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IMPACT OF MERCURY CONTAMINATION IN SOIL AND CROP ECOSYSTEM WITH ADVANCED APPROACHES OF MITIGATION: A REVIEW

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ABSTRACT

The escalation of heavy metal pollution in agricultural soils mirrors the rapid industrialization process. Mercury, a hazardous heavy metal, widely contaminates ecosystems as a pervasive pollutant. Its presence poses a significant ecological threat globally, driven by its extensive utilization in industrial activities and subsequent release into the environment. This cycle of contamination is particularly alarming due to mercury's lack of essentiality and beneficial properties, coupled with its potential toxicity. The repercussions of environmental mercury contamination extend to food chains, with plants absorbing mercury from soil and water, thus facilitating its incorporation into the human diet. Hg's well-documented genotoxic and carcinogenic characteristics, monitoring its behavior within the soil-plant system is crucial to comprehend its potential for contaminating the food chain and subsequent human exposure. This review delves into the intricate interplay between mercury concentrations, its various chemical forms in soil (speciation), water and its availability to plants. It investigates the mechanisms underlying mercury accumulation in plants, scrutinizing both its harmful effects on plants and the detoxification processes occurring within plant tissues. To mitigate the toxic impact of mercury, strategies such as genetic modification, phytoremediation, the use of plant growth-promoting rhizobacteria and salicylic acid, as well as electro-remediation techniques have proven to be effective approaches.

Key words : Contaminant, Heavy metal, Mercury, Phytoremediation, Pollutant.

Introduction

Mercury poisoning has emerged as a pressing issue due to widespread environmental contamination globally. Approximately two-thirds of mercury input into the environment originates from natural sources, with human activities accounting for the remaining one-third. The utilization of mercury as a toxic substance has been documented since ancient times, appearing in the literature of ancient Oriental and Roman civilizations. Additionally, there was a belief in the healing properties of mercury (Hg), leading to its inclusion as an ingredient in numerous traditional medicines (Pal *et al*., 2014).

In contemporary times, mercury (Hg) is recognized as a significant global pollutant due to its enduring presence, tendency to accumulate in living organisms, and its toxic nature in the environment. The elemental form, Hg^0, commonly known as "metallic mercury," exists as a shiny liquid and is the most well-known variant. Inorganic mercury, present as either Hg^+ (mercurous) or Hg^{2+} (mercuric), is often found in compounds such as HgS, $HgCl$ and $Hg(OH)$, which may be associated with organic materials or particulate matter. The absorption of mercury varies across diverse plant species, encompassing bryophytes, lichens, wetland flora, woody vegetation and crops. Multiple factors influence this uptake process, such as soil or sediment organic content, carbon exchange capacity, oxide and carbonate presence, redox potential, formulation types and overall metal content. Typically, the level of mercury uptake in plants tends to correspond with pollution levels. During periods of low mercury pollution, crop mercury levels generally remain

below permissible thresholds. Aquatic plants are particularly adept at accumulating mercury, especially when it is in organic form. Mercury concentrations in plant components, such as stems and leaves are typically elevated when the metal is introduced organically. In freshwater aquatic vascular plants, uptake rates vary based on factors like plant species, seasonal growth rate fluctuations and the specific metal ion being absorbed. Some of the mercury released into the atmosphere is absorbed by plant leaves and subsequently transported to humus via fallen leaves. Certain plant species, such as oats, barley and wheat (C3 species), display notably higher mercury-vapor uptake by leaves compared to others like corn, sorghum, and crabgrass (C4 species). This variance in uptake is largely attributed to internal resistance to mercury-vapor binding. Airborne mercury significantly contributes to the mercury content of crops, thereby affecting human intake through food consumption. Despite similar internal mercury concentrations in treated plants, accumulation, toxicity response and mercury distribution differ between plants exposed through shoots or roots.

Plants may come into contact with mercury compounds either intentionally, such as when used as antifungal agents in crop plants through methods like seed treatment or foliar spray, or inadvertently through accidental exposure. Key criteria assessed in studies typically include seed germination, seedling growth, relative root and shoot growth and occasionally, evaluations of leaf-area index, internode development and other anatomical features. Accidental exposures may occur due to soil, water, or air contamination. Toxicity levels are commonly evaluated in laboratory settings, where different concentrations and durations of exposure are tested. In Australia, a larger share of mercury in the environment is linked to natural sources and re-emission, as opposed to human activities (ranging from 95 to 297 Mg compared to 10 to 20 Mg). This trend reflects positively on the management of human-generated waste in the country (Nelson *et al.*, 2012).

Characteristics of mercury

Mercury is ranked sixteenth from the bottom among all elements on Earth in terms of abundance, making it a scarce element. It is present in minute amounts in all lithosphere, hydrosphere, atmosphere and biosphere environments, including all types of igneous rocks. Mercury concentrations in ordinary soil typically range from 20 to 150 parts per billion (ppb). On the other hand, these levels can rise sharply, possibly as high as 80%, in close proximity to known deposits (WHO, 1976). Except

in situations where mercury leaks from municipal landfills, mercury usually forms strong bonds with the organic components of soil, limiting its mobility through leaching and lowering the possibility of groundwater contamination.

With an atomic mass of 200.59 grams per mole and a specific gravity 13.5 times that of water, mercury exhibits unique physical properties. It possesses a melting point of -38.9°C and a boiling point of 356.7°C, distinguishing it as the sole metal to maintain a liquid state at room temperature. Liquid mercury forms shiny, silver-white droplets with notable surface tension, appearing rounded on flat surfaces. Its high mobility and low viscosity facilitate easy combination of droplets. Mercury, with an atomic number of 80, exists in three distinct valence states in nature. Firstly, elemental mercury (Hg^0) remains electrically neutral. Additionally, it can take on two positively charged states: Hg^{2+} (mercuric) and Hg^{1+} (mercurous). The mercuric cation, known for its stability, is typically associated with inorganic compounds containing sulfur (*e.g.*, cinnabar), chlorine (*e.g.*, mercuric chloride), oxygen, and hydroxyl ions. Hg^{2+} is also present in organic compounds like dimethylmercury (Me_2Hg), which is exceptionally toxic and prone to bioaccumulation in living organisms' tissues. Due to its affinity for small particles, some scientists denote elemental mercury attached to or absorbed into a particle as Hg(p). As an element, mercury lacks biodegradability. It undergoes various abiotic and biogeochemical transformations and can be transported through the atmosphere, altering its form and accessibility to organisms. Despite these changes, mercury remains persistent in the environment.

