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INVESTIGATION AND EVALUATION OF THE TRANSFER OF HEAVY METALS FROM THE SOIL TO THE TREE

Summary of Doctoral Dissertation
Technological Sciences, Environmental Engineering and Landscape Management (04T)

1378

VGTU LEIDYKLA TECHNIKA

Vilnius 2007

VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

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VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS

Edita BALTRĖNAITĖ

SUNKIŲJŲ METALŲ PERNAŠOS IŠ DIRVOŽEMIO Į MEDĮ TYRIMAI IR ĮVERTINIMAS

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General Characteristic of the Dissertation

The problem

Heavy metals (HMs) are natural components of the earth crust the geochemical and biochemical balance of which is undergoing drastic changes caused by anthropogenic activities. Rapid urbanisation, industrialisation, growing transport intensity as well as agricultural activities create problems of soil contamination with HMs. The environmental pollution with HMs is an acute problem because, according to the Korte index designed to show hazard to life, health and heridity, HMs are among such major ecological problems as contamination with pesticides, acid rain, oil spills, chemical fertilizers, and noise. Large areas of land are contaminated with HMs formed in sewage, waste incineration plants, in farming with fertilizers and pesticides, as well as in industrial metal and leather processing, etc. HMs are long-term contaminants with the ability accumulate in the soil and plants, and cannot disappear in a natural way. The most hazardous are toxic metals (e.g. lead, chromium, nickel, copper, zinc, manganese and others), including their soluble compounds. Some HMs (e.g. zinc, manganese, nickel) are nutrients essential to plants, whereas lead and cadmium are more harmful elements. The transfer of HMs to the plant and their distribution therein make an impact on plant nutrition. Each year witness an accumulation of around 200 000 tons of sewage sludge in Lithuania. The sludge is being stored and used for fertilisation, yet the amount of the stored sludge is constantly increasing, whereas due to high concentrations of HMs sludge is prohibited from being used for fertilisation. The environment-friendly methods of sewage sludge treatment based on the principles of sustainable development should to be followed.

Topicality of the work

HMs in forms of dry and wet sedimentation are transported from local and long-distance contamination sources to the soil and plants thus being involved in biogeochemical processes. Roots and leaves of long-term vegetation plants such as trees are able to uptake and accumulate HMs in their separate parts. On account of those characteristics, the trees are considered the bio-indicators of environmental pollution. Trees are used as bio-indicators of environmental pollution in the examination of HMs concentrations in needles, leaves, bark and tree annual rings. Needles contain the amounts of HMs of the last three–four years, leaves accumulate the concentrations of the last year, a bark can record the amounts of HMs during the whole vegetation period, whereas new rings uptake HMs of the last year. Thus the information about the past environmental contamination recorded in the tree enables to observe the trends of contamination alteration as well as to determine local contamination sources. It also allows to examine the interaction between HMs and pathogens in the affected tree in the particular years. Therefore the determination of HMs in wood samples made of as few annual rings as possible is assuming a growing importance. About 10 % of pines in Lithuania are affected by fungus diseases, anthropogenic activities, abiotic stresses, rodents, etc. Despite birches being much more resistant to those infections, fungus diseases have affected 1.3 % and 1.2 % of pines and birches respectively. The most spread fungus disease among pines is root rot (*Heterobasidion annosum* (Fr.) Bref.). A considerable amount of research has been conducted worldwide on plant resistance to the biotic factors that involve HMs accumulation, and resent years see a new field of study on the signals of the plant affected by the pathogen and metabolism changes. The paper presents results on the change of HMs concentrations in the pinewood affected by root rot (*Heterobasidion annosum* (Fr.) Bref.) and considers the hypothesis on the interaction between HMs and the pathogen. A lot of efforts are going into research on plants capable to rapidly accumulate HMs in the above-ground part and consequently reduce the amount of HMs in the soil. Although, generally speaking, trees do not fall into the category of such plants, the individual species are capable to transfer from the soil to trunks up to some 60 % of HMs found in the soil. Those trees are good to be planted on the soils treated by sludge. The spreading of sewage sludge in the wood cutting sites as well as the planting of tree seedlings allow the alternative of sewage sludge treatment. There is, however, a scarcity of information concerning the transfer of HMs to trees and the accumulation effectiveness of trees of different tree species under natural conditions.

Aim and tasks of the work

Aim of research is to determine HMs concentration in the soils with different contamination levels and in trees of different species as well as to evaluate their transfer from the soil to the tree.

