

1.1 Introduction to Heavy metals

Heavy metals are conventionally defined as elements with metallic properties and an atomic number >20 (1). They have density in the range of $3.5-7\text{g/cm}^3$ and are transition metals with incompletely filled d- orbital which make them highly reactive and toxic(2). Some of the metals include Pb, Cd, Hg, Cr, Cu, Fe, Zn, Ni, Mn, As. It is a well known fact that heavy metals cannot be chemically degraded and insist on to be physically removed or be transformed into nontoxic compounds. Sources of heavy metals include volcanoes, forest fires, fossil fuels, mining and smelting of ores, electroplating operations, fungicides and pesticides, sewage and sludge from treatment plants, cosmetics, jewelry, paints and electronics(3).

1.2 Health hazards associated with Heavy metal toxicity

Most of the heavy metals are in fact micronutrients that function as catalytically active cofactors in enzymes, others have enzyme activating functions and yet others fulfill a structural role in stabilizing proteins, i.e. essential in small quantities for normal growth of plants and animals, but in larger quantities are lethal(4). Urbanization and industrialization has led to the accumulation of heavy metals in water, vegetables, fruits, sea foods etc. Heavy metals have long biological half-life (5), therefore they can accumulate in the body causing various diseases and disorders. The main threat to human health from heavy metals is associated with exposure to lead, mercury, arsenic and cadmium. Humans get associated with these toxic substances through drinking water, food crops cultivated with water and soil contaminated with heavy metals. Neurological disorders, CNS destruction, and cancers of various body organs are some of the reported effects of heavy metal poisoning. Low birth weight and severe mental retardation of newborn children have been reported in some cases where the pregnant mother ingested toxic amounts of heavy metals (3). Lead competes with calcium and affects normal functioning of the nervous, renal, cardiovascular systems and is considered to be the cause for some of the cancers (6). It binds to sulfhydryl groups and alters cellular metabolism, competing effects of lead with other cations such as ferrous and zinc leading to the activation or inactivation of many enzymes (7). Lead may displace zinc in the zinc- dependent enzyme δ -aminolevulinic acid dehydratase (ALAD), thereby inhibiting the synthesis of heme, an important component of hemoglobin and heme-containing enzymes, such as the various cytochromes(8). Chromium is a known human

carcinogen and induces lung cancers among exposed workers. Chromium is a strong oxidizing agent which affects the biological membranes and can be easily accumulated in the cells as insoluble chromium hydroxides (6). The mechanism of chromium (Cr^{+6}) carcinogenicity in the lung is believed to be its reduction to Cr^{+3} and generation of reactive intermediates, leading to bronchogenic carcinoma (8).

1.3 Case studies

The most significant example of human intoxication is itaiitai disease which was diagnosed in Japan in 1940, due to the consumption of rice contaminated with cadmium. Patients suffering from this disease showed signs of osteomalacia, calcification and pyelonephritis (2). Another important public health disaster was in Minamata Bay, Japan due to mercury (9). Accumulation of mercury in testicles may inhibit spermatogenesis. Thyroid dysfunction caused by mercury may be due to inhibition of 5' deiodonases. Methyl mercury is shown to reduce the activity of natural killer (NK) cell activity. It is believed that lead targets the learning and memory processes of the brain by inhibiting the N-methyl-D-aspartate receptor (NMDAR), which is essential for hippocampus-mediated learning and memory (10).

1.4 Phytotoxicity due to Heavy metals

Phytotoxicity in soil is caused due to high levels of heavy metals. Metals get associated with soil particles in the following ways:

1. Free metal ions or/and soluble metal complexes;
2. Adsorbed at ion exchange sites of inorganic soil constituents;
3. Bound to soil inorganic matter;
4. Precipitated as oxides, hydroxides, carbonates;
5. Nested within the structure of silicate minerals

Toxicity may induce interaction with sulfhydryl groups, leading to inactivation of plant proteins and activities of microorganisms which promote growth of plant may be affected. Increased uptake of heavy metals by root and shoot interact with cellular components, metabolic functions etc. The reason for these damages may be mainly due to reactive oxygen species and hydroxyl radicals (11). Membrane proteins mediate the transport of metal ions into the cells (12). Mercuric chloride toxicity in plants may cause reduction in chlorophyll synthesis and photosynthesis.

