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THE CRUCIAL ROLE OF SULFUR IN A PHYTOREMEDIATION PROCESS – LESSONS FROM THE POACEAE SPECIES AS PHYTOREMEDIATS: A REVIEW

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ABSTRACT

Among living organisms plants are the most tolerant to pollution. This fact, emphasizes their utility for phytoremediation, a promising technology for environmental cleanup. Many botanical families include multiple species which exhibit a notable phytoremediation potential. Each of these species enjoys certain advantages, but at the same encounters some limitations with respect to its application as phytoremediants. Careful selection of the appropriate family and genotype to match the particular pollutant and environment is crucial for successful phytoremediation; the Poaceae family seems to be one of the most important for this technology.

Phytoremediation of inorganic and organic pollutants largely depends on sulfur (S) metabolism. Therefore, S sufficient conditions and efficient S metabolism constitute the prerequisites for the effectiveness of the process. In the modern societies, heavy-metal pollution of soils is causing ever greater problems, exacerbated by the fact that most heavy metals accumulated in plants may, either directly or indirectly, find their way into animals and human beings. Wheat, rice and maize are among the world's most prominent crops, whilst cadmium (Cd) and nickel (Ni) are among the most toxic metals. Therefore, the physiological adaptations induced in cereals, by Cd for example, are alarming and subsequently, the responsiveness of these species has been studied extensively as model plants. Studies with *Arundo donax* as phytoremediant have proven that this species is tolerant to increased concentrations of Cd and Ni in its rhizosphere, and as a consequence, it can be cultivated in contaminated areas for phytoremediation and energy production purposes.

S-deficiency of crops is frequently reported, especially during the past two decades, worldwide. The main reasons for this deficiency are: the reduction of sulfur dioxide emission from power plants and various industrial sources, the ever increasing use of high-analysis low-S-containing fertilizers and the decreasing use of S-containing fertilizers, S-containing fungicides, pesticides and high-yielding varieties. A sufficient S supply of cereal crops is required in early growth stages, which cannot be fully compensated by S fertilization during later growth. Elemental S proved to contribute continuously to the crop's S nutrition due to its constant release after oxidation. Therefore, the early diagnosis of S deficiency, the profiling of S forms in the soil of the phytoremediation site and the prediction of S-fertilizer requirements are of key importance for achieving a successful process.

Keywords

graminaceous species, thiols, Poaceae, S metabolites, sulfur, phytomanagement, phytoremediants

1. INTRODUCTION

Human activities have resulted in changes of the elemental composition of the biosphere through the release of large amounts of potentially toxic trace elements (TEs; e.g., heavy metals), such as Zn, Cd, and Pb. Large areas have been contaminated over centuries with TEs and organic pollutants by industrial, mining and military activities, as well as farming and waste disposal. Contamination does pose a threat to the environment and to natural resources and they are a danger to public health, because they can enter the food chain. Phytoremediation is a technology for the remediation of contaminated environments, based on the use of plants and their associated microorganisms, to decrease the bio-availability of the contaminants, and/or their total concentration below the limits established by regulatory agencies (Rennenberg and Peuke, 2005)

During the last decade, different "phyto-approaches" (phytoextraction, phytodegradation, phytovolatilization, rhizofiltration, phytostabilization and phytorestoration) have not only received scientific but also commercial attention (Robinson at al., 2009). In this paper phytoremediation is mainly discussed in relation to the removal of TEs from the environment, although it has been proven that it can be useful to effectively remove from soils organic pollutants, radioactive isotopes and excesses of plant nutrients. In particular, we focus our attention on the role of sulfur (S) nutrition, since the use of higher plants in phytoextraction of TEs from polluted soil is based not only on their ability to take up, translocate and accumulate the metals in the aerial parts, but also on mechanisms able to alleviate their toxic effects (Salt at al., 1998). Under this context, adaptation of sulfate uptake and assimilation is thought to be critical for plant survival in a wide range of adverse environmental conditions, since different S containing compounds are involved in plant responses to heavy metal stress (May et al., 1998; Rausch and Wachter, 2005).

