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Potential toxic elements phytoremediation: Review.

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ABSTRACT

However some heavy metals including zinc, copper, lead, nickel, cadmium, cobalt, and chromium at lower concentration play a significant role in growth and productivity of most plants; its considerer the main contaminants to the environment. Therefore, it takes a more concern to clean up the environment from these pollutants. Phytoremedation using the hyper-accumulator plants with or without some amendments can overcome this problem. The current study is (1) a meta analyses of the literature on the adverse effect of some heavy metals on plants and human health, (2) it comprises the databases of hyper-accumulator plants and heavy metals removed by plant species, and (3) and the factors that affect the level of phytoremedation processes.

Keywords: Arsenic, Cadmium, Chromium, Cupper, Mercury, Hyper-accumulators, Transgenic Plants, Lead, Nickel, Selenium, Zinc

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INTRODUCTION

No doubt, phytoremediation is a talented attractive biotechnology for cleaning contaminated soils irrigated with sewage effluent due to its cheap cost and flexibility [1]. Plant species had been used for *Potential toxic elements* (PTEs) accumulation and most of the studies had been done on hyperaccumulator tolerant species [1], [2], [3]. PTEs hyperaccumulator plants though useful to phyto-extract PTEs contaminant from soil, had many shortcomings such as low biomass, edible nature and difficult to harvest. Hyper accumulators naturally use metal accumulation as a defense against herbivores and pathogens, and therefore deal with accumulated metals in very specific ways of complexation and compartmentation, different from non-hyperaccumulator plants and also non-hyper accumulated metals [3]. More than 400 plant species have been identified to have potential for soil and water remediation [4].

Phyto-extraction of PTEs is frequently limited by contaminant bioavailability and plant uptake rates. Inorganic amendments could be added to increase the uptake and translocation of PTEs to aerial biomass [2]. Many factors affect phytoremediation such as PTEs content, pH value and nutrient status in the surface soil layer. Care should be exercised in selecting the plants to be used phytoremediation and only restricted on those that do not accumulate high concentrations of PTEs to edible portions of harvests. Phytoremediators should possess high capacity to mount up the targeted PTEs, could tolerate high accumulated PTEs concentrations and characterized with a speedy PTEs buildup biomass as well as with ease growing and harvesting [1], [6]. In the enormous published papers, it was established that PTEs hyper-accumulators plants are able to uptake more or less 100-fold more of PTEs compared to other plants [7]. More than 400 species of terrestrial plants are recognized as hyper-accumulators for different PTEs and capable of enduring and gathering high amounts of PTEs in their shoots [8]. The hyper-accumulators plants compared to other plants are characterized by superior rates of PTEs cleaning. Some plants concentrate PTEs of up to quite a few percentages of their dried shoot biomass [9].

Arsenic (As)

Transgenics with the ability to convert the inorganic forms of arsenic to these or similar compounds could be viable phyto-rmediators. They were able to greatly increase the arsenic tolerance and accumulation of Arabidopsis with only two genes. Constitutive over expression of γ- glutamyl cysteine synthetase (γ-ECS) from the glutathione biosynthesis pathway coupled with the leaf specific expression of arsenate reductase (arsC) from *E. coli* increased the fresh weight of arsenate challenged plants by ~5-fold and the shoot accumulation ~3-fold. While these significant improvements were not enough to make Arabidopsis into a viable phyto-remediator, this showed promise for adding arsenic tolerance and extraction capabilities to other hyperaccumulator species [10]. It proposed that a detoxification pathway for arsenate (AsO_4^{-3}) is by conversion to arsenate (AsO_2) upon its uptake into root [11].

X-ray spectroscopy showed that, at most, 20% of the arsenic in the fronds was coordinated to S suggesting that most of the arsenic stored in the vacuole is aqueous, but uncomplexed with thiols [12]. They added that arsenic is thought to be sequestered in extra- or sub-cellular compartments in *Pteris vittata* to prevent interaction between arsenic and cellular components. X-ray spectroscopy detected the majority of arsenic intracellularlly in the frond epidermal cells, probably in the vacuole.

