



Review Article

Chromium: As an Environmental Pollutant

Satish A. Bhalerao* and Amit S. Sharma

Environmental Sciences Research Laboratory, Department of Botany, Wilson College,
University of Mumbai, Mumbai – 400 007 M.S. India

*Corresponding author

ABSTRACT

In recent years, contamination of the environment by chromium (Cr) has become a major area of concern. Chromium is the 17th most abundant element in the earth's mantle. Chromium is used on large scale in many industries including metallurgical, electroplating, production of paints and pigments, tanning, wood preservation, chemical production and pulp and paper production. Cr exists in several oxidation states but the most stable and common forms are Cr (0), Cr (III) and Cr (VI) species. Cr toxicity in plant depends on its valence state. Cr (VI) is being highly mobile is toxic. Cr (III) as less mobile is less toxic. Chromium is known to be a toxic metal that can cause severe damage to plant. Toxic effects of Cr on plants growth and development include alterations in the process of germination, growth of roots, stem and leaves, which may affect total dry matter production and yield. Cr also causes detrimental effects on the plant physiological processes such as photosynthesis, water relations, mineral nutrition, oxidative imbalance and inhibition of enzymatic activities. Chromium can affect antioxidant metabolism in plant. Chromium- induced oxidative stress involves induction of lipid peroxidation in plants that causes severe damage to cell membrane. Cr is able to induce genotoxicity in several plant species. The use of biological remediation technologies such as bioremediation and Phytoremediation for the cleanup of Cr-contaminated areas has received increasing interest from researchers worldwide. This paper includes an overview of the literature about Cr toxicity in the environment, especially in water and soil and provides new insights about Cr toxicity in plants.

Keywords

Chromium,
Oxidative stress,
Antioxidant,
Cr (III),
Cr (VI),
Phytoremediation,
Bioremediation,
Photosynthesis

Introduction

Chromium (Cr) is the 17th most abundant element in the Earth's mantle (Avudainayagam et al., 2003). It occurs naturally as chromite (FeCr_2O_4) in

ultramafic and serpentine rocks or complexed with other metals like crocoite (PbCrO_4), bentorite $\text{Ca}_6(\text{Cr,Al})_2(\text{SO}_4)_3$ and tarapacaite (K_2CrO_4), vauquelinite

($\text{CuPb}_2\text{CrO}_4\text{PO}_4\text{OH}$), among others (Babula et al., 2008). Cr is widely used in industry as plating, alloying, tanning of animal hides, inhibition of water corrosion, textile dyes and mordants, pigments, ceramic glazes, refractory bricks, and pressure-treated lumber (Avudainayagam et al, 2003). Due to this wide anthropogenic use of Cr, the consequent environmental contamination increased and has become an increasing concern in the last years (Zayed and Terry, 2003). Chromium exists in several oxidation states, but the most stable and common forms are Cr (0), the trivalent Cr (III), and the hexavalent Cr (VI) species. Cr(0) is the metallic form, produced in industry and is a solid with high fusion point usually used for the manufacturing of steel and other alloys. Cr(VI) in the forms of chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and CrO_3 is considered the most toxic forms of chromium, as it presents high oxidizing potential, high solubility, and mobility across the membranes in living organisms and in the environment. Cr (III) in the forms of oxides, hydroxides, and sulphates is less toxic as it is relatively insoluble in water, presents lower mobility, and is mainly bound to organic matter in soil and aquatic environments. Moreover, Cr (III) forms tend to form hydroxide precipitates with Fe at typical ground water pH values. At high concentrations of oxygen or Mn oxides, Cr (III) can be oxidized to Cr (VI) (Becquer et al., 2003; Peralta et al, 2009).

Chromium in the environment

Chromium in water

Chromium may enter the natural waters by weathering of Cr-containing rocks, direct discharge from industrial operations, leaching of soils, among others. In the aquatic environment Cr may suffer reduction, oxidation, sorption, desorption,

dissolution, and precipitation (Kimbrough et al, 1999). The aqueous solubility of Cr (III) is a function of the pH of the water. Under neutral to basic pH, Cr (III) will precipitate and conversely under acidic pH it will tend to solubilize. The forms of Cr (VI) chromate and dichromate are extremely soluble under all pH conditions, but they can precipitate with divalent cations (Kimbrough et al, 1999). The recommended limits for Cr concentration in water are $8 \mu\text{g L}^{-1}$ for Cr (III) and $1 \mu\text{g L}^{-1}$ for Cr (VI). In the effluents in the vicinity of Cr industries the levels of Cr range from 2 to 5 g L^{-1} (Chandra et al, 1997).

Chromium in soil

The concentration of Cr in the soils may vary considerably according to the natural composition of rocks and sediments that compose them (Kimbrough et al, 1999). The levels of chromium in the soil may increase mainly through anthropogenic deposition, as for example atmospheric deposition (Rosas et al, 1989), also dumping of chromium-bearing liquids and solid wastes as chromium byproducts, ferrochromium slag, or chromium plating baths (Kimbrough et al, 1999). Generally, Cr in soil represents a combination of both Cr (III) and (VI). As in aquatic environment, once in the soil or sediment, Cr undergoes a variety of transformations, such as oxidation, reduction, sorption, precipitation, and dissolution (Kimbrough et al, 1999). The oxidants present in the soil (e.g., dissolved oxygen and MnO_2) can oxidize Cr (III) to Cr (VI) (Fendrof et al, 1992); however, it seems that oxidation of Cr (III) by dissolved O_2 is residual when compared with MnO_2 . The forms of Cr (VI) are on the other hand reduced by iron, vanadium, sulphides, and organic materials (Cary, 1982). However, when the reducing capacity of the soil is overcome, Cr (VI) may persist in the soil or

sediment for years, especially if the soils are sandy or present low levels of organic matter. (López-Luna et al., 2009) compared the toxicity of Cr (VI), Cr (III), and Cr tannery sludge respecting to Cr mobility in the soil and toxicity in wheat, oat, and sorghum plants and found that Cr (VI) was more mobile in soil and caused higher toxicity on those plant seedlings, while tannery sludge was the least toxic (López-Luna et al., 2009).

