The solubility of Cr(III) and Cr(VI) compounds in soil and their availability to plants

K.L. Mandiwana [a,*], N. Panichev [a], M. Kataeva [b], S. Siebert [c]

[a] Department of Chemistry, Tshwane University of Technology, Private Bag X31, Rosslyn 0200, South Africa
[b] Department of Botany, University of Pretoria, Pretoria 0001, South Africa
[c] Department of Botany, University of Zululand, KwaDlangezwa, South Africa

Abstract

The mystery surrounding high concentrations of Cr(III) in plants has been uncovered. It is attributed to the presence of low molecular weight organic acids (LMWOA) in soil in which the plants are growing. Apart from that, the factors influencing solubility of Cr(VI) in soil have also been investigated. It was found that the solubility of Cr(VI) species is governed by the presence of CO_3^{2-} ions in a soil solution that resulted when atmospheric CO_2 dissolves in soil–water.

Concentrations of Cr(VI) and Cr(III) were determined in plants, collected on unpolluted soils in different geographical areas. It was found that the concentration of Cr(VI) in plants correlated with the soluble fraction of Cr(VI) in soil, while Cr(III) concentration in plants is limited by concentration LMWOA in soil. It can therefore be concluded that the high level of Cr(III) in plants is also due to the direct absorptions of the species from soil rich in organic acids.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Cr(VI); Carbon dioxide; Cr(III); Low molecular weight organic acids; Plants

1. Introduction

Understanding the bio-geochemical cycling of contaminants in terrestrial ecosystems is the basis for the prediction of elements behavior in the environment. This is especially applicable to chromium (Cr) because its toxicity depends on its oxidation state. While Cr(III) is considered as an essential microelement [1–3], Cr(VI) is regarded as a carcinogenic agent [4,5]. The carcinogenicity of Cr(VI)-containing compounds has been covered extensively in several reviews [6–10] as well as in documents produced by governmental organizations [11,12] and international agencies [13]. The toxic and carcinogenic properties of Cr(VI) compounds arise from the possibility of free diffusion of chromate (CrO_4^{2-}) ions across cell membranes and the action of this form as an oxidizing agent, as well as from the formation of free radicals during the reduction of Cr(VI) to Cr(III) inside the cell [14–16].

Trace element uptake by roots depends on both soil and plant factors such as chemical form of elements in soil, pH, organic matter, and plant species. Consequently, element mobility and plant availability are very important when assessing the effect of soil contamination on plant metal uptake and related phytotoxic effects.

The major factor governing the metals in soil to be available to plants is their solubility that is associated with solid phase, since in order for root uptake to occur, a soluble species must exist adjacent to the root membrane [17]. In general, trace element uptake by plants depends on soil composition (endogenous metal concentration, mineralogy, and particle size distribution) and soil processes (e.g., mineral weathering, microbial activity), as these influence the metal concentration in solution and the form of soluble chemical species. Consequently, element mobility and their availability to plants is a combination of many factors, which are quite different for Cr(III) and Cr(VI) species.

Hexavalent chromium is always present in relatively small amounts as compared with Cr(III) in any kind of unpolluted soil. Cr(VI) may form moderately-to-sparingly soluble chromates (e.g., $CaCrO_4$, $BaCrO_4$, $PbCrO_4$) in soil [18]. The equilibrium concentration of CrO_4^{2-} ions, formed due to partial dissocia-

tion is rather small ($\leq 1.75\,\mu g\,g^{-1}$), but in the presence of CO_3^{2-} ions it can be much higher [19]. The CrO_4^{2-} ions can therefore be taken up by plants or easily leached out into the deeper soil layers causing ground and surface water pollution [20,21].

In soils, Cr is present mostly as insoluble Cr_2O_3, $Cr(OH)_3(aq)$ or as Cr(III) adsorbed to soil components, which prevents Cr leaching into the ground water or its uptake by plants [22]. The equilibrium concentration of Cr(III) ions in soil solution, calculated on the base of solubility product of $Cr(OH)_3$, can be estimated as $0.5\,\mu g\,l^{-1}$. At such concentration, the consumption of Cr(III) by the plants would be negligible.