Tasks of the work:

1. Evaluate bio-indicator properties of the Scots pine (*Pinus sylvestris* L.) and the birch (*Betula pendula* Roth) based on the concentrations of HMs in annual rings, on climate conditions, and on the past environmental contamination with HMs of the site studied.
2. Compare HMs concentrations in differently sampled tree ring wood.
3. Determine and evaluate distribution of HMs in the soil under tree foliage.
4. Determine and evaluate the correlation between HMs concentrations and the rot pathogen in the pine wood.
5. Determine and evaluate the transfer of HMs from the soil treated by sludge to the seedlings of the local Lithuanian trees (Scots pines, birches and black alders).
6. Perform a mathematical modelling of the transfer of HMs to the tree.

Scientific novelty

The novelty of the research consists of the complex studies of HMs in trees, which include a theoretical analysis of the transfer of HMs from the soil to the trees, experimental studies and the modelling of the HMs transfer from the soil to the tree. The complex studies are presented with a view to evaluating the transfer of HMs from the soil with different contamination to the trees of distinct species, as well as of different age and growth conditions. The research is concerned with HMs concentrations in a separate annual ring and discusses the interaction between HMs and the pathogen.

Practical value

The concentrations of HMs in tree rings provide the information about the soil contamination with HMs in the past, as well as about the intensity of contamination sources and its alteration. The sampling methods improved and proposed by the research allowed to increase the accuracy of tree ring sampling by using growing trees. The findings of the transfer of HMs from the soil treated with sewage sludge to the three species of the seedlings of Lithuanian trees give practical information regarding the ability of different trees to uptake HMs and offer valuable assistance in selecting sludge treatment alternatives as well as in choosing tree species.

Defended propositions

- Distribution of HMs and their chemical forms varies depending on the nature of the pollution.
- The seedlings of a pine, birch or a black alder can also serve the purpose of treating the sludge spread on the soil.

The scope of the scientific work

The scientific work consists of the general characteristic of the dissertation, 5 chapters, conclusions and recommendations, lists of literature, author’s publications and presentations on the subject of the dissertation in scientific conferences. The total scope of the dissertation – 153 pages, 54 pictures and 25 tables.

Approval of the results

The research findings of the following 13 papers are published: 2 scientific articles in magazines with the ISI citation index; 1 paper in conference reports with the ISI Proceedings index; 2 papers in foreign review publications; 2 scientific articles in magazines put on the LL list; 5 papers in other Lithuanian scientific publications. Lithuanian patent for methodology No 5325 B has been obtained. The results of the thesis have been discussed in 6 international conferences and 5 republican scientific conferences; besides 10 scientific publications have been included into report materials of the conferences.

1. Transfer of HMs in the System Soil–Tree

The transfer of HMs to trees has several significant aspects. Firstly, being the plants of long-term vegetation, trees are capable to accumulate a considerable amount of HMs. An examination of the transfer processes of HMs to trees provides valuable information about environmental contamination in the past, the source of pollution, etc. For example, HMs concentration in separate annual ring record environmental contamination with HMs in given years in the past. Secondly, the knowledge of interaction between HMs and the pathogens of trees (as well as of other plants) is still scarce. Some hypotheses have been proposed concerning interaction processes of HMs and pathogens not only in plants accumulating large amounts of HMs but also in the trees with bio-indicator properties only. For example, HMs are supposed to have defensive properties when faced with the pathogens in the tree. Thirdly, trees are planted in the soil with sewage sludge. The sludge accumulates particularly heavy concentrations of Zn, Ni, Cu, the HMs of anthropogenic origin, which often are highly mobile. In such case knowledge about the transfer of HMs to different tree species and HMs translocation in the parts of a tree is of major importance in the evaluation of HMs proportion in the above-ground tree parts and in the soil after some time, in the estimation of HMs migration rate, the HMs probability of reaching underground waters, and, yet again, in the evaluation of the possibility of spreading the sludge on the soil as one of the sludge treatment methods. Although being familiar, the method of sludge treatment has, however, been little studied depending upon the properties of tree species, sludge characteristics, and HMs translocation in the tree parts. The information concerning the abilities of distinct tree species to uptake different HMs, as well as the impact of soil and sludge properties on the transfer of HMs is still scarce.

