The effect of iron and manganese oxyhydroxide soil fraction on the occurence of Cr(VI)

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The objective of the present paper was to study the effect of soil natural oxidants (Fe/Mn oxides) on the occurrence of Cr(VI) in soil in order to better understand and predict the fate, mobility and toxicity of chromium in the environment. Thirty five surface soil samples were examined for Cr(VI) content in their aqueous and alkaline leachates. The reducible iron and manganese oxides in soils, that could promote the oxidation of Cr(III), were extracted using acidified hydroxylamine hydrochloride solution (BCR procedure). Liquid phase extraction was used for redox speciation of Cr. The results obtained indicated that the Cr(III) oxidation in soils occurs *via* interactions with iron and manganese oxides. Cr(VI) was the predominant form in aqueous leachates (44–145 μ g kg⁻¹ Cr). For the main part of the samples the dissolved alkaline Cr(VI) presented 80 – 89 % of the total soil chromium dissolved in 0.1 mol l⁻¹ NaOH.

Key words: Chromium (VI), Soils, Reducible soil fraction, Chemometrics

INTRODUCTION

Chromium is a common trace element in rocks and soils, found as amorphous Cr(III) hydroxides, eskeolaite (Cr_2O_3) and chromite [FeCr(III)₂O₄], all Cr(III) forms [1, 2]. They exhibit very low solubility and of the mobile, toxic and carcinogenic Cr(VI) species in the environment is typically associated with anthropogenic activities [3-7]. But a significant number of studies in the scientific literature have reported geogenic origin of hexavalent chromium in soil and groundwater. The natural oxidation of Cr(III) to Cr(VI) proceeds in the presence of Mn(III/IV) hydroxides or oxides and bacteria [8-12]. Oxides and oxyhydroxides of iron and manganese constitute an appreciable fraction of the soils. Under common environmental conditions Mn-oxides are considered to be the only environmentally relevant Cr(III) oxidant [13, 14]. Manganese oxides and hydroxides can oxidize Cr(III) in soils transforming it to more mobile Cr(VI) species [12, 15–17].

The importance of the high surface reactivity and redox chemistry of Fe oxides/oxyhydroxides (Fe-oxide) [18] was evaluated in terms of i) development of Fe amendment technologies during treatment of polluted soils and sediments [19–21] and ii) sorption of the reduced form of Cr on the Fe-oxide as a sorbent [22, 23]. To the best of our knowledge, the potential oxidative reactivity of Fe oxides to generate Cr(VI) in soils is not studied yet. How the presence of both oxides (Fe/Mn oxides) in soils would affect the actual potential of chromium(VI) release in soils is not known. In order to better understand and predict the fate, mobility and toxicity of chromium in the environment, it is important to elucidate the oxidation potential of the soil fraction containing Fe/Mn oxides.

The purpose of the present paper was to study the effect of soil natural oxidants on the occurrence of Cr(VI) in soil. The soil oxidation capacity was investigated using the soil extract obtained in the second step (leaching of reducible Fe/Mn-oxides with acidified hydroxylamine hydrochloride solution) of the modified BCR fourstep sequential extraction procedure [24, 25]. The following experiments were performed: i) extraction and separation of the Fe/Mn-oxide fraction in soils and determination of Fe and Mn content; ii) determination of chromium in aqueous and alkaline soil extracts as total chromium [Cr(III) Cr(VI)] and Cr(VI); iii) chemometrical +interpretation of the data.

EXPERIMENTAL

Samples, reagents and instrumentation

Thirty five soil samples were collected in the surroundings of a former steel mill Kremikovtsi located about 20 km northeast of the Bulgarian capital, Sofia. The sampling was performed on grassland from soils not treated by fertilizers. Soil types were Luvisols (Chromic) and Fluvisols (Arenic). The samples were collected from the top soil layer (0–10 cm) according to ISO 10381-2002. The samples were air-dried, then gently crushed, cleaned from extraneous material, sieved to < 2 mm and stored at 4 °C. The examined soils had a pH in the range of 6.8–7.1, equivalent calcium carbonate content was between 0.1 and 22%, total organic matter (TOM) – from 5 to 11 %.

