београду, Немањина 16, 11081 Београд*

У раду је праћена дистрибуција хрома између земљишта и инфилтрационих вода. Природни процес перколирања кишнице кроз земљиште је симулиран у лабораторијским условима помоћу екстракције и излуживања у колони. Миграција хрома у земљишту је праћена у зависности од нивоа загађења земљишта хромом, садржаја органске материје земљишта и киселости кишнице. Хром(III) и хром(VI) су одређени спектрофотометријски помоћу дифенилкарбазида у киселој средини. Специјација хрома у инфилтрационим водама добијена експерименталним модел системом је у сагласности са специјацијом добијеном прорачуном геохемијским моделом Visual MINTEQ. Концентрација хрома у инфилтрационим растворима показује значајну зависност од садржаја органске материје земљишта. Компјутерски геохемијски модел – Stockholm хумински модел, који је коришћен за евалуацију експерименталних резултата може се применити у специјацији хрома у урбаном земљишту и органском супстрату, који су испитивани у раду.

(Примљено 16. децембра 2010, ревидирано 20. фебруара 2011)

REFERENCES

1. L. Campanella, in: *Element Speciation in Bioinorganic Chemistry*, S. Caroli, Ed., Wiley Interscience, New York, 1996, p. 419
2. J. Kotas, Z. Stasicka, *Environ. Pollut.* **107** (2000) 263
3. K. P. Lee, C. E. Ulrich, R. G. Geil, H. J. Trochimowicz, *Sci. Tot. Environ.* **86** (1989) 83
4. J. M. Pacyna, J. O. Nriagu, in *Chromium in Natural and Human Environments*, J. O. Nriagu, E. Nieboer, Eds., Wiley Interscience, New York, 1988, p. 105
5. D. C. Adriano, *Trace Elements in the Terrestrial Environment*, Springer, New York, 1986
6. L. X. Zhou, J. W. C. Wong, *J. Environ. Qual.* **30** (2001) 878
7. A. V. Zomeren, R. N. Comans, *Environ. Sci. Technol.* **38** (2004) 3927
8. E. M. Perdue, J. H. Reuter, R. S. Paerish, *Geochim. Cosmochim. Acta* **48** (1984) 1257
9. J. P. Gustafsson, *J. Colloid Interface Sci.* **244** (2001) 102
10. D. G. Kinniburgh, W. H. van Riemsdijk, L. K. Koopal, M. Borkovec, M. H. Benedetti, M. J. Avena, *Colloids Surf., A* **151** (1999) 147.
11. A. Walkley, L. A. Black, *Soil Sci.* **37** (1934) 29
12. M. Linde, *Trace Metals in Urban Soils – Stockholm as a Case Study*, PhD thesis, Swedish University of Agricultural Sciences, Uppsala, 2005
13. A. Tunceli, A. R. Turker, *Talanta*. **57** (2002) 1199
14. V. Gomez, M. P. Callao, *Trends Anal. Chem.* **25** (2006) 10
15. J. E. T. Andersen, *Anal. Chim. Acta* **361** (1998) 125
16. J. P. Gustafsson, J. W. J. van Schaik, *Eur. J. Soil Sci.* **54** (2003) 295
17. J. P. Gustafsson, D. B. Kleja, *Environ. Sci. Technol.* **39** (2005) 5372
18. M. Jakovljević, M. Pantović, *Chemistry of Solis and Waters*, Naučna knjiga, Beograd, 1991, p. 27 (in Serbian)
19. M. M. Kononova, *Soil Organic Matter*, 2nd ed., Pergamon Press, Oxford, 1966
20. T. Andjelkovic, R. Nikolic, A. Bojic, D. Andjelkovic, G. Nikolic, *Maced. J. Chem. Chem. Eng.* **29** (2010) 215
21. T. Andjelkovic, J. Perovic, M. Purenovic, S. Blagojevic, R. Nikolic, D. Andjelkovic, A. Bojic, *Anal. Sci.* **22** (2006) 1553
22. M. D. Jakovljević, N. M. Kostić, D. Stevanović, S. Blagojević, M. J. Wilson, Lj. Martinović, *Appl. Geochem.* **12** (1997) 637
23. B. R. James, R. J. Bartlett, *J. Environ. Qual.* **12** (1983) 173
24. B. R. James, R. J. Bartlett, *J. Environ. Qual.* **12** (1983) 177
25. B. R. James, R. J. Bartlett, in: *Chromium in Natural and Human Environments*, J. O. Nriagu, E. Nieboer, Eds., Wiley Interscience, New York, 1988, 265
26. A. R. Walsh, J. O'Halloran, *Water Res.* **30** (1996) 2393
27. F. C. Richard, A. C. M. Bourg, *Water Res.* **25** (1991) 807.