

## Chromium: toxicity and tolerance in plants. A review

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**Abstract.** The metals that have a greater density than  $5 \text{ g cm}^{-3}$  are called heavy metals. These heavy metals sum up 53 of the total 90 elements that occur naturally. Of these 53 heavy metals, 17 are significant to the plants and animals from various ecosystems and are available for living cells from the solubility in physiological conditions' point of view. Moreover, there are only a few heavy metals that are non-toxic at low concentrations: Zn, Ni, Cu, V, Co, W and Cr. In photosynthetic organisms, heavy metals with stress effect result in the modification of some of these organisms' characteristics as: plasma membrane damages, formation of oxygen radicals, appearance of free metal ions in cytosol, disorders of nutrient uptake, water balance and photosynthesis, limited growth, reduced production of flowers and seeds. Direct and indirect effects are produced by these types of modifications.

**Key Words:** heavy metals, chromium, green algae, toxicity.

**Introduction.** Heavy metals are great pollutants to the environment (Angelone & Bini 1992; Berry 1986) and their presence in soils depends on certain natural processes, especially on the lithogenic and pedogenic processes as well as on anthropogenic factors, such as mining, the burning of fossil fuels and urban waste, sewage treatment, and on the sites of municipal solid waste disposal.

The increase in the amount of heavy metals in the soil could also be attributed to such factors as soil properties or different agricultural practices, such as applying sewage sludge to agricultural land (Foy et al 1978).

Soils contaminated with heavy metals exceeding the limit allowed Pb to lower agricultural yields (Nellessen & Fletcher 1993; Akinola & Ekiyoyo 2006). The accumulation of heavy metals in the environment is now becoming a major cause of environmental pollution.

**Toxicity of heavy metals.** Out of the known metals,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  at elevated levels are toxic to plants, while  $\text{Pb}^{2+}$  has been observed to generally cause phytotoxicity (Foy et al 1978). The concentration of Cd in the unpolluted soil ranges from 0.04 mM up to 0.32 mM and a concentration between 0.32 mM and approximately 1 mM can be described as polluting (Sanita di Toppi & Gabbriellini 1990). Among heavy metals, Cd is an industrial pollutant of high importance especially in areas associated with zinc melting and intense road traffic (Somasekaraiah et al 1992; Das et al 1997).

High concentrations of heavy metals in soil are toxic to most plants (Baker & Brooks 1989; Ernst 1980; Macnair 1993). There are two types of causality relationships between the high concentration of heavy metals in soil and the symptoms of toxicity. On the one hand, heavy metals compete with the absorption of essential nutrients and minerals, thus upsetting the mineral nutrition of plants (Clarkson & Luttge 1989) and on the other hand, after the absorption, the metal accumulates in the tissues and cells of the plants preventing the functioning of their general metabolism (Turner 1997).

**Chromium toxicity.** Chromium is a hard, stiff, silver-white, smooth metal. In the periodic table, it is situated in the d block of the elements. The atomic number of chromium is 24, the atomic mass is 51.996, the density  $7.2 \text{ g cm}^{-3}$ , the melting point is  $1857^\circ\text{C}$  and the boiling point is  $2672^\circ\text{C}$  (Kotás & Stasicka 2000). Chromium was discovered by the French chemist Vauquelin in 1798 after examining the crocoite ore (lead chromate) in Siberia. It received its name on account of its glossy color (Losi et al 1994). It is the 21st most abundant element (Krauskopf 1979), making up 0.0083% of the Earth's crust according to National Academy of Sciences USA (1974). The occurrence

rate of chromium in the continental shelf is  $125 \text{ mg kg}^{-1}$ . The concentration in some serpentine minerals can reach  $125\,000 \text{ mg kg}^{-1}$  (Adriano 1986).

It can be found only in compounds, never as an element. Similarly to the d block elements, it can have several oxidation states - 2, 3, 4, 5, 6 - but only the compounds Cr(III) and Cr(VI) are stable in nature (Saleh et al 1989).

Most of the forms of Cr(VI) occur in the environment as a result of industrial activity, having as main source the chromite, also known as iron chromate and chrome. The ideal composition is  $\text{FeCr}_2\text{O}_4$ , but here and there in the occurrence areas they can contain Mg and Al; in such cases we describe it as the  $[(\text{Fe}, \text{Mg}) (\text{Cr}, \text{Al}, \text{Fe})_2\text{O}_3]$  composition. The world annual production of chromium is 11 megatons, the vast majority is extracted in South Africa, Zimbabwe, Russia, Albania and India, and the annual processed quantity increases constantly (Kotás & Stasicka 2000). The largest consumers are the galvanic industry, ceramic industry, metallurgy, the magnetic tape manufacturers, the leather industry and the paint manufacturing industry. These industries are the largest emitters; with a great waste water quantity they introduce a large quantity of chromium in the environment (Langard 1980).

