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THE PRESENCE OF CHROMIUM IN AGRICULTURAL SYSTEMS. A COMPREHENSIVE REVIEW

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Abstract

Currently, the entire world is facing major challenges related to agricultural practices and heavy metals contaminations of agricultural systems and food production. On the other hand, the structure, texture, and properties of the soil have deteriorated as a result of intensive conventional agriculture based on the addition of different inputs. Along with these, toxic metals affect agricultural soils, crops, food chain, becoming a major threat to living systems. Among these is chromium (Cr), an element naturally occurring in rocky soils and volcanic dust. The increased use of chromium in several multiple activities causes soil and water contamination. Differently from other heavy metals like lead, cadmium, and copper, chromium presents different degrees of toxicity depending on its chemical form. In the present review, we present data regarding chromium abundance in agricultural systems, factors favouring the absorption in the plant and bioaccumulation in different organs and tissues, bioaccumulation and translocation factors, its toxicity in plants, animals, and human through the food chain, and how it can be quantified using different types of analysis.

Key words: *chromium toxicity, chromium uptake and transport, environmental pollutant.*

INTRODUCTION

Environmental pollution with toxic metals became one of the most important issues that undermines global environmental sustainability efforts. In the last decades, the contamination, especially with hexavalent chromium [Cr (VI)] form in both terrestrial and aquatic ecosystems increased rapidly with industrialization, severely impacting our environment and natural resources, especially water and soil (Usman et al., 2020). If the crops are cultivated on a polluted agricultural soil, the toxic elements are translocated in crops and then through the entire food chain.

Contamination of water and soil with chromium can be made by fertilizers, fungicides, plastic film, sewage irrigation and industrial activities (mining, chemical industry, tannery wastes) and also from exhaust smoke of vehicles (Reijonen & Hartikainen, 2016; Li et al., 2020; Ahmad et al., 2021).

Having in view that chromium has a lot of environmental implications and negative effects on human and animal health, the aims of this paper were to review the literature data concerning chromium and to present its influence in agricultural systems, the bioaccumulation in different organs and tissues, its toxicity in plants, animals, and human through the food chain.

For the present study, several scientific journal articles, proceedings papers, reports and official methods were selected and reviewed. The literature search was carried out using the most important and commonly practical databases, such as Web of Science, Science Direct, Scopus, PubMed and Google Scholar.

Firstly, the following specific words were chosen: chromium in health, chromium in soil, chromium abundance in agricultural soil, chromium accumulation in plant organs, and toxicity of chromium, methods of extraction and analysis.

The publications were chosen, collected and reviewed based on the criteria of this paper which is correlated to the objective.

1. Chromium in soil

Governmental authorities and international organizations have set maximum permissible limits for chromium in soil.

The Word Health Organization (WHO) recommended safe limits for Cr (VI) in wastewater and soils used for agriculture are 0.05 $mg\cdot L^{-1}$ and 0.1 $mg\cdot kg^{-1}$ respectively (Kinuthia et al., 2020). In the agricultural soil, limit values for chromium are: in US 26 $mg\cdot kg^{-1}$, Spain 80 $mg\cdot kg^{-1}$, Croatia 80-120 $mg\cdot kg^{-1}$, Czech Republic 200 $mg\cdot kg^{-1}$and 64 $mg\cdot kg^{-1}$ in Canada (Broomandi et al., 2020; Christou et al., 2021). In Romania the safe limits for Cr 30 $mg\cdot kg^{-1}$, and for Cr (VI) 1 $mg\cdot kg^{-1}$, according to Environmental protection law no.137/1995. The use of irrigation water can have harmful effects on health because it can contain trace elements like chromium (Cr), nickel (Ni), cadmium (Cd). The maximum limits for irrigation water according to the policies of Netherlands and Spain and Belgium are 2 $mg\cdot L^{-1}$ for Cr (VI) and 5 $mg\cdot L^{-1}$ for total chromium in EU Member States (Tumolo et al., 2020).

The presence of high concentrations of Cd and Cr salts produce negative effects on chlorophyll and photosynthetic activities in plants (Del Bubba et al., 2013; Nawaz et al., 2021).

Cr mobility and bioavailability in soil is influenced by physiological and chemical properties of the soil such as: pH, electrical conductivity (EC), organic carbon content, cation exchange capacity (CEC). Soil properties are interconnected with plant growth and development.

