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Plant-Heavy Metal Interaction: Phytoremediation, Biofortification and Nanoparticles

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1. Introduction

Contamination of ecosystems and action of toxic metals to plants is one of the major problems of all over the world. Most of these metals are present in the environment as a consequence of geological and/or anthropogenic activities. Metal contamination in agricultural environments can originate from atmospheric pollution, pesticide applications, contamination by chemical fertilizers, and irrigation with wastewater of poor quality. Although, some of metals are bioelements (macro- and micronutrients) at normal concentration, they can cause harmful effects on the plants in excess. Moreover, these metals have strong impact on human health through the food chain. Toxic metals or metals, as bioelements in higher than normal concentrations, are group of substances belonging to the xenobiotics. Frequently is also used term heavy metals, that are metals with specific weight higher than 5 gcm^{-3}, e.g. Cd, Hg, Pb, Cr, Ag and Sn (di Toppi & Gabbrielli, 1999). Knowledge of dominant fluxes of metals in the soil-root-shoot continuum can also help agronomic strategy to address the problem of crop growth under metal-excess, biomass production and food quality. In addition to the highly toxic heavy metals, light metals (e.g. Mg, Al) and metalloids (e.g. As and Se) are of great environmental and health significance. Extraordinarily dangerous for both humans and plants are mainly metals that attack activity of the enzymes containing –SH group (e.g. Cd, Hg and Pb). These metals can initiate acute or more dangerous and frequently occurring chronic diseases. Therefore, new and environmental-friendly technologies, such phytoremediation appeared to remove the harmful metals from the environment. Based on their strategy, plants growing on soil containing metal can be classified as accumulators and excluders. Later the following groups of plants were suggested: metal excluders and metal non-excluders (indicators, hyperaccumulators) (in detail see Masarovičová et al., 2010).

Medicinal plants have an increasing economic importance and the food, pharmaceutical and cosmetic industry produce important goods with these plants. Products based on natural substances enjoy an increasing value. However, anthropogenic activity and its effects on environment recently showed that medicinal plants have also responded on the changing environmental conditions. Some medicinal plants produce specific secondary metabolites, which can detoxify some of toxic metals. Thus, medicinal plants can also have non-traditional use e.g. in phytoremediation technologies. In the last years the practical use of

alternative medicine in healing processes showed continually increasing tendency. Several species of medicinal plants can be used as supplementary nutrition due to their ability to accumulate some essential nutrition elements (e.g. Se, Zn, and Fe) in the edible parts of these plants. Such fortification of plants with essential nutrients (phytofortification) in an easily assimilated form can help to feed the rapidly increasing world population and improve human health through balanced mineral nutrition. In general, data related to toxic metal contents (e.g. Cd) in pharmaceutically utilized parts of the medicinal plants are also considered from the aspect of „food safety". Therefore it should be stressed that cultivation and use of medicinal plants have to respect the potential hazard connected with environmental contamination, mainly with toxic metals (Masarovičová & Kráľová, 2007).

2. Crops

While the green revolution resulted in the development of new cultivars of crops suited to high input of fertilizer and water, many regions of the world rely on contaminated soils utilized for food production. The continuous application of large amounts of fertilizers and other soil amendments to agricultural land has raised concern regarding the possible accumulation of elevated levels of trace element constituents and potential harm to the environment. Furthermore, increasing amounts of urban and industrial wastes which may contain also significant quantities of toxic metals are being disposed on the agricultural lands (Raven and Leoppert, 1997). Mining, processing metal ore, wastewater irrigation, solid waste disposal, sludge application, vehicular exhaust and many industrial activities are the major and harmful sources of soil contamination with toxic metals. Therefore, an increased uptake of toxic metals by food crops grown on such soils together with human health risks are often recorded. Excessive accumulation of toxic metals in agricultural soils and the aforesaid elevated toxic metal uptake by crops affect both food quality and safety. Numerous regions in the world are known where cultivation of food and feed crops is irresponsible due to the presence of excessive amounts of plant-available toxic metals, leading to economic losses and negative effect for food chain (Meers et al., 2010). Severe toxic metal contamination of soil may cause a variety of problems, including the reduction of crop yield, serious damage of plants and intoxication of animals and humans.

2.1 „Second" green revolution

According to Lynch (2007) at present we need a "second" green revolution, to improve the yield of crops grown in infertile (or low fertile) soils by farmers with little access to fertiliser. Just as the green revolution was based on crops responsive to high soil fertility, the "second" green revolution will be based on crops tolerant to low soil fertility. Root architecture is critically important for both soil exploration and nutrients and water uptake. Architectural traits that enhance topsoil foraging are important for acquisition of phosphorus from infertile soils. Genetic variation in the length and density of root hairs is important for the acquisition of immobile nutrients such as phosphorus and potassium. Genetic variation in root cortical aerenchyma formation is important in reducing the metabolic costs of root growth and soil exploration. Genetic variation in rhizosphere modification through the efflux of protons, organic acids and enzymes is important for the mobilisation of nutrients such as phosphorus and transition metals, and the avoidance of aluminum toxicity. Manipulation of ion transporters may be useful for improving the

acquisition of nitrate and for enhancing salt tolerance. Genetic variation in these traits is associated with substantial yield gains in low-fertility soils. In breeding crops for low-fertility soils, selection for specific root traits through direct phenotypic evaluation or molecular markers is likely to be more productive than conventional field screening. Crop genotypes with greater yield in infertile soils will substantially improve the productivity and sustainability of low-input agroecosystems, and in high-input agroecosystems will reduce the environmental impacts of intensive fertilisation. Above mentioned author stressed that population growth, ongoing soil degradation and increasing costs of chemical fertiliser will make the „second" green revolution a priority for plant biology in the 21st century.

2.2 Effect of metals on physiological processes

In general, the metals play an important role in the metabolic pathway during the growth and development of plants, when available in appreciable concentration. Bioelements are essential for many proteins in plants, although they are toxic in excess. Plants differ greatly in metal uptake and accumulation characteristics. Thus, uptake and distribution of metals in plant body depends upon availability and concentration of metals as well as on plant species.

Kranner & Colville (2011) published review paper providing information of metal impact on seed of plants (including the crops and medicinal plants) from the aspect of biochemical and molecular implications and their significance for seed germination. The authors noticed that metals generally affect seed variability and germination in a strictly concentration-dependent manner when exogenously applied in the micro- to mili-molar range. The seeds of metal tolerant plants and hyperaccumulators may have a substantially higher threshold for toxicity than non-tolerant ones. However, knowledge of the effects of metals on seeds is only starting to emerge, in particular on the mechanisms of damage. In addition, more studies are needed that investigate the effects of metals on seed germination *in situ*. It was found, that the inhibition of seed germination by certain metals, e.g. Cd, may be reversible by rinsing the seeds in water. There is some evidence that Cd and Cu can inhibit seed water uptake, which has the potential to impact on germination. On the other hand, seed dormancy status can also be affected by low metal concentrations, but the precise mechanisms of action are far from understood. Moreover, it is largely unknown where metals are deposited in developing seeds and which levels are toxic to the embryo as compared to the endosperm or cotyledons. More work is needed to understand how seed longevity is affected by metals. According to the authors, regarding the mechanism of damage and seed stress response, surprising few studies have concentrated on the detoxification of metals by phytochelatins in seed, although some papers have reported on metallothioneins. Importantly, for a more comprehensive understanding of the effects of metals on seed viability and dormancy, the signalling networks need to be explored including the interaction of seed hormones with metals. Similarly, Shanker et al. (2005) published review article devoted to the chromium toxicity in plants. It was stressed that toxicity of Cr to plants depends on its valence state: Cr(VI) is highly toxic and mobile whereas Cr(III) is less toxic. Since plants lack a specific transport system for this metal, it is taken up by varied transporters of essential ions such as sulphate or iron. Toxic effects of Cr on plant growth and development include alterations in the germination process as well as the growth of roots, stems and leaves, which may affect total dry mass production and yield.

Cr also causes deleterious effects on plant physiological processes such are photosynthesis, water relations and mineral nutritions. Metabolic alterations due to Cr exposure have also been described in plants by a direct effect on enzymes or other metabolites or by its ability to generate reactive oxygen species which may cause oxidative stress. These authors noticed that Cr, in contrast to other toxic metals like Cd, Pb, Cu or Al, has received little attention from plants scientists. Its complex electronic chemistry has been major hurdle in unravelling its toxicity mechanism in plants.

We have already mentioned that Cd and Cu were very often used for investigation of their negative effects on plants. Thus, Hattab et al. (2009) studied physiological effects of Cd and Cu on growth and photosynthesis of pea (*Pisum sativum* L.). It was found, that root and shoot lengths, the concentration of photosynthetic pigments and the rate of photosynthesis were affected by the high metal concentrations. The analysis of metal accumulation showed that leaves significantly accumulate Cd for all tested concentrations. However, Cu was significantly accumulated only with the highest tested dose. These findings can explain the higher inhibitory effects of Cd on growth and photosynthesis in pea plants. These results are valuable for understanding the biological consequences of toxic metals contamination particularly in soils devoted to organic agriculture. Similarly, Shukla et al. (2003) examined the influence of cadmium on the wheat (*Triticum aestivum* L.) plant. The root, shoot-leaf length and the root, shoot-leaf biomass progressively decreased with increasing Cd^{2+} concentration in the nutrient medium. Cd^{2+} uptake and accumulation was found to be maximum during the initial growth period. Cd^{2+} also interfered with the nutrients uptake, especially Ca^{2+}, Mg^{2+}, K^+, Fe^{2+}, Zn^{2+}, and Mn^{2+} from the growth medium. Growth reduction and altered levels of major biochemical constituents such as chlorophyll, protein, free amino acids, starch, and soluble sugars, that play a major role in plant metabolism, were observed in response to varying concentrations of Cd^{2+} in the nutrient medium. In this paper the effects of Cd^{2+} on growth, biomass productivity, mineral nutrients, chlorophyll biosynthesis, protein, free amino acid, starch, and soluble sugars content in wheat plants were estimated to establish an overall picture of the Cd^{2+} toxicity at structural and functional levels.

According to the Gupta & Gupta (1998) nutrient toxicities in crops are more frequent for manganese and boron than for other nutrients. Manganese toxicity was found on acid soils in many parts of the world, boron toxicities occurred in irrigated regions where irrigation waters were exceptionally high in B. Most other nutrient toxicities occurred when large amounts of nutrients in question have been added in waste, e.g. sewage sludge. Crops grown near mines and smelters were prone to nutrient toxicities. In general, the symptoms of toxicity in crops occurred as burning, chlorosis and yellowing of leaves. Toxicities can result in decreased yield and/or impaired crop quality. Use of crop species and genotypes less sensitive to toxicity were recommended where toxicity is suspected.

Tudoreanu & Phillips (2004) in their paper concluded that there is currently only a limited understanding and quantification of key parameters which would allow a comprehensive mechanistic model of Cd uptake by different plant genotypes to be constructed, and also that there is a limited number of empirical observations of key endpoints for an empirical model. Further work on these aspects is essential to facilitate the construction of effective models to control excessive Cd accumulation in the food chain.