By means of soil erosion, it finds its way into surface waters and is released into the atmosphere when the Earth's crust and oceans naturally release gas. Roughly two thirds of the total input come from natural emissions, and the remaining third comes from releases caused by human activity.

Occurrence of mercury in soil

The buildup of heavy metals in soil can result in adverse effects on plants, such as hindering enzyme activity, inducing oxidative stress and displacing nutrients (Sarma *et al.*, 2024). Cinnabar, a sulphide ore formed by hydrothermal mineralization associated with volcanic processes, is the source of most commercially produced mercury (Kabata-Pendias and Mukherjee, 2007). Although, it may be more concentrated in argillaceous sediments and coal deposits, mercury is relatively rare in the Earth's crust, usually ranging from 0.02 to 0.06 mg/kg (Kabata-Pendias and Mukherjee, 2007). Although, mercury can form inorganic compounds in the HgI

oxidation state (Hg^{2+}), it is more commonly encountered in the Hg II oxidation state, which is much more stable in soil environments (Schlüter, 1993 and Steinnes, 1995). In natural soil solutions, the mercuric cation (Hg^{2+}) is rarely found due to its strong tendency to form complexes with different anions (such as Cl^-, OH^- and S^{2-}) and humic substances. As an alternative, most of it is adsorbed onto inorganic mineral surfaces or bound within soil minerals.

About 1-3 percent of the total mercury in surface soils is methylated, with HgII compounds making up the majority of the compounds (Kabata-Pendias and Mukherjee, 2007). Mercury levels in the soil from a closed chlor-alkali plant in Botany Bay, New South Wales, Australia, are nearly 300 times higher than the recommended safe level established by Australia (Mahbub *et al.*, 2017). Because simple salts and elemental mercury have the ability to release toxic vapours, they pose the greatest risk to soil-plant systems' phytoavailability and toxicity. The toxicity and specific form of mercury are dependent on their sorption to soil. Different plants can absorb different amounts of mercury. For example, some plants can withstand higher concentrations of mercury in contaminated areas, which means that their edible parts have higher concentrations of mercury than those from natural soils. Several investigations have revealed that mercury builds up in plant roots, but it can also move throughout the plant to other areas like shoots and seeds (Schlüter, 1993; Kabata-Pendias and Mukherjee, 2007). The topic of inorganic mercury dermal absorption was studied by Sartorelli *et al.* (2003). When they looked into the skin absorption of mercuric chloride from loamy soil, they discovered that while absorption was observed from a buffered solution, mercury concentrations in penetrated fluids were undetectable.

Research has demonstrated that, after crops are harvested, the amount of mercury accumulated in the soil decreases at different rates for each crop, with the following crops ranking lowest: According to Wang *et al.* (1982), *Oryza sativa>Brassica oleracea* var. *capitata >Brassica rapa > Zea mays > Sorghum vulgare > Triticum aestivum.* Permissible levels of soil mercury are outlined in regulatory guidelines. The levels are capped at 0.5 ppm and are 17 mg/kg for calcareous soils and 6 mg/kg for acidic soils. It has been discovered that elements like high soil pH, lime content, and salt buildup reduce plants' ability to absorb mercury (Xuexun and Linhai, 1991).

By atmospheric deposition, anthropogenic mercury is deposited into soil. Because soil is one of the most significant Hg pools and has a long retention period, soil is essential to the biogeochemical cycle of Hg (Martín and Nanos 2016). Adsorption and desorption processes regulate the complex behaviour of mercury in soil (Montoya *et al.*, 2019). Airborne Hg^0 is deposited in soil over a broad geographic and temporal range (Lin *et al.*, 2010; O'Connor *et al.*, 2019), whereas atmospheric Hg^{2+} is deposited into soil either dry or wet quite quickly.

Pre-treating seeds is a widespread practice in many countries to avoid the introduction of fungi upon importation, especially for important crops like wheat and barley, as well as oats, rye, maize, rice, seed potatoes and various fodder crops. Because they are so effective, organomercury compounds are frequently used for this purpose; however, because of the way that mercury binds to humic acid, they cause direct soil contamination. Seed treatment within recommended dosages generally has a positive effect on germination rates. However, increasing application rates exacerbate seed injury.

According to Martín and Nanos' (2016) analysis of soil Hg contents, the average concentration of Hg in Spanish soil was found to be 0.0672 mg/kg, with a range of 0.001 to 7.564 mg/kg. According to the findings, 66% of the soil samples had Hg concentrations above the 0.025 mg/kg threshold, while 50% of the soil samples had Hg concentrations below the 0.037 mg/kg threshold. The investigation also showed that top soils had a higher Hg content, which was caused by the deposition of Hg-containing FA in the vicinity of coal-fired TPPs.

