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Remediation of Toxic Metals by Forest Trees: Concepts and Strategies

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ABSTRACT

Toxic metals are ubiquitous in the environment, and increasing as a result of human activities through discharge of various toxic effluents from industries, thermal power plants and vehicles exhausts to different components of the environments. Among the various toxic elements present in the environments, the most common toxic elements are: Cd, Cu, Cr, Pb, Zn and Hg. Once the concentration of these toxic metals crosses certain threshold level, they start accumulating in the living organisms including humans in higher amounts through bio-magnification and cause various harmful effects. Among various methods used for the removal of toxic elements from the contaminated sites, phyto-remediation has been considered as the most effective, low-cost and environment friendly technology. However, most of the phyto-remediation studies have been conducted on the small plants particularly from the water bodies, which needs further processing of these short-lived plants to stop the absorbed toxic metals into their body to reach the soil and water ecosystems. On the other hand, trees are long-lived and thus, the accumulated toxic elements can be resided for a longer time. Trees are reported to remove toxic metals through Phyto-accumulation, Phyto-filtration, Phyto-extraction, Phyto-stabilization, Phyto-degradation, and Phyto-volatiozation in Phyto-accumulation, Phyto-filtration, Phyto-extraction, Phyto-stabilization, Phyto-degradation, and Phyto-volatiozation. This paper reviews the mechanism and removal efficiencies of toxic metals by forest trees. The mechanism of removal of toxic metals from different environmental components by trees involves; a) uptake of toxic metals by roots of the trees, b) translocation of these toxic metals from roots to aerial tissues, and c) sequestration of toxic metal tolerance capacity of trees. The removal of toxic metals from the soil through these mechanisms varies among tree species. Further, screening of various forest trees for their capacity to remove toxic metals from the contaminated sites (i.e., soil and water) will be useful in the selection of tree species for their plantation on various contaminated sites.

Keywords Toxic metals, Forest tree species, Phyto-remediation mechanism.

INTRODUCTION

Toxic metals are characterized by high atomic weight and high density which are generally present in traces (Kabata-Pendias and Pendias 2001). However, when

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the concentration of these metals increases in the environmental components, they are becoming highly dangerous for living organisms, particularly humans through bio-magnification (Chen *et al*. 2021) Toxic metals have been classified into two groups (viz., essential and non-essential) on the basis of their role in biological systems. Essential toxic metals (E-TM) are those which are directly involved in the vital biochemical and physiological functioning of an organism, e.g., Cu, Mn, Ni, Fe and Zn (Ali *et al*. 2013). Essential toxic metals are important components of various enzymes and play a vital role in oxidation-reduction reactions (WHO 1996). In contrast, non-essential toxic metals (NE-TM) are those which aren't directly involved in the biochemical, physiological or enzymatic functions, but they play an important role in biological systems. Non-essential Toxic metals (NE-TM) include Pb, As, Cd, Cr and Hg (Suzuki *et al*. 2001, Cobbett 2003, Peng *et al*. 2009, Dabonne *et al*. 2010 and Lasota *et al*. 2020).

When the concentration of heavy metals goes beyond their threshold limits in the environment, they become toxic to the biological systems (Tchounwou *et al*. 2012). The toxicity induced by toxic metals occurs through different mechanisms and still many of them are not clearly understood. The level of heavy metal toxicity depends on many factors like dose, exposure route and chemical species, and on the age, gender, genetics and species of the exposed individual. The current economic development taking place across the globe has increased the concentration of toxic metals in different components (Igwe and Abia 2006, Semeraro *et al*. 2020). The contamination of environment by heavy metal is becoming a severe problem across the globe (Roozbaha *et al*. 2014). About 90% of people on earth breathe air that is more polluted than allowed, according to the World Health Organization, making it the fifth biggest risk factor for mortality globally (Locosselli *et al*. 2020). The rapid industrialization, urbanization and poor management of industrial effluent are increasing the threat of heavy metal accumulation in different ecosystems (Danek *et al*. 2015, Cocozza *et al*. 2021). Toxic metals have negative impact on human, animal and plant health, soil microorganisms and even a minute amount of some toxic metals can act as carcinogenic agents (Thakur *et al*. 2016, Asati *et al*. 2016 and Altaf *et al*. 2021). Toxic metals first accumulate in the tissues of a living organism (bio-accumulation), then the concentration of these toxic metals increases when they pass through trophic levels (bio-magnifications).

