Chapter 8
Chromium Dynamics in the Soil-Plant Continuum

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Abstract Heavy metal use is playing a crucial role in economic development of a country. Another side, generated waste may be affected the quality of natural resources during unscientific disposal. This situation is grimmer in developing countries, where much effort is needed to scientific disposal of waste. Chromium (Cr), one

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of the heavy metals, is extremely important to the metal, leather, and wooden industries and releases a sizable amount of effluent into water or onto soil surfaces. Crop production potential and soil health indices were both decreased by higher Cr concentrations in the soil. It mediated metabolic activities in plants and organs functionality in human body. An excessive concentration in the human body can have a cancerous effect and shorten life. By the help of scientific tool and techniques, we can manage the Cr pollution prior to discharge in natural bodies. The removal of Cr using physical, chemical, and biological approaches can significantly increase crop production potential. Increase the people's participation and awareness to reduce the Cr toxicity effect through food chain contamination are much needed. Many research and policy organizations are working on Cr toxicity issues to remove/immobilization process without affecting the environmental health. This chapter discusses the significance of Cr, its origins and chemistry in soil, as well as its toxicity to plants and people, effect on soil microbial count and diversity and management options for reducing the Cr toxicity in soil.

Keywords Crop sustainability · Chromium toxicity · Dynamics in soil-plant · Human health · Phytoremediation techniques · Soil contamination

8.1 Introduction

By 2050, India's population will have increased to 1.66 billion, and it would require 333 million tonnes (mt) of grain to feed that population (Minhas et al. 2021). Present scenario of agriculture having improved varieties, tool and techniques of balance fertilizer application, better weather forecasting, friendly production and protection technologies, modern application of extension process are helped to enhance the food grain production 50 mt in 1950 to 309 mt in the year 2022 (Dotaniya et al. 2022c). These achievements are not easy to achieve, but the contentious efforts of researcher and policy maker to strengthen the food production programme in collaboration of national and international institutes. However, growing populations feed on limited natural resources are a big challenge to researchers. Developing countries are increased the rate of industries installation to boost the economic growth of the country. Another side of the coin, these industries are generating huge volume of effluents and discharging into water bodies or on the soils (Solanki et al. 2020). These waste substances are containing huge amount of salt/acid or significant amount of heavy metals (Dotaniya et al. 2022a). While not all types of industries are in the same predicament, the majority of them in developing nations have subpar treatment facilities. There are 269 sewage treatment plant (STP) constructed in India

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and 38254 million liters per day (MLD) of wastewater is produced, but only 12,000 MLD of processing power has been developed. On an average, 38% of generated sewage is treated and most of the parts are dumping in different waste channels. It degrades ecosystem quality by raising metal and salt toxicity in soil and water sources (Dotaniya et al. 2018a).

Chromium (Cr), which has an atomic number of 46 and a molecular weight of 52 u, is one of the most poisonous heavy metal. However, it is one of the major metal used in industrial sector and significant amount reached into soils. It is presents in many forms and oxidation states ranged from −4, −2, −1, 0, +1, +2, +3, +4, +5, +6 (Dotaniya et al. 2014a). The Cr hexavalent (Cr^{6+}) is toxic form, whereas, trivalent Cr is nontoxic in nature (Dotaniya et al. 2019). Use of tannery effluent for agricultural crop growing resulted in more than 972 mg/kg total Cr being deposited in the soil (Dotaniya et al. 2016). Applying Cr at a dosage of 100 mg/kg influences the soil's microbial biomass carbon mineralization rate by 66% (Dotaniya et al. 2017a). Similarly, Wyszkowska et al. (2007) mentioned that long term application of Cr, an excessive concentration in the soil solution mediated the number and diversity of soil microorganisms. Dotaniya et al. (2017a) mentioned by an application of Cr upto 100 mg/kg drastically reduced the soil enzymatic activities (71.3% DHA, 40% FDA) and microbial count.

Chromium reaching in food stuffs via food chain contamination. Excessive concentration of Cr intake impaired with metabolic functions of human body. These symptoms are very much detective and extreme cases living organism may die. In crop plants, higher concentration of Cr in soil restricted the mineral and water uptake process by affecting the root connecting tissues (Sharma et al. 2020). It was observed that, root tissues are damaged due to Cr toxicity and poor health of crop was reported in tannery irrigated areas. Inter-conversion of Cr^{3+} to Cr^{6+}, however, by moderating the impact of organic matter and the presence of other metal ions (Mn, Fe, Cu). By immobilizing Cr in the soil, the addition of organic C enhances soil health indicators. Application of organic matter through FYM at 10 t/ha decreased the amount of accessible Cr in the soil solution and directly decreased the amount of Cr that spinach crops absorbed in vertisol (Dotaniya et al. 2022b).

