HEAVY METALS LEAD, CHROMIUM, AND COPPER IN CEREAL CROPS: SOURCES, ROLES, IMPACTS, STRATEGIES

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ABSTRACT

Heavy metals are metal elements generally harmful to human health and the environment. Heavy metals can cause stress and toxicity to plants, including cereal crops. Sources of heavy metals can come from nature or anthropogenic activities such as industry and agriculture. Heavy metals can accumulate in the environment and enter the food chain, thus endangering human health. It is very harmful to plants because it can cause reduced growth, deformation of cellular structures, ion homeostasis, decrease chlorophyll biosynthesis and photosynthesis, cause hormonal imbalances, and induce excessive production of reactive oxygen species (ROS) in plants. Heavy metals such as lead (Pb), chromium (Cr), and copper (Cu) have direct toxic effects on the growth and development of cereal crops. Strategies are needed to reduce the negative impact of heavy metal stress by using organic materials such as manure, compost, or biochar to reduce heavy metal levels in the soil. In addition, microorganisms such as phosphate-solubilizing bacteria, endophytic bacteria, and arbuscular mycorrhizal fungi can bind heavy metals and increase plant tolerance to heavy metal stress.

Keywords: cereal crops; heavy metals; microorganisms; organic matter; toxicity

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INTRODUCTION

Heavy metals are elements with an atomic weight of more than 63.5 and a specific gravity higher than 5.0, and they are generally harmful to human health and the environment (Ajoku et al., 2023). The main elements included in this class are lead (Pb), chromium (Cr), copper (Cu), cadmium (Cd), cobalt (Co), iron (Fe), arsenic (As), nickel (Ni), zinc (Zn), and mercury (Hg) (Nkwunonwo et al., 2020). Sources of heavy metals can come from natural (rock) and metal mining, smelting, waste disposal, combustion, pesticides, and chemical fertilizers used in agriculture (Ciont et al., 2022). The use of heavy metals is becoming an overuse in agriculture to maintain quality as the use of metals in industry, despite the various benefits provided to humanity, continues to cause significant ecological imbalances that can harm agriculture, thus having a particular impact on food quality and safety, food resources, and consumer health (Scutarasu & Trincå, 2023).

Cereals are the primary source of human food because they have various health benefits for the human body, which are related to the nutritional content contained in cereals (Laskowski et al., 2019). Cereals are fundamental sources of proteins, fiber, vitamins, minerals, and carbohydrates (Baniwal et al., 2021). The significance of cereals is further corroborated by the fact that global food security is critically dependent on cereal production, which attains approximately 2,600 million tons annually (Laskowski et al., 2019). To facilitate this, the growth and development of cereal crops necessitate systematic observation to optimize yields and sustain food security (Wang et al., 2018). Nevertheless, multiple impediments exist, such as environmental deterioration, which can threaten cereal crop development. A notable illustration is heavy metal toxicity, which detrimentally influences crop yields.

Heavy metals can cause stress and toxicity in plants, including cereal crops (Handayanto et al., 2017). Heavy metals can have a severe and lasting impact on the growth and development of cereal crops, leading to reduced yields and grain quality (Herman, 2022). The stress caused by heavy metals has its mechanisms in cereal crops, such as inhibition of photosynthesis by reducing the rate of photosynthesis and decreasing biomass production, causing oxidative stress to damage plant cells, disruption of nutrient uptake that disrupts plant growth, and making cell structure damaged (Vasilachi et al., 2023). After the occurrence of these mechanisms, there are adverse effects on cereal plants, such as chlorosis due to lack of chlorophyll content, inhibiting plant growth, damaging plant roots so that the plant's ability to absorb water is reduced, and inhibiting seed germination and seedling growth (Abbas et al., 2021; Vasilachi et al., 2023).

