Metal Transporters in Plants

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Abstract Several transition metals are essential for plants as for most other organisms. These elements have been needed in the course of evolution because of their chemical properties such as redox activity under physiological conditions (Cu, Fe) or Lewis acid strength (Zn). The properties that make transition metal ions indispensable for life, however, are also the reason why they can easily be toxic when present in excess. The main threat lies in their ability to produce reactive oxygen species (ROS). Unfortunately, toxic metals such as cadmium, lead, mercury, etc., as well as the essential ones can also produce ROS. In the course of industrialization, emissions of metals have risen tremendously and significantly exceed those from natural sources for practically all metals. Due to this mobilization of metals into the biosphere, their circulation through soil, water, and air has greatly increased. The main aim of this chapter is to discuss the effects of metal ions on a plant cell, to summarize the current state of the art in the field of thiol-rich compounds like phytochelatins to detoxify metal ions.

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Contents

1 Introduction

Several transition metals are essential for plants as for most other organisms (Pilon et al. 2009; Puig and Penarrubia 2009). These elements have been acquired in the course of evolution because of their chemical properties such as redox activity under physiological conditions (Cu, Fe) or Lewis acid strength (Zn) (Welch 1995; Palmer and Guerinot 2009). The same properties that make transition metal ions indispensable for life, however, are also the reason why they can easily be toxic when present in excess. The main threat lies in their ability to produce reactive oxygen species (ROS) (Gratao et al. 2005). Unfortunately, toxic metals such as cadmium, lead, mercury, etc., as well as the essential ones can also produce ROS (Rodriguez-Serrano et al. 2009; Martins et al. 2011), see in Fig. 1.

In the course of industrialization, emissions of metals have been tremendously raised and significantly exceed those from natural sources for practically all metals. Due to this mobilization of metals into the biosphere, their circulation through soil, water, and air has greatly increased (Kafka and Puncocharova 2002; Cheng 2003; Boran and Altinok 2010; Yabe et al. 2010). Investigation of the influence of metals on an organism as well as of their transport and of maintaining their levels inside a cell is thus very topical. The main aim of this chapter is to discuss the effects of metal ions on a plant cell, to summarize the current state of the art in the field of thiol-rich compounds like phytochelatins to detoxify metal ions, and to review methods used for detection and determination of both metal ions and thiols (Fig. 2).

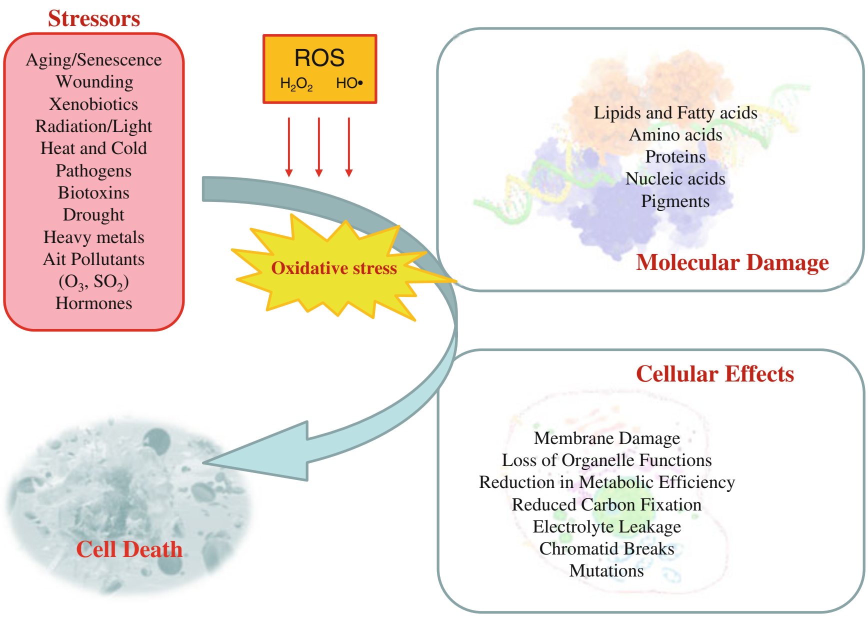

Fig. 1 Scheme showing some of the initiators (stressors) of reactive oxygen species (ROS) and the biological consequences leading to a variety of physiological dysfunctions that can lead to cell death