Al(III) and Fe(III) forms soluble complexes with organic ligands with low molecular weight organic acids. The most common organic acids identified in soils are oxalic, citric, succinic, tartaric, malic and salicylic acids [23]. The main source of oxalic acid in soil is fungi, particularly in acidic forest soils and may occur in soils at concentrations ranging from 0.025 to 1.0 mM [24]. The origin of citric acid in soil is plants where it is excreted from roots of plants like white lupin [25]. By forming soluble complexes with polyvalent cations from rocks and minerals, organic acids play an important role in dissolution, transportation, and concentration of elements in the earth's surface as well as in soil formation and plant nutrition [26].

The similarity of chemical properties of Cr(III) ions with Fe(III) and Al(III) allows us to predict higher solubility of Cr(III) in soil solution in the presence of organic acids and, as a result, their high bioaviability to plants. The aim of present study is to show that the solubility of Cr(III) in soil depends on the presence of low molecular weight organic acids (LMWOA) while that of Cr(VI) compounds is governed by the presence of carbonate compounds and ultimately both species are available to plants separately.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer atomic absorption spectrophotometer model AAnalyst 600 with Zeeman-effect background correction system was used for all measurements. The spectrophotometer was equipped with an AS-800 autosampler and the system was controlled by means of AAWinlab software running under Microsoft Windows. A Cr hollow cathode lamp (Perkin-Elmer), operating at 25 mA, was employed. All determinations were accomplished on Cr 357.9 nm resonance line in transversely heated graphite tubes (THGA), fitted with integrated L'vov platform (Perkin-Elmer, part N B050-4033). L'vov platform is a small plate of solid pyrolytic graphite that is inserted into the graphite tube to isolate the sample from the tube walls to allow more reproducible atomization of the sample through indirect heating. Argon (Afrox, South Africa) was used as a protective gas throughout.

2.2. Reagents

Standard stock solutions containing $1000\,mg\,l^{-1}$ Cr(III) and Cr(VI) as $CrCl_3$ and K_2CrO_4 (Merck), respectively, were used

for the preparation of working standards for each oxidation state of chromium. Ultra-pure water (resistivity $18.2\,M\Omega\,cm$), obtained from a Milli-Q water purification system (Millipore Corp., USA) was used for all dilutions and sample preparation. Citric and oxalic acid (Merck) were of analytical reagent grade. CO_2 99.99% purity (Air Products, South Africa) was used for the leaching of Cr(VI). Hydrophilic PVDF $0.45\,\mu m$ filters (Millipore Millex, USA) were used for the filtration of all solutions for Cr(VI) determinations.

2.3. Samples and samples preparation.

Samples of top soil were taken at Thorncliff in Mpumalanga Province, South Africa (the site of a new chromium mine). They were dried and ground to a particle size less than $75\,\mu m$ in a tungsten carbide milling vessel. Plant samples were taken from Polar Ural Mountains (Russia) and in South Africa. The soil samples where the plants were taken were typically sandy clay with high water holding capacity. The samples were air-dried and homogenized by grinding.

2.3.1. Determination of the solubility of Cr(VI) in soil in the presence of CO_2

The nominal mass of 0.25 g sub-sample of soil was weighed and transferred into plastic tubes in which 25.0 ml of deionized water was added. The mixture was periodically shaken for a minimum period of 24 h. Before bubbling CO_2, the soil sample solution containing only water soluble fraction of Cr(VI) were taken for analysis from each tube.

CO_2 was then bubbled through the suspension of soil samples in deionized water for period ranging from 5 min to 24 h at a flow rate of $50\,ml\,min^{-1}$. One millimeter of the bubbled sample was filtered through hydrophilic PVDF $0.45\,\mu m$ filter every 5 min into the sampling cup and analyzed by electrothermal atomic absorption spectrometry (ET-AAS).