Arsenite-PC complexes are not the dominant form of arsenite in *P. vittata* as neither PC nor total S are present in sufficient quantities in *P. vittata* for the expected arsenic: thiol ratio which was found in populations of arsenic tolerant non-accumulators [13], [14]. **A**rsenite-PC complexes in *Holcus lanatus* were most likely vacuolar [15].

Stated that However non-accumulators plants had a phytotoxic threshold at approximately 5-100 mg kg^{-1} arsenic dry weight, *H. lanatus* could accumulate up to 560 mg kg^{-1}arsenic and *P. vittata* could accumulate up to 27,000 mg kg^{-1} arsenic dry weight, with phytotoxic symptoms appearing around 10,000 mg kg^{-1} [16]. Therefore, various studies recommended using *P. vittata* for phytoremediation of soil and water. Field experiments had indicated that *P. vittata* could remediate contaminated soil sites in 10 years or less. The ideal phytoremediator would accumulate arsenic at levels similar to *P. vittata*, but store it in a less toxic form [17].

Arsenate could be reduced to arsenite enzymatically by arsenate reductase as shown *in vitro* and non-enzymatically by *Glutathione synthetase* (GSH) or ascorbic acid as shown in yeast followed by the formation of an arsenite-thiol (AsO_2--SH) complex. Phytochelatins (PCs) had also been proposed as arsenic chelators in *H. lanatus* [18]. After growing *P. vittata* in soils with a similar distribution pattern of arsenic in different fractions in a sequential extraction, with more than 60% of the total arsenic being associated with the fraction thought to represent amorphous and poorly-crystalline hydrous oxides of Fe and Al, it was found that the concentration of arsenic in the fronds ranged from 84 to 3600 mg kg^{-1}, with 0.93% of the total soil arsenic being taken up by *P. vittata* [19]. While in high contaminated soil (contained 5500 mg cupper kg^{-1} and 1242 mg zinc kg^{-1}), *P. vittata* suffered from phytotoxicity and accumulated little arsenic (0.002% of total). In a separate experiment, neither phosphate addition (50 mg P kg^{-1} soil) nor liming (4.6 g $CaCO_3$ kg^{-1} soil) was found to affect the arsenic concentration in the fronds of *P. vittata*, even though phosphate addition increased the arsenic concentration in the soil pore water. Between 4 and 7% of the total soil, arsenic was taken up by *P. vittata* in 4 cuttings in this experiment. The results indicate that *P. vittata* could hyper accumulate arsenic from naturally contaminated soils, but might be suitable for phytoremediation only in the moderately contaminated soils [19]. Nitrogen fertilizer levels had little effect on arsenic removal by *P. vittata* plant, whereas low level of P was more effective than high P and arsenic was reduced to <5 g L^{-1} in 28 d compared to 35 d. Reused ferns (*P. vittata*), with or without harvesting the arsenic-rich fronds, took up arsenic more rapidly so the arsenic concentration in the groundwater declined faster (130 to 10 g L^{-1} in 8 h). It was found that most arsenic (85-93%) located in the aboveground tissue (rhizomes and fronds)..Low-P treatment coupled with reuse of more established ferns with or without harvesting fronds could be used to effectively remove arsenic from contaminated water using *P. vittata* [20].

Cadmium (Cd)

Cadmium is a toxic PTE and probable carcinogen and presenting a significant health hazard. Ecotypes of *T. caerulescens accumulate a* wide range of cadmium levels. The Ganges and Vivez eco-types could accumulate up to 10,000 mg kg^{-1} cadmium dr^{y} weight (DW) and 12, 500 mg kg^{-1} cadmium DW′ respectively, without showing signs of toxicity; however, the Puy de Wolf and Prayon ecotypes could only accumulate 2,300 mg cadmium kg^{-1} DW and 4,800 mg kg^{-1} cadmium DW′ respectively [21], [22]. In addition, *Thlaspi aerulescens had constitu*tively high levels of antioxidant enzyme activity like catalase, 300-fold higher than *N. tabaccum* w*hich might* contribute to cadmium tolerance. While cadmium treatment did not induce phytochelatin (PC) synthesis in non-tolerant plants like *A .thaliana* m*ost PTEs to*lerant plants did not accumulate phytochelatin-PTEs complexes in response to PTEs toxicity [23]**.** Although *T. caerulescens and T. arvense* ha*d increase*d PCs following cadmium treatment, total PCs were lower in the hyperaccumulator *T. caerulescens, and PC leve*ls did not correlate with increased tolerance in this plant [24]**.** Several of the zinc iron sporting ZIP genes in plants had been shown to transport cadmium, although with a wide range of affinities [25]**.**