8.2 Role of Metal in Plant Nutrient Dynamics

Metals are the essential part of plant nutrients systems. To complete the life cycles of plant needs 17 essential nutrients based on the criteria of Arnon and Stout (1939). These nutrients include carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulphur, calcium, and magnesium. These nutrients are classed as macronutrients, which means they require a bigger amount than 100 mg/kg dry weight. However, crop plant need smaller amount of nutrient concentration (<100 mg/kg dry weight) classified as micro nutrient (iron, copper, manganese, zinc, molybdenum, boron, nickel, chlorine). Certain essential plant metals are found in greater concentrations in soil, behave like poisonous metals, and slow down the intake of other vital plant nutrients. Reactive oxygen species (ROS), which are produced when metals are accumulated in excess, cause poor plant development and lower yields. In this line many metals are clearly identified as trace metal or heavy metal like cadmium, chromium, arsenic, lead, mercury, arsenic etc. These metals in small amount may retard the adsorption and uptake mechanism of essential nutrients or uptake of more concentration of toxic metal (Xu et al. 2011). These metals initially adsorbed and taken up by root tip/hairs and reach to the cellular levels and mediated the different process of plant metabolism (Fig. 8.1). Some of the sensitive organs are reduced the working capacity or show the toxicity symptoms on different parts of plants. In extreme cases, plant reduces water and mineral nutrient leads dead of organs.

8.3 Heavy Metal Sources and Toxicity

The majority of heavy metals are metals with relative densities greater than water (1 g/cc) (Tchounwou et al. 2012). These are mentioned in periodic table of element with yellow color. Some of the essential plant nutrients are also behaving as heavy metals described in different groups of periodic table (Fig. 8.2). These metals are used for examination of a disease or curing an illness of an organ across the globe. Cobalt −60 used for the detection of different disease in human. Cobalt (Co) alloys have been used in a number of medical devices, such as hip and knee implants, surgical instruments, and vascular stents, for over 70 years because of their excellent biocompatibility, durability, and mechanical qualities (Britannica 2022). When harmful compounds accumulate inside an organism at a pace that is quicker than their rate of breakdown, this is known as bioaccumulation. High blood sugar can result from a Cr deficiency. However, too much exposure to these heavy metals can cause poisoning and other severe health issues. Iron and copper, for instance, might build up in the liver. If this occurs, the liver won't operate normally. Such ill effect is affected the majority of the living organisms. However, some of the microorganism likes bacteria, fungi and algae are less affected by metal toxicity and transformed the metal toxicity form into less toxic form (Figs. 8.3, 8.4 and 8.5).

The majority of heavy metals have a significant negative impact on both human and animal health through modulating plant nutrient absorption dynamics, soil organic carbon (SOC) mineralization dynamics, soil microbial development and diversity. Long-term application of marginal quality agricultural imputes during crop production by knowleging and unknowledgingly; accumulated significant amount of pollutant in soil-water ecosystems. Application of fertilizers and pesticides during the crop production contaminated the soil environment with different heavy metals. These pollution sources may be classified into non point sources of metal pollution. The intensity of metal toxicity is depending on form, eco-system properties, the age of living things and their daily metal consumption. Table 8.1 lists the sources of metal pollution in the food chain and how they affect human health.