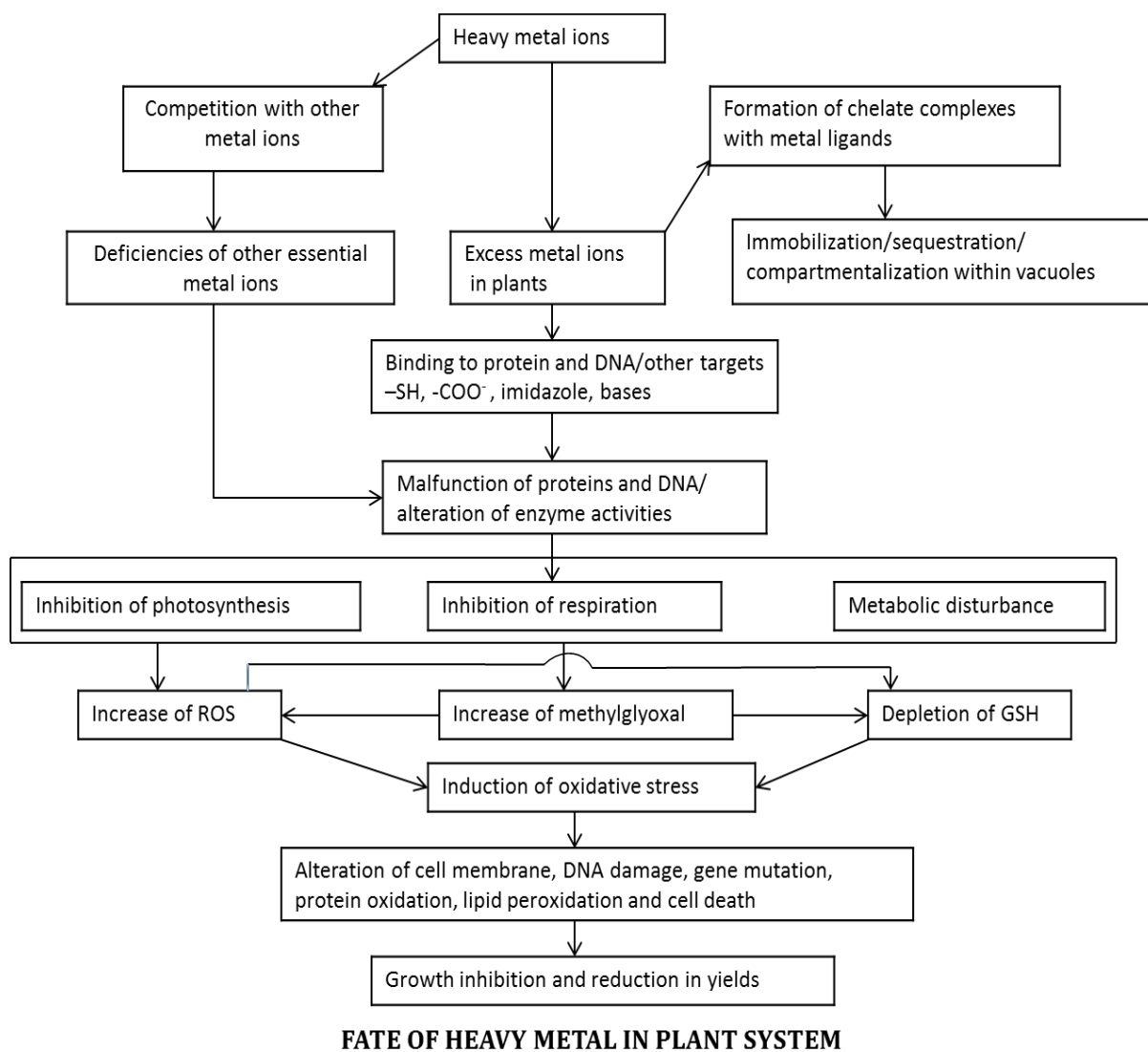


Fig 1: Fate of heavy metal in plant system

This toxicity is due to complexation of heavy metal ions by phytochelatins, metallothioneins, and organic acids and in turn alters the metabolic pathways of plants (13). Hg has high affinity for phosphate groups altering functions of many proteins like changes in permeability of cell membrane and is the reason for decrease in DNA, RNA content. It is also known to induce spindle and chromosomal alterations. N and O atoms, ribose groups might be potential binding sites for Hg leading to nucleobase impairment (14). The metals that are exchangeable and found in an easily available form are zinc and cadmium, while their counterpart is lead. Plants do not have channels for lead, instead bind to mucilage uronic acids via carboxylic groups on the surface of roots. Cationic channels, especially calcium ion channels help in uptake of lead from the medium by roots. Accumulation of proline is seen in root tissue when treated with lead (15). Studies have shown that pH plays an important role in uptake of Pb by plants; low pH levels increases the uptake by increasing the mobility of Pb. It uses transpiration conductive system to move in apoplastic space. Plants respond to ion stress including chelation, expression of stress protein genes. It can decrease the number of mitochondrial cristae lowering the capacity of oxidative phosphorylation (16). Lead toxicity increases reactive oxygen species causing inhibition in ATP production, lipid peroxidation and DNA damage.