Chemical properties of chromium

Chromium is the 21st most abundant mineral in the crust of the earth; the average Cr concentration in US soils is around 40 mg/kg (Barnhart, 1997). The results of research focusing on the content of risk elements in farm land throughout the Czech Republic in 1991–1994 have been published by (Mazanec 1996). Although chromium (relative atomic mass 51.996 g) may theoretically occur in all oxidation states from –2 to +6, it is most often found in 0, +2, +3 and +6. Elemental chromium (0) is not naturally present in the earth crust and is biologically inert. Almost all naturally found Cr is trivalent while hexavalent Cr is mostly of industrial origin. Most Cr compounds are halides, oxides or sulphides.

Divalent chromium (Cr^{2+}) is a strong reductant; the form is readily oxidised when in contact with air, producing Cr^{3+} . This explains why divalent Cr is not available in biological systems.

Hexavalent chromium (Cr^{6+}) is the second most stable form and a strong oxidising agent, especially in acidic media. Hexavalent chromium is bound to oxygen as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) with a strong oxidative capacity. This form of Cr crosses biological membranes easily, reacting with protein components and

nucleic acids inside the cell while being deoxygenated to Cr^{3+} . The reaction with genetic matter provides for the carcinogenic properties of Cr^{6+} .

Trivalent chromium (Cr^{3+}) is the most stable oxidation state in which Cr is found in living organisms. It does not have the capacity to cross cell membranes easily (Mertz, 1992) and has a low reactivity, which is the most significant biological feature distinguishing it from Cr^{6+} . Trivalent Cr forms a number of coordination complexes, hexadentate ligands being the basic form. Some forms of Cr^{3+} (e.g. Cr_2O_3) are, thanks to their low reactivity and absorption from the gastrointestinal system, used as markers in the study of digestion processes (Furnival et al., 1990a,b).

Chromium as an environmental contaminant

Cr and its compounds have multifarious industrial uses. They are extensively employed in leather processing and finishing (Nriagu, 1988), in the production of refractory steel, drilling muds, electroplating cleaning agents, catalytic manufacture and in the production of chromic acid and specialty chemicals. Hexavalent chromium compounds are used in industry for metal plating, cooling tower water treatment, hide tanning and, until recently, wood preservation. These anthropogenic activities have led to the widespread contamination that Cr shows in the environment and have increased its bioavailability and biomobility. A detailed review on the critical assessment of Cr in the environment has been published by Kimbrough et al. (1999), Kotas and Stasicka (2000). The leather industry is the major cause for the high influx of Cr to the biosphere, accounting for 40% of the total industrial use (Barnhart, 1997). In India, about 2000–32,000 tons of elemental Cr

annually escapes into the environment from tanning industries. Even if the recommended limit for Cr concentration in water are set differently for Cr(III) (8 Ag L₋₁) and Cr(VI) (1 Ag L₋₁), it ranges from 2 to 5 g/L in the effluents of these industries (Chandra et al., 1997). In the United States, 14.6 Ag L₋₁ in ground water and 25.9 gd kg₋₁ in soil have been found in the vicinity of chrome production sites (Zayed and Terry, 2003).

Uptake of chromium

The pathway of Cr uptake in plants is not yet clearly elucidated. However, being a nonessential element, Cr does not have any specific mechanism for its uptake and is also dependent on Cr speciation. Plant uptake of Cr (III) is a passive process, that is, no energy expenditure is required by the plant (Zayed and Terry, 2003; (Skeffington et al., 1976). The uptake of Cr (VI) is thought to be an active mechanism performed by carriers for the uptake of essential elements such as sulphate (Kim et al., 2006; Cervantes et al., 2001. Cr also competes with Fe, S, and P for carrier binding (Shanker et al., 2005). Cr (VI) has higher solubility and thus bioavailability is more toxic at lower concentrations than Cr (III), which tends to form stable complexes in the soil (L'opez-Luna et al., 2009). There are conflicting results concerning the uptake and translocation of Cr (VI). While some authors defend that Cr (VI) is reduced to Cr (III) on the root surface (Ramchandran et al., 2001; Zayed et al., 1998), others suggest that dissolved Cr (VI) is taken up by plants without reduction (Mishra et al., 1995). Thus, Cr toxicity is dependent on metal speciation, which is determinant for its uptake, translocation and accumulation. Cr is toxic for agronomic plants at about 0.5 to 5.0 mgmL⁻¹ in nutrient solution and 5 to 100 mg g⁻¹ in soil (Hossner, 1996). Under normal conditions, concentration of Cr in

plants is less than 1 µg g⁻¹ (Mortvedt and Giordano., 1976).

Chromium accumulation and translocation

Cr accumulates mainly in roots and shoots; however roots accumulate the major part, being usually only a small part translocated to the shoots (Paiva et al., 2009; Sundaramurthi et al., 2010). In pea plants exposed to Cr there was an increase in concentration of Cr in different parts of the plant with the increase of Cr supply.

Accumulation of Cr in the different parts of the plant was in the following order roots > stem > leaves > seed (Tiwari et al., 2009). Corroborating these results are the findings of several works and for instance, Huffman and Allaway (Huffman and Allaway., 1973) found that bean seeds accumulated about 0.1% Cr, while roots accumulated 98%. Furthermore, Liu and coworkers (Liu et al., 2008) studied hydroponically grown *A. viridis* L. under different concentrations of Cr(VI) and found that Cr was accumulated primarily in roots (Liu et al., 2008). Another study performed by Vernay et al., (2007) in *Lolium perenne* grown in the presence of 500 µM of Cr(VI) showed that roots accumulated 10 times more Cr than leaves. Spinach (*Spinacia oleracea* L. cv. "Banarasi") grown in the presence of Cr(VI) showed more accumulation of Cr in the roots than in leaves and stem showed the least accumulation (Gopal et al., 2009). Also, in celery seedlings grown in the presence of C(III) most Cr was accumulated in roots (Scoccianti et al., 2006). These results may conclude that Cr is mainly accumulated in roots, followed by stems and leaves; however only small amounts of Cr are translocated to leaves. This pattern seems independent of the form of Cr tested.