Upon cadmium exposure, *Nicotiana tabaccum* hairy roots had five times more reactive oxygen species (ROS) than *T. caerulescens* hairy roots [26]. They found that cadmium in the apoplast and vacuoles of *T. caerulescens*, and most cadmium in *T. caerulescens* hairy roots appears to be localized in the cell walls. Transgenic approaches to either make *T. caerulescens* grow larger or to make *B. juncea* accumulate more cadmium and zinc could make cadmium phytoextraction feasible. *Brassica juncea* plants genetically modified with bacterial genes to overproduce γ-glutamylcysteine synthetase (ECS) or glutathione synthetase (GS) were found to accumulate 1.5 times more cadmium and Zn compared to wild type *B. juncea* growing on PTEs-contaminated soil**.**

Transgenic Arabidopsis overexpressing (AtPCS1) resulting in 1.3 to 2.1-fold increase PCs, compared with wild-type plant; however, the transgenic lines were hypersensitive to cadmium stress as measured by root growth and this hypersensitivity could be alleviated by the addition of glutathione [27].

The regulation of glutathione levels and perhaps the entire S assimilation pathway is important for cadmium tolerance and accumulation [28].

Hyper accumulation of cadmium in *Arabidopsis hallerii* had been reported by [29]**.** Cadmium uptake is likely mediated through transporters or channels for other divalent ions. They demonstrated that cadmium/zinc transport capacity in leaf mesophyll protoplasts and affinity for PTEs were indistinguishable in *T. caerulescens Ganges*, *A. halleri*, and *T. caerulescens* Prayon ecotypes; however, cadmium accumulation

increased in Ganges protoplasts but decreased in *A. halleri* protoplasts in conjunction with Cd pre-exposure, hence, there might be multiple cadmium transport systems in the leaves. *T. caerulescens* accumulates in in the cell wall/apoplast of their leaves ~35% cadmium [30]. While [31] showed that cadmium accumulation in the shoots of *Solanum nigrum* was significantly higher than that of *S. melongena*. The accumulation of cadmium in the leaves of *S. nigrum* ranged from 2.0 to 167.8 g DW, but only from 1.2 to 64.0 g DW in *S. melongena* which was considerably less tolerant to cadmium than *S. nigrum*. Approximately 20% of the total cadmium in *S. nigrum* leaves was water-soluble, suggesting that some accumulated cadmium was associated with water-soluble compounds such as organic acids. Malic acid in the leaves of *S. nigrum* was the most abundant organic acid (up to 115.6–145.7 mol g^{-1}) fresh weight FW), but this acid was not significantly affected by the cadmium concentration in soil. However, the level of malic acid in *S. melongena* plants was much lower, only 16.3–75.4 mol g^{-1}. The significant positive correlations between total cadmium and water-soluble cadmium concentrations and both acetic and citric acid concentrations in the leaves of *S. nigrum* were observed. In contrast, there was no correlation between concentrations of the two acids and cadmium concentrations in the leaves of *S. melongena*. Their results indicated that acetic and citric acids in the leaves of *S. nigrum* might be related to its cadmium hyper accumulation.

Tobacco is a well-known efficient accumulator of cadmium and the genotypic differences in cadmium uptake and the response to cadmium was not determined [32]. They added that cadmium level affected the number of leaves and dry matter accumulation, and there were differences among the different tobacco cultivars tested. Furthermore, some cultivars showed a higher reduction in growth than others, indicating that they are more sensitive to cadmium level in the soil. Moreover, differences existed among the cultivars for the cadmium concentration and uptake. There also were negative correlations between cadmium and zinc concentrations; as cadmium accumulation increased, zinc accumulation decreased, which showed that the two PTEs were antagonistic. They suggest that tobacco cultivars differed greatly in their growth and developmental responses to cadmium and in the concentration and uptake of cadmium and zinc; hence it is possible to use certain tobacco cultivars to lower the cadmium concentration in the soil.