Excessive concentration of toxic metals (viz., Cr, Cd, As, Ni, Se and Pb) has been found in the soil of agriculture fields, cities and industrial areas (Rajindran *et al*. 2015). Toxic metals and other trace elements have the potential to accumulate in the soil. The soil adsorption characteristics of toxic metals are influenced by factors such as soil texture, organic matter, mineralogy, pH, water content and temperature as well as the particular characteristics which can affect the capacity of the soil to absorb each metal ion (Lasota *et al*. 2020). The relationship between plants and soil should be taken into consideration and focus should be given on a greater number of studies related to behavior of toxic metals in soil and plants (Xu *et al*. 2017). Dendrogeochemistry is based on in-depth and detailed analysis of the chemicals found in trees especially in growth rings, and is widely used to assess the environment impacts associated with contamination events on a local or regional scale while establishing the chronological references related to these events (Hagemeyer *et al*. 1992, Gustin *et al*. 2015, Cocozza *et al*. 2021, Semeraro *et al*. 2020, Balouet and Oudijk 2006).

Dendrochemistry is the chemical makeup of tree rings corresponding to the yearly variations in ambient chemical quality of the site at the time of ring formation. The toxic metals tended to translocate within of the tree components through moving between the phloem and the xylem. The process of movement and accumulation of metals is affected by environmental and tree physiological factors. Thus, the knowledge of elements present in tree rings tell us about the condition of the forest health, soil chemistry, pollution, climate, and environmental occurrences during the course of time (Chen *et al*. 2021, Ballikaya *et al.* 2022). Studies have shown that tree growth rings can serve as an indication of environmental contamination events affecting soil and water bodies (Chen *et al*. 2021). These events can be detected through the analysis of tree ring growth (i.e., dendrochronology) and through the chemical composition of the rings directly in the wood cells (i.e., dendrochemistry)

(Burken *et al*. 2011, Cocozza *et al*. 2021). Likewise, the forest tree species have the ability to accumulate and sequester toxic metals in different tissues. Still, there is a gap in knowledge and information regarding the role of forest tree species in the accumulation of toxic metals from the environment. In this context, the present review has been structured to find out the current state of knowledge on the role of forest tree species in the removal of toxic metals from the contaminated environment.

Source of toxic metals in the environment

The environmental contamination by toxic metals occurs from natural or anthropogenic sources. Because of the weathering of parent materials during pedogenetic processes, toxic metals naturally occur in the soil at amounts that are classed as trace (1000 mg kg^{-1}) which is rarely hazardous (Wuana and Okieimen 2011). The natural factors which cause the release of toxic metals into the environment are weathering of minerals, volcanic activity, and soil erosion. Whereas, the major sources of anthropogenic activities releasing toxic metals into the environment are industries, mining, metallurgic operations, pesticides (Modaish *et al*. 2004, Chehregani and Malayeri 2007, Wuana and Okieimen 2011). Most of the toxic metals are released by industrial activities and fossil fuel burning (Table 1).

Table 1. The sources of toxic metals in the environment.

Sl. No.	Heavy metal	Source	Reference
1	Copper (Cu)	Decaying vegetation, forest fires, sea spray, mining, metallurgic pesticides, leather processing and automotive brake pads	Shotyk 2020
2	Iron (Fe)	paints and ceramic products, caulking, and pipe solder	Fazekasova and Fazekas 2020
3	Manganese (Mn)	Sewage sludge, mining, mineral processing, alloy, metallurgic operations, burning of fossil fuels, municipal wastewater discharge	Matveeva *et al*. 2022
4	Nickel (Ni)	alloys, pigments, and batteries	Maja *et al*. 2018, Genchi *et al*. 2022
5	Zinc (Zn)	Mining and metallurgic operations	Wei *et al*. 2021
6	Lead (Pb)	Burning of fossil fuels, mining, manufacturing, paints, caulking, ceramic products and pipe solder	Yang *et al*. 2020
7	Cadmium (Cd)	Marine phosphate, Alloy Industries, Pigment Industries, Batteries	Kubier *et al*. 2019, Zhang *et al*. 2021
8	Chromium (Cr)	Metal processing, chromate production, tannery facilities, stainless steel welding, chrome and ferrochrome pigment production	Maja *et al*. 2018, Tumolo *et al*. 2020
9	Mercury (Hg)	Electrical industry, dentistry, production of caustic soda, nuclear reactors, antifungal agent, wood processing, preservative	Rodrigues *et al*. 2012, Sundseth *et al*. 2017
10	Arsenic (As)	Industries, insecticides, Fungicides, Herbicides, algicides Sheep dips, dye-stuff and wood preservatives	Raju 2022

Toxic metal absorption mechanism and its stress

A simple and effective method for eliminating toxic metals and the recovery of the contaminated sites to counteract the negative impacts of toxic metals is phytoremediation. Various plant species with a high capacity for absorbing toxic metals can be employed in phytoremediation (Altaf *et al*. 2021). The stress or the toxicity of these metals to the organisms can occur when the level of these element concentrations in the environment increases the tolerance limit of a biological organism. Consequently, this increased level critically affects the normal functioning of an organism. However, little amount of these metals is essential for basic physiological and biochemical metabolisms of the organisms. The molecular mechanisms of metal toxicity are based on chemical activity and biological features.