Lead, chromium, and copper have direct toxicity effects on the growth and development of cereal crops (Aslam et al., 2021). The effects significantly impact cereal crops' growth, yield, and quality, making them essential environmental pollutants to manage and mitigate (Rashid et al., 2023). The presence of heavy metals in cereal crops makes heavy metals pollute the environment, leading to water pollution (Kapoor et al., 2021). Examples of countries that experience water pollution due to the three heavy metals are Vietnam, Thailand, and Laos (Brindha et al., 2017)

Research by Ngoc et al. (2020) revealed that Vietnam reported heavy metal contamination in food sources and public water in the northern coastal region of Vietnam. Chromium, cadmium, lead, and arsenic concentrations were found to be very high in water, seafood, and vegetable samples, with concentrations two times higher than the permissible standards of the WHO (World Health Organization), which can damage human health. WHO standards for food content of agricultural food: chromium at 1.0 mg/kg; copper at 1.3 mg/kg of food by weight; and copper at 25 μg/kg of food by weight (Wu, 2014). In addition to Vietnam, based on research by Ahimbisibwe et al. (2022), Uganda found plastic cups commonly used by the public found large amounts of copper, lead, and chromium in beverages, exceeding the WHO and USEPA permissible limits.

Lead, copper, and chromium, the three heavy metals, are often found in cereal crops, so they are toxic to cereal crops. This journal will discuss the sources of these three heavy metals, their role in cereal crops, their effects on cereal crops, and strategies to reduce heavy metals availability.

SOURCES OF HEAVY METALS

Sources of Lead (Pb)

Lead is a non-essential element for plants whose content ranges from 0.1-10 ppm (Soepardi, 1983). Lead is a heavy metal that can be found in nature. Lead naturally comes from soil rocks in the Earth's crust and is dispersed into nature in small amounts through natural processes, including volcanic eruptions and geochemical processes (Wiria, 2009). In addition to natural sources, lead is also sourced from human activities such as those from motor exhaust gases; industrial manufacturing activities that use lead, such as lead-acid battery production, metal manufacturing, glass production, and the paint industry, can produce lead emissions to air, water, and soil (Wiria, 2009). Lead ions (Pb^{2+}) are commonly found in polluted waters (Faisal, 2015).

Treshow and Anderson (1989) stated that the amount of lead in the air is influenced by the volume or density of traffic, distance from highways, industrial areas, engine speed, and wind direction. In addition, the amount of lead in plants is influenced by sedimentation and collisions. According to Gidding (1973), particles emitted by motor vehicles are between 0.004 and 1.0 µm in size. Before falling into water, soil, and plants, slight lead will float in the free air. The fall of lead is caused by sedimentation due to gravity and precipitation associated with rain.

Sources of Chromium (Cr)

Chromium (Cr) is a metal element that forms naturally in the Earth's crust as chromite ore (Nabiela et al., 2020). Chromium is mainly found in the mineral chromite ($FeCr_2O_4$) and other minerals in ultrabasic igneous rocks, such as peridotite and dunite. The primary sources are stratiform and podiform chromite deposits formed during magmatic processes (Mukherjee & Das, 2019). Serpentinites, alteration products of ultrabasic rocks, can contain dispersed chromite and sometimes chromite deposits (Bacińska et al., 2021). Chromium can also be found in sedimentary rocks such as limestone, shale, and sandstone due to weathering and erosion of chromium-bearing rocks (Mukherjee & Das, 2019).

Apart from the weathering of parent rocks, chromium can come from human activities such as using fertilizers, pesticides, and industrial waste (Shahid et al., 2017). Chromium has an oxidation state that varies from Cr (II) to Cr (VI) (Jobby et al., 2018). Hexavalent chromium ions (Cr^{6+}) are commonly found in the effluents of electroplating, tanning, cement, mining, textile, fertilizer, and photography industries (Khare et al., 2018). It is easily absorbed by plant roots if in high concentrations and can cause plant poisoning, while trivalent chromium ions are not dangerous (Nugroho, 2021).

Source of Copper (Cu)

Copper metal (Cu) is an element that occurs naturally in nature in various forms. Sulfide mineral ores such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4), and Cuprite (Cu_2O) are the primary sources of copper in nature (Reed, 2018). Copper oxide minerals such as cuprite (Cu_2O) and tenorite (CuO) are also sources of copper in nature, although they are less common than sulfide ores (Marin et al., 2020). Copper can also be found in varying concentrations in rocks such as granite, basalt, and other igneous rocks (Ayoubi et al., 2019). Copper is present in soil due to weathering rocks containing copper minerals. Copper concentrations in soil vary depending on soil type and location (Shamilishvili et al., 2015).