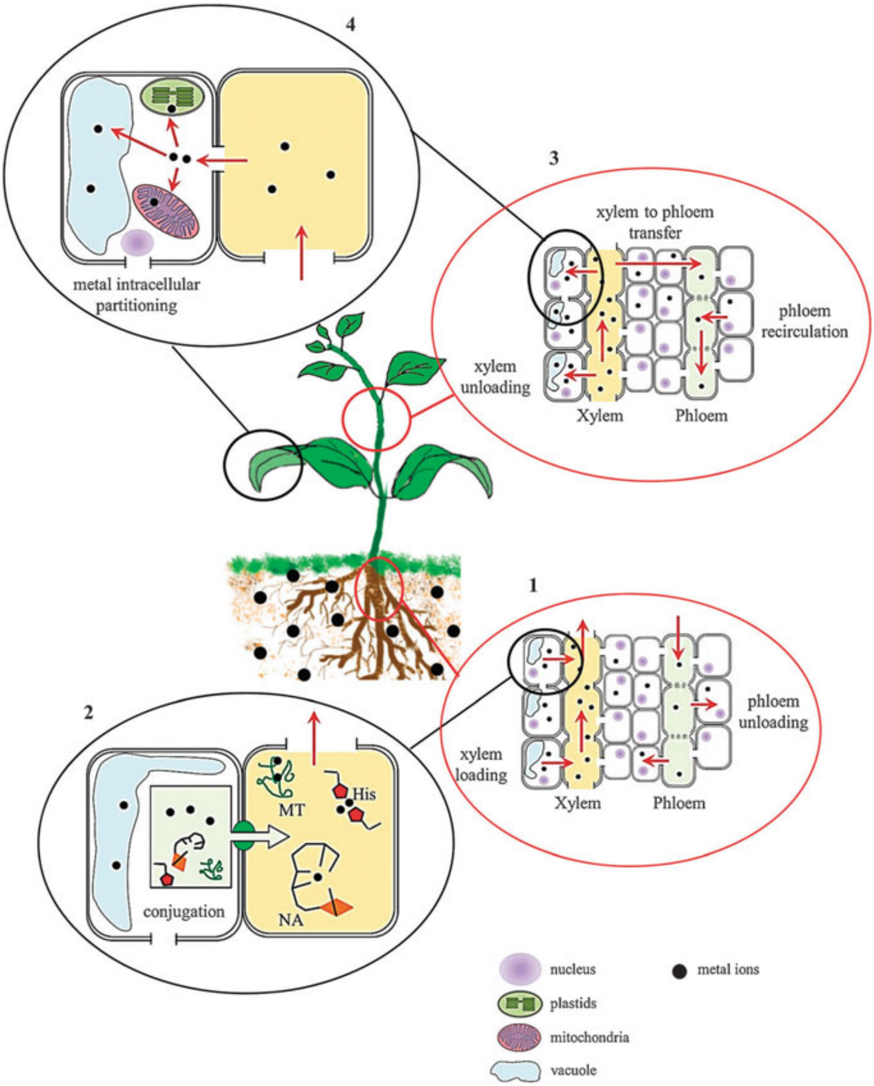

Fig. 8.1 Plant nutrient uptake routs (1) root adsorption metal ions, (2) free ion forms, (3) metal reach to the leaf, (4) metal deliver to the cell/detoxification process. Adopted from DalCorso et al. (2014)

8.4 Chromium Sources and Toxicity

Rapid industrialization and uncontrolled urbanization have caused the entry of heavy metals into water and soil through the inappropriate disposal of industrial wastes directly on land and into water bodies (Mahmoud 2022; Chaukura et al. 2022;

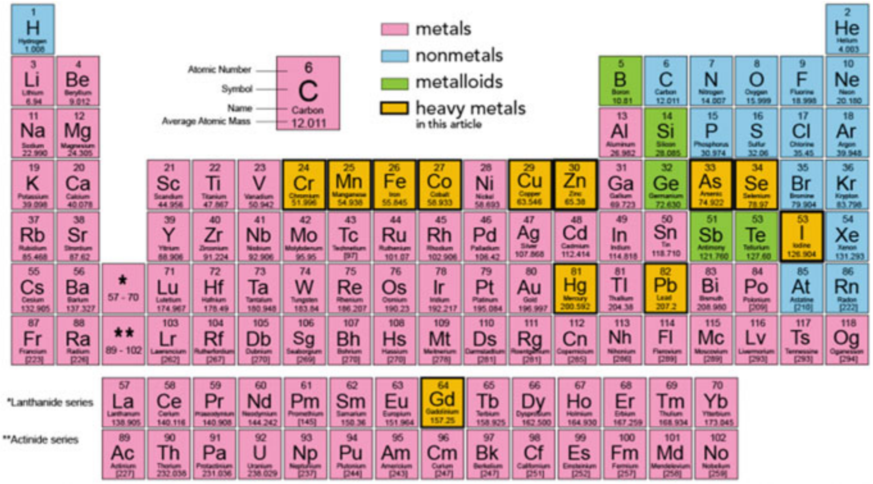

Fig. 8.2 Position of heavy metals in periodic table. Adopted from Letstalk Science (2022)

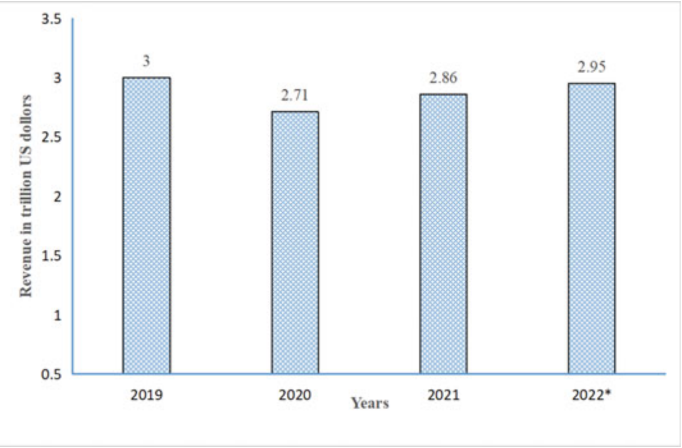

Fig. 8.3 Revenue generation across the globe during 2019–2022 (Statista 2022)

Mahmoud and Kathi 2022; Mahmoud et al. 2021a, b). Pollutants including heavy metals and pesticides cause soil contamination (Sawick et al. 2021; Mahmoud et al. 2016; Mahmoud et al. 2022a). Here, we concentrate on Cr. It is the seventh most prevalent chemical element in the crust of the Earth. Chromium is mostly used in metallurgical processes (67%) as well as refractories (18%) and chemicals (15%) (Saha et al. 2011). It may thus be found in a variety of sectors, including electroplating, tanning, industrial water cooling, paper & pulp manufacture, and petroleum refining. About 35% of the utilised chromium is released as trivalent and hexavalent chromium in the effluent (Sun et al. 2009). The top 20 most dangerous chemicals

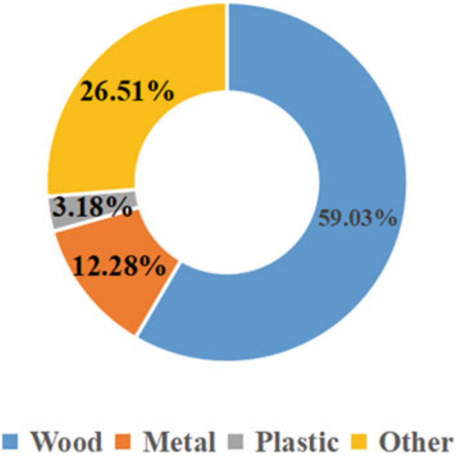

Fig. 8.4 Share of different components in furniture global market in the year 2020