2. Methodology of Research

A total of 6 trees (5 pines and 1 birch) from habitats with different levels of HMs contamination were studied. Two pines (1P and 2P) grew in the Rukla-Gaižiūnai Military Ground (Jonava District). The third pine (3P) grew in the Kairiai Military Ground (Klaipėda District); the fourth pine and the birch (4P and B) grew at a distance of 10 km from the centre of the town of Alytus; the fifth pine (5P) grew in the Neris Regional Park (Vilnius District). Samples of tree seedlings (pine, birch and black alder) were taken in area treated by industrial sewage sludge. The soil samples were taken in each tree habitat area at a depth of 0–40 every 10 cm. Mobile and potentially mobile forms of HMs, as well as soil characteristics were determined in collaboration with Norwegian experts at the Norwegian University of Life Sciences. The intercalibrative measurements of HMs in the soil and wood were taken at Mikkeli Technical

High School in Finland. Fungi in the pinewood were determined by experts at the Laboratory of Phytopathogenic Microorganisms of the Institute of Botany. HMs concentration in solutions of the tree parts and of soil samples was analysed with FAAS and GFAAS. The transfer factors of HMs from soil (TFs) to a tree were calculated dividing average HMs concentrations in the trunk wood by average HMs concentrations in soil. The translocation factors (TcFs) were calculated dividing HMs concentration in leaves and needles of tree seedlings by the HMs concentration in fine roots. The statistical methods (ANOVA, T-test, Spearman' rank correlation) were employed in the research.

3. The Results

3.1. Comparison of tree ring sampling methods. Wood sampling to determine wood physical properties as well as to carry out dendrochronological and dendroindicative experiments is well documented, whereas tree ring sampling for HMs analysis is still scarce. This research is concerned with the methods of tree sampling that involve the use of the four tools: common chisels, arched chisels, a plane and increment borer. The results of ANOVA analysis on HMs concentrations in tree ring wood sampled with four different tools have demonstrated no significance statistical difference, hence, all the methods concerned can serve the purpose of ring sampling and HMs analysis. Yet the sampling with the increment borer means the lowest coefficients of variance and lowest mean standard square deviations. The increment borer is superior in its simple use and is less time consuming as it does not involve the cutting down of a tree as well as produces small yet sufficient amount of samples for analysis. No additional measures (e.g. workforce, tree cutting skills, etc.) are needed. With the exception of Cr and Ni, other HMs mean concentrations in ring samples of 0.10 g, 0.15 g, and 0.20 g respectively had no significance difference. Therefore a 0.10 g ring sample can be used for Pb, Zn, Mn and Cu analysis both statistically and practically.

3.2. Findings of the intercalibrative measurements of HMs in the wood. The concentrations of HMs (Ni, Pb, Cu, Cr, Mn and Zn) were determined in the same wood samples at the laboratories of Mikkeli Technical High School (MPI) and of the Department of Environmental Protection at Vilnius Gediminas Technical University (VGTU) by employing the statistical methods of the Spearman's rank correlation coefficient and T-test (Table). Spearman's rank correlation coefficients among HMs concentrations in the wood for all the HMs, except Pb, were higher than 0.50: values for Mn, Zn, and Ni sometimes exceeded 0.80; for Cu and Cr were higher than 0.50 and showed a close correlation between the HMs values determined at different laboratories.

Coefficients of mean values, of variance and of Spearman's rank correlation among mean values

HM	Mean value, $mg \cdot kg^{-1}$		Variance, $mg^2 \cdot kg^{-2}$		Spearman 's rank correlation
	VGTU	**MPI**	**VGTU**	**MPI**	
Zn	3.14	2.76	1.31	0.751	**0.85**
Mn	7.92	8.65	1.54	2.90	**0.83**
Pb	0.462	0.686	0.0655	0.0921	0.15
Cu	0.666	0.600	0.0560	0.113	**0.57**
Cr	0.0911	0.0734	0.00427	0.00185	**0.72**
Ni	0.166	0.174	0.00599	0.00372	**0.85**

Just for Pb the correlation coefficient was lower than 0.50 and showed a poor correlation between the values of Pb concentrations. The results of a statistical T-test suggested that there is no significance difference between the concentrations of HMs determined at different laboratories. That implies that the preparation of wood employing a wet extraction method or digestion makes no considerable impact on the analysis of HMs present in the wood. Thus both methods can be applied for the preparation of wood samples, and their results can be compared.