2 Plants and Heavy Metals

Heavy metals represent a group of metallic elements of density higher than 5 g/cm^3. Some of them are essential for normal plant growth and development because they are integral parts of many enzymes and other proteins (Welch 1995; Grusak et al. 1999; Darrah and Staunton 2000; Shaul 2002; Kramer et al. 2007). However, elevated concentrations of both essential and non-essential heavy metals lead to symptoms of toxicity with growth and development processes affected. Heavy metal phytotoxicity may result from alterations of numerous physiological processes caused at cellular/molecular level by inactivating enzymes, blocking functional groups of metabolically important molecules, displacing or substituting for essential elements, and disrupting membrane integrity (Sergio et al. 2000; Rakhshaee et al. 2009; Douchiche et al. 2010a). A rather common consequence of heavy metal poisoning is the enhanced production of ROS due to interference with electron transport activities. This increase in ROS exposes cells to oxidative stress leading to lipid peroxidation, biological macromolecule deterioration, membrane dismantling, ion leakage, and DNA-strand cleavage (Fig. 1). Plants resort to a series of defense mechanisms that control uptake, accumulation, and translocation of these dangerous elements and detoxify them by excluding the free ionic forms from the cytoplasm. In addition, heavy metals can replace essential metallic element(s) with symptoms of

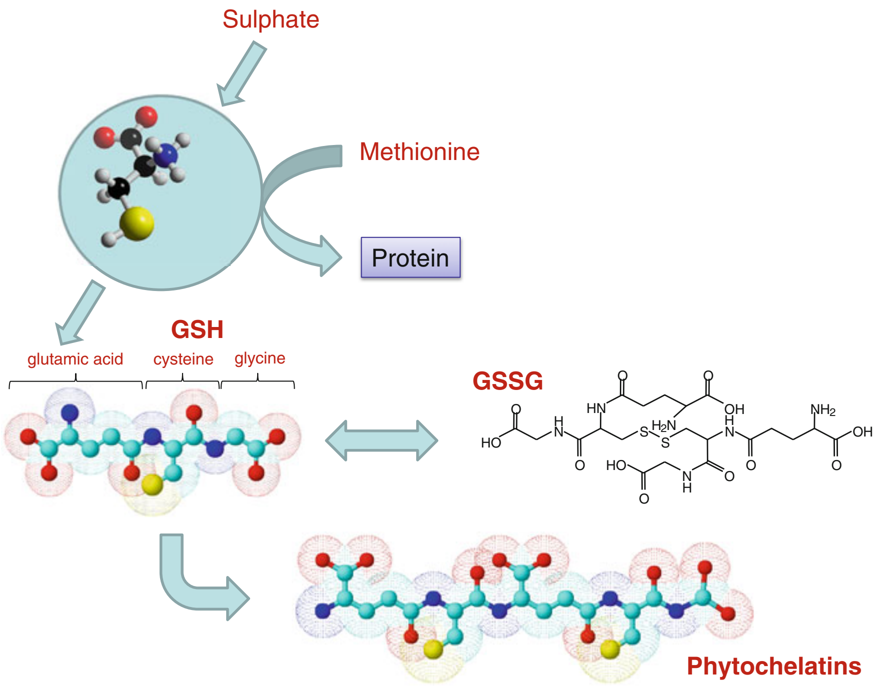

Fig. 2 Consequence of synthesis of biologically active thiols from cysteine to phytochelatins