Metal toxicity is influenced not only by metal concentration, but also by mineral composition and organic substances in the soil, pH, redox-potential and presence of other metals in the soil. The most important factor which modifies metal toxicity is relationship to the mineral substances in the plants grown in contaminated areas. Toxic metals can induce excessive input or output of elements from plants and thus also modify metal content in the plants. It was found that, e.g. Cd acts negatively on uptake of many nutrients through deterioration of plasmatic membrane of the roots (lipid peroxidation, protein degradation), by effect on ATP-ses and other carriers, as well as by respiration decrease of root with following decrease of active uptake and transport of nutrients. Decline of essential elements in the plants can be also consequence of their washing out from the damaged roots and immobilisation of elements in the roots (Siedlecka, 1995). This author found that Cd also induced Fe deficiency despite the fact that Fe was in medium in sufficient amount. As a consequence of negative effect of Cd there were observed leaf –rolling, –yellowing, –darkening or leaf wilting (e.g. Hagemeyer et al., 1986). Cd decreased water potential and transpiration rate as a consequence of decrease of stomatal conductance (Barceló & Poschenrieder, 1990). This metal seriously damaged photosynthetic apparatus, induced inhibition of both photosystems (PS I and PS II), non-cyclic transport of electrons (Siedlecka & Krupa, 1996) as well as Calvin cycle including activity of Rubisco and PEP-carboxylase (e.g. Stiborová et al., 1986). The other authors (e.g. Šeršeň & Kráľová, 2001) confirmed direct interaction Cd^{2+} with photosynthetic apparatus, namely with light phase of photosynthesis. Cadmium ions can interact with tyrosine radicals located on 161st position of D1 or D2 proteins as well as with reaction centre of PS I. These ions can release Mn^{2+} from manganese cluster which is component of water splitting complex. As a mechanism of action it is supposed formation of complexes of Cd^{2+} with amino acids of proteins in photosynthetic centres. Effect of Cd on respiration rate was found at low Cd concentration stimulative and at high Cd concentration inhibitive (influence of Krebs cycle) (Burzynski, 1990). In our recent review paper (Masarovičová et al., 2011) we presented comprehensive outline related to the effect of metals on cytology, anatomy, physiology and production of crops used as a food, fodder as well as technical plants.

2.3 Defense reactions of plants

Plants respond to stress induced by cadmium using some defense reactions such are immobilization, exclusion, accumulation of cadmium ions in vacuole, synthesis of phytochelatins and stress proteins as well as production of ethylene (e.g. di Toppi & Gabbrielli, 1999). Immobilization in both, cell wall and extra cellular polysaccharides (mucilage, callose) is the first barrier against Cd^{2+} transport into the root. Exclusion represents prevention of Cd^{2+} enter into the cytosol through plasmatic membrane. However, in the case of higher Cd^{2+} concentration the plasmatic membrane can be seriously damaged (in detail see Budíková & Mistrík, 1999). One of the frequent mechanism of plant detoxification is synthesis of phytochelatins which form with their–SH group and cadmium ions various types of complexes (Grill et al., 1985). Formation of stress proteins is induced by any stress factors including toxic metals. In root cells contaminated by cadmium was found production of specific m-RNA transcripts which control synthesis of stress proteins (in detail see Tamás et al., 1997). Plants under Cd stress produce more ethylene, whereby higher amount of this gas is formed in roots than in the shoots (Rodecap et al. 1981).

Subsequently, the further reactions are initiated such are lignine formation (Ievinsh et al., 1995), induction of ascorbate peroxidase activity (Mehlhorn, 1990) and change in gene expression (Whitelaw et al., 1997).

2.4 Food – Quality, sufficiency, safety, and human health risks

Since food production lag behind the rate of growth in population, it is necessary to develop not only high-yielding varieties of food crops but also to develop strategies for integrated nutrient management, integrated pest management, and efficient utilization of water and soil resources. The identification of the origin, quality and authenticity of food, including ingredients and food sources is of prime importance for the protection of consumers. Moreover, traceability of substances in food plays important role for both food safety and human health risks. It means the ability to trace the substances in food "through all stages of production, processing and distribution": primary production, storage, transport, sale, importation, manufacture, distribution, supply (Regulation EC/178/2002 – General Food Low).

World Health Organisation (WHO) has stated its commitment on food safety as an essential public health issue and jointly with the Food and Agriculture Organisation (FAO) sponsor the Codex Alimentarius Commission where international standards on guidance are prepared for member and non-member states. In Europe, the European Food Safety Authority (EFSA) was also constituted for need to guarantee a high level of food safety.

Means and opportunities by which to satisfy the health and nutritional needs (using also GM crops) of impoverished nations and communities differ significantly from those who enjoy greater affluence. The planet´s resources and scientific ingenuity are sufficient to satisfy everyone´s need, but not everyone´s greed. Present and predictable world-wide demand for bioscientists and bioengineers exceeds best estimates of supply. Systematically planned, long-term investments by governments and bioindustries to generate adequate qualified people are urgently needed. (Hulse, 2002).

Food chain contamination is one of the important pathways for entry toxic metals as well as excessive and so harmful concentration of essential nutrients into the human body. The consumption of plants produced on contaminated agricultural soils together with inhalation of contaminated particles are two principal factors contributing to human exposure to metals. Wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust and various industrial activities also contribute to both soil and food crops contamination with toxic metals. Especially, wastewater-irrigated plants were contaminated with Cr, Cu, Ni, Pb and Cd and exceeded the permissible limits for vegetables set by SEPA (State Environmental Protection Administration, China) as well as WHO. Both, adults and children consuming food crops grown in wasterwater-irrigated soil ingest significant amount of the metals studied (in detail see Khan et al., 2008).

Potential health risks of humans and animals from consumption of food and fodder can be due to metal uptake from contaminated soils through plant roots or direct deposition of contaminants from the atmosphere onto plant surfaces. In the absence of a basic understanding of metal behavior in each specific situation, a more precautionary approach to toxic metal additions to soils is warranted (McBride, 2003). Therefore information about

toxic metal concentrations in food products and their dietary intake is very important for assessing their risk to human health (Zhuang et al., 2009).

It can be concluded that cultivation of crops for human (food) or livestock (fodder) consumption on soils contaminated by toxic metals can lead to the uptake and accumulation of these metals in the edible parts of plants with potential risk to both, animal and human health. However, different metals can behave entirely differently in the same soil, as can a particular metal in different soils. Detailed knowledge of the soil at the application site, especially pH, buffering capacity, organic matter and clay content, is so essential (McBride, 2003).

3. Medicinal plants

Chemical studies concerning therapeutical properties of medicinal plants are mostly directed to the determination of the structure of organic substances, especially those which might have to do with their medicinal uses. The importance of their mineral constituents is often overlooked in spite of evidence that many of them are essential to the medicinal plants themselves, and in most cases the synthesis of these organic compounds requires the action of enzymes containing metallic ions at their active centres. Furthermore, one has to consider that these same elements are important to animal and human beings and the knowledge of their concentration could help to explain the therapeutical properties of medicinal plants. Elements such are manganese, iron, copper or zinc operate as activators or enzymes important for healing process – synthesis of extracellular substances, cellular division, digestion of necrotic tissue etc. Considering that the elements are complexed with organic substances they can help to concentrate organic substances responsible for the action or the action can be due to the whole complex (in detail see Pereira & Felcman, 1998). Moreover, it could be stressed that toxic substances including toxic metals (or essential bioelements in higher than physiological concentration) are also very serious factor which negatively influences not only growth, production, structure and function of these important group of plants but also diminish their phytotherapeutical action.

3.1 Response of medicinal plants to metal presence

As has already been mentioned, medicinal plants have also responded on the changing environmental conditions. In our laboratory we focused on three medicinal species: *Hypericum perforatum* L., *Matricaria recutita* L. and *Salvia officinalis* L. which are in general the most frequent medicinal plants used in phytotherapy. Major constituents of *Hypericum perforatum* L. extracts include several classes of compounds exemplified by flavonols, flavonol glycosides, biflavones, naphthodianthrones, phloroglucinols, tannins, coumarins, essential oils, xanthophylls and others (Nahrstedt & Butterweck, 1997). These compounds are very important for this medicinal plant to preserve it against toxic metal stress. Thus, we studied tolerance of *H. perforatum* to toxic effect of copper and cadmium with respect to metal accumulation in individual plant organs (Kráľová & Masarovičová, 2004). It was confirmed that as the most sensitive parameter to Cu treatment was found to be the root dry mass. The length of shoot as well as shoot dry mass was not significantly affected. Lower values of root dry mass could be explained with significant reduction of lateral roots and root hairs by Cu treatment. The roots of *H. perforatum* accumulated markedly higher

concentrations of Cu than the shoots. The metal accumulation in both plant organs showed an increase with increasing metal concentration. Bioaccumulation factors (BAF), i.e. quotients obtained by dividing the concentration of the metal in dry mass of individual plant tissues (root and shoot, respectively) by its concentration in the external exposure medium, were also calculated. Taking into account the actual dry mass of individual plant organs (root and shoot), Cu portion in shoot was in the investigated concentration range approximately 20 % from the total uptaken metal content by the whole plant. With respect to relatively high Cd content in the shoot dry mass (1087 μg g^{-1}) *H. perforatum* could be classified as Cd hyperaccumulator. In this paper was firstly discussed possible contribution of the formation of metal complexes with secondary metabolites of *H. perforatum* to the plant metal tolerance. Later we stated (Masarovičová & Kráľová, 2007) that for plants producing specific secondary metabolites (medicinal plants) the further, additive mechanism of tolerance arose. This additive mechanism is connected with chelatation of metal ions by some specific secondary metabolites such are hypericin and pseudohypericin (Fig. 1) produced by *H. perforatum.* The toxic ionic form of metal is thus changed into non-toxic metal chelate. This assumption was based on the findings of Falk and Schmitzberger (1992) and Falk and Mayr (1997) who stated that the pronounced acidity of the *bay*-region hydroxyl groups of hypericin make salt formation a definite possibility: hypericin is present in the plant material mainly as its potassium salt. In addition, in structurally similar *bay*-hydroxylated fringelites salt formation with divalent ions, such as Ca^{2+} yields polymeric systems, which because of their extreme insolubility are highly stabile in fossils.

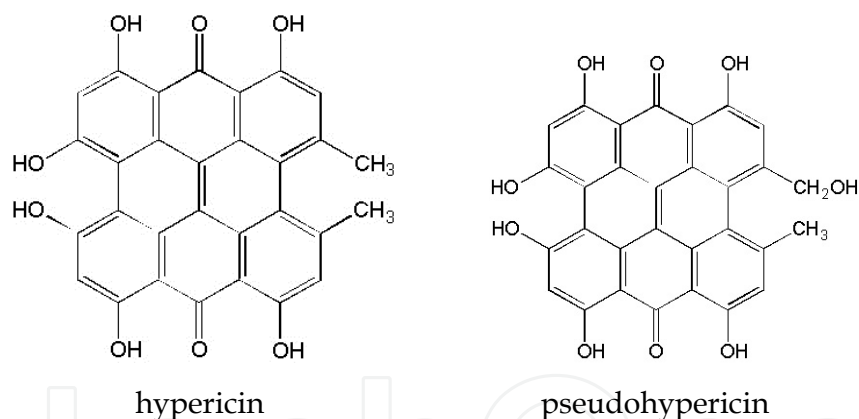hypericin   pseudohypericin

Fig. 1. Structures of hypericin and pseudohypericin.

The *peri*-hydroxyl groups situated in the neighbourhood of the carbonyl groups display the best prerequisites to form chelates with transition metal ions. Such coordination complexes could be characterized in the case of fringelite D and Zn^{2+} (Falk & Mayr, 1997).