Plants in Poland were found to have different levels of mercury in them; vegetables grown in greenhouses had the highest concentrations, followed by plants grown in industrialised areas. Cucumbers, tomatoes and potatoes had the lowest concentrations, while lettuce and parsley leaves displayed the highest. There was no discernible relationship between soil mercury levels and plant mercury concentrations, and fruits and grains showed less bioaccumulation than vegetables (Szymczak and Grajeta, 1992). According to Arbestain *et al.* (2009), there was a high concentration of mercury (> 6500 mg/kg) in the soil near an old plant that produced mercury fulminate. Soils near an abandoned mercury mine waste in Spain had the highest concentration of mercury (10197 mg/kg) and the concentration decreased with increasing distance from the mining site (Fernández-Martínez *et al.*, 2005). The deposition of mercury through precipitation in forest catchment regions is contingent upon seasonal variations in atmospheric mercury levels, a phenomenon observed notably in Scandinavia (Iverfeldt, 1991). In industrialized areas, the accumulation of mercury particles is influenced

by factors like increased trichome density and dust-trapping efficiency of certain tropical plants, including *Cassia siamea*, *Calotropis procera*, *Ipomoea fistulosa, Zizyphus mauritiana* and *Mangifera indica* (Rao and Dubey, 1992).

40% of Mediterranean calcareous soil samples exceeded the specified reference value of 0.025 mg Hg/kg, according to Gil *et al*. (2010). 53 soil samples were gathered for Hg analysis as part of the study and the findings revealed that the samples' Hg contents ranged from 0.0094 to 1.585 mg/kg. The threshold value, or 0.3 mg Hg/kg, is the level at which mercury toxicity in soil can be detected (Martín and Nanos 2016).

Toxic metal ions, including mercury, are presumed to enter cells via uptake mechanisms akin to those facilitating essential micronutrient metal ions. Mercury, classified as a class B metal, exhibits an affinity for sulphur- and nitrogen-rich ligands, such as amino acids. According to Soares *et al.* (2015), soils in tropical regions accumulate Hg^0. After gaseous Hg has been retained by soils, gaseous Hg^0 is oxidised. The type of soil affects how much mercury it can retain. The study's findings also showed that, for a given type of soil, the A-horizon or top layer, adsorbed more mercury than the B-horizon, or subsoil. Because organic matter is crucial to the adsorption of gaseous mercury in soil, more mercury is found in the A-horizon (high organic matter) of soil. During the growing season, trees—especially deciduous trees—are also regarded as mercury sinks. Thus, the dropping of Hg-containing plant leaves on the ground constitutes another method of Hg deposition to soil in addition to FA (Alloway 2013). The parent material's composition and edaphogenetic parameters primarily determine the concentration of mercury in soil (Gil *et al*., 2010). A large body of research has shown that crop mercury levels typically stay below allowable limits in areas where mercury pollution is less prevalent. Several investigations conducted globally, such as those in South India, Taiwan and Czechoslovakia, where fertilizers or irrigation caused soil contamination, discovered that crop levels of mercury were below the World Health Organization's recommended daily intake (Srikumar, 1993). Studies have investigated mercury uptake and excretion in various plant species, including seedlings of woody plants (Kotov, 1983), shoots of oats and lettuces (Staiger, 1983), the eelgrass *Zostera marina* (Lyngby and Brix, 1982), crops grown on sludge-treated soil (Davis, 1984) and spruce (*Picea abies*) seedlings (Godbold and Huettermann, 1985). Around a chloralkali factory in India, plant species exhibited the highest mercury accumulation in leaves, followed by stems and roots. Significant correlations were

observed between soil mercury concentrations and mercury levels in plant tissues, as well as among different plant tissues (Lanka *et al*., 1992).

Contamination of mercury in water

In water bodies around Wroclaw, Poland, where atmospheric pollution, chemical factory effluents and groundwater contamination are prevalent, aquatic macrophytes have been identified as bioaccumulators of mercury. Concentrations of mercury in these macrophytes exceed average values found in background reference sites. For instance, the liverwort *Scapania undulata*, originally from a pristine forested mountain stream, exhibited increased mercury content when cultivated in solutions containing 70-100% sewage from a chemical factory, showing a 40-fold increase in 100% sewage and a 20-fold increase in 70% sewage (Samecka and Kempers, 1996). Since mercury strongly binds to soil organic matter, leaching of mercury into ground waters is typically only found in sandy soils with low levels of SOM (Teršiè *et al*., 2014). The biggest anthropogenic source of mercury emissions into water bodies is the Hg-cell chlor-alkali industry, which releases metal and alkali processing discharges. Dental amalgam use exposes dental staff to health risks because of mercury exposure (Nagpal *et al*., 2017). Due to its use in the extraction of gold, liquid metallic mercury contaminates rivers through discharge (Mbanga *et al.*, 2019).

A study comparing mercury bioaccumulation capacity in four rooted macrophytes (*Elodea densa, Ludwigia natans, Lysimachianum mularia* and *Hygrophila onogaria*) revealed significant differences in accumulation after 18 or 21 days of exposure. Mercury concentrations in the plants were consistently higher when introduced in organic form, with greater disparities observed when initial contamination occurred via sediment. Bioaccumulation from water sources was approximately 10 times greater than from sediment and substantial interspecies differences emerged in mercury burdens accumulated by the plants. After one week of exposure to mercury concentrations of 25, 50 and 75 ppm, the level of mercury in *Eichhornia crassipes* was approximately 70-75%. Additionally, the concentration of total free amino acids and enzymes such as alanine aminotransferase and aspartate aminotransferase increased with rising mercury concentrations (Hussain and Jamil, 1990).