2. BACKGROUND

2.1 A survey of primary S metabolism in higher plants

Sulfur is an essential element for all leaving organisms, since it is found in a broad variety of biological compounds playing pivotal roles in a number of metabolic processes (Leustek et al., 2000). The main S source for plants is the sulfate ion of the rhizosphere, which is taken up by roots through specific high-affinity sulfate transporters (Buchner et al., 2010; Takahashi et al., 2011). Once inside the plant, sulfate is allocated via the xylem and phloem routes to different sinks, and undergoes intracellular channelling to chloroplast and vacuole, where it is assimilated into organic S compounds or compartmentalized as S store, respectively. Different sulfate transport systems are involved in mediating the sulfate fluxes through the whole plant in order to satisfy the S requirement for growth, which varies during development and under different environmental conditions. The main pathway of sulfate assimilation in plants involves activation of the anion and its stepwise reduction to sulfide which is finally incorporated into cysteine (Cys), a key intermediate (Fig. 1) from which methionine (Met), glutathione (GSH) and most of S containing compounds are synthesized (Saito, 2004; Takahashi et al., 2011).

2.2 Phytoremediation largely depends on S metabolism and S availability

Plants have the basic capability of extracting inorganic ions from soils and accumulating them in their biomass. An improved understanding of plant metal homeostasis (Kraemer and Clemens, 2005) can aid in the development of cost-effective plant-based technologies for the clean-up of polluted soils.

Absorption and detoxification processes of metals may depend on the synthesis of chelating compounds. These chelators include S-rich peptides, such as GSH, phytochelatins (PCs) and metallothioneins (MTs), and other molecules, such as nicotianamine (NA) and phytosiderophores

(PSs), the synthesis of which is closely depending on S metabolism. S metabolism is also involved in the detoxification of xenobiotic organic compounds, since the sulfhydryl group in the GSH structure readily reacts with a wide range of electrophylic compounds to form covalent bound glutathione S-conjugates (Leustek et al., 2000). This kind of reaction, catalyzed by glutathione S-transferases (GSTs), has been shown to be essential in the detoxification processes of toxins, xenobiotics and catabolic products (Marrs, 1996; Leustek et al., 2000). Moreover, S availability on the rhizosphere may strongly influence the functional equilibrium between roots and shoots and TEs bioavailability for plant uptake.

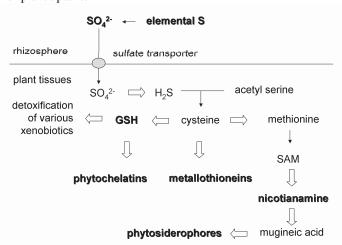


Figure 1 – The elemental sulfur is converted to sulfate in the rhizosphere, which is transported actively into the plant tissues and assimilated to cysteine. Then cysteine is converted to various primary S-metabolites, which contribute to the phytoremediation processes. Production of siderophores characterizes the graminaceous (Poaceae) species.

The central role of GSH in plant defense - GSH is a tripeptide with the formula γ -Glu-Cys-Gly, which represents the major form of nonprotein thiol compounds in plant cells (Kunert and Foyer, 1993). The pathway for GSH biosynthesis from Cys is well known and involves two sequential ATP-dependent reactions in plastids and cytosol (Noctor et al., 2011). In the first step, γ glutamylcysteine (γ -EC; γ -Glu-Cys) is synthesized by the enzyme γ -EC synthetase through the formation of an unusual peptide bond between the amine group of Cys and the γ -carboxyl group of the glutamate (Glu) side chain. In the second step GSH synthetase catalyzes the addition of a glycine (Gly) molecule to the C-terminal of γ -EC to produce GSH. GSH plays pivotal functions in both defense and protection (Rausch and Wachter, 2005; Noctor et al., 2011). Such a molecule mainly acts as a redox buffer in protecting cells from reactive oxygen species which may accumulate in response to abiotic and biotic stresses, and in homeostatic adjustment of the cellular redox potential too. Furthermore, GSH has been described as involved in several other processes, including regulation of S metabolism and inter-organ S allocation, control of development and cell cycle, calcium signalling, gene expression, and xenobiotic and heavy metal detoxification (Noctor et al., 2011; Takahashi et al., 2011). Changes in intracellular GSH concentration may thus be expected to have important consequences on cells, through modification of redox status, gene transcription and metabolic functions.