deficiency. Some of them, such as cadmium or lead, induce formation of reactive oxygen/nitrogen species-free radicals, which are responsible for damage of biomolecules including DNA (Deng et al. 2010b; Iannone et al. 2010; Liu et al. 2010b). However, plants have many detoxification and tolerance mechanisms that enable to survive in a polluted soil containing toxic levels of heavy metal/metals. These mechanisms include (i) establishment of symbiotic associations with soil microorganisms such as mycorrhiza that restrict movement of heavy metal ions and uptake by the plant (Lin et al. 2007; Amir et al. 2008; Arriagada et al. 2009; Iram et al. 2009), (ii) binding to the cell walls and eventually to root exudates (Douchiche et al. 2010b; Colzi et al. 2011; Lang and Wernitznig 2011), (iii) reduced influx through the plasma membrane (Courbot et al. 2007; Gonzalez-Mendoza and Zapata-Perez 2008; Xiao et al. 2008; Lang and Wernitznig 2011), (iv) chelation in the cytosol by various ligands such as phytochelatins and metallothioneins and further heavy metals compartmentalization in vacuole (Prasad 1995; Hall 2002; Hasan et al. 2009), (v) action of proteins connected with the stress caused by heavy metals (heat shock proteins) (Neumann et al. 1994; Wollgiehn and Neumann 1999). Plants with enhanced tolerance to heavy metal ions are able to survive, grow, and reproduce on polluted soils and are, therefore, usually connected with processes of soil decontamination and remediation (Ow 1996; Navari-Izzo and Quartacci 2001; Sonmez et al. 2008). As it will be discussed in Sect. 3, decontamination and remediation of the polluted environment by using modern, non-destructive, and environment-friendly technologies is a topical theme to study. One of such technologies is called phytoremediation, which describes the treatment of environmental problems using plants (Jabeen et al. 2009; Kotrba et al. 2009; Karami and Shamsuddin 2010; Shao et al. 2010; Vamerali et al. 2010). Therefore, plant species with the best properties to grow and remediate the heavy metal polluted environment are intensively searched for. There are many promising plants usable in phytoremediation, especially in *Brassicaceae* family as *Thlaspi caerulescens, Thlaspi praecox, Thlaspi goesingense*, and *Arabidopsis halleri* (Gawronski and Gawronska 2007).

2.1 Glutathione and Related Thiols

Glutathione is one of the most significant thiol compounds occurring in the plant and animal kingdoms. It occurs in all living organisms—in prokaryotic as well as eukaryotic. GSH is redox buffer protecting the cytosol and other parts of cells against reactive oxygen radicals (ROS), which are induced by biotic and abiotic stress. In organisms, glutathione occurs in two forms, as reduced glutathione (GSH) and oxidized glutathione (GSSG). Both glutathione forms are strictly maintained ratios, whose disturbance is able to indicate stress elicited by various stress factors (Anderson 1998; Asensi et al. 1999; Garrido et al. 2010; Bielawski and Joy 1986). GSSG originates by formation of disulfide bind/linkage between two molecules of GSH, when two arisen H^+ atoms participate in the ascorbate–glutathione cycle toward generated ROS elimination. Regressive GSSG molecule regeneration proceeds under GSH catalysis by reduction and oxidation of NADPH + H^+ (Ogawa 2005; Paradiso et al. 2008), which is shown in Fig. 2. Its concentration varies in plants in the range from 0.1 to 10 mM (Meister and Anderson 1983).

The earliest reference to glutathione is from 1888, when its presence in yeasts was demonstrated. Glutathione structure was described as late as in 1935. In the 1960s, GSH was intensively studied because of its connection with human body liquids (McGovern et al. 1958; Manso and Wroblewski 1958; Pisciotta and Daly 1960a, b); though Dr. Alton Meister had indisputably the most contribution on glutathione metabolism clarification (Meister and Anderson 1983), which is proved by more than 4300 citations of his work on Web of Science server. GSH is a tripeptide containing γ-glutamyl-cysteinyl-glycine (Mullineaux and Rausch 2005).

In higher plants, GSH has many important functions that have crucial roles in maintenance of cellular redox homeostasis, and also participates in heavy metals and xenobiotics detoxification. In consequence to these functions, GSH is also used as a signal molecule in cells. GSH/GSSG couple reduction (redox) potential is not only influenced by reciprocal rate of GSH/GSSG, but also by changes in GSH synthesis as well as degradation (Schneider et al. 1992; Herschbach and Rennenberg 1994; Gelhaye et al. 2003; Rausch et al. 2007; Liedschulte et al. 2010).