Chromium toxicity in plants

Growth and development

Plant growth and development are essential processes of life and propagation of the species. They are continuous and mainly depend on external resources present in soil and air. Growth is chiefly expressed as a function of genotype and environment, which consists of external growth factors and internal growth factors. Presence of Cr in the external environment leads to changes in the growth and development pattern of the plant.

Germination

Since seed germination is the first physiological process affected by Cr, the ability of a seed to germinate in a medium containing Cr would be indicative of its level of tolerance to this metal (Peralta et al., 2001). Seed germination of the weed *Echinochloa colona* was reduced to 25% with 200 AMCr (Rout et al., 2000). High levels (500 ppm) of hexavalent Cr in soil reduced germination up to 48% in the bush bean *Phaseolus vulgaris* (Parr and Taylor, 1982). Peralta et al. (2001) found that 40 ppm of Cr (VI) reduced by 23% the ability of seeds of lucerne (*Medicago sativa* cv. Malone) to germinate and grow in the contaminated medium. Reductions of 32–57% in sugarcane bud germination were observed with 20 and 80 ppm Cr, respectively (Jain et al., 2000). The reduced germination of seeds under Cr stress could be a depressive effect of Cr on the activity of amylases and on the subsequent transport of sugars to the embryo axes (Zeid, 2001). Protease activity, on the other hand, increases with the Cr treatment, which could also contribute to the reduction in germination of Cr-treated seeds (Zeid, 2001).

Root growth

Besides germination, also root growth is frequently affected by heavy metals. Peralta and coworkers (Peralta et al., 2001) showed that 5 mg L⁻¹ of Cr(VI) increased root growth comparatively to the control, and at higher doses (20 and 40 mg L⁻¹) there was a dose-inhibition effect. Cr(VI) in concentrations up to 200 mg L⁻¹ decreased growth of paddy (*Oriza sativa* L.) (Sundaramurthi et al., 2010). Sensitive mungbean cultivars also showed decreased root growth when exposed to Cr(VI) (Rout et al., 1997). Samantary (Samantary, 2002) found that there was no root elongation in mungbean exposed to Cr(VI) concentrations between 96 and 1928 µM, but in lower concentrations, sensitive cultivars showed root elongation similar to the control. Also, development of lateral roots and root number was also affected by Cr exposure (Samantary, 2002). Moreover, roots of *Zea mays* L. treated with Cr(VI) were shorter and brownish and presented less number of roots hairs.

Shoot growth

Adverse effects of Cr on plant height and shoot growth have been reported (Rout et al., 1997). When Cr was added at 2, 10 and 25 ppm to nutrient solutions in sand cultures in oats, Anderson et al. (1972) observed 11%, 22% and 41% reduction in plant height, respectively, over control. Reduction in plant height due to Cr (VI) on *Curcuma sativa*, *Lactuca sativa* and *Panicum miliaceum* was reported by Joseph et al. (1995). Barton et al. (2000) observed that Cr(III) addition inhibited shoot growth in lucerne cultures. Sharma and Sharma (1993) reported that after 32 and 96 days, plant height reduced significantly in wheat cv. UP 2003 in a glasshouse trial when sown in sand with 0.5 AM sodium dichromate. There

was a significant reduction in plant height in *Sinapsis alba* when Cr was given at the rates of 200 or 400 mg kg⁻¹ soil along with N, P, K and S fertilizers (Hanus and Tomas, 1993). The reduction in plant height might be mainly due to the reduced root growth and consequent lesser nutrients and water transport to the above parts of the plant. In addition to this, Cr transport to the aerial part of the plant can have a direct impact on cellular metabolism of shoots contributing to the reduction in plant height.

Leaf growth

Leaf growth, area development and total leaf number decisively determine the yield of crops (Table 3). Leaf number per plant reduced by 50% in wheat when 0.5 mM Cr was added in nutrient solution (Sharma and Sharma, 1993). Tripathi et al. (1999) found that leaf area and biomass of *Albizia lebbek* seedlings was severely affected by a high concentration (200 ppm) of Cr(VI). These authors noted that leaf growth traits might serve as suitable bioindicators of heavy metal pollution and in the selection of resistant species.

Primary and trifoliolate leaves of bush bean plants grown in 1–10 Ag cm⁻³ Cr showed a marked decrease in leaf area; trifoliolate leaves were more affected by Cr than the primary leaves (Barcelo et al., 1985). Dry leaf yield of bush bean plants was found to decrease up to 45% when 100 ppm of Cr(VI) was added to soil (Wallace et al., 1976). Karunyal et al. (1994) studied the effect of tannery effluent on leaf area and biomass and reported that all the concentrations tested decreased leaf area and leaf dry weight in *Oryza sativa*, *Acacia holosericea* and *Leucaena leucocephala*.

In a study on the effect of Cr(III) and Cr(VI) on spinach, Singh (2001) reported that Cr

applied at 60 mg kg⁻¹ and higher levels reduced the leaf size, caused burning of leaf tips or margin and slowed leaf growth rate. Jain et al. (2000) observed leaf chlorosis at 40 ppm Cr that turned to necrosis at 80 ppm Cr. In a study with several heavy metals, Pedreno et al. (1997) found that Cr had a pronounced effect on leaf growth and preferentially affected young leaves in tomato plants. Reduction in leaf biomass was correlated with the oxalate acid extractable Cr in *P. vulgaris* by Poschenrieder et al. (1993).

Total dry weight production

The first prerequisite for higher yields in plants is an increase in biomass production in terms of dry matter. Carbon compounds account for 80–90% of the total dry matter produced by plants. Higher source size and increased photosynthetic process was found to be the basis for the building up of organic substances and dry matter production under heavy-metal stress in general and Cr in particular (Bishnoi et al., 1993a,b).

