



CHROMIUM IN ANTHROPOGENICALLY POLLUTED AND NATURALLY ENRICHED SOILS: A REVIEW*

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Chromium (Cr) is a very important element examined for last decades on many expert fields. Its toxicity, mobility and bio-availability are strongly dependent on its oxidation state, Cr(III) and Cr(VI). Hexavalent form Cr(VI) is a known carcinogen with many harmful effects on living organisms, on the other hand trivalent Cr(III) form is an important micronutrient necessary for lipid metabolism. Contamination of the environment by Cr may come from anthropogenic industrial pollution or from naturally enriched sites, especially ultramafic rocks and their derived soils. Environmental conditions of soils and water represent a very complex system, which makes reliable assessment of its fate and potential toxicity and transport a really difficult task. A number of studies have been performed to describe Cr behaviour in these systems, as well as to optimize its determination, especially speciation methods. The main objective of this contribution is to summarize and present the today's knowledge about the occurrence, speciation, and behaviour of Cr in soil environment, with a specific emphasis to description of differences between naturally enriched and anthropogenically contaminated soils.

speciation, mobility, serpentine soils, contamination, toxicity



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INTRODUCTION

Elemental chromium (Cr) was discovered by French chemist Louis Vauquelin (1797) in the mineral crocoite (PbCrO_4) in a Siberian gold mine (Nriagu, Nieboer, 1988; Barceloux, Barceloux, 1999; Mohan, Pittman, 2006).

Cr is a natural component of the Earth's crust (average content 100–200 mg kg^{-1}), and belongs to 24 most common elements occurring in a variety of rock materials (igneous, metamorphic, sedimentary, etc.), especially ultramafic rocks and their derived soils. These materials form 1% of the terrestrial landscape, mostly within populated areas of the Circum-Pacific

and Mediterranean regions (Oze et al., 2007; Izbiicki et al., 2008; Mandal et al., 2011; Farkas et al., 2013; Scancar, Milacic, 2014).

As Cr is a relatively common element, especially in soils, its behaviour and toxicity strongly depend on its oxidation state. Cr occurs in the environment mostly as trivalent Cr(III) or hexavalent Cr(VI) ions (mainly as CrO_4^{2-} anions). In metallic form Cr exists in its zero-valent state as elemental Cr(0) (Bartlett, James, 1979; Barceloux, Barceloux, 1999; Kimbrough et al., 1999; Legrand et al., 2004; Scancar, Milacic, 2014).

In soils, Cr naturally occurs primarily as trivalent Cr(III) cations, strongly bound to negatively charged

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soil particles, binding on iron and aluminum oxides and hydroxides or/and complexes with organic compounds in a slightly acidic and alkaline conditions. Thus Cr(III) is only slightly mobile, less subjected to leaching in the soil profile and much less toxic than Cr(VI) (Bartlett, James, 1979; Zayed, Terry, 2003; Dhal et al., 2013; Scancar, Milacic, 2014). Cr(III) is discussed as an important micronutrient, and also less susceptible to biological uptake (Pechova, Pavlata, 2007).

On the other hand, Cr(VI)-oxyanions are known as highly toxic and mobile compounds, only weakly adsorbed by soil particles, soluble in the full pH range and stable under strongly alkaline conditions. These properties make Cr(VI) easily leached into groundwater and more readily available for uptake by plants, due to the active mechanism of plant acceptance by transportation through tissues. Although Cr(III) is considered as a very stable form in common soils, presence of oxidized Mn (as electron acceptor for oxidation) may rapidly change its form from Cr(III) to Cr(VI) (Bartlett, James, 1979; Hossner et al., 1998; Zayed, Terry, 2003; Guha, 2004; Banks et al., 2006; Cheung, Gu, 2007; Onweremadu, Uhegbu, 2007; Barrera-Diaz et al., 2012; Dhal et al., 2013; Scancar, Milacic, 2014; Choppala et al., 2015; Mandal et al., 2016; Kunhikrishnan et al., 2017).

GEOCHEMISTRY – NATURAL OCCURRENCE OF HIGH CHROMIUM CONCENTRATIONS IN THE ENVIRONMENT

Serpentine soils formed on ultramafic rocks (peridotite and pyroxenite) or serpentinite (metamorphosed ultramafic rock), mainly ophiolitic serpentinites, belong to primary natural sources of Cr with typically elevated Cr concentrations exceeding 200 mg kg^{-1} . The main sources of Cr are chromite (trivalent Cr; $\text{Fe}(\text{Fe},\text{Cr})_2\text{O}_4$) and Cr-magnetite (hexavalent Cr; $\text{Fe}(\text{Fe},\text{Cr})_2\text{O}_4$) (minerals from spinel group) (Becquer et al., 2003; Oze et al., 2004a, b).

Serpentine soils typically show a high content of Mg, Fe and trace elements Ni, Cr, Cd, Co, Cu, Mn and, on the contrary, significantly decreased levels of plant nutrients as Ca, K, N, P. Especially the elevated levels of Cr and Ni pose an environmental risk, the same as high concentrations (generally more than 200 mg kg^{-1}) of Mn, namely in oxidized forms, which may indicate a significant potential for oxidation of Cr(III) to Cr(VI). However Cr-chromite and Cr-magnetite phases do not weather easily, thus present Cr occurs mostly in its trivalent Cr(III) state, bound in Cr-spinels, Cr-bearing silicates and clay minerals (Cr-chlorite, Cr-garnet, Cr-mica, and Cr-epidote) (Becquer et al., 2003; Oze et al., 2004b; Bilbao et al., 2008; Chang et al., 2013; Baumeister

et al., 2015). Fe occurs in a variety of Fe(III) oxides (magnetite and hematite) and Fe(III) (oxy)hydroxides. Phyllosilicates consist of serpentines and chlorites and the most common clays are smectites and vermiculites. The pH of these soils is then ranging from 4 to 9, but mostly is slightly acidic (± 6) (Oze et al., 2004b).