Water hyacinth (*Eichhornia crassipes*), common cattail (*Typha latifolia*), burr reed (*Sparganium minimum*) and *Menyanthes trifoliata* roots were observed to readily absorb mercury ions from aqueous solutions. The hydrophilic parts of the roots accumulated
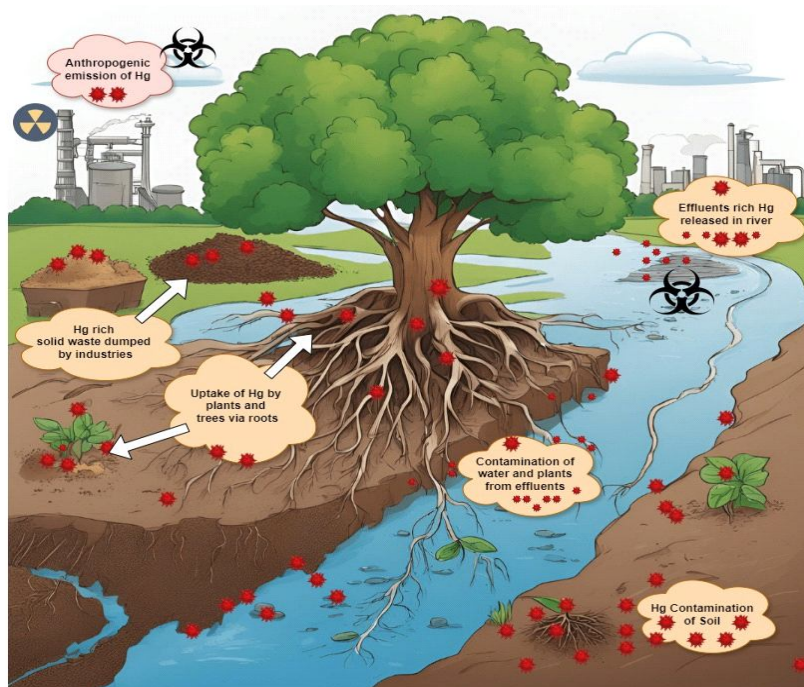
Fig. 1 : Mercury contamination in the environment.

significantly more mercury than the hydrophobic parts (Robichaud *et al*., 1995).

Uptake of mercury by plants

Soil contamination with mercury often occurs through the introduction of this heavy metal via fertilizers, lime, sludges and manures. The relationship between the quantity of mercury present in the soil and its absorption by plants is nonlinear and is influenced by various factors such as cation-exchange capacity, soil pH, soil aeration and the species of plants involved. Uptake may decrease in soils with elevated pH levels and/or abundant lime and salts. Another influencing factor on the extent of mercury accumulation is the plant species and variety (McGrath *et al*., 2001). Indeed, more than 45 plant families are known to include species that accumulate metals (Reeves and Baker, 2000). The majority of plants that uptake mercury tends to sequester it in their roots while some have the capacity to accumulate moderate levels in their shootseither through translocation or direct absorption of the vapor form. Research conducted by Suszcynsky and Shann (1995) demonstrated that plants exposed to elemental mercury can absorb and accumulate it in their shoots, with no subsequent translocation to the roots. Research on the reaction of terrestrial plants to soil contaminated with mercury has been carried out in the last few decades. These studies have demonstrated that, on average, plants are less able to absorb mercury through their roots than through parts of their bodies that are above ground (Fernández-Martínez *et al*., 2015; Patra and Sharma, 2000). When attached to fulvic acid, inorganic

mercury forms are usually easier for roots to absorb from the soil (Hongtao *et al*., 2004; Meng *et al*., 2012). Mercury has been shown to bind intracellularly to phosphate, other active groups in ADP and ATP, and -SH groups. This has been shown to have an impact on the replacement of necessary cations, mitochondrial activity, and cell membrane permeability (Nagajyoti *et al*., 2010). These results have been supported by more recent research, which also offered new information. For example, although fish has long been thought to be the main source of mercury pollution for humans, new findings indicate that rice may also play a significant role.

When added as a single contaminant to artificial soil, mercury has been shown to significantly inhibit the germination of cucumber and cress at concentrations of 25 mg/kg; however, when combined with other heavy metals, the toxic concentration of mercury can be as low as 1-2 mg/kg (Italian regulatory limits for residential and commercial use) (Baderna *et al*., 2015). Age is a significant factor that affects the bioavailability of mercury to plants, but it was not taken into consideration in this study. Rice seeds containing 16–584 µg/kg total mercury and 2–132 µg/ kg methylmercury were found in a study on rice (*Oryza sativa*) grown in a Chinese mining site where soil samples contained 2–186 mg/kg total mercury, 2–8 µg/kg methylmercury and less than 0.1% soluble mercury (Meng *et al*., 2014).

On the other hand, methylmercury accumulation in seeds and water-soluble mercury in soil were found to be directly correlated by this study. Rothenberg *et al*. (2011), on the other hand, contended that soil pH and rice genotypes have a greater influence on mercury accumulation and that water-soluble mercury in soil does not accurately predict the species of mercury present in rice grains. In contrast to inorganic mercury, which was dependent on phytochelatins for uptake and bioaccumulation, this form of mercury was more easily deposited in the endosperm of the rice grain during growth in methylmercury-contaminated soil, up to 800 times higher (Rothenberg *et al*., 2011)

Examination of approximately 2,500 vegetable samples and 650 soil samples revealed that a significant portion of vegetables, particularly those with edible roots, contained mercury, typically in the range of thousandths of milligrams per kilogram (Zawadzka *et al*., 1990). Similar findings were reported in cultivars of strawberry

and raspberry collected from five regions (Surdel, 1991). Mercury accumulation in rice was found to be higher than the permissible level (20 µg/ kg) in all Chinese investigations (CNSA, 2013). Higher soil contamination levels resulted in lower Bioaccumulation Factors (BAFs) for other plants like *Phyllitis scolopendrium*, *Calluna vulgaris* and *Brassica* spp. This could be because the soil's higher organic matter content limited the amount of mercury that was bioavailable (Fernández-Martínez *et al.*, 2015; Wang *et al.*, 2004). In the Boashen district of Shanghai, the mercury contents of vegetables were found to be elevated, with leafy vegetables having the highest levels, followed by root tubers and fruit vegetables (Feng *et al.*, 1993).

Research conducted by Lima *et al.* (2019) documented that Hg-contaminated soil affects both common beans and oats. While common beans are less affected by Hg concentrations above 20 mg kg^{-1}, oats are more affected at lower Hg concentrations in the soil (20 mg kg^{-1}). These effects are more pronounced for common beans in soils that contain less clay and organic matter. The properties of the soil as well as the types of plants that grow there have an impact on the sensitivity of the soil microbial community to Hg concentrations. According to this study, the critical concentration of mercury in soils above which plant and soil organisms will be impacted is 0.36 mg kg^{-1}.

