Chapter 4
A Critical Evaluation of Chromium(III) Ecotoxicity to Aquatic and Terrestrial Plants

Elsa Salles, Vincent Normant, and Davide A. L. Vignati

Abstract Current research on chromium (Cr) ecotoxicity primary focuses on the adverse effects of Cr(VI). Concerns about high levels of Cr(III) in the environment are mostly driven by its possible (re)oxidation to the highly toxic hexavalent form, but trivalent chromium is considered of limited ecotoxicological relevance. However, Cr(III) can also elicit a large range of responses in aquatic and terrestrial plants including inhibition of growth and seed germination, damage to chloroplasts, reduced photosynthesis, oxidative stress, and alteration of nutrient balance, organelles and cellular function. Furthermore, most studies pay little if any attention to the complex chemistry of Cr(III) in the ecotoxicological test media used in controlled laboratory studies. In particular, Cr(III) can rapidly undergo hydrolysis that transforms soluble Cr^{3+} ions into Cr oxy-hydroxides—$Cr(OH)_3$. Given the very low theoretical solubility of $Cr(OH)_3$ (about 5 μg/L), their formation can markedly decrease the Cr(III) levels to which test organisms are actually exposed during the tests. These phenomena make comparison among studies far from straightforward and question the validity of many concentrations *vs.* response relationships reported for Cr(III). Although the high ecotoxicity of Cr(VI) is unquestionable, the critique presented in this chapter suggests that current consensus suffer from a general underestimation of Cr(III) ecotoxicity.

Keywords Plants · Cr(III) toxicity · Ecotoxicology · Cr speciation · Cellular effects

4.1 Introduction

A great deal of research exists on the biological responses induced by Cr in terrestrial and aquatic plants. The vast majority of published studies is concerned with the adverse effects triggered by exposure to Cr(VI) (Cervantes et al. 2001; Shadid et al.

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2017; Shanker et al. 2005) and justifies the large interest on possible techniques for remediation of Cr(VI)-contaminated sites (Beretta et al. 2018; Ao et al. 2022; Murthy et al. 2022). On the other hand, current consensus usually regards Cr(III) as being of little ecotoxicological significance and limits the risks related to the presence of Cr(III) to its potential (re)oxidation to Cr(VI) following abiotic or biologically-mediated reactions (Gorny et al. 2016; Liang et al. 2021).

The high ecotoxicity of Cr(VI) is linked to its structural analogy with phosphate and sulphate anions that facilitates intracellular uptake (Viti et al. 2014). Possible mechanisms of Cr(III) entrance into cells involve Fe(III) transporters, internalization of hydrophobic Cr(III) complexes or endocytosis of Cr-bearing particles (Beyersmann and Hartwig 2008). Inside cells, Cr(VI) is rapidly reduced to Cr(III) (Zhitkovich et al. 2005; Viti et al. 2014). The reduction of Cr(VI) results in the formation of reactive oxygen species that are associated with the severe ecotoxicological effects of Cr(VI), but also in the production of intracellular Cr(III) that reacts with cellular constituents and eventually causes DNA damage (Viti et al. 2014; Medeiros et al. 2003). Indeed, Cr(III) is the predominant or sole oxidation state of Cr inside cells (Zayed et al. 1998; Montes-Holguin et al. 2006). In higher plants, Cr(III) is also the oxidation state that is transported in sap from roots to shoots and leaves, regardless of the Cr form to which the plants are exposed (Marković et al. 2022). A similar situation likely occurs in unicellular algae. Aharchaou et al. (2017) showed that chromium had the same distribution among operationally defined subcellular fractions in cells of *Chlamydomonas reinhardtii* exposed to either Cr(VI) and Cr(III). Overall, a proper understanding of the possible risks linked to Cr contamination requires a solid knowledge of Cr(III) uptake and effects on living organisms.

This chapter provides a critique of the current knowledge on the ecotoxicity of Cr(III) to aquatic and terrestrial plants. It specifically focuses on studies performed under controlled laboratory conditions that allow to establish clear relationships between exposure to Cr and biological responses in the absence of confounding factors that may exist in natural soils and waters. Despite the consensus considering Cr(VI) as much more toxic than Cr(III), studies showing a higher toxicity of Cr(III) are regularly published. In this chapter, we will try to reconcile the results of such studies with the current consensus and to evaluate if studies documenting low Cr(III) ecotoxicity can suffer from unknown bias.

4.2 An Ecotoxicological Perspective of the Chemistry of Cr(III)

Cr has several oxidation states, but only Cr(III) and Cr(VI) are ecotoxicologically relevant for exposures via environmental matrices (Gorny et al. 2016). Cr(VI) occurs in the form of chromate anions that show little reactivity toward environmental particles, usually bearing a negative net charge (Warren and Haak 2001), and exhibit high mobility and long-distance transport (Gorny et al. 2016). At the opposite, Cr(III)

predominantly occurs as cationic species (Rai et al. 1989; Giusti and Barakat 2005) that are easily adsorbed onto negatively charged environmental particles. Redox interconversions between the two oxidation states do occur in the environment and are mainly linked to the presence of reduced iron and sulphur for reduction of Cr(VI) to Cr(III) and of Mn oxides for oxidation of Cr(III) to Cr(VI) (Gorny et al. 2016). Bacterial activity can also facilitate both oxidation and reduction reactions. In aquatic ecosystems, particle-bound Cr(III) progressively accumulates into bed sediments via gravitational settling of suspended particulate matter and colloidal pumping (Dominik et al. 2007). In terrestrial (and aquatic) ecosystems, the formation of Cr(III) organic complexes can remobilize Cr (Löv et al. 2017; Liao et al. 2020; Zhu et al. 2022) and oxidation of Cr(III) to Cr(VI) can result in groundwater contamination even in the absence of anthropogenic inputs of chromium (Oze et al. 2007). Although sediments and soils act as large reservoirs of potentially bioavailable Cr, chromium uptake by terrestrial and (rooted) aquatic plants is linked to the presence of soluble Cr pools. It is therefore particularly important to understand the aqueous chemistry of Cr(III), especially when exposure is performed in controlled conditions by the addition of soluble Cr salts, which is common practice in ecotoxicological studies using the aqueous exposure route.

Three aspects of the aqueous chemistry of trivalent chromium are particularly relevant during ecotoxicological experiments: hydrolysis, solubility, and possible oxidation to Cr(VI). Ecotoxicological studies with Cr(III) are usually performed by amending appropriate (aqueous) test media with soluble Cr(III) salts such as $CrCl_3 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$. Following addition to aqueous media, the soluble salts dissociate into Cr(III) cations and the corresponding counter ions. At pH values above 4, free Cr^{3+} ions rapidly undergo hydrolysis according to the following reaction:

$$Cr(H_2O)_6^{3+} + xH_2O = Cr(H_2O)_{6-x}(OH)_x^{(3-x)} + xH_3O^+ \quad (4.1)$$

Because hydrolysis is accompanied by the release of protons (Eq. 4.1), addition of soluble Cr(III) salts can acidify ecotoxicological test media if their buffering capacity is exceeded by e.g., addition of large quantities of Cr(III) for experimental purposes. Following hydrolysis, the predominant Cr(III) species are expected to be $CrOH^{2+}$ in the pH range 3.8–6.3, $Cr(OH)_3$ at pH between 6.3 to 11.5 and $Cr(OH)_4^-$ for pH > 11.5 (Rai et al. 1989).