3.3. HMs in the soils and trees in potentially contaminated areas. The study revealed HMs concentrations in the annual rings of the pines grown in the military grounds of Rukla-Gaižiūnai (Jonava District) and Kairiai (Klaipėda District), as well as in the pine and birch trees grown in the district of Alytus. Those concentrations were compared with the literature found naturally detected, deficiency, excessive and phytotoxic concentrations of HMs in plants. The results of the study indicated that HMs concentrations in trees grown in potentially contaminated areas exceeded neither excessive nor phytotoxic concentrations in plants. The HMs concentrations in the pinewood (*Pinus sylvestris)* in the growth places under study ranged within 0.1–3.50 $mg \cdot kg^{-1}$for Ni; 0.1–1.50 $mg \cdot kg^{-1}$for Cr; 0.25–3.00 $mg \cdot kg^{-1}$ for Cu; 10–160 $mg \cdot kg^{-1}$ for Mn; 2–75 $mg \cdot kg^{-1}$ for Zn; 0.05–2.80 $mg \cdot kg^{-1}$ for Pb, whereas the concentration in the birch (*Betula pendula*) varied within 0.90–3.20 $mg \cdot kg^{-1}$ for Ni; 0.90–2.50 $mg \cdot kg^{-1}$ for Cr; 40–130 $mg \cdot kg^{-1}$ for Mn; 1.0–3.50 $mg \cdot kg^{-1}$ for Pb (Fig 3.1). With Ni, Pb and Cr being constituents of internal-combustion engine emissions, the decrease of concentrations in the wood can be attributed to the decline in military activities (especially after Lithuania gained independence in 1990). The fall in concentrations were observed from 1986 to 1995, when the climate favoured tree increment. Neither tree had the factor of HMs transfer from the soil to the tree exceeding 1.0. Values of HMs transfer to the wood identified in the study ranged within 0.001–0.55 for Ni; 0.04–0.45 for Cu; 0.03–0.6 for Zn; 0.001–0.75 for Mn; 0.002–0.085 for Pb, and 0.005–0.11 for Cr.

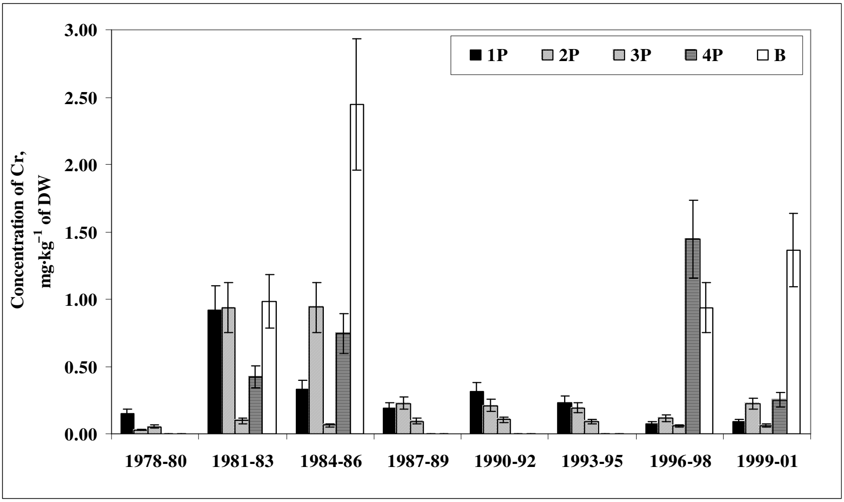

Fig 3.1. Cr concentration pine and birch trees during the period of 1978–2001

Values of transfer factors (TFs) for Mn, Cr and Pb were higher in the birch than in the pines, even in the pine and birch growing in the same soil and under the same conditions. This can be accounted for about 1.7–4 times larger amount of roots in birch than in pine. The study revealed higher TFs values of HMs from the soil depth of 20–30 cm, which might be associated with the highest density of fine roots actively participating in the uptake of elements at a depth of 0–30 cm. Mean Cr, Ni, Mn and Zn concentrations in the soil (0–40 cm) in the leeward from the trunk were observed to be lower (from 1.2 times for Zn and up to 2.5 for Mn) compared to the opposite direction. Thus the impact of the prevailing wind direction on the distribution of HMs in the soil under tree foliage was highlighted.

3.4. HMs in the pine affected by fungi. The accumulation of HMs in the wood is conditioned by the main physical and chemical stresses: the processes taking place in the tree and wood, as well as environmental biotic and abiotic stresses. Variation of HMs concentration in plants can be determined not only by the nature of the pollution but also by the physiological state of the plant and its changes. There is no extensive literature on the research into the interaction between HMs and diseases as well as their pathogens that are the factors making a major impact on the physiology of plants. A wood pathogen Heterobasidion *annosum* (Fr.) Bref. was determined in the pine wood from 1959 to 1960, where 4 and 7 times higher than mean concentrations for Ni and Cr during the study period were observed (Fig 3.2).