Afterwards Palivan et al. (2001) investigated the formation of copper complexes with hypericin in solutions using EPR spectroscopy and found that hypericin forms a four-coordinated copper species where the solvent participates to the coordination sphere of the metal. Taking into account the above mentioned results concerning complex formation between hypericin and copper it could be assumed that this secondary metabolite of *H. perforatum* as well as structurally similar pseudohypericin will form similar complexes with further transition metal ions (Fig. 2). Due to such interaction the concentration of free metal ions will decrease and their toxic effect will diminished. Thus, formation of complexes

between heavy metals and the above mentioned secondary metabolites could be regarded as a further additive mechanisms contributing to enhanced tolerance of *H. perforatum* against divalent metals such as copper and cadmium.

The above-described chelatation of cadmium ions with hypericin could contribute to enhanced tolerance of *H. perforatum* plants to cadmium stress and to their cadmium hyperaccumulating ability (in detail see Masarovičová et al., 2011). Classification of this medicinal plant species as a Cd hyperaccumulator firstly was confirmed by Marquard and Schneider (1998) and consequently also in our research (Masarovičová et al., 1999; Kráľová et al., 2000).
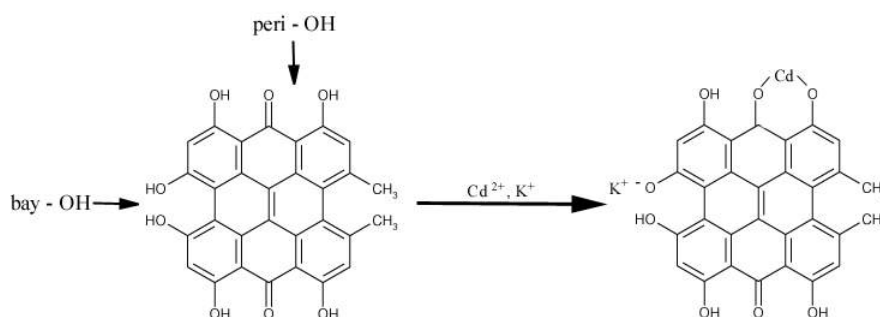

Fig. 2. Complex of hypericin with metal ions Cd^{2+} and K^+.

According to Murch et al. (2003) metal contamination can change the chemical composition of *H .perforatum,* thereby, seriously impacting the quality, safety and efficacy of natural plant substances produced by medicinal plant species. The seedlings of *H. perforatum* lost completely the capacity to produce or accumulate hyperforin and demonstrated a 15-20-fold decrease in the concentration of pseudohypericin and hypericin. Several authors confirmed that *M. recutita* species tolerate Cd concentrations corresponding to the middle-strong contaminated soils (Grejtovský & Prič, 2000; Masarovičová et al., 2003) and high Cd concentration in shoots assigns also this medicinal plant to Cd hyperaccumulators.

In our further paper (Kráľová et al., 2000) the effect of cadmium (12 µM $Cd(NO_3)_2$; pH = 5.5) on growth, plant biomass (root and shoot) and root dark respiration rate of *H. perforatum* (cultivated hydroponically) as well as cadmium accumulation in all plant organs was investigated. On the basis of found results it could be concluded that Cd enhanced the permeability of membranes in both root and shoots. Consequently, above mentioned metal ions were transported into the leaves where their higher content was estimated. Cd administration did not affect the growth and dry biomass of the shoot and root and the root:shoot ratio. However, the root dark respiration rate of the Cd-treated plants was faster than those of control plants.

It has been already mentioned that *M. recutita* L. belongs to the most favoured medicinal plants not only in Slovakia but also over the world (Masarovičová & Kráľová, 2007). This species produces a variety of volatile secondary metabolites, e.g. chamomillol, gossonorol, cubenol, α-cadinol, chamazulene, β-farnesene, (-)-α-bisabolol, (-)-α-bisabololoxide A, (-)-α-bisabololoxide B, 1-azulenethanol acetate and (-)-α-bisabolol acetate, herniarin, etc. Traditionally, in Eastern Slovakia large regions are used for commercial chamomile

cultivation. As chamomile species are long-term cultivated in field conditions, it is important to know how many of Cd is taken up from the soil, transported and accumulated in individual parts of plants. Therefore Cd content in the pharmaceutical important plant part - anthodium was also estimated (Šalamon et al., 2007).

Marquard & Schneider (1998) were the first to confirm that chamomile plants had the potential to accumulate high levels of cadmium from the soil. In our paper (Pavlovič et al., 2006) two tetraploid cultivars of *Matricaria recutita* L. (cv. Goral and cv. Lutea) were investigated in response to Cd application. Significant inhibition of root growth was observed in both chamomile cultivars after Cd-treatment. We did not found any differences in Cd accumulation in root between cultivars, but cv. Lutea accumulated slightly higher amount of Cd in the shoot. In root test we observed fragility, browning and twisting of roots. In shoots leaf roll, chlorosis and leaf growth inhibition occurred. During the root test chamomile plants cv. Goral formed the anthodia in all concentrations except control, despite the fact that the plants were only 3 weeks old. According to our observation, the plants started blossoming when they are 8 – 12 weeks old, however Cd treatment resulted in reduced size of flowers. The measurements confirmed higher inhibition of photosynthesis in cv. Lutea, although these plants accumulated less Cd than cv. Goral. Similar decrease of shoot dry weight in both cultivars was also detected. Decrease of net photosynthetic rate could be due to structural and functional disorders in many different levels. Shoot and root respiration rates were not changed significantly in both chamomile cultivars. We confirmed that chamomile belongs to the group of Cd accumulator species. If we take into account high content of Cd in chamomile shoot (over 300 µg g^{-1} at 12 µmol dm^{-3} Cd in solution), only small extent of damages occurred in Cd treated plants. Therefore this medicinal plant species exhibited high tolerance to Cd treatment. This fact was also confirmed by Masarovičová et al. (2003) when the effect of cadmium and zinc separately (10 µmol dm^{-3} for Cd and 50 µmol dm^{-3} for Zn), as well as combined application of these ions on physiological processes (photosynthetic rate and dark respiration rates of leaves and roots, chlorophyll concentration) and production parameters (shoot and root biomass, shoot:root ratio, length of shoots and roots) of young plants of *H. perforatum* and *M. recutita* was investigated. As the applied metal concentrations did not significantly affect studied parameters (except of root respiration rate) we can conclude that both investigated medicinal plants could be used in phytoextraction and subsequent remediation of soils contaminated by cadmium and zinc. Jakovljevic et al. (2000) investigated the influence of the different doses of sodium selenate (0, 100 and 500 g Se per hectare) applied by foliar spraying on the yield and quality of chamomile. The applied doses of Se did not influence the formation of dry chamomile flowers yield and the content of essential oil. However, the applied Se caused the significant increase of the content of bisabolol oxide A and B, followed by the decrease of the chamazulene content in the chamomile essential oil. Significant increase of Se content in the chamomile flowers (12.9 to 53.6 ppm) has also been observed.

Salvia officinalis L. is in general also one of the most important medicinal and aromatic plants with the great spectrum of application in phytotherapy, cosmetic and food industry. The genus *Salvia* includes more than 400 species. *S. officinalis* as a perennial plant originates from the Mediterranean region. In regard to the analysis of sage essential oil the major compounds are thujone, cineole, camphor and caryophyllene. These secondary metabolites are biologically active compounds in *herba salviae* having application in phytotherapy. In

food industry this aromatic plant species is recommended as a spice or additive substance (cf. Langer et al., 1996; Perry et al., 1999). From all above-mentioned aspects it is important to have information of toxic metal effects on growth and metal accumulation into the different plant organs of this species. Since Marquard & Schneider (1998) characterised *S. officinalis* as excluder of cadmium we studied effect of large external concentration range of cadmium (30 – 480 µmol dm^{-3} Cd(NO$_3$)$_2$) on production characteristics (length of roots and shoots as well as dry mass of roots and shoots) of this species. We tested two cultivars: cv. Krajova (Slovakian provenance) and cv. Primorska (Yugoslavian provenance). Two months old plants were cultivated hydroponically seven days under controlled conditions in Hoagland solution without and in the presence of Cd(NO$_3$)$_2$ (Masarovičová et al., 2004). There were found differences in phenology and production parameters between two tested cultivars of different provenance. Cv. Krajova was already sensitive to the concentration of 60 µmol dm^{-3} Cd(NO$_3$)$_2$ when the oldest leaves dried. At concentration of 120 µmol dm^{-3} Cd(NO$_3$)$_2$ all older leaves were dried and younger leaves were wilt. At the concentration 240 µmol dm^{-3} Cd(NO$_3$)$_2$ the brown spots were observed on the leaves and at the both applied highest metal concentrations (360 and 480 µmol dm^{-3} Cd(NO$_3$)$_2$) the all leaves were dried and on apical side of the leaves depigmentation was observed. Cultivar Primorska seems to be more tolerant to metal treatment. Visual changes occurred at the concentration of 120 µmol dm^{-3} Cd(NO$_3$)$_2$ when dried only some of older leaves of the plant. At the concentration of 240 µmol dm $^{-3}$ Cd(NO$_3$)$_2$ the leaves were dried but they were green coloured. This fact confirms the disturbance of water regime and indicated strong water stress. At highest tested Cd concentrations (360 and 480 µmol dm^{-3} Cd(NO$_3$)$_2$) all leaves were already dried and the damage of leaf pigmentation as the brown coloured spots was observed. In spite of high concentration of Cd (360 – 480 µmol dm^{-3}) length of the roots in both cultivars was almost not influenced. Also for the shoots of both cultivars only a slight reduction of length was found. On the other hand, dry mass of the shoots decreased at all applied Cd concentrations more expressively than the dry mass of the roots. The negative effect of the high Cd concentrations on the shoot dry mass was manifested mainly in cv. Krajova. Both cultivars uptaken the greatest portion of Cd into the roots, but cv. Primorska accumulated in the shoot app. two-times more Cd than cv. Krajova. However, differences were found in translocation of cadmium from roots into the shoots. Cv. Krajova did not allocate Cd from roots into the shoots already at 240 µmol dm^{-3} Cd(NO$_3$)$_2$ which confirm existence of some barriers in the roots.