In a study conducted on *Vallisneria spiralis* to evaluate the Cr accumulation and toxicity in relation to biomass production, it was found that dry matter production was severely affected by Cr(VI) concentrations above 2.5 Ag mL⁻¹ in nutrient medium (Vajpayee et al., 2001).

Yield

Plant yield is dependent on leaf growth, leaf area, and number. As Cr affects most of the biochemical and physiological process in plants, productivity and yield are also affected. Cr (VI) in irrigation water decreased significantly grain weight and yield (kg ha⁻¹) of paddy (*Oryza sativa*) up to 80% under 200 mg L⁻¹ of Cr (Sundaramurthi et al., 2010).

Physiological processes

Photosynthesis

Chromium stress is one of the important factors that affect photosynthesis in terms of CO₂ fixation, electron transport, photophosphorylation and enzyme activities (Clijsters and Van Assche, 1985). In higher plants and trees, the effect of Cr on photosynthesis is well documented (Foy et al., 1978). However, it is not well understood to what extent Cr-induced inhibition of photosynthesis is due to disorganization of chloroplast ultrastructure (Vazques et al., 1987), inhibition of electron transport or the influence of Cr on the enzymes of the Calvin cycle. Chromate is used as a Hill reagent by isolated chloroplast (Desmet et al., 1975). The more pronounced effect of Cr(VI) on PS I than on PS II activity in isolated chloroplasts has been reported by Bishnoi et al. (1993a,b) in peas. Nevertheless, in whole plants, both the photosystems were affected. Zeid (2001) observed in peas that Cr at the highest concentration tested (10⁻² M) decreased photosynthesis drastically. Krupa and Baszynski (1995) explained some hypotheses concerning the possible mechanisms of heavy-metals toxicity on photosynthesis and presented a list of key enzymes of photosynthetic carbon reduction, which were inhibited in heavy-metal treated plants (mainly cereal and legume crops).

Water relations

Wilting of various crops and plant species due to Cr toxicity has been reported (Turner and Rust, 1971), but little information is available on the exact effect of Cr on water relations of higher plants. Barcelo et al. (1985) observed a decrease in leaf water potential in Cr treated bean plants. Excess Cr decreased the water potential and

transpiration rates and increased diffusive resistance and relative water content in leaves of cauliflower (Chatterjee and Chatterjee, 2000). Decreased turgor and plasmolysis was observed in epidermal and cortical cells of bush bean plants exposed to Cr (Vazques et al., 1987). Toxic levels of Cr in beans were found to decrease tracheary vessel diameter, thereby reducing longitudinal water movement (Vazques et al., 1987). Impaired spatial distribution and reduced root surface of Cr-stressed plants can lower the capacity of plants to explore the soil surface for water. The significantly higher toxic effect of Cr(VI) in declining the stomatal conductance could be due to the high oxidative potential of Cr(VI), which in turn may be instrumental in damaging the cells and membrane of stomatal guard cells.

Mineral nutrition

Chromium, due to its structural similarity with some essential elements, can affect mineral nutrition of plants in a complex way. Interactions of Cr with uptake and accumulation of other inorganic nutrients have received maximum attention by researchers. Cr(III) and Cr(VI) are taken up by the plants by different mechanisms (Zaccheo et al., 1985). It has been suggested that both species can interfere with uptake of several other ionically similar elements like Fe and S (Skeffington et al., 1976). Nutrient solution with 9.6 AM Cr(VI) decreased the uptake of K, Mg, P, Fe and Mn in roots of soybean (Turner and Rust, 1971). Excess Cr interfered with the uptake of Fe, Mo, P and N (Adriano, 1986). Barcelo et al. (1985) described the inhibition of P, K, Zn, Cu and Fe translocation within the plant parts when bean plants were exposed to Cr in nutrient solutions. Sujatha et al. (1996) reported that tannery effluent irrigation caused micronutrient deficiencies in several agricultural crops.

Enzyme and other compounds

Nitrate reductase

Nitrate reductase (NR) activity of leaves was significantly increased over control values and negatively correlated with root and shoot length, leaf area and biomass of the plants, indicating stress due to Cr(VI) in *A. lebbek* (Tripathi et al., 1999). Cr concentrations up to 200 AM resulted in significant inhibition of NR activity in *Nelumbo nucifera* (Vajpayee et al., 1999) and *Nymphaea alba* (Vajpayee et al., 2000). Seedlings treated with 1 AM Cr resulted in increased NR activity, whereas higher Cr concentrations were toxic and reduced the enzyme activity significantly in wheat (Panda and Patra, 2000).

Root Fe (III) reductase

Chlorosis induced by heavy metals has been generally correlated with low plant Fe content, suggesting effects on Fe mobilisation and uptake. Under Fe-deficient conditions, dicotyledonous plants enhanced root Fe(III) reductase activity, thus increasing the capacity to reduce Fe(III) to Fe(II), the form in which roots absorb Fe (Alcantara et al., 1994). Cr is reported to affect Fe uptake in dicots either by inhibiting reduction of Fe(III) to Fe(II) or by competing with Fe(II) at the site of absorption (Shanker, 2004).

Chromium application to iron-deficient *Plantago lanceolata* roots increased the activity of root-associated Fe(III) reductase. This effect was evident only with acceptors of the turbo reductase and was not observed in iron-sufficient plants (Wolfgang, 1996). In split-root experiments, which allowed only a part of the root system to receive Cr while the other portion was grown in iron-

free medium, roots subjected to either treatment showed an intermediate FeEDTA reductase activity with respect to non-split control plants (Wolfgang, 1996). The addition of Cr (III) at 2 AM slightly inhibited ferric chelate reductase in roots of plants grown under iron-limited conditions; Cr (III) at 10 AM stimulated ferric chelate reductase in roots from both iron-limited and iron-sufficient media (Barton et al., 2000).