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All reagents used were of analytical reagent grade (Merck). High-purity water (Milli-Q 50, Millipore) was used throughout. For Cr(III), Fe(III) and Mn(II) ready for use standard solutions for AAS (Merck) were used for preparation of calibration solutions. The stock standard solution with concentration of 1 g l⁻¹ Cr(VI) was prepared from (NH₄)₂CrO₄ delivered from Sigma-Aldrich.

The applied instrumentation was: inductively coupled plasma optical emission spectrometer (Perkin Elmer ICP-OES 6000, MiraMist nebulizer) for measurement of *aqua regia* soluble content of Cr, Fe and Mn in soils; flame (Perkin Elmer, Aanalyst 400) and electrothermal atomic absorption spectrometer (ETAAS) (Perkin Elmer Zeeman 3030, HGA-600) for determination of elements (Cr, Fe, Mn) in the extracts.

Extraction procedures

The procedure for extraction and determination of Cr(VI) in soils is described in our previous work [26]. In brief, one gram of soil sample was shaken with 20 ml of Milli-Q water or 20 ml of 0.1 mol 1⁻¹ NaOH for 2 h at 150 rpm. After centrifugation the samples were filtered through 0.45 µm syringe filter for determination of total dissolved chromium [Cr(III)+Cr(VI)]. Then an appropriate volume (from 1.0 to 5.0 ml) of the filtrate was placed into an extraction tube. After dilution to 10 ml with Milli-Q water, 2.0 ml of 2% solution of Aliquat 336 in xylene was added and the extraction was performed by up and down shaking for 8 min. In the organic phase Cr(VI) was determined by ETAAS. The certified reference material CRM041-30G Chromium VI-Soil (Fluka, Sigma-Aldrich) was used for proving the reliability of the procedure.

of iron and The content manganese oxides/oxyhydroxides in soils was evaluated using the leachate from the second step of the BCR threestep sequential extraction procedure [24] which represents the reducible (Fe/Mn associated with Fe/Mn oxyhydroxides) soil fraction. The soil residue obtained after the first procedural step was treated with a mixture of 0.5 mol 1⁻¹ NH₂OH.HCl and 0.05 mol 1⁻¹ HNO₃. The reduction of insoluble Fe(III)/Mn(IV) oxyhydroxides leads to formation of Mn(II) soluble and Fe(II) species. The concentration of the dissolved Fe and Mn corresponds to the reducible Fe/Mn oxyhydroxide content in the soil. The accuracy of the procedure was controlled with CRM BCR-701.

Aqua regia soil extracts (ISO 11466) were used for determination of total element contents. With each run two CRMs (Stream Sediments STSD-1 and STSD-3) were analyzed in parallel. In all cases recoveries in the range of 94–105 % were classified as satisfactory.

Chemometric methods

Cluster analysis is a widely used chemometric approach. In order to cluster objects characterized by a set of variables, one has to determine their similarity. A preliminary step of data scaling is necessary (e.g., autoscaling or z — transform) to avoid dimension impact on the clustering. Then, the similarity between the objects in the variable space can be determined using, for instance, the Euclidean distance or squared Euclidean distance. Typical method for linkage of similar objects into clusters is the Ward's method offering a very stable procedure of clustering. The graphical presentation of the results of the clustering is normally a treelike hierarchical scheme called dendrogram. The cluster significance is determined by the Sneath's index.

Principal components analysis (PCA) is a multivariate method, which allows estimating the data structure. PCA uses the formation of linear combination of the original columns in the data matrix - responsible for the description of the input variables. These linear combinations represent a type of abstract variables being better descriptors of the data structure than the original variables. Usually, the new abstract variables are called latent factors. Just a few of the latent variables account for a large part of the data set variation. Thus, the data structure in a reduced variable space can be observed and interpreted. The initial PCs represent the direction in the data, containing the largest variation. The projections of the data on the plane of PC 1 and PC 2 can be computed and shown as a plot (score plot) where similarity groups could be distinguished. It is important to note that PCA very often requires scaling of the input raw data to eliminate dependence on the scale of the original values. For better representation of the results a mode called Varimax rotation is applied.

