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Heavy metals in the vascular plants of Tatra Mountains

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Introduction

Heavy metals deriving from anthropogenic activities are important pollutants in the environment. The term "heavy metals" is used for the group of elements with the density higher than 5 g.cm^{-3}. Some of them are necessary for living organisms (Cu, Zn, Mn, Cr, Co), but they can have a toxic effect in the greater amounts. The others are inessential and risk due to their toxicity and ability of accumulation in soils and organisms because they are not degradable. Heavy metals naturally occur in pure form or in salts and they can be transported in biological and geochemical cycles. Anthropogenic emissions originate mainly from mining, industrial production, combustion of fossil fuels and application of fertilizers and pesticides.

Plant uptake of heavy metals in relation to their content in soil

Metals of anthropogenic origin are generally considered as more available from soils than those originating from parent rock (Grupe and Kuntze 1988). Effects of heavy metal pollution are most long lasting in soils due to relatively strong adsorption of many metals onto the humus and clay colloids. The duration of contamination may be for hundreds and thousands years in many cases, e.g. first half lives: Cd 15 – 1,100 years, Cu 310 – 1,500 years and Pb 740 – 5,900 years depending on the soil type and physico-chemical parametres (Alloway and Ayres 1994).

The form in which the metals are present in the soil, i.e. metal speciation, greatly influences the rate of their uptake. Metals in soil solution, exchangeable metals and organically bound metals are considered as easily or potentially available (Kabata-Pendias and Pendias 1992). The heavy metals generally regarded as highly mobile in soils are Mn, Cd, Co, Zn, Ni, on the contrary, Pb, As, Cu are characterised by lower mobility in soils. The important parametres for the input of heavy metals from soil into plants are: soil reaction, content and quality of organic matter, nutrition of plants, cation exchange and sorptive capacity, microbiological activity, oxidation and reduction potential, amount and quality of the clay fraction of soil and method of soil cultivation (Alloway 1990).

Barančíková (1998) divides heavy metals depending on pH values into two groups: the former contains elements as Cd, Cr, Pb, Zn and Ni that dispose of maximal mobility in soil at pH lower than 5.5. The latter is typical for Cu and As with maximal mobility below 4.5 and above 7.0. The mobility of Hg is independent of the soil reaction. The quality of soil organic matter significantly influences behaviour of heavy metals and their bioavailability. Humic acids share in retaining of heavy metals and decreasing of their content in soil solution (Brümmer *et al.* 1986). On the other hand fulvic acids and their complexes can increase mobility and toxicity of heavy metals. Some elements are characterized by high affinity to organic matter in soil, e.g. Pb and Cu. The mineral part of soil plays an important role in immobilization of metals, especially chemisorption, irreversible process, and reversible electrostatic adsorption belong to mechanisms that can be used in soil detoxication.

Heavy metal contamination of soils in mountainous regions of Slovakia is at the margin of interest, main attention is devoted agricultural soils. Kobza (2002) noted that in accordance with obtained results contamination of mountainous soils with cadmium and lead, particulary with zinc has been confirmed. Their highest values in surface layer of soils indicated an atmospheric deposition. Thóth *et al.* (2009) researched content of Cd, Co and Ni in agricultural soils at the foot of the High and Low Tatras and their transfer into agricultural plants. The results of monitored heavy metals prove that portion of Cd and Ni is the main polluting factor of soils in this region. Hajdúk (1988) ascertained the content of some heavy metals in TANAP soils in relation to the effect of industrial emissions. Pb content near the trunk of a beech tree (*Fagus sylvatica*) close to a gully was higher by 100 % and Cu by about 50 % than at a distance three metres away. Near rocky walls, Pb content in most samples proved to be higher than or at least equa to that in soil 2 - 8m from the rock. Above mentioned facts support the theory that higher concentrations of some metals reveal in the localities, where these elements are washed up by the rain water from larger surfaces on smaller ones. Heavy metal deposition in Tatras mountain relates with automobility and on northern aspects there is evident the effect of transboundary air pollutants from Polland (Katowice). In the highest ridge positions without terrain barriers is prevailing north-west convection (Konček *et al.* 1973).

Heavy metals in plants

Plant uptake of metals is generally dependent on (1) movement of elements from the soil to the plant root,

(2) elements crossing the membrane of epidermal cells of the root, (3) transport of elements from the epidermal cells to the xylem, in which a solution of elements is transported from roots to shoots, and (4) possible mobilization from leaves to storage tissues in the phloem transport system (John and Leventhal 1995). Metal mobility in plants is various and decreases in the order Zn > Cd > Pb (Borůvka *et al.*1997a). In plants, some metals are accumulate in roots (especially Pb), probably due to some physiological barriers against metal transport to aerial parts, while others are easily transported in the plants, for example Cd (Kabata-Pendias and Pendias 1992).