The detailed mechanism and effects of metal toxicity on animals and plants are shown in Fig. 1. The mechanistic steps of toxic elements on the organisms are as:

The toxic metal binds with the various protein groups and inactivates different enzymes.
The toxic metal stress alters hormonal synthesis, transport, action and degradation.
The toxic metal stress can cause ROS (Reactive ox-

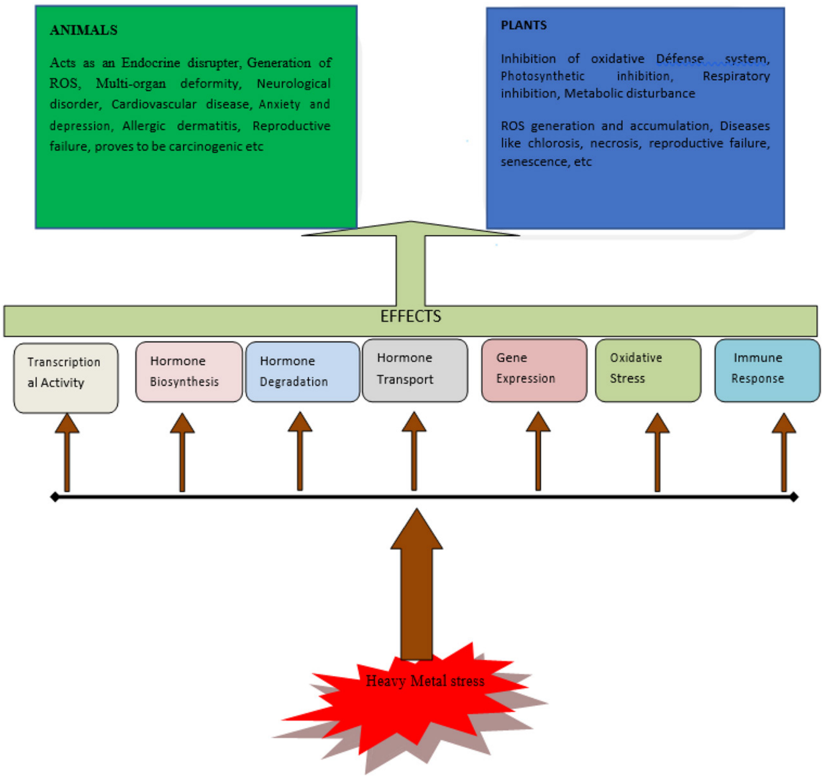

Fig. 1. Action mechanism and effects of heavy metal stress in animals and plants.

ygen species) generation and accumulation, which develops oxidative stress.

The heavy metal stress modulates DNA synthesis, DNA repair, gene regulation, expression, mutations, and apoptotic mechanism.

The heavy metal stress alters all physiological and biochemical metabolisms.

Some toxic metals block or mimic the actions of other metals and thus alter the functioning of the biological system.

Heavy metal stress can affect the signaling pathway of a biological system.

Removal of toxic metals from the environment by plants

One of the biggest issues facing our civilization today is the need to clean up the contaminated soil and water in order to maintain ecosystem processes and functioning. There have been numerous physical, chemical and biological methods used to clean up environmental pollution, but their use has been constrained by labor and resource costs, safety issues, and ecosystem problems (Ali *et al*. 2013). Phytoremediation is an effective method which is becoming popular, accepted and used. Using green plants to retain, sequester, or detoxify toxins from contaminated soil and water through phytoremediation is both economically and environmentally advantageous (Ashraf *et al*. 2019).

Phytoremediation employs a variety of mechanisms, including degradation (e.g., phyto-degradation, rhizo-degradation), accumulation (i.e., phyto-extraction, rhizo-filtration), dissipation (i.e., phyto-volatilization), and immobilization (i.e., hydraulic control and phyto-stabilization). Plants use one or more of these processes to lower the amounts of pollutants in soil and water, depending on the contaminants.

