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Exogenous Mineral Regulation Under Heavy Metal Stress: Advances and Prospects

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Abstract

Heavy metals (HMs) contaminate the soil through various natural and anthropogenic resources and are transported to the plant systems. These heavy metals are translocated within the plant system by the apoplast and symplast through various transporters such as HMAs, ZIP, ABC. HMs disturb plant metabolism, cause oxidative stress and nutrient dearth. Many researchers have applied exogenous minerals to alleviate these negative impacts caused by HMs. Minerals mitigate the HMAs induced negative impacts by the enhancement of biochemical reactions and physiological processes in plants. In the present article the role of exogenous mineral regulation under heavy metal toxicity is being discussed.

Keywords: Heavy metals; Exogenous minerals; Oxidative stress; Transporters

Toxicity of heavy metals in plants and role of mineral nutrients in its alleviation

Heavy metal contamination in our environment has become a huge problem for all living things. Heavy metals comprise of an imprecise group of elements, such as lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni). These contaminants occur due to the hastened rate of industrialization and enormous usage of pesticides in agriculture. Mining, gasoline, paints, sewage, sludges, coal combustion rock weathering are some of the other sources through which these contaminants get entry into the ecosystem [1,2]. Heavy metals are also deemed to be trace elements because of their minimal, but indispensable requirement in plant growth and development [3]. These HMs have immense roles in biochemical and physiological functions and are important constituents of various key enzymes and redox reactions when present in limited concentrations [4]. Metal mobilization takes place with the cell wall of root cells and various transporter proteins make easier the uptake of heavy metals across the plasma membrane due to their higher affinities with heavy metals [5]. Plant cell has various transporters such as ATPases (HMAs), Nramps (natural resistance associated macrophage proteins), the cation diffusion facilitator (CDF) , the ZIP (ZRT, IRT-like proteins) family and ABC transporters (ATP-binding cassette) [6]. These individual transporters may have a broad range like IRT1 transports Fe^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}; ZIP4 transports Zn^{2+}, Cu^{2+}; NRAMP3/4 transports Fe^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+} and HMA1 transports, Cu^{2+}, Cd^{2+}, Zn^{2+} and Co^{2+} [6]. At higher concentrations these HMs disturb the equilibrium within the plant by affecting the cellular components like cell membrane, mitochondria, lysosome and endoplasmic reticulum, alters the behavior of various enzymes involved in metabolism, detoxification and damage repair [7] (Figure 1). HMs also induces the oxidative stress in plants [4]. However, Singh et al. [8] reported the induction of ROS in *Zea mays* seedling in response to Pb and Cr stress. Moreover, Tripathi et al. [9] reported the generation of oxidative stress due to chromium toxicity in wheat seedlings. Plants have developed diverse and orchestrated mechanisms to overcome from the adverse impacts of heavy metals. Although, it has been already revealed that metal transporters plays prominent role in intracellular metal homeostasis of plants [10] however, plants have developed a well-off defence system in the form of enzymatic and non-enzymatic antioxidants [8,9]. Enzymatic antioxidants like superoxide dismutase (SOD), peroxidase (POD), catalase (CAT) and glutathione-*S*-transferase (GST) convert various reactive oxygen species into hydrogen peroxide, water and oxygen. Whereas, non-enzymatic antioxidants such as ascorbic acid, flavonoids, glutathione and proline directly scavenge the free radicals [11]. Consequently at a certain level of toxicity these defense mechanism works, but at the edge of toxicity cell apoptosis occur. Therefore, besides these self defensive strategy of plant, researchers have evolved the usage of some substances by exogenous supplementation that can alleviate the heavy metal toxicity to increases the plant growth and production (Figure 1). In the recent era, the use of mineral nutrients is a celebrated approach in the regulation of heavy metals toxicity (Figure 1). Mineral nutrients are essential element for plant growth and development in both normal and stressed conditions. Heavy metals may cause mineral deficiencies that can be invalidated by the addition of mineral nutrients. Moreover, the availability of nutrients diminishes the HM accumulation and reduces its toxicity by provoking several physiological mechanisms [12]. Various experiments have been conducted to show the ameliorative behavior of minerals against the heavy metal toxicity. For instance, Gajewska et al. [13] reported the alleviation of Ni toxicity by the application of selenium in *Triticum aestivum*. They further discussed that, Se mitigated Ni induced reduction in concentration of