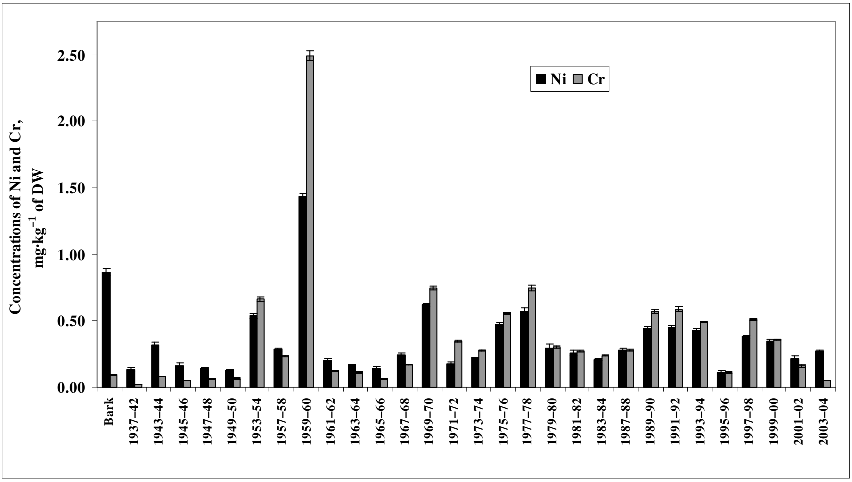

Fig 3.2. Concentrations for Ni and Cr in the annual rings and the bark of the affected pine from 1937–2004

The rise is supposed to be related to the fall in lignin production in the affected pine and, as a result, to the increase in the production of ferulic acid glycosides, actively transporting nutrients and possibly HMs. The depositions of Ni on the walls of plant cells increase their permeability thus stepping up metabolism, whereas Cr is essential to the production of glucose, which, in turn, produces glycosides and lignin. In the examination of the affected pine, the results have substantiated the two hypotheses: the defensive function of HMs and the HMs induced fortification of plants.

3.5. Transfer of HMs from sewage sludge to the seedlings of trees. Six years after the seedlings of the trees were planted in the soil treated by industrial sewage sludge (a layer of 2–3 cm), the elements most effectively transported to the trees were Zn (to the birch) and Ni (to the pine and the black alder) (TF>0.7), lower TFs were determined for Mn, Cu and Pb (TF = 0.2–0.7) (Fig 3.3). TFs values for Pb and Cu to the trees grown in the soil treated by sludge were higher as compared to naturally growing trees (0.01 and 0.05 respectively). The transfer of HMs to the trees was observed to likely be prompted by acid soil environment (pH 4.0–5.0), and by the higher level of dissolved organic carbon (some 2 times higher as compared to the control soil), and in some cases by the higher level of Al (some 4 times higher in comparison with the control soil). Depending upon the tree species, a little higher mean transfer of HMs was characteristic to the birch (TF = 0.51) and the black alder (TF = 0.49) than to the pine (TF = 0.44).

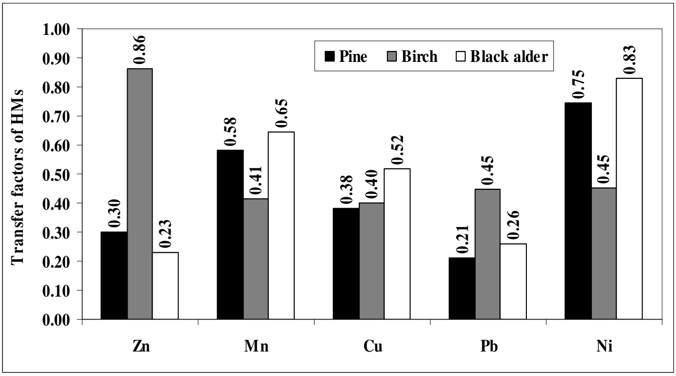

Fig 3.3. Factors of HMs transfer from the soil treated by sludge to the tree

This approves of the fact that *Betula pendula*, though not seen as a hyperaccumulator, can effectively be used to uptake HMs from contaminated soils. *Alnus glutinosa* is numbered among the tree species accumulating in the roots not only huge amounts of Zn, but also containing high levels of Mn and Ni in the above-ground parts.

3.6. Distribution of HMs chemical forms in the soils of the growth places of the trees. The uneven distribution of mobile and potentially mobile (MPM) forms of HMs varies depending on soil characteristics, the origin of HMs, influence of trees, the nature of growth places, etc.