The species $Cr(OH)_3$ is characterized by a very low solubility product ($K_{sp} = 6.7 \times 10^{-31}$; Gorny et al. 2016), corresponding to a theoretical solubility limit of about 1.5 $\mu g\ L^{-1}$ of chromium. This value agrees well with data reported by Rai et al. (1987) who estimated the solubility of Cr(III) at about 4 $\mu g\ L^{-1}$ in a non-complexing perchlorate medium. Furthermore, Rai et al. (1987) obtained similar results in solutions amended with $Cr(NO_3)_3 \cdot 9H_2O$ or $CrCl_3 \cdot 6H_2O$. Otherwise stated, the formation of $Cr(OH)_3$ precipitates seems independent from the initial composition of the Cr solution; an important observation considering that ecotoxicity testing can be carried out with different Cr(III) salts across different studies. Indeed, Vignati et al. (2008) and Aharchaou et al. (2018) observed a similar decrease in Cr concentrations in algal

ISO medium 8692 (ISO 2012) amended with Cr nitrate, chloride or sulphate. The presence of EDTA in ISO 8692 medium did not prevent Cr(III) precipitation because Cr(III) complexation with multidentate chelators such as EDTA is sluggish compared with the kinetics of hydrolysis (Vignati et al. 2010). The solubility of Cr(III) is further decreased in the presence of iron following the formation of mixed Cr–Fe hydroxides (Sass and Rai 1987). Finally, hydrolysis takes place within microseconds (Giusti and Barakat 2005) and $Cr(OH)_3$ formation can occur within tens of minutes (Pettine et al. 2008; Aharchaou et al. 2018). The kinetics of both processes is therefore very fast compared with the typical duration of ecotoxicity tests (hours to several days). In summary, amending aqueous ecotoxicological test media with soluble Cr(III) salts will result in the rapid formation, and possible precipitation, of insoluble $Cr(OH)_3$ if the added Cr concentrations exceed the corresponding solubility limit of a few $\mu g\ L^{-1}$. These chemical processes have two major ecotoxicological consequences: the decrease of the actual soluble (bioavailable) Cr(III) concentrations in the exposure medium during the test and the formation of a pool of nano-particulate Cr(III) in the exposure medium (Aharchaou et al. 2018). Correct interpretation of Cr(III) ecotoxicity in aqueous media must consider both phenomena and cannot be achieved without an exhaustive knowledge of Cr speciation, including its possible changes over the test duration. In particular, neglecting the decrease in soluble (bioavailable) concentration over time can lead to an underestimation of the actual ecotoxicity of Cr(III).

The examples in Table 4.1 show that few studies provide sufficiently detailed information on Cr(III) chemistry and speciation during ecotoxicity testing. Even basic analytical verification of exposure concentrations is not common practice although the range of added Cr(III) concentrations usually includes concentrations well above the theoretical solubility limit of $Cr(OH)_3$. At the same time, formation of poorly soluble $Cr(OH)_3$ appears very likely in most studies, considering that the pH of most ecotoxicological test media fall in the window favouring $Cr(OH)_3$ formation (6–11 units). In such situations, measurements of total concentrations (e.g., Yu et al. 2008; Yu and Gu 2008b, 2007; Ponce et al. 2019) may include a fraction of Cr-containing nanoparticles whose bioavailability may differ from that of soluble Cr ions. The formation of Cr-containing particles (80–140 nm) has been documented by Aharchaou et al. (2018) in ISO medium 8692 for freshwater algae. Finally, the presence of organic ligands in test medium can affect Cr(III) speciation via the formation of organic-Cr(III) complexes again with possible consequences on chromium bioavailability.

These considerations do not question the quality of the studies listed in Table 4.1 nor the ecotoxicological significance of their results. They simply highlight two major caveats in Cr(III) ecotoxicology. First, Cr(III) speciation markedly changes among test media. Comparisons among studies are therefore far from straightforward when analytical information on (total) exposure concentration is available and close to meaningless when only nominal concentrations are provided. Second, in the absence of analytical verification, relationships between exposure concentrations and biological responses may underestimate Cr(III) ecotoxicity by including both soluble and insoluble Cr species in the pool of chromium bioavailable to the test organisms.

Table 4.1 Examples of studies examining the responses of aquatic and terrestrial plants to Cr(III). The selected items allow to verify possible issues linked with Cr(III) speciation. AAM, Algal Assay medium

Group	Plant species	Added Cr(III) form	Medium	Exposure concentrations (range)	Measured (Y/N)		Other possible issues related to Cr speciation	References
					Cr	pH		
Green alga	*Dictyosphaerium chlorelloides* (wild type)	$CrCl_3 \cdot 6\,H_2O$	BG-11	10–200 μM	N	N	Presence of organic component in the medium	Pereira et al. (2013)
Green alga	*Dictyosphaerium chlorelloides* (Cr-resistant mutant)	$CrCl_3 \cdot 6\,H_2O$	BG-11	300–10000 μM	N	N	Presence of organic components in the medium	Pereira et al. (2013)
Cyanobacteria	*Synechococcus* PCC 7942	$CrCl_3 \cdot 6\,H_2O$	BG-11	50–300 μM	N	**Y**	Presence of organic components in the medium	Thompson et al. (2002)
Cyanobacteria	Nostoc PCC 7120	$CrCl_3 \cdot 6\,H_2O$	BG-11	500 μM–3 mM	N	**Y**	Presence of organic components in the medium	Thompson et al. (2002)
Green alga	*Raphidocelis subcapitata*[$]	Trivalent Cr	AAM	10–1000 $\mu g\ L^{-1}$	N	N	–	Turbak et al. (1986)
Green alga	*Raphidocelis subcapitata*[$]	$CrCl_3 \cdot 6\,H_2O$	AAM	50–400 $\mu g\ L^{-1}$	N	N	–	Greene et al. (1988)
Green alga	*Raphidocelis subcapitata*	$CrCl_3 \cdot 6\,H_2O$ $Cr(NO3)3 \cdot 9$ H2O $KCr(SO_4)_2 \cdot 12\,H_2O$	ISO 8692	9–2250 $\mu g\ L^{-1}$	Y total and filterable, multiple time points	Y info provided	–	Aharchaou et al. (2018)

(continued)

Table 4.1 (continued)