4. Classification of metallophytes and plant strategies for metal uptake

A metallophyte is a plant that can tolerate high levels of toxic (heavy) metals. Such plants range between "obligate metallophytes" (which can only survive in the presence of these metals), and "facultative metallophytes" which can tolerate such conditions but are not confined to them. Metallophytes commonly exist as specialised flora found on spoil heaps of mines. Primarily these plants have potential for use for phytoremediation of contaminated ground. In our earlier paper (Masarovičová et al., 2010) classification of metallophytes and actual theory of the strategies in the response of plants to toxic metals were presented, and for hyper/accumulators and excluders the bioaccumulation and translocation factors were discussed. Based on this review the following outline could be described. Strategies of the plants grown on the metal containing soil, classified as accumulators and excluders, were first time published by Baker in 1981 (Baker, 1981) based on the ratio between leaf: root

metal concentration. Later this conception was improved suggesting the following two groups of plants: metal excluders and metal non-excluders (indicators, hyperaccumulators). The plant strategy of hyperaccumulators was originally introduced to define plants containing > 0.1 % (1000 μg g^{-1} on dry matter –DM-basis) of Ni in dried plant tissues (Brooks et al., 1977). For other metals such as Zn and Mn the threshold is 10 000 μg g^{-1} (1%) of metal in aerial dry mass. Baker et al. (1994) determined threshold for Cd 100 μg g^{-1} (0.01%). Nowadays the accepted concentration defining hyperaccumulation for Cd is still 0.01 % of this metal in the shoot. Hyperaccumulator plants can be regarded as one subset of a larger category of metal-tolerant plants. However, the exact relationship between metal tolerance and metal hyperaccumulation has not yet been fully resolved (Pollard et al., 2002). Recently, conditions for above-mentioned classification of plant strategies were improved by two further characteristics: bioaccumulation factor (BF or BAF) and translocation factor (TF). Both factors have to be considered for evaluation whether a particular plant is a metal hyperaccumulator (Ma et al., 2001). The term BF, defined as the ratio of metal concentrations in plant dry mass (μg.g^{-1} DM) to those in soils (μg g^{-1} soil), has been used to determine the effectiveness of plants in removing metals from soils (Tu and Ma, 2002). The term TF, defined as the metal concentration in plant shoot to this in the roots, has been used to determine the effectiveness of plants in translocating metal from the root to the shoot (Stoltz and Greger, 2002; Tu and Ma, 2002; Deng et al., 2004). However, fraction of accumulated metal allocated in shoots related to the total amount of metal accumulated by plants respects also actual plant biomass. Consequently, relative high value of this fraction could be also reached when TF value is lower, however actual shoot biomass is high. In the course of hyperaccumulation the following processes are usually observed: (a) higher metal uptake connected with high effectiveness of metal translocation from the root into the shoot, (b) preference of biomass allocation into the root where also high metal concentration occurs (c) development of larger root system in comparison with shoot biomass, which is favourable for total ion uptake by the plant (Cosio, 2004). These features are currently included in BAF. It should be stressed that complex study of plant species is needed to assort it to group of metal hyper/accumulators, metal excluders or plants tolerant to the tested metal. Moreover, all important parameters (e.g. bioaccumulation factor, translocation factor) should be estimated before recommendation if tested plant species is utilizable in phytoremediation technology.

4.1 Hyperaccumulating plants – How and why do they do it?

Recently appeared paper (Rascio & Navari-Izzo, 2011) describing three basic hallmarks to distinquish hyperaccumulators from related non-hyperaccumulating species: a strongly enhanced rate of toxic metal uptake, a faster root-to-shoot translocation and greater ability to detoxify and sequester metals in the leaves. An interesting breakthrough that has emerged from comparative physiological and molecular analyses of hyperaccumulators and related non-hyperaccumulators is that most key steps of hyperaccumulation rely on different regulation and expression of genes found in both kinds of plants. In particular, a determinant role in driving the uptake, translocation into the leaves, sequestration in vacuoles or cell walls of great amounts of toxic metals, is played in hyperaccumulators by constitutive overexpression of genes encoding transmembrane transporters. Among the hypotheses proposed to explain the function of hyperaccumulators, most evidence has supported the "elemental defence" hypothesis, which states that plants hyperaccumulate

toxic metals as defence mechanisms against natural enemies, such as herbivores. According to the most recent hypothesis of "joint effects", toxic metals can operate in concert with organic defensive compounds leading to enhanced plant defence overall. Above-mentioned authors stressed, that more elements and a larger number of hyperaccumulators need to be examined to validate the hypothesis of defensive effects of toxic metals. Moreover, the investigations need to move from laboratory to field conditions to provide realistic information about defence mechanism of the plants under natural stand. It should be emphasized the interest in the potential exploiting of hyperaccumulators as a rich genetic resource to develop engineered plants with enhanced nutritional value for improving public health or for contending with widespread mineral deficiencies in human vegetarian diets (Palmgren et al., 2008). This aspect concerning biofortification is discussed in the section 6 of this chapter.

5. Phytoremediation: Environmental-friendly, cost-effective and natural green biotechnology

Rapid expansion and increasing sophistication of various industries in the last century has remarkably increased the amount and complexity of toxic or hazardous substances, such are heavy metals, radionuclides, organic and inorganic wastes, pesticides, etc. which may be bioremediated by suitable organisms (plants and microbes). This technology was termed as bioremediation or phytoremediation (in detail see Singh & Tripathi, 2007). Phytoremediation is environmental-friendly, cost-effective and natural green biotechnology for the removing xenobiotics, including toxic metals, from the environment using some species of the plants. It seems unbelievable, that these pioneering ecological approaches appeared over the last 20 years. However, problem of toxic metals contamination of environment is still continuously worsening due to intensive, various and mostly negative human activities. This unfavourable state leads to intensification of research dealing with phytotoxicity of the metals and with mechanisms used by plants to face against their harmful effects. Great interest has been gained by the behaviour of hyperaccumulators growing on metalliferous soils, which accumulated toxic metals in the leaves at concentration much higher than other plant species. Aims of studying these hyperaccumulators has been to highlight physiological and molecular mechanisms underlying the hyperaccumulation ability, to discover adaptive functions performed by hyperaccumulation in these plants and to explore the possibility of using them as tools to remove metals from contaminated or natural metal-rich soils. However, in spite of important progress made in recent years by the numerous studies accomplished, the complexity of hyperaccumulation is far being understood and several aspects of this remarkable feature still await explanation (c.f. Rascio & Navari-Izzo, 2011).

5.1 Phytoremediation classification and principles

There are several types of phytoremediation technologies currently and quite successfully available for clean-up of both contaminated soils and water. The most important of them could be characterised as follows: reduction of metal concentration in the soil by cultivating plants with a high capacity for metal accumulation in the shoots **(phytoextraction)**, adsorption or precipitation of metals onto roots or absorption by the roots of metal-tolerant aquatic plants **(rhizofiltration)**, immobilization of metals in soils by adsorption onto roots or

precipitation in the rhizosphere **(phytostabilization)**, absorption of large amounts of water by fast growing plants and thus prevent expansion of contaminants into adjacent uncontaminated areas **(hydraulic control),** decomposition of organic pollutants by rhizosphere microorganisms **(rhizodegradation),** and re-vegetation of barren area by fast grown plants that cover soils and thus prevent the spreading of pollutants into environment **(phytorestauration) (**in detail see Masarovičová et al., 2009).

It was found that the most effective but also the most technically difficult phytoremediation technology is phytoextraction. This technology is based on hyperaccumulation of the metals into the whole plants. This approach involves cultivation of metal-tolerant plants (hyperaccumulators) that concentrate metals in the aboveground organs of the plant. At the end of the growing season, plant biomass is harvested, dried, and the contaminant-enriched mass is deposited in a special dump or added into a smelter. The energy gained from burning of the biomass could support the profitability of this technology, if the resultant fumes can be cleaned appropriately. For phytoextraction to be effective, the dry biomass or the ash derived from aboveground tissues of a phytoremediator crop should contain substantially higher concentrations of the contaminant than the polluted soil (Krämer, 2005).

Metal-tolerant species (including some of energetic crops such are *Hordeum vulgare, Triticum aestivum, Brassica napus, Brassica juncea, Helianthus annuus,*) can accumulate high concentration of some toxic metals in their aboveground biomass. As has already been mentioned, one group of metallophytes are hyperaccumulators (metal extractors). However, besides hyperaccumulators the fast-growing (high-biomass-producing) plants (e.g. *Salix* spp., *Populus* spp.) can also be used in phytoremediation technology. In spite of lower shoot metal-bioaccumulating capacity of these species, the efficient clean-up of contaminated substrates is connected with their high biomass production. Aronsson et al. (2002) have already recognized that it is both environmentally and economically appropriate to use vegetation filters of short rotation willow to purify waters and soils.

Capability of the plants to reduce the amount of heavy metals in contaminated soils depends on plant biomass production and their metal bioaccumulation factor, which is the ratio of metal concentration in the shoot tissue to the soil. The bioaccumulation factor is determined by the ability and capacity of the roots to take up metals and load them into the xylem, by the mass flow in the xylem stream as driven by transpiration, and by the ability to accumulate, store and detoxify metals while maintaining metabolism, growth and biomass production (Guerinot & Salt, 2001). With the exception of hyperaccumulators, most plants have metal bioconcentration factors less than 1, which means that it takes longer than a human lifespan to reduce soil contamination by 50%. To achieve a significant reduction of contaminants within one or two decades, it is therefore necessary to use plants that excel in either of these two factors, e.g. to cultivate crops with a metal bioconcentration factor of 20 and a biomass production of 10 tonnes per hectare (Mg/ha), or with a metal bioconcentration factor of 10 and a biomass production of 20 Mg/ha (Peuke & Rennenberg, 2005).

It was concluded that the most frequent practical application has phytoextraction which has been growing rapidly in popularity worldwide for the last twenty years. In general, this process has been tried more often for extraction of toxic metals than for organic substances. Phytoextraction as an environment friendly approach could be used for cleaning up sites that are contaminated with toxic metals. However, the method has been questioned because

it produces a biomass-rich secondary waste containing the extracted metals. Therefore, further treatment of this biomass is necessary - gasification (i.e. pyrolysis) which could help make phytoextraction more cost-effective. Hence, processing of biomass to produce energy and valuable ash in a form which can be used as ore or disposed safely at low cost is advantageous. Recovery of energy by biomass burn or pyrolysis could help to make the phytoextraction a cost-effective technology (Li et al., 2003).

5.2 Phytoattenuation

In general, term „ attenuation" is used in physics (in some context also called extinction) as a gradual loss in intensity of any kind of flux through a medium. Recently (Meers et al., 2010) appeared the first time term „phytoattenuation" for risk-reduction of metals in the produced biomass while allowing maximum economic valorisation of marginal land as main objectives. Before this notice, Meers et al. (2005) observed that of four biomass producing crops – energy plants (*Brassica rapa, Cannabis sativa, Helianthus annuus and Zea mays*) maize exhibited the highest biomass potential on moderately metal contaminated land, with the lowest metal accumulation in the harvestable plant parts. This fits well within the intended scope of phytoattenuation, namely risk-reduction of metals in the produced biomass (by using an excluder species) while allowing maximum economic valorisation of marginal land as main objectives. Otherwise, the primary objective in the current context is allowing an optimal economic use of marginal/contaminated land with risk-reduction of the metals in the produced biomass, whereas the second objective is the gradual "attenuation" of the metals from the soil.

It was recognized, that worldwide there are numerous regions where conventional agriculture is affected by the presence of elevated amounts of plant-available trace elements, causing economic losses and endanger or diminish food and feed quality and safety. Phytoremediation as a soil remediation technology only appears feasible if the produced biomass might be valorised in some manner. It was proposed the use of energy crops (such are maize, sunflower, or sorghum) aiming at risk-reduction and generation of an alternative income for agriculture, yet in the long run also a gradual reduction of the pollution levels. Since the remediation aspect is demoted to a secondary objective with sustainable risk-based land use as first objective, Meers et al. (2010) suggested and introduced the term "phytoattenuation". This concept is in analogy with "natural attenuation" of organic pollutants in soils where also no direct intended remediation measures but a risk-based management approach is implemented. In the current field experiment, cultivation of energy maize resulted in 33,000-46,000 kW h of renewable energy (electrical and thermal) per hectare per year which by substitution of fossil energy would imply a reduction of up to 21 tons ha^{-1} year^{-1} CO_2 if used to substitute a coal fed power plant. Metal removal was very low for Cd and Pb but more significant for Zn with an annual reduction of 0.4-0.7 mg kg^{-1} in the top soil layer. Above mentioned authors stressed that removal efficiency could be further enhanced by introducing winter crops for bio-energy purposes in crop rotation. The use of whole plant for industrial purposes is currently the only realistic scenario to combine phytoremediation with risk-based soil management. Metal concentrations in the green maize shoot were too high for use as fodder, but still were acceptable use as feedstock for anaerobic digestion. However, climatic conditions also play important role. Thus for warmer more southern regions in

Europe other crops such are maize, sunflower or sorghum may potentially serve as alternative energy crops for similar purpose. There is also an urgent need to find and characterize other hyperaccumulators, to cultivate them and better assess agronomic practices and management to enhance plant growth and metal uptake by selective breeding and gene manipulation. Even then, metal uptake might pose environmental risks, unless the biomass produced during the phytoremediation process could be rendered economically by burning it to produce bio-ore and converting it into bioenergy. However, according to the authors Rascio & Navari-Izzo (2011) it is only matter of time before the commercialization of phytoextraction using high-biomass hyperaccumulator plants becomes widespread, considering that not only will it remediate contaminated sites but will generate income from agricultural lands otherwise not utilized.