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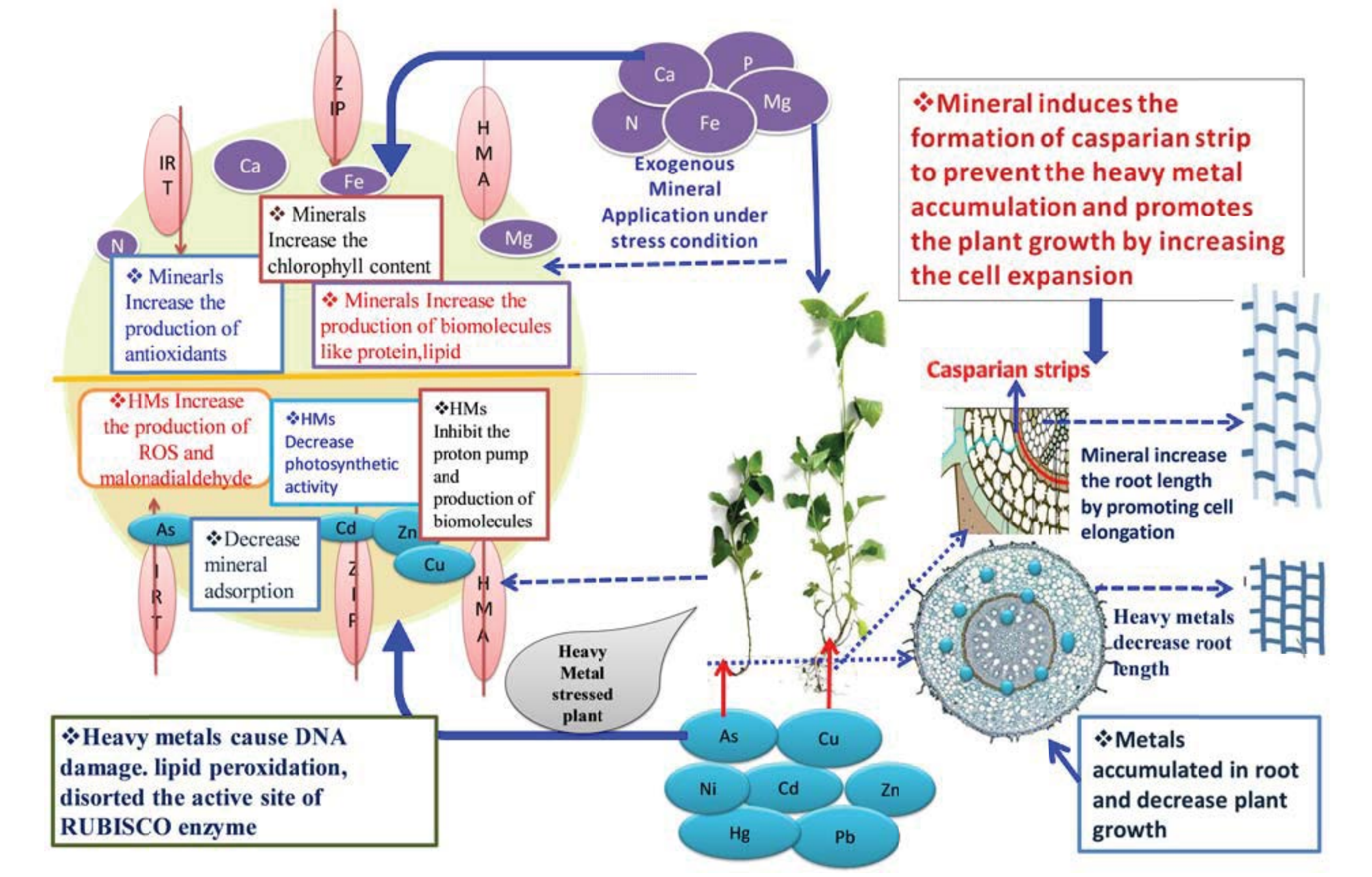