Oryza sativa (rice) is one example of a plant that

may absorb the residues of fungicides or insecticides containing mercury, which may then build up in the edible parts of the plant. Plant ageing has been found to be accelerated and photosynthesis disrupted by compounds such as phenyl-Hg salts. Additionally, if seeds are stored with too much moisture or if the concentration of mercury in the mercurial solution is too high, applying mercurial solutions as seed treatments may have a detrimental effect on the viability of the seeds. These elements emphasise the complex connection between plant absorption, soil mercury levels and possible threats to plant health and food safety.

Mercury (Hg) comes in many forms, and some of them have been linked to seed damage and decreased viability. Mercury destabilises sulfhydryl (SH) groups through interactions that result in S-Hg-S bridges. This can have negative effects on embryo growth and seed germination, especially in tissues with high concentrations of SH ligands. Research has revealed that mercury chloride suppresses the gravimetric response of seedlings and prevents *Zea mays* primary roots from elongating (Patra *et al.*, 2004). The author also observed that Vigna radiata seedlings' respiration rates decrease in response to increases in the concentration of this heavy metal, as do reductions in the amount of sugar and nitrogen in total as well as in DNA and RNA. Additionally, photosynthesis, transpiration rate, water uptake and chlorophyll synthesis can all be lowered by mercury exposure. It has been demonstrated that exposure to both organic and inorganic mercury causes an accumulation of iron and a loss of manganese, magnesium and potassium (Boening, 2000). These reductions compromise the integrity of the cell membrane, which explains variations in its permeability. One form of mercury that can alter the plasma membrane is Hg^{2+}, which could account for the toxicity that plants experience in their aerial sections. Nevertheless, some writers contend that the toxicity seen in the shoots is caused by damage to the roots.

The primary impact of mercury likely targets the embryo itself, with effects on the endosperm being of secondary importance. Mercury disrupts the -SH system within living cells, leading to the formation of -S-Hg-S- bridges. This disruption can significantly affect both germination and subsequent embryo growth, particularly as these tissues contain abundant -SH groups.
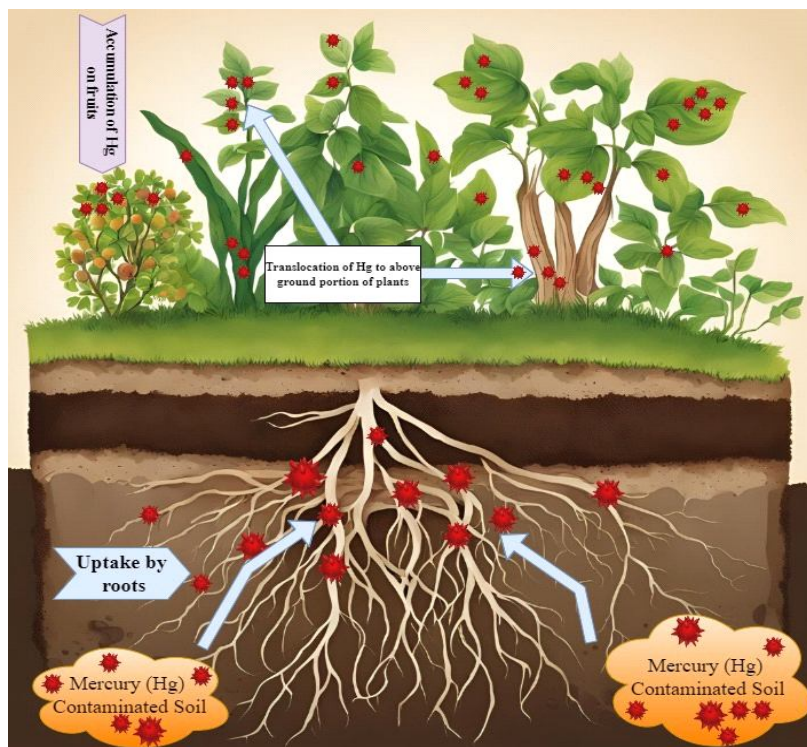

Fig. 2 : Mercury uptake by roots through contaminated soil.

Distinct alterations were triggered by varying concentrations of $HgCl_2$ (0.5-2.0 mM) on the root and stem morphology of *Triticum aestivum* cv. WL 711, with pronounced anatomical changes observed at higher doses. Mercury exposure led to the secretion of a gelatinous substance on the epidermal surface and inhibited root differentiation. In the stems, there was a reduction in diameter, number of vascular bundles, and cell sizes, alongside an increase in cell-wall thickness in the epidermal and hypodermal tissues (Setia *et al*., 1994). Pollen germination and tube growth of *Lilium longiflorum* were affected by concentrations of 3-100 µM of chlorides of Hg^{2+}, primarily causing abnormal cell-wall organization (Sawidis and Reiss, 1995). Foliar administration of different formulations of phenyl mercury acetate to *Sorghum vulgare* cv. CSH 5 in field trials did not impact grain or fodder yields or yield components (Kaore *et al*., 1993). The production of reactive oxygen species (ROS) such as superoxide radicals, hydroxyl radicals and hydrogen peroxide is increased by heavy metals, which is known to cause oxidative stress in plants and various cellular damages (Sharma *et al*., 2012). Mercury can cause oxidative stress in a variety of plant species, according to a number of recent studies. Mercury-induced damage from oxidative stress has been found to inhibit root and shoot growth, interfere with the production of chlorophyll and oxidative enzymes in a variety of terrestrial plant species, such as wheat (*Triticum aestivum*) (Sahu *et al*., 2012), mint (*Mentha arvensis*) (Manikandan *et al*., 2015), Indian mustard (*Brassica juncea* L.) (Ansari *et al*., 2009), hummingbird tree (*Sesbania grandiflora*) (Malar *et al*., 2015), cucumber (Cargnelutti *et al*., 2006), tomato (*Lycopersicon esculentum*) (Cho and Park, 2000), Chinese brake fern (*Pteris vittata*) and Boston fern (*Nephrolepis exaltata*) (Chen *et al*., 2009), physic nut (*Jatropha curcas*) (Gao *et al*., 2010), alfalfa (*Medicago sativa*) (Zhou *et al*., 2008) and rice (*Oryza sativa*) (Chen *et al*., 2012). Depending on the type of plant, a critical mercury content of 0.05 to 100 mg/L was needed to cause oxidative stress. Nonetheless, the interplay among metal, soil, and seed is essential and has the potential to alter the level of toxicity noted in experiments in which soil is not employed as a medium. Growing plants in hydroponic systems, moistened filter paper, or laboratory culture media like Hoagland nutrient solution or agar medium spiked with mercury were the most common methods used in studies on mercury-induced oxidative stress in plants. In these experimental configurations, the concentration of bioavailable mercury was elevated.