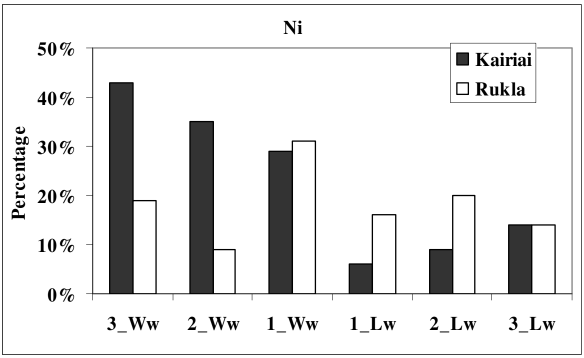

Fig 3.4. Ni MPM distribution in the soils of pine growth places (0–40 cm) in the prevailing wind directions in the Kairiai and Rukla–Gaižiūnai Military Grounds (3 m, 2 m, 1 m are the distances from the pines in the windward (Ww) and leeward (Lw) directions respectively

The concentrations of MPM forms of HMs in the soil treated by industrial sewage sludge were observed to be 2 (for Zn), 4 (for Ni) and 5 (for Cu and Pb) times higher than in control soil, whereas higher distribution of HMs in MPM forms of all the HMs studied (except Pb and Mn) at a depth of 20–40 cm was 1.5–2.0 times larger than in the whole 0–40 cm soil layer under study. The downward trend of MPM forms of HMs (mostly for Mn, Ni and Cr) was observed in the prevailing wind direction as compared to the opposite direction (Fig 3.4). This leads to the conclusion that a prevailing wind direction can make an indirect impact on the distribution of HMs in MPM forms in the soil under tree foliage.

4. Model of HMs Transfer from the Soil to the Tree. The HMs transfer from the industrial sewage sludge spread on the soil to the seedlings of trees was based on the simplified model of the transfer of contaminants from the soil to plants made by Hung and Muckay. The model evaluates the HMs transfer to the plant from the soil and air. The uptake of HMs from the soil to plants rests upon the factors of distribution of contaminants in various environments (soil, water, transpiration flow, ect.), as well as upon metabolic rate and steady factors of contaminant concentration. When employing the model for modelling of HMs transfer from the soil treated by industrial sewage sludge to the seedlings of coniferous and leafy trees (Fig 3.5) some adjustments were made by evaluating the equilibrium partition coefficients for HMs in octanol and water (K_{ow}); by introducing the equilibrium partition coefficients for HMs in soil and water (K_d), which are dependant on the soil pH and the level of organic matter; by introducing the overall coefficient (K_T) of HMs solubility in water as well as by introducing corrective coefficients.

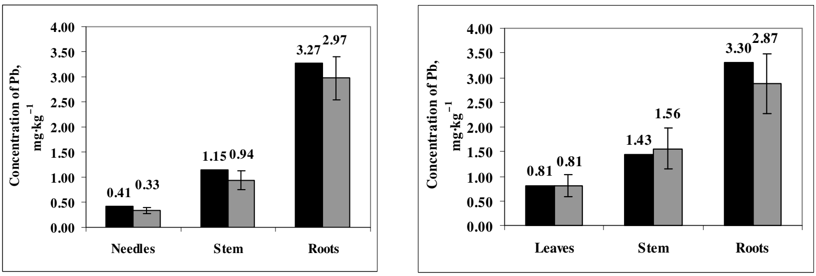

Fig 3.5. Pb concentrations in the parts of the seedlings of coniferous (a) and leafy (b) trees: black colour represents modelling results; grey colour stands for the results of the experiments

By employing the model, a mean corrective coefficient of HMs transfer from the soil treated by sludge to the roots of leafy trees was 2.0, from roots to the trunk 0.28, and from the trunk to leaves 2.9.

A mean corrective coefficient of HMs transfer from the soil treated by sludge to the roots of coniferous trees was 1.8, from roots to the trunk 0.31, and from the trunk to needles 2.56.

5. Developed and Applied Methods and Tools. Increment borer used in the forestry was adapted to the sampling of tree annual rings and the studying of HMs concentration. It is superior in its **simple use** and is **less time consuming** as it does not involve the cutting down of the tree and produce small yet sufficient amount of samples for analysis. **No additional measures** (e.g. workforce, tree cutting skills, etc.) are needed. Increment borer is a **practical method** for sampling the tree rings to determine HMs concentrations without cutting down the tree. The method is also **simple technically**: the sampling is quick, without using saws for cutting the tree. The increment borer as well as its samples are easy to carry or transport. Using this method means greater accuracy of separating the annual rings as compared to other methods (splitting, planing, scraping etc.) as well as leads to the precise concentration of HMs accumulated in the wood. The samples are taken without doing any harm to tree studied, as the mass of one sample is relatively very small (0.1–0.2 g), and the bore in the trunk can be easily sealed with a wood splinter to avoid infection. **Lithuanian patent for methodology No. 5325 B has been obtained to determine HMs concentration by sampling separate rings with increment borer in 2006.**