Group	Plant species	Added Cr(III) form	Medium	Exposure concentrations (range)	Measured (Y/N)		Other possible issues related to Cr speciation	References
					Cr	pH		
Terrestrial plant	*Oryza sativa L. XZX 45*	$Cr(NO_3)_3 \cdot 9 H_2O$	Modified ISO 8692	12–40 mg L^{-1}	N	N	–	Fan et al. (2020)
Terrestrial plant	*Chenopodium quinoa Willd*	$CrCl_3 \cdot 6 H_2O$	½ Hoagland + perlite (semi-hydroponic)	0.52–260 mg L^{-1}	N	N	–	Scoccianti et al. (2016)
Terrestrial plant	*Salix babylonica L and Salix matsudana Koidz*	$CrCl_3 \cdot 6 H_2O$	Modified ISO 8692	1.51 mg L^{-1}	Y total	N	Ascribes temporal decrease in Cr concentration to sequestration to plants	Yu and Gu (2008b)
Terrestrial plant	*Salix matsudana Koidz*	$CrCl_3 \cdot 6 H_2O$	Modified ISO 8692	About 1–2 mg L^{-1}	Y total start/stop	N	Different nitrogen levels	Yu and Gu (2008a)
Terrestrial plant	*Salix matsudana Koidz x Salix alba L. and Salix babylonica L.)*	$CrCl_3 \cdot 6 H_2O$	Modified ISO 8692	About 1.5 mg L^{-1}	Y total start/stop	N	Presence of EDTA in some exposure scenarios	Yu and Gu (2008c)
Terrestrial plant	*Salix matsudana Koidz x alba L*	$CrCl_3 \cdot 6 H_2O$	Modified ISO 8692	2.5–30 mg L^{-1}	Y total Start/ stop	N	Different behaviour at <7.5 mg/L versus 15 and 30 mg/L	Yu and Gu (2007)
Terrestrial plant	*Actinidia deliciosa var. deliciosa*	$CrCl_3 \cdot 6 H_2O$	Agar medium with 0.29 mM sucrose and 0.4 mM boric acid	0–75 μM	N	N	Medium with sucrose	Speranza et al. (2007)
Terrestrial plant	*Convolvulus arvensis L*	$Cr(NO_3)_3 \cdot 9 H_2O$	Modified Hoagland medium as per Peralta et al. (2001)	1–20 mg L^{-1}	N	N	Agar based medium	Montes-Holguin et al. (2006)

(continued)

Table 4.1 (continued)

Group	Plant species	Added Cr(III) form	Medium	Exposure concentrations (range)	Measured (Y/N)		Other possible issues related to Cr speciation	References
					Cr	pH		
Terrestrial plant	*Salsola kali*	$Cr(NO_3)_3 \cdot 9H_2O$	Modified Hoagland medium as per Peralta et al. (2001)	0–20 mg L^{-1}	N	N (initially adjusted to 5.8)	Agar based medium. Initial pH value may redude/prevent Cr(III) precipitation	Gardea-Torresday et al. (2005)
Aquatic plant	*Fontinalis antipyretica Hedw*	$Cr(NO_3)_3 \cdot 9H_2O$ $CrCl_3 \cdot 6H_2O$	Volvic mineral water	6.25×10^{-5}–50 mM	N	N	$Cr(OH)^{2+}$ predicted as predominant species (MINEQL+) at all concentrations and for both forms	Dazy et al. (2008)
Terrestrial plant	*Apium graveolens (celery)*	$CrCl_3 \cdot 6H_2O$	Heller medium + Fe-EDTA + sucrose + 0.8% agar	0.01–10 mM	N	N	Agar containing medium	Scoccianti et al. (2006)
Terrestrial plant	*Oryza sativa* L. cv. XZX 45	$Cr(NO_3)_3 \cdot 9H_2O$	Modified ISO 8692	0–40 mg L^{-1}	N	N	Modifications not specified. Possibly same as other studies from the same research group	Yu et al. (2018a, b)
Terrestrial plant	*Lycopersicon esculentum* Mill. cv. Juncal (Tomato)	$CrCl_3 \cdot 6H_2O$	Half-stregth Hoagland medium	0–50 μM	N	N		Henriques (2010)

(continued)

Table 4.1 (continued)

Group	Plant species	Added Cr(III) form	Medium	Exposure concentrations (range)	Measured (Y/N)		Other possible issues related to Cr speciation	References
					Cr	pH		
Terrestrial plant	*Vigna unguiculata*	$Cr(NO_3)_3 \cdot 9H_2O$	Hydroponic cultivation setup	0.05–0.5 mM	N	N	Unspecified medium composition	Chow et al. (2018)
Aquatic plant	*Eichhornia crassipes (Mart.) Solms*	Cr_2O_3	Hoagland medium	1 and 10 mM	N	N	Insoluble/sparingly soluble Cr form	Paiva et al. (2009)
Terrestrial plant	*Salvinia rotundifolia*	$CrCl_3 \cdot 6H_2O$	Tap water (±buffer), composition provided	5 and 20 mg L^{-1}	Y (data not shown)	Y (medium buffered at 4.0; 6.0 and 7.6 units, data not shown)	Cr speciation issue considered in experimental set-up	Ponce et al. (2019)

$, Named with its former name of *Selenastrum capricornutum* in the original study

A similar situation is observed with regard to pH, with a very limited number of studies providing information on the temporal stability (or lack thereof) of this parameter over the course of the experiments. Because of hydrolysis (Eq. 4.1), changes in the pH of test medium may occur following the release of protons. One early study warned about possible strong decreases in pH values in a simple test medium (0.05% K_2HPO_4, 0.05% KH_2PO_4, 0.05% $(NH_4)_2SO_4$, 0.05% KNO_3; initial pH just below 7) amended with chromium chloride (Den Dooren de Jong and Roman 1965). Thompson et al. (2002) documented that initial pH differed by about 1.5 units between BG-11 medium amended with 50 μM Cr(III) (pH = 7.27) and 300 μM Cr(III) (pH = 6.14). Most interestingly pH values were comparable at about 9.5 units at the end of the test regardless of the added Cr(III) concentration. However, the differences in pH at the beginning of the test suggest that Cr speciation and its temporal evolution probably depended on the initial concentration of added Cr(III). In practice, exposure conditions may not be fully consistent even within an individual study. As in the case of analytical verification of exposure concentrations over the test duration, monitoring of pH values during the tests should always be performed at least for the lowest and highest tested concentrations.

Information is equally scant as to the possible Cr(III) to Cr(VI) interconversions in the test medium during ecotoxicological experiments. In the absence of biologically mediated reactions, oxidation of Cr(III) to Cr(VI) could be catalyzed only by Mn oxides that are not a standard component of test media. Aharchaou et al. (2018) used ion chromatography ICP-MS to verify the possible occurrence of Cr(III) to Cr(VI) redox interconversion in ISO medium 8692 for freshwater algae (ISO 2012) and did not observe any changes in the oxidation state of chromium. Because Mn enters in the composition of ISO medium 8692 as soluble $MnCl_2$, the general applicability of these results to other aqueous media remains to be verified. The situation is much more complicated in experiments involving the use of synthetic or, especially, natural soils where the presence of some form of organic matter and Fe and Mn oxides is the norm. Similarly, in natural waters, including pore waters and soil solutions, the behavior of Cr(III) can be modified by the presence of natural organic matter (NOM) and other colloidal carrier phases. In particular, adsorption on NOM can increase Cr(III) solubility by avoiding precipitation of Cr hydroxides (Fukushima et al. 1995; Gustafsson et al. 2014). Nonetheless, the presence of colloidal Cr_2O_3 has been documented in soils (Zhu et al. 2022) and polynuclear species have been detected in natural waters (Hu et al. 2016). These considerations confirm that ecotoxicological laboratory studies should start paying much more attention to Cr(III) speciation to correctly assess its actual toxicity and to facilitate extrapolation of laboratory results to real-field conditions.