6. Biofortification a phytofortification

Biofortification is the process of increasing the bioavailable concentrations of essential nutrients in edible portions of food crops through agronomic intervention or genetic selection (White & Broadley, 2005). Phytofortification as a part of biofortification is the fortification of plants with essential nutrients, vitamins and metabolites during their growth and development, there by making these additives more readily available for human/animal consumption (in detail see Kráľová & Masarovičová, 2006). The idea of fortifying food crops with the essential minerals required for a healthy diet is thus relatively new. As many of the metals that can be hyperaccumulated are also essential nutrients, it is easy to see that food fortification and phytoremediation are two sides of the same coin (Guerinot & Salt, 2001).

Plants are at the beginning of food chain, therefore improving the nutrients uptake from soil and enhancing their movement and bioavailability in the edible parts (see below) of crops will provide benefits for both, animal and humans. It can be stated that biofortification provides a truly feasible means of reaching malnourished populations in relatively remote rural areas, delivering naturally-fortified foods to population groups with limited access to commercially-marketed fortified foods. According to Palmgren at al. (2008), there are two main challenges ahead: (i) to develop crops that have an increased content of essential nutrients in the edible parts of plant but that at the same time exclude toxic elements that exhibit similar chemical properties; and (ii) to avoid sequestration of nutrients in the inedible parts of plants, for example in the roots. A breeding approach to produce nutritionally improved food crops relies on genetic diversity in natural populations that can be crossbred to introduce traits/genes from one variety or line into a new genetic background.

Phytofortification is divided into agronomic and genetic phytofortification. The first one uses soil and spray fertilizers enriched by individual essential elements (e.g. Fe, Zn and Se). This approach has been adopted with success in Finland for enrichment of crops by Se. Agronomic biofortification could be used as a cost-effective method to produce high-Se wheat products that contain most Se in the desirable selenomethionine form. Increasing Se content in wheat is a food systems strategy that could increase the Se intake of whole populations. Genetic phytofortification presents the possibility to enrich food crops by selecting or breeding crop varieties, which enhanced Se accumulation characteristics

(Broadley et al., 2006). A strategy of genetic phytofortification offers a sustainable, cost-effective alternative to conventional supplementation and fortification programs. Genc et al. (2005) suggested that a combined strategy utilising (a) plant breeding for higher micronutrient density, (b) maximising the effects of nutritional promoters (e.g. inulin, vitamin C) by promoting favourable dietary combinations, as well as by plant breeding; and (c) agronomic biofortification (e.g. applying selenate to cereal crops by spraying or adding to fertiliser) is likely to be the most effective way to improve the nutrition of populations. Because selenium as an essential micronutrient for humans and animals is deficient in at least a milliard people worldwide, selenium-accumulating plants are a source of genetic material that can be used to alter selenium metabolism and tolerance to help develop food crops that have enhanced levels of anticarcinogenic selenium compounds (Ellis and Salt, 2003). Wheat (*Triticum aestivum* L.) is a major dietary source of Se. Agronomic biofortification (e.g. application of selenate on soil) could be used by food companies as a cost-effective method to produce high-Se wheat products that contain most Se in the desirable selenomethionine form. Increasing the Se content in wheat is a food systems strategy that could increase the Se intake of whole human population (Lyons et al., 2003, 2005). Finland, for example, fortifies with Se, although there is not strong evidence of selenium deficiency-related public health problems (Aro et al., 1998).

Finally, it has to be emphasized the interest in the potential exploiting of hyperaccumulators as a rich genetic resource to develop engineered plants with enhanced nutritional value for improving public health or for contending with widespread mineral deficiencies in human vegetarian diets (Palmgren et al., 2008). However, the strategies of food crop biofortification are still in infancy, even though that importance of biofortification for the humans makes this an exciting line of future research in the field of hyperaccumulation of essential bioelements.

7. Nanoparticles and plants

Nanoparticles (nano-scale particles = NSPs) are atomic or molecular aggregates with dimension between 1 and 100 nm that can drastically modify their physico-chemical properties compared to the bulk material. NSPs can be made from variety of bulk materials and they can act depending on chemical composition, size or shape of the particles. According to the Ruffini-Castiglione & Cremonini (2009) there were identified three types of NSPs: natural (e.g. volcanic or lunar dust, mineral composites), incidental (resulting from anthropogenic activity, e.g. diesel exhaust, coal combustion, welding fumes) and engineered. To the last type of NSPs belong also metal based materials – quantum dots, nanogold, nanozinc, nanoaluminium, TiO_2, ZnO and Al_2O_3 (Li & Xing, 2007). There is now an extensive discussion about the risks of the anthropogenic or engineered NSPs into environment, plants as well as human health. Handy et al. (2008) in their recent paper summarized information concerning the current status, knowledge gaps, challenges and future needs of NSPs ecotoxicology. These authors concluded that NSPs can be toxic to bacteria, algae, invertebrates and fish species, as well as mammals. However, much of the ecotoxicological data is limited to species used in regulatory testing and freshwater organism. Data on bacteria, terrestrial species, marine species and higher plants is particularly lacking. Till now only some studies have focused on the effects and mechanisms of nanomaterials on higher (vascular) plants. The results of these studies have been reported

by Ruffini-Castiglione & Cremonini (2009) with the aim to provide further insight into connections between plants and NSPs.

Stampoulis et al. (2009) studied effect of Ag, Cu, ZnO, and Si nanoparticles and their corresponding bulk counterparts on seed germination, root elongation, and biomass production of *Cucurbita pepo* plants which were grown in hydroponic solutions. It was found that seed germination was unaffected by any of the treatments, but Cu nanoparticles reduced emerging root length by 77% and 64% relative to untreated controls and seeds exposed to bulk Cu powder, respectively. Biomass of plants exposed to Ag nanoparticles was reduced by 75%. Although bulk Cu powder reduced biomass by 69%, Cu nanoparticle exposure resulted in 90% reduction of biomass relative to control plants. For Ag and Cu metals it was found, that half of the observed phytotoxicity originated from nanoparticles. Similarly, Li & Xing (2007) investigated effects of some metal nanoparticles (Al, Zn, ZnO) on seed germination and root growth of six plant species (radish, rape, rye-grass, lettuce, corn, and cucumber). Seed germination was not affected except for the inhibition of nanoscale zinc on ryegrass and zinc oxide on corn at 2000 mg/L. Inhibition on root growth varied greatly among nanoparticles and plants. Suspensions of 2000 mg/L nano-Zn or nano-ZnO practically terminated root elongation of the tested plant species. Fifty percent inhibitory concentrations (IC_{50}) of nano-Zn and nano-ZnO were estimated to be near 50 mg/L for radish, and about 20 mg/L for rape and ryegrass. The inhibition occurred during the seed incubation process rather than seed soaking stage.

Saison et al. (2010) studied toxic effect of core–shell copper oxide nanoparticles on the green alga *Chlamydomonas reinhardtii* with regards to the change of algal cellular population structure, primary photochemistry of photosystem II and reactive oxygen species formation. Algal cultures were exposed to 0.004, 0.01 and 0.02 g/L of core–shell copper oxide nanoparticles for 6 h. It was found that core–shell copper oxide nanoparticles induced cellular aggregation processes and had a deteriorative effect on chlorophyll by inducing the photoinhibition of photosystem II. The inhibition of photosynthetic electron transport induced a strong energy dissipation process via non-photochemical pathways. The deterioration of photosynthesis was interpreted as being caused by the formation of reactive oxygen species induced by core–shell copper oxide nanoparticles. However, no formation of reactive oxygen species was observed when *C. reinhardtii* was exposed to the core without the shell or to the shell only.

7.1 Biosynthesis of metal nanoparticles

In modern nanotechnology one of the most exciting area of research is the formation of nanoparticles (biosynthesis of metal nanoparticles) through the biological interventions. It is known, that plants also have inherent capacity to reduce metal through their specific metabolic pathway. Shekhawat & Arya (2009) used seedlings of *Brassica juncea* prepared *in vitro* to produce silver nanoparticles. Two weeks old seedlings were transferred into nutrient solution augmented with silver nitrate. After seven days (in hydroponics cultivated) plants were harvested and analyzed through UV-VIS spectrophotometer and by Transmission Electron Microscopy (TEM) that confirmed the nanoscale silver nanoparticles. Beattie & Haverkamp (2011) investigated sites for the reduction of metal ions Ag^+ and Au^{3+} to Ag^0 and Au^0 metal nanoparticles in *Brassica juncea* plants. Harvested plants were sectioned and

studied by transmission electron microscopy, total metal content was analysed by atomic absorption spectroscopy and chemical state of the both metals was determined using X-ray absorption spectroscopy. Nanoparticles of Ag^0 and Au^0 were found in leaves, stem, roots and cell walls of the plants at a concentration of 0.40% Ag and 0.44% Au in the leaves. It is interesting, that the sites of the most abundant reduction of metal salts to nanoparticles were chloroplasts, regions of high reducing sugar (glucose and fructose) content. Above mentioned authors proposed that these sugars are responsible for the reduction of these metals. At present these gold nanoparticles are also named „green-gold“. Similarly, Ankamwar (2010) reported synthesis of gold nanoparticles in aqueous medium using *Terminalia catappa* leaf extract as the reducing and stabilizing agent. On treating chloroauric acid with this leaf extract rapid reduction of chloroaurate ions was observed leading to the formation of highly stable gold nanopaticles in solution. Gold nanoparticles ranged in size from 10 to 35 nm with mean size of 21.9 nm. It was stressed by Kumar & Yadav (2009) that biosynthetic processes for nanoparticles would be more useful if nanoparticles were produced extracellularly using plants or their extracts and in a controlled manner according to their size, dispersity and shape. Plant use can also be suitably scaled up for large-scale synthesis of nanoparticles. These authors summarized plant species which can form silver and gold nanoparticles, to which belong well known species such are *Triticum aestivum, Avena sativa, Medicago sativa, Cicer arietinum, Pelargonium graveolens, Aloe vera* or many other species, e.g. *Cymbopogon flexuosus, Cinnamommum camphora, Azadirachta indica, Tamarindus indica, Emblica officinalis*, etc.