Specific properties of serpentine soils create a quite extreme environment for plants and organisms, resulting in special plant biotopes called 'serpentine syndrome'. This vegetation is typical by reduced stature, increased tolerance to high levels of Mg and Ni, and in comparison with plants on other types of soil it shows better developed root systems but slower growth (Kruckeberg, 2004; Oze et al., 2004a, b; Baumeister et al., 2015).

After release by weathering from chromite, Cr(III) is mainly adsorbed on clay minerals, precipitates with Al(III) or Fe(III)-hydroxides in its trivalent form (Oze et al., 2007).

Natural oxidation of Cr(III) occurs basically in the presence of Mn(IV/III)-oxides, commonly birnessite, forming surface coatings on soil minerals, which are the most important naturally occurring oxidants of Cr(III) and under conditions of $\text{pH} < 9$ (Milacic, Stupar, 1995; Becquer et al., 2003; Oze et al., 2007).

In common soils and rocks Cr occurs mostly in Cr(III) trivalent form as amorphous Fe(III)-Cr(III)-hydroxide, eskolaite (Cr_2O_3) and chromite. Its concentrations reach to 200 mg kg^{-1} , in dependence on the texture of matrix, when soils with fine-grain sizes have higher concentrations than sandy sediments (large-grained), granite and carbonates. In soils developed on ultramafic rocks the levels of Cr reach up to $10\,000 \text{ mg kg}^{-1}$. As mentioned above, high levels of Cr(VI) are mostly caused by anthropogenic activity, serpentine soils have been reported as a natural source raising Cr(VI) in the environment as well (Becquer et al., 2003; Hawley et al., 2004; Oze et al., 2004a, b, 2007).

The highest levels of released Cr(VI) from serpentine soils have been found in New Caledonia, where displacement of Cr(VI) from mineral surfaces by phosphate (coming from nutrient amendments) was the main factor of contamination by Cr(VI) (Oze et al., 2007). Significant amounts of Cr(VI) were detected under vegetation at these soils, where concentrations of soluble Cr increased (from 15 to $700 \mu\text{g l}^{-1}$) after application of phosphorus fertilizer (Becquer et al., 2003; Novak et al., 2014).

Also a study focused on contamination by Cr(VI) leached from serpentine soils in ground- and surface waters from New Caledonia, California, Italy, and Mexico found levels of aqueous Cr(VI) up to $73 \mu\text{g l}^{-1}$ (exceeding the World Health Organization's limit for drinking water – $50 \mu\text{g l}^{-1}$) (WHO, 2003; Oze et al., 2007).

Study of Kierczak et al. (2008) demonstrated higher mobility of Cr from anthropogenic pollution

than from lithogenic matrices (Kierczak et al., 2008). It even seems that mobility of Cr in serpentine soils is quite limited; once river or groundwater are draining ultramafic (also metamorphic, volcanic or limestone) rocks, ideal conditions for Cr release and redox cycling are created.

Alkaline river water in ultramafic catchments is also naturally enriched with Cr (up to $30 \mu\text{g l}^{-1}$) as the alkaline environment enhance Cr(VI) (MgCrO_4 , CrO_4^{2-}) and also Cr(III) ($\text{Cr}(\text{OH})_3$, $\text{CrOH}(\text{CO}_3)_2^{2-}$) (McClain, Maher, 2016) leaching from Cr(III)-containing minerals under oxic conditions. Concentrations of Cr(VI) dissolved from chromite (FeCr_2O_4) are linearly increasing in dependence on residence time of water (Novak et al., 2014; Saputro et al., 2014; Manning et al., 2015; McClain, Maher, 2016).

ANTHROPOGENIC POLLUTION

There is a wide range of anthropogenic pollution sources such as: metallurgical industry and steel slag, pigments in leather tanning and dyeing, wastes, fungicides, corrosion inhibitors in cooling water and drilling muds, wall papers, photographic films, magnetic tapes, printing inks, sewages, gas contaminants, electroplating, chemical manufacturing, wood treatment, glass, ceramics and cement products, and contaminations caused by poor storage and improper disposal practices during these work processes, as well as from the burning of natural gas, oil, or coal (Palmer, Wittbrodt, 1991; EPA, 1998; Kotas, Stasicka, 2000; Leita et al., 2009; U.S. ATSDR, 2012; Yao et al., 2012; Allue et al., 2014; Scancar, Milacic, 2014; Radziemska et al., 2016). Once Cr is released from liquid and solid waste sources, it can be found in air, soil, and water. While Cr is not stable in the atmosphere, the main polluted deposits are soils, surface- and groundwaters (Palmer, Wittbrodt, 1991; Guha et al., 2001; Jacobs, Testa, 2004; U.S. ATSDR, 2012). Even settlements, deforestation, agriculture, recreational activities and soil erosion may be sources of Cr contamination of the drinking water resources (Iqbal et al., 2013). Thus occurrence in atmosphere, waters and soils and possible transport to plants and via food chains to animals, makes Cr potentially harmful. For humans the most dangerous intake of Cr is via inhalation, drinking, eating and skin (U.S. ATSDR, 2012).

The major Cr ore is chromite (FeCr_2O_4) and less common sources are crocoite (PbCrO_4) and eskolaite (Cr_2O_3). Chromium ore is mined mainly in South Africa, Russia, Kazakhstan, India, Turkey and Philippines (Cornelis et al., 2005; Mohan, Pittman, 2006).

Reserves found in India belong to the world's 30 most polluted places due to mining processes and natural oxidation of chromite (Dhal et al., 2013).

Natural concentrations of total aqueous Cr in groundwater are typically below $10 \mu\text{g l}^{-1}$ while at contaminated sites levels of Cr(VI) are generally reaching 300 to $500 \mu\text{g l}^{-1}$ (Hawley et al., 2004). Also anomalous natural Cr(VI) concentrations, related with high redox potential, pH values exceeding 10, and high concentrations of Na in groundwaters of the sandstone aquifer in the Brazilian Bauru Basin reaching the highest concentrations of Cr(VI) $130 \mu\text{g l}^{-1}$ have been reported (Bertolo et al., 2011). A yellow colour is imparted to the water at about $1000 \mu\text{g l}^{-1}$ Cr(VI) (Palmer, Wittbrodt, 1991).