2.3.2. Determination of Cr(VI) in plants

Sub-samples of 0.25 g of ground leaves were weighed into a glass beaker and 25.0 ml of $0.1\,M\,Na_2CO_3$ were added and the mixtures were boiled for 15 min. After filtration through Whatman No. 540 filter paper, the precipitates were washed with $0.1\,M\,Na_2CO_3$ several times [27]. The final volumes of the sample solutions were diluted to 25.0 ml with deionized water. The sample solutions were filtrated through hydrophilic PVDF $0.45\,\mu m$ filter before analysis by ET-AAS.

2.3.3. Determination of Cr(III) in plants

The precipitates, which were left after the filtration of samples treated with $0.1\,M\,Na_2CO_3$, were transferred on the filter paper to a Teflon digestion vessel (CEM type) and 5.0 ml of concentrated HNO_3, 3.0 ml HF and 1.0 ml HCl were added. The vessels were capped and the samples were digested in microwave at a pressure 120 psi for 20 min. After cooling, the cap was removed and the open vessel was heated on a hot plate to evaporate the excess acid. The final volume of each sample solutions was adjusted to 25.0 ml with deionized water. The resulting solution was then analyzed by ET-AAS.

Table 1
Temperature program for the determination of Cr

Step	Temperature ($^\circ$C)	Ramp (s)	Hold (s)	Ar (ml min^{-1})
1	110	1	10	250
2	250	5	20	250
3	1400	5	30	250
4	2450	0	5	0
5	2450	1	3	250

2.3.4. Determination of solubility of Cr(III) in organic acids

Approximately 1 g soil or chromite ore (FeO $\times$ Cr$_2$O$_3$) were placed in separate 500 ml beakers and 250 ml of 1–100 mM solutions of either citric or oxalic acids were added. The mixtures were periodically shaken for 48 h. The concentration of Cr(III) in these solutions was measured at 24 h time intervals.

Plants surrounding each individual plant in an area of approximately 1 m^2 were removed. The soil around the plant was well prepared so that the irrigated water stands still around the plant. The plant was then irrigated daily with 1 l of 0.1 M of either citric or oxalic acid for a period of 5 days. Plants were sampled after 7 days and were treated as in Sections 2.3.2 and 2.3.3.

2.3.5. Determination of total concentration of Cr in plants

A nominal mass of 0.25 g of plant leaves was weighed into a teflon digestion vessel (CEM type) and 5.0 ml of concentrated HNO$_3$, 3.0 ml HF and 1.0 ml HCl were added. The vessels were capped and the samples were digested in microwave at a pressure 120 psi for 20 min. After cooling, the cap was removed and the open vessel was heated on a hot plate to evaporate the excess acid. The final volume of each sample solutions was adjusted to 25.0 ml with deionized water.

3. Results and discussion

3.1. Analytical results of total Cr determination in reference samples and plants

As recommended by Panichev et al. [19], the temperature program summarized in Table 1 was used for the determination of Cr in all samples. The temperature program utilizes two drying stages, thus avoiding spattering of the liquid. Pyrolysis was conducted at 1400 $^\circ$C in order to remove excess Na$_2$CO$_3$ matrix. The atomic profiles of Cr obtained in samples and aqueous standard solutions had the same shape and appearance time. These indicated that the high pyrolysis temperature had effec-
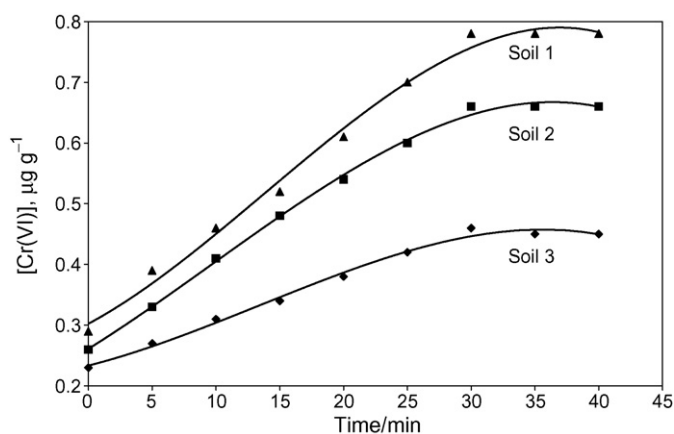

Fig. 1. The concentrations of Cr(VI) leached from soil suspensions by bubbling CO$_2$ through them as a function of time: (▲) Soil 1; (■) Soil 2; (♦) Soil 3.

tively removed the majority of the matrix prior atomization and that the residual amount of Na$_2$CO$_3$ had no influence on the release of Cr during atomization.