Figure 1: Heavy metals transport in the plant cell by the transporters such as IRT,ZIP and HMA [6]. Heavy metals induce the DNA damage, Lipid peroxidation, disrorted the binding sites of various enzymes, ROS production [9] and cause mineral deficiency in plant [7].While the exogenous application of minerals alleviate the heavy metal toxicity by competing at the binding sites of transporters [13] increase the production of antioxidant enzyme [14], Mineral also prevent the heavy metal accumulation by the formation of apoplastic barrier like casparian strips [17] as well as ncrease the root length by inducing the cell expansion [31,32].

Fe and Mg in shoot, diminished chlorophyll content and increased electrolyte lekage from the root and shoot cells by competing with metal ions at the binding sites. Malik et al. [14] described the ameliorating effects of selenium in mungbean in response to arsenic stress by increasing the activity of enzymatic and non-enzymatic antioxidants. The reduced activity of enzymes under As contamination occure by the diminished active sites [15]. Se helps in ameliorating As toxicity by checking As uptake and increasing its own accummulation for plant growth. Se also reported to increase the concentration of metallothioneins (MTs), thiols and glutathione-*S*-transferase (GST) in As stressed plants [16]. Similarly ,Wang et al [17] suggested the use of selenium (Se) to mitigate the mercury toxicity. The study was conducted on both hydroponic and soil potted seedlings of *Oryza sativa* and results showed that due to the application of Se less mercury accumulation occured in both seedlings. Se develoved apoplastic and symplastic barrier in rice seedling by the formation of casparian bands and suberin lamellae and via lowering the activity of membrane transporters. Some studies also suggested the utilization of mineral elements like Fe, S, Si in inducing the changes in the root anatomy, these minerals interrupts the uptake and accumulation of heavy metal [18,19]. Srivastva and D'Souza [20] described the role of sulphur in arsenic stressed plant *Hydrilla verticulata*. As stress was evident by generation of ROS and scarce activity of antioxidants like thiols, GSH and GSSH. Sulphur mitigate those stress by increasing the metal accumulation ability of plant. Several studies have been conducted to show the ameliorative role of silicon against the manganese (Mn) toxicity. For instance, Si reported to mitigate the manganese toxicity in Rice plants. Exogenously applied Si reduced the increased concentration of hydrogen peroxide and malonadialdehyde under high Mn concentration in rice seedling [21]. Similar results were also obtained by the exogenous supplementation of Si on Mn stressed cucumber plants. Si increased the tolerancy of cucumber plant for Mn by increasing the efficiency of the ascorbate-glutathione cycle [22]. These study explored that the Si increases the Mn tolerancy in plants by increasing the activity of non-enzymatic antioxidants [23]. Tripathi et al. [9] reported the silicon regulation in response to Cr uptake in rice seedlings. According to the study, chromium decreased the Mg, Ca, K, Zn and Fe transportation and thus damaged the plant anatomical structures like xylem, phloem and mesophyll cells. However, Si application diminished those abnormalities by decreasing Cr accumulation and transportation and by increasing uptake of minerals and improving the antioxidant system of plants. Anayat et al. [24] propounded about the mitigation of Cd and Hg toxicity with the help of nitrogen application in *Foeniculum vulagre*. In their study, Hg was reported to be more toxic than Cd, Hg decreased the chlorophyll a and chlorophyll b at 0.252 $mgg^{-1}Fw$ and 0.290 $mgg^{-1}Fw$ concentration, while Cd reduced the Chl a and Chl b at 0.290 and 0.309 $mg^{-1}Fw$ concentration [24]. Their investigation revealed that exogenous application of nitrogen increased the metal tolerance capacity of plant by increasing the reduced level of chlorophyll a and b and carotenoid content and also by reducing the elevated level of proline in stressed plants. Similarly, Pankovic et al. [25] reported the effect of exogenous supplementation of nitrogen in Cd-treated sunflower. Nitrogen application to the plant ameliorated the toxicity generated by the Cd treatement. Toxicity was displayed in terms of reduced photosynthetic activity by affecting the PS II reaction centers and regeneration of ribulose-1,5-bisphosphate. Gaafar et al. [26] reported the Cd toxicity in *Triticum aestivum* and its detoxification by sulphur (S). Cadmium increased the MDA concentration due to the excess production of ROS, decreased plant growth by reducing Chl a, Chl b, and inhibited the growth of rice seedling by inhibiting root length and shoot length and biomass. While, S showed mitigating effects in plants by enhancing Chl a, Chl b content and by increasing the activity of CAT, POD and SOD. It has also been accounted that Cd inhibits proton pumps which are responsible for the cell elongation [27]. Several studies have been conducted to explore the ameliorative effects of Si application on heavy metal stressed plants [28,29]. Exogenous application of Ca and Si restores plant growth and mitigate all the negative impacts imposed by HMs. Ca reportedly reduced the Cd activity at plasma membrane level in root cells [30,31] and Si take parts in enhancing the cell wall expansion [31,32]. Silicon and Zinc were successfully used with glutathione in the alleviation of Cd and Cr toxicity in rice. Cadmium and chromium also documented to reduce the activity of antioxidant enzymes such as APX and CAT and increase the accumulation of MDA in plant cells. While the exogenous applications of Se and Zn in combination to glutathione suppress the ROS production by increasing the APX and CAT activity [33]. Gunes et al.[34] reported the phytotoxicity of arsenic in chickpea and its mitigation by using the phosphorus. Phosphorus at high concentration decreased the elevated level of free radical production and lipid peroxidation under As stress. Moreover, phosphorus protects plants from arsenic toxicity because arsenate and phosphate are chemical analogues and are absorbed by the plant from the same transport system [35]. Wang and Song [36] reported that exogenous application of calcium in alleviating the cadmium toxicity. Cadmium decreased the plant length, biomass, chlorophyll and protein content and increased free radical production and lipid peroxidation. However, Ca mitigated the Cd induced toxicity and further increased the plant growth and biomass and the concentration of antioxidant enzymes [37]. In another investigation treatment of $MnSO_4$ documented to reduce the cadmium toxicity, it playes a defensive role for improving the photosynthetic tissues in the Cd-stressed plants [38]. Mn increases the antioxidant concentration and also reduces the Cd acquisition because Cd and Mn share common transporters. Therefore, that is how Mn regulates the Cd concentration at the transportation level [12, 30, 39,40].