Toxic metals (TM) are absorbed by the plants and stored in their tissues and lowering the toxicity of the resources from the soil and water by storing them in organic form (Saleem *et al*. 2020). Depending on the kinds, forms and medium of the contaminants, different plants use various techniques or combinations of them to remediate soil and water. Phyto-degradation, phyto-volatilization, rhizo-filtration and rhizo-degradation are used for cleaning up contaminated groundwater, whereas, rhizo-degradation, phyto-degradation or rhizo-defiltration are used to clean surface and wastewater contamination.

Contaminations caused by soil, sediment, or sludge are cleaned up using phytoextraction, phyto-degradation, phyto-stabilization, rhizo-degradation, or phyto-volatilization. The best plant species for phytoremediation should have characteristics such as hardiness, high biomass production, tolerance to the harmful effects of metals and pollutants, ease of cultivation, high absorption capacity, and herbivore repellent (Kafle *et al*. 2022). Plant species frequently struggle to perform well and require assistance to improve phytoremediation. Some of these tools are soil amendments like biochar (Paz-Ferreiro *et al*. 2014), ethylene diamine tetra acetic acid (EDTA) (Shahid *et al*. 2014), endophytic bacteria (Afzal *et al*. 2014), arbuscular mycorrhiza (Gaur and Adholeya 2004), or even transgenic plants. The contaminant, the plant type and the soil all affect how effective remediation is. The effectiveness of remediation is significantly influenced by plant biomass and metabolism, as well as soil pH, electric conductivity, organic matter content, microbial activities and other soil additives (Kafle *et al*. 2022). The increase in environmental contamination by Toxic metals such as Cr, Cd, As, Ni, Se and Pb and their negative effects on human, animals and plants is a worst global problem (Rajindiran *et al*. 2015). Year to year there is an increase in the concentration of Toxic metals in the environment (Govindasamy *et al*. 2011). Heavy metal accumulation in soil and water have been reported across the globe (Xia 2004, Shanker *et al*. 2005, Rajindiran *et al*. 2015, Masindi and Muedi 2018, Briffa *et al*. 2020, Alengebawy *et al*. 2021). In India heavy metal accumulation in soils and water have been reported from different areas due to anthropogenic activity (Sachan *et al*. 2007, Deka and Bhattacharyya 2009, Rajindiran *et al*. 2015, CWC 2019). The destroyed lands by heavy metal accumulation remain devoid of vegetation, in addition to the destroyed water quality falls out of proper standards limits. Therefore, before the area under heavy metal contamination would increase more and more, cleanup up of these sites is utmost necessity to reduce the adverse effects (Gerhardt *et al*. 2017, Hasan *et al*. 2019).

The removal of heavy metals from the contaminated environment is a challenging activity in reference to cost and technical complexity (Barcelo and Poschenrieder 2003). Till today a number of approaches like incineration, landfill, excavation, soil washing, vitrification, soil flushing, soil stabilization and soil solidifications have been employed for this purpose (Sheoran *et al*. 2011, Wuana and Okieumen 2011, DalCorso *et al*. 2019). But, all of these approaches suffer a lot of limitations viz., high cost, labor intensive, large skill, change in soil micro-environment, creation of secondary pollution. Further the concept of phytoremediation came into existence, which basically refers to the “use of plants and associated microbes to reduce the concentration or toxic effects of contaminants in the environment” (Greipsson 2011). This novel approach has proved to be cost-effective, efficient, and eco-friendly method for removing the contaminants from environment. With respect to other contamination, a phytoremediation is also a good option for removal of a toxic metal accumulation from the environment. This method have been successfully adapted for clean up of many sites from toxic metal pollution (Lone *et al*. 2008, Yan *et al*. 2020, Wei *et al*. 2021). Since, a number of plant species have been used to remove Toxic metals from environment (Lone *et al*. 2008, Devi and Kumar 2020, Yan *et al*. 2020, Hrotko *et al*. 2021, Samara *et al*. 2021, Bortoloti and Baron 2022). Across all these species, forest trees have played a remarkable role in removing the Toxic metals from the contaminated environment (Ukpebor *et al*. 2010, Karmakar and Padhy 2019, Gunthardt-Goerg *et al*. 2022). There are two methods commonly used to assess the phytoremediation potential of plants (Wu *et al*. 2011) for example, Bioconcentration Factor (BCF)

- the ratio of concentration of pollutants in plant parts and in the contaminated sites and Translocation Factor (TF) - the ratio of elemental accumulation in a plant shoot compared to the plant roots.