Depending on the pH values, chromium can be found as trivalent chromium [Cr (III)] or hexavalent chromium [Cr (VI)]. Cr (VI) can be reduced to Cr (III) by Fe (II), phosphate, organic matter. Cr (III) it is almost precipitated in acidic media (pH 5.5). For plants, toxicity of Cr is dependent on oxidation state, Cr (VI) being more toxic than Cr (III). Cr (VI) as chromate (CrO_4^{2-}), it is water soluble and it is more mobile and toxic than Cr (III). Cr (VI) can be found in the soils that have a high pH (>7.5), low organic matter and a high Mn content. If it is found in the soil of a high-valent Mn as electron acceptor, it causes the oxidation of Cr (III) to (VI). In soil, redox reactions of Cr and Mn are strongly influenced by microbial activity as well as by physico-chemical soil properties (Del Bubba et al., 2013; Ding et al., 2014; Reijonen & Hartikainen, 2016; Hamilton et al., 2020; Tumolo et al., 2020). Some researchers (Zhang et al., 2021) demonstrated in a study that distribution factor values in silt-clay for both total Cr were 1.27 and 2.29 for Cr (IV) times higher than those in coarse sand samples. It can be said that fine soil particles have a high environmental risk because of their stronger accumulation ability and mobility. High levels of Cr in soil can affect microbial diversity and enzyme activities like cellulase (Li et al., 2021).

The ratio of soluble and stable organic C and Fe, Al, and Mn concentrations found in organic matter are involved in the process of Cr adsorption/desorption. Soils that have a high level of organic matter can stimulate the reduction of hexavalent chromium. Cr (VI) could stay in the soil for years, especially in sandy soils and those with a low level of organic matter (Del Bubba et al., 2013).

2. Chromium in crops

Crops can take and accumulate Cr (VI) in their edible tissues, from polluted soils. This is a concern related to the food chain, people and animal health. In the plants, Cr toxicity have a negative impact on physiological and biochemical processes such as: photosynthesis, transpiration, pigment biosynthesis, root growth and nutrient uptake, leading to perturbations in redox homeostasis and signalling, damages in membrane lipids, DNA, proteins and enzymes, affect also enzymatic activities linked to starch synthesis and N-metabolism, seed germination, flowering, fruit setting, crop yield loss, and deteriorate food quality (Del Bubba et al., 2013; Singh et al., 2013; Stambulska et al., 2018; Sharma et al., 2020; Christou et al., 2021).

The reduction of sugar content in chromium stressed plants was also observed, this probably being related with the photosynthetic inhibition or stimulation of respiration for higher energy requirements. Soluble sugar content can be an important parameter for assessing the effects of Cr on plants (Kakkalameli et al., 2021; Sharma et al., 2020). Very low concentration (<1mg·kg^{-1}) of Cr (VI) in soils can produce ecotoxic effects.

High content in chromium can influence the uptake of plant nutrients like: iron (Fe), magnesium (Mg), phosphorus (P) and calcium (Ca). In rice, an excessive chromium exposure leads to a decrease in the uptake of: N, P, K, Zn, Cu and Fe (Singh et al., 2013; Sharma et al., 2020). A study conducted by Ding et al. (2014) regarding the influence of Cr on the carrots cultivated in soils with pH below 7.5 evidenced that its application generated the decrease of carrot fresh weight and yield.

Nawaz et al. (2021) in their study showed that Cd had the maximum translocation from soil to wheat (*Triticum aestivum* L.) shoot, followed by N, Cr and Ni.

In wheat, maize, peas, rice, beans, sunflower, canola and sorghum, Cr have toxic effect on: photosynthetic pigments, photosynthetic apparatus, inhibit the electron transport, inactivate the Calvin cycle enzymes, decreased CO_2 fixation, decrease the activity of Ribulose-1,5-bis-phosphatecarboxylase/oxygenase (RuBisCO), change the morphology of leaves, reduced root length, lamellar structure, the ultrastructure of chloroplasts, enhance hydrogen peroxide (H_2O_2) production and lipid peroxidation. Cr (VI) decrease leaf water potential, which can develop water stress in plants (Del Bubba et al., 2013; Singh et al., 2013).

In bush beans, sunflower, mung bean, chromium reduced water potential, increased transpiration rate, reduced diffusive resistance, and wilting, reduced diameter of the tracheal vessels.