According to the World Health Organization provisional guideline values are $50 \mu\text{g l}^{-1}$ for total Cr concentrations, common levels of total Cr in drinking water are usually less than $2 \mu\text{g l}^{-1}$, but even actual concentrations reaching $120 \mu\text{g l}^{-1}$ have been detected (WHO, 2008).

Due to known toxic effects of Cr, its concentrations present in water, soil and food are controlled. EPA's maximum contaminant level goal for total Cr in drinking-waters is $100 \mu\text{g l}^{-1}$ (U.S. EPA, 2017). For example, the State of California standard in line with European Council Directive as well as the Czech Republic standard state a limit for total Cr content in drinking water not exceeding $50 \mu\text{g l}^{-1}$ (Decree 252/2004 Coll.; Council Directive 98/83/EC, 1998; Choppala et al., 2013a; EPA, 2017; Economou-Eliopoulos et al., 2017).

The maximum threshold level of Cr(III) in waste and groundwaters is $5000 \mu\text{g l}^{-1}$. For Cr (total), the maximum permissible limit is $2000 \mu\text{g l}^{-1}$ for surface waters, while goal for Cr(VI) in landfill discharge is $100 \mu\text{g l}^{-1}$, and for drinking water only $50 \mu\text{g l}^{-1}$ of Cr(VI) (Choppala et al., 2013a; Mandal et al., 2016).

Common condition of high Cr leaching from soils or rocks into ground- and surface waters is considerably acidic or alkaline pH. Anthropogenically contaminated soils are generally more susceptible to Cr leaching, compared to only slightly weathered rocks and naturally enriched soils. However, leaching is controlled by a variety of other factors, such as present complexing agents (organic matter, S^{2-} , Fe(II), Na, PO_4^{3-} , etc.), phase (liquid/solid/gas) of the contaminant, age of the binding and others (Jacobs, Testa, 2004; Scancar, Milacic, 2014; Manning et al., 2015; McClain, Maher, 2016). More detailed description of Cr behaviour in the soil environment is described in the following section.

CHROMIUM OCCURRENCE IN THE ENVIRONMENT AND ITS TOXICITY

Chromium toxicity

First cases of carcinogenic effects – nose tumors caused by Cr pigments of Cr(VI) and lung cancer

described in 1830s led to many discoveries on Cr chemical and physical properties. While trivalent Cr is after years known as an important nutrient (demonstrated in 1959) essential to normal carbohydrate, lipid and protein metabolism with recommended daily dose for humans about 20–200 µg (Kotas, Stasicka, 2000; Pechova, Pavlata, 2007; Li et al., 2012; U.S. ATSDR, 2012; Choppala et al., 2013a; Rockett et al., 2015), hexavalent Cr is a strongly toxic element, which harmfully affects plants and living organisms including humans.

Due to its high oxidative capacity, Cr(VI) forms cross biological membranes readily and their reactions with genetic matter lead to carcinogenic and mutagenic effects and skin dermatitis (Zayed, Terry, 2003; Banks et al., 2006; Pechova, Pavlata, 2007; Scancar, Milacic, 2014). Also Cr(III) may cause harmful effects, but in comparison with Cr(VI) it is far less toxic (Scancar, Milacic, 2014).

Speciation of chromium in the soil environment

Information about the presence, oxidation state and study of the fate of Cr in soil and groundwater ecosystems have a great importance due to high toxicity and carcinogenicity of Cr(VI) and potential transport of Cr via surface- or groundwater (U.S. DOE, 2006; Leita et al., 2009). Differences in behaviour are coming from different (+/-) charges of Cr(III) and Cr(VI) compounds and their various physical and chemical properties and reactivity. Distribution and speciation is governed by a combination of geochemical processes as oxidation, reduction, adsorption, and precipitation, however the oxidation state mainly depends on the pH and redox conditions (Kotas, Stasicka, 2000; Guha et al., 2001; Li et al., 2012).

Cr behaviour depends on its negative correlation with pH and redox potential. Reduction occurs most readily at acidic pH, whereas oxidation is faster at strongly alkaline pH. These extremely basic conditions are barely found in the natural environment, however they can occur at anthropogenically contaminated sites (Cornelis et al., 2005; Barrera-Diaz et al., 2012).

Thus, soil pH is a key factor affecting geochemical behaviour of Cr in soil–water systems, especially sorption and desorption and speciation (Shahid et al., 2017). Low temperature slows the kinetics of oxidizing reaction as well (Nriagu, Nieboer, 1988).

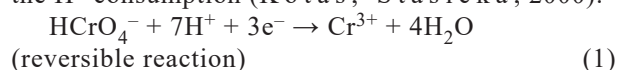
When Cr occurs in the aquatic environment, with no present agents except H₂O and OH⁻, then Cr(III) exists as hexa-aqua Cr(H₂O)₆³⁺ complex (Cr³⁺) when the pH of solution is higher than 4.0. In less acidic solution Cr(H₂O)₆³⁺ hydrolyzes to the form Cr(H₂O)₅(OH)²⁺ (abbreviated as Cr(OH)²⁺) and Cr(H₂O)₄(OH)₂⁺ (abbreviated as Cr(OH)₂⁺). From the neutral to alkaline pH region, reduced Cr precipitates as a relatively insoluble Cr(OH)_{3(s)}. When alkaline solution pH is higher than 11.5, the precipitate is dissolved forming

tetrahydroxo Cr(OH)₄⁻ complex. In solutions with Cr(III) concentrations above 10⁻⁶ mol l⁻¹, Cr(III) leads up to polymerization (Palmer, Wittbrodt, 1991; Scancar, Milacic, 2014).