Always the highest translocation from roots to aerial corn and sunflower organs was found in the case of Cd and Pb (57and 83% of Cd, 56 and 76% of Pb) [33].

Chromium (Cr)

Five weed species that are harmless, non-edible in nature (*Lpomoea carnea*, *Dhatura innoxia, Phragmytes karka, Cassia tora* and *Lantana camara*), with two accumulator plants (*Brassica juncea* and *Brassica campestris*) were investigated and compared in a pot study to assess chromium uptake in the range of 5 to 200 mg/kg^{-1} soil [2]. Their results indicated that *P. karka* showed much greater tolerance to PTEs than other plants, though the uptake was low. It was more effective at translocating chromium from soil to plant shoot. The order of chromium extraction was *I. carnea* > *D. innoxia* > *C. tora* > *P. karka* > *B. juncea* > *L. camara* > *B. campestris*. Among the studied plants *I. carnea* showed maximum chromium extraction and biomass growth, but the difference of shoot by root chromium concentration was least. Other than *Lantana camara,* all the tested weeds were better for chromium extraction than the accumulator *Brassica* species.

Copper (Cu)

Copper is an essential element and enzyme co-factor for oxidases (cytochrome oxidase, superoxide dismutase) and tyrosinases, however, plants could accumulate toxic levels. At super optimal levels, copper is highly toxic to plants and copper ligands in plants are citrate, PC, PC, and PTElothioniens [34]. Correspondingly, most copper -tolerant plants are excluders, and no confirmed copper accumulators had been identified. It was originally thought that *Elsholtzia splendens* was a copper hyperaccumulator, but after further investigation, [35] concluded that it might be a tolerant excluder like *Elsholtzia argyi***.** Thirty seven taxa of copper hyper accumulators such as *Silene vulgaris* were detected [36]. In addition, soil amendments, like phosphate, increase copper uptake, and therefore, might further phytoremediation efforts [37]. *Arbuscular microrrhyzea* (AM) inoculation in the high contaminated soils irrigated with sewage effluent resulted in elevated depression in Cu content in roots and shoots of sunflower reaching 31.4% and 64.3%, respectively. Based on the distinctive decontamination rate of every studied PTE and Zn equivalent values, the cleaning potency of corn plant far exceeded that of sunflower plants for Cu and Ni [1].

Mercury (Hg)

Instead of using plants to phyto-extract mercury, several studies had focused on converting organ omercurials to HgO, which is volatile and is released into the atmosphere. The most toxic forms of mercury are organ omercurials like methyl-Hg and phenyl mercuric acetate, followed by ionic mercury (II), with elemental HgO as the least toxic form.

Organomercurials and ionic mercury are toxic to plants, and to date mercury hyper accumulating plants had not been identified [38**]**. However, the mercury hyper accumulating mushroom *Amanita muscaria* had been found that accumulates 96-1900 ng g^{-1} DW in the caps and 61-920 ng g^{-1} DW in the stalks depending on the soil. MerB severs the mercury-carbon bond and MerA reduces ionic mercury to elemental mercury. Transgenic poplar and cottonwood trees expressing merA and/or merB could be used as phytoremediators which do not require harvesting or replanting each season [39]. In an elegant demonstration of the importance of proper subcellular targeting, [40] created ER and cell wall targeted versions of MerB. This appears to have targeted the MerB activity to the secretary pathway, which is thought to be the main location of hydrophobic organomercurials within the cells. Even though the plants produced tenfold or less targeted MerB than the untargeted MerB. They were able to identify lines that converted equivalent amounts of elemental Hg0. Also, [41] were able to express merA and merB in chloroplasts which allows for high levels of protein production as well as other possible advantages. While, these approaches showed great promising from a scientific and technical perspective, there was a great deal of public resistance to a technology which volatilizes mercury, even if it is in a form that is 200 times less toxic than the form present in soil. The majority of the mercury among *Salix spp*. was accumulated and retained in the cell wall of the roots and only 0.45-0.65% was translocated to the shoots [42].