Plasma membrane H⁺ ATPase

ATPase plays a significant role in the adaptation to heavy-metal conditions and it is regulated at the molecular and biochemical level (Dietz et al., 2001). A toxic effect of Cr on the transport activities of plant cell plasma membrane was suggested by Zaccheo et al. (1982). After a short-term exposure to 2 AM Cr(VI), a strong inhibition of both H⁺ and K⁺ uptake in maize root segments was observed, while the transmembrane electric potential was unchanged (Zaccheo et al., 1985). Pillay (1994) found that ATPase activity increased at higher treatment concentrations in a study on the effects of soil Cr treatment on different metabolites and certain enzymes of *Helianthus suaveolens* and *Helianthus annuus* leaves.

The inhibition of ATPase activity could be due to disruption of the membrane because of free radical formation. The decrease in ATPase activity causes a decrease in proton extrusion. This in turn could cause a decrease in the transport activities of the root plasma membrane, thus reducing the uptake of most nutrient elements. It is also possible that Cr interfered with the mechanism controlling the intracellular pH; this possibility is supported by the fact that Cr could be reduced in the cells thereby utilizing the protons (Zaccheo et al., 1985).

Antioxidant enzymes

Induction and activation of superoxide dismutase (SOD) and of antioxidant catalase are some of the major metal detoxification mechanisms in plants (Prasad, 1998). Gwozdz et al. (1997) found that at lower heavy metal concentrations, activity of antioxidant enzymes increased, whereas at higher concentrations, the SOD activity did not increase further and catalase activity decreased. Pea plants exposed to environmentally relevant (20 AM) and acute (200 AM) concentrations of Cr(VI) for 7 days affected total SOD activity of root mitochondria differently. At 20 AM Cr(VI), SOD activity was found to increase by 29%, whereas 200 AM Cr(VI) produced a significant inhibition (Dixit et al., 2002). A decline in the specific activity of catalase with increase in Cr concentration from 20 to 80 ppm was observed (Jain et al., 2000). Excess of Cr (0.5 mM) restricted the activity of catalase in leaves of cauliflower (Chatterjee and Chatterjee, 2000). H₂O₂ levels increased in both roots and leaves of sorghum treated with either 50 AM Cr(VI) or 100 AM Cr(III). A similar increase in lipid peroxidation, in terms of malondialdehyde formation, was observed with these treatments.

Plants with potential of phytoremediation of Cr contamination

Literature survey shows that very few workers have reported ameliorative measures for Cr toxicity in crop plants. This is largely due the reason that most of the research has been focused on enhancing phytoaccumulation of Cr by plants and trees for its use in phytoremediation. Impaired mineral nutrition due to Cr toxicity has been corrected by the application of mycorrhizal inoculation. Khan (2001) reported the potential of mycorrhizae in protecting tree

species *Populus euroamericana*, *Acacia arabica* and *Dalbergia sisso* against the harmful effects of heavy metal and phytoremediation of Cr contamination in tannery effluent-polluted soils. Shanker et al. (in press) have reported the possible use of *Albizia amara* as a potential Cr phytoaccumulator. Karagiannidis and Hadjisavva Zinoviadi (1998) studied the effect of the vesicular arbuscular mycorrhizal fungus (VAMF) *Glomus mosseae* on growth, yield and nutrient uptake of durum wheat and reported that VAMF enhanced yield in wheat and simultaneously decreased the Cr content in the plant. In a study on the effects of Cr on the uptake and distribution of micronutrients (Fe, Mn, Cu and Zn) in mycorrhizal soybean and maize in sand culture, Davies et al. (2001) found that VAMF enhanced the ability of sunflower plants to tolerate Cr; similarly, Davies et al. (2002) reported that VAMF had a positive effect on tissue mineral concentration, growth and gas exchange in Cr-treated plant

Concluded remark

This paper includes an overview of the literature about Cr toxicity in the environment, especially in water and soil and provides new insights about Cr toxicity in plants. Cr exists mainly in three oxidative states Cr (0), Cr (III), and Cr (VI), which are the most stable forms of Cr. As Cr (0) is the metallic form, the forms of Cr (III) and Cr (VI) are the most preponderant in soils and water. Once in water/soil, Cr suffers a variety of transformations such as oxidation, reduction, sorption, desorption, precipitation, and dissolution. While Cr (III) solubility is dependent on pH, Cr (VI) is extremely soluble under all pH conditions. Cr as being a nonessential element for plants does not have any specific mechanism for its uptake. Cr (III) uptake is a passive process,

whereas Cr (VI) uptake is performed by carriers of essential elements such as sulphate. Cr accumulates mainly on plant roots, being translocated to shoots in small levels, independently of Cr specie. Despite known toxicity of Cr to plants, there are several plants that hyper accumulate this metal contributing to its removal from soil/water, showing good potential for application in Cr phytoremediation strategies. Cr affects several processes in plants, namely, seed germination, growth, yield and also physiological processes as photosynthesis impairment and nutrient and oxidative imbalances. Also, it has been shown that Cr is able to induce genotoxicity in several plant species.