4.3 Cr(III) Transport and Distribution

4.3.1 Cr(III) Uptake

Cr is not an essential nutrient for plants that, consequently, do not have Cr specific transporters (Panda and Choudhury 2005; Adhikari et al. 2020). However, plants can import both Cr(III) and Cr(VI), the general consensus being that Cr(VI) is more easily taken up than Cr(III) due to its higher transmembrane transport efficiency and solubility (Shanker et al. 2005). However, the accumulation of Cr(VI) and Cr(III) in *Arabidopsis thaliana* was similar (Ding et al. 2019) and Cr(III) is the main form present inside plant tissue (Zayed and Terry 2003; Markovich et al. 2022). Cr(VI) uptake occurs mainly via sulphate or phosphate transporters in some bacteria, fungi, algae and plants because of their structural similarities with chromate anions (Tang et al. 2023; Viti et al. 2014; Xu et al. 2021). Mechanisms involving Cr(III) uptake by plants are not yet completed understood. Cr(III) uptake could mainly be via the same carriers as for essential ion elements (ion channels) such as Fe, Ca, Mg or K or through the simple diffusion of cations exchanges sites in the cell wall (Ding et al. 2019; Singh et al. 2013; Ao et al. 2022). In *Leersia hexandra* Swartz, the antagonistic effect of Fe(III) on Cr(III) uptake by root cells suggests that Cr(III) uptake may be mediated partly by Fe(III)-phytosiderophore complex transporters (Liu et al. 2011). Cr(III) can also be transported by passive mechanism, by cation diffusion facilitators (Skeffington et al., 1976). In this study, *Hordeum vulgare L.* was exposed to Cr(III) and Cr(VI) in presence and absence of metabolic inhibitors and Cr uptake was measured. They demonstrated that the uptake of Cr(VI) was reduced by the inhibitors whereas Cr(III) uptake was not affected, suggesting different uptake mechanisms for the two forms. However, the passive and active uptake mechanisms are not clearly established and evidence of this process is still needed. Precautions needs to be taken as Skeffington et al. (1976) proposed that Cr(VI) was the only form of Cr inside root cells which was corrected later: in this case, Cr(III) was detected in apoplast of root cells (Zayed and Terry 2003). Cr(III) can also be retained by the cation-exchange sites of the cell walls (Marschner 1995). The complexation of Cr(III) with organic acid (e.g. carboxylic acid or amino acid) enhance root uptake of Cr(III), suggesting that organic complexation of Cr(III) would contribute to Cr(III) uptake (Srivastava et al. 1999; Panda and Choudhury 2005). Cr(III) uptake clearly occurs in plant cells and Cr(III) can cross biological membranes, although the exact mechanisms are not yet fully understood.

4.3.2 Cr(III) Translocation and Accumulation

In root cells, Cr(III) ions are highly stabilized by complex formation with organic molecules, such as proteins (glutathione), carbohydrates (especially pentoses),

NAD(P)H, $FADH_2$, and probably also with organic acids, and stored and immobilized in root cell vacuoles in precipitated form (Caldelas et al. 2012; Zeng et al. 2011) or in apoplast in cell walls, which is the reason for restricted mobility of chromium in plants (Shanker et al. 2004; Mangabeira et al. 2011; Babula et al. 2008). Cr has a lower migration rate from root to shoot, than other heavy metals such as Hg, Cd and As (Shanker et al. 2005). For most terrestrial and aquatic plants, Cr distribution in different parts is in the order of roots > stem > leaves > fruits. Many studies showed that Cr(III) is accumulated mostly in roots and only a small part of Cr(III) is translocated to shoots (Paiva et al. 2009). Little translocation of Cr(III) to aerial part was reported in *G. americana*, with a concentration of 45 and 50 mg kg^{-1} in leaves and stems respectively, and most of the Cr(III) immobilized and stored in the roots, with accumulation concentration in the roots of 3841 mg kg^{-1} (Barbosa et al. 2007). In this case, Cr(III) is poorly translocated due to formation of Cr(III) insoluble complexes. Organic compounds, like citrate or EDTA are involved in Cr(III) translocation in xylem vessels and plant distribution. Cr(III)-citrate or Cr(III)-EDTA complexes are therefore more soluble and easily transported by the plants or immobilized and stored after translocation to leaves or fruits (Yu et al. 2008c; Juneja and Prakash 2005). Moreover, a study on *Taraxacum officinale* roots suggested that Cr(III) transport only occurs as Cr(III)-organic complexes with organic acids no matter if the plant is exposed to Cr(VI) or Cr(III), suggesting that Cr(VI) is reduced to Cr(III) inside the plants to be translocated and that Cr(III) is more mobile after complexation with organic compounds as suggested before (Markovich et al. 2022). In parenchyma cells, Cr(III) is accumulated in vacuoles and in the cell wall of xylem cells (Mangabeira et al. 2011; Vazquez et al. 1987). The leafy vegetables that tend to accumulate Fe (i.e., spinach, turnip leaves) appear to be the most effective in translocating Cr to the shoot. The leafy vegetables that do not accumulate relatively high concentrations of Fe in their leaves (i.e. lettuce and cabbage) are substantially less effective in translocation of Cr to the leaves (Cary et al. 1977a, b). Onion, spinach, chive and celery have a higher shoot/root concentration ratio than cabbage, peas, kale, cauliflower and lettuce after Cr(III) exposure (Zayed et al. 1998). Cr(III) is mainly retained in the roots, in epidermal cells. Depending on the chosen biological model, Cr(III) can be transported to the stem (xylem cells), leaf and fruits and could be transported as Cr(III)-organic complex (Fig. 4.1).

4.4 Biological Effects

4.4.1 Effects on Plant Morphology

Studies reported a decrease of total biomass and plant growth (Davies et al. 2001; Arduini et al. 2006; Lopez-Luna et al. 2009). Cr(III) also caused inhibition of growth in *Brassica oleracea* after exposure to 0.5 mM (Chatterjee and Chatterjee 2000).

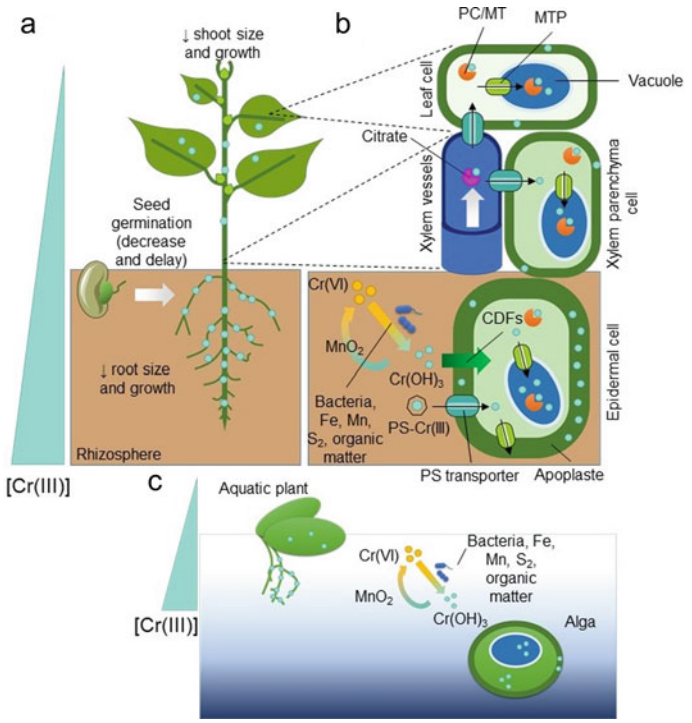

Fig. 4.1 Plant uptake, translocation and accumulation of Cr(III) from soil and water. **a** Cr(III) induce effects on seed germination, shoot and root parts and Cr(III) accumulation is more important in root than shoot. **b** Uptake and translocation of Cr(III) at cellular level in epidermal, xylem parenchyma, and leaf cells and translocation in xylem vessels. **c** Accumulation of Cr(III) in algae and aquatic plants. PS: phytosiderophores, CDFs: cation diffusion facilitators, PC: phytochelatins, MT: metallothioneins MTP: metal tolerance proteins