The calibration curve for Cr was linear up to 70 μg l^{-1} and is described by the following equation: $Y = 0.0064x + 0.0056$, where x is the analyte concentration (μg l^{-1}) and Y is the integrated absorbance, with correlation coefficient of $R^2 = 0.9909$ ($n = 5$). The limit of detection (LOD) for Cr determination was established using blank solutions of Na$_2$CO$_3$. The LOD, calculated according to the equation: LOD $= x_{bl} + 3s_{bl}$ ($n = 25$), was found to be 0.7 μg l^{-1} for a 10 μl sample aliquot. The LOD is comparable to that reported earlier [28,29].

The results for total chromium determination in certified reference materials are shown in Table 2, with good agreement between the certified and found values.

3.2. Results of Cr(VI) determination in soil treated with CO$_2$

The kinetics for the determination of Cr(VI) after the bubbling CO$_2$ through the soil suspension at different time intervals is shown in Fig. 1. The amount of Cr(VI) leached from soil was found to be directly proportional to the time carbon dioxide was bubbled and reaches its limit when the solution becomes saturated with the gas. The maximum concentration of Cr(VI) leached was approximately 2.5-fold in excess, in comparison with the concentration of Cr(VI) formed in the water soluble fraction. Therefore, the presence of atmospheric CO$_2$ in soil–water leaches Cr(VI) into water and make it available to plants that absorb it through their roots.

Table 2
Results of total chromium determination in certified reference materials

CRM	Certified value (μg g^{-1})	Found value[a] (μg g^{-1})
SRM 2704, river sediments	134 ± 5	132 ± 6
PACS–2, marine sediments	90.7 ± 4.6	92.2 ± 3.4
CRM 281, rye grass	2.15 ± 0.12	2.20 ± 0.20

[a] Average of six determinations at 95% level of confidence: mean $\pm t_{0.05} \times s/\sqrt{n}$.

3.3. Mechanism of the leaching of Cr(VI) with CO₂

The mechanism of the action of CO_2 can be explained with aid of the following equations:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq) \tag{1}$$

$$BaCrO_4(s) + CO_3^{2-}(aq) \rightarrow BaCO_3(s) + CrO_4^{2-}(aq) \tag{2}$$
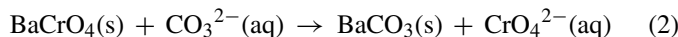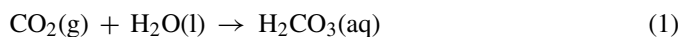
According to Eq. (2), the treatment of samples with CO_3^{2-} removes all common metals, including Cr(III), as insoluble carbonates, leaving chromates that have been originally present as insoluble Cr(VI) compounds.

Carbon dioxide forms CO_3^{2-} ions when it is dissolved in water. The concentration of CO_3^{2-} ions formed is proportional to the partial pressure of CO_2 and is governed by Henry's law [30], i.e.

$$[CO_2(sol)] = K \times p_{CO_2} \tag{3}$$

where $K = 3.34 \times 10^{-4}$ mol l kPa.

It follows from Eqs. (1) to (3), that the amount of Cr(VI) leached should be proportional to the partial pressure of CO_2 in soil:

$$\left[CrO_4^{2-} \right] = K \times p_{CO_2} \tag{4}$$

Though the concentration of CO_2 in rainwater is in equilibrium with atmospheric CO_2, the carbon dioxide content becomes extremely high when in contact with the soil due to the presence of decaying vegetation, plant respiration in the rooting zone and microbial decomposition of organic matter [31].
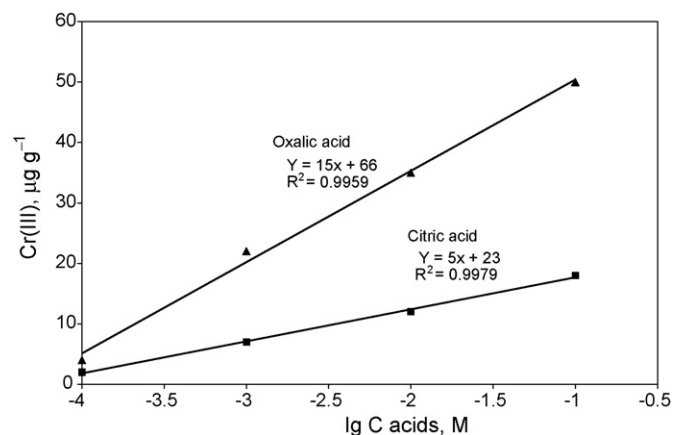

Fig. 2. The level of Cr(III), which is soluble in different concentrations of low molecular weight organic acids: (▲) oxalic acid; (■) citric acid.

3.4. Solubility of Cr(III) in organic acids

The solubility of Cr(III) in organic acids was tested by shaking soil or ore sample with different concentrations of oxalic or citric acids. Though Cr(III) compounds are reputed to form insoluble complexes, they were found to be soluble in low molecular weight organic acids. Fig. 2 shows that Cr(III) is soluble to both citric and oxalic acids and the amount leached is directly proportional to the concentration of the acids. Therefore, the presence of organic acids in soil at significant levels probably leaches Cr(III), thereby making it available to plants.

The concentrations of Cr(III) in plants after the irrigation with citric or oxalic acids were compared with Cr(III) concentrations found before irrigation, to check whether the presence of organic acids in soil enhances the leaching of Cr(III) and their

Table 3
Distribution of chromium species in different types of plants

Sample	[Cr(VI)] ($\mu g\,g^{-1}$)	[Cr(III)][a] ($\mu g\,g^{-1}$)	[Cr(III)][b] ($\mu g\,g^{-1}$)		Total Cr concentration[c] ($\mu g\,g^{-1}$)
		Without irrigation	Oxalic acid	Citric acid	
Terminalia prunioides[d]	0.29[e] ± 0.04	3.23[e] ± 0.25	6.00[e] ± 0.90	4.95[e] ± 0.95	3.80[e] ± 0.40
	0.49[f] ± 0.15	4.86[f] ± 0.30	7.29[f] ± 1.50	5.82[f] ± 1.20	5.20[f] ± 0.60
Lydenburgia cassinoides[d]	0.74[e] ± 0.11	9.28[e] ± 0.85	15.3[e] ± 1.30	12.9[e] ± 1.50	10.2[e] ± 0.90
	0.78[f] ± 0.12	11.4[f] ± 1.50	20.5[f] ± 1.75	15.0[f] ± 1.10	12.1[f] ± 1.00
Leucas capensis[d]	0.16[e] ± 0.05	4.93[e] ± 0.90	9.25[e] ± 0.69	7.30[e] ± 0.73	5.80[e] ± 0.55
	0.75[f] ± 0.15	8.84[f] ± 1.00	17.1[f] ± 1.50	12.3[f] ± 0.85	10.6[f] ± 1.00
Thalictrum alpinum[g]	0.25[e] ± 0.04	0.33[e] ± 0.02	0.61[e] ± 0.02	0.35[e] ± 0.02	0.70[e] ± 0.25
	0.45[f] ± 0.10	0.49[f] ± 0.05	1.05[f] ± 0.06	0.80[f] ± 0.06	0.83[f] ± 0.07
Alyssum obovatum[g]	0.13[e] ± 0.06	0.95[e] ± 0.03	2.00[e] ± 0.07	1.45[e] ± 0.06	1.55[e] ± 0.40
	0.57[f] ± 0.14	2.20[f] ± 0.75	5.70[f] ± 0.45	3.50[f] ± 0.55	2.36[f] ± 0.50
Salix reticulata[g]	0.16[e] ± 0.05	1.67[e] ± 0.80	4.95[e] ± 0.75	3.15[e] ± 0.60	2.35[e] ± 0.15
	0.66[f] ± 0.12	3.54[f] ± 0.65	5.50[f] ± 0.86	4.40[f] ± 0.70	3.73[f] ± 0.30