According to Baker (1981), there are three basic types of tolerance strategy to heavy metals: (1) indication – the content of metals in the plants reflects their quantity in external environment, (2) exclusion – the uptake and transport of metals are restricted, the metals are immobilized in root system, (3) accumulation – the plants due to specific physiology active concentrate the metals in aerial parts. The extreme level of metal tolerance in vascular plants is hyperaccumulation. Hyperaccumulators are defined as higher plant species whose shoots contain > 100 mg Cd kg^{-1}, > 1,000 mg Ni, Pb and Cu kg^{-1}, or 10,000 mg Zn and Mn kg^{-1} (dry weight) when grown in metal-rich soils (Baker and Brooks 1989, Baker *et al.* 1994). *Thlaspi caerulescens* is the example of hyperaccumulator in Slovakia, *T. caerulescens* ssp. caerulescens can accumulate 30 g Ni kg^{-1}, 43 g Zn kg^{-1}, 2 g Cd and Pb kg^{-1}, *T. caerulescens* ssp. *tatrense* accumulates 20 g Zn kg^{-1} dry weight (Dercová *et al.* 2005). The accumulation capacity of these plants can be used in the phytoremediation techniques to eliminate metal contamination of large areas.

The toxicity of heavy metals generally declines in order: Hg > Cd > Ni > Pb > Cr and lies in substitution of the essential metals in the enzymes and in the important biomolecules (Makovníková *et al.* 2006). Recently the great attention has been devoted the toxic effect of lead and cadmium. The plants in higher concentrations of Cd answer by reduction of photosynthetic activity together with extension of respiratory processes, by damage of membranous structures, by chlorosis and necrosis of leaves and by total decrease of biomass. Cadmium is generally reported as mobile in plants, at high concentrations it can be also accumulated in roots (Kabata-Pendias and Pendias 1992). Some foliar uptake was also assumed for Cd. This is in accordance with Hovmand *et al.* (1983) who considered grasses as plants with a high ability for foliar uptake of Cd. Borůvka *et al.* (1997a) researched the relationship between the metal concentration in plant roots and shoots and the concentration of metal fraction in topsoil (0 – 150mm) in heavily polluted soils. The cadmium content in plants root correlated with topsoil concentration of its exchangeable and 2 mol.l^{-1} HNO_3 extractable forms. Uptake of Cd in plants increases in the presence of chlorine in soil due to creation of easily soluble chlorocomplexes Cd. On the contrary, Zn is the known competitive inhibitor of Cd-uptake by plants (Makovníková *et al.* 2006).

The plants catch lead in the very small amounts, lead deposits mainly in root, at the same time 80 % of lead accumulation comes from direct atmospherical deposition (Beneš 1993). There are some factors that influence of lead uptake by the plant root system and his translocation, primarily low pH value, low content of phosphorus and of ligands in soil. Lead precipitates with phosphates under creation the insoluble compounds (Makovníková *et al.* 2006). The phytotoxicity of lead in tolerant plants displays at the extremly high concentrations, some authors present the values from 100 to 500 ppm, so these plants on Pb-contaminated areas can successfully survive in conditions with the inadmissible concentration of lead for animal organisms (Beneš 1994). In spite of it, excess lead content in plants interferes and inhibits various physiological process (Balsberg Pahlsson 1989). Responses of plants to lead exposure include decrease in root elongation and biomass (Fargasova 1994), inhibition in chlorophyll biosynthesis (Miranda and Ilangovan 1996), induction or inhibition of several enzymes (Van Assche and Clijsters 1990) as well as cell disturbances and chromosomal lesions (Balsberg Pahlsson 1989).

According to Borůvka *et al.* (1997a), the lead content in plant roots correlated with the topsoil concentration of 2 mol.L^{-1} HNO_3 extractable forms, but the correlation with the exchangeable form content was rather weak (correlation coefficient in the slightly polluted area was as low as 0.045). It was supposed to be due to adsorption of Pb on specific adsorption sites in soil (Borůvka *et al.* 1997b). Pb-uptake by plants is higher in soils with low values of cation exchange capacity (Makovníková *et al.* 2006).