Roots are the first organ in contact with Cr(III) and Cr(III) preferentially accumulates in plant roots. Several studies showed an inhibition of roots growth, reduction of roots lengths, volume and roots dry weight (Davies et al. 2001; Arduini et al. 2006; Barcelo et al. 1993; Lopez-Luna et al. 2009; Liu et al. 1992; Vajpayee et al. 2011). The reduction of root length is correlated to an increase of the Cr(III) concentration (Table 4.2) (Lopez-Luna et al. 2009; Liu et al. 1992; Barbosa et al. 2007). Opposite effects on root dry weigh, at low concentration of Cr(III) (0.05 mg L^{-1}) were observed on roots of *Phaseolus vulgaris*. Moreover, the root dry weight increased more in presence of Cr(III) when *P. vulgaris* was grown in Fe-deficient conditions (Barcelo et al. 1993). Arduini et al. (2006) observed an increase of root dry weight of *Miscanthus sinensis* after Cr(III) treatment (50 and 100 mg L^{-1}). Changes in root morphology can indicate Cr(III) stress, with a stimulation of root elongation below 150 mg L^{-1} of Cr(III) and a severe inhibition of root length observed at concentrations equal or higher than 150 mg L^{-1} which demonstrates that Cr(III) affects root morphology at all level of concentration (Arduini et al. 2006). In addition, Cr(III) can

also affect aerial parts of plants and cause a decrease in leaf size and number (total and green leaves), growth rate, biomass and dry weight and affect the morphology of leaves (Wallace et al.1976; Chatterjee and Chatterjee 2000; Davies et al. 2001; Barbosa et al. 2007; Arduini et al. 2006; Chatterjee and Chatterjee 2000). Increase of leaf dry weight in *P. vulgaris* was observed after exposure to low concentration of Cr(III) (1 μM) (Barcelo et al. 1993).

Cr(III) have negative effects on roots and aerial parts of the plants. Studies reported that root growth was a more sensitive indicator than shoots for Cr(III) toxicity because Cr(III) is uptake via roots and accumulates more on roots than leaves (Chatterjee and Chatterjee 2000; Fargasova et al. 2012). Some studies also reported an opposite

Table 4.2 Effects of Cr(III) on seed germination and plant development

Plant species	Effects	Cr(III) concentration	Compound	References
Allium cepa	Reduction in root growth	0.01–10400 mg L^{-1}	$Cr(NO_3)_3$	Liu et al. (1992)
Avena sativa	Inhibition of root growth	1000–4000 mg kg^{-1}	$CrCl_3$	López-Luna et al. (2009)
Brassica oleracea	Decrease in leaf size, chlorosis and wilting	25 mg L^{-1}	$Cr_2(SO_4)_3$	Chatterjee and Chatterjee (2000)
Genipa americana	Reduction in root, leaf, stem and total biomass	5–30 mg L^{-1}	$CrCl_3$	Barbosa et al. (2007)
Helianthus annuus	Decrease root dry weight	520 mg L^{-1}	$CrCl_3$	Davies et al. (2001)
Miscanthus sinensis	Decrease leaf and flower dry weight	104–520 mg L^{-1}	$CrCl_3$	Davies et al. (2001)
	Increase root length	50–100 mg L^{-1}	$Cr(NO_3)_3$	Arduini et al. (2006)
	Decrease shoot growth and aerial part	50–200 mg L^{-1}	$Cr(NO_3)_3$	Arduini et al. (2006)
	Decrease length and roots biomass	>150 mg L^{-1}	$Cr(NO_3)_3$	Arduini et al. (2006)
Phaseolus vulgaris	Reduction of leaf size and leaf biomass	0.5–5 mg L^{-1}	$Cr_2(SO_4)_3$	Wallace et al. (1976)
	Increase in root and leaf dry weight	0.05 mg L^{-1}	Not specified	Barcelo et al. (1993)
	Decrease in dry weight and chlorophyll content	1–4 mg L^{-1}	Not specified	Barcelo et al. (1993)
Raphanus sativus	Inhibition of roots and shoots growth	50–250 mg L^{-1}	$Cr(NO_3)_3$	Fargašoavà et al. (2012)
Salix alba	Inhibition of roots and shoots growth	50–250 mg L^{-1}	$Cr(NO_3)_3$	Fargašoavà et al. (2012)
Sorghum bicolor	Inhibition of root growth	100–4000 mg kg^{-1}	$CrCl_3$	Lopez-Luna et al. (2009)
Triticum aestivum	Inhibition of root growth	500–4000 mg kg^{-1}	$CrCl_3$	Lopez-Luna et al. (2009)
	Inhibition of germination	25–100 mg L^{-1}	Cr_2O_3	Vajpayee et al. (2011)
Vicia Sativa	Inhibition of roots and shoots growth	50–250 mg L^{-1}	$Cr(NO_3)_3$	Fargašoavà et al. (2012)
Zea mays	Inhibition of roots and shoots growth	50–250 mg L^{-1}	$Cr(NO_3)_3$	Fargašoavà et al. (2012)

effect on roots and leaves of Cr(III) in specific conditions such as low concentration of Cr(III) and imbalanced nutrient supply of Fe (Barcelo et al. 1993; Arduini et al. 2006). However, it is important to consider all parameters for roots, because an increase in length could also indicate a stress reaction when the morphology of the roots is changed (Arduini et al. 2006).

4.4.2 Reproduction and Seed Germination

Cr(III) has a negative effect in the seed germination. Cr(III) exposure and accumulation in seeds delay, decrease and inhibit germination process. For *Triticum aestivum*, a treatment under 10 mg L^{-1} of Cr(III) showed no impact on the germination but treatment of 25, 50 and 100 mg L^{-1} led to 5–19% reduction of germination (Vajpayee et al. 2011). Cr(III) affected germination and growth of wheat (*T. aestivum*) and sorghum (*Sorghum bicolor*) after treatment of 500–1000 mg kg^{-1} of soil, but no effect on germination was observed for oat (*Avena sativa*), more resistant to Cr(III) than the other two species. This is confirmed by the EC_{50} of oat of 2216.84 mg kg^{-1} in roots, two times higher than EC_{50} of wheat and sorghum, 1631.14 and 1089.01 mg kg^{-1} respectively (Lopèz-Luna et al. 2009). Cr(III) has also been reported to interfere with structure and function of male gametophyte in kiwifruit (*Actinidia deliciosa var. deliciosa*) and can inhibit pollen germination and tube growth and induce alterations in pollen tube shape. Modification of callose deposition pattern and arabinogalactan protein distribution in kiwifruit pollen wall was also observed after Cr(III) exposure (Speranza et al. 2007, 2009). The reduction of α-amylase and β-amylase activities observed after Cr(III) treatment and causing a reduction of sugar supply required for the embryo development may be linked to germination reduction rate (Dua and Sawhaney 1991; Zeid 2001; Singh et al. 2013).