Conclusions and Recommendations

1. A direct connection has been determined between the concentrations of HMs in the wood, soil and unfavourable climate conditions for the increment of trees.
2. A prevailing wind direction has been determined to have influence over the distribution of HMs in the soil under tree foliage: HMs concentrations at a depth of 0–40 cm in the leeward direction from the trunk were from 1.2 for (Zn) to 2.5 for (Mn) times lower than to the windward direction.
3. The increase of HMs in mobile and potentially mobile forms in the soil of the growth places of the study trees has been identified to depend on the nature of the soil pollution (in the soil treated by sewage sludge distribution of Zn, Pb, Ni and Cu was 2, 5, 4 and 5 times respectively larger in mobile and potentially forms than in control soil); the depth of the soil (with the exception of Mn and Pb, distribution of other HMs in the mobile and potentially mobile forms at a depth of 20–40 cm, was 1.5–2.0 times higher

than in the whole 0–40 cm soil layer under study); a prevailing wind direction (mobile and potentially mobile forms of HMs found in the leeward direction from the trunk showed a tendency to decline in comparison with the windward direction).

4. A prevailing downward trend of concentrations has been observed along the trunk toward the tree top for Cr, Ni and Zn, whereas the upward trends were detected for Pb, Mn and Cu.
5. A pathogen *Heterobasidion annosum* detected in the ring of the pinewood in 1959–1960 had no decisive influence over the transfer of Mn, Zn, Cu and Pb from the soil, whereas mean concentrations for Ni and Cr in the wood of the year in question increased some 5 times in comparison with the mean concentrations during the study period.
6. Different methods can serve the purpose of tree ring sampling for further HMs analysis: splitting with common and arched chisels, planing and boring with increment borer.
7. The intercalibrative measurements taken at the research laboratories of the Department of Environmental Protection (Vilnius Gediminas Technical University) and of Mikkeli Technical High School (Finland) have suggested that wood samples can be prepared by a wet extraction and digestion, because T-test showed no significant difference between the mean values of HMs concentrations (the calculated value of T criteria was lower than the critical two-tailed value thereof).
8. When using Hung and Muckay, a model of the transfer of contaminants from the soil to plants, adapted to the experimental conditions, the results of modelling differed around 6 % in leaves, 5 % in trunk and 8 % in roots as compared with those of experimental measurements.
9. According to the Lithuanian patent No 5325 B for method, the increment borer is recommended for determining HMs concentration, as with the mass of a sample being reduced up to 0.10 g and a mean relative error of HMs concentration was 9 %. The method should involve accurate grinding of the wood, which is advisable to be kept in nitrogen acid (65 %) prior to digestion for at least 24 hours.
10. The spreading of sewage sludge on the soil as well as the planting of the seedlings of trees are recommended for the treatment of the sludge. The highest transfer factor to pine was 0.75 for (Ni), to birch 0.86 for (Zn), to black alder 0.83 for (Ni).

List of Published Works on the Topic of the Dissertation

In the scientific periodical publications included in ISI Master List

1. BALTRĖNAITĖ, E.; BUTKUS, D. Investigation of heavy metals transport from the soil to the pine tree. *Water Science and Technology*, 2004, Vol 50(3), p. 239–244. ISSN 0273-1223.
2. BALTRĖNAITĖ, E.; BUTKUS, D. Heavy metals in *Pinus Sylvestris L.* and *Betula pendula* annual rings. *Ekologija*, 2007, No 1, p. 29–36.

In the conference proceedings included in ISI Proceedings List

3. BALTRĖNAITĖ, E.; BUTKUS, D.; POURU, M. Intercalibrative measurements of heavy metals concentration in pinewood and soil. In: *Proceedings of the VI International Conference Environmental Engineering held in 26–27th May 2005 in Lithuania*. Vilnius: Technika, 2005, p. 7–11. ISBN 9986-05-850-3.

In the scientific periodical publications included in international databases of reviewed scientific periodical publications

4. BUTKUS, D.; PALIULIS, D.; BALTRĖNAITĖ, E. Sorbtion of heavy metals from polluted water and their migration in the system soil–tree. *Journal of Environmental Engineering and Landscape Management*, 2004, Vol 12(4), p. 120–125. ISSN 1648-6897, (CSA, EBSCO, COMPEDEX, ICONDA, VINITI, SCOPUS).