In vivo substitution of magnesium, the central atom of chlorophyll, by mercury is a significant mechanism of damage. This substitution hinders photosynthetic light harvesting in affected chlorophyll molecules, leading to photosynthesis breakdown. The reaction is dependent on light intensity. Under low light irradiance, heavy metals, including mercury can access all central atoms of chlorophylls, forming heavy-metal chlorophylls with enhanced stability. This stability can maintain greenness in plants even after death. However, in high light conditions, almost all chlorophyll decays, indicating limited accessibility of chlorophyll to heavy-metal ions (Kupper *et al*., 1996). In their study, Lomonte *et al*. (2009) proposed that plants have defence mechanisms activated by mercury stress and that these mechanisms probably explain why the tested plant species produced more sulphur compounds, which promoted their growth.

Since chromium has no known biological function, is hardly soluble in soil, and is not readily available for plant uptake, it is possible that this has prevented the identification of Hg-hyperaccumulating plants. In *Zea mays* cv. Tisa seedlings, higher concentrations of mercury led to increased glutathione transferase activity in shoots and a slight decrease in roots, with activity peaking in roots three days after exposure to 30 µM mercury (Komives *et al*., 1994). Treatment of *Bacopa monnieri* plants with various mercury concentrations over different durations revealed an initial increase in cysteine, total - SH, reduced glutathione and ascorbic acid content, contributing to mercury tolerance. However, higher metal concentrations resulted in decreased chlorophyll protein content due to mercury toxicity (Sinha *et al*., 1996). Proteins called aquaporins, which help move water through cell membranes, are mercury-sensitive. Because Cys-116, a mercury-sensitive cysteine residue, is present in *Arabidopsis*, the aquaporin *d-TiP*, which is found in the tonoplast, displays water-channel activity that is mercury-sensitive. Cys-116 was found to be the mercury-sensitive site in *d-TiP* by site-directed mutagenesis, indicating its function in aquaporin mercury sensitivity (Daniels *et al.,* 1994, 1996).

Segments of *Helianthus annuus* cv. Giganteum hypocotyl inner tissue, primarily ground-tissue parenchyma, showed rapid extension in water, reversible in hypertonic osmoticum. Sub millimolar concentrations of $HgCl_2$ affected water uptake or loss rates, indicating sensitivity to mercury and suggesting alterations in water channel turgor changes (Hejnowicz and Sievers, 1996).

Mitigating strategies for mercury toxicity

1. **Genetic modification :** Processing plants for heavy metals present viable and eco-friendly solutions for

removal and sequestration. *MerA*, an enzyme that transforms toxic Hg^{2+} into less dangerous, comparatively inert Hg^0, is one such example. However, conditions that are unfavourable for efficient expression, such as CpG dinucleotide richness and skewed codon usage, impede the expression of bacterial *merA* sequences in plants. In order to address this, a modified *merA* sequence known as MerApe9 was created and put under the control of plant-regulatory elements. This modified the flanking region and 9% of the coding region. Despite being toxic to multiple control plants, transgenic *Arabidopsis thaliana* seeds expressing *merApe9* successfully germinated and showed growth, flowering and seed set even in the presence of $HgCl_2$ concentrations ranging from 25-100 μM (5-20 ppm). Additionally, these transgenic seedlings developed considerable resistance in comparison to controls and the rate of evolution of mercury resistance and the degree of resistance corresponded with the steady-state mRNA level, indicating that the expression of the MerApe9 enzyme plays a role in conferring resistance (Rugh *et al*., 1996; Wilde *et al*., 1994).

Researchers engineered *Arabidopsis thaliana* to express a modified bacterial gene, *merBpe*, which encodes *MerB* under the control of a plant promoter, in order to investigate the potential of plants in extracting and detoxifying methylmercury. *MerB* helps the carbon-mercury bond to be protonolyzed, which releases the less mobile form of mercury, Hg (II) and separates the organic ligand. When exposed to various concentrations of organic mercurials, transgenic plants expressing *merBpe* grew vigorously, whereas plants lacking the gene experienced significant inhibition or even died. Different transgenic lines displayed different amounts of *merBpe* mRNA and *MerB* protein synthesis; even very little *merBpe* expression provided resistance against organic mercurials. According to this study, native macrophytes like grasses, trees and shrubs that have been genetically modified to express *merBpe* may be able to degrade methylmercury at polluted locations and sequester mercury (II) for later removal. (Bizily *et al*., 1999).