4.4.3 Effect of Cr(III) on Photosynthesis and Chloroplast Structure

As other trace elements, Cr(III) can affect plant photosynthesis and cause ultrastructural changes in the chloroplasts leading to inhibition of photosynthesis (Panda and Choudhury 2005; Panda and Patra 2000). Do Nascimiento et al. (2018) observed chloroplast damages after they exposed cocoa plants (*Theobroma cacao*) to a high concentration of Cr(III) (600 mg kg^{-1}). Alteration in shape of leaf chloroplasts resulting in the structural disarrangement of thylakoids and stroma was observed in *Alternanthera philoxeroides* and *Borreria scabiosoides* under Cr(III) stress (Mangabeira et al. 2011). Cr(III) treatment reduced chlorophyll contents in celery seedlings at 1 mM (Scoccianti et al. 2006), in genipayer (*Genipa americana*) seedlings at 30 mg L^{-1} (Barbosa et al, 2007), and in cauliflower (*Brassica oleracea*)

at 0.5 mM (Chatterjee and Chatterjee 2000). At the same concentration of Cr(III) and Cr(VI), Cr(III) was much less toxic than Cr(VI) on photosynthesis parameters of water hyacinth (*Eichhornia crassipes*) and might eventually increase photosynthesis and chlorophyll content (Paiva et al. 2009). One mM of Cr(III) stimulated growth and photosynthetic parameters such as photosynthetic rate and stomatal conductance on aquatic hyacinths after a 2 day treatment, but a decrease of photosynthetic rate and signs of toxicity (chlorosis) were observed for plants treated with 10 mM of Cr(III) for 4 days (Paiva et al, 2009). Similar results were shown for *P. vulgaris;* low (1 μM) or moderate (100 μM) concentrations of Cr(III) in irrigation solution increased chlorophyll a and b, and carotenoids content in leaves, but high Cr(III) concentration (10 mM) reduced the contents of chlorophylls and carotenoids (Zeid 2001). In mosses (*Fontinalis antipyretica*), Cr(III) modified chlorophyll a/b ratio. Cr(III) as $Cr(NO_3)_3$ decreased total chlorophyll content whereas Cr(III) as $CrCl_3$ lead to chlorophyll accumulation at low concentration of Cr(III). The effect on chlorophyll seem to depend on Cr(III) form and Cr(III) as a nitrate salt seems to be more toxic (Dazy et al. 2008). Like Pb, Cd or Hg, Cr may reduce δ-aminolevulinic acid dehydratase (ALAD) activity or degrade ALAD, an important enzyme involved in chlorophyll biosynthesis, thereby affecting the δ-aminolevulinic acid (ALA) utilization resulting in the increase of ALA and reducing chlorophyll production (Stobort et al. 1985; Prasad and Prasad 1987; Vajpayee et al. 2011). In cells, Cr(III) may compete with Mg and Fe for assimilation and transport to leaves, affecting therefore pigment biosynthesis (Vernay et al. 2007). Cr(III) exposure can also increase the production of ROS (Shanker and Pathmanabhan 2004). The ROS induce damages in pigment-protein complexes located in thylakoid membranes followed by pheophytinization (two H^+ ions replace the Mg^{2+} ion found in the center of the porphyrin ring of chlorophylls) and destruction of thylakoid membranes (Juarez et al. 2008). Cr(III) decrease the photosystem II (PSII) activity in *Datura innoxia* (Vernay et al. 2008). Barton et al. (2000) observed that Cr(III) at 10 μM increased the ferric chelate reductase activity in alfalfa (*Medicago sativa L.*) roots in iron-limited media. Cr(III) also induced chlorosis on plants (Barton et al. 2000; Schmidt et al. 1996). Chlorosis is generally correlated with Fe-deficiency in plant (Kaya and Ashraf 2019; Jin et al. 2007; Briat et al. 2015). It is possible that chlorosis is due to an inhibitory effect of Cr(III) on iron reductase involved in Fe(III) uptake (Alcántara et al. 1994). Cr(III) could also compete with iron for entry in root cells or interfere with iron uptake (Skeffington et al. 1976).

4.4.4 Gas Exchanges

Leaf gas exchange monitored by photosynthetic rate, stomatal conductance and transpiration was severely affected by Cr(III) in the first 24 h of treatment of *T. cacao* (Do Nascimiento et al. 2018). Severe changes in leaf gas exchange have also been reported for the macrophytes *Alternanthera philoxeroides*, *Borreria scabiosoides*, *Polygonum ferrugineum, Eichhornia crassipes* (Mangabeira et al. 2011), *Genipa americana*

(Santana et al. 2012) and *Eichirnia crassipes* (Paiva et al. 2009) subjected to Cr(III) stress. The leaf gas exchanged and stomates opening can be linked to photosynthesis rate, as a decrease in CO_2 will reduce optimal rates of photosynthesis.

4.4.5 Alteration of Organelles and Cellular Functions

Under Cr(III) stress, the shapes of chloroplast and nuclei were altered in two aquatic macrophytes *Alternanthera philoxeroides* (alligator grass) and *Borreria scabiosoides*. At 50 mg L^{-1} of Cr(III), disintegration of the nucleus and deformation of chloroplasts were observed leading to structural disarrangement of thykaloids and stroma (Mangabeira et al. 2011). Damage to chloroplast can affect photosynthesis and plant growth. Alteration of mitochondrial cristae and dense electron material in mitochondria was also observed for both *Allium cepa* and *Borreria scabiosoides* treated with Cr(III) (Mangabeira et al. 2011; Liu and Kottke 2003). In kiwi pollen, similar findings have been reported with an alteration of the shape of mitochondria (swelling and loss of mitochondrial cristae) and the shape of endoplasmic reticulum (Speranza et al. 2007). Cytoplasmic vacuolization was also observed in kiwi pollen after Cr(III) treatment, usually a sign of cell death (Speranza et al. 2007). The impact of Cr(III) on organelles can affect cellular function of the plant.

The presence of Cr(III) produce mitotic irregularities (i.e. anaphase bridges or mitosis lagging), chromosomal aberrations (i.e. chromosome stickiness, chromosome fragmentation) (Liu et al. 1992; Qian 2004; Kumar et al. 2015), chromatin condensation (Speranza et al. 2007) and nuclear abnormalities (nuclear bud, micro nucleus, nuclear notch) (Kumar et al. 2015). These chromosomal irregularities and DNA damage could be linked to the production of ROS (Kumar et al. 2015) or to the formation of DNA adducts with Cr(III) (Viti et al. 2014). The chromosomal aberration observed can be linked with the production of ROS, as Cr(III) induced the formation of ROS and antioxidant enzyme induced to counter oxidative stress can cause chromosomal aberration (Kumar et al. 2015). Cr(III) induces the expression of genes encoding for proteins involved in cellular stress responses. These proteins are also induced in pathogen defence, senescence process and heavy metal stress, suggesting the existence of a common ROS-mediated mechanism of gene regulation (Quaggiotti et al. 2007).