Nickel (Ni)

The majority of intracellular nickel is localized in the vacuole, and *T. goesingense* accumulates twice as much as *T. arvense* even though there was no observed difference in the vacuole sizes of the two species [43**]**. However, root exudation of histidine and citrate might help reduce nickel uptake for the non-accumulator *T. arvense***,** these exudates did not appear to be involved in the hyper accumulation of nickel by *T. goesingense*. overexpression of *T. goesingense* PTE-tolerance proteins (MTPs) members of the cation diffusion facilitator (CDF) family conferred resistance to nickel, cadmium, cobalt and zinc in yeast [44].

Alyssum lesbiacum and *Thlaspi goesingense* were both nickel hyper accumulating plants in the Brassicaceae family. In the genus *Alyssum* alone, 48 different species had been discovered containing between 1000 µg g^{-1} and 30000 µg g^{-1} nickel in leaf dry biomass [45]. Nevertheless, a comparison of the uptake mechanisms of *A. lesbiacum* and *B. juncea*, a non-accumulator, indicated that nickel is taken up independently as a free cation. Nicotianamine is thought to be involved in nickel detoxification in *T. caerulescens* [46].

Ninicotianamine-nickel complexes had been shown to be transported from the roots to the shoots and across plant membranes in a manner similar to nicotianamine-Fe complexes [47]. However, [48] stated that little is known about Ni uptake into roots. Evidence that histidine chelates nickel suggests that it might assist root uptake of Ni. *Alyssum lesbiacum* had constitutively high free Histidine levels, and when *Salmonella typhimurium* ATP phosphoribosyl transferee's enzyme (StHisG) was expressed in *A. thaliana*, the Histidine increased twofold and biomass increased 14-40-fold when grown on nickel.

Nicotianamine synthade (NAS) was constitutively expressed at high levels in both *T.caerulescens* and *A.halleri* which strongly suggests a role for nicotianamine in Ni/Zn hyperaccumulation [47]. Much of the intracellular nickel of *T.goesingense* associated with citrate.

Nickel had a higher affinity for both nitrogen and oxygen ligands than S ligands, and the observed absence of Ni-S ligands indicated a lack of PC binding [49]**.** Reduced cell wall binding in *T. arvense* might alternatively be explained by pH changes resulting from exposure to a toxic concentration of nickel.

Lead (Pb)

Lead elemental was insoluble and the most water soluble forms of lead compounds were lead acetate (2 mg ml^{-1}), lead chloride (0.009 mg ml^{-1}) and lead nitrate (5 mg ml^{-1}) [50]. Atmospheric lead mostly exists as PbSO and PbCO. *Brassica juncea* showed reduced growth at a 645 ug g^{-1} lead in the soil substrate but could accumulate 34.5 g kg^{-1} shoot dry weight although significant shoot accumulation was not observed until lead reached saturation levels in the roots. Most of the lead accumulation was found in stems and not leaves suggesting that lead is relatively insoluble [51]. The biggest challenge to effective phytoremediation of lead is its extremely low solubility, as only ~0.1% of soil Pb is available for extraction [52].

Lead phyto extraction by *Brassica juncea* and *Brassica nigra* had high PTEs-accumulating ability (Table 1) [53]**.** Other salient findings include cultivar 426308 of *Brassica juncea* was the most efficient shoot accumulator (3.5% lead on a dry weight basis), tight binding of lead to soils and plant material partially explains relatively low mobility in soils and plants, the rate of lead uptake to roots decreased and the rate of translocation to the shoots increased as a function of exposure time, and insoluble inorganic complexes in soil and the plant significantly reduces phyto extraction efficiency of *Brassica juncea*. Lead concentrations in plant shoots (DW basis) of several plants growing on contaminated sites were reported to range from 130 to 8,200 mg kg^{-1}.

The prospects for phytoremediation of lead depend on the development of novel systems for solublizing lead and for transporting it to the leaves. The expression of the glutahione-Cd vacuolar transporter YCF-1 in Arabidopsis had been found to increase the tolerance and slightly increases the accumulation of lead [36].