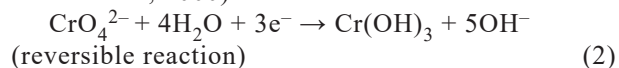
In the natural environment Cr species of Cr(III) as CrOH²⁺, Cr(OH)₃⁰, Cr(OH)₄⁻, and Cr(OH)₂²⁻ are the most frequent, which are slightly soluble and therefore less mobile than those of Cr(VI). The Cr(VI) mostly occurs as soluble anion over a wide pH range in chromates (CrO₄²⁻), hydrochromates (HCrO₄⁻), and dichromates (Cr₂O₇²⁻), especially in strongly oxidizing environments (Bartlett, 1991; Sharma, Forster, 1995; Barrera-Diaz et al., 2012; Choppala et al., 2012). Cr(VI) present as oxyanion is easily adsorbed on the surface of minerals at low pH range due to positive charge of the surface bearing inorganic hydroxyl groups (clay particles of iron, aluminium and manganese), but adsorption is limited at high pH values (Palmer, Wittbrodt, 1991; Kimbrough et al., 1999; Leita et al., 2009; Fibbi et al., 2012; Landrot et al., 2012; Choppala et al., 2013b; Scancar, Milacic, 2014). The reduction process at acidic pH is faster than in alkaline pH (Leita et al., 2009; Landrot et al., 2012; Choppala et al., 2013b; Scancar, Milacic, 2014).

The Cr(VI) form H₂CrO₄, a strong acid, deprotonated when the pH is higher than 1, produces HCr₂O₇⁻ which occurs within the pH range 1–6.5. CrO₄²⁻ are the only ions existing when the pH is higher than 6.5. At higher Cr(VI) concentrations (more than 10⁻² mol l⁻¹) HCr₂O₇⁻ begins to polymerize, resulting in Cr₂O₇²⁻ dimer formation (Palmer, Wittbrodt, 1991; Mohan, Pittman, 2006; Scancar, Milacic, 2014). Main thermodynamically stable Cr species diluted in aqueous solutions in dependence on pH and redox potential are shown in the Pourbaix Eh-pH diagram (Fig. 1).

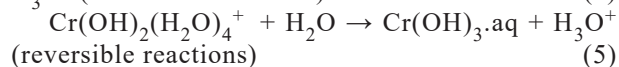
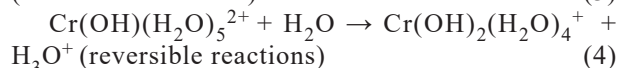
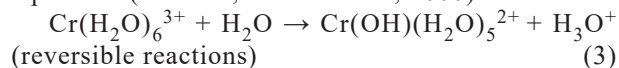
Equation (1) shows the Cr(VI) reduction in acidic solution, where Cr has a very high positive redox potential. The reduction of HCrO₄⁻ is accompanied by the H⁺ consumption (Kotas, Stasicka, 2000):



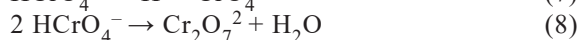
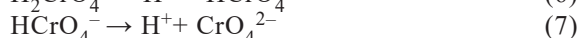
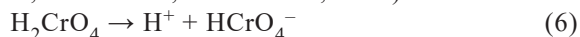
In more basic solution the reduction of CrO₄²⁻ proceeds according to the following reaction (Kotas, Stasicka, 2000):



In the absence of complexing agents, other than H₂O or OH⁻, Cr(III) occurs as hexa-aquachromium and its products of hydrolysis, shown in the following equations (Kotas, Stasicka, 2000):



The following reactions (6–8) illustrate several Cr(VI) species, as they are dependent on both pH and total Cr(VI) concentration (Kotas, Stasicka, 2000; Scancar, Milacic, 2014):



Redox behaviour of chromium

There are a number of agents, which can mitigate the toxicity of Cr(VI) by its reduction to Cr(III) species (Choppala et al., 2012). Reduction of Cr(VI) to Cr(III) can proceed in the presence of electron donors such as available carbon and reduced Fe(II) ions, increasing in acid conditions. Generally, reduction of Cr(VI) to Cr(III) affecting immobilization of Cr(III) via adsorption and precipitation belongs to the main reducing processes (Park et al., 2005, 2006; Mohan, Pittman, 2006; Choppala et al., 2015).

Due to reduction processes, when Cr(VI) in soils undergoes proton (H^+) consumption (or hydroxyl (OH^-) release) forming Cr(III), soil pH is increasing (Park et al., 2006). This leads to enhanced Cr(III) adsorption, related to pH-dependent surface charge and precipitation as $\text{Cr}(\text{OH})_3$ (Park et al., 2006; Choppala et al., 2015; von der Heyden, Roychoudhury, 2015).

Reduction of chromium

Influence of Fe. Chromium present in soils is associated with Fe-phases, Fe(II)-bearing minerals and

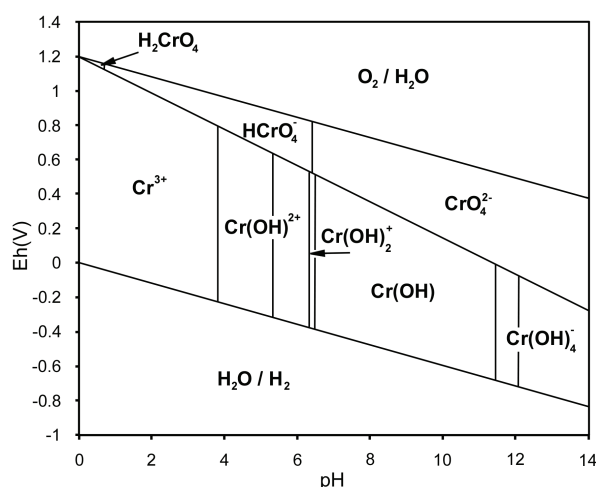


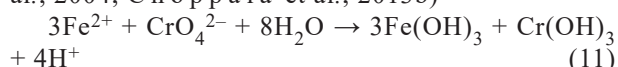
Fig. 1. Pourbaix diagram (Eh-pH diagram). Main thermodynamically stable Cr species diluted in aqueous solutions (no other complexing agents than H_2O or OH^-) in dependence on pH and redox potential. Concentration of total Cr is 10^{-6} mol l $^{-1}$ (according to Scancar, Milacic, 2014)

dissolved Fe(II) species, respectively (Legrand et al. 2004; Gao, Schulze, 2010). Ferrous oxides and oxyhydroxides as ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$), goethite (FeOOH) and hematite (Fe_2O_3) can reduce toxic Cr(VI) to less toxic Cr(III), especially due to their abundant occurrence and large surface area (surface area decreases in the order ferrihydrite > goethite > hematite) (Legrand et al., 2004; Stanin, 2004; Gao, Schulze, 2010; Choppala et al., 2013b; Longmire et al., 2013; von der Heyden, Roychoudhury, 2015).