Exposure to Cr(III) induced proteasome misfunction in kiwi (*A. deliciosa var. deliciosa*) pollen that generated accumulation of misfolding and damaged proteins. Similar results were observed after Cr(VI) exposure, but molecular targets at proteasome level may be different (Vannini et al. 2011). The 20S proteasome α-subunit expression was decreased in presence of Cr(III) and the 26S regulatory subunit Rpn11 level was decreased after Cr(VI) exposure (Vannini et al. 2011).

4.4.6 Effects of Cr(III) on Mineral Nutrition

Like other trace elements, Cr(III) is structurally similar to other essential elements and may affect plant mineral nutrition. In rhizosphere soil, excessive Cr reduces the accumulation of essential nutriments (Fe, Cu, Mg, Zn Ca, S and P) by masking adsorption sites and forming insoluble or low-bioavailability complexes (Woke et al. 2019; de Oliveira et al. 2015, 2016; Sharma et al. 2020). There is also evidence of increased Fe availability and uptake for plants in presence of Cr(III) in soil (Cary et al. 1977a, b). Yu et al. (2018a, b) found that Cr(III) exposure decreased Mn and Zn concentration in root cells and Zn concentration in shoot cells in rice seedlings. Mn and Zn concentrations were also decreased in tomato root cells after Cr(III) exposure. A decrease of Fe and Cu concentrations was also observed in tomato roots (Moral et al. 1996). Gardea-Torresdey et al. (2005) showed in *Salsola kali* roots a decrease of K, P, Mg and Cu after Cr(III) treatment. In *Phaseolus vulgaris* L., very small quantities of Cr(III) are transported to leaves, but Cr(III) exposure induces a decrease of Fe, Zn and Mo and to a lesser extent a decrease of K, Ca and Mg in leaves (Wallace et al. 1976). Davies et al. (2001) reported that Cr(III) treatment decrease N, P and K levels in *Helianthus annuus* leaves, but enhance Al, Fe and Zn concentration. These effects were enhanced by the presence of mycorrhiza (Davies et al. 2001). These decreases in nutrient uptake are probably due to deterioration of root nutriment penetration under Cr(III) stress and the decline in root growth (Ao et al. 2022; Sharma et al. 2020). The decrease in nutrient uptake could indicate that Cr(III) displaces ions from physiologically important binding sites in plant cells, thus affecting signal transduction, photosynthesis or plant nutrient metabolism (Cipriani et al. 2012; Sharma et al. 2020). Also, the Cr(III) accumulation in the plant cell wall may damage the plasmodesmata, which are important for mineral nutrients transport channels, thus leading to an imbalance in mineral nutrient metabolism (Ao et al. 2022; Fujita 2015; Kitagawa et al. 2015). In presence of 1 μM of Cr(III), nitrate reductase (NR) activity was enhanced suggesting a request in ammonium (NH_4^+) or nitric oxide (NO) during the cellular response to Cr(III), whereas in presence of Cr(VI) (≥2 μM) NR activity decreased in *T. aestivum* (Panda and Patra 2000). Nitrogen is an essential macro-element and plays a role in growth and in plant development and is available as nitrate NO_3^-. An enhanced nitrate reductase could indicate an increased demand of energy, due to a dysfunction of photosynthesis or mitochondrial respiration.

4.4.7 ROS Production, Lipid Peroxidation and Antioxidative Mechanisms

Exposure to heavy metals induces the overproduction of ROS (reactive oxygen species) including superoxide radicals ($O_2^{\cdot -}$), hydroxyl radicals ($OH^{\cdot}$), oxygen singlets ($^1O_2$) and hydrogen peroxide (H_2O_2). Hyperaccumulation of ROS affects the growth and development of plants (Maiti et al. 2012; Xie et al. 2019). Redox active

metals such as Fe, Cu, Co or Cr have the capacity to produce ROS via Haber-Weiss and Fenton reactions (Sharma et al. 2020; Bokare and Choi 2014). Plants can develop antioxidant enzyme systems for scavenging excessive accumulation of ROS under metal stress. The enzymatic antioxidants include the key enzymes such as superoxide dismutase (SOD), catalase (CAT), peroxidases (POD), guaiacol peroxidase (GPX), ascorbate peroxidase (APX), glutathione reductase (GR), glutathione S-transferases (GST), single dehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR) (Ahmad et al. 2010). Under normal condition, ROS are generated in little quantities in cellular organelles of plants (Maiti et al. 2012) and play important roles in regulating and controlling essential metabolisms, such as signal transduction for programmed cell death, seed dormancy, senescence, and growth (Pourrut et al. 2011). In many studies, Cr(III) exposure induces an increase of antioxidant enzyme activities including SOD, CAT, POD, GPX, APX, GR, MDHAR and DHAR (see references in Table 4.3). Some studies showed a downregulation of antioxidant enzyme activities like CAT and POD in *Brassica oleracea* (Pandey and Sharma 2003; Chatterjee and Chaterjee 2000) and GR in *T. cacao* (Do Nascimiento et al. 2018). CAT uses heme (iron-porphyrin) as a cofactor. Reduction in CAT activity indicates that Cr has the potential to interact with iron in metabolic pool or it may influence the presence of active form of iron (Sharma et al. 2003, 2020). The non-enzymatic antioxidant responses (i.e. ascorbic acid, glutathione (GSH), phenolic acid) are also observed in presence of Cr(III). In *S. bicolor*, after Cr(III) treatment, the GSH/GSSH ratio decreases only in roots but not in leaves, suggesting an increase of oxidative species in root cells (Shanker and Pathmanabhan 2004). Dehydroascorbate (root and leaf) and total ascorbate (root) levels exhibited a high degree of significant increase irrespective of speciation or concentration of Cr(III) in the medium (Shanker and Pathmanabhan 2004). Cr(III) affects the membrane potential by inducing lipid peroxidation. Malondialdehyde (MDA), a biomarker of lipid peroxidation is excessively produced due to lipid peroxidation increase after Cr(III) treatment in root and leaf (Shanker and Pathmanabhan 2004). Oxidative damages resulting from ROS towards biomolecules such as lipids, proteins and nucleic acids is well documented for plant species (Kanazawa et al. 2000; Singh et al. 2006).