In addition, Cu is widely found in the environment due to human activities such as the metal industry, smelting, and paint manufacturing, which can release copper into the environment through liquid waste, dust, or air emissions (Izydorczyk et al., 2021). Fertilizers and pesticides containing copper compounds can contaminate soil and surface water if used excessively (Lepp, 2012). Cu^{2+} metal ions are found in various environments, including industrial processes, biological systems, soil and sediments, and food and drinking water.

THE ROLE OF HEAVY METALS IN CEREAL CROPS

Heavy metals are needed in plant growth and development but can be toxic in excessive concentrations (Arif et al., 2016). Some heavy metals such as Lead (Pb), Chromium (Cr), and Copper (Cu) have benefits for plants.

Lead (Pb) is a significant environmental heavy metal pollutant and highly detrimental to living organisms, plant productivity, and human health. However, lead has a valuable role due to its mechanical properties; however, its non-biodegradable nature and excessive use are the reasons for its increasing toxicity (Nas & Ali, 2018). In plants, lead concentrations at low levels can increase plant biomass and yield (Wang & Wu, 1997), while lead is toxic to plants at high concentrations (Zulfiqar, 2019).

Chromium has a role in plant growth. Studies have shown that low concentrations of chromium (10-100 µM) can increase rice plant growth, including plant height, biomass, and yield (Samantaray et al., 1998). It can also increase plant resistance to abiotic stresses such as drought, salinity, and other heavy metals. Chromium plays a role in inducing the synthesis of protective compounds such as proline and increasing the activity of antioxidant enzymes

(Malik et al., 2021). Research conducted by Zahoor et al. (2017) showed that chromium can increase the activity of enzymes involved in carbohydrate metabolism, such as sucrose synthase and invertase, and enzymes involved in protein metabolism in wheat plants.

Copper (Cu) is an essential micronutrient that plants need in small amounts. It plays a role in photosynthesis, respiration, carbohydrate, and protein metabolism, increasing plant resistance to environmental stress (Mir et al., 2021). Cu also plays a vital role as a micro fertilizer in peatlands to support plant growth. In peat soils that tend to have low Cu availability, the application of Cu fertilizer can help overcome the deficiency and meet the Cu needs of plants (Suswanti et al., 2021).

EFFECT OF HEAVY METALS IN CEREALS CROP

Heavy metals affect cereal crops in high and low concentrations (Vasilachi et al., 2023). Heavy metals can threaten cereal crops due to toxicity, interfering with metabolic processes and plant growth. When heavy metals accumulate in excessive amounts in plant tissues, they can cause symptoms of phytotoxicity, affecting normal plant metabolism, morphological and physiological characteristics, plant growth, and productivity (Ashraf et al., 2015). Heavy metal accumulation often leads to reduced growth, deformation of cellular structures, ion homeostasis, decreased chlorophyll biosynthesis, decreased photosynthesis, hormonal imbalances, and induces excessive production of reactive oxygen species (ROS) in plants (Hassanuzaman et al., 2021). In addition, heavy metals in plants can cause a decrease in stomatal conductance and, therefore, limit photosynthetic capacity (known as the stomatal limitation factor) (Gill et al., 2012). Some studies found that heavy metal stress can increase the activity of carbon assimilation-related enzymes such as Rubisco (Hossain et al., 2012).

Heavy metals will be toxic at high concentrations, such as the heavy metal Lead (Pb), a harmful plant pollutant. Lead ions (Pb^{2+}) can bind to the functional groups of some enzymes (e.g., mercapto groups, ^{-}SH) and replace essential metal elements in the protein. Such replacement can change the conformation of biological macromolecules and inhibit their activity, resulting in decreased photosynthetic capacity (Marmiroli et al., 2013). Among the non-stomatal factors, besides the inactivation of key enzymes involved in carbon assimilation, another major limiting factor is the decrease in the photochemical activities of photosystem II (PSII) and photosystem I (PSI).