[a] Concentration of Cr(III) in plants before irrigation of plants with organic acids.
[b] Concentration of Cr(III) in plants after irrigation of plants with organic acids.
[c] Total concentration of Cr in plants before irrigation of plants with organic acids.
[d] Plant samples from South Africa.
[e] Leaves.
[f] Roots.
[g] Plant samples from Polar Ural mountains, Russia.

availability to plants. Table 3 confirms that the presence of low molecular weight organic acids in soil is responsible for high concentrations of Cr(III) species in plants as the concentrations of Cr(III) before irrigation is much smaller than after irrigation with organic acidic solution.

3.5. Validation of the method for the determination of Cr(III) in plants

The validation of the method of leaching Cr(III) with either citric or oxalic acid using certified reference materials was impossible, since such materials with certified values of chromium species are not yet available in the market. Therefore, the only available alternative was to compare the sum of [Cr(III)] and [Cr(VI)] with total [Cr] obtained independently from the same plant sample. A comparison of the concentration of the sum of chromium species should be equivalent to the total chromium [32].

The results of the determination of Cr in South African and Russian plants shown in Table 3 confirm that the sum of concentrations of Cr(III) and Cr(VI) in plants before irrigation of plants with either citric or oxalic acid is equal to the total concentration of Cr determined by an independent method at 95% level of confidence. Therefore, it can said with 95% level of certainty, that LMWOA leached Cr(III) successfully from finely ground plant samples, for statistically, there was no difference between the sum of the concentrations of the chromium species and the total chromium concentration, as determined through an independent method.

3.6. Analytical results for the determination of chromium in plants

The analysis of South African and Russian plants were influenced by their common features such as growing on soils rich in chromium and that they are endemic for these regions [33]. It was, therefore, interesting to compare their ability to accumulate this element. The results summarized in Table 3 indicate that the average concentration of Cr(III) and total Cr in the analyzed South African plants is higher than in the Russian plants, with more of the analyte found in the roots than in the leaves.

The root/leaves concentration ration of both Cr(VI) in roots ranges between 1 and 5, while that of Cr(III) was approximately 2, for all experiments. The highest and lowest [Cr(III)]/[Cr(VI)] were found in *Leucas capensis* and *Thalictrum alpinum*, where the concentration ration of approximately 50 and 2, respectively, were recorded. Similar pattern were recorded after the plants were irrigated with oxalic and citric acids. The highest concentrations of Cr(III) and total Cr was found to be 0.78 and 12.1 μg g^{-1}, respectively.

3.7. The correlation between water soluble Cr(VI) species in soil and Cr(VI) in plants

The amount of Cr(VI), in soil, that is naturally soluble in water was compared with the amount of Cr(VI) in plants to check any correlation between them. It was found that the concentration
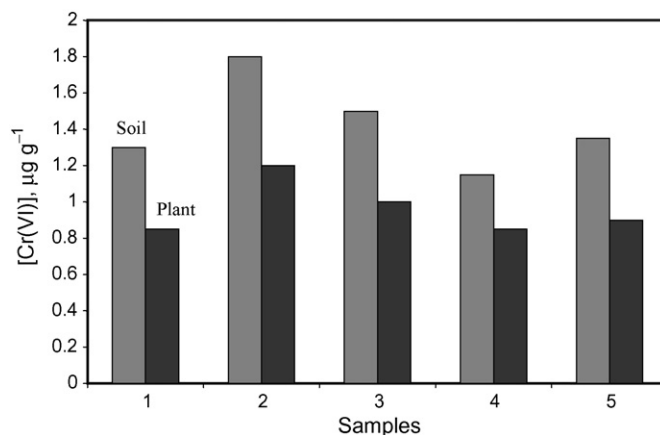

Fig. 3. Comparison of the concentration of Cr(VI) in South African plants to that of water soluble Cr(VI) found in their respective soils.

of water soluble Cr(VI) in soil is always higher than that in the respective plant as illustrated in Fig. 3. Therefore, the levels of water soluble fraction of Cr(VI) in soil can be used as an indicator to estimate the maximum levels of this pollutant that can be accumulated by plants. Fig. 3 also shows that the levels of Cr(VI) in plants is approximately two-thirds of that of the water soluble fraction of Cr(VI) in soil.