The remarkable ability of transgenic plants to extract mercury ions from methylmercury compounds, transform them into metallic mercury, absorb the metallic mercury through their roots, and release less elemental mercury at concentrations well below OSHA guidelines is demonstrated. This novel method reduces mercury toxicity by an astounding factor of 10,000 while meeting or exceeding regulatory requirements and offering a sustainable, aesthetically pleasing and cost-effective solution. The bacterial genes that break down methylmercury and lower mercury ions have been altered and inserted into these plants. The first gene to be successfully inserted into plants was *merA*, which codes for the enzyme mercuric-ion reductase, which transforms ionic mercury into an elemental form that is less harmful. An organomercurial lyase protein, encoded by the *merB* gene, is responsible for separating highly toxic methylmercury compounds from mercury ions. Studies have indicated that methylmercury can be detoxified in soil and water by plants that have the *merB* gene. Different plant species, including *Liriodendron tulipifera* (tulip poplar), *Nicotiana tabacum* (tobacco), *Brassic*a (mustard) and *Arabidopsis thaliana*, have all had both genes successfully activated. More plant species, such as cattails, wild rice and Spartina, a distinct wetland plant are being converted as part of ongoing efforts (Phytoworks, 1997).

Hussein *et al*. (2007) conducted a study utilizing genetically modified tobacco plants to explore the phytoremediation potential of mercury by examining the absorption of different mercury forms into the roots and shoots of tobacco plants. These plants were engineered with bacterial *merA* and *merB* genes incorporated into the chloroplast genome.

2. **Phytoremediation :** An investigation done by Lafabrie *et al.* (2011), the bioaccumulation of mercury (Hg) in *Vallisneria neotropicalis*, a submerged aquatic plant species was examined. The study found that Vallisneria species played a significant role in Hg bioaccumulation and could serve as an indicator of Hg pollution in sediments. Isaksson *et al*. (2007) conducted a study on Hg accumulation in *Lemna minor*, an aquatic plant, and discovered that *L. minor* effectively stored Hg within its biomass. The research illustrated a positive correlation between Hg concentrations in plant tissues and water, suggesting that *L. minor* is highly suitable for Hg removal from water through phytoremediation. Furthermore, aquatic macrophytes such as *Azolla pinnata* and *Pistia stratiotes* were explored as potential candidates for removal from wastewater in open-pit coal mines. *Typha domingensis* was employed in a constructed wetland for removing mercury from water using phytoremediation. The findings indicated that these aquatic macrophytes possess significant potential for mercury removal from polluted water owing to their ability to accumulate high levels of mercury, as evidenced by their accumulation capacity of 273.3515 ± 0.7234 mg/kg (Gomes *et al*., 2014).

In a pot experiment, researchers discovered that *Cyrtomium macrophyllum*, a wild plant widely found in China, exhibits significant potential for phytoremediation of mercury (Hg). Even when grown in soil with high Hg levels (500 mg/kg), *C. macrophyllum* showed no signs of toxicity during its growth. The study revealed that this plant species possesses remarkable abilities for translocating and accumulating Hg, making it a promising candidate for remediating highly polluted soil contaminated with mercury (Xun *et al*., 2017)

Cassina *et al*. (2012) employed two plant species—*B. juncea* and *Helianthus annuus*—for the efficient remediation of mercury. They found that while the sunflower plant responded better in terms of plant biomass production, *B. juncea* was more effective in absorbing mercury. The study also discovered that the application of thioligands and plant hormones (cytokinin) enhanced the ability of plants to perform phytoremediation.

Enzymatic antioxidants and some nonenzymatic antioxidants, such as glutathione, phytochelatin, salicylic acids, ascorbic acid, selenium, proline, and tocopherols, are examples of detoxification mechanisms to counteract Hg-induced oxidative stress.

3. **Response of PGPR :** Research conducted by Gontia-Mishra *et al*. (2016) demonstrated that applying the mercury tolerant PGPRs (HG 1, HG 2, and HG 3) shielded plants from the harmful effects of mercury and successfully encouraged *Triticum aestivum* growth. The isolated PGPRs were excellent candidates for plant inoculation because they exhibited a variety of characteristics that promote plant growth. Better root development is explained by ACC deaminase activity and IAA productions, while P, Zn and K solubilization may aid in the mobilisation of nutrients and so promote plant growth in mercury-stressed environments. One could draw the conclusion that the PGPRs employed in this study have a lot of promise for the phytoremediation process in soil contaminated with mercury.

4. **Response of Salicylic acid :** The application of salicylic acid (SA) triggers Systemic Acquired Resistance (SAR) in plants, providing substantial protection against diverse biotic and abiotic stresses. Apart from bolstering defence mechanisms against pathogens and infections, SA also mitigates the detrimental impacts of various abiotic stressors like heavy metals, temperature fluctuations, water scarcity, and salinity stress (Ansari *et al*., 2023). Salicylic acid (SA) serves as a recognized signaling molecule within plants, playing a crucial role in enhancing their tolerance to stress. Indeed, SA facilitates plant adaptation to challenging environmental circumstances by overseeing a range of physiological and biochemical activities (Zhang, 2018). It has been observed that applied SA reduces lipid peroxidation and electrolyte leakage, improves water and nutrient uptake, antioxidant activity, and photosynthetic features, and increases the tolerance of exposed plants under metal toxicity (Li *et al*., 2019).

According to a study conducted by Safari *et al*. (2019), mercury (Hg) toxicity led to oxidative stress and severely hampered plant growth. Nevertheless, the use of salicylic acid (SA) enhanced growth parameters and lessened the harmful effects of mercury stress. As evidenced by DPPH radical scavenging and FRAP assays, which shielded cellular compartments from reactive oxygen species-induced oxidative damage, this improvement was associated with an increase in antioxidant capacity (ROS). A reduction in lipid peroxidation levels, which suggests improved membrane integrity, provided additional evidence for this. SA's regulatory function in the antioxidative system was suggested at the molecular level by the up-regulation of the PAL gene, a crucial part of the phenylpropanoid pathway. By raising proline levels, preserving leaf relative water content and preserving chlorophyll content—all of which are supported by increased transcript levels of the crucial biosynthetic gene chlorophyll synthase (CHLG)—salicylic acid also induced tolerance mechanisms against mercury stress. These results have applications and advanced the practical knowledge of how SA reduces mercury stress in lemon balm and possibly other plant species.