Pb metal stress often causes a decrease in PSII and PSI activities of plants (Tuba et al., 2010; Bayçu et al., 2017). Pb can inhibit electron transfer on the acceptor side of PSII and oxygen-evolved complex (OEC) activity on the donor side of PSII. In chloroplasts, ROS cause oxidative damage to the photosynthetic apparatus, resulting in photoinhibition of photosystem II (PS II) and Photosystem I (PS I). In particular, the photoinhibition of PSI is mainly related to the surrounding ROS. After entering the chloroplast stroma, ROS can inactivate some critical enzymes in the Calvin cycle, resulting in reduced CO_2 fixation capacity (Zhang et al., 2011). Based on the research of Kalaji & Loboda (2007) and Yao et al. (2009), they also found that the cause of PSII photoinhibition in maize and barley leaves under Pb stress is mainly related to OEC damage.

As a non-redox metal, Pb affects ROS production and causes oxidative stress in plant cells (Singh et al., 2016). Once produced, these ROS readily attack biological structures and biomolecules, resulting in metabolic dysfunction (Clemens, 2006). ROS can occur when excess electrons in the photosynthetic electron transport chain attack free O2, producing superoxide anion (Ahmed et al., 2009). Oxygen molecules will be mutated into ROS, such as H_2O_2, forming highly reactive hydroxyl free radicals. It damages the redox balance in plants, causing cell membrane peroxidation and oxidative damage to cellular structures (De Silva et al., 2012). Pb stress causes an increase in H_2O_2 content in maize leaves (Anjum et al., 2015) and paddy leaves (Wang et al., 2014).

In cereal plants, cases of poisoning caused by heavy metals often occur in rice plants. This poisoning is because the soil and water for planting rice are contaminated with heavy metals such as Pb, Cr, and Cu. Based on previous research, Pb toxicity can cause phytotoxicity, which affects several physiological functions, resulting in excess production of reactive oxygen species (ROS), which oxidize essential cell structures and cell membranes as well as reduce photosynthetic pigments and induce oxidative stress with increased production of hydrogen peroxide in rice plants (Ashraf et al., 2017). Pb toxicity is the same as the impact caused by the 6-valent heavy metal chromium (Cr) ion on cereal plants, which can also increase the production of reactive species (ROS), damaging lipid, protein, and nucleic acid biomolecules. ROS production will inhibit photosynthesis, respiration, and chlorophyll biosynthesis (Ali et al., 2020; Pandey et al., 2021). Based on several studies that have been conducted, Cr can inhibit the growth of roots, stems, and leaves in rice; this causes a decrease in biomass and yields (Khan et al., 2019; Amin et al., 2018).

Lack of heavy metals in plants can also have a negative impact, although not as severe as the impact of excess heavy metals. Certain heavy metals, such as Copper (Cu), are plant micronutrients. Lack of these heavy metal micronutrients can disrupt plant physiological and metabolic processes. According to research by Marschner (2012), Cu deficiency can cause chlorosis in young leaves, inhibit shoot growth, and reduce flower fertility. Research on wheat plants shows that Cu deficiency causes a decrease in plant height, number of tillers, and biomass weight (Tan et al., 2018). In addition, copper deficiency in high concentrations can cause poisoning.

Saha et al. (2020) showed that high concentrations of metal ions (Cu^{2+}) in rice plants could have an impact on increasing the production of reactive oxygen species (ROS), especially superoxide anions (O^{2-}) and hydrogen peroxide (H_2O_2), in chloroplasts (Maksymiec, 1997). Inhibition of antioxidant enzymes in high concentrations can inhibit the activity of antioxidant enzymes, such as superoxide dismutase (SOD), catalase (CAT), and other enzymes that play a role in ROS detoxification (Thounaojam et al., 2012). These enzymes aid in neutralizing harmful oxidants produced during metabolism, helping to preserve cellular health and function. (Jeeva et al., 2015).