References

- Adriano, D.C. 1986. Trace Elements in the Terrestrial Environment. New York7 Springer Verlag; p. 105– 23.
- Alcantara, E., Romera, F.J., Canete, M., De la Guardia, M.D. 1994. Effects of heavy metals on both induction and function of root Fe (III) reductase in Fedeficient cucumber (*Cucumis sativus* L) plants. *J Exp Bot.* 45: 1983–1998.
- Anderson A.J., Meyer, D.R., Mayer, F.K., 1972. Heavy metal toxicities: levels of nickel, cobalt and chromium in the soil and plants associated with visual symptoms and variation in growth of an oat crop. *Aust J Agric Res.* 24:557–71.
- Anderson T. A., and Coats J. R., Eds., vol. 664 of ACS Symposium, pp. 274–282, DC7 American Chemical Society, Washington, DC, USA.
- Avudainayagam S., Megharaj M., Owens G., Kookana R. S., Chittleborough D., and Naidu R., 2003. “Chemistry of chromium in soils with emphasis on tannery waste sites,” *Reviews of Environmental Contamination and Toxicology.*178: 53–91.
- Babula P., Adam V., Opatrilova R., Zehnalek J., Havel L., and Kizek R., 2008. “Uncommon heavy metals, metalloids and their plant toxicity: a review,” *Environmental Chemistry Letters.* 6 (4)189–213.
- Barnhart J. 1997. Occurences, uses, and properties of chromium. *Regulatory Toxicology Pharmacology*, 26, S3–S7.
- Barton L.L., Johnson G.V., O’Nan A.G., Wagener B.M. 2000. Inhibition of ferric chelate reductase in alfalfa roots by cobalt, nickel, chromium, and copper. *J Plant Nutr.* 23:1833– 1845.
- Barcelo J., Poschenriender C., Ruano A., Gunse B. 1985. Leaf water potential in Cr (VI) treated bean plants (*Phaseolus vulgaris* L). *Plant Physiol Suppl.* 77:163– 164.
- Becquer T., Quantin C., Sicot M., and Boudot J. P., 2003. “Chromium availability in ultramafic soils from New Caledonia,” *Science of the Total Environment.* 301 (1–3): 251– 261.
- Bishnoi N.R., Chugh L.K., Sawhney S.K. 1993a. Effect of chromium on photosynthesis, respiration and nitrogen fixation in pea (*Pisum sativum* L) seedlings. *J Plant Physiol.* 142:25–30.
- Bishnoi N.R., Chugh L.K., Sawhney S.K. 1993b. Effect of chromium on seed germination, seedling growth and yield of peas. *Agric Ecosyst Environ.* 47:47–57.
- Cary, E. E. 1982. “Chromium in air, soils, and natural waters,” in *Biological and Environmental Aspects of Chromium*, S. Langard, Ed., pp. 49–63, Elsevier Biomedical, New York, NY, USA.
- Cervantes C., Garc’ia J. C., Devars S. et al., “Interactions of chromium with microorganisms and plants,” *FEMS*

- Microbiology Reviews. 25 (3): 335–347, 2001.
- Chandra P., Sinha S., and Rai U. N., 1997. “Bioremediation of Cr from water and soil by vascular aquatic plants,” in *Phytoremediation of Soil and Water Contaminants*, Kruger E. L., Chatterjee J., Chatterjee C. 2000. Phytotoxicity of cobalt, chromium and copper in cauliflower. *Environ Pollut.* 109: 69–74.
- Clijsters H., Van Assche F. 1985. Inhibition of photosynthesis by heavy metals. *Photosynth Res.* 7:31–40.
- Davies F.T., Puryear J.D., Newton R.J., Egilla J.N., Grossi J.A.S. 2001. Mycorrhizal fungi enhance accumulation and tolerance of chromium in sunflower (*Helianthus annuus*). *J Plant Physiol.* 158:777–786.
- Davies F.T., Puryear J.D., Newton R.J., Egilla J.N., Grossi J.A.S. 2002. Mycorrhizal fungi increase chromium uptake by sunflower plants: influence on tissue mineral concentration, growth, and gas exchange. *J Plant Nutr.* 25: 2389–407.
- Desmet G.A., de Ruyter G.A., Rigoet A. 1975. Absorption and metabolism of Cr (VI) by isolated chloroplasts. *Phytochemistry.* 14: 2585–2588.
- Dietz K.J., Tavakoli N., Kluge C., Mimura T., Sharma S.S., Harris G.C., et al. 2001. Significance of the V-type ATPase for the adaptation to stressful growth conditions and its regulation on the molecular and biochemical level. *J Exp Bot.* 52:1969–80.
- Dixit V., Pandey V., Shyam R. 2002. Chromium ions inactivate electron transport and enhance superoxide generation in vivo in pea (*Pisum sativum* L.cv. Azad) root mitochondria. *Plant Cell Environ.* 25:687–690.
- Fendorf S. E. and Zasoski R. J., 1992. “Chromium (III) oxidation by δ -MnO₂. 1. Characterization,” *Environmental Science and Technology.* 26 (1): 79–85.
- Furnival E.P., Corbert J.L., Inskip M.W. (1990a): Evaluation of controlled release devices for administration of chromium sesquioxide using fistulated grazing sheep. I. Variation in marker concentration in faeces. *Australian Journal of Agricultural Research*, 41: 969–975.
- Furnival E.P., Ellis K.J., Pickering F.S. (1990b): Evaluation of controlled release devices for administration of chromium sesquioxide using fistulated grazing sheep. II. Variation in rate of release from the device. *Australian Journal of Agricultural Research*, 41: 977–986.
- Foy C.D., Chaney R.L., White M.C. 1978. The physiology of metal toxicity in plants. *Ann Rev Plant Physiol.* 29: 511–66.
- Gopal R., Rizvi A. H., and Nautiyal N., 2009. “Chromium alters iron nutrition and water relations of spinach,” *Journal of Plant Nutrition.* 32 (9): 1551–1559.
- Gwozdz E.A., Przymusinski R., Rucinska R., Deckert J. 1997. Plant cell responses to heavy metals: molecular and physiological aspects. *Acta Physiol Plant.* 19:459–65.
- Hanus J., Tomas J. 1993. An investigation of chromium content and its uptake from soil in white mustard. *Acta Fytotech.* 48:39–47.
- Hossner, L. R. 1996. “Phytoaccumulation of selected heavy metals, uranium, and plutonium in plant systems,” *Quarterly Progress Report*, Texas A&M University: College Station, TX, Project UTA96–0043.