Phytochelatins - PCs is a principal class of heavy metal chelators known in plants and fungi; they are Cys-rich small peptides consisting of only three amino acids: Glu, Cys and Gly, with the Glu and Cys residues linked through a γ -carboxylamide bond. In PCs, two or more repeating γ -EC units are followed by a terminal Gly residue giving the general structure (γ -Glu-Cys)n-Gly, where n

ranges from 2 to 11 (Zenk, 1996). PCs are nontranslationally synthesized from GSH in a stepwise reaction, catalyzed by the enzyme PC synthase (PCS). Biosynthesis of PCs occurs within minutes following exposure to different metals or metalloids; among these, Cd is the strongest inducer, whereas Cu, Zn, Pb, and Ni are less effective and generally require higher external levels for induction (Grill et al., 1987; Maitani et al., 1996). Large numbers of plant species have been shown to respond to Cd and other TEs by producing PCs (Rauser, 1995). Such thiol compounds have largely been shown to be involved in Cd chelation and vacuolar sequestration, although new and intriguing roles for PCs have been hypothesized in Cd mobility (Gong et al., 2003). The mechanism by which PCs bind Cd ions reducing their free amounts into cells has been largely investigated in fungi and plants. Once inside the vacuole, the low molecular weight complexes incorporate S²⁻ and other Cd ions, evolving into the more stable high molecular weight Cd-PCs complexes. Several features of this model have also been found in higher plants (Clemens, 2006).

Metallothioneins - MTs are Cys-rich proteins able to bind metal ions through the thiol groups of their Cys residues. The structure of plant MTs, the number of metal ions bound and the dissociation energies required for metal release have been only recently explored. The metal—thiolate clusters formed in MTs show different pH stabilities but it is not yet clear how these relate to the functions of the different MTs *in vivo*. One of the most stable clusters is the Zn(II)-thiolate cluster of *Triticum aestivum*. Metallothioneins bind Zn, Cd and Cu ions. The combination of high thermodynamic but low kinetic stability is one of the main features of the metal-MT complexes: they bind the metals ions very tightly, a part of which is easily available to other proteins (Hassinen et al., 2009).

Nicotianamine - NA is a non-proteinogenic amino acid, ubiquitous in higher plants. NA biosynthesis originates in the S assimilation and Met biosynthetic pathways. The enzyme nicotianamine synthase catalyses the biosynthesis of NA from three molecules of S-adenosylmethionine, releasing three molecules of 5'-methylthioadenosine. NA serves as a metal chelator; it chelates Fe(II), Co(II), Zn(II), Ni(II), Cu(II) and Fe(III) with high affinities. In most plant species, excess metal ions are primarily immobilized in the root either in the apoplast or, by sequestration, presumably inside the vacuoles. The proportion of metals that is kept mobile is translocated from cell to cell towards and into the stele, followed by a final export from the cytoplasm of xylem parenchyma cells into the apoplastic xylem. Inside the xylem sap, chelation by ligands, for example, NA or organic acids, and the exchange with cell wall binding sites determine the rate of movement of a metal cation into the shoot with the transpiration stream (von Wiren et al., 1999; Clemens, 2001; Kraemer and Clemens, 2005).

Phytosiderophores - PSs are high-affinity low-molecular-weight chelators, which are derived from NA by consecutive replacement of amino groups by hydroxyl groups at various positions and to different degrees. This is initiated by the formation of 2'-deoxymugineic acid involving the enzyme nicotianamine aminotransferase and the oxygenase deoxymugineic acid synthase. Compared to NA, the replacement of amino by hydroxyl groups stabilizes the complexes with Fe(III) and renders PS-metal complexes more stable at low pH values that may be encountered in the immediate surroundings of the roots. So far, PSs have only been detected in graminaceous plants. Under Fe deficiency, roots of graminaceous plants produce and secrete PSs, which chelate Fe(III) in the rhizosphere. The Fe(III)-PS complexes are taken up by specific transport systems, among which the yellow-stripe-1 transporter (YS1) is likely to be the primary uptake system in maize. Maize roots can also take up Zn(II)-PS complexes. YS1 operates as a metal-phytosiderophore proton cotransporter and can mediate cellular uptake of complexes of the PS 2-deoxymugineic acid with Fe(III), Ni(II), Zn(II), Cu(II) and, at lower rates, Mn(II) and Cd(II). Evidence that YS1 is capable of mediating cellular import of NA complexes of Ni(II), Fe(III), and Fe(III) has also been obtained.