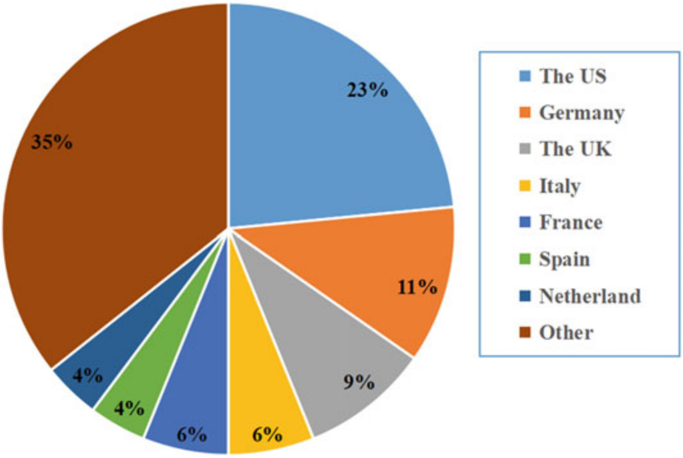

Fig. 8.5 India leather and leather product export during 2021–2022 (DGCI and S 2022)

according to the Agency for Toxic Substances and Disease Registry include the heavy metal chromium (Oh et al. 2007). Due to its nonbiodegradable nature and destructive impacts on living things, chromium is extremely poisonous (Mahmoud et al. 2021a, b, 2022b).

Around 1.29 × 10^5 tonnes of Cr are discharged into the environment each year, the majority of which has accumulated in soil and resulted in substantial Cr pollution (Ao et al. 2022). The entrance of Cr into cells and its harmful effects are significantly influenced by its chemistry. There are two main oxidation states of Cr in water, ground water, and soil: oxidized hexavalent chromium (Cr^{6+}) and less

Table 8.1 Sources of heavy metals and their impact on human health

Metals	Metal form	Sources	Implication for human health
Arsenic	Trivalent As	Metal smelters, fungicides, and pesticides	Skin, respiration problems
Cadmium	Cd^{2+}	Solding, electroplating, chemical formulations, fertilizers, Cd–Ni dry batteries	Lung functions irregularity and renal dysfunction, bone defects, increase blood pressure, kidney damage, gastrointestinal disorder, cancer
Lead	Organic form of Pb, Pb^{2+}	Paint and varnish, agri-pesticide, smoking, automobile emission, mining, burning of coal	Mental retardation of children, developmental delay, congenital paralysis, sensory neural deafness, malfunctions in nerve system, infection in liver and kidney, mediated function of gastrointestinal
Mercury	Hg^{o}	Insecticide/pesticides, dry batteries, pulp and paper industry	Tremors, gingivitis, minor psychological modifications, premature abortion, malfunctions to nervous system, acute protoplasm poisoning
Chromium	Cr(VI)	Mineral industries, tanning process in leather industry, wooden furnishing	Malfunctions in nervous system, fatigue, irritability
Zinc	Zn^{2+}, Zn^{4+}	Refineries, brass manufacture, metal plating and solding	Skin diseases, nervous system problems
Copper	Cu^{2+}, Cu^{4+}	Mineral & mining sector, insecticide/pesticide production, chemical sector, metal pipe industry	Malfunctions in liver and kidney, stomach itching, problem in intestinal irritation

Adopted from Singh et al. (2011), Dotaniya et al. (2018b)

oxidized trivalent chromium (Cr^{3+}) (Zhang et al. 2022). In comparison to hexavalent chromium compounds, trivalent chromium compounds are very slightly soluble in water. Under acidic circumstances, the resultant hexavalent chromium solutions are potent oxidizing agents; but, under basic conditions, they are less potent (Dotaniya et al. 2014a). In chemical laboratories, for instance, chromic acid (H_2CrO_4) is frequently used to clean glassware by oxidizing organic residues. As a result, groundwater contains substantially more hazardous and mobile hexavalent chromium than it does comparatively stationary trivalent chromium (Fei et al. 2022). Depending on the quantity and acidity, hexavalent chromium can exist as chromate (CrO_4^{2-}) or dichromate (CrO_4^{2-}). The two species of dissolved chromium that are most common are $HCrO_4^-$, CrO_4^{2-}, and CrO_4^{2-} (hexavalent chromium). Which entity will prevail in a particular environment depends on a number of specific factors, including pH, Eh (redox potential), the total concentration of Cr, and the overall aqueous chemistry (Ao et al. 2022). Other metal ions, organic matter, soil moisture, and soil biota are major mediators of the absorption kinetics of Cr in soil (Dotaniya et al. 2017b, 2019). It is well recognized that certain soil characteristics, including pH, cation exchange capacity (CEC), organic matter (OM), and metal oxide concentration, affect both the heterogeneity of natural soils and the bioavailability of metals (Jiang et al. 2020).