2.2 Metallothionein-like Proteins and Metallothionein Expression

These proteins are polypeptides sharing low molecular mass, high cysteine content with absence of aromatic amino acids and histidine, high metal content, and abundance of CysXCys sequences where X is an amino acid other than cysteine (Suh et al. 1998; Liu et al. 2000; He et al. 2002; Lu et al. 2003). Metallothioneins (MT) with molecular weight varying from 2 to 16 kDa are subdivided into three classes based on their structure (Class I: polypeptides with a location of cysteines closely related to those in equine renal metallothioneins; Class II: polypeptides with locations of cysteine only distantly related to those in equine renal MT; Class III: atypical, non-translationally synthesized metal thiolate polypeptides (Liu et al. 2000). The metalloproteins have the ability to bind both physiological metal (Zn, Cu) as toxic (Cd, Pb, As) through thio group (−SH) of cysteine residues. The family of metallothione-like proteins with a carboxy-terminal (further in text C-terminal) Gly was for the first time characterized in the yeast *Schizosaccharomyces pombe* exposed to cadmium (Plocke 1991). Shortly thereafter, a larger series within the same peptide family was found in several plants exposed to various heavy metals. Phytochelatins have a structural relationship to glutathione; the homologues related to homoglutathione were called homophytochelatins and those related to hydroxymethylglutathione were designated as hydroxymethylphytochelatins. Peptides having a C-terminal amino acid other than Gly are named as isophytochelatin with the parenthetic addition of the C-terminal amino acid. The prefix iso- was chosen to signify the equal called γ-GluCys peptides based on the common structural element. Specific thiols are named according to the sequence of amino acids (Grill et al. 1986; Rauser 1990; Cobbett 2000, 2001; Cobbett and Goldsbrough 2002; Pal and Rai 2010). There were also prepared plants carrying MT gene as a way to increase the ability of a plant to withstand metal ions (Diopan et al. 2008; Janouskova et al. 2005a, b; Kotrba et al. 1999; Macek et al. 2002, 1996; Pavlikova et al. 2004; Shestivska et al. 2011).

2.3 Induction of Thiols by Heavy Metals

Various metals cause the appearance of thiols in plants (Kneer and Zenk 1992; Patra and Sharma 2000; Schmoger et al. 2000; Lee and Korban 2002; Abercrombie et al. 2008; Torres et al. 1997; Davis et al. 2006; Wang and Wang 2011). Induction of phytochelatins depends on the type of heavy metal as well as on the plant chosen. Silver through Cu (I) are class B metal ions that seek out nitrogen and sulfur centers in biological systems. Copper (II) and zinc are borderline metals that can form stable complexes with ligands offering oxygen, nitrogen, or sulfur atoms. Selenate, Te, and W are outside the grouping. All metals induced phytochelatins, except those members of the order of *Fabales* without glutathione, where homophytochelatins were accompanied by the (γ-GluCys)$_n$ family except with Ni and Se (Tukendorf et al. 1997; Gupta et al. 2004; Loscos et al. 2006). Initial reports of induction by Ni, Se, Te, and W could not be repeated perhaps reflecting analytical problems at low phytochelatins levels. The abundance and length of induced γ-GluCys peptides varied with the used type of metal. In some cases, a somewhat effective metal at one concentration could not be tested at higher concentrations because its toxicity killed the cells. Cadmium is generally considered the most effective inducer of phytochelatins, but was surpassed by Ag in *Rubia tinctorum* (family *Rubiaceae*) root in vitro culture (Maitani et al. 1996). No phytochelatin induction was found for Al, Ca, Cr, Cs, K, Mg, Mn, Mo, Na, or V. Apart from Cr and Mn that are borderline metals, the above list of metals are all class A metals that share a strong preference for ligands with oxygen as the donor atom. Metals always inducing phytochelatins synthesis are Ag, Pb, Cd, and Zn. For details, see works focused on glutathione, metallothionein-like proteins and phytochelatins (Prasad 1995; di Toppi and Gabbrielli 1999; Zhang et al. 1999; Cobbett 2000; Clemens 2001; Cobbett and Goldsbrough 2002; Hall 2002; Pal et al. 2006; Mullainathan et al. 2007; Rausch et al. 2007; Ernst et al. 2008; Clemens and Persoh 2009; Jabeen et al. 2009; Yadav 2010; Hassinen et al. 2011).

3 Accumulation of Heavy Metals by Different Plant Species

3.1 Phytoremediation

Phytoremediation is a widely accepted, aesthetically pleasant, solar-energy driven, passive technique that can be used to clean up sites with shallow, low to moderate levels of contamination (Padmavathiamma and Li 2007; Doran 2009; Jabeen et al. 2009; Memon and Schroder 2009; Zhao and McGrath 2009; Nwoko 2010). Phytoremediation is not only a growing science, it is also a growing industry. This technique can be used along with or, in some cases, in place of mechanical clean-up methods. Early estimates on the costs for remediating contaminated sites have shown that plants could do the same job as a group of engineers for one-tenth of the cost. The soil or water does not need to be gathered in and stored as hazardous waste, requiring large amounts of land, money, and manpower. Plants can be sown, watered, and then harvested with less manpower. The storage of the harvested plants as hazardous waste is seldom required and when needed it is less demanding than traditional disposal techniques. However, the main drawback of this novel technology is that it is not applicable to all sites. Several mechanisms may be involved in the direct and indirect action of phytoremediation in contaminated soils (Fig. 3).