Different forms of chromium can be found in the soil, water and even in the air. Around 60% of the chromium in the air is anthropic, it occurs naturally (by volcanic eruptions, fires). Gaseous chromium cannot be found in the atmosphere, chromium binds itself to the solid particles or to the atmospheric aerosol drops. Two (2)  $\mu\text{m}$  wide and even smaller particles can travel long distances and if they are inhaled and remain in the lungs, they can lead to cancer (Kotás & Stasicka 2000).

The chromium in the water originates from dust from the air, from cliff erosion and from pollution by emissions. The chromium content in freshwater ranges from 0.1 to  $800 \mu\text{g dm}^{-3}$ ; polluted areas can contain an even higher level of chromium (Gaines 1988). In natural waters Cr(III) and Cr(VI) are stable.

The main natural sources of chromium in soils are their own parent rocks, as a result, the amount of chromium in different soils is very diverse. The chromium content in pristine soils is between  $10 \text{ mg kg}^{-1}$  and  $150 \text{ mg kg}^{-1}$ , with the average value of  $40 \text{ mg kg}^{-1}$  (Losi et al 1994).

The concentration of the two chromium types ( $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$ ) depends on the physico-chemical features and the phenomena in the environment (Mertz 1969). In an environment rich in oxygen and with the  $\text{pH} \geq 7$ , the presence of the ions  $\text{CrO}_4^{2-}$  is expected, while Cr(III) ions are expected in an environment poor in oxygen and with the  $\text{pH} \leq 6$ . In transient pH intervals, the concentrations of Cr(III) and Cr(VI) depend on the oxygen concentration and on the reducing agents such as Fe(II) and on the oxidation agents such as manganese oxides (Schroeder & Lee 1975). With the exception of the aerated surface waters with a higher level of oxygen, Cr(VI) occurs in the form of  $\text{H}_2\text{CrO}_4$  only at a low level of pH. Cr(III) occurs in the normal pH intervals in the form of hydro-complexes, organic complexes and  $\text{Cr}(\text{OH})_3$  precipitations (Rai et al 1989). The complex formation decreases the chances for the precipitation formation. Organic complexes oxidise harder than hydro-complexes (Rai et al 1989; Stein & Schwedt 1994).

The chromium content in soils originates from the parent-rocks erosion which can be enhanced by the chromium containing waste from the air originated from industrial activities. In pH neutral soil most of Cr(III) is found in the form of hydroxide precipitation; this has a low agility and cannot be assimilated by plants. In acidic soils with  $\text{pH} < 4$  mainly  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and  $\text{CrOH}^{2+}$ .aq are found (Bartlett & Kimble 1976 a, b). In neutral or alkaline soils, Cr(VI) is found generally in the form of high solvency  $\text{Na}_2\text{CrO}_4$ ; alkalino-earthly chromates and Pb chromates can be found as well. The reduction possibilities and the catalysts  $\text{CrO}_4^{2-}$  and  $\text{HCrO}_4^-$  are similar to those described in the water environment; reversely, in this case, the manganese oxides (III, IV) and hydroxides are catalysts (Eary & Ray 1987; Makino et al 1998).

The chromium content in the air varies on a large scale. As they were researching the chromium content in the air in Antarctica, Greenland and the Norwegian North Pole, Pacyna & Nriagu (1988) had the following result:  $5.0 \times 10^{-6}$  and  $1.2 \times 10^{-3} \mu\text{g m}^{-3}$ . This chromium comes from natural chromium sources such as volcanic eruptions and from the

pollution carried by the wind to those areas; their quantity is  $3.9 \times 10^3$ ,  $50 \times 10^3$  tones per year.

**Toxic effects on plants. Transport and accumulation in plants.** The results of studies regarding the way chromium is transported and accumulated in plants, are contradictory. This is because, during the lengthy experiments in the soil or in aqueous environments, the interconversion of the two main states of oxidation of chromium: + 6 to + 3 may take place (Akinola & Ekiyoyo 2006).