While many studies were aimed to metal uptake by plants, particularly with regard to phytoremediation and hyperaccumulation, only few have distinguished between metal deposition and metal salt accumulation. Therefore Haverkamp & Marshall (2009) described the uptake of $AgNO_3$, $Na_3Ag(S_2O_3)_2$, and $Ag(NH_3)_2NO_3$ solutions by hydroponically cultivated plants of *Brassica juncea* and the quantitative measurement of the conversion of these salts to silver metal nanoparticles. It was found that there is a limit on the amount of metal nanoparticles that may be deposited, of about 0.35 wt.% Ag on a dry plant basis, and that higher levels of silver are obtained only by the concentration of metal salts within the plant, not by deposition of metal. The limit on metal nanoparticle accumulation, across a range of metals, is proposed to be controlled by the total reducing capacity of the plant for the reduction of the metal species and limited to reactions occurring at an electrochemical potential greater than zero volts. Metal nanoparticles in plants were observed for gold, silver and copper. However, silver is very often used as a model compound because this metal not only can form metal nanoparticles in plants, but high levels of silver have been `achieved in plants, silver nanoparticles exhibit good catalytic properties, this metal has a high electrochemical reduction potential and also other useful properties.

It should be noticed, that not only vascular plants but also microorganisms such as bacteria, yeasts, algae, fungi and actinomycetes can be used for biosynthesis of nanoparticles (in detail see Sastry et al., 2003). However, Navarro et al. (2008) stressed, that there is a remarkable lack of information on some key aspects, which prevents a better understanding and assessment of the toxicity and ecotoxicity of nanoparticles, especially engineered nanoparticles to living organisms - vascular as well as non-vascular plants. Therefore, collaboration between ecotoxicologists, toxicologists, biologists, chemists, biophysicists, and analytical researchers is needed.

8. Utilization of metallomics for better understanding of metal-induced stress in plants

In the future for elucidation of the physiological roles and functions of biomolecules binding with metallic ions in the biological systems increasingly widespread use of metallomics could be expected. The term "metallome" was first coined by Williams (2001) who referred to it as an element distribution, equilibrium concentrations of free metal ions, or as a free element content in a cellular compartment, cell, or organism and the ensemble of research activities related to metal ions in biological systems has been recently referred to as "metallomics" (Haraguchi, 2004). Later it was proposed that the term "metallome" should be extended to the entirety of metal and metalloid species present in a cell or tissue type (Szpunar, 2004). In the study of metallomics, elucidation of the physiological roles and functions of biomolecules binding with metallic ions in the biological systems should be the most important research target. According to Haraguchi (2004), metallomics may be called, in another words, "metal-assisted function biochemistry". The wider use of molecular biology methods is expected to complement the *in vivo* bioanalytical data with *in vitro* molecular genetic data and lead to an understanding of metal functions at the molecular level (Mounicou and Lobinski, 2008). Lombi et al. (2011) summarized in detail the main techniques used to investigate metal(loids) *in situ* in plants, including histochemical techniques, autoradiography, laser ablation inductively coupled plasma mass spectrometry ((LA)-ICP-MS), secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), proton/particle induced X-ray emission (PIXE), synchrotron techniques (utilising high energy X-rays), X-ray fluorescence spectroscopy, tomography—differential absorption, tomography—fluorescence, as well as X-ray absorption spectroscopy (XAS). However, it could be stressed that sample preparation will continue to be a critical step for the majority of *in situ* techniques and in this regard the physiological aspects, in relation to sample preparation, should be at least as important as the methodological needs. Comprehensive review papers related to metallomics were published by Mounicou et al. (2009), Lobinski et al. (2010) and Arruda &Azevedo (2009).

9. Some aspects of bioethics

It should be stressed that negative effects of toxic metals on crops and medicinal plants is manifested not only in undesirable decrease of yield but also in endangered food safety what is serious action and intervention into the whole human population (cf. Nasreddine & Parent-Massin, 2002; Prasad 2004; Reeves & Chaney, 2008). From global aspect it can be stated that crops have dominant use as a food and fodder. Only in advanced and highly-developed countries these plants are also used as technical plants (e.g. for alternative source of energy or environment protection). Therefore it is so stressed ethical aspect if the crops (e.g. maize, cereals, potatoes, rapeseed, and sunflower) could be used exclusively for alimentary purposes or also as an alternative energy source. Moreover, topic of the effect of toxic substances including heavy metals on physiological and production characteristics of the both, crops and medicinal plants is in general extraordinarily important.

10. Conclusion

Numerous regions in the world are known where cultivation of food crops and medicinal plants is irresponsible due to the presence of excessive amounts of plant-available toxic

metals, leading to economic losses and negative effects for the human food chain as well as for human health. It was stressed that cultivation and use of crops and medicinal plants have to respect the potential hazard connected with environmental contamination, mainly with toxic metals. Although, some of metals are bioelements (macro- and micronutrients) at normal concentration, they can cause harmful effects on the plants in excess. Therefore, new and environmental-friendly, cost-effective and natural green technologies, such phytoremediation appeared to remove the harmful metals from the environment. This review has illustrated from the known behaviour of toxic metals that broad assumptions about the general behaviour and bioavailability of metal contaminants should be considered from many aspects including the metal nanoparticles – their formation as well as action on physiological processes of the plants. It was described that there were developed strategies of the plants grown on the metal containing soil, classified as metal excluders and metal non-excluders (indicators, hyperaccumulators). Since anthropogenic activity also affects medicinal plants it was mentioned that this group of plants likewise have non-traditional use in phytoremediation and biofortification technologies. Moreover, crops and medicinal plants can be used as supplementary nutrition due to their ability to accumulate some essential nutrition elements (e.g. Se, Zn, and Fe) in the edible parts of these plants. Such fortification of plants with essential nutrients (phytofortification) in an easily assimilated form can help to feed the rapidly increasing world population and improve human health through balanced mineral nutrition. It was stated that crops have dominant use as a food and fodder. However, only in advanced and highly-developed countries these plants are also used as technical plants. Therefore it was stressed ethical aspect if the crops could be utilised exclusively for alimentary purposes or also as an alternative energy source.

11. Acknowledgments

12. References

Ankamwar, B. (2010). Biosynthesis of gold nanoparticles (green-gold) using leaf extract of *Terminalia catappa*. *E-Journal of Chemistry*, Vol. 7, No. 4, (October – December 2010), pp. 1334-1339, ISSN 0973-4945

Aro, A.; Alfthan, G.; Ekholm, P. & Varo, P. (1998). Effects of selenium supplementation of fertilizers on human nutrition and selenium status. *Environmental Chemistry of Selenium*, Book Series: *Books in Soils Plants and the Environment*, W.T. Frankenberger & R.A. Engberg, (Ed.), Vol. 64, pp. 81-97

Aronsson, P.; Heinsoo, K.; Perttu, K. & Hasselgren, K. (2002). Spatial variation in above-ground growth in unevenly wastewater-irrigated willow *Salix viminalis* plantations. *Ecological Engineering,* Vol. 19, No. 4, (October 2002), pp. 281-287, ISSN 0925-8574

Arruda, M.A.Z. & Azevedo, R.A. (2009). Metallomics and chemical speciation: towards a better understanding of metal-induced stress in plants. *Annals of Applied Biology*, Vol. 155, No. 3, pp. 301-307, ISSN 0003-4746

Baker, A.J.M. (1981). Accumulators and excluders – strategies in the response of plants to heavy metals. *Journal of Plant Nutrition*, Vol. 3, No. 1-4, pp. 643–654, ISSN 0190-4167

Baker, A.J.M.; Reeves, R.D. & Hajar A.S.M. (1994). Heavy-metal accumulation and tolerance in British populations of the metallophyte *Thlaspi caerulescens* J and C pressl (Brassicaceae). *New Phytologist*, Vol. 127, No. 1, (May 1994), pp. 61–68, ISSN 0028-646X

Barceló, J. & Poschenrieder, C. (1990). Plant water relations as affected by heavy metal stress: A review. *Journal of Plant Nutrition*, Vol. 13, No. 1, (January 1990), pp. 1-37, ISSN 0190-4167

Beattie, I.R. & Haverkamp, R.G. (2011). Silver and gold nanoparticles in plants: sites for their reduction to metal. *Metallomics*, Vol. 3, No. 6, (May 2011), pp. 628-632, ISSN 1756-5901

Broadley, M.R.; White, P.J.; Bryson, R.J.; Meacharn, M.C.; Bowen, H.C.; Johnson, S.E.; Hawkesford, M.J.; McGrath, S.P.; Zhao, F.J.; Breward N.; Harriman, M. & Tucker, M. (2006). Biofortification of UK food crops with selenium. *Proceedings of the Nutrition Society*, Vol. 65, No. 2, (May 2006), pp.169-181, ISSN 0029-6651

Brooks, R.R.; Lee, J.; Reeves, R.D. & Jaffré, T. (1977). Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *Journal of Geochemical Exploration*, Vol. 8, No. 3, pp. 49–57. ISSN 0375-6742

Budíková, S. & Mistrík, I. (1999). Cultivar characterization of aluminium tolerance of barley seedlings by root growth, aluminium and callose distribution. *Biologia (Bratislava)*, Vol. 54, No. 4, (August 1990), pp. 447-451. ISSN 0006-3088

Burzynski, M. (1990). Activity of some enzymes involved in NO_3^- assimilation in cucumber seedlings treated with lead or cadmium [NADH-glutamate synthase]. *Acta Physiologiae Plantarum*, Vol. 12, No. 2, pp. 105-110. ISSN 0137-5881

Codex alimentarius. Available from http://www.codexalimentarius.net/

Cosio, C. (2004). Phytoextraction of heavy metal by hyperaccumulating and non hyperaccumulating plants: comparison of cadmium uptake and storage mechanisms in the plants. PhD Thesis, École Polytechnique Fédérale de Lausanne, 119 p, Available from
http://biblion.epfl.ch/EPFL/theses/2004/2937/EPFL_TH2937.pdf

Deng, H.; Ye, Z.H.; Wong, M.H. (2004). Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal contaminated sites in China. *Environmental Pollution*, Vol. 132, No. 1, (November 2004), pp.29-40, ISSN 0269-7491

di Toppi, L.S. & Gabbrielli, R. (1999). Response to cadmium in higher plants. *Environmental and Experimental Botany*, Vol. 41, No. 2, (April 1999), pp.105-130, ISSN 0098-8472

Ellis, D.R. & Salt, D.E. (2003). Plants, selenium and human health. *Current Opinion in Plant Biology*, Vol. 6, No. 3, (June 2003), pp. 273-279, ISSN 1369-5266

Falk, H. & Schmitzberger, W. (1992). On the nature of soluble hypericin in *Hypericum* species. *Monatshefte für Chemie*, Vol. 123, No. 8-9, (August-September 1992), pp. 731-739, ISSN 0026-9247

Falk, H. & Mayr, E. (1997). Concerning bay salt and peri chelate formation of hydroxy-phenanthroperylene quinines (fringelites). *Monatshefte für Chemie*, Vol. 128, No. 4, (April 1997), pp. 353-360, ISSN 0026-9247

Food and Agriculture Organization of United Nations.Available from http://www.fao.org/

Genc, Y.; Humphries, M.J.; Lyons, G.H. & Graham, R.D. (2005). Exploiting genotypic variation in plant nutrient accumulation to alleviate micronutrient deficiency in

populations. *Journal of Trace Elements in Medicine and Biology*, Vol. 18, No. 4, (June 2005), pp.319-324, ISSN 0946-672X

Grejtovský, A. & Prič, R. (2000). The effect of high cadmium concentration in soil on growth, uptake of nutrient and some heavy metals on *Chamomilla recutita* (L.) Rauschert. *Journal of Applied Botany-Angewandte Botanik*, Vol. 74, No. 5-6 (December 2000), pp. 169-174, ISSN 0949-5460