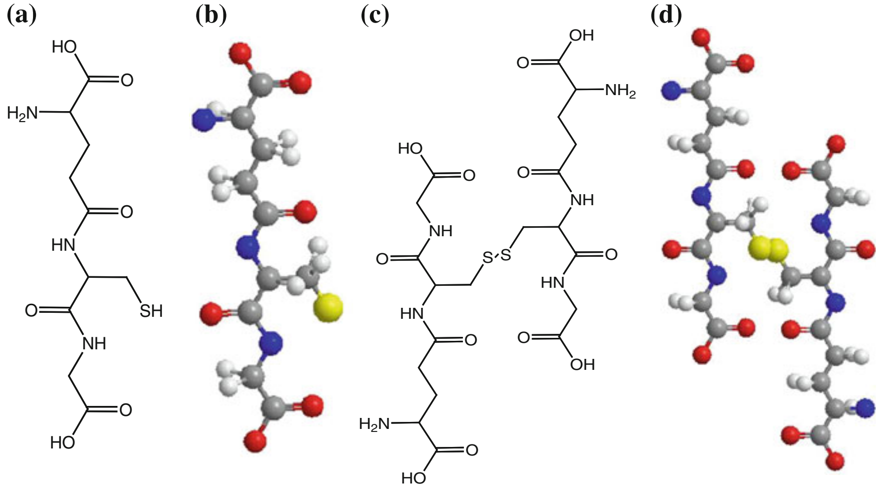

Fig. 3 Phytoremediation describes the treatment of environmental problems (bioremediation) using plants that mitigate the environmental problem without the need to excavate the contaminant material and dispose of it elsewhere. A range of processes mediated by plants or algae are useful in treating environmental problems as phytoextraction, phytostabilization, and (phyto) rhizofiltration. Phytoremediation consists of mitigating pollutant concentrations in contaminated soils, water, or air, with plants able to contain, degrade, or eliminate metals, pesticides, solvents, explosives, crude oil and its derivatives, and various other contaminants from the media that contain them

Therefore, phytoremediation of heavy metals can be divided into three groups:

1. Phytoextraction; the use of metal-accumulating plants to remove toxic metals from soil (Lasat 2002; McGrath and Zhao 2003; do Nascimento and Xing 2006; Van Nevel et al. 2007).
2. Phytostabilization; the use of plants to eliminate the bioavailability of toxic metals in soils (Cunningham and Berti 2000; Petrisor et al. 2004; Frerot et al. 2006; Kshirsagar and Aery 2007; Ehsan et al. 2009; Madejon et al. 2009; Andreazza et al. 2011).
3. (Phyto)rhizofiltration, the use of plant roots to remove toxic metals from polluted waters (Eapen et al. 2003; Verma et al. 2006; Khilji and Firdaus e 2008; Lee and Yang 2010; Yadav et al. 2011).

3.2 Basic Mechanisms of Phytoremediation

The remediation of soils contaminated with heavy metals is based on mechanisms of phytoextraction and phytostabilization. Phytoextraction, or phytoaccumulation, is referred to as the uptake and translocation of metal contaminants in the soil via the roots into the aboveground portions of the plants (Lasat 2002; McGrath and

Zhao 2003; do Nascimento and Xing 2006; Van Nevel et al. 2007). Risk element uptake by plants from soil depends on the level of pollution, forms of the element in soil, its mobility in the soil–plant system, and on plant species (Boruvka and Vacha 2006). Certain plants called hyperaccumulators absorb unusually large amounts of metals in comparison to other plants (e.g. up to 0.1 % chromium, cobalt, copper, or nickel or 1 % zinc, manganese in the aboveground shoots on a dry weight basis) (Xie et al. 2009; Masarovicova et al. 2010; Mengoni et al. 2010). Such hyperaccumulators are taxonomically widespread throughout the plant kingdom and are relevant to phytoremediation (Cunningham et al. 1995; Cunningham and Lee 1995). Phytoextraction is the using of hyperaccumulating plant species to remove metals from the soil by absorption into the roots and shoots of the plant. Metal concentrations in the shoots of some known hyperaccumulators can reach of extremely high levels (summarized by Cunningham and Ow 1996).