Table 1: Lead content of roots and shoots of crop *Brassica* and other plants [53].

Plant species	mg of Pb per g dry weight ± SE	
	Shoot	Root
Brassica juncea (L.) Czern.	10.3 ± 2.9	103.5 ± 12.3
Brassica nigra (L.) Koch	9.4 ± 2.5	106.6 ± 10.7
Brassica campestris L.	7.2 ± 2.2	103.4 ± 7.7
Brassica carinata A. Br.	4.6 ± 2.6	108.9 ± 13.9
Brassica napus L.	3.4 ± 1.0	61.2 ± 11.9
Brassica oleracea L.	0.6 ± 0.2	52.7 ± 3.8
Helianthus annuus L.	5.6 ± 1.3	61.6 ± 3.3
Nicotiana tabacum L.	0.8 ± 0.3	24.9 ± 7.8
Sorghum bicolor L.	0.3 ± 0.0	8.2 ± 0.6
Amaranthus hybridus L.	0.3 ± 0.04	8.7 ± 0.7
Amaranthus paniculata L.	0.4 ± 0.04	8.9 ± 0.3
Zea mights L.	0.2 ± 0.1	14.7 ± 0.9

Several plant species could hyper accumulate soluble lead in the soil. It had been reported that *Sesbania drummondii*, a leguminous shrub, and several Brassica species could accumulate significant amounts of lead in their roots. *Piptathertan miliacetall*, a grass, accumulated lead directly correlating to soil concentrations without symptoms of toxicity for three weeks [54]. They noted that *S. drummondii* could tolerate lead levels up to 1500 mg L-1 and accumulated ~40 g kg-1 shoot DW. Microanalysis spectra data through *S. drummondii* root sections showed a decreasing gradient of lead contents from the epidermis to the root central axis, and electron microscopy of S. drummondii roots revealed lead deposition in the cell membrane and cell wall.

Many plants might have a strategy of lead exclusion as *Thlaspi praecox*, which hyperaccumulates cadmium and zinc but not lead [55].

Selenium (Se)

Selenium naturally leaches from the soil, but becomes concentrated where leachates from highly irrigated soils accumulated toxic levels in shallow groundwater regions or wetlands. *B. juncea* had shown to accumulate 50 mg kg^{-1} dry mass in the field [56]. While there is no direct evidence that selenate reduction in *A. bisulcatus* occurred via the ATP sulfurylase/APS reductase pathway as a Se-specific selenate reductase had not been identified. Selenium non-accumulating species accumulate seleno-Methionine (SeMet) and Se-methylseleno-Met (Se-MeSeMet), while MeSeCys accumulates *A.bisulcatus*, if SeMet or Se-MeSeMet was incorporated into proteins, the seleno-protein was non-functional resulting in cellular toxicity. In contrast, *A. bisulcatus* forms MeSeCys from the methylation of SeCys by SMT [57].

Bioinorganic forms of selenium isolated from plants suggested that selenium metabolism is similar to the selenium metabolic pathway and that selenium analogs of selenium assimilated into selenium path-ways [58]. MeSeCys and proteins incorporating it are not toxic to the plant, and therefore, accumulate to high concentrations. It was suggested that mature leaves of *A. bisulcatus* could export Se- MeSeCys to younger tissues, and Se-MeSeCys was likely incorporated in seeds [59]. MeSeCys is an intermediate in the formation of dimethyl diselenide, a volatile form of selenium. Dimethyl diselenide is the primary volatile of *A. bisulcatus*, the distinctive malodorous, signature smell of the plants. Identification of all of the enzymes involved in the metabolic pathway of Se-MeSeCys in *A. bisulcatus* would clarify this pathway, and further elucidate the mechanisms whereby this plant establishes its hyper accumulation capabilities. They added that selenium hyper accumulators such as *Astragulus bisulcatus*, the two-grooved milk-vetch, had been shown to accumulate Se up to 0.65% (w/w). *A. bisulcatus* accumulated high concentrations of Se-methylseleno-Cysteine (Se-MeSeCys) in young leaves, while mature leaves had predominately selenate and 40 to 60-fold less Se-MeSeCys. Seleno-Cys methyl transferase (SMT1), which catalyzes Se-MeSeCys from seleno-Cys (SeCys) and S-methyl-transferase, was present in leaves of all ages. This suggested that the synthesis of Se-MeSeCys in older leaves must be blocked at an earlier metabolic step and that mature leaves could not reduce selenate (SeO4-2) to selenite (SeO3-2). Selenate (SeO4-2) and sulfate (SO4-2) metabolism in plants were parallel to selenate and sulfate accumulations in mature *A. bisulcatus* leaves and non-accumulators [60].