All multivariate statistical calculations were performed by STATISTICA (data analysis software system), StatSoft, Inc. (2007) version 8.0. www.statsoft.com.

RESULTS AND DISCUSSION

Iron and manganese species in soils. The *aqua regia* soluble content of iron and manganese in soils (Table 1) varied remarkably between the 35 samples. The concentration of iron ranged from 22 to 301 g kg⁻¹ Fe, and that of manganese from 1.2 to 14.7 g kg⁻¹ Mn. The variation in metal concentrations could be assigned to geogenic, as well as to anthropogenic origin. The results for the reducible part of Fe and Mn are presented in Table Ts. Voyslavov et al.: The effect of iron and manganese oxyhydroxide soil fraction on the occurence of Cr(VI)

1. The reducible part of Fe presents 0.28–10.4 % of the total Fe. The reducible Mn species were found to be in the range 31–74.4 % of the *aqua regia* soluble soil manganese*Chromium species in the soils*. The ranges of chromium species content in soils are shown in Table 2. The total soil chromium was less than the permissible level of Cr in agricultural (200 mg kg-1 Cr) and urban (250 mg kg-1 Cr) soils according to the national regulatory standard [27]. The studied soil samples could be considered as not contaminated with Cr.

The aqueous and the alkaline leachates were analyzed for both total Cr and Cr(VI). The difference between the two values approximates the amount of soluble Cr(III) present in a given sample. The results show that only a negligible part of total soil Cr can be dissolved in water or sodium hydroxide. As expected, the aqueous soluble Cr was mainly in the form of Cr(VI) species. Cr(VI) in the soil usually exists in the form of HCrO₄⁻ and CrO_4^{2-} depending on pH of the surrounding aqueous environment. At a pH above 7, most of the Cr(VI) exists in the form of CrO_4^{2-} , whereas at lower pH, Cr(VI) tends to be in the form of $HCrO_4^{-}$ [7]. The less negatively charged anions are stronger adsorbed on the soil surface, because the surface of the most natural soils is negatively charged. Thus, CrO_4^{2-} is weaker adsorbed on the soil compared to $HCrO_4^{-}$ [28].

The presence of Cr(III) in the aqueous extracts could be explained with probable desorption of $Cr(OH)_{2^+}$ or $Cr(OH)_{2^+}$ species from the soil surface [29] or dissolution of Cr(III) complexes with soil fulvic acids dissolved at soil pH. The solubility of chromium increased in NaOH still remaining in the µg kg⁻¹ range (Table 2). The higher Cr concentrations under alkaline conditions could be explained with Cr-silicate mineral dissolution which could lead to higher rates of Cr(VI) generation [30, 31].

Table 1. Iron and manganese in soils as *aqua regia* soluble (Fe_{total}, Mn_{total}) and as reducible oxides (Fe_{OX}, Mn_{OX}). SD: standard deviation (*n*=3)

	Unit	Min	Max	Mean	SD
Fe _{total}	g kg ⁻¹	22	301	66.6	58
Feox	g kg ⁻¹	0.06	6.42	2.66	1.40
Fe _{OX} / Fe _{total}	%	0.3	10.4	4.7	1.9
Mn _{total}	g kg ⁻¹	1.2	14.7	4.9	4.3
Mn _{OX}	g kg ⁻¹	0.54	5.42	2.07	1.45
Mn _{OX} / Mn _{total}	%	31	74	46.5	10.7

Table 2. Soil chromium species: *aqua regia* soluble Cr (Cr_{total}), total aqueous soluble Cr (Cr_{H2O}), aqueous soluble Cr(VI) (Cr(VI)_{H2O}), total alkaline soluble Cr (Cr_{OH}), alkaline soluble hexavalent Cr (Cr(VI)_{OH}). SD: standard deviation (n=3).