In various cereals and legumes chromium affects the uptake of nutritive elements, inhibiting assimilatory enzymes. In beet, a high concentration of Cr inhibits electron transport sites in photosynthesis in isolated chloroplasts, affecting the photosynthesis. In Chinese cabbage, Cr inhibits seed germination and development and subsequently reduces the dry matter production and yield (Del Bubba et al., 2013).

In tomato plants was observed an increased accumulation of chromium due to the presence of citrate, aspartate and oxalate, which converted inorganic chromium into organic complexes, which are available for the plant to uptake. In *Brassica rapa* and *Spinacia oleracea*, Cr uptake and translocation to aerial parts is made through Fe channels (Sharma et al., 2020).

Cr (VI) unlike other metals it directly reacts with DNA, forming DNA–protein and DNA–DNA cross-links, being very mutagenic in plants like: *Brassica napus*, *Arabidopsis thaliana*, *Trifoliumrepens*. It can also induce DNA mutation; chromosomal aberrations and mitotic aberrations in: *A. cepa* and *V. faba*. In roots of *P. sativum* it was observed that Cr (VI) alter cell cycle dynamics and ploidy levels (Singh et al., 2013).

There are plants that can accumulate chromium (1000 mg·kg^{-1}) and are categorized as chromium hyperaccumulators. For example, *Helianthus annuus* it is a moderate chromium accumulator in shoots and *Brassica napus* is a low accumulator in whole plant (Singh et al., 2013).

Cr (VI) being very soluble than Cr (III) (which is immobile in ambient environments, being found bound to organic matter) can lead to more toxic effects on animals and human's health.

Soil and crops contamination with chromium it is reflected in water, beverages and food, throughout the whole food chain.

Maximum permissible limits set for foodstuff by FAO 2002 are 1 mg·kg^{-1}fresh weight (F.W.), and for fruits and vegetables of 2.3 mg·kg^{-1} F.W. (FAO 2011; Christou et al., 2021). According to EFSA's tolerable daily intake (TDI) of 0.3 mg·kg^{-1} body-weight/day is for Cr (III).

Contamination of drinking water and food with high levels of Cr (VI) has a 60-fold increase in the rate of gastric cancer, which leads to loss of life expectancy (Del Bubba et al., 2013).

The main form of Cr found in food is Cr (III), the food and beverages consumed by humans should be examined for this priority toxic element (Yaman, 2020). The United States

Environmental Protection (USEPA) listed Cr (VI) as one of the seventeen metals that are dangerous to human health (Usman et al., 2020).

3. Chromium effects on human health

Cr (VI) is classified as belonging to group 1 carcinogen element by the International Agency for Research on Cancer (IARC) and it is very common in polluted environments and industrial places (Wang et al., 2017). Absorption of Cr depends on particle size, oxidation state and its solubility and health effects depend on dose, exposure level and duration (Shekhawat et al., 2015; Tumolo et al., 2020). Absorption and metabolism of chromium species in the human body can be realized through oral, dermal and inhalation pathway Cr (III) it is less absorbed than Cr (VI), so the transport to cells will be different. Cr (III) enters in the cell by passive diffusion or phagocytosis (Shekhawat et al., 2015; Wang et al., 2017).

Cr (VI) enters into the cell via a non-specific anion channel and in the cell is reduced by glutathione to Cr (V) and after that converted to Cr (III).

In red blood cells Cr (III) binds to the cellular components and then it is unable to leave the cells. As a result of this process, hydrogen peroxide and free radical species are produced, which generate high levels of oxidative stress that lead to lipids, protein and DNA modification. These modifications limit the DNA repair capacity of the cells. Cr also can induce tumor suppressor gene p53 (Shrivastava et al., 2002; Shekhawat et al., 2015; Wang et al., 2017; DesMarais& Costa, 2019; Engwa et al., 2019; Tumolo et al., 2020; Yaman, 2020). The main reduction of Cr (VI) to Cr (III) takes place in tissue of lungs (Shekhawat et al., 2015).

It was found also that chromium competes for one of the binding sites on transferrin, in this way there were several studies that investigated possible interactions between iron and chromium (Yaman, 2020).

The Cr (VI) is considered the most toxic, causing acute and chronic toxicity. The most important heath reactions after contact, inhalation, or ingestion of Cr (VI) are the following: dermatitis, allergic and eczematous skin reactions, skin and mucous membrane ulcerations, perforation of the nasal septum, allergic asthmatic reactions, bronchial carcinomas, damage to the lower respiratory tract, gastro-enteritis, hepatocellular deficiency, renal oligo-anuric deficiency, anaemia and possibly death (Baruthio, 1992; Wilbur et al., 2012; Wang et al., 2017; Engwa et al., 2019; Li et al., 2020).