Plants usually have three mechanisms of tolerance to the effects of heavy metals, namely, (a) passive mechanisms (plants develop various types of physical barriers against the absorption of heavy metals), (b) inducible mechanisms (detoxification of metals and their excretion into the extracellular space), and (c) activation of the antioxidative defense system (which includes enzymatic and non-enzymatic antioxidants) to scavenge ROS (Ashraf et al., 2015). Antioxidants, both enzymatic such as superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), and ascorbate peroxidase (APX), and non-enzymatic such as reduced glutathione (GSH) react with superoxide to form oxidized glutathione (GSSG) involved in the direct and indirect detoxification of ROS in cereal plants (Mishra & Choudhary, 1998; Mittler, 2002). Apart from antioxidants, plants accumulate various organic compounds, proline osmolytes, and soluble sugars to protect critical cellular structures and maintain cell osmotic potential (Ali et al., 2014). However, this is not necessarily the case for all plants; therefore, strategies are needed to deal with heavy metal stress to reduce the detrimental impact of heavy metal stress on cereal plants.

STRATEGIES TO REDUCE HEAVY METAL AVAILABILITY IN CEREAL CROPS

Organic Materials and Plants Reduce Heavy Metals

Heavy metals in cereal crops can be excessive, hence the need for strategies to reduce their availability. One strategy that can be used is to absorb heavy metals using organic matter. Organic matter can absorb and immobilize these metals in the soil. Based on the research of Aslam et al. (2021), it was revealed that organic materials can reduce heavy metal levels in soil and can be in the form of manure, compost, or biochar. Under field conditions, its application increases root branching, surface area, and fine roots; organic matter reduces toxicity, affecting root growth so that organic matter can increase root branching.

Organic modification is a solar-based, cost-effective, and environmentally friendly method that preserves the natural properties of soil (using plants and microbes) (Marathe et al., 2021). Organic matter can also increase microbial activity to reduce heavy metal uptake by cereal crops while using plants such as *Erigeron canadensis*, *Digitari aciliaris*, and *Solanum nigrum* that can mitigate the carcinogenic potential of Pb as bioremediation (Al-Wabel et al., 2015).

Microorganisms binding to Heavy Metals

Strategies to help overcome heavy metal stress's impact on cereal crops include using microorganisms such as phosphate-solubilizing bacteria. Based on research showed that phosphate-solubilizing bacteria such as *Pseudomonas aeruginosa* and *Bacillus subtilis* can improve wheat growth under Pb stress with mechanisms such as phosphate solubilization, siderophore production, and antioxidant enzyme activity (Mushtaq et al., 2022; Bai et al., 2014). Phosphate-solubilizing bacteria can produce siderophores that can chelate metals and form metal-siderophore complexes, reducing the bioavailability of heavy metals (Gomes et al., 2024).

In addition, arbuscular mycorrhizal fungi such as *Rhizophagus intraradices* and *Funneliformis mosseae* can increase wheat tolerance to Cr stress through increased nutrient absorption and accumulation of phenolic compounds (Ahammed et al., 2023). In addition, based on research conducted by Shahzad et al. (2019) stated that endophytic bacteria can alleviate heavy metal stress (Cu, Cr, and Pb) in rice plants through the regulation of changes in plant metabolism, such as increased biosynthesis of phenol compounds and amino acids. Endophytic bacteria can stimulate plants to produce more phenol compounds that act as antioxidants and metal chelators, which can bind heavy metals and reduce their toxicity. In addition, phenol compounds can also protect plant cells from oxidative damage caused by heavy metals (Rajkumar et al., 2016). Endophytic bacteria can also increase the production of specific amino acids, such as proline and histidine. These amino acids play a role in metal binding. Some amino acids can form complexes with metal ions, reducing their bioavailability and toxicity (Ahemad & Kibret, 2014).

CONCLUSION

Heavy metals can affect cereal crops' growth, yield, and quality. Excess of heavy metals can be reduced in two ways: using organic materials and plants that can reduce heavy metals and microorganisms that can bind heavy metals. The organic materials used include manure, compost, and biochar, which absorb heavy metals in the soil, reducing their levels. Bioremediation of heavy metals also can use some of plant species. The microorganisms used are phosphate-solubilizing bacteria, arbuscular mycorrhizal fungi, and endophytic bacteria, increasing the tolerance of cereal plants to heavy metal toxicity.

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