Chromium species	Unit	Valid N	Min	Max	Mean	SD
Cr _{total}	mg kg ⁻¹	35	24	189	89	38
Cr _{H2O}	μg kg ⁻¹	35	44	145	88	28
Cr(VI) _{H2O}	μg kg ⁻¹	35	41	142	85	27
Cr _{OH}	µg kg⁻¹	35	57	548	210	111
Cr(VI) _{OH}	μg kg ⁻¹	35	45	502	174	105
Cr(VI) _{H2O} /Cr _{H2O}		35	1.04	0.96	0.80	0.05
Cr(VI) _{OH} /Cr(III) _{OH}		32	1.1	12.2	3.2	3.2
Cr(VI) _{OH} /Cr _{OH}		35	0.52	0.99	0.82	0.12
Cr(VI) _{OH} /Cr(VI) _{H2O}		35	0.85	4.83	1.99	1.01

The trivalent chromium species in alkaline soil extracts (evaluated as difference between total and hexavalent Cr) represented less than 20 % (for 22 samples) of the total alkaline soluble Cr. The occurrence of Cr(III) was most probably connected with the dissolution of its complexes with soil humic acids at pH 13 (0.1 mol 1^{-1} NaOH).

In most of the studied sites (22 samples) the content of Cr(VI) in the alkaline extracts was 1.1 to 2.3 times higher than in aqueous soil leachates. It

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could be explained with the higher solubility of hexavalent chromium species in alkaline media. For 3 samples the difference between aqueous and alkaline Cr(VI) was not significant. For two samples the ratio between Cr(VI) in alkaline and aqueous extracts was 0.85. This is probably due to partial reduction of Cr(VI) in presence of soil organic substances dissolved at pH 13.

For the main part of the samples the dissolved alkaline Cr(VI) represented 80 - 89 % of the total chromium dissolved in 0.1 mol 1⁻¹ NaOH. In nine samples the dissolved hexavalent chromium species were 91 - 99 % of all dissolved chromium species. For 6 samples Cr(VI) was 70 ± 2 % of total alkaline dissolved Cr.

The equilibrium ratio between Cr(VI) and Cr(III) in the alkaline extracts ranged from 1.07 to 66 (Table 2). But for the half of the sites (17 samples) this ratio was between 1.1 and 5, for 15 samples – between 5 and 12. For two samples the Cr(VI)/Cr(III) ratio was 20 and 30, and for one single sample – 66. The latter three samples were not included in the calculation of the average values and of the standard deviation.

Chemometric analysis

Correlation analysis. In Table 4 the correlation matrix for the data set is presented. The statistically significant correlation coefficients are marked. Two levels of significance are highlighted: strong correlation indicated by bold and significant

correlation marked by italics. The rest of the correlation coefficients are statistically non significant.

It could be readily seen that Cr(VI) content in the alkaline leachates ($Cr(VI)_{OH}$) is strongly correlated with the content of Mn(IV) (r=0.80) and Fe(III) (r=0.89) species in the soils. These results confirm the oxidizing role of Mn oxyhydroxides reported in previous studies. The present paper shows for the first time the potential of soil iron oxides to generate Cr(VI) species. Even Cr(VI) in aqueous soil extracts is significantly well correlated (r=0.44) with Fe(III) species and does not correlate with Mn(IV).

The correlation between the content of the hexavalent chromium in both aqueous and alkaline soil leachates and the total Cr dissolved in these extracts is extremely strong. It agrees with the results from the redox speciation analysis for Cr, presented in Table 2.

This consideration is a solid preliminary background for searching more detailed relationships between the variables of interest.

Cluster analysis. As already mentioned above, the cluster analysis was performed after z-transform of the raw input data, squared Euclidean distances as similarity measures and Ward's method of linkage. The cluster significance was determined according to Sneath's criterion.