In the liver, kidney, spleen and bone was found a higher concentration of chromium, than in other organs (Shekhawat et al., 2015; Yaman, 2020). The main routes for the excretion of chromium are via kidney/urine and the bile/faeces (Shrivastava et al., 2002).

Cr (VI) is considered to be reduced in the stomach to Cr (III), which presents low ability to enter cells (Yaman, 2020).

Drinking chromium contaminated water can lead to mouth ulcers, indigestion, acute tubular necrosis, vomiting, abdominal pain, kidney failure and even death (Shekhawat et al., 2015).

Lee et al. (2019) found that is a correlation between soils contaminated with high levels of Cr and Sjogren's syndrome, which is an autoimmune disorder with symptoms like dry eyes and dry mouth, patients with this syndrome can have also lymphocytic infiltration into extra glandular tissues, not only in lacrimal and salivary glands (Fox, 2011).

4. Chromium effects on animal health

Studies on rats and mice showed that if Cr (VI) is given in drinking water then it shows the ability to cross the placenta and reach to fetal tissue. Also, different health effects that includes cellular infiltration in the liver, pancreatic and small intestine was observed and carcinogenic activity (intestines and oral carcinogenicity) in both the sexes of rats and mice if they drink contaminated water (Shekhawat et al., 2015). In the studies on hamsters and mice parenteral administration of Cr (III) or Cr (VI) results in embryotoxicity or fetotoxicity and teratogenicity (WHO 1996). We can say that chromium is responsible for the toxic effects in humans and in animals also. Cr (VI) is mainly responsible for all carcinogenic activity in comparison to trivalent chromium (Shekhawat et al., 2015).

5. Chromium remediation

There are some soil remediation techniques such as: chemical stabilization, reduction, transformation using adsorption, desorption, precipitation and oxidation-reduction reactions, solidification, soil washing, membrane filtration, photocatalysis, bioremediation using microorganisms, nano-particles and phytoremediation using terrestrial and aquatic plants (Sathya et al., 2020; Azeez et al., 2021; Li et al., 2021; Prasad et al., 2021; Sharma et al., 2021; Wang et al., 2021). Soil phytoremediation can be performed by: phytoextraction, rhizofiltration, phytostabilization, phytovolatilization, phytodegradation and rhizodegradation (Aparicio et al., 2021).

Yang et al. (2021) in their study mentioned the reductants such as: iron-based reductants (elemental Fe and Fe (III)), sulfur compounds (sodium sulfite and sodium thiosulfate) and organic amendments (humic, tartaric acids, isopropyl alcohol) that can be used for soil remediation.

6. Extraction methods of chromium from different matrices

Strictly analytically, various extraction procedures have been studied in order to determine Cr species in soil and plant samples. The sample extractions have to be chosen according to what chromium species we need to identify and quantify.

Sample preparation before analysis

Before conducting each analysis, the several different soil samples were dried in air (~ 25ºC) and then passed through a 2 x 2 mm stainless steel sieve (Franco et al., 2011).

As a rule, the decomposition of the matrix is a mandatory step before their elemental analysis (Szymczycha-Madeja et al., 2014).

For soil sample preparation there are official methods like:

- EPA Method 3050B, for acid digestion of sediments, sludges, and soils;
- EPA Method 200.2. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements.

Extraction solvents

Extraction solvents that can be used for the identification of Cr (VI) in soil and plant samples are: oxidants (H_2O_2), acids at various concentrations (e.g., acetic acid, nitric acid, hydrofluoric acid), buffered salts (e.g., ammonium acetate), neutral salts ($CaCl_2$, Na_3PO_4 or Na_2CO_3), chelating agents (e.g., EDTA, DTPA, EDDS) (Leśniewska et al., 2017).

Methods of extraction

For soil and plants, there are several **conventional methods**, as:

a) open vessel hot-plate wet digestion;

b) closed vessel microwave-assisted wet digestion. The conventional extraction methods have *advantages* as:

- large sample amounts;
- complete destruction of organic matter;
- simplification to a variety sample;
➢ - application to a variety sample;

Also, the conventional extraction methods have *disadvantages* as:

- like slow, laborious, time-consuming;
- loss of volatile analytes;
- possible contaminations of samples;
- high temperature treatments, lower precision.

a) Open vessel hot-plate wet digestion method has a series of *advantages*: - large sample amounts;
- lower temperatures as compared to dry ash;
- application to a variety sample.