Cr toxicity, which typically inhibits plant growth, alters the ultra-structure of the cell membrane and chloroplast, causes chlorosis to affect the root cells, reduces pigment content, disrupts water relations and mineral nutrition, impairs transpiration and nitrogen assimilation, and alters a number of enzymatic activities (Cervantes et al. 2007; Ali et al. 2015; Farooq et al. 2016; Reale et al. 2016; Anjum et al. 2017a, b). An overabundance of reactive oxygen species (ROS), which eventually affects the redox balance in plants, may be the root cause of all of these detrimental effects of Cr (Anjum et al. 2017a, b). The germination, root, and shoot growth of the wheat (Dotaniya et al. 2014b) and pigeon pea (Dotaniya et al. 2014c) crops were inhibited by Cr toxicity. Chromium in crop plants affected different metabolic process (Table 8.2).

When untreated wastewater is used to irrigate these food crops, Cr accumulates in the soil and is transported to the edible sections of the plants. Despite relatively low Cr levels in the effluent, Cr-enhanced soil to plant bioaccumulation did occur. The steady accumulation of Cr in the soil was most definitely caused by the treatment of water sources (Chen et al. 2022). It was confirmed by Zhang et al. (2022) that the toxicity of Cr to microbes varied significantly across soil samples, and it was discovered that Cr toxicity was significantly ($p \leq 0.05$) negatively correlated with soil OM content. This finding was in line with earlier studies that found low bioavailability and toxicity of Cr(VI) to plants in soils with a high OM content. It is generally known that soil organic matter (OM) is important for metal mobility, bioavailability, and sorption/desorption.

OM may move Cr and other heavy metals in soil. Additionally, when employed as an electron donor, soil OM may facilitate the reduction of Cr(VI) (Andrade et al. 2022). Oxyanions may be reduced to trivalent forms by electron donors like OM with ease due to soil's high levels of Cr(VI) oxidation. According to research by Palma et al. (2018), high OM concentrations increased Cr(VI) reduction, which may account for the observed inverse relationship between soil OM and Cr(VI) toxicity and likely explains part of the heterogeneity in Cr toxicity. Depending on the pH and the quantity of hexavalent chromium, oxoforms of various species exist as hexavalent chromium in aqueous solutions. Saha et al. (2011) mentioned three major pH zones for the oxo-species of hexavalent Cr were determined (Table 8.3).

Table 8.2 Chromium toxicity effects in different crops

Plant species	Physiological response	References
Tea	Mediated SOD and CAT action in plants	Sharma et al. (2020); Tang et al. (2014)
Chili pepper	Carotenoid concentration positively improved	Oliveira (2012)
Rice	Lower down glutathione level	Qiu et al. (2013)
Chamomile	Enhanced Malondialdehyde	Kováčik et al. (2013)
Chickpea	Yield and yield attributes	Singh et al. (2020)
Deccan grass	Enhanced catalase and peroxidase biochemical activities	Samantaray et al. (2001)
Kandelia candel (species of mangrove)	Elevated Malondialdehyde level, and level of stress enzymes (Catalase and Superoxide dismutase)	Rahman et al. (2010)
Wheat	Reduced root and shoot growth	Rafique et al. (2022)
Holy basil/tulsi	Stimulated proline concentration	Rai et al. (2004)
Rice	Elevated Peroxidase concentration	Ma et al. (2016)
Maize	Stress created by Increased elevating concentration of lipid peroxidation and hydrogen peroxide	Maiti et al. (2012)
Spinach	Reduced biomass	Dotaniya et al. (2017b)
Rice	Enhanced ethylene production	Trinh et al. (2014)
Rice	Enhanced catalase and superoxide dismutase level	Sharma et al. (2020), Zhang et al. (2010)
Rice	Enhanced peroxidase level	Sharma et al. (2020), Xu et al. (2011)
French bean	Drastically lower down carotenoids level	Aldoobie and Beltagi (2013)
Pea	Lower down ascorbate peroxidase content	Duhan (2012)
Pterogyne	Enhanced spermidine content	Sharma et al. (2020), Paiva et al. (2014)
Radish	Enhanced glycine-betaine level	Sharma et al. (2020), Choudhary et al. (2012)
Wheat	Stimulated Malondialdehyde level	Ali et al. (2015)
Wheat	Enhanced lipid peroxidation activities	Zhang et al. (2010)

(continued)

Table 8.2 (continued)

Plant species	Physiological response	References
Mung bean	Lower down glutathione content	Sharma et al. (2020), Shanker et al. (2004)
Maize	Enhanced Superoxide dismutase and Guaiacol peroxidase level	Maiti et al. (2012)
Pigeon pea	Germination, root elongation and coleoptile growth	Dotaniya et al. (2014c)

Table 8.3 Chromium species affected by soil pH

pH value	Chromium species
$pH < 0$	H_2CrO_4
2–6	$HCrO_4^-$, $Cr_2O_7^{2-}$
$pH > 6$	CrO_4^{2-}

8.5 Chromium Pollution is a Necessary Evil?

Chromium is a transitional metal and popular for wooden industries, leather industries, steel industries and medical industries. It is having the hard in nature and mostly used for corrosion resistance. Some of the important industries are having essentially of Cr metal.