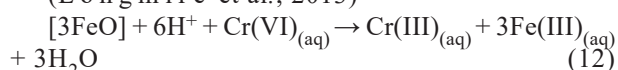
The main reduction equations (9–12) are as follows:

$$3\text{Fe}^{2+} + \text{CrO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow 3\text{Fe}^{3+} + \text{Cr}^{3+} + 8\text{OH}^- \quad (9)$$

$\text{Cr}^{6+} + 3\text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+}$ respectively (Palmer, Wittbrodt, 1991; Legrand et al., 2004; Choppala et al., 2013b)



(Longmire et al., 2013)



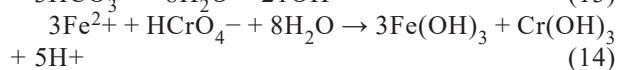
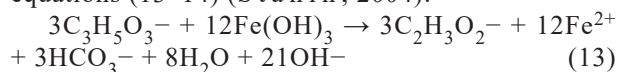
Stanin, 2004).

Trivalent state Cr(III), the most thermodynamically stable form of Cr in soils, co-precipitates with goethite (a- FeOOH) forming an a-(Fe,Cr)OOH solid solution. This happens due to the structural similarity between the host Fe(III) mineral and the pure Cr surface precipitate phase (a- CrOOH) (Charlet, Manceau, 1992; Leita et al., 2009; Landrot et al., 2012).

The reduction of Cr(VI) by ferrous iron can be described by the overall reaction (Eq. 10), when the pH of solution is less than 10 and concentrations of PO_4^{3-} are less than 0.1 mM (Palmer, Wittbrodt, 1991). Phosphate (PO_4^{3-}) and common use of phosphorus amendments into the soil are known to increase the rate of oxidation of Fe(II) by dissolved oxygen, thus decreasing the reduction potential of ferrous iron. Also phosphate may substitute Cr(VI), due to the competition for the same sites in alkaline pH from mineral surfaces, which leads to the increase of Cr(VI) concentrations (Nriagu, Nieboer, 1988; Palmer, Wittbrodt, 1991; Oze et al., 2007).

Other reducing agents. Besides ferrous oxides, Cr(VI) can be naturally reduced to Cr(III) by other various reducing agents as S^{2-} ions of sulfides, dissolved organic carbon in organic matter (DOC) and also by microbial communities, even though increasing levels of Cr in soils decrease microbial respiration and plant growth as well. Simultaneously organic carbon stimulates microorganisms and increases levels of DOC, which is an important electron donor in the reduction processes of Cr(VI) ions (Palmer, Wittbrodt, 1991; Wittbrodt, Palmer, 1997; Stanin, 2004; Cheung, Gu, 2007; Choppala et al., 2012; Scancar, Milacic, 2014). A reducing effect of the brown seaweed *Ecklonia sp.* biomass has been published (Park et al., 2005). Microbial respiration

commonly accompanying reduction processes and respiratory by-products is presented in the following equations (13–14) (Staniin, 2004):



Further, Cr(VI) can be immobilized by reduction and sorption onto soil colloids, a mechanism depending on their special properties (quality and quantity of the clay-minerals, inorganic carbon, cation exchange capacity and pH conditions), although under alkaline to sub-neutral conditions the process of sorption Cr(VI) does not work (Wittbrodt, Palmer, 1997; Banks et al., 2006; Leita et al., 2009; Landrot et al., 2012; Scancar, Milacic, 2014). Inorganic Cr(III) can be sorbed by silicates, due to their partially negatively charged surfaces, while Cr(III) organic complexes are rather sorbed by organic matter. Actual behaviour and kinetics of these processes are strongly dependent on pH, extent of surface area, number of active sites, and temperature (Cornelis et al., 2005).

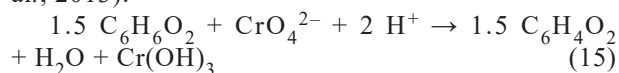
It is possible that both Cr(VI) reduction (i.e. proton-consuming reaction) and Cr(III) immobilization (i.e. proton release reaction) can occur simultaneously in soils. The Cr(VI) reduction accompanied by Cr(III) immobilization leads to the decrease of H⁺ consumption, resulting in smaller increase in pH than predicted (Choppala et al., 2013b).

Chromium complexes with natural organic matter are important for Cr speciation in different environments. While information on the coordination of chemistry and stability of Cr with natural organic matter are still not completely clear, a number of studies have described some of these relationships in the Cr–soil–water–organic matter system. Organic matter, such as humic acids and fulvic acids and also farmyard and poultry manures and composts, enables the reduction of free Cr(VI) ions in the soil solution under acidic conditions, because of its high redox potential value (> +1.3 V under standard conditions). Humic substances with Cr(III) form kinetically stable complexes which significantly affect its mobility in the environment. Bounding of these complexes on soil particles makes Cr(III) just slightly mobile, while soluble organic matter increases its mobility rapidly (Cornelis et al., 2005; Banks et al., 2006; Park et al., 2006; Choppala et al., 2012, 2013b, 2015; Gustafsson et al., 2014).

The presence of organic carbon provides a stock of electron donors, which is also the energy source for the microbial communities (Park et al., 2006; Choppala et al., 2012, 2015).

The reducing potential of organic carbon depends on its reactivity, concentration of pollution, and microbial activity (Choppala et al., 2012). Addition of organic amendments belongs, due to their functions, to remediation processes (Choppala et al., 2015).