3.3 Hyperaccumulator

To physically remove metals from the contaminated site, the aboveground shoots of the hyperaccumulator plants are harvested and subsequently disposed of as hazardous wastes or treated for the recovery of the metals. Phytoremediation can be used to remove not only metals (e.g. Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn) (Juwarkar et al. 2010) but also radionuclides (e.g. 90Sr, 137Cs, 239Pu, 234U, 238U) (Cook et al. 2009; Fulekar et al. 2010; Hegazy and Emam 2010; Cerne et al. 2011) and certain organic compounds (i.e. petroleum hydrocarbons) (Abhilash et al. 2009; Gerhardt et al. 2009; Hussain et al. 2009; Perelo 2010; Megharaj et al. 2011). Plants growing in metal contaminated environments can accumulate toxic metal ions and efficiently compartmentalize them into various plant parts. Several studies indicated that the partitioning of heavy metals at the whole plant level can broadly be divided into three categories. For instance, Chaney and Giordano classified Mn, Zn, Cd, B, Mo, and Se as elements, which were readily translocated to the plant shoots; Ni, Co, and Cu, were intermediate, and Cr, Pb, and Hg were translocated to the lowest extent (Alloway 1995).

Jaffre et al. (1976) first applied the term hyperaccumulation to describe a highly abnormal level of metal accumulation in the title of their paper on nickel concentration in the tree S*ebertia acuminata* (family *Sapotaceae*) (Jaffre et al. 1976). The specific use of hyperaccumulation to denote a defined concentration (higher than 1000 mg kg^{-1} of Ni kg^{-1}) was introduced by (Brooks et al. 1977) in discussing Ni concentration in species of *Homalium* (family *Flacoutiaceae*) and *Hybantus* (family *Violaceae*) from various parts of the world (Brooks et al. 1977). To date, more than 440 hyperaccumulator species have been described, three quarters of these being Ni accumulators from extensive occurrences of Ni-rich ultramafic soils found in many parts of the world (Martens and Boyd 1994; Borhidi 2001; Reeves 2006; Bani et al. 2009; Cecchi et al. 2010). Chaney (1983) first suggested the concept of using hyperaccumulator plants to accumulate high quantities of metals in plant biomass to remove heavy metals from contaminated soils (Chaney 1983). In addition to the low cost, phytoaccumulation has several other important advantages over the traditional soil removal/replacement remediation methods. For example, it is in situ, preserves top soil, reduces the secondary waste stream, is environmentally sustainable, and the plant ash may have economic value (Garbisu and Alkorta 2001; Hetland et al. 2001). The main attraction of using hyperaccumulators for phytoremediation that remove and concentrate large amounts of a particular element is the possibility of employing species that remove and concentrate large amounts of a particular element from the soil without significant chemical intervention, other than classical application of fertilizers. It is important that the metal concentration in harvested plant tissue is greater than that in soil. To define, e.g., Ni hyperaccumulation more precisely, Reeves (2006) defined the hyperaccumulator as a plant that can accumulate a metal concentration of at least 1000 mg kg^{-1} in the dry matter of any above-ground tissue (Reeves 2006).

Baker and Brooks (1989) have reported about 400 metal-accumulating wild plants that accumulate high concentrations of heavy metals in their shoots (Baker and Brooks 1989). Natural hyperaccumulator plants often grow slowly and have low biomass yield. *T. caerulescens* (family *Brassicaceae*) was reported as a hyperaccumulator of cadmium and zinc (Plessl et al. 2010; Tuomainen et al. 2010; Leitenmaier and Kupper 2011; Leitenmaier et al. 2011; Liu et al. 2011). It can accumulate over 3 % of zinc and at the same time over 0.1 % of cadmium per dry biomass. The practical use of this plant for phytoremediation is restricted by its small biomass yield (Robinson et al. 1998). Metal hyperaccumulators are highly attractive model organisms as they have overcome major physiological bottlenecks limiting metal accumulation in biomass and metal tolerance.