8.5.1 Steel Industry

In steel industry, it is mostly preferred for increasing the strength of the alloy. Most of the parts of the automobiles are Cr plated and increasing the hardness protect during the accident. In India, accordingly to the automobile sector expert told that annual transaction of Rs 7.5 lakh crore including 3 lakh crore foreign exchange. Across the globe this sector is growing very fast and contributing significant role in boosting the economic growth of a country. If we were studied the global exchange of automobiles sector depicted approximant 3 trillion US dollars during each year's 2019–2022 (Fig. 8.3). This figure generates huge amount of revenue in associate industries. The prediction of expert from different automobiles firm are expecting more durable, efficient, less corrosive and environmental friendly vehicle lead the world in 2030. In this situation, use of Cr metal would be increased and chunk of it discharged as a waste in the form of solid and liquid. These effluents are partly recycled and major portion of it discharged in different ecosystems. The recovery cost of Cr from automobiles industry effluent needs technological advancement, and lot of cost at initially installation of treatment/recovery plants.

8.5.2 Wooden Industry

It is another priority area of economy of a country. Chromium is preferably used for the preservation of wooden from insect and pest attack, strength, an unmistakable lustre, and a high level of rust resistance. Most of the wooden industries are using Cr as chrome as a trade name. It is manufacturing by adding with different metals like chromium, copper and arsenic as per the need of strength and need of the product (Fig. 8.4). In furniture industries, copper chrome arsenate (CCA) also a popular product used for wooden preservative. Due to significant concentration of different heavy metals, consumers directed not to use for buring and formation of woody items for young children. The global furniture market was US dollors 475.4 billion in the year 2020. It is expected to grow US doller 720.2 billion by the year 2028 with compound annual growth rate (CAGR) 5.5% in the duration 2021–2028-time frame (MRR 2022).

8.5.3 Leather Industries

India's second most revenue generating industry having huge value for economic growth of the country. More than 2000 small and medium sector leather industries are located mostly at Kanpur (UP), Howrah (WB) and Ambur (TN) as household and commercial units. More than 80–90% leather industries are using Cr as a trivalent salt of Cr for tanning purpose. Chromium stabilizes the leather quality by cross-linking the collagen strands during tanning. Approximately, 4–5% of treated Cr strongly bound with leather product component protein. It is adding the strength and smoothness to the leather. Some of the industries are claiming that they are using vegetable dye instead of the Cr metal during the tanning process. India produces roughly 13% of the world's leather hides and skins, and the country's leather industry also produces a substantial amount of leather annually—nearly 3 billion square feet. In India, leather products were exported $402.61 million in May 2022 with a $48.53% increase from May 2021 (IBEF 2022) (Fig. 8.5).

8.5.4 Medical Industries

Many heavy metals are using in different medical industries. Cobalt and selenium are using for mental related medicine. Iron, manganese (Mn), and gadolinium (Gd) are heavy metals that may have been utilized as dyes or contrast agents. These dyes aid in creating a clear image that enables medical professionals to spot tumors or cancerous cells. The treatment of disease is possible with therapeutic radio-pharmaceuticals. For instance, cancer cells can be eliminated from a brain tumour by directing a gamma ray of the isotope cobalt-60 (Co-60) at the tumour.

8.6 Effect of Chromium Toxicity on Soil Health

Worldwide, soil health and its sustainable management are the major areas of concern in the present-day scenario, since soils are a valuable and non-renewable resource (Lal 2015). The dynamic equilibrium of the soil ecosystem is maintained by healthy soil with a good structure, functional state, and buffering capacity. The microbial diversity makes up the majority of arable soil biomass. In order to improve productivity, it is crucial to maintain the health of the soil. Global environmental catastrophes and resource depletion have put achieving food and nutrition security, as well as environmental sustainability, in danger. Therefore, soil health is a focal point for sustainability in food security, plants, animals and human health, and sustainable ecosystems (Babu et al. 2022). The soil's health and crop yield are both seriously threatened by the presence of heavy metals and hazardous chemicals (Li et al. 2020). Due to extended exposure to wastewater and trash disposal, heavy metals that are not biodegradable continue to build and reach harmful levels in the soil. The production of Cr salts, industrial coolants, textile dyeing, leather tanning, chromate plating, and solid waste disposal are the principal anthropogenic activities that cause environmental contamination with Cr (Zhang et al. 2022). Heavy metal pollution has lately emerged as a significant environmental issue worldwide due to its increased concentration over the permitted limits (Srivastava et al. 2021). Some heavy metals, like Cr, for instance, stop nutrients from being absorbed by the soil by forming insoluble compounds. Therefore, there has been a lot of interest in the biological toxicity of heavy metals in soil (Zhang et al. 2022; Louhar et al. 2020). Additionally, the widespread usage of toxic substances like chromium in the environment and a lack of facilities for ethical waste management contribute to significant soil contamination (Paz-Ferreiro et al. 2018). As a result, crops produced in polluted soils accumulate Cr content, posing a major hazard to human health through the food chain (Alengebawy et al. 2021). However, some research has emphasized that compared to other organisms; soil microbes are more vulnerable to heavy metal contamination. Chromium toxicity has been linked to negative impacts on enzyme activity, soil microorganisms, and microbial processes, according to a number of studies (Table 8.4).