Epstein *et al.* (1999) found obvious correlation of lead accumulation with accumulation of EDTA. This fact was verified by observation of Pb complexed with EDTA in the xylem sap of *Brassica juncea* immediately after exposure of Pb-EDTA. The solubility of Pb in the complex Pb-EDTA apparently allows the transport of this metal from the root into the shoot, where Pb is accumulated.

Many studies on heavy metals in plants are focused to their content and cumulation in agricultural plants. It is very important to research heavy metal loading of the natural ecosystems for assessment of environmental contamination. Maňkovská *et al.* (2008) investigated the atmosphere loading of the Slovak Carpathians using bryophyte technique. In comparison to the median northern Norway values of heavy metal contents in moss the Slovak atmospheric deposition loads of the trace elements were found to be higher than average. Kuklová and Kukla (2007) determined the content of risk elements (Cd, Hg, Al, Pb, Ni, Cr) in aboveground phytomass of herb species selected in spruce ecosystems of Central Spis Region. The concentration of Al, Ni, Pb, Cd and Hg in the species *Vaccinium myrtillus, Luzula luzuloides* and *Dryopteris dilatata* were mostly found exceeding the limits of natural occurence of these elements in plants.

In mountainous regions, arising altitude, local orographic and related meteorological conditions determine the distribution of heavy metal atmospheric deposition. Investigation of differences in heavy metal deposition in respect to different altitudes seems to be necessary. Generally it is known that there is a strong correlation between orography, the amount of wet deposition and rainfall composition (Fowler *et al.* 1993). The rate of atmospheric element deposition in mountains may vary within short distances. Although precipitation generally increases with altitude along transects in small mountainous areas (Zechmeister 1995), the precipitation patern is usually affected by a complex interplay of factors, especially geographic location and slope aspect (Fliri 1975). Dry deposition of gases and particles is depended on factors influencing turbulent transport, particularly wind speed, but also on the structure and heigh of the plant canopy (Erisman and Draaijers 2003). In accordance with Clough (1975) heavy metals spread as small particles and their deposition closely relates to windspeed, which increases above the tree line.

Few studies have addressed relationship between element concentration in moss tissues and altitude. Those studies reported partly contrasting results so that the mechanisms through which altitude can influence element contents in moss tissues are far from being fully understood (Gerdol and Bragazza 2006). Zechmeister (1995) and Šoltés (1998) reported increasing concentrations of trace metals, especially Pb, Cd and Zn with altitude in forest mosses and *Sphagnum* mosses. High levels of precipitation are strongly correlated with heavy metal deposition, and seem to be the main source of heavy metal fallout at higher altitudes.

On the contrary Gerdol and Bragazza (2006) found that element concentration varies with altitude even in the absence of any precipitation pattern related to elevation. Concentrations of Pb and Cd in mature *Hylocomium* tissues peaked at mid altitude (1,400 - 1,800m) where frequency of cloud cover was the highest, and so occult deposition by cloud-water may account for a significant fraction of the total deposition of anthropogenic trace metals, in close relation to cloud cover frequency. Although the hydrological input by cloud water in mountainous regions is negligible (< 5%) compared to the hydrological input by rainwater, the deposition fluxes of trace metals and major ions by cloud-water interception can account for a major fraction (up to over 50%) of atmospheric wet deposition. Cini *et al.* (2002) also found high Pb and Cd concentration in cloud-water at a mountain site in northern Italy.

Bednářová and Bednář (1978) surveyed the lead content in the plants of Tatra national park along transects chosen perpendicularly on the direction of the communication and at different distances from the border of the road. The ascertained Pb concentrations in the plant tissues were much higher than their natural level and pollution was proved in the distance of 150m from the road communication. Higher amounts of Pb was recorded in populations of plants colected in 1,600m above s. l. The authors accent the relevant differences in Pb deposition in various plants in dependence on plant morphology and anatomy. Šoltés *et al.* (1992) also confirmed heavy metal loading of vascular plants, moss growths and lichens in the High Tatra and Belianske Tatra Mountains. Seasonal fluctuations in the lead concentrations of foliar parts of alpine plants have been recorded with higher values in winter and early spring months than in summer months in connection with acidification of habitats (Janiga 2008).

Conclusion

Heavy metals often in lower concentrations impact as stress factor for many sensitive plants. Stunted growth, chlorosis and necrosis, leaf epinasty and red-brownish discoloration are visible symptoms of metal phytotoxicity. At the metabolic level, enzyme capacity can be substantially inhibited. Contaminated plant nutrition represents potential risk for herbivores and through the food chain for carnivores with the ability of cumulation. Mountainous and alpine regions belong to more sensitive ecosystems affected besides by local pollutors mainly by the long-range transport of emissions.

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