Also, the method has *disadvantages* like:

- the slow, time-consuming;
- laborious;
- loss of volatile analytes;
- contaminations of samples;
- use of large amounts of strong oxidizing reagents;
- pre-concentration of reagent impurities, incomplete solubilisation of sample constituents;
- high temperature treatments.

According to literature, quantification by flame atomic absorption spectrometry (FAAS) could be achieved by using:

- dry ash 0.25 g, 450°C, 8 h, 5 mL HNO_3 (25%), final volume 10 mL (Narin et al., 2004);
- 5.0 g, 500°C, 6 h ash: 2 mL HCl (6 $mol \cdot L^{-1}$), final volume 25 mL (Chen et al., 2009).

For the samples that will be analysed by inductively coupled plasma - optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), it can be used:

- a mixture of HNO_3 (10 mL), 3h, (0.25 g + 10 mL), brought to a final volume of 25 mL (Kara 2009);
- a mixture of HNO_3 (10 mL), 1h, + $HClO_4$ (1 mL), 1h, (0.5g + 11 mL), brought to a final volume of final volume 100 mL (Ashraf and Mian, 2008).

b) Closed vessel microwave-assisted wet digestion

The method has a series of *advantages:*

- closed system;
- reduce volume of aggressive reagents;
- minimal contamination;
- lack of loss volatile analytes;
- minimal contaminations of samples;

➢ good precision and accuracy. Also, the method has *disadvantages* such as:

- high cost of equipment;

➢ small sample amounts;

- time required for cooling;
- cleaning vessel;
- control of process;
- the matrix may require a different microwave program.

For this type of digestion, there are reported the following protocols:

- HNO_3 (20 mL), extraction time 70 min, (2.0g + 20 mL), to a final volume of 50 mL, (Shen and Chen, 2008); - HNO_3 (3 mL), 30 min, + H_2O_2 (0.5 mL), 30 min (0.25 g + 3.5 mL), to a final volume of 25 mL for ICP-OES and AAS detection (Dash et al., 2008).

7. Quantification methods for chromium

a) *solid matrices* - US EPA method 3060A.

Generally, the Cr in *soil samples* is quantified by using the following techniques:

- flame atomic absorption spectrometry (FAAS) (Aksuner et al., 2012);
- graphite furnace atomic absorption spectrometry (GF AAS) (Dash et al., 2008);
- inductively coupled plasma optical emission spectrometry (ICP-OES) (McKenzie et al., 2010);
- inductively coupled plasma mass spectrometry (ICP-MS) (Kara, 2009);
- X-ray fluorescence spectrometry (XRFS) (Salvador et al., 2002).

b) *water samples*

Generally, the Cr in water samples is achieved by using:

- ISO 11885, ISO 17294-2, ISO 15586, ISO 18412 (Cr VI), ISO 23913 (Cr VI), ISO 9174 (Section 4), EPA 200.8 (using ICP-MS), recommended by Codex Alimentarius;
- EPA 218.7 for determination of hexavalent chromium in drinking water by ion chromatography with post-column derivatization and UV-VIS spectroscopic detection;
- EPA 200.9 for Determination of Trace Elements by Stabilized Temperature Graphic Furnace Atomic Absorption.

c) *other matrices*

- EN 13804:2002, EN 13805:2002, EN 13806:200, EN 14082:2003, EN 14083:2003, CEN/TS 15506:2007 and AOAC 974.27 (using AA spectrophotometer), recommended by European Commission in 2012 regarding food;
- EN 14082, EN 14083, AOAC 2006.03, AOAC 2011.19 (using ICP-MS) / ISO 20649 |IDF 235, according to the FAO/WHO Food standards programme codex from 2015, regarding infant formula.

CONCLUSIONS

Our review study revealed that Cr is present in water, soil, plants, and food in various concentrations. Its availability depends on different agricultural systems factors and it can have both positive and negative influence on soil, plants, human and animal health depending on the concentration and oxidation state. Cr (VI) species are toxic and carcinogenic, meanwhile Cr (III) plays an important role in molecular mechanisms of biological systems.

From agricultural point of view, there are technologies for remedying contaminated soils and irrigation water that can be used.

There are currently advanced techniques for chromium quantification even at trace levels from various samples (soil, plant, water, etc).

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