- Huffman Jr. E. W. and Allaway H. W., 1973. "Chromium in plants: distribution in tissues, organelles, and extracts and availability of bean leaf Cr to animals," *Journal of Agricultural and Food Chemistry*. 21 (6): 982–986.
- Jain R., Srivastava S., Madan V.K., Jain R. 2000. Influence of chromium on growth and cell division of sugarcane. *Indian J Plant Physiol*. 5:228–31.
- James B.R. 1996. The challenge of remediating chromium-contaminated soils. *Environ Sci Technol*. 30:248A–51A.
- Joseph G.W., Merrilee R.A., ; 1995. Raymond E. Comparative toxicities of six heavy metals using root elongation and shoot growth in three plant species. The symposium on environmental toxicology and risk assessment, Atlanta, GA, USA. p. 26–29.
- Kimbrough D. E., Cohen Y., Winer A. M., Creelman L., and Mabuni C. 1999. "A critical assessment of chromium in the environment," *Critical Reviews in Environmental Science and Technology*. 29 (1): 1–46.
- Karunyal S., Renuga G., Paliwal K. 1994. Effects of tannery effluent on seed germination, leaf area, biomass and mineral content of some plants. *Bioresour Technol*. 47:215–8.
- Kimbrough D.E., Cohen Y., Winer A.M., Creelman L., Mabuni C. A. 1999. critical assessment of chromium in the environment. *Crit Rev Environ Sci Technol*. 29:1–46.
- Karagiannidis N., Hadjisavva Zinoviadi S. 1998. The mycorrhizal fungus *Glomus mosseae* enhances growth, yield and chemical composition of a durum wheat variety in 10 different soils. *Nutr Cycl Agroecosyst*. 52:1–7.
- Khan A.G. 2001. Relationships between chromium bio magnification ratio, accumulation factor, and mycorrhizae in plants growing on tannery effluent-polluted soil. *Environ Int* . 26:417–423.
- Kim Y. J., Kim J. H., Lee C. E. et al., "Expression of yeast transcriptional activator MSN1 promotes accumulation of chromium and sulfur by enhancing sulfate transporter level in plants," *FEBS Letters*. 580 (1):206–210, 2006.
- Kotas J and Stasicka Z. 2000. Commentary: chromium occurrence in the environment and methods of its speciation. *Environ Pollut*. 107:263–283.
- Krupa Z. and Baszynski T. 1995. Some aspects of heavy metals toxicity towards photosynthetic apparatus—direct and indirect effects on light and dark reactions. *Acta Physiol Plant*.17:177–190.
- Liu D., Zou J., Wang M., and Jiang W., 2008. "Hexavalent chromium uptake and its effects on mineral uptake, antioxidant defence system and photosynthesis in *Amaranthus viridis* L.," *Bioresource Technology*. 99 (7): 2628–2636.
- Mortvedt J. J. and Giordano P. M., 1975. "Response of corn to zinc and chromium in municipal wastes applied to soil," *Journal of Environmental Quality*. 4 (2): 170–174.
- Mertz W. 1993: Chromium in human nutrition: a review. *The Journal of Nutrition*, 123: 626–633.
- Mazanec O. 1996. The content of risk elements in farm land throughout the Czech Republic (in Czech). In: Microelements. *Ceska spolecnost chemicka*, Prague. 56–59.
- Mishra S., Singh V., Srivastava S. et al., 1995. "Studies on uptake of trivalent and hexavalent chromium by maize

- (*Zea mays*),” *Food and Chemical Toxicology*. 33 (5): 393–397.
- Nriagu J.O. 1988. Production and uses of chromium. Chromium in natural and human environment. New York, USA7 John Wiley and Sons; pp. 81–105.
- Opez-Luna J. L., Gonz´alez-Ch´avez M. C., Esparza-Garc´ıa F. J., and Rodr´ıguez-V´azquez R., 2009. “Toxicity assessment of soil amended with tannery sludge, trivalent chromium and hexavalent chromium, using wheat, oat and sorghum plants,” *Journal of Hazardous Materials*. 163 (2-3): 829–834.
- Panda S.K., Patra H.K. 2000. Nitrate and ammonium ions effect on the chromium toxicity in developing wheat seedlings. *P Natl Acad Sci India B*. 70:75– 80.
- Paiva L. B., de Oliveira J. G., Azevedo R. A., Ribeiro D. R., da Silva M. G., and Vitoria A. P., 2009. “Ecophysiological responses of water hyacinth exposed to Cr³⁺ and Cr⁶⁺,” *Environmental and Experimental Botany*. 65 (2-3): 403–409.
- Parr P.D., Taylor Jr F.G. 1982. Germination and growth effects of hexavalent chromium in Orocol TL (a corrosion inhibitor) on *Phaseolus vulgaris*. *Environ Int.*7:197–202.
- Pedreno N.J.I., Gomez R., Moral G., Palacios J., Mataix J. 1997. Heavy metals and plant nutrition and development. *Recent Res Dev Phytochem*. 1: 173– 9.
- Peralta J.R., Gardea Torresdey J.L., Tiemann K.J., Gomez E., Arteaga S., Rascon E., et al. 2001. Uptake and effects of five heavy metals on seed germination and plant growth in alfalfa (*Medicago sativa*) L. *B Environ Contam Toxicol*. 66(6):727– 34.
- Peralta-Videa J. R., Lopez M. L., Narayan M., Saupe G., and Gardea-Torresdey J., 2009. “The biochemistry of environmental heavy metal uptake by plants: implications for the food chain,” *International Journal of Biochemistry and Cell Biology*. 41 (8-9): 1665–1677.
- Pillay S.V. 1994. Biochemical changes in *Hyptis suaveolens* (L) Poit and *Helianthus annuus* L in response to chromium treatment. *J Phytol Res* 7:165 – 7.
- Poschenrieder C., Gunse B., Barcelo J. 1993. Chromium-induced inhibition of ethylene evolution in bean (*Phaseolus vulgaris*) leaves. *Physiol Plant*. 89:404– 8.
- Prasad M.N.V. 1998. Metal-biomolecule complexes in plants: occurrence, functions, and applications. *Analisis*. 26-28.
- Ramachandran V., D’Souza T. J., and Mistry K. B., 1980. “Uptake and transport of chromium in plants,” *Journal of Nuclear Agriculture and Biology*. 9 (4): 126–128.
- Rosas I., Belmomt R., Baez A., and Villalobos-Pietrini R., 1989. “Some aspects of the environmental exposure to chromium residues in Mexico,” *Water, Air, and Soil Pollution*. 48 (3-4): 463–475.
- Rout G.R., Samantaray S., Das P. 1997. Differential chromium tolerance among eight mungbean cultivars grown in nutrient culture. *J Plant Nutr*. 20:473– 83.
- Rout G.R., Samantaray S., Das P. 2000. Effects of chromium and nickel on germination and growth in tolerant and non-tolerant populations of *Echinochloa colona* (L). *Chemosphere* 40:855–9.
- Samantary S. 2002. “Biochemical responses of Cr-tolerant and Crsensitive mung