Conclusion and future prospects

In the recent scenario, lack of nutritional value is one of the major problems acknowledged by the world health organization. Minerals are the indispensable constituents of nutrients for animals and plants. Though contamination of heavy metals in soil disturbs the uptake and transportation of mineral elements and reduces the plant growth and development by causing nutrient scarcity, ROS generation and reduction in photosynthetic activity. However, Optimum availability of nutrient elements mitigates the toxicity of heavy metals by regulating various physiological, biochemical and molecular reactions. Antioxidant system, photosynthetic activity and transporters are the chief components which take part in heavy metal homeostasis. Although, at some extent these homeostasis mechanisms of plant system worked, but at higher concentration of heavy metal plant cell and their physiological mechanism get affected. To alleviate or evade these negative impacts addition of mineral elements to the plants by the exogenous application is effective. Use of minerals enhances the plant growth and mitigate heavy metal toxicity by interfering in various physiological and biochemical mechanisms. Hence mineral regulation offers an approach to alleviate the heavy metal toxicity. Use of minerals to mitigate heavy metal toxicity is predicted to becoming an emerging trend in the agricultural field in future. This article recapitulates the current advancement in understanding the mitigating behavior of exogenous minerals applications, but besides these understandings, the pathway of mineral mediated alleviation of metal toxicity is inadequate. Therefore, further research is required for the better understanding of mineral homeostasis in heavy metal toxicity at physiological and molecular level. Attention should be paid on the signaling process of metal homeostasis and to work out the probable interactions among various nutrients and metal toxicity. As well as ingenious, extensive and enduring fields experiment is required to assess the possibility of mineral application for the remediation of metal contaminated soils. More attention required to fertilize the contaminated crops with the beneficial mineral elements, which may boost the crop production.

Conflict of Interest

Authors declare that they have no conflict of interest.

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