Retention of toxic metals by forest trees

Forest species have been playing a vital role in phytoremediation as an elite green solution against the problem of toxic metal contamination. Forest trees have multiple features that make them ideal in removing the toxic metals from the environment (Merkle 2006). The following characters of forest tree species have made them promising solution of bio-remediation of toxic metals from the environment:

Massive root and shoot system make them ideal to intercept, absorb, degrade and/or detoxify the heavy metal contamination.

Long life cycle of forest trees can accumulate the toxic metals for a long time.
High growth rate of forest trees helps them in rapid biomass production.
High rates of water uptake and evapo-transpiration helps them to rapidly remove the metal ions from the soil.
Occurrence of forest trees in a wide range of habitats.
The phenomenon of secondary growth has reported the sequestration of Toxic metals in the tree growth rings which is absent in monocots.
Good adaptation to the prevailing environment and climatic conditions.
Resistance against disease and pests.
Some fast-growing trees like Salix, Poplar and Eucalyptus proved a successful solution in soil stabilization towards heavy metal contamination.
Many forest trees have properties of hyper-accumulators, thus can prove to be excellent candidate for phyto-remediation.
High tolerance level of forest trees to the toxic effects of target Toxic metals.
High rate of translocation of Toxic metals from branched network of roots to massive shoot system.
Indirectly forest trees improve the microclimate which in turn decreases the rate of chemical reactions, thus it decreases the toxicity of Toxic metals.
Forest tree provides surface for air borne Toxic metals to be accumulated on the surface of trees rather than soil and water.
The large and dense crown of forest trees stops movement and diffusion of air borne Toxic metals.

Forest tree species by their ideal metabolisms capture the toxic metals from roots and stomata, and fix them in different tissues. The techniques and strategies adopted by trees for phytoremediation of heavy metal contaminates are described (Table 2). Almost all parts like root, stem, leaves, fruits, bark and branches are involved in the sequestration of toxic metals from the contaminated environment.

Researchers have reconstructed the history of contamination events by analyzing the chemical composition of the tree rings (dendro-chemistry) and integrating it with soil and water chemistry and atmospheric parameters (Cutter and Guyette 1993, Yanosky and Vroblesky 1992, Vaitkute and Baltrenas 2011, Hietz *et al*. 2014, Jankovski *et al*. 2012, Liu *et al*. 2018). This ability of trees have made them a focus of research which dealing with the problems of heavy metal contamination. The ability of different forest tree species for the retention of heavy metals in different tissues are provided (Table 3).

Table 2. Techniques of bio-remediation towards heavy metal contamination by forest trees.

Sl.No.	Technique	Description of strategy
1	Phyto-extraction	Accumulation of Toxic metals in biomass
2	Phyto-degradation	Breakdown or transformation of metals by enzymes within enzymes.
3	Phyto-filtration	Sequestration of Toxic metals from water by trees
4	Phyto-volatilization	Converts metals into volatile form and are released into atmosphere through leaf surfaces of trees
5	Phyto-stabilization	Limits mobility and availability of Toxic metals in soil by tree roots
6	Rhizo(sphere)-degradation	Degradation of Toxic metals by tree rhizospheric micro-organisms
7	Phyto-desalination	Removal of excess Toxic metals from soil by halophytic trees

Table 3. Retention of Toxic metals by different forest tree species.