When ATP sulfurylase, an enzyme that reduces selenate to selenite, was over expressed in *B. juncea*, selenium accumulation in shoots was twofold greater and greater biomass than the selenium hyperaccumulator *Stanleya pinnata* [61] indicating that *B.juncea* ATP sulfurylase over expressors had the potential to successfully phytoremediate selenium contaminated soils. As *B juncea* plants over expressing ATP sulfurylase already had a bioconcentration factor of ~10, any improvement in accumulation or vitalization could make these plants suitable for efficient phytoremediation.

Two bioinorganic pathways could convert SeCys to a volatile compound, either to dimethyl selenide or dimethyl diselenide. Cystathionine-γ-synthade catalyzes Se- Cys to dimethyl selenide, and overexpression of cystathionine-γ-synthade in *B. juncea* increased selenium tolerance and enhanced selenium vitalization. Overexpression of SMT from *A. bisulcatus* in Arabidopsis and *B.juncea* increased selenium tolerance, accumulation of MeSeCys and vitalization of selenium [60], [62]. These transgenic plants were more tolerant to selenite than to selenate, indicating that the reduction of selenate to selenite was limiting. Overexpression of ATP sulfurylase with selenocysteine lyase, cystathionine- γ-synthade or SMT could therefore have synergistic effects.

Zinc (Zn)

The difference in transporter concentration could account for the observation that the hyper-accumulator and the non-accumulator had the same affinity for zinc, but the hyperaccumulator had a higher rate of uptake [63]. They added that both *T. caerulescens* and *T. arvense* store similar amounts of zinc in their root apoplasts, indicating that cell wall compartmentation was not a tolerance mechanism. The higher concentration of zinc in the root vacuoles of the non-accumulator noted above suggested that root vacuole accumulation was a tolerance mechanism for non accumulators which lack a mechanism to transport to the leaves. Although malate is the most common organic acid in *T. caerulescens* shoots, no zinc-malate complexes were detected with X-ray absorption spectroscopy [64]. Instead, the predominant form of zinc in the roots was zinc-histidine with the remaining 30% bound to the cell wall. In the xylem sap, most of the zinc existed as the free hydrated Zinc2+cation with ~20% as zinc-citrate, while in the leaves all four forms were

found with citrate being the most common. Leaf vacuoles are the primary site of zinc sequestration in *T. caerulescens* [65]. X-ray microanalysis of shoot tissue indicated that zinc is sequestered in the vacuoles of epidermal and sub-epidermal leaf cells in *T. caerulescens* [66].

The first zinc hyper-accumualtor identified was *T. caerulescens*. This plant was reported to accumulate between 25,000 and 30,000 µg g^{-1} total zinc before exhibiting symptoms of toxicity, although *T.caerulescens* could accumulate a maximum dry weight reaching 40,000 ug g^{-1} zinc in its shoots [67]. *Arabidopsis halleri* had also been found to increase in its shoot zinc concentration from 300 ug g^{-1} DW at 1 µM zinc to 32 000 ug g^{-1} at 1000 µM zinc without phytototoxicity [68]. ZINCT1 expression was higher in the hyperaccumulator *T. caerulescens* than in the non-accumulator *T. arvense*, possibly leading to a higher density of zinc transporters in the root-cell plasma membrane.

