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HEAVY METAL PHYTOEXTRACTION BY WETLAND WEED AND RUDERAL MACROMYCETES IN ENVIRONMENTALLY ENDANGERED AREAS

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Abstract
Current research efforts focus now-a-day on expanding phytoremediation to address contaminated soils, waters and atmospheric pollutants. Plants that hyperaccumulate normally toxic metals are rare and taxonomically widespread throughout the remote areas. Phyto- (or green plant based) remediation is not a new concept and constructed wetlands, reed beds as well as floating plant systems have been common for the treatment of some types of wastewater for many years. The objective of our current study was to testify heavy metal bioaccumulation in wetland weed indicators grown near the West Carpathian Záhorie (Konopiská) Landscape, designed as the most valuable part of well preserved and developed complex of diverse wetlands in Slovakia.

Key words: wetland weed, heavy metals, bioaccumulation, AAS, phytoextraction, phytoremediation

Introduction

The uptake or absorption of metals by terrestrial plants is still poorly understood. The bioavailability of an element in the soil is the resultant of a competition between surface complexation at the plant root system, at various soil solid phases, remaining in solution and atmospheric foliar imput (uptake path) as well. In the last case, metal movement into the plant seems to involve diffusion through the cuticle and uptake by leaf cells.

There is a tendency for many elements to become concentrated as the growing season is over, i.e. towards autumn and winter in temperate climate due to continuous accumulation during the growing season and due to aerosols deposition in the as long as possible time period, consequently to both foliar and root system uptakes[1].

Several plant species have been reported to be hyperaccumulators; they lead to bioaccumulation of heavy metals of considerably higher concentrations, often by a factor between ca. 10 and 1000, than found for other plant species in the same localities. Usually, they grow in environments, that have already high concentrations of available metals in the soil.

In the places where land is available easily, treatment for sewage through natural systems is considered to be the best option and provide a viable treatment alternative. One of the emerging technology out of the various natural systems available is Root Zone Constructed Wetland Technology, which has been used since the last 40 years for the treatment of domestic wastewater, storm water management and industrial wastewater containing organic pollutants. Constructed wetlands (CW) consist of a shallow depression in the ground with a level bottom or channels, with a natural or constructed subsurface of clay or geotechnical material to prevent seepage and a suitable substrate to support rooted emergent macrophytes. In Slovakia, at Grey Bear Tále Golf Playground Project the CW system for water protection was applied, too.

The objective of our current study was to testify heavy metal bioaccumulation in wetland weed indicators grown near the West Carpathian Záhorie (Konopiská) Landscape, designed as most valuable part of well preserved and developed complex of diverse wetlands in Slovakia[2]. Consequently to a closed natural resource of carbonates, siliceous sands and energy intensive cement manufacturing process affecting environmental pollution since several decades, the targeted area was situated downstream with the most seasonal wind fronts intensities of this territory[3].

Materials and Methods

As already emphasized, the element concentration of a plant is essentially determined by the plant species, by the plant compartment to be studied, by seasonal concentration fluctuations and the influence of various parameters such as soil type, influence of wind intensities, plant age, height, streams obstacles, etc. [3, 4, 5].

To avoid the most resistant and hardly pulverised weed parts to be necessarily pre-treated for instrumental analysis, the sampling strategy based only on the collection of over the ground weed parts, i.e. without gathering of their roots and stalks. The 10 grid squares with the same number of samples were undertaken for AAS analysis of following heavy metals: Cu, Hg, Mn, Cd and Pb.

Drying of the samples, which usually serves to protect the plants against microbial decomposition during subsequent storage and ensure a constant dry weight, was done at laboratory PREMED KBC drier for 2 hrs by 60°C.

Homogenization and grinding of the dried sample material was achieved manually in agate mortar and pestle equipment.

In order to provide chemical element analysis and avoid the matrix constituent's interferences, the samples needed to be decomposed. A high-pressure ashing or microwaves decomposition in closed or half-closed quartz vessels achieves usually satisfactory results for subsequent AAS procedure. Acid decomposition of our samples (about 2.0 g of analytical weight) was performed in the semiclosed glass apparatus in a mixture of 7 ml 65% v/v HNO_3 (suprapur), 7 ml H_2O_2 (30% v/v, suprapur) and 3 ml deionised H_2O. After the procedure the solutions were transferred into 50 ml calibrated flasks and fulfilled up to the mark with D.I. water.

The toxic metal concentrations in all samples were analysed by Atomic Absorption Spectrometer (AAS) using an Apparatus Philips PU 9400X with (air - acetylene) flame technique. The sensitivity for Cd was improved by using slotted tube atom trap. The instrumental parameters of AAS for heavy metal determination shows Table 1. Mercury was determined by amalgamate AAS technique on the apparatus AMA-254 (Altec - Czech Republic). The samples for this measurement were inserted into device without above acid decomposition, whereas inside apparatus drying time of samples was 30 sec and decomposition procedure and waiting lasted 50 sec.

The methods and procedure were validated using certificated reference material: CRM Bowens Kale, H.J.M. Bowen, University Reading, Berks U.K. All analyses were done in triplicate and one blank sample was included for every ten samples analysed.

Results and Discussion

As generally known, in Central Europe climate zone mostly species like Thlaspi, Alyssum, Urtica and Chenopodium use to be responsible for the rhizospheric phytoextraction, phytoaccumulation or phytostabilization processes utilizing more or less plant complexation excretes. Phyto- (or green plant based) remediation is not a new concept and constructed wetlands, reed beds as well as floating plant systems have been common for the treatment of some types of wastewater for many years [6,7].