Soil organic matter containing hydroquinone (C₆H₆O₂) (natural organic matter) acts as potential electron donors for the reduction of Cr(VI) according to the following equation (15) (Longmire et al., 2013):



It has been reported that humic acids may prevent reduction of Cr(VI) via supramolecular interaction between Cr(VI) and humic acids micelles. Thus humic acids may increase the uptake by plants, bioavailability and mobility of Cr in the environment leading to venting the toxicity of hyper-accumulated Cr(III) (Leita et al., 2009; Wittbrodt, Palmer, 1997). The accumulation of Cr(III) by plants is increased in the presence of organic acids: while amino acids are less effective, carboxylic acids are more effective in the mobilization of Cr from soil (Srivastava et al., 1999; Leita et al., 2009).

Oxidation of chromium

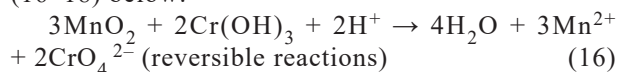
Kinetics of the Cr(III) oxidation depends on a variety of factors as biological, geological and chemical conditions, including pH, redox and occurrence of present nutrients, as well as microbial activity making the actual ratio of Cr(VI)/Cr(III) very complex (Hawley et al., 2004). Oxidation of Cr in soil can be facilitated by present low molecular mass organic acids (citrate, gallic acid, etc.), which increase mobility and solubility of Cr(III). On the other hand, complexation with high molecular mass organic ligands is very stable and relatively dissociation- and oxidation- resistant (Nriagu, Nieboer, 1988).

Oxidation by manganese oxides. The trivalent form Cr(III) creates strong complexes widely bound to soil minerals. This makes it less soluble, less available for plant uptake, thereby much less toxic for plants and organisms (Choppala et al., 2013b).

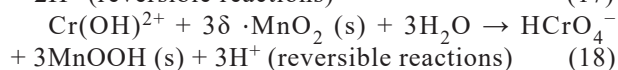
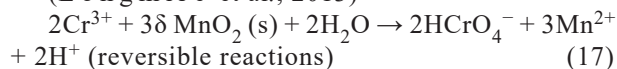
Mn oxides, which occur commonly as coatings on mineral grains and are the only known naturally occurring oxidants of Cr, catalyze the oxidation of Cr(III) to Cr(VI) (Guha et al., 2001). However Cr(III) ions are also sorbed to Mn oxides, especially at acidic pH range, when soluble Cr(III) is easily adsorbed on the surface of negatively charged Mn(IV) oxides (zero point of charge is in the range of 2–5). The oxidation process by Mn(IV) oxides can be increased in the presence of low-molecular-mass organic ligands in soil. Therefore Mn(IV) oxides are the most important natural oxidants for Cr(III) in soils, sediments, and waters (Reddy, DeLaune, 2008; Landrot et al., 2012; Scancar, Milacic, 2014).

In the presence of the base anhydrides such as MgO, FeO, and CaO, pH is rapidly increased. Once alkaline pH releases their respective hydroxides into water, combination of increased alkalinity of water, oxidation by ferrous–ferric conversion and the presence

of Mn oxides lead to the transformation of Cr(III) to Cr(VI) (Dhal et al., 2013). Chromium reactivity in the presence of Mn(IV) oxides is shown in equations (16–18) below:



(L ong m i r e et al., 2013)



(S t a n i n , 2004).

Even though Mn oxides are important agents in natural oxidation of Cr(III), reduction by organic matter is a significant competitor changing the Cr(III) and Cr(VI) ratio in soils (N r i a g u , N i e b o e r , 1988).

Oxidation of Cr by Mn agents can be also blocked by Mn(IV) reduction to Mn(II) ions, formed during Cr oxidation bonded on the surface of Mn(IV) oxides. This corresponds to the findings that Cr oxidation is increasing as extractable Mn is decreasing (N r i a g u , N i e b o e r , 1988).

Elementary transformation, oxidation and reduction processes of Cr in soil and soil solution are schematized in Fig. 2 presenting an overview of general oxidation-reduction processes of Cr in soil and soil solution.

The transformation scheme shows the Cr–soil–water transport system, where Cr(III) is mobile in both directions, from soil to water via solubilization or complexation and from the water to soil via adsorption or precipitation, while Cr(VI) passes only from soil to the water system via desorption or diffusion or stays adsorbed in soil.

Knowledge on chromium oxidizing (KMnO_4 , H_2O_2 , HClO_4 , MnO_2 , PbO_2 , $\text{K}_2\text{S}_2\text{O}_8$, bromine water ($\text{Br}_2 + \text{H}_2\text{O}$), CCl_4 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, etc.) and reducing (H_3SO_3 , $\text{Fe}(\text{OH})_2$, ascorbic acid, hydroquinone, SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, etc.) agents was used in many studies

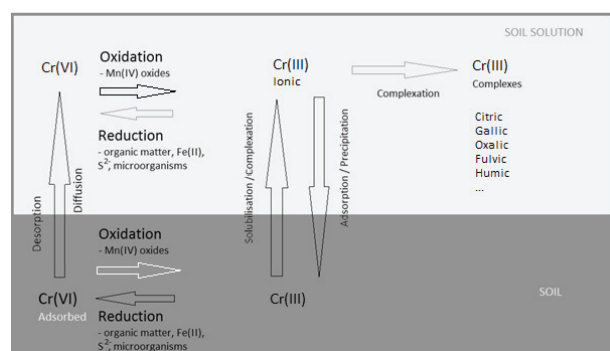


Fig. 2. Transformation, oxidation and reduction processes of Cr in soil and soil solution (according to S c a n c a r , M i l a c i c , 2014)

(L i c h t i n , 1930; Y a m a m o t o , O h a s h i , 1970; H a r a , 1983; D u l s k i , 1996; R e v a n a s i d d a p p a , K i r a n K u m a r , 2001; B o r g e s e t . a l . , 2002; M a , T a n n e r , 2008; S c a n c a r , M i l a c i c , 2014). At present, however, methods for the use of complexing agents, precipitation, adsorption and, above all, the effort to analyze natural samples in unchanged form come to the fore.