All plants have the capacity to absorb a wide range of metals from the soil. Most of them absorb only metals that are essential for their development and survival. There is, however, a smaller number of plants, making an exception to that rule, which may absorb and tolerate higher amounts of heavy metals, which would be toxic to almost any other organisms. In this category of plants, called hiper-accumulators, are those plants that can contain  $> 100 \text{ mg kg}^{-1} \text{ Cd}$ ;  $> 1000 \text{ mg kg}^{-1} \text{ Ni}$  and  $\text{Cu}$ ; or  $> 10000 \text{ mg kg}^{-1} \text{ Zn}$  and  $\text{Mn}$  (dry weight). Given this extraordinary ability to concentrate heavy metals, these plants can be used for the remediation of lands affected by pollution with these contaminants, process known as phytoremediation (Akinola & Ekiyoyo 2006).

However, they are not used yet for this purpose on a large scale, one of the main causes being the lack of knowledge regarding the mechanisms of absorption, transport and accumulation of heavy metals.

Salt laid down the hypothesis that a series of plants developed certain mechanisms for growing their capacity to absorb metallic ions in the soil, especially those absorbed at the surface of the soil particles. A first mechanism proposed by Vonwiren is that these plants have the ability to produce a range of organic products (such as muconic and avenic acid) that can cause a complexation, solubilisation and thus mobilisation of the metals absorbed at the surface of soil particles. The second possible mechanism, proposed by Crowley, explains solubilising and the mobilisation of metals absorbed at the surface of soil particles, as the capacity of the plants to remove protons through roots, thus resulting in a soil acidification (Vondrackova et al 2014).

As in the case of microorganisms,  $\text{CrO}_4^{2-}$  ions transport in plants is carried out through an ionic exchange mechanism with sulfate ions. The accumulation of chromium in plants depends on the oxidation state of the chromium, its concentration in the environment, as well as the nature of the plants. Therefore, in an experiment conducted on ten plant species, the chromium accumulation was higher in seven of them, when they were contaminated with Cr (VI), as compared to the situation when they were contaminated with Cr (III) (Tomar & Jajoo 2015).

In studies conducted on beans (*Phaseolus vulgaris*) and wheat (*Triticum aestivum*) there was no difference between the absorption of Cr(III) or Cr(VI). The chromium complexation by organic compounds is considered to be a factor that favors the plants' ability to absorb chromium. For example, wheat plants to which, besides  $\text{CrCl}_3$ , oxalic and maleic acid or glycine was introduced in their culture environment, have accumulated more chromium in their roots than plants that have been administered only Cr(III) (Tomar & Jajoo 2015). There are studies which indicate that the absorption mechanisms of Cr(III) and Cr(VI) are different; thus, by using metabolic inhibitors a substantial decrease of Cr(VI) absorption was observed, but that was not the case for the Cr(III) absorption (Sharma et al 2016). There are also studies indicating that the Cr(III) and Cr(VI) absorption mechanisms are different; by using certain metabolic inhibitors a substantial decrease in the Cr(VI) was observed, however this was not the case for Cr(III). There are also studies based on the enhancement of Cr(III) and Cr(VI) absorption by plants indicating that the Cr(III) and Cr(VI) absorption mechanisms are identical (Berry 1986).

The degree of chromium accumulation in various parts of the plants is different. For example, roots accumulated 10-100 times more chromium than the buds or other tissues. In studies conducted on beans, only 0.1% of the total accumulated chromium was found in kidney beans, while the roots retained 98% of the total accumulated chromium. Plants with great ability to accumulate chromium have been identified, some of which are aquatic plants in the family *Eichhornia crassipes* whose roots may

accumulate  $6 \text{ mg Cr g}^{-1}$ ; plants such as cauliflower and various types of cabbages, have the ability to accumulate  $160\text{-}350 \text{ mg Cr kg}^{-1}$  in the roots (Foy 1979).

**Conclusions.** Chromium is found in nature in the form of various mineral complexes and in different valences, the most toxic being hexavalent and trivalent chromium. The studies have shown that out of the two forms, hexavalent chromium has more harmful effects, it can even cause cancer. The toxicity of the hexavalent chromium is given by its property to be easily transported inside cells.

Every form of biological life, from the unicellular life form to most evolved life forms, to man, is indicated to have an acute toxicity of the hexavalent form. Although the hexavalent form of chromium is known for good reason to be the most toxic, the trivalent form, unable to penetrate living cells on account of its high insolubility, must not be overlooked. If Cr(III) could penetrate the cell membrane, it could cause severe damage. However there have been reported cases of acute intoxication even when chromium was in its trivalent form.

In conclusion, it is not recommended to use nutritional supplements based on Cr(III) in large doses over long periods of time. Recently, cases of accidents involving chromium compounds have become increasingly rare owing to the environmental rules which have highlighted the toxic effect of this element and the law was amended accordingly.

Cr(VI) is on the first place in the top of dangerous substances (a compiled list containing 275 substances which are considered to be the highest risk for humans); this proves once again the risk for the human health.

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