Mechanisms of zinc detoxification, chelation, and sequestration are species- specific. Zinc was mostly found coordinated to malate in *A. halleri* leaves [69]. ZINCT1 from *T.caerulescens* mediates low affinity zinc uptake as expected for a plant that grew on high concentrations of zinc [67]. The ZIP family of proteins (ZRT/IRT-like proteins) transports zinc into the plants [25].

A solute transfer model to predict the concentration of zinc in the rhizosphere solution [zinc] extract of *Thlaspi caerulescens*, a hyperaccumulator species was developed [70] and could be exploited for zinc phyto-extraction. Their model predicts that zinc accumulation by *Thlaspi caerulescens* is sub-optimal when the zinc concentration in the bulk soil solution is <27 µM. Such a high [zinc] ext is rare in contaminated agricultural soils, but is possible in the PTE liferous substrates where *Thlaspi caerulescens* is endemic. Sensitivity analyses indicate that zinc diffusion is more important than transpiration-driven mass flow for zinc delivery to the root, implying that management of soil physical and hydrological properties will improve phytoextraction. Sensitivity analyses also imply that strategies to enhance the zinc absorption power of the root will not necessarily be successful for enhancing phytoextraction per se. Thus, research into enhancing zinc availability and mobility in soil will be as important as understanding and manipulating zinc uptake by plants. Sunflower plants contained more Zn compared to those of corn plants [1]. They added that based on the distinctive decontamination rate of every studied PTE and Zn equivalent values, the cleaning potency of corn plant far exceeded that of sunflower plants for Zn, Cu and Ni.

Phytoremediation of trichloroethylene (TCE) from contaminated groundwater had been extensively studied using the hybrid poplar tree (*Populus spp*.). Several metabolites of TCE had been identified in the tissue of poplar including trichloroethanol (TCEOH) and dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) [71]. In addition to the use of hybrid poplar for the phytoremediation of TCE, it was important to screen native tree species that could be successful candidates for field use. They examined Longleaf pine (*Pinus palustris*), Leyland cypress (*X Cupressocyparis leylandii*), two varieties of Loblolly pine (*Pinus taeda*), and hybrid poplar species H11-11 (*Populus trichocarpa x deltoides*) for the concentration of TCE and its metabolites in their tissue following treatment with either a low (50 mg L^{-1}) or high dose of TCE (150 mg L^{-1}) for 2 month. Also, the amount of water taken up, change in height of the tree, TCE transpiration, and total fresh weight of various tissue types were measured. They found that all trees contained detectable levels of TCE in their root and stem tissue. TCEOH was found only in the tissue of longleaf pine, suggesting that TCE metabolism was occurring in this tree. TCAA was only detected in the leaves of hybrid poplar and piedmont loblolly pine. Conifers took up less water over the 2-month treatment period than hybrid poplar and grew at a slower rate. However, phytoremediation field soils might benefit from the evergreen's ability to transpire water throughout the winter months.

Plants of Cucurbitaceae family are known to up take organochlorines. So, study was designed to screen seven cultivars of the *Lagenaria siceraria* species of the Cucurbitaceae family to determine their capacity to remediate heptachlor- and heptachlor epoxide-contaminated soil [72].

The seven *Lagenaria* cultivars were grown in contaminated and uncontaminated Molokai soil for 13 weeks. Their results showed that all the plants tolerated heptachlor and heptachlor epoxide at levels of 0.169 and 0.376 g g^{-1}, respectively, in the soil and were able to bear a limited number of immature fruits during the short study period. All seven *Lagenaria* cultivars showed some ability to up take heptachlor epoxide into their vines with bioaccumulation factors varying from 1.0 to 5.2. The two contaminants were not detected in the fruits and heptachlor itself was not detected in the vines. The mean concentrations of heptachlor in the soil of

all the pots including the no-plant control were not significantly different from that in the initial soil, which might be due to the gradual release of the soil soil-bound heptachlor residues. In the soil, all pots showed a significant decrease for heptachlor epoxide as compared to the initial level, but there was no significant difference between the no-plant control pots and the planted pots of six of the seven cultivars. The local Hyotan cultivar showed the largest decrease, from 0.376 down to 0.050 g g^{-1} dry soil, and was the only cultivar showing a significant difference in the soil heptachlor epoxide concentration with the no-plant control.

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