There are two general approaches to phytoextraction: continuous and chemically enhanced phytoextraction (do Nascimento and Xing 2006; Nowack et al. 2006; Evangelou et al. 2007; Meers et al. 2008; Rajkumar et al. 2009; Saifullah et al. 2009; Rajkumar et al. 2010). The first approach uses naturally hyperaccumulating plants with the ability to accumulate an exceptionally high metal content in the shoots. Hyperaccumulating plants usually hyperaccumulate only a specific metal and metals that are primarily accumulated (Ni, Zn and Cu) are not among the most important environmental pollutants. No plant species has yet been found that demonstrates a wide spectrum of hyperaccumulation (Watanabe 1997). Hyperaccumulators are also mostly slow growing, low biomass-producing species, lacking good agronomic characteristics (Cunningham et al. 1995). There is no evidence that natural hyperaccumulator plants can access a less soluble and bio-available pool of metals in soil.

In non-hyperaccumulating plants, factors limiting their potential for phytoextraction include small root uptake and little root-to-shoot translocation of heavy metals. Chemically enhanced phytoextraction has been shown to overcome the above problems (Banaaraghi et al. 2010; Barrutia et al. 2010; de Araujo and do Nascimento 2010; Komarek et al. 2010; Zaier et al. 2010; Lomonte et al. 2011; Zhao et al. 2011). Common crop plants with high biomass can be triggered to accumulate high amounts of low bioavailable metals, when their mobility in the soil and translocation from the roots to the green part of plants was enhanced by the addition of mobilizing agents when the crop had reached its maximum biomass. The feasibility of chemically enhanced phytoextraction has been primarily studied for Pb and chelating agents as soil additives; less attention has been given to other metals and radionuclides or their mixtures (Meers et al. 2005).

3.3.1 Nickel

About 360 species worldwide are known to act as Ni hyperaccumulators (Reeves 2006). The plant families most strongly represented are the *Brassicaceae, Euphorbiaceae, Asteraceae, Flacourtiaceae, Buxaceae,* and *Rubiaceae*. About 90 other species are from more than 30 families, distributed throughout the plant kingdom.

3.3.2 Zinc and Lead

The discovery of zinc accumulation in certain *Viola* and *Thlaspi* species in the nineteenth century was followed by other species with more than 10,000 mg kg^{-1} Zn accumulation, notably *A. halleri.* This plant is one of the closest relatives of *A. thaliana.* It has colonized calamine soils, which are highly contaminated with Zn, Cd, Pb as a consequence of industrial activities. In addition, some populations have been reported to contain more than 100 μg g^{-1} dry biomass Cd in their leaves. In hydropony, *A. halleri* has been shown to tolerate at least 30-fold higher Zn and 10-fold higher Cd concentrations in roots than *A. thaliana* can tolerate (Roosens et al. 2008).

Lead is present in most soils and rocks at concentrations below 50 mg kg^{-1} and generally shows relatively low mobility in soils and in vegetation which typically have less than 10 mg kg^{-1} Pb. In cases when Pb does enter the plant roots in larger concentrations from Pb-enriched soils, significant translocation to the upper parts of the plant is uncommon. Increased concentrations of Pb in aboveground tissues can be caused by entering of the metal bound with dust and fine soil particles directly to leaves through stomata.

3.3.3 Cadmium

Cadmium is a nonessential heavy metal widespread in our environment because of contamination by power stations, metal industries, and waste incineration. Toxicity to living cells occurs at very low concentrations, with suspected carcinogenic effects in humans. However, the biological effects of this metal and the mechanisms of its toxicity are not yet clearly understood (Suzuki et al. 2001). Cd is one of the increasingly frequent contaminants of agricultural soils, where it is usually present at 0.1–0.2 mg kg^{-1} but occasionally has been detected at much higher levels in some regions. Cadmium contamination in agricultural soils is due to either excessive phosphate fertilization, use of sewage sludge as a soil amendment, or due to naturally high background levels (de Borne et al. 1998). Cadmium has no essential function in plants and at high concentrations is toxic to plants and animals. Uptake of Cd by plant roots depends on the concentration, the oxidation state of this metal in solution, and on the physical–chemical characteristics of the soils such as pH content of clay, minerals, and organic matter (Brokbartold et al. 2011; Gao et al. 2011; Hou et al. 2011; Kovacik et al. 2011; Mleczek et al. 2011; Redjala et al. 2011). Few plant species have shown to accumulate more than 100 mg kg^{-1} into their tissue (*T. caerulescens* and *A. halleri,* both *Brassicaceae*) (Ozturk et al. 2003; Zhao et al. 2003; Ueno et al. 2004; Tolra et al. 2006; Liu et al. 2008). Recently, high accumulation abilities by *Salix* (*Salicaceae*) were shown (Kuzovkina et al. 2004; Tlustos et al. 2007; Mleczek et al. 2011).