Sl.No.	Forest tree species	Heavy metal retained	Reference
1	*Pinus nigra*	Cd, Co, Cr, Cu, Fe, Mn, Ni and Zinc	Samara *et al.* 2021
2	*Cupressus arizonica*	Cd, Co, Cr, Cu, Fe, Mn, Ni and Zinc	Samara *et al.* 2021
3	*Robinia pseudoacacia*	Cd, Co, Cr, Cu, Fe, Mn, Ni and Zinc	Samara *et al.* 2021
4	*Populus nigra*	Cd, Co, Cr, Cu, Fe, Mn, Ni and Zinc	Samara *et al.* 2021
5	*Acacia retinoides*	Cu and Pb	Pyatt 2001
6	*Eucalyptus torquatain*	Cu and Pb	Pyatt 2001
7	*Quercus ilex*	Cu, Pb, Zn and Cd	Alfani *et al.* 1996, Avila *et al.* 2003 Maisto *et al.* 2004
8	*Hypnum cupressiforme*	Cd, Cu, Zn and Pb	Sardans and Penuelas 2005
9	*Pinus halepensis*	Cd, Cu, Zn and Pb	Sardans and Penuelas 2005
10	*Quercus ilex*	Al, Fe, Cu, Zn and P	Gratani *et al.* 2008
11	*E. camaldulensis*	Cd, Cu and Pb	Yasin *et al.* 2021
12	*M. alba*	Cd, Cu, Zn and Pb	Nikolova 2015, Alahabadi *et al.* 2017 Jiang *et al.* 2019, Yasin *et al.* 2021 Zeng *et al.* 2020
13	*Pinus eldarica*	Zn, Cd, Cu, and Pb	Alahabadi *et al.* 2017
14	*Wistaria sinensis*	Zn, Cd, Cu, and Pb	Alahabadi *et al.* 2017
15	*Morus alba*	Zn, Cd, Cu, and Pb	
16	*Nigral morus*	Zn, Cd, Cu, and Pb	Alahabadi *et al.* 2017
17	*Quercus ilex*	Cr,Cd, Cu, Fe, Pb, V and Zn	De Nicola *et al.* 2008, Drava *et al.* 2017
18	*Ficus nitida*	Pb,Cu,Cd	El-Khatib *et al.* 2020
19	*Tectona grandis*	Mn, Cu, Pb, Cr and Cd	Ipeaiyeda and Dawodu 2014
20	*Terminalia catappa*	Mn, Cu, Pb, Cr and Cd	Ipeaiyeda and Dawodu 2014
21	*Anacardium occidentale*	Mn, Cu, Pb, Cr and Cd	Ipeaiyeda and Dawodu 2014
22	*Gmelina arborea*	Mn, Cu, Pb, Cr and Cd	Ipeaiyeda and Dawodu 2014
23	*Eucalyptus spp.*	Arsenic	King *et al.* 2008
24	*Eucalyptus camaldulensis*	As, Pb and Cd	Madejon *et al.* 2017, Fine *et al.* 2013
25	*Pinus spp.*	Cd, Pb,As and Hg	Matin *et al.* 2016
26	*Dalbergia sissoo*	Pb	Naveed *et al.* 2010
27	*Prosopis juliflora*	Pb	Naveed *et al.* 2010
28	*Aesculus hippocastanum*	Cd, Cr, Cu, Pb, V and U	Petrova *et al.* 2012
29	*Tilia spp.*	Mn, Cu, Pb, Cr and Cd	Anicic *et al.* 2011
30	*Populus alba*	Cd,Cr and Ni	Rafati *et al.* 2011
31	*Ficus microcarpa*	Cd, Cu, Fe, Pb, Mg and Zn	Rossini *et al.* 2004
32	*Acacia mangium*	Pb	Meeinkuirt *et al.* 2012
33	*Platanus orientalis L.*	Mn, Mg, Cu, Pb, Cr, Zn,Fe, Ni and Cd	Sawidis *et al.* 2011, Norouzi *et al.* 2016
34	*Salix spp.*	Cd, Co, Mn, Cu, Fe, Pb, Mg and Zn	Pulford and Watson 2003, Robinson *et al.* 2000, Meers *et al.* 2007, Mleczek *et al.* 2009, Wahsha *et al.* 2012
35	*Olea europaea*	As,Cu,Cd,Pb,Sb and Zn	Domínguez *et al.* 2008
36	*Acacia holosericea*	Cu	Reichman *et al.* 2004
37	*Melaleuca leucadendra*	Cu	Reichman *et al.* 2004
38	*Eucalyptus grandis*	Mn	Xie *et al.* 2015
39	*E. urophylla*	Mn	Xie *et al.* 2015
40	*Betula sp.*	Al, Cd, Cr, Ni and Pb	Piczak *et al.* 2003
41	*Acer sp.*	Al, Cd, Cr, Ni and Pb	Piczak *et al.* 2003
42	*Tilia tomentosa*	Pb, Fe, Ni, Zn and Cu	Hrotko *et al.* 2021
43	*Fraxinus excelsior*	Pb, Fe, Ni, Zn and Cu	Hrotko *et al.* 2021
44	*Cassia siamea*	Cd, Pb and Fe	Gajbhiye *et al.* 2016
45	*Aesculus sp.*	Cd, Pb, Ni and Zn	Baycu *et al.* 2006
46	*Lagerstroemia floribunda*	Pb	Meeinkuirt *et al.* 2012
47	*Robinia sp.*	Cd, Pb, Ni and Zn	Baycu *et al.* 2006
48	*Pinus halepensis*	Cd, Pb, Ni and Zn	Al-Alawi *et al.* 2007
49	*Salix subfragilis*	Cd, Pb, Mn, Cu and Zn	Kim and Kim 2018
50	*Salix cinerea*	Cd, Mn and Zn	Vandecasteele *et al.* 2005
51	*Shorea robusta*	Pb, Cd, Cu, Cr, Fe, Ni, Zn and Mn	Karmakar *et al.* 2019

Table 3. continued.