Current research efforts focus now-a-day on expanding phytoremediation to address contaminated soils and atmospheric pollutants. Plants that hyperaccumulate normally toxic metals are rare and taxonomically widespread throughout the remote areas. For example, a member of the Brassica family, Thlaspi caerulescens can accumulate up to 4% zinc in its tissue without apparent damage or a small tree growing on outcroppings of metalliferous soils, Sebertia accuminata takes up 25% nickel by dry weight. However, most hyperaccumulators grow slowly and have small biomass. Moreover, a little is known about physiology of these plants so far [8].

Consequently to these factors, especially Brassica family has been cultivated as new mutant that might yield useful heavy metal hyperaccumulators. Genetic engineered mutant Pisum sativum accumulates 10-100 - fold more iron or mutant Arabidopsis 10 - fold more manganese than do the wild types.

Investigation the mechanisms of organic and inorganic contaminants under field conditions poses significant analytical challenges. Phytodecontamination techniques are still in the early stages of research and development and results from field trials involving metal phytoextraction show that metal removal rates currently remain too low to be commercially useful. The role of plants is to increase the sequestration of the contaminant by altering water flux through the soil, incorporating residual free contaminant into roots and preventing wind and rain erosion. Plants are chosen for altering or further sequestering pollutants by mechanisms such as redox reactions, e.g. chromium (VI) to (III), precipitating the metal into an insoluble form (Pb into lead phosphate) or incorporating organics into the plant lignin (subsequently unextractable in chemical solvents and animal feeding tests).

Table 1 AAS instrumental parameters for heavy metal determination

Element	**Analysis time, [sec]**	**Wavelength [nm]**	**Bandass [nm]**	**Fuel flow [l/min]**	**Lamp current [mA]**
Mn	4.0	279.5	0.5	1.0	7.5
Cu	3.0	324.8	0.5	1.1	4.5
Pb	3.0	217.0	0.5	1.1	7.5
Cd	4.0	228.8	0.5	1.2	6.0

Table 2 Statistical data on trace element concentrations in sampled wetland weed [mg/kg]

Variable	**Manganese**	**Copper**	**Lead**	**Cadmium**	**Mercury**
EU 178/2002 Guidelines	250	125	10	0.2	0.1
Sample size	10	10	10	10	10
Arithmetic mean	120.59	13.51	4.36	0.1568	0.0133
Median	99	13.65	1.25	0.0645	0.013
Mode	92.5	13	0	0	0.01
Standard deviation	65.2075	2.5124	7.4823	0.3154	0.0034
Standard error	20.6204	0.7944	2.3661	0.0997	0.0010
Minimum	47.3	9.7	0	0	0.01
Maximum	224.5	17.4	21.8	1.046	0.02
Range	177.2	7.7	21.8	1.046	0.01
Lower quartile	68.9	11.4	0.4	0.03	0.01
Upper quartile	183.2	15.4	2.3	0.101	0.015
Interquartile range	114.3	4	1.9	0.071	0.005
Coefficient of variation	54.0738	18.5965	171.613	201.167	25.3244

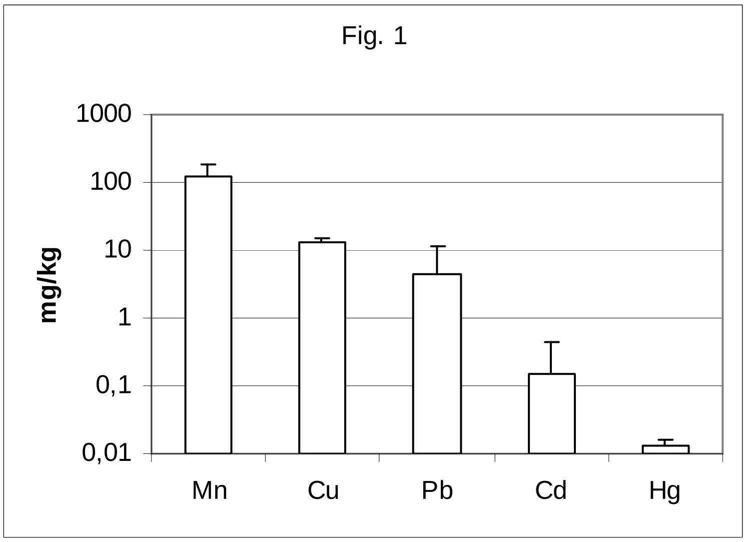

Fig. 1: Column diagrams of mean heavy metal concentrations with standard deviation (by 95% percentile) for the sampled weeds

Table 2 presents the computed statistical results of heavy metal contents of the sampled weed mixture at the Konopiská wetland (approximately 100 x 100 m area) supposed to be impacted especially by closed industrial activities of cement production. Following plant species of domestic wetland were predominantly sampled: Typha latifolia, Lemna trisulca, Glycera maxima, Phragmites australis. According to the EU 178/2002 Guidelines, that limit the heavy metal contents in animal feed, only 3 spots of the monitored raster area exhibited enhanced metal concentrations, i.e. 2 samples of the up to 2 times higher Pb concentration and one sample for the 5 times higher Cd concentration, however no extra hard roots and stalks of the plants, that are usually not cropping feed for animals, were collected. Otherwise, it may be supposed that the heavy metal content would be greater. Fig. 1 presents column diagrams of mean heavy metal concentrations with standard deviation (by 95% percentile) for the sampled weeds.

Conclusions

Exploring the synergy between traditional disciplines may eventually provide low cost, low impact, visually benign and environmentally sound remediation strategy. In Central Europe climate zone, e.g. poplar trees with higher lignin or oil contents in the roots may fulfil for near future the appropriate phytoremediation and phytostabilization sanitary actions to recover natural ecosystems. In our study the common wetland weed collected mostly without the hard roots and stalks did not confirm a potential endargement for wild animal feeding, despite the long time cement production in the closed vicinity.

Acknowledgments

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