Mugineic acid (MA) is one of the phytosiderophores. Evidence for uptake into YS1-expressing yeast cells was obtained for Fe(III)-MA, Fe(II)-MA, Cu(II)-MA and Co(II)-MA complexes (Pilon-Smits and Pilon, 2002; Callahan et al., 2006).

2.3 Some aspects related to Cd accumulation in maize

Realization of an effective phytoextraction of TEs requires a good knowledge of the physiology of the plant species which are used. Among the class of non essential metals, Cd is one of the major concern with respect to both plant exposure and human food-chain accumulation. Its relevance as environmental pollutant and its relatively high mobility in the soil-plant system have made this toxic metal the most widely studied in plants (Clemens, 2006). Here, we summarize some aspects related to Cd accumulation in maize, with particular regard to PC biosynthesis and related metabolisms. It has widely been reported that Cd accumulation in maize rapidly induces PC biosynthesis and the activity of key enzymes involved in the sulfate reductive assimilation pathway and GSH biosynthesis, indicating the activation of a wide range of adaptive responses involving GSH consuming activities (Nussbaum et al., 1988; Rüegsegger and Brunold, 1992). In fact, GSH not only acts as a direct or indirect antioxidant in mitigating Cd-induced oxidative stress, but also represents the key intermediate for the synthesis of PCs essential for Cd detoxification. Comparative analyses of thiol compound levels in plants exposed to Cd stress reveal that PCs concentration (expressed as GSH equivalent) may reach values several fold higher than those of their direct precursor GSH, which instead represents the main nonprotein thiol in non-stressed plants (Nocito et al., 2002; Drąźkiewicz et al., 2003). The large amount of PCs produced by Cd stressed plants may represent an additional sink for reduced S able to increase the total amount of S request by plants and then the rate of sulfate assimilation. Interestingly, the need for maintaining a high rate of PC biosynthesis and adequate GSH levels under Cd stress may be also met by modulating sulfate influx into the root, and thus the total amount of S taken up from the environment. This finding arises from the observation that both short and prolonged exposures to micromolar Cd concentrations increase sulfate uptake capacity of maize roots by the up-regulation of ZmST1; I, a gene encoding a rootexpressed high-affinity sulfate transporter (Nocito et al., 2002; 2006). Moreover, the modulation of sulfate uptake seems to be dependent on the nutritional request for reduced S, as suggested by the observation that both changes in ZmST1;1 transcript levels and sulfate uptake capacity of the roots are closely related to the strength of Cd-induced additional sink for thiol compounds (Nocito et al., 2006). The regulation of sulfate uptake may thus represent the first step of the adaptive process required to ensure an adequate S supply for Cd detoxification.

The massive synthesis of PCs under Cd stress has important implication on carbon metabolism, since the induction of additional sinks for thiol compounds not only increases the need for S, but also enhances the metabolic demand for reducing equivalents and carbon skeletons which are essential to sustain the biosynthesis Cys, Gly and Glu, the amino acid monomers of GSH and PCs. Experimental evidences indicate that these additional needs may be supported through a carbohydrate overflow toward glycolysis, the pentose-phosphate pathway and anaplerotic reactions producing tricarboxylic acid cycle intermediates essential to sustain GSH and PC biosynthesis (Sarry et al., 2006; Nocito et al., 2008). Moreover, it is also important to note that this metabolic scenario, though it is essential to sustain Cd detoxification, may rapidly induce cell acidosis, since: i) both glycolysis and pentose phosphate pathways are H⁺-producing processes; ii) Cd accumulation into the root cells may affect plasma membrane lipid composition resulting in a progressive reduction of the plasma membrane H⁺-ATPase passive permeability to H⁺ (Astolfi et al., 2005; Nocito et al., 2008). Such aspects need to be taken into account to improve PC-based Cd detoxification processes in cereals of biotechnological interest.