Sl. No.	Forest tree species	Heavy metal retained	Reference
52	*Acacia nilotica*	Mn, Cr, Pb, Fe, Cd, Co, Zn, Ni and Hg	Kulhari *et al.* 2013
53	*Terminalia bellirica*	Mn, Cr, Pb, Fe, Cd, Co, Zn, Ni and Hg	Kulhari *et al.* 2013
54	*Pterocarpus macrocarpus*	Pb	Meeinkuirt *et al.* 2012
55	*Terminalia chebula*	Mn, Cr, Pb, Fe, Cd, Co, Zn, Ni and Hg	Kulhari *et al.* 2013
56	*Ficus religiosa*	Mn, Cr, Pb, Fe, Cd, Co, Zn, Ni and Hg	Kulhari *et al.* 2013
57	*Delonix regia*	Cd, Pb, Zn and Cu	Ukpebor *et al.* 2010
58	*Casuarina equisetifolia*	Cd, Pb, Zn and Cu	Ukpebor *et al.* 2010
59	*Acacia auriculiformis*	Pb, Cd, Cu, Cr, Fe, Ni, Zn and Mn	Karmakar and Padhy 2019
60	*Azadirachta indica*	Pb, Cd, Cu, Cr, Fe, Ni, Zn and Mn	Karmakar and Padhy 2019
61	*Leucaena leucocephala*	Pb	Meeinkuirt *et al.* 2012
62	*Nerium oleander*	Cd, Cu, Fe, Pb, Mg and Zn	Rossini *et al.* 2004

Mechanism of heavy metal accumulation by forest trees

Forest trees have been proved to be efficient in removing the toxic metals from contaminated environment. Trees can absorb the heavy metal ions from the soil through their massive root system. Then these toxic metals are translocated, and fixed in different tissues of trees. The whole mechanism of heavy metal mobilization, uptake by massive root system, xylem loading, translocation, cellular compartmentation, and sequestration of heavy metals in forest trees is described as under (Fig. 2).

The toxic metals present in soil occur as insoluble form that isn't available to plants. They become available to plants by releasing a number of root exudates, which change the rhizophere pH, increase microbial activity, retains water, and thus, increases toxic metal solubility (Dalvi and Bhakerao 2013). Since trees are large terrestrial plants with a massive network of root system, they develop massive rhizosphere which releases large root exudates and can make more heavy metal solubility and availability. The available toxic metals move to roots through mass (bulk) flow and diffusion. Plant roots come in direct contact with the heavy metal associated with the soil particles and start to absorb them. Here, the rate of heavy metal absorption through root interception depends on the root surface area (or rhizosphere area), concentration

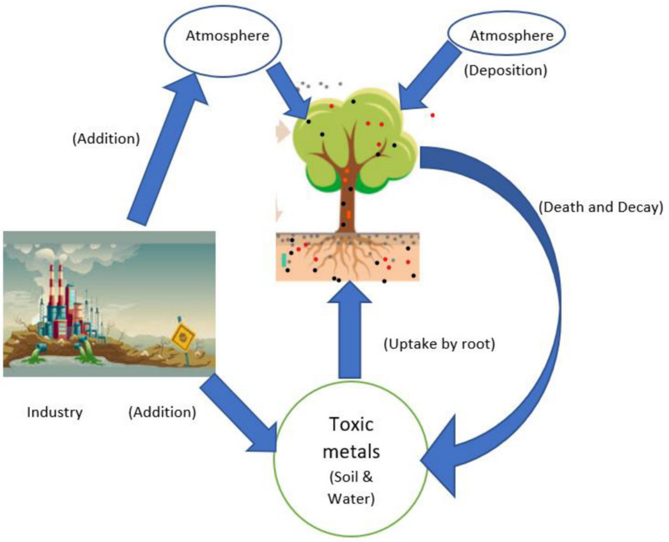

Fig. 2. Toxic metal removing from soil and water, atmosphere.

of heavy metals and root morphology. In this context, forest tree species bear a massive root surface area, thus it results in more interception and absorption than other plants. The toxic metals now move across the cellular membrane into the root cells. Basically, root cell wall has the ability to bind the heavy metal ions through high-affinity binding sites and a localized transport system of the plasma membrane.