Though a number of articles have showed that that some plants like *Eichhornia crassipes* (water hyacinth), *Prosopis spp.* (mesquite) and *Allium sativum* (garlic) have the ability to reduce toxic Cr(VI) to non-toxic Cr(III) completely, and accumulate detoxified Cr into roots and leaf tissues [34–36], it is doubtful that the analyzed plants have similar capabilities, since trace amount of Cr(VI) were found in both roots and leaves.

4. Conclusions

The results of investigation show that Cr is generally mobile in soils to the extent that a fraction of their total mass is bioavailable to plants. Both atmospheric CO_2 and low molecular weight organic acids are responsible for the leaching of Cr(VI) and Cr(III) species, respectively, in soil. Data presented here show that low molecular weight organic acids are effective chelators of Cr(III) and that these ligands therefore play an important role in the leaching and availability of this metal species to plants. The level of Cr(VI) in plants is concentrated more on the roots than in leaves.

References

[1] E. Nieboer, A.A. Jusys, Biologic chemistry of chromium, in: J.O. Nriagu, E. Nieboer (Eds.), Chromium in Natural and Human Environments, Wiley Interscience, New York, 1988, p. 2181.

[2] R.A. Anderson, Chromium as an essential nutrient for humans, Regul. Toxicol. Pharmacol. 26 (1997) S35–S41.

[3] A.M. Zayed, N. Terry, Chromium in the environment: factors affecting biological remediation, Plant Soil 249 (2003) 139–156.

[4] S. De Flora, M. Bagnasco, D. Serra, P. Zanacchi, Genotoxicity of chromium compounds, Mutat. Res. 238 (1990) 99-L172.

[5] International Agency for Research on Cancer (IARC), IARC Monographs of the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Chromium, Nickel and Welding, IARC, Lyon, 1990. p. 49.

[6] V. Bianchi, A.G. Levis, Review of genetic effects and mechanisms of action of chromium compounds, Sci. Total Environ. 71 (1988) 351–355.

[7] S. De Flora, Threshold mechanisms and site specificity in chromium(VI) carcinogenesis, Carcinogenesis 21 (2000) 533–541.

[8] K.D. Sugden, D.M. Stearns, The role of chromium(IV) in the mechanism of chromate-induced oxidative DNA damage and cancer, J. Environ. Pathol. Toxicol. Oncol. 19 (2000) 215–230.

[9] E.T. Snow, Metal carcinogenesis: mechanistic implications, Pharmacol. Ther. 53 (1992) 3165.

[10] J. Singh, D.L. Carlisle, D.E. Pritchard, S.R. Patierno, Chromium-induced genotoxicity and apoptosis: relationship to chromium carcinogenesis, Oncol. Rep. 5 (1998) 1307–1318.

[11] EPA Locating and Estimating Air Emissions from Sources of Chromium, Office of Air Quality Planning and Standards, US Environmental Protection Agency, Research Triangle Park, NC, 1984.

[12] EPA Health Effects Assessment for Hexavalent Chromium, Office of Emergency and Remedial Response, US Environmental Protection Agency, Cincinnati, OH, 1984.

[13] IARC Monograph on the Evaluation of Carcinogenic Risk to Humans, Chromium, Nickel and Welding, Lyon, France, 1990.

[14] T.J. O'Brein, S. Ceryak, S.R. Patierno, Review. Complexities of chromium carcinogenesis: role of cellular response, repair and recovery mechanisms, Mutat. Res. 533 (2003) 336.

[15] C.S. Gad, Acute and chronic systematic chromium toxicity, Sci. Total Environ. 86 (1989) 149–157.

[16] A. Kortenkamp, Z. Ozolins, D. Beyersmann, P. O'Brien, Generation of PM2 DNA breaks in the course of reduction of chromium(VI) by glutathione, Mutat. Res. 216 (1989) 1926.