3. THE APPLICATION

3.1. S-deficiency and the need for S addition for effective phytoremediation

Successful phytoremediation demands enhanced carbon allocation to the aerial portion of the plant, to be harvested along with the TEs carried by it. Functional equilibrium between overground and underground plant parts is an old story (Hunt and Lloyd, 1987), and it is well established that the partitioning of dry matter and N between shoots and roots is flexible and can respond to environmental limitations (Cooper and Clarkson, 1989). One of the mechanisms used by plants in order to adjust to an imbalance of exogenous resources is the allocation of new biomass to the organs involved in acquiring the scarcest resources. The root is devoted to mineral nutrient acquisition and is the first organ to sense and signal mineral deficiency. A model of plant response to nutrient shortage by allocating biomass to specific organs has been discussed by Hermans et al (2006). Among environmental limitations, S-deficiency is an increasing problem in agriculture, mainly due to reduced industrial emissions of S to the atmosphere, and the consequent decreased deposition of S onto agricultural land worldwide (Scherer, 2009). S plays an important role in plant growth and development. The importance of S nutrition on plant metabolism has received large attention. A series of specific responses aimed at optimizing acquisition and utilization are induced by S-limitation in all plant species studied today (Hawkesford and De Kok, 2006). In maize, adaptations to increase sulfate acquisition include modifications of root architecture in order to maximize sulfate-acquisition efficiency, which coincide with an increased root length, increased root mass, increased root-to-shoot ratio and lateral root proliferation (Hopkins et al., 2004; Bouranis et al., 2008). For these reasons, adequate sulfate must be found in the rhizosphere for a successful phytoremediation process. The general pattern of S metabolism of higher plants is modified by the S supply of the environment and by the variability of the S demands among plants. During the evolution of higher plants the S requirement by plants has resulted in species-specific and sometimes even family-specific demands. Cereals and wild grasses may extract per annum from the soil 10-15 kg S ha⁻¹. Finally, it is interesting to note that an adequate S nutrition may alleviate the toxic effect exerted by TEs accumulation into plant tissues. Such a behavior is likely due to an effect of S on GSH biosynthesis and then on the GSH-consuming mechanisms related to TEs detoxification (Nocito et al., 2006).

Phytoextraction, is often limited by low availability of the polluting metals in the soil. Elemental S has been used as an agent that increases the solubility of TEs for plant uptake. Shoot Zn concentration in Zea mays L. is increased by application of elemental S. The concentration of Cd was also increased in Z. mays L. after the application of elemental S in pot experiments. The oxidation of the elemental S by microbial activity to sulfuric acid leads to a decrease in soil pH, depending on the soil's buffering capacity. Solubility is dependent on soil pH and strongly increases for most cationic metal pollutants at pH range of 5 - 6. Further decrease in pH by additional S applications bears an excessive risk of decreasing yields and increasing metal leaching out of the root zone. A decrease in soil pH to values below 4.5 - 5 would lead to irreversible soil degradation and complete leaching of macronutrient cations such as Ca, Mg and K. Also, toxic effects due to the solubilisation of the polluting metals and Al would become a problem for crop plant growth and water quality (Cui et al., 2004; 2005). In contrast to S deficiency in not-well-fertilized agricultural ecosystems, environments enriched anthropogenically or naturally with one or more heavy metals are characterized by good or high S supply. Therefore, in such environments, plants have metabolically to regulate not only a surplus of metal(loid)s, but also a surplus of S (Ernst et al., 2008).

3.2 Members of the Poaceae family as phytoremediants

The grass family is one of the most important for phytoremediation. Maize (Zea mays) and tall varieties of wheat (Triticum aestivum) and barley (Hordeum vulgare) have been recommended for phytoremediation, because they are highly productive in terms of biomass and tolerant to TEs and petroleum. When a polluted site is saline, barley is the most tolerant of the cereals (Seckin et al., 2010). Lolium multiflorum, Lolium perenne (rye grasses), Festuca arundinacea, Festuca ovina and Festuca rubra (fescue grasses) are pasture grasses tolerant of polycyclic aromatic hydrocarbons and petroleum hydrocarbons, therefore frequently present on polluted roadsides. Agrostis alba and Agrostis tenuis (bent grasses) are suitable for phytostabilization because they are characterized by a particularly high level of resistance to TEs, achieved by restricting pollutants to the roots. Wheat grass (Agropyron repens), a frequent coloniser of polluted sites in the temperate zone, is very tolerant to salinity and TEs, accumulating them in high amounts in underground rhizomes. The ornamental species Deschampsia cespitosa (hair grass) and Vetiveria zizanioides (vetiver grass) are grasses also exhibiting a high phytoremediation capacity. Phragmites australis (reed) is temperate species, very tolerant to a wide range of pollutants including high salinity, thus suitable for phytoremediation of water and sediments,. Phalaris arundinacea (canary grass) and Miscanthus sp (silver grass) are adapted to warmer climates. Miscanthus giganteus accumulates a large amount of biomass and is sufficiently frost tolerant to survive the Central European winter. An advantage of this family is that plant material is not fragile after cutting and drying. Most species possess rather shallow root systems, but root density is high. Pasture grasses produce less biomass than grain crops, but they can be cut several times during the season, allowing absorbed pollutants to be removed before they are eluted from the plants by rain. (Gawronski and Gawronska, 2007). Ryegrass has been frequently used to evaluate the feasibility of plant establishment and growth in amended metal-contaminated soils and mine tailings (Goecke et al., 2011).