5. **Soil washing :** Using water to reduce the concentration of mercury in the soil is known as "soil washing," a physical method of removing mercury from soil (Dermont *et al*., 2008; Xu *et al*., 2015). The idea behind the soil washing procedure is that the majority of harmful substances attach themselves to the fine soil particles, such as slit and clay and that these contaminants are washed away with the particles when the soil is washed with water (USEPA, 2007). Chemical extraction is the term for the process of removing mercury from soil by application of chemicals; this technique can be combined with physical separation. In order to lower the levels of mercury in coal, Ghosh *et al*. (1994) proposed that beneficiation of coal could also be done before it is used in different industries. The primary benefit of this technology is the decreased amount of soil that

requires additional treatment or disposal. But when there is a strong bond between mercury and soil particles, this process is not possible (Xu *et al.*, 2015).

6. **Electro-remediation :** The deliberate application of direct current between electrodes through the soil is known as electro-remediation. The entire system consists of three compartments: a soil compartment situated between the two electrode compartments and two electrode compartments. Ions travel from the soil to the electrodes via an ion exchange membrane, when Hg-contaminated soil is treated (Pazos *et al.*, 2010). In their investigation into the electro-dialytic remediation of soil, Hansen *et al.* (1997) discovered that adding oxidising agents and chloride to the soil would mobilise mercury, thereby speeding up the removal of mercury from the soil. The findings demonstrated that chelates improved the soil's Hg solubility and improved the electroremediation process' effectiveness. The soil's pH, the solubility of mercury in the soil, and the amount of organic matter present all have a significant impact on the process's efficiency. The primary drawback of this method is that it requires acidic conditions to be treated (Virkutyte *et al.*, 2002).

Minamata convention on Mercury

The international community is obligated by the Minamata Convention on Mercury to reduce mercury emissions and take other steps to control the supply and trade of mercury as well as products containing mercury and manufacturing processes that use mercury. With its implementation, the harmful effects of mercury on the environment and human health were acknowledged on a global scale. At the Conference of Plenipotentiaries on the Minamata Convention on Mercury, which took place in Kumamoto, Japan, from October 7–11, 2013, the Convention was adopted. It came into effect on August 16, 2017. The Minamata Convention's primary aspects include a ban on new mercury mines, the phase-out of existing ones, the reduction and elimination of mercury's use in a variety of goods and processes, air emission limits, water and land release regulations, and control measures for the unofficial artisanal and small-scale gold mining industry. The Convention also covers sites contaminated by mercury, health concerns and the interim storage of mercury and its eventual disposal once it becomes waste.
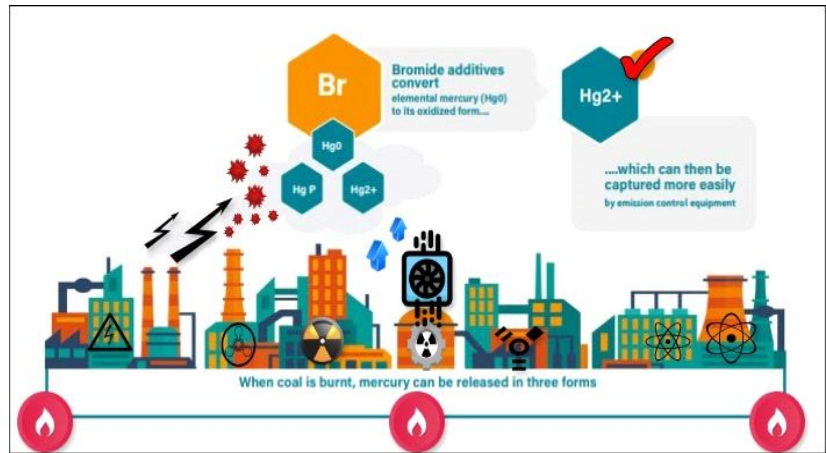

Fig. 3 : Use of bromine to decrease mercury emission from industries.

Use of bromine to reduce Mercury emission into the atmosphere

Bromine-based technologies have been demonstrated to effectively decrease mercury emissions, particularly in coal-fired power plants and industrial settings, achieving reductions of over 90%. Mercury emissions from burning coal typically occur in three forms: oxidized (Hg^{2+}), particulate (Hg P) and elemental (Hg^0). Elemental mercury poses a challenge for capture as it is gaseous at combustion temperatures. Therefore, it must first be converted to its oxidized form, which can then be more easily captured by emission control systems. Factors influencing the oxidation of elemental mercury include the presence of halides (*e.g.*, fluoride, chloride, bromide), flue-gas temperature, catalysts and constituents. Increased halide content, particularly bromide, enhances mercury capture efficiency. Additionally, the use of bromide additives surpasses chloride in oxidizing elemental mercury.

Furthermore, these technologies offer secondary benefits such as reduced fuel ash and sulfur content. The oxidized mercury can be captured by standard emission control equipment, like bag filters and disposed of safely. One significant advantage is the potential for easy retrofitting to existing plants, provided they already have standard emission control measures in place.

Conclusion

In conclusion, mercury contamination poses significant risks to soil and crop ecosystems, with far-reaching implications for environmental and human health. The accumulation of mercury in soil can lead to toxic effects on crops, hindering growth and productivity. Furthermore, mercury can bioaccumulate in the food chain, potentially impacting human consumers. Efforts to mitigate mercury contamination must prioritize

comprehensive monitoring, effective remediation strategies, and sustainable agricultural practices. By implementing measures to reduce mercury emissions, promoting soil conservation, and enhancing crop resilience, we can safeguard soil and crop ecosystems from the detrimental effects of mercury contamination, ensuring a safer and more sustainable agricultural future for generations to come.

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