4.4.8 Regulation of Phytochelatins, Metallothioneins and Metal Tolerance Proteins

To cope with Cr(III) induced stress, plants have developed different strategies involving morphological, anatomical and molecular defence mechanisms. In order to regulate the uptake and accumulation of trace elements, plants can sequester and chelate metals with metal binding ligands such as metallothioneins (MT), phytochelatins (PC) and metal tolerance proteins (MTP), produced within the plant cells to aid in heavy metal transport and sequestration. These metal chelators protect plants against high heavy metal concentrations through different mechanisms, such

Table 4.3 Effects of Cr(III) on antioxidant enzyme activities

Plant species	Cr(III) concentration	Antioxidant enzyme activities	References
Oryza sativa L. XZX 45	12–40 mg L^{-1}	↑ DHAR ↑ MDHAR ↑ GPX ↑ GR ↑ APX ↑ POD = CAT = SOD	Fan et al. (2020)
Brassica oleracea L var. capitata cv. Snowball	500 µM	↓ CAT ↓ POD	Pandey and Sharma (2003)
Theobroma cacao L	0–600 mg kg^{-1}	↑ CAT, ↑ GPX ↑ SOD = GR	Do Nascimento et al. (2018)
Vigna unguiculata	0.05–0.5 mM	↑ POD ↑ CAT ↑ APX	Chow et al. (2018)
Micrasterias denticulata	10 nM–1 mM	= SOD = CAT	Volland et al. (2012)
Sorghum bicolor (L.) Moench cv CO 27	50–100 µM	↑ SOD, ↑ CAT, ↑ APX, ↑ DHAR, ↑ GR = MDHAR	Shanker and Pathmanabhan (2004)
Brassica oleracea	500 µM	↓ CAT	Chatterjee and Chaterjee (2000)
Parthenium hysterophorus L	1 mM	↑ SOD	UdDin et al. (2015)
Solanium nigrum L	1 mM	↑ SOD	UdDin et al. (2015)
Zea mays	30–150 µmol L^{-1}	↑ SOD	Anjum et al. (2017)
Theobroma cacao	>400 mg kg^{-1}	↓ GR	Do Nascimiento et al. (2018)
Allium cepa	1–100 µg mL^{-1}	↑ SOD	Kumar et al. (2015)
Fontinalis antipyretica	0.625 µM–50 mM	↑ SOD ↑ CAT	Dazy et al. (2008)

↑ Increase enzyme activity ↓ Decrease enzyme activity = activity was not modified

as chelation, sequestration (MT and PC) or efflux (MTP). MT are cysteine-rich proteins that play a crucial role in heavy metals detoxification, metal homeostasis and metabolism via binding through the thiol group (SH) in cysteine residues. MT are transcribed constitutively or induced in response to several types of stress including heavy-metal exposures (Ziller and Fraissinet-Tachet 2018). The increased expression of MT-like protein in sorghum exposed to Cr(III) can indicate a potential role of metal binding ligands in Cr(III) detoxification (Shanker et al. 2004). After chelation, Cr can be compartmentalized in the cell wall and vacuoles. In plants, the cell wall is mainly composed of cellulose, hemicelluloses and pectins (Carpita and McCann 2000; Wolf and Greiner 2012). In the cell wall of root cells, Cr(III) can bind cellulose and pectin (Wang and Lee 2011; Yamada and Shiiba 2015). In *Oryza sativa* tissues, expression of MT genes was increased after Cr(III) exposure suggesting a role of MT in Cr(III) chelation (Yu et al. 2019). PC are synthesized in the cytoplasm under heavy metals toxic stress (Sharma et al. 2016). Biosynthesis of PC is

catalysed by phytochelatin synthase (PCS) that is constitutively expressed. However, PCS activity is increased in the presence of heavy metals (Sharma et al. 2016). PT are low-molecular-weight, cysteine-rich small polypeptides with a general structure $(\gamma\text{-Glu-Cys})_n\text{Gly}$ ($n = 2$–11) (Mirza et al. 2014). PC are one of the most important classes of metal chelators. PC-metal complexes are very stable and are formed and sequestered in vacuoles (Sharma et al. 2016). Several studies on metal detoxification via PC have suggested the important role of PC in the detoxification of heavy metals including Cr (Ao et al. 2022). MTP are described as metal efflux transporters such as Fe, Zn, Mn, Cd, Co and Ni from the cytoplasm generally to vacuoles or extracellular spaces to prevent cytoplasmic damages (Ricachenevsky et al. 2013). In *O. sativa*, expression of several mRNA encoding for MTP was induced after Cr(III) exposure in root and shoot (Yu et al. 2018a, b). However, few studies have investigated the detoxification response of MTP to Cr(III) exposure and the transport mechanisms of Cr(III) by MTP in plant remain unclear (Ao et al. 2022).

4.5 Conclusions

Cr(III) clearly has a variety of impacts on terrestrial and aquatic plants and therefore deserves full consideration by ecotoxicologists, stakeholders and regulators. Current consensus regards Cr(VI) as much more toxic than Cr(III) and underpins extensive research efforts to find economically viable processes based on the reduction of Cr(VI) to Cr(III) for remediation purposes. However, Cr(III) chemistry in ecotoxicological studies requires much better consideration to correctly understand the biological effects of this form of chromium. In particular, too few studies have checked the actual speciation of Cr(III) in the exposure media along with the measured biological responses. The lack of information on actual Cr(III) speciation in ecotoxicological studies can lead to an underestimation of Cr(III) toxicity and complicates both comparisons across studies and extrapolation of laboratory findings to real field situations.

The effects of Cr(III) on plants include inhibition of plant growth, seed germination process, damage to chloroplast, reduced photosynthesis, oxidative stress associated with generation of ROS, and alteration of nutrient balance, organelles and cellular function (Fig. 4.2). More knowledge is needed on Cr(III) speciation in ecotoxicological test media to establish reliable concentrations *vs.* responses relationships for all these effects and improve risk assessment for this important oxidation state of chromium in natural environments.

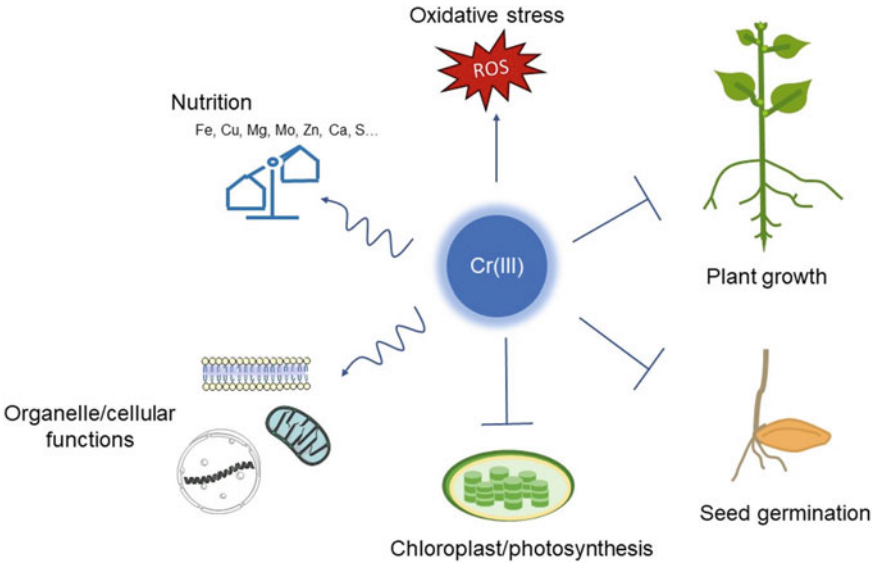

Fig. 4.2 Possible mechanisms of Cr(III) toxicity in terrestrial and aquatic plants

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