3.3.4 Cobalt and Copper

Normal concentrations of Co and Cu in plants are in the ranges 0.03–2 and 5–25 mg kg^{-1}, respectively. The tupelo or black gum of the southeastern United States (*Nyssa sylvatica*, *Cornaceae*) is remarkable in being able to accumulate as much as 845 mg kg^{-1} Co from normal soils (McLeod and Ciravolo 2007). However, even on cobalt-enriched soils, such as those derived from ultramafic rocks, plant Cu rarely exceeds 20 mg kg^{-1}.

Extensive screening of many sites of mining and smelting activity throughout Zaire, through plant and soil sample collections and analysis, identified 30 hyperaccumulators of cobalt and 32 of copper, with 12 species being common to the two lists (Homer et al. 1991; Keeling et al. 2003; Li et al. 2003; Faucon et al. 2007; Ghaderian et al. 2009; Wang et al. 2004; Wang and Zhong 2011). The Co and Cu accumulators have been found in more than dozen families. It can be mentioned that Co and Cu hyperaccumulators are not restricted only to metalliferous soils.

3.3.5 Manganese

Manganese is an essential element activating some of the enzymes involved in citric cycle (tricarboxylic acid cycle) and a central role of manganese cluster complexes in oxidation of water to oxygen has been reported. Toxic levels fall in the range 1000–12,000 mg kg^{-1}, depending on the plant species. Some species have been found with 1000–5000 mg kg^{-1} Mn on soils with manganese mineralization (more than 1 % Mn) and on soils with lower concentrations. Ultramafic soils may have 1000–5000 mg kg^{-1}, which is not regarded as strongly abnormal. Most records of Mn hyperaccumulation come from these areas. Other hyperaccumulators were found on ultramafic soils in New Caledonia with concentrations around 1000 mg kg^{-1} (Reeves 2006), in six plant species concentrations exceeded

10,000 mg kg^{-1}, nine species had at least one specimen above this level. Mn hyperaccumulators can be found among *Apocynaceae, Celastraceae, Clusiaceae, Myrtaceae, Phytolaccaceae,* and *Proteaceae* families (Xue et al. 2004, 2006, 2007, 2009; Fernando et al. 2006, 2008; Min et al. 2007; Mizuno et al. 2008; Peng et al. 2008; Yang et al. 2008; Dou et al. 2009; Deng et al. 2010a; Liu et al. 2010a).

3.3.6 Selenium

Selenium is an essential element for animal and human health, with remarkably narrow range between levels required to prevent deficiency diseases and those producing symptoms of toxicity. Soil content is generally 0.01–2 mg kg^{-1}. Se-rich soils can be found in the western part of United States, Ireland, Queensland, Colombia, and Venezuela. In plant dry matter, Se concentrations are generally below 1 mg kg^{-1}, 0.01 mg kg^{-1} in areas of low Se soils. Plants with more than 100 mg kg^{-1} are considered as hyperaccumulators since normal levels in plants are below 2 mg kg^{-1} (Reeves 2006). Plant genera in which extreme accumulation of Se can be found include *Astragalus* (*Fabaceae-Leguminosae*), *Stanleya* (*Brassicaceae*), *Haplopappus,* and *Machaeranthera* (*Asteraceae*) (Pickering et al. 2003; Cruz-Jimenez et al. 2004; Freeman et al. 2006; Galeas et al. 2007; Hung and Xie 2008; Freeman et al. 2009; Freeman and Banuelos 2011). Plants show a very wide variation in Se accumulation, as much as two orders of magnitude and even within a single locality.

Metal tolerant species and hyperaccumulators are a valuable and potentially useful biological resource which represent great potential for use in a variety of strategies for soil bioremediation, but some of them have been very rarely collected (Reeves 2006). There seems to be an urgent need for greater exploration of European metalliferous soils, so that more species of hyperaccumulating plants can be found and the distribution and rarity of these species can be better defined.

4 Conclusion

To consider whether the specific plant specie is able or not to remediate the polluted environment, not only heavy metals content in the plant tissues, but also the distribution of such metal ions in the tissues must be analyzed. Coupling of chromatographic technique for determination of heavy metal stress-induced plant peptides and spectrometric method for detection of spatial distribution of metals of interest seems to be suitable toward this aim.

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