Table 3. Correlation matrix [*-strong correlation (ρ <0.01); **-significant correlation (ρ <0.05)]

	ТОМ	Fe(III) species	Mn(IV) species	Cr _{tot}	Cr _{H20}	Cr(VI) _{H2O}	Cr _{OH}
Fe(III)							
species	-0.10						
Mn(IV)							
species	-0.18	0.60*					
Cr _{tot}	-0.11	0.04	-0.15				
Cr _{H2O}	-0.27	0.40**	0.25	0.24			
Cr(VI) _{H2O}	-0.29	0.44**	0.28	0.24	0.98*		
Croh	-0.16	0.88*	0.80*	0.01	0.50**	0.52**	
Cr(VI) _{OH}	-0.13	0.89*	0.80*	-0.03	0.47**	0.50**	0.97*

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Fig. 1. Hierarchical dendrogram for clustering of 8 variables



Fig. 2. Biplot PC1 vs. PC2 for factor loadings

In Fig. 1 the hierarchical dendrogram showing the clustering of the variables is presented.

Two major clusters are formed:

K1 [Mn(IV), Cr(VI)- OH, Cr (OH), Fe(III)]

K2 [Cr(VI)-H2O, Cr(H2O), Cr(total)]

TOM is a typical outlier which differs from the rest of variables.

In K2 Cr(total) also slightly differs from the other members of the cluster K2. In general, the results from the hierarchical clustering of variables confirm those from correlation analysis. *Principal components analysis*. In order to confirm the results from correlation analysis and hierarchical cluster analysis the input data were subjected to principal components analysis (PCA). It was found that two principal components explain over 75 % of the total variance. It means that two significant factors are responsible for the data structure. In Fig. 3 the biplot for the factor loadings PC1 *vs.* PC2 is presentedAs in cluster analysis, there is close relationship between chromium species with water

extraction, on one hand, and between chromium species after OH-extraction along with Fe(III) and Mn(IV) species, on the other. It can be concluded that the two latent factors determining the data structure are conditionally "water extraction" and "alkaline extraction". Again, total Cr and TOM are not closely related to the other soil features. It is obvious that TOM negatively correlated to all other species.

CONCLUSION

The Cr(III) oxidation in soils occurs *via* interactions with iron and manganese oxides. Multivariate statistical analysis revealed information about the probable mechanism for Cr(III) oxidation in soils: the soil fraction containing Fe(III) and Mn(IV) species is the phase that promotes the oxidation of Cr(III). The BCR sequential extraction procedure and the isolation of the soil fraction bound to amorphous Fe/Mn oxyhydroxides can be a useful tool for evaluating the oxidation capacity of the soils.

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REFERENCES

- 1. K. Shiraki, Resour. Geol., 47, 319 (1997).
- 2. F. C. Richard, A. M. Bourg, Water Resources, 25, 807 (1991).
- 3. D. S. Becker, E. R. Long, D. M. Proctor, T. C. Ginn, Environ. Toxicol. Chem., 25, 2576 (2006).
- 4. W. J. Berry, W. S. Boothman, J. R. Serbst, P. A. Edwards, *Environ. Toxicol. Chem.*, 23, 2981(2004).
- 5. W. Ding, D. I. Stewart, P. N. Humphreys, S. P. Rout, I. T. Burke, Sci. Total Environ., 541, 1191 (2016).
- 6. J. F. Papp, Mineral Commodity Summaries: Chromium, U.S. Department of the Interior, U.S. Geological Survey, Washington, DC, 2001.
- 7. C. H. Wang, C. P. Huang, P. F. Sanders, Pract. Period. Hazard. Toxic Radioact.Waste Manag., 6, 6 (2002).
- 8. S. E. Fendorf, R. J. Zasoski, Environ. Sci. Technol., 26, 79 (1992).
- 9. P. S. Nico, R. I. Zasoski, Environ. Sci. Technol., 34, 3363 (2000).
- 10. C. D. Palmer, P. R. Wittbrodt, Environ. Health Persp., 92, 25 (1991).
- 11. L. M. Zhang, F. Liu, W. F. Tan, X. H. Feng, Y. G. Zhu, J. Z. He, Soil Biol. Biochem. 40, 1364 (2008).
- 12. Z. Stepniewska, K. Bucior, R. P. Bennicelli, Geoderma, 122, 291(2004).
- 13. L. E. Eary, D. Rai, Environ. Sci. Technol., 21, 1187 (1987).
- 14. S. E. Fendorf, Geoderma, 57, 65 (1995).
- 15. B. R. James, J. C. Petura, R. J. Vitale, G. R. Mussoline, J. Soil Contam., 6, 569 (1997).
- 16. C. Yingxu, C. Yiyi, L. Qi, H. Ziqiang, H. Hong, W. Jianyang, Pedosphere, 7, 185 (1997).
- 17. M. Debra, D. M. Hausladen, S. Fendorf, Environ.