ANALYTICAL SPECIATION METHODS AND PROBLEMS ASSOCIATED WITH Cr(III)/Cr(VI) DETERMINATION

Environmental conditions of soils and water evidently represent a very complex system and thus there are a number of factors affecting Cr speciation, resorption, coprecipitation, fractionation and distribution as summarized in the literature review. These findings suggest reliable assessment of Cr fate and potential toxicity and transport is a really difficult task and determination of its species is quite limited.

Errors occurring during sample processing and during extraction lead to over- or under- estimation of each Cr(III)/Cr(VI) concentration results.

To reach relevant and close to original speciation data it is necessary to fulfill the requirements for sampling, conservation of species during the sample storage, sample pretreatment, extraction, separation and the determination of Cr species.

Performance of the speciation analysis directly after sampling has a great importance as well (K a r a t e p e e t a l . , 2010; L a n d r o t e t a l . , 2012; S c a n c a r , M i l a c i c , 2014; M a r c i n k o w s k a e t a l . , 2016).

Processes affecting the Cr form during treatment have been described. The water content (naturally moist/dried sample) quite significantly affects manganese oxidation-reduction processes in soil important for potential Mn oxidation of Cr (K a b a t a - P e n d i a s , M u k h e r j e e , 2007; T r e b i e n e t a l . , 2011; W o l f e t a l . , 2011). Refrigeration or freezing of leachates for Cr speciation disturbs the speciation of the real sample after quite a short time (W o l f e t a l . , 2011). Also the type of polypropylene and glass vials or PVC tubes may affect reliability of the analysis due to background contamination (M a r c i n k o w s k a e t a l . , 2016).

Changes in Cr speciation during a few-day storage depending on the content of organic matter, concentration of Cr and pH of soil have been observed (K o z u h e t a l . , 2000).

As Cr(VI) converts rapidly to Cr(III) under acidic conditions, according to USEPA methods aqueous samples must be preserved at pH of 9.0–9.5 and analyzed within 24 h (W o l f e t a l . , 2011).

Sensitivity of the instrumental technologies for Cr determination had been rather insufficient until the mid-1980s. To determine Cr(VI) in natural samples,

generally preconcentration was necessary, feasible rather for specialized laboratories than regular monitoring (Catalani et al., 2015).

Since then numerous studies have been performed to disclose the behaviour of Cr in complex environmental systems, as well as to optimize its determination, especially speciation methods. Selective techniques for the speciation and determination of Cr include liquid to liquid or solid phase extraction, coprecipitation, electrodeposition followed by appropriate instrumental analysis (Karatepe et al., 2010).

However, for each speciation method it is necessary to avoid errors and to set up the method correctly, as the Cr species are not stable. Some complications which may occur during the Cr determination have been described (IAEA, 2007; Karatepe et al., 2010; Novotnik et al., 2013; Scancar, Milacic, 2014; Catalani et al., 2015; Marcinkowska et al., 2016).

Alkaline extraction with sodium carbonate or sodium hydroxide was one of frequently used methods for Cr(VI) determination in environmental matrix samples. During the extraction process soluble Cr(III) can be oxidized, which may lead to falsely positive detection of Cr(VI). This was the case of the Cr(VI) detection in food samples when measuring Cr using electrothermal atomic absorption spectrometry (ETAAS) after alkaline extraction. It was a serious issue, as Cr(VI) should be reduced to Cr(III) in the presence of organic matter, once it is not stable in this matrix (Novotnik et al., 2013, 2015; E F S A , 2014; Vacchina et al., 2015).

Also Cr(VI) determination in coloured samples by spectrophotometry, interference effects caused by the presence of coloured species as turbidity and

colloidal particles occur. Thus the coloured species must be removed by selective retention sorbents, for example columns filled with Florisil in the determination of Cr(VI) in dyed leathers (Scancar, 2007a; Scancar, Milacic, 2014).

In the case of using HPLC for Cr determination, parameters such as column type, eluent composition and pH, as well as injection volume must be optimized (Catalani et al., 2015).

A number of factors needed to be taken into account while measuring Cr with LC-ICP-MS technique have been described. Matrix effect of high salt content, chlorides, sulphates, carbon compounds, organic ligands, corrosion of metallic parts of the instrument, underestimation of Cr(VI) in acidic samples due to the reduction caused by electron donors of the eluent or chlorine polyatomic interferences, belong to complications of the method (Scancar, Milacic, 2014).

Multielement analyses are known for interferences which may disturb Cr speciation due to different separation conditions for Cr in the presence of other elements. Thus the application of complexing agent is needed (Marcinkowska et al., 2016).

The detection limits of selected Cr determination techniques are presented in Table 1.

CONCLUSION

Despite the Cr toxicity, mobility and speciation in the environment having been studied for decades, there are still numerous issues concerning how to pretreat and determine Cr in environmental samples properly because of the well-known Cr(VI) lability. Cr(VI) reacts with a lot of reducing agents, thus at small

Table 1. Determination methods

Method	Specie	Detection limits ($\mu\text{g. L}^{-1}$)	Detection limits ($\mu\text{g.kg}^{-1}$)	Detected values ($\mu\text{g. L}^{-1}$)	Detected values ($\mu\text{g.kg}^{-1}$)	References
HPLC-ICP-MS	Cr(tot)					Hagendorfer, Goessler, 2008; Mesheehy Nash, 2008; Bednar et al., 2009; Catalani et al., 2015; Marcinkowska et al., 2015, 2016, 2017; Sakai et al., 2013; Vacchina et al., 2015
including HPLC/ICP-DRC-MS	Cr(VI)	0.02–0.5	1–10	0.25–50	11–14530	
	Cr(III)	0.1–2.13		0.7–6.4	13–1800	
IC-ICP-MS	Cr(tot)					Rodriguez-Gonzalez et al., 2005; Sakai et al., 2005; Kutscher et al., 2012, 2016
	Cr(VI)	0.0009–10	0.0002	0.055–0.34	0.0425–77.50	
	Cr(III)	0.0132–10	0.00038	0.05	69.67–71.44	