8.7 Chromium Chemistry in Soil

The two primary oxidation states of chromium in soils are +3 and +6 in nature. The +3 oxidation state is represented by the Cr^{+3} cation and Cr^{+6} in chromate (CrO_4^{2-}). Both of these states are hazardous, non-biodegradable pollutants (Wang et al. 2022). But in several nations, hexavalent chromium is considered a priority pollutant. Normal soil conditions are good for the Cr^{+3}, which is very immobile and unavailable because of strong complexations and chemi-sorption's with soil oxides, silicates, and organic materials. The persistent form of Cr^{+6} in the soil is extremely dangerous to biota. In the presence of organic matter and acidic conditions, the

Table 8.4 Effect of chromium toxicity on microbial activity, enzymatic activity, and microorganisms in soil

Concentrations (mg/kg)	Effects	Location/type of soil	References
150–300	*Azotobacter* sp. & *Pichia* sp. biomass reduced by Cr (VI) by more than 50%	Romania; ando soil	Diaconu et al. (2020)
0–300	Slowed down the microbial activity	China	Zhang et al. (2022)
0.2–0.6	Reduced Urease activity by 50%	Poland; peat soil	Samborska et al. (2004)
950–2240	Significantly reduces microbial population and dehydrogenase activity	China	Huang et al. (2009)
50–400	Significantly reduces microbial activities	Nigeria, Sandy loam	Chibuzor et al. (2018)
50–2000	Significantly decreased alkaline phosphatase and dehydrogenase activities	China; ferralic cambisol	Peng et al. (2009)
0–150	Decreased the activity of the urease, dehydrogenases, and alkaline phosphatases enzyme	Poland; brown soil	Wyszkowskaw (2002)
0–20	Reduced catalase enzyme activity	Poland; Mollic Gleysol	Stpniewska et al. (2009)
0–100	Fluorescein diacetate, alkaline phosphatase, and DHA activities were all decreased up to 70%	India, Vertisol	Dotaniya et al. (2017a)
0–20	Reduced dehydrogenase activity	Poland; Haplic Luvisol	Stpniewska et al. (2005)
10–100	Decreased the microbial activity	USA; Sandy loam	Ross et al. (1981)
0–800	Reduced dehydrogenase, catalase enzyme and soil respiration activities	China	Quazi et al. (2014)
200–1600	Decreased soil microbial population and enzyme activities	China; paddy soil	Liu et al. (2014)
3–3300	Significantly reduced the microbial activities	USA	Shi et al. (2002)
4700	Significantly slow down the microbial activities	France	Desjardin et al. (2002)

majority or all of the hexavalent chromate ions that enter the soil along with contaminated irrigation are swiftly transformed to Cr^{+3}. On the other hand, the oxidation of Cr(III) to Cr(VI) may increase the availability and toxicity of Cr in soil solution (Saha et al. 2017a). Because, Cr^{+6} is more mobile and soluble than Cr^{+3}, it is thought to be more damaging to living organisms in soil systems. (Vignati et al. 2010). In soil, Cr^{+6} is typically converted to Cr^{+3} in the presence of oxidizing chemicals, which also reduced its carcinogenicity. Additionally, as pH increases, Cr availability falls off quickly. A minor portion of Cr^{+3} may be converted to soluble chromate when the pH is higher (DesMarias et al. 2019).

8.8 Factor Affecting Chromium Availability

The type and concentration of cations and anions in the soil, the availability of other metals, soil moisture, soil microbial activity, and other factors all have a role in the Cr in soil solution and its absorption by crop plants. These factors are mostly converting Cr forms into different meta forms. Major factors are affecting Cr availability and toxicities are as.

8.8.1 Effect of Organic Matter on Chromium Bioavailability

Organic matter (OM), a crucial component of soil, regulates the mobility, bioavailability, and sorption of heavy metals in the ground. The amount of organic matter in the soil is essential for lowering the likelihood of Cr contamination. Soil organic matter has been discovered to have a significant influence on the mobility of chromium in soil because of its tendency to convert mobile Cr(VI) to the more stationary Cr(III). The effect of soil organic matter on the decrease of Cr(VI) has also been the subject of several investigations. It was discovered that a high quantity of organic materials hindered the Cr. A key indicator of toxicity and potential mobility is the degree of chromium oxidation in contaminated soils. Numerous studies have investigated how OM affects movement of Cr in soil-plant dynamics. The ratio of chromate CrO_4^{2-} ion to total Cr was found to be lower in columns with higher OM than in those with lower OM. Consequently, the most significant effect on the mobility of chromium was caused by the presence of organic materials (Banks et al. 2006). Studies have showed that Cr(VI) reduction increased together with soil total organic carbon (TOC) concentration. When exposed to TOC, Cr^{+6} is converted to Cr^{+3}, and in the majority of situations, this causes it to get immobilized in the soil. The chromium oxidation and reduction processes are controlled by organic matter and different acids (Xu et al. 2004) . According to a report, Cr(III) is mostly found in the organic matter-bound fraction in soils in dry zones with saturated conditions (Eckbo et al. 2022; Han et al. 2004).

8.8.2 Effect of pH, Metals, Cations and Anions on Chromium Bioavailability

Soil pH controls the geochemical behaviour of heavy metals in both the solid and solution phases of the soil (Chung and Eum 2001). The pH of the soil affects the sorption and desorption of Cr and other heavy metals in soils. Soil pH has a significant impact on the geochemical behaviour of chromium. Cr(III) is poorly soluble at pH values lower than 5.5. However, beyond this pH, Cr(III) almost totally precipitates. Contrarily, Cr(VI) is incredibly unstable in soil and continues to be mobilized in both acidic and alkaline soil. Additionally, the quantity of Cr(III) that was sorbed rose when soil pH, CEC, clay, and OM increased (Shahid et al. 2017).