3.3 Phytomanagement through Poaceae

In Greece, severe contamination with Cd, Ni, Pb, As and Zn has been reported in the area of Kamariza in Eastern Attica and in the extended area of Lavrion-Attica, SSE of Athens. The Lavrion peninsula presents a high level of soil contamination with multiple heavy metals, including cadmium (at 66 mg kg⁻¹) and nickel (at 73 mg kg⁻¹); this area is heavily contaminated due to the intensive mining and metallurgical activities that took place over a period of 2700 years. High Ni concentrations are found in regions different to Cd, away from mining sites, which indicate that its origin is probably due to the nature of parent material (Papazoglou et al., 2005; 2007). Efficient phytoextraction techniques require large biomass yield, fast growth rate, easy harvest, metal accumulation ability and tolerance to heavy metal stress. Arundo donax (giant reed, Poaceae) is widely spread in Lavrion peninsula. It is a fast growing, robust, invasive perennial grass, wildgrowing in southern European regions and other Mediterranean countries. Giant reed can easily adapt to different ecological conditions and grows in all types of soils, it is a highly pest-resistant crop and it produces high biomass yield (32-37 tons or dry mass per hectare). Growth and photosynthesis of giant reed was not affected by high cadmium and nickel soil content (Papazoglou et al., 2005; 2007). For these reasons giant reed is a potentially high-yielding nonfood crop, which displays many attractive characteristics for the production of biomass, of pulp and paper and of activated carbons. Agropyron elongatum (Poaceae), another energy plant, is also fast growing plant with a large biomass yield and is fairly tolerant to different habitats; therefore, potentially suitable for phytoextraction (Vashegyi et al., 2011).

Phytoextraction as a stand-alone technology is unlikely to find widespread use for the cleanup of contaminated sites. After phyto-extraction the loaded plant material has to be further processed to extract the elements and to condense them for a reuse in the chemical industry, i.e. the material cycle needs to be optimized. Therefore, "phyto" management is needed, aiming at the engineering

or manipulation of soil-plant systems to control the fluxes of TEs or xenobiotics in the environment. Phytomanagement is a long-term technology; contaminated site phytomanagement requires the production of valuable biomass as well as reducing environmental risk. Bioenergy production on contaminated land has several advantages over production on non-contaminated fertile soils. Productive agricultural land will not be taken out of food production, which, in the case of bioenergy production, has led to increased food costs. The biomass of vegetation from a phytomanagement program may have other non-food uses. Phytomanagement that combines phytoextraction, phytostabilization and the production of valuable biomass could be used extensively worldwide. The plants may be other than standard crop species, particularly concerning TEs tolerance and accumulation (Robinson et al., 2009). Interestingly, on this issue Dickinson et al. (2009) have argued that the wider practical applications of phytoremediation are too often overlooked. They proposed that an additional focus on biomass energy, improved biodiversity, soil protection, carbon sequestration, and improved soil health is required for the justification and advancement of phytotechnologies.

4. CONCLUDING REMARKS

Elemental S has been used as an agent that increases the solubility of transition elements for plant uptake. The elemental S is oxidized by microbial activity to sulfuric acid and sulfate is taken up by roots through specific high-affinity sulfate transporters. Inside the plant, sulfate is assimilated to cysteine, the precursor molecule for the production of several primary S-containing compounds. Glutathione, phytochelatins, methionins, nicotianamine and phytosiderophores play important roles in managing the biological activity of transition elements and several classes of xenobiotics. Various graminaceous species have been used effectively for phytoremediation processes and several aspects of the molecular basis of this efficiency have been studied in details. Their particularities concerning a specific strategy for managing iron, include phytosiderophores in their arsenal, thus enhancing their capacity as phytoremediants and rendering them as useful tools for developing efficient and profitable phytomanagement.

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