GC-ICP-MS	Cr(tot)	0.0039–0.02		0.132–0.154		Yang et al., 2004
	Cr(VI)					
	Cr(III)					
CE-ICP-MS	Cr(tot)					Li, Yan, 2007; Chen et al., 2015
	Cr(VI)	0.1–1.9		25–40	5.14×10^5 -9.3×10^5	
	Cr(III)	0.18–1.8		25–42.5	4.71×10^5 -1.03×10^6	
ICP-MS	Cr(tot)	0.15–2.5	0.063–10		2.9 -1.842×10^4	van de Wiel, 2003; Balarama Krishna et al., 2005; Rodriguez-Gonzalez et al., 2005; Wilbur et al., 2012; Khan et al., 2013; Zhang et al., 2013
	Cr(VI)	1–5	2.4	0.04–970		
	Cr(III)	1–5	1.2	0.09–1940		
ICP-OES/AES	Cr(tot)	0.65–36*	4.443	3.75	1.7×10^3 -1.5×10^5	Miyazaki, Barnes, 1981; Hwang, Wang, 1994; van de Wiel, 2003; Narin et al., 2006; Wilbur et al., 2012; Khan et al., 2013; Coelho, 2016
	Cr(VI)	0.4–6		200–2000	3.38×10^3 -2.7×10^4	
	Cr(III)	0.81–6				
IC with suppressed conductivity detection	Cr(tot)					Madden et al., 2011; Aggrawal, Rohrer, 2016
	Cr(VI)	0.17–0.64	1.711–4.66 ppt	1.17–11.4	21.01 ppt –1.17 ppb	
	Cr(III)					
IC-UV/Vis with postcolumn derivatization	Cr(tot)					Dionex, 2003; Thermo Fisher Scientific, 2012; Wilbur et al., 2012; Basumallick, Rohrer, 2016
	Cr(VI)	0.001–1		0.0032 –0.2690		
	Cr(III)					
FPLC-ETAAS/ CIM-ETAAS	Cr(tot)					IAEA, 2007; Scancar et al., 2007b
	Cr(VI)	1.5	15–20	47–71.4	1.27×10^5 -1.035×10^6	
	Cr(III)					
ET-AAS	Cr(tot)	0.18		0.05–0.5		Sperling et al., 1992; Husakova et al., 2005
	Cr(VI)	0.16		0.05–0.5		
	Cr(III)					
AAS/GFAAS/FAAS	Cr(tot)	5		$15-5 \times 10^4$		Sperling et al., 1992; Narin et al., 2006; Wilbur et al., 2012
	Cr(VI)	0.3–2.3		$5-5 \times 10^4$		
	Cr(III)	0.1–1		20–2000		

NAA/RNAA	Cr(tot)	5	4.88		1390–5450	Wilbur et al., 2012; Kuzelewska et al., 2016
	Cr(VI)					
	Cr(III)					
GC-FPD	Cr(tot)	2		0.1–19.6		Ding et al., 2005
	Cr(VI)					
	Cr(III)					
XRF	Cr(tot)		< 10 ppm –0.05 µg.kg ⁻¹ **		< 2.265 × 10 ⁸	Hurst et al., 2011
	Cr(VI)					
	Cr(III)					
DPAdSV	Cr(tot)	0.00957		0.178 –1.134 × 10 ⁴		Dominguez et al., 2001; Dominguez , Arcos, 2002; Dominguez-Renedo et al., 2008
	Cr(VI)	0.057 –0.644		0.04 –3.510 × 10 ³		
	Cr(III)	1.56		0.053 –1.134 × 10 ⁴		
CAdSV	Cr(tot)	0.002		0.05–1.51		Bobrowski et al., 2004; Husakova et al., 2005; Bas, 2006
	Cr(VI)	0.00988 –0.00416		0.097–0.60		
	Cr(III)					
Coulometry	Cr(tot)					Manova et al., 2007
	Cr(VI)	1.9		< 1.9–51		
	Cr(III)					
Spectrophotometry	Cr(tot)					Wrobel et al., 1997; Scancar et al., 2007a; Nagaraj et al., 2009; Rezic, Zeiner, 2009
	Cr(VI)	0.06–15	500–2500	< 0.5–716	300–3000	
	Cr(III)					

HPLC = high pressure liquid chromatography, ICP = inductively coupled plasma, MS = mass spectrometry, LC = liquid chromatography, GC = gas chromatography, CE = capillary electrophoresis, IC = ion chromatography, OES = optical emission spectrometry, AES = atomic emission spectrometry, FPLC = fast protein liquid chromatography, ETAAS = electrothermal atomic absorption spectrometry, CIM = convective interaction media, AAS = atomic absorption spectrophotometry, GFAAS = graphite furnace atomic absorption spectrometry, FAAS = flame atomic absorption spectroscopy, NAA = neutron activation analysis, RNAA = radiochemical neutron activation analysis, FPD = flame photometric detector, XRF = X-ray fluorescence analysis, CSPE = carbon screen-printed electrodes, DPAdSV = differential pulse adsorptive stripping voltammetry, CAdSV = catalytic adsorptive stripping voltammetry

*Detection limit (DL) value = 0.7 µg. L⁻¹ based on own experience,**DL value < 10 ppm based on own experience

concentrations it may not be considered a threat. In the case of known enormous contamination, however, the situation becomes difficult to handle, as Cr(VI) at high concentrations may be more stable and much more mobile.

Once Cr is a part of contamination in many production fields, it is transported in the soil-water system and also by atmospheric deposition. The need for the most accurate determination of possible toxic effects is therefore very strong. The most difficult task in studying the Cr speciation is to most accurately simulate and describe the influence of the environment in which it is present. Previous findings suggest that there is still a large field for application studies as to optimize the storage, methodology for pretreatment to increase reliability of Cr(III)/Cr(VI) separation and sensitivity of analytical instruments.

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