Grill, E.; Winnacker, E.L. & Zenk, M.H. (1985). Phytochelatins: the principal heavy-metal complexing peptides of higher plants. *Science*, Vol. 230, No. 4726, (November 8, 1985), pp. 674-676, ISSN 0036-8075

Guerinot, M.L. & Salt, D.E. (2001). Fortified foods and phytoremediation. Two sides of the same coin. *Plant Physiology*, Vol. 125, No. 1, (January 2001), pp. 164-167, ISSN 0032-0889

Gupta, U.C. & Gupta, S.C. (1998). Trace element toxicity relationships to crop production and livestock and human health: Implications for management. *Communications in Soil Science and Plant Analysis*, Vol. 29, No. 11-14, pp. 1491-1522, ISSN 0010-3624

Hagemeyer, J.; Kahle, H.; Breckle, S.W. & Waisel, Y. (1986). Cadmium in *Fagus sylvatica* L. trees and seedlings: leaching, uptake and interconnection with transpiration. *Water, Air and Soil Pollution*, Vol. 29, No. 4, (August 1986), pp. 347-359, ISSN 0049-6979

Handy, R.D., Owen, R. & Valsami-Jones, E. (2008). The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges and future needs. *Ecotoxicology*, Vol. 17, No. 5, (July 2008), pp. 315-325, ISSN 0963-9292

Haraguchi, H. (2004). Metallomics as integrated biometal science. *Journal of Analytical Atomic Spectrometry*, Vol. 19, No. 1, (January 2004), pp. 5-14, ISSN 0267-9477

Hattab, S.; Dridi, B.; Chouba, L.; Kheder, M.B. & Bousetta, H. (2009). Photosynthesis and growth response of pea *Pisum sativum* L. under heavy metals stress. *Journal of Environmental Sciences*, Vol. 21, No. 11, pp. 1552-1556, ISSN 1001-0742

Heverkamp, R.G. & Marshall, A.T. (2009). The mechanism of metal nanoparticle formation in plants: limits on accumulation. *Journal of Nanoparticle Research*, Vol 11, No. 6, (August 2009), pp. 1453-1463, ISSN 1388-0764

Hulse, J.H. (2002). Ethical issues in biotechnologies and international trade. *Journal of Chemical Technology and Biotechnology*, Vol. 77, No .5, (May 2002), pp. 607-615, ISSN 0268-2575

Ievinsh, G.; Valcina, A. & Ozola, D. (1995). Induction of ascorbate peroxidase activity in stressed pine *(Pinus sylvestris* L. *)* needles: a putative role for ethylene. *Plant Science*, Vol. 112, No. 2, (December 1995), pp. 167-173, ISSN 0168-9452

Jakovljevic, M.; Antic-Mladenovic, S.; Ristic, M.; Maksimovic, S. & Blagojevic, S. (2000). Influence of selenium on the yield and quality of chamomile (*Chamomilla recutita* (L.) Rausch.). *Rostlinná Výroba-Plant Production*, Vol. 46, No. 3, pp. 123-126, ISSN 0370-663X

Khan, S.; Cao, Q.; Zheng, Y.M.; Huang, Y.Z. & Zhu, Y.G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*, Vol. 152, No. 3, (April 2008), pp. 686-692, ISSN 0269-7491

Kráľová, K.; Masarovičová, E. & Bumbálová, A. (2000). Toxic effect of cadmium on *Hypericum perforatum* plants and green alga *Chlorella vulgaris*. *Chemia i Inžynieria Ekologiczna*, Vol.7, No. 11, pp. 1200-1205, ISSN 1231-7098

Kráľová, K. & Masarovičová, E. (2004). Could complexes of heavy metals with secondary metabolites induce enhanced metal tolerance of *Hypericum perforatum*? In: *Macro and Trace Elements. Mengen- und Spurenelemente*. ed. M. Anke et al., 411-416. 22. Workshop, Jena, 24.-25.09, Friedrich Schiller Universität

Kráľová, K. & Masarovičová, E. (2006). Plants for the future. *Ecological Chemistry and Engineering*, Vol. 13, No. 11, pp. 1179-1207, ISSN 1231-7098

Krämer, U. (2005). Phytoremediation: novel approaches to cleaning up polluted soils. *Current Opinion in Biotechnology*, Vol. 16, No. 2, (April 2005), pp. 133-141, ISSN 0958-1669

Kranner, I. & Colville, L. (2011). Metals and seeds: Biochemical and molecular implications and their significance for seed germination. *Environmental and Experimental Botany*, Vol. 72, No. 1, (August 2011), pp. 93-105, ISSN 0098-8472

Kumar, V. & Yadav, S.K. (2009). Plant-mediated synthesis of silver and gold nanoparticles and their application. *Journal of Chemical Technology and Biotechnology*, Vol. 84, No. 2, (February 2009), pp. 151-157, ISSN 0268-2575

Langer, R.; Mechtler, C. & Jurenitsch, J. (1996). Composition of essential oils of commercial samples of *Salvia officinalis* L. and *S. fruticosa* Mill.: a comparison of oils obtained by extraction and steam distillation. *Phytochemical Analysis*, Vol. 7, No. 6, (November-December 1996), pp. 289-293, ISSN 0958-0344

Li, Y.M.; Chaney, R.; Brewer, E.; Roseberg, R.; Angle, J.S.; Bake, A.; Reeves, R. & Nelkin, J. (2003). Development of a technology for commercial phytoextraction of nickel: economic and technical considerations. *Plant and Soil*, Vol. 249, No. 1, (February 2003), pp. 107-115, ISSN 0032-079X

Lin, D. & Xing, B. (2007). Phytotoxicity of nanoprticles: inhibition of seed germination and root growth. *Environmental Pollution,* Vol.150, No. 2, (November 2007), pp. 243-250, ISSN 0269-7491

Lobinski, R.; Becker, J.S.; Haraguchi, H. & Sarkar, B. (2010). Metallomics: Guidelines for terminology and critical evaluation of analytical chemistry approaches (IUPAC Technical Report). *Pure and Applied Chemistry,* Vol. 82, No. 2, (February 2010), pp. 493–504, ISNN 0033-4545

Lombi, E.; Scheckel, K.G. & Kempson, I.M. (2011). *In situ* analysis of metal(loid)s in plants: plants: State of the art and artefacts. *Environmental and Experimental Botany*, Vol. 72, No. 1, (August 2011), pp. 3–17, ISSN 0098-8472

Lynch, J. P. (2007). Roots of the second green revolution. *Australian Journal of Botany*, Vol. 55, No. 5, pp. 493-512, ISSN 0067-1924

Lyons, G.; Stangoulis, J. & Graham, R. (2003). High-selenium wheat: biofortification for better health. *Nutrition Research Reviews*, Vol. 16, No. 1, (June 2003), pp. 45-60, ISSN 0954-4224

Ma, L.Q.; Komar, K.M.; Tu, C.; Zhang, W.H.; Cai, Y. & Kennelley, E.D. (2001). A fern that hyperaccumulates arsenic - A hardy, versatile, fast-growing plant helps to remove arsenic from contaminated soils. *Nature,* Vol. 409, No. 6820, (February 2001), p. 579, ISSN 0028-0836

Marquard, R. & Schneider, M. (1998). Zur Cadmiumproblematik im Arzneipflanzenbau. In: *Fachtagung Arznei- und Gewűrzpflanzen*. R. Marquard & E. Schubert, (Ed.), 9-15, 1.-2. 10.1998, Giessen, Germany.

Masarovičová, E.; Kráľová, K.; Šeršeň, F.; Bumbálová, A. & Lux, A. (1999). Effect of toxic effects on medicinal plants. In: *Mengen- und Spurelemente,* M. Anke et al., (Ed.), 189-196, 19. Arbeitstagung, Jena, 3 - 4. 2. 1999, Leipzig, Verlag Harald Schubert

Masarovičová, E.; Kráľová, K. & Streško, V. (2003). Effect of metal ions on some medicinal plants. *Chemia i Inžynieria Ekologiczna,* Vol. 10, No. 3-4, pp. 275-279, ISSN 1231-7098

Masarovičová, E.; Kráľová, K. & Streško, V. (2004). Comparative study of uptake, accumulation and some effects of cadmium in two cultivars of *Salvia officinalis* L. *Chemia i Inžynieria Ekologiczna,* Vol. 11, No. 2-3, pp. 209-214, ISSN 1231-7098

Masarovičová, E. & Kráľová, K. (2007). Medicinal plants – past, nowadays, future. *Acta Horticulturae,* Vol. 749, pp. 19- 27, ISSN 0567-7572, ISBN 978 90 6605 530 8

Masarovičová, E.; Kráľová, K. & Peško, M. (2009). Energetic plants – Cost and benefit. *Ecological Chemistry and Engineering* S, Vol.16, No.3, pp. 263-276, ISSN 1231-7098

Masarovičová, E.; Kráľová, K. & Kummerová, M. (2010). Principles of classification of medicinal plants as hyperaccumulators or excluders. *Acta Physiologiae Plantarum*, Vol. 32, No. 5, (September 2010), pp. 823-829, ISSN 0137-5881

Masarovičová, E.; Kráľová, K. & Šeršeň, F. (2011). Plant Responses to Toxic Metal Stress. In: *Handbook of Plant and Crop Stress*, 3rd Edition, M. Pessarakli, (Ed.), 595-634, Boca Raton, CRC Press, ISBN 978-1-4398-1396-6

McBride, M.B. (2003). Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? *Advances in Environmental Research,* Vol. 8, No. 1, (October 2003), pp. 5-9, ISSN 1093-0191

Meers, E.; Ruttens, A.; Hopgood, M.; Lesage, E. & Tack, F.M.G. (2005). Potential of *Brassica rapa, Cannabis sativa, Helianthus annuus* and *Zea mays* for phytoextraction of heavy metals from calcareous dredged sediment derived soils. *Chemosphere*, Vol. 61, No, 4, (October 2005), pp. 561-572, ISSN 0045-6535

Meers, E.; Van Slycken, S.; Adriaensen, K.; Ruttens, A.; Vangronsveld, J.; Du Laing, G.; Witters, N.; Thewys, T. & Tack, F.M.G. (2010). The use of bio-energy crops (*Zea mays*) for „phytoattenuation" of heavy metals on moderately contaminated soils: A field experiment. *Chemosphare*, Vol. 78, No. 1, (January 2010), pp. 35-41, ISSN 0045-6535

Mehlhorn, H. (1990). Ethylene-promoted ascorbate peroxidase activity protects plants against hydrogen peroxide, ozone and paraquat. *Plant Cell and Environment*, Vol. 13, No. 9, (December 1990), pp. 971-976, ISSN 0140-7791

Mounicou, S. & Lobinski, R. (2008). Challenges to metallomics and analytical chemistry solutions. *Pure and Applied Chemistry,* Vol. 80, No. 12, (December 2008), pp, 2565–2575, ISSN 0033-4545

Mounicou, S.; Szpunar, J. & Lobinski, R. (2009). Metallomics: the concept and methodology. *Chemical Society Reviews*, Vol. 38, No. 4, pp. 1119-1138, ISSN 0306-0012