[17] A. Kabata-Pendias, Soil-plant transfer of trace element: an environment issue, Geoderma 122 (2004) 143.

[18] R.J. Bartlett, B.R. James, Chromium, in: D.L. Sparks (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods, SSSA, WI, Madison, 1996.

[19] N. Panichev, K. Mandiwana, G. Foukaridis, Electrothermal atomic absorption determination of Cr(VI) in soil after leaching of Cr(VI) species with carbon dioxide, Anal. Chim. Acta 491 (2003) 81–89.

[20] L.M. Calder, Chromium contamination of ground water, in: J.O. Nriagu, E. Nieboer (Eds.), Chromium in Natural and Human Environments, Wiley Interscience, New York, 1988, pp. 215–231.

[21] B.K. Handa, Occurrence and distribution of chromium in natural waters of India, in: J.O. Nriagu, E. Nieboer (Eds.), Chromium in Natural and Human Environments, Wiley Interscience, New York, 1988, pp. 189–215.

[22] R.J. Bartlett, J.M. Kimble, Behavior of chromium in soils: I. trivalent form, J. Environ. Qual. 5 (1976) 379–382.

[23] I.S. Kaurichev, T.N. Ivanova, K.A. Nozdrunova, Low-molecular organic acid content of water-soluble organic matter in soil, Sov. Soil (1963) 223–229.

[24] G. Sposito, The chemistry of soils, Oxford Univ. Press, Oxford, 1989.

[25] B. Dinkelaker, V. Römheld, H. Marschner, Citric acid excretion and precipitation of calcium citrate in the rhizosphere of white lupin (*Lupinus albus* L.), Plant Cell Environ. 12 (1989) 1365–3040.

[26] W.H. Huang, W.D. Keller, Organic acids as agents of chemical weathering of silicate minerals, Nature 239 (1972) 149–151.

[27] N. Panichev, K. Mandiwana, M. Kataeva, S. Siebert, Determination of Cr(VI) in plants by electrothermal atomic absorption spectrometry after leaching with sodium carbonate, Spectrochim. Acta Part B 60 (2005) 699–703.

[28] A.G. Coedo, T. Dorado, I. Padilla, F.J. Alguacil, Speciation of chromium in steelmaking solid wastes by selective retention on ion-exchange media and determination by isotope dilution inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 15 (2000) 1564–1568.

[29] R. Chakraborty, A.K. Das, M.L. Cervera, M. de la Guardia, Determination of chromium by electrothermal atomic absorption spectrometry after rapid microwave-assisted digestion of sediment and botanical samples, J. Anal. At. Spectrom. 10 (1995) 353–358.

[30] J.E. Brandy, J.R. Holum, Chemistry, second ed., Wiley, NY, 1996.

[31] Soil chemistry: basic elements, in: G.H. Bolt, BruggenwertF M.G. (Eds.), in: Developments in Soil Science, vol. 5A, Elsevier, Amsterdam, 1978.

[32] J. Kotaś, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 107 (2000) 263–283.

[33] M.N. Kataeva, N.V. Alexeeva-Popova, I.V. Drozdova, A.I. Beljaeva, Chemical composition of soils and plant species in the Polar Urals as influenced by rock type, Geoderma 122 (2004) 257–268.

[34] G. Micera, A. Dessl, Chromium adsorption by plant roots and formation of long-lived Cr(V) species: an ecological hazard? J. Inorg. Biochem. 34 (1988) 157–166.

[35] C.M. Lytle, F.W. Lytle, N. Yang, J. Qian, D. Hansen, A. Zayed, N. Terry, Reduction of Cr(VI) to Cr(III) by wetland plants: potential for in situ heavy metal detoxification, Environ. Sci. Technol. 32 (1998) 3087–3093.

[36] M.V. Aldrich, J.L. Gardea-Torredey, J.R. Peralta-Videa, J.G. Parsons, Uptake and reduction of Cr(VI) to Cr(III) by mesquite(*Prosopis spp.*): chromate–plant interaction in hydroponics and solid media studied by XAS, Environ. Sci. Technol. 37 (2003) 1859–1864.