1.5 Treatment for Metal Poisoning:

Glutathione super system is the body's main detoxification system, it binds to heavy metals with assistance of enzymes, antioxidants and transport proteins and help in the removal of these toxins from the body (mainly for mercury). Food sources such as green apples, cabbage, flaxseeds, nuts, bananas, grapes, parsley, beets, and citrus fruits contain pectin that have the potential to chelate heavy metals and eventually help the body to excrete through urination. Cilantro is an excellent metal chelator that can cross blood brain barrier and remove heavy metals from brain. Zeolite, a naturally occurring mineral compound specifically clinoptilolite is a cage shaped compound that carries a negative charge, it captures the toxic heavy metals containing positive charge including Hg, Pb, Cd, Al etc. Heavy metals gets trapped into the zeolite molecule and are impossible them to escape this bond. Zeolite is incredibly fast acting and gets completely removed from the body in 5-7 hours and hence does the trapped metals.

Treatment of metal exposure to prevent or reverse toxicity is done with chelating agents or antagonists. Chelation is the formation of a metal ion complex, in which the metal ion is associated with an electron donor ligand. Metals may react with O⁻, S⁻, and N⁻ containing ligands (e.g., -OH, -COOH, -S-S-, and -NH₂). Chelating agents need to be able to reach sites of storage, form nontoxic complexes, not readily bind essential metals (e.g., calcium, zinc), and be easily excreted. One of the first clinically useful chelating drugs was British anti- Lewisite (BAL [2, 3- dimercaptopropanol]), which was developed during World War II as an antagonist to arsenical war gases. BAL is a dithiol compound with two sulfur atoms on adjacent carbon atoms that compete with critical binding sites involved in arsenic toxicity. Although BAL will bind a number of toxic metals, it is also a potentially toxic drug with multiple side effects. In response to BAL's toxicity, several analogs have now been developed. Examples of chelating drugs used to treat metal toxicity: British anti - lewisite (BAL [2, 3 - dimercaptopropanol]), dimercaprol DMPS (2, 3 - dimercapto-1-propanesulfonic acid), DMSA (meso-2, 3- dimercaptosuccinic acid), EDTA (ethylenediaminetetraacetic acid, calcium salt), DTPA (diethylenetriaminepentaacetic acid, calcium salt), DTC (dithiocarbamate), Penicillamine (β-β- dimethylcysteine), hydrolytic product of penicillin. Pectasol chelation complex is a tablet that is used to detoxify the heavy metals.

1.6 Main objectives of the study:

- To detect & estimate the concentration of heavy metals in soil, water and food crops.
- To study the phytotoxic effects and bioaccumulation of heavy metals in vegetables and food crops.
- To carry out morphological, cytological and phytochemical studies on plants and its correlation to human toxic effects.
- To assess the public health risks arising from the presence of these toxic contaminants in foods.
- To design small scale filtration system using rice husk, bagasse, muskmelon peel and sawdust as potential biosorbents of heavy metal.

1.7 Overview of the study

Our study focuses on analyzing the heavy metal contamination in Byramangala reservoir and Hebbal Lake. Byramangala reservoir is spread over an area of 412 hectares. Over 1600 hectares of agricultural land in and around this lake is irrigated with this polluted water. Due to industrial revolution and high cost of effluent treatment the lake has been receiving untreated sewage and effluents mainly from the Bidadi industrial zone (1). Cytological studies using these water samples were done on Onion (*Allium cepa*). Phytotoxicity and morphological alterations in Green gram (*Vignaradiata*), Tomato (*Solanumlycopersicum*), Spinach (*Spinaciaoleracea*) and Ragi (*Eleusinecoracana*) were assessed subjecting them to growth using mercuric chloride (HgCl_2), lead nitrate [$\text{Pb}(\text{NO}_3)_2$] and lead acetate [$\text{Pb}(\text{CH}_3\text{COO})_2$]. Design of a small scale filtration system as detoxification system for contaminated water.

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