- bean cultivars grown on varying levels of chromium,” *Chemosphere*, 47 (10): 1065–1072.
- Sharma D. C., Sharma C. P. 1993. Chromium uptake and its effects on growth and biological yield of wheat. *Cereal Res Commun.* 21:317–21.
- Sharma D.C., Pant R.C. 1994. Chromium uptake and its effects on certain plant nutrients in maize (*Zea mays* L. cv. Ganga 5). *J Environ Sci Health A.* 29:941–8.
- Shanker A.K., Djanaguiraman M., Sudhagar R., Chandrashekar C.N., Pathmanabhan G. 2004a. Differential antioxidative response of ascorbate glutathione pathway enzymes and metabolites to chromium speciation stress in green gram (*Vigna radiata* (L) R Wilczek, cv CO 4) roots. *Plant Sci.* 166:1035–43.
- Shanker A.K., Ravichandran V., Pathmanabhan G. Phytoaccumulation of chromium by some multipurpose tree seedlings. *Agroforestry Systems*; in press.
- Scoccianti V., Crinelli R., Tirillini B., Mancinelli V., and Speranza A., 2006. “Uptake and toxicity of Cr(III) in celery seedlings,” *Chemosphere.* 64 (10): 1695–1703.
- Singh A.K. 2001. Effect of trivalent and hexavalent chromium on spinach (*Spinacea oleracea* L). *Environ Ecol.* 19:807–10.
- Skeffington R. A., Shewry P. R., and Peterson P. J., 1976. “Chromium uptake and transport in barley seedlings (*Hordeum vulgare* L.),” *Planta.* 132 (3): 209–214.
- Sujatha P., Gupta A. 1996. Tannery effluent characteristics and its effects on agriculture. *J Ecotoxicol Environ Monit.* 6:45–8.
- Sundaramoorthy P., Chidambaram A., Ganesh K. S., Unnikannan P., and Baskaran L., 2010. “Chromium stress in paddy: (i) nutrient status of paddy under chromium stress; (ii) phytoremediation of chromium by aquatic and terrestrial weeds,” *Comptes Rendus Biologies.* 333 (8): 597–607.
- Tiwari K. K., Dwivedi S., Singh N. K., Rai U. N., and Tripathi R. D., 2009. “Chromium (VI) induced phytotoxicity and oxidative stress in pea (*Pisum sativum* L.): biochemical changes and translocation of essential nutrients,” *Journal of Environmental Biology.* 30 (3): 389–394.
- Tripathi A.K., Tripathi Sadhna, Tripathi S. 1999. Changes in some physiological and biochemical characters in *Albizia lebbek* as bio-indicators of heavy metal toxicity. *J Environ Biol.* 20:93–8.
- Turner M.A., Rust R.H. 1971. Effects of chromium on growth and mineral nutrition of soybeans. *Soil Sci Soc Am Proc.* 35:755–8
- Vajpayee P., Sharma S.C., Tripathi R.D., Rai U.N., Yunus M. 1999. Bioaccumulation of chromium and toxicity to photosynthetic pigments, nitrate reductase activity and protein content of *Nelumbo nucifera* Gaertn. *Chemosphere.* 39:2159–69.
- Vajpayee P., Tripathi R.D, Rai U.N., Ali M.B., Singh S.N. 2000. Chromium (VI) accumulation reduces chlorophyll biosynthesis, nitrate reductase activity and protein content in *Nymphaea alba* L. *Chemosphere.* 41:1075–82.
- Vajpayee P., Rai U.N., Ali M.B., Tripathi R.D., Yadav V., Sinha S., et al. 2001. Chromium induced physiological changes in *Vallisneria spiralis* L and its role in phytoremediation of tannery

- effluent. *Bull Environ Contam Toxicol.* 67(2):246– 56.
- Vazques M.D., Poschenrieder Ch., Barcelo J. 1987. Chromium (VI) induced structural changes in bush bean plants. *Ann Bot.* 59: 427–38.
- Vernay P., Gauthier-Moussard C., and Hitmi A., 2007. “Interaction of bioaccumulation of heavy metal chromium with water relation, mineral nutrition and photosynthesis in developed leaves of *Lolium perenne* L.,” *Chemosphere.* 68 (8): 1563–1575.
- Wallace A., Soufi S.M., Cha J.W., Romney E.M. 1976. Some effects of chromium toxicity on bush bean plants grown in soil. *Plant Soil.* 44: 471– 3.
- Wolfgang S. 1996. Influence of chromium (III) on root-associated Fe (III) reductase in *Plantago lanceolata* L. *J Exp Bot.* 47:805– 10.
- Zayed A., Lytle C. M., Qian J. H., and Terry N., 1998. “Chromium accumulation, translocation and chemical speciation in vegetable crops,” *Planta,* 206 (2): 293–299.
- Zayed A, Terry N. 2003. Chromium in the environment: factors affecting biological remediation. *Plant Soil.* 249:139–56.
- Zaccheo P., Genevini P.L., Cocucci S. 1982. Chromium ions toxicity on the membrane transport mechanism in segments of maize seedling roots. *J Plant Nutr.* 5:1217– 1227.
- Zaccheo P., Cocucci M., Cocucci S. 1985. Effects of Cr on proton extrusion, potassium uptake and transmembrane electric potential in maize root segments. *Plant Cell Environ.* 8:721– 6.
- Zeid I.M. 2001. Responses of *Phaseolus vulgaris* to chromium and cobalt treatments. *Biol Plant.* 44:111 – 5.