Murch, S.J.; Haq, K.; Rupasinghe, H.P.V. & Saxena, P.K. (2003). Nickel contamination affects growth and secondary metabolite composition of St. John's wort (*Hypericum perforatum* L.). *Environmental and Experimental Botany*, Vol. 49, No. 3, (June 2003), pp. 251-257, ISSN 0098-8472

Nahrstedt, A. & Butterweck, V. (1997). Biologically active and other chemical constituents of the herb of *Hypericum perforatum* L. *Pharmacopsychiatry*, Vol. 30, Suppl. 2, (September 1997), pp. 129-134, ISSN 0176-3679

Nasreddine, L. & Parent-Massin, D. (2002). Food contamination by metals and pesticides in the European Union. Should we worry? *Toxicology Letters*, Vol. 127, No. 1-3, February 2002), pp. 29-41. ISSN 0378-4274

Navarro, E.; Baun, A.; Behra, R.; Hartmann, N.B.; Fisler, J.; Miao, A.J.; Quigg, A.; Santschi, P.H. & Sigg, L. (2008). Environmental behaviour and ecotoxicity of engineered nanoparticles to algae, plants and fungi. *Ecotoxicology*, Vol. 17, No. 5, (July 2008), pp. 372-386, ISSN 0963-9292

Palivan, C.G.; Gescheidt, G. & Weiner, L. (2001). The formation of copper complexes with hypericin, in solutions: An EPR study. *Journal of Inorganic Biochemistry*, Vol. 86, No. 1, (August 2001), pp. 369-369, ISSN 0162-0134

Palmgren, M.G.; Clemens, S.; Williams, L.E.; Krämer, U.; Borg, S.; Schjorring, J.K. & Sanders, D. (2008). Zinc biofortification of cereals: problems and solutions. *Trends in Plant Science*, Vol. 13, No. 9, (September 2008), pp. 464-473, ISSN 1360-1385

Pavlovič, A.; Masarovičová, E.; Kráľová, K. & Kubová, J. (2006). Response of chamomile plants (*Matricaria recutita* L.) to cadmium treatment. *Bulletin of Environmental Contamination and Toxicology*, Vol. 77, No. 5, (November 2006), pp. 763-771, ISSN 0007-4861

Pereira, C.E.D. & Felcman J. (1998). Correlation between five minerals and the healing effect of Brazilian medicinal plants. *Biological Trace Element Research*, Vol. 65, No. 3, (December 1998), pp. 251-259, ISSN 0163-4984

Perry, N.B.; Anderson, R.E.; Brennan, N.J.; Douglas, M.H.; Heaney, A.J.; McGimpsey, J.A. & Smallfield, B.M. (1999). Essential oils from dalmatian sage (*Salvia officinalis* L.): variations among individuals, plant parts, seasons, and sites. *Journal of Agricultural and Food Chemisry*, Vol. 47, No. 5, (May 1999), pp. 2048-2054, ISSN 0021-8561

Peuke, A.D. & Rennenberg, H. (2005). Phytoremediation. *EMBO Reports*, Vol. 6, No. 6, (June 2005), pp. 497–501, ISSN 1469-221X
http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1369103

Pollard, A.; Powell, K.; Harper, F. & Smith, J. (2002). The genetic basis of metal hyperaccumulation in plants. *Critical Reviews of Plant Sciences*, Vol. 21, No. 6, pp. 539– 566, ISSN 0735-2689

Prasad, M.N.V. (2004). *Heavy metal stress in plants: from biomolecules to ecosystems*, 2nd ed., Berlin: Springer, ISBN 3-540-40131-8

Prescott, V.E. & Hogan, S.P. (2006). Genetically modified plants and food hypersensitivity diseases: Usage and implications of experimental models for risk assessment. *Pharmacology & Therapeutics*, Vol. 111, No. 2, (August 2006), pp. 374-383, ISSN 0163-7258

Rascio, N. & Navari-Izzo, F. (2011). Heavy metal hyperaccumulating plants: How and why do they do it ? And what makes them so interesting ? *Plant Science*, Vol. 180, No. 2, (February 2011), pp. 169-181, ISSN 0168-9452

Raven, K.P. & Leoppert, R.H. (1997). Trace element composition of fertilizers and soil amendments. *Journal of Environmental Quality*, Vol. 26, No. 2, (March-April 1997), pp. 551-557, ISSN 0047-2425

Reeves, P.G. & Chaney, R.L. (2008). Bioavailability as an issue in risk assessment and management of food cadmium. A review. *Science of the Total Environment*, Vol. 398, No. 1-3, (July 2008), pp. 13-19, ISSN 0048-9697

Regulation (EC) No 178/2002 of the European Parliament and of the Council of 28 January 2002, Available from
  http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32002R0178:EN: NOT

Rodecap, K.D.; Tingey, D.T. & Tibbs, J.H. (1981). Cadmium-induced ethylene production in bean plant. *Zeitschrift für Pflanzenphysiologie*, Vol. 105, pp. 65–74, ISSN 0044-328X

Ruffini-Castiglione, M. & Cremonini, R. (2009). Nanoparticles and higher plants. *Caryologia*, Vol. 62, No. 2, (April 2009), pp. 161-165, ISSN 0008-7114

Saison, C.; Perreault, F.; Daigle J.C.; Fortin, C.; Claverie, J.; Morin, M. & Popovic, R. (2010). Effect of core-shell copper oxide nanoparticles on cell culture morphology and photosynthesis (photosystem II energy distribution) in the green alga, *Chlamydomonas reinhardtii. Aquatic Toxicology*, Vol. 96, No. 2, (January 2010), pp. 109-114, ISSN 0166-445X

Šalamon, I.; Kráľová, K. & Masarovičová, E. (2007). Accumulation of cadmium in chamomile plants cultivated in Eastern Slovakia regions. *Acta Horticulturae. (ISHS)*, Vol. 749, pp. 217-222, ISSN 0567-7572, ISBN 978 90 6605 530 8

Sastry, M.; Ahmad, A.; Khan, M.I. & Kumar, R. (2003). Biosynthesis of metal nanoparticles using fungi and actinomycete. *Current Science*, Vol. 85, No. 2, (July 2003), pp. 162–170, ISSN 0011-3891

Seršeň, F. & Kráľová, K. (2001). New facts about $CdCl_2$ action on the photosynthetic apparatus of spinach chloroplasts and its comparison with $HgCl_2$ action. *Photosynthetica*, Vol. 39, No. 4, pp. 575-580, ISSN 0300-3604

Shanker, A.K.; Cervantes, C.; Loza-Tavera, H. & Avudainayagam, S. (2005). Chromium toxicity in plants. *Environment International*, Vol. 31, No. 5, (July 2005), pp. 739-753, ISSN 0160-4120

Shekhawat, G. S. & Arya, V. (2009). Biological synthesis of Ag nanoparticles through i*n vitro* cultures of *Brassica juncea* Czern. *Nanomaterials and Devices: Processing and Applications*. Book Series: Advanced Materials Research, Vol. 67, pp. 295-299, ISSN 1022-6680, ISBN 978-0-87849-328-9

Shukla, U.C.; Singh, J.; Joshi, P.C. & Kakkar, P. (2003). Effect of bioaccumulation of cadmium on biomass productivity, essential trace elements, chlorophyll biosynthesis, and macromolecules of wheat seedlings. *Biological Trace Element Research*, Vol. 92, No. 3, (June 2003), pp. 257-273, ISSN 0163-4984

Siedlecka, A. (1995). Some aspects of interactions between heavy metals and plant mineral nutrients. *Acta Societatis Botanicorum Poloniae*, Vol. 64, No. 3, pp. 265-272, ISSN 0001-6977

Siedlecka, A. & Krupa, A. (1996). Interaction between cadmium and iron and its effects on photosynthetic capacity of primary leaves of *Phaseolus vulgaris. Plant Physiology and Biochemistry*, Vol. 34, No. 6, (November-December 1996), pp. 833-842, ISSN 0981-9428

Singh, S.N. & Tripathi, R.D. (2007). Environmental bioremediation technologies. Springer Verlag, Berlin, Heidelberg, Pp. 518, ISBN 978-3-540-34790-3

Stampoulis, D.; Sinha, S.K. & White, J.C. (2009). Assay-dependent phytotoxicity of nanoparticles to plants. *Environmental Science and Technology*, Vol. 43, No. 24, (December 2009), pp. 9473-9479, ISSN 0013-936X

Stiborová, M.; Doubravová, M. & Leblová, S. (1986). A comparative study of the effect of heavy metal ions on ribulose-1,5-bisphosphate carboxylase and phosphoenol-pyruvate carboxylase. *Biochemie und Physiologie der Pflanzen*, Vol. 181, No. 6, pp. 373-379, ISSN 0015-3796

Stoltz, E. & Greger, M. (2002). Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plant species growing on submerged mine tailings. *Environmental and Experimental Botany*, Vol. 47, No. 3, (May 2002), pp. 271-280, ISSN 0098-8472

Szpunar, J. (2004). Metallomics: a new frontier in analytical chemistry. *Analytical and Bioanalytical. Chemistry*, Vol. 378, No. 1, (January 2004), pp. 54-56, ISSN 1618-2642

Tamás, L.; Mistrík, I. & Huttová, J. (1997). Accumulation of apoplasmic proteins in barley primary leaves induced by aluminium and pathogen treatment. *Biologia* (Bratislava), Vol. 52, No. 4, (August 1997), p. 585-589, ISSN 0006-3088

Tu, C. & Ma, L.Q. (2002). Effects of arsenic concentrations and forms on arsenic uptake by the hyperaccumulator ladder brake. *Journal of Environmental Quality*, Vol. 31, No. 2, (April 2002), pp. 641–647, ISSN 0047-2425

Tudoreanu, L. & Phillips, C.J.C. (2004). Modeling cadmium uptake and accumulation in plants. *Advances in Agronomy*, Vol. 84, Book Series: Advances in Agronomy, pp. 121-157, ISSN 0065-2113

White, P.J. & Broadley M.R. (2005). Biofortifying crops with essential mineral elements. *Trends in Plant Science*, Vol. 10, No. 12, (December 2005), pp. 586-593, ISSN 1360-1385

Whitelaw, C.A.; Le Huquet, J.A.; Thurman, D.A. & Tomsett, A.B. (1997). The isolation and characterisation of type II metallothionein-like genes from tomato (*Lycopersicon esculentum* L.). *Plant Molecular Biology*, Vol. 33, No. 3, (February 1997), p. 503-511. ISSN 0167-4412

Williams, R.J.P. (2001). Chemical selection of elements by cells. *Coordination Chemistry Reviews*, Vol. 216–217, (June-July 2001), pp. 583-595, ISSN 0010-8545

Zhuang, P., McBridge, M.B., Xia, H., Li, N. & Li, Z. (2009). Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan, South China. *Science of the Total Environment*, Vol. 407, No. 5, (February 2009), pp. 1551-1561, ISSN 0048-9697
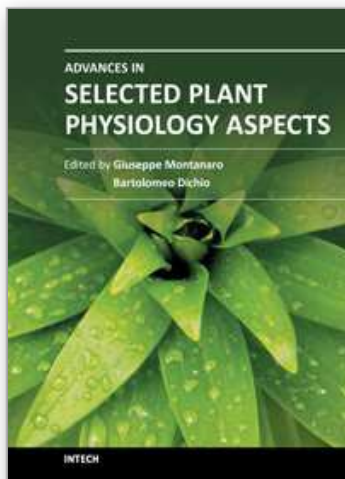
Advances in Selected Plant Physiology Aspects

Edited by Dr. Giuseppe Montanaro

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