The uptake of toxic metals occurs through two different pathways; i.e., a) apoplastic pathway also known as passive diffusion (occurs towards the electrochemical potential gradients) and b) symplastic pathway also know as active transport (occurs against the electrochemical potential gradients). Since, all plants absorb the minerals including metal according to the diffusion pressure gradient of cell and soil solution (passive diffusion). But in case we have to deal with the heavy metal stress, which means that the absorption of these metals can't be regulated by the passive diffusion, as the absorption have to take place against diffusion pressure gradient. Under such conditions the uptake of toxic metals is commonly regulated by the symplastic pathway (Peer *et al*. 2005), thereby reclaiming the heavy metal contaminated soil and stabilize the soil fertility (Jacob *et al*. 2018, Dal-Corso *et al*. 2019). Once the heavy metal ions reach into the root cells, they form complexes with various chelators; these complexes are then immobilized into extracellular space (Apoplastic cellular walls) or intracellular spaces (symplastic compartments, like vacuoles) (Ali *et al*. 2013). After heavy metals are entered into the plant roots, they accumulated within the vacuoles then transported into the stele and reaches into the xylem stream through root symplasm, and then translocated to shoot through vascular bundles (Prasad 2004, Jabeen *et al*. 2009, Thakur *et al*. 2016). Further, through apoplast or symplast pathway these heavy metal ions are transported and distributed in the leaves, where these ions are sequestered in cell wall or plant vacuole, thus accumulation of free metal ions in cytoplasm is prevented (Tong *et al*. 2004, Denton *et al*. 2007, Sheoran *et al*. 2011). In this way, the heavy metal ions are removed from cell cytosol and thus reduce the interaction of heavy metal ions with the metabolic activities of cell (Assuncao *et al*. 2003).

The accumulation of toxic metals ions in different parts of forest tree species have been reported by different authors (Ukpebor *et al*. 2010, Meeinkuirt *et al*. 2012, Samara *et al*. 2021, El- Khatib *et al*. 2020). Laurent *et al*. (2009) reported the presence of lead and other toxic metals (As, Cd, Cu, Ni and Zn) in the xylem of the trees and identified the contamination events on time-scale. Hristovski and Melovski (2010) reported that pith contains higher trace elements than middle and outermost rings of the European beech (*Fagus sylvatica* L). The presence of heavy metal contaminants detected in tree-rings reflected industrial activities over time and varied with distance of tree with industrial plant (Perone *et al*. 2018). The movement of the toxic metals from the soil solution to different parts of the forest tree species is regulated by various molecules. These molecules are involved in cross membrane transport, complexation and sequestration of toxic metals. Further, the uptake of toxic metals in plants is mediated by some specialized transporters (channel protein) or H+ coupled carrier proteins, which are present in the plasma membrane of roots (Griepsson 2011).

CONCLUSION

The economic development as result of industrialization, urbanization and agriculture development across the globe has resulted into the release of toxic metal contaminations in the environment. Toxic metal contaminations have negative impact on living organisms (i.e. human, animal and plant health, soil microorganisms) and sometimes even a minute level of some toxic metals can act as carcinogen. Various methods have been used to clean up the ecosystem from heavy metal toxicity, however, the phytoremediation has been regarded as most effective, low-cost technology and eco-friendly. Forest tree species in specific have been regarded as a major player in the phytoremediation of heavy metals where the studies are limited.

The long-life cycle, large biomass, massive root and shoot system, large biomagnifications property have made trees most efficient agent for cleaning the environment from toxic metal contaminants. Forest tree species by their ideal metabolisms capture the toxic metals from roots and stomata and fix them in different tissues. Almost all parts like root, stem, leaves, fruits, bark and branches are involved in the sequestration of toxic metals from the contaminated environment. Forest trees take up heavy metal which often travel as part of soluble organic compounds (ligands) and usually become fixed as parts of cell wall. Reports suggest that trees have been involved in retaining the toxic metals efficiently than other plants. Research is in progress to screen native forest tree species for bioremediation of target toxic metals from the contaminated environment. However, further research is required to develop and identify more and more hyper-accumulator forest tree species. The elite approach of genetic engineering in the present context has emerged as a powerful tool in terms of developing fast growing species, high biomass production, high heavy metal accumulation and tolerance. In addition, there is a requirement of basic research to identify proteins and/or genes involved in cross-membrane transport, vacuolar accumulation of toxic metals and signaling pathway for developing ideal tree species for phytoremediation. The advancement and achievements in the molecular studies of heavy metal sequestration by forest tree species will help in understanding the basic mechanism of phytoremediation.

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