Chromium soil toxicity can be reduced by reducing Cr(VI)–Cr(III), which is controlled by the availability of protons and electrons (Choppala et al. 2013). Cr(III) is less toxic to biota and binds firmly to soil minerals because it is relatively insoluble and less easily absorbed by plants. It functions as a Lewis acid and forms complexes with a range of ligands. Cr(III) is a stable cation in soils and is required for human health, in contrast to Cr(VI), which causes cancer and is a mobile anion in soils. Some oxides, such manganese oxides (MnOx), converted soil containing Cr(III) into Cr(VI). On the other hand, Chromium(VI) was reduced by Fe(II), organic matter, and sulphide to Cr(III). Free Cr(VI) ions are easily reduced in the presence of organic materials when they are present in acidic conditions (Han et al. 2004).

Plants may absorb Cr in both its (III) and (VI) valence states. On the other hand, plants passively take up Cr(III) through the cation exchange sites in their cell walls. Through diffusion at the cell wall's cation exchange site, plants passively absorb Cr(III) sulfate transporters help Cr(VI) actively enter plant cells. Whereas, phosphate and sulfate have structural similarities with Cr(VI), its uptake happens via phosphate and sulfate transporters via an active mechanism that requires energy (Srivastava et al. 2021).

8.9 Management of Chromium Toxicity

The amount and type of organic matter, the presence of other metals, the microbial community, root exudates, crop type and stage; all have a significant impact on the chemistry of Cr in soil. Chromium hexavalent converts into trivalent Cr over a period in present of organic matter. This form is less toxic to hexavent chromium. Based on the mode of action and living organism are classified into two groups.

8.9.1 Immobilization Through Organic and Inorganic Substance

In this process, different organic and inorganic substances are using to reduce the Cr toxicity in soil. Lime is mostly used for the immobilization of Cd, Ni, Pb; phosphate salt for Pb and Cd; fly-ash for Cr, Cd, Pb; slag for Cr and Pb, Cd; portland cement for Cr and Zn. However, some of the salt containing Ca or sulphate ions reduced the Cr availability in soil solution. Adding organic matter to the soil enhances soil health and crop productivity while lowering the toxicity of Cr. Addition of FYM, poultry manure, crop residues are also reducing the active ions of Cr. Organic substances are acted as bioabsorber to immobilize the Cr in soil (Nagar et al. 2022).

8.9.2 Bioremediation

In this living organisms are using for Cr removal/immobilization process to minimize the toxicity. It could consist of green plants, actinomycetes, bacteria, or fungus. Some bacteria may be able to lower metal toxicity through various metabolic processes (Solanki et al. 2019). Many plant species that accumulate larger concentrations of Cr in various sections of their bodies without compromising the development of the plant are known as hyperaccumulator plants, and the process is known as phytoremediation (Dotaniya et al. 2020). Phytoremediation processes are classified in divers group based on the action mechanism and Cr reduction/removal media (Table 8.5).

8.10 Future Suggestions/Research

- Basic and applied research related to uptake kinetics of Cr in presence of multi metal containing effluent.
- Immobilization process of Cr in soil with respect to climate change phenomena.
- Safe disposal of Cr content during phytoremediation process.

8.11 Epilogue

Chromium is a toxic metal; huge adverse impact on soil–plant-human health. It is having many important uses in different industries those contributing significant economic boost up in Gross domestic product (GDP) in India. Chromium contaminated effluents are mediated the plant nutrient dynamic in soil; uptake kinetic in plant, metabolic disorder in living system are the consequences of toxicity. Long-term use of waste water tainted with Cr led to soil pollution, which then reached

Table 8.5 Strategies for phytoremediation techniques

Phytoremediation techniques	Action process	Medium treated
Phytoextraction	Direct pollutant buildup in plant shoots followed by removal of the plant shoots	Soil
Rhizofiltration (Phytofiltration)	Roots of plants that absorb contaminants	Both root-pumped water and surface water
Phytostabilization	Metals precipitate as a result of root exudates, and biomass becomes less bioavailable	Groundwater, soil, mine tailings
Phytovolatilization	Some metal ions and volatile organics are evaporated by plants	Soil, groundwater
Phytodegradation (plant–assisted bioremediation)	Degradation caused by microbes in the rhizosphere	The soil's rhizosphere and groundwater
Phytotransformation	Degradation and organic pollutant absorption by plants	Surface/groundwater
Elimination of airborne pollutants	Different volatile organics are absorbed by leaves	Air

Adopted from Yang et al. (2005), Dotaniya and Lata (2012)

human bodies through the food chain. Researchers are continuously working on different organic and inorganic substances to immobilize the Cr in soil. However, many soil microorganisms are also identified to reduce the Cr toxicity and plant are using for phytoremediation purpose. In all above, we have to use the Cr contaminated waste water for agricultural crop production system with proper treatment. Create awareness among the local peoples with the help of different agencies and periodically quantify the toxicity of metals in polluted environments.

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