18. R. M. Cornell, U. Schwertmann, The iron oxides: structure, properties, reactions, occurrences and uses, John Wiley & Sons, 2006.

- 19. A. B. Cundy, L. Hopkinson, R. L. Whitby, Sci. Total Environ., 400, 42 (2008).
- 20. M. Komárek, A. Vaněk, V. Ettler, Environ. Pollut., 172, 9 (2013).
- 21. J. Kumpiene, A. Lagerkvist, C. Maurice, Waste Manag., 28, 215 (2008).
- 22. E. C. Butler, L. Chen, C. M. Hansel, L. R. Krumholz, A. S. E. Madden, Environ. Sci.: Processes Impacts, 17, 1930 (2015).
- 23. D. Fandeur, F. Juillot, G. Morin, L. Olivi, A. Cognigni, J. P. Ambrosi, F. Guyot, E. Fritsch, American Mineralogist, 94, 710 (2009).
- 24. G. Rauret, J. F. Lopez-Sanchez, A. Sahuquillo, E. Barohona, M. Lachica, A. M. Ure, C. Davidson, A. Gomez, D. Luck, J. Bacon, M. Yli-Halla, H. Muntau, Ph. Quevauviller, J. Environ. Monit., 2, 228 (2000).
- 25. J. M. Serafimovska, S. Arpadjan, T. Stafilov, K. Tsekova, J. Soils Sed., 13, 294 (2013).
- 26. C. Voyslavov, S. Tsakovski, S. Arpadjan, Turkish J. Chem., 40, 944 (2016).
- 27. Regulation № 3 /01/08/2008 on the allowable limits of toxic substances in the soils. www.government.bg/bg/legislation/soil/normipochv i.doc.
- 28. K. R. Krishna, L. Philip, J. Hazard. Mat., 21, 109 (2005).
- 29. E. I. Hawley, R. A. Deeb, M. C. Kavanaugh, J. R. G. Jacobs, Chromium(VI) Handbook. Chapter 8: Treatment Technologies for Chromium (VI), CRC Press, Florida, 2004, p. 273.
- 30. C. Oze, D. K. Bird, S. Fendorf, Proc. Nat. Acad. Sci. USA, 104, 6544 (2007).
- 31. A. U. Rajapaksha, M. Vithanage, Y. S. Ok, C. Oze, Environ. Sci. Technol., 47, 9722 (2013).

ВЛИЯНИЕ НА ПОЧВЕНАТА ФРАКЦИЯ, СЪДЪРЖАЩА ЖЕЛЕЗНИ И МАНГАНОВИ ОКСИХИДРОКСИДИ, ВЪРХУ НАЛИЧИЕТО НА Cr(VI)

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(Резюме)

Целта на настоящата работа е да се изучи влиянието на природните окислители в почвата (Fe/Mn оксиди) върху наличието на Cr(VI) в почвата с оглед по-доброто разбиране и предсказване на промените, мобилността и токсичността на хрома в околната среда. Водни и алкални извлеци от 35 образци от повърхностния слой на почвата са изследвани за съдържанието на Cr(VI). Редуцируемите железни и манганови оксиди в почвата, които биха могли да промотират окислението на Cr(III), са екстрахирани с използване на подкислен разтвор на хидроксиламин хидрохлорид (BCR процедура). Течна екстракция е използвана за определяне на редокс формите на Cr. Установено е, че окислението на Cr(III) в почвите се извършва посредством взаимодействие с железните и мангановите оксиди. Cr(VI) е преобладаващата форма във водните извлеци (44-145 µg kg⁻¹ Cr). За по-голямата част от образците, разтворимият в алкален разтвор Cr(VI) представлява 80 - 89 % от тоталния почвен хром, разтворен в 0.1 mol 1⁻¹ NaOH.