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5. BUTKUS, D.; BALTRĖNAITĖ, E.; KAZIUKONIENĖ, D. Estimation of heavy metals accumulation in tree rings (in Lithuanian). *Environmental Engineering* (Aplinkos inžinerija), 2002, Vol 10(4), p. 156–160. ISSN 1392-1622.
6. BALTRĖNAITĖ, E.; BUTKUS, D.; KAZIUKONIENĖ, D. Evaluation of heavy metals accumulation in pine and birch wood. *Известия Академии Промышленной Экологии,* 2004*,* No 4, p. 65–70, (in Russian).

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8. BALTRĖNAITĖ, E.; BUTKUS, B. Access and accumulation of heavy metals in trees (in Lithuanian). In: *Proceedings of the V Conference of Young Scientists "Lithuania without science – Lithuania without the future", organized in Vilnius, 21st March 2002. Environmental Engineering*. (5-osios jaunųjų mokslininkų konferencijos „Lietuva be mokslo – Lietuva be ateities", įvykusios Vilniuje 2002 m. kovo mėn. 21 d., medžiaga.

Aplinkos inžinerija). Vilnius: Technika, 2002, p. 103–110. ISBN 9986-05-564-4.

9. BALTRĖNAITĖ, E.; BUTKUS, D. Evaluation of heavy metals transportation from different types of soil to the pine (in Lithuanian). In: *Proceedings of the VI Conference of Young Scientists "Lithuania without science – Lithuania without the future", organized in Vilnius, 20th March 2003*, *Environmental Engineering*. (6-osios jaunųjų mokslininkų konferencijos „Lietuva be mokslo – Lietuva be ateities", įvykusios Vilniuje 2003 m. kovo mėn. 20 d., medžiaga. Aplinkos inžinerija). Vilnius: Technika, 2003, p. 234–244. ISBN 9986-05-645-4.
10. BALTRĖNAITĖ, E.; BUTKUS, D. Intercalibration of measurements of heavy metals concentration in soil around a pine tree (in Lithuanian). In: *Proceedings of the VII Conference of Lithuanian Junior Scientists „Lithuania Without Science – Lithuania Without the Future", 25th March 2004. Environmental Engineering*. (7-osios jaunųjų mokslininkų konferencijos „Lietuva be mokslo – Lietuva be ateities", įvykusios Vilniuje 2004 m. kovo 25 d., medžiaga. Aplinkos inžinerija). Vilnius: Technika, 2004, p. 212–221. ISBN 9986-05-755-8.
11. BALTRĖNAITĖ, E.; BUTKUS, D. Different tree rings sampling methods and their assessment (in Lithuanian). In: *Proceedings of the VIII Conference of Lithuanian Junior Scientists "Lithuania Without Science – Lithuania Without the Future", 24th March 2005. Environmental Engineering*. (8-osios jaunųjų mokslininkų konferencijos „Lietuva be mokslo – Lietuva be ateities", įvykusios Vilniuje 2005 m. kovo 24 d., medžiaga. Aplinkos inžinerija). Vilnius: Technika, 2005. p. 178–184. ISBN 9986-05-876-7.
12. BALTRĖNAITĖ, E.; BUTKUS, D. Distribution of heavy metals concentration in *Pinus sylvestris* L. infected with pathogens. In: *Proceedings of the IX Conference of Lithuanian Junior Researchers "Science – the Future of Lithuania", 30th March 2006, Vilnius. Environmental Engineering.* (9-osios jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis", įvykusios Vilniuje 2006 m. kovo 30 d., medžiaga. Aplinkos inžinerija). Vilnius: Technika, 2006, p. 213–219. ISBN 9955-28-037-9.

Patent

BALTRĖNAS, P.; BUTKUS, D.; BALTRĖNAITĖ, E. Nr. LT 5325 B. Int. Cl. G01N 33/46. Method to determine concentration of heavy metals in annual tree ring (Sunkiųjų metalų koncentracijos nustatymo metinėje medienos rievėje būdas). Invention patent No 5325 has been obtained in 2006. 5 p.

About the author

Edita Baltrėnaitė was born in Kaunas on 28 August 1980. In 2002 she took a Bachelor's Degree in Environmental Engineering at Vilnius Gediminas Technical University. In 2004 she obtained a Master's Degree in Environmental Protection Management and Clean Production at the Faculty of Environmental Engineering at Vilnius Gediminas Technical University. Edita Baltrėnaitė worked at the Research Institute of Environmental Protection from 2000 to 2004 and was a doctoral student at Vilnius Gediminas Technical University from 2004 to 2007. She was a Socrates-Erasmus student at Lulea University of Technology in Sweden from January to March 2001. Edita had traineeships at Mikkeli Technical High School in Finland and at Norwegian University of Life Sciences in 2003 and 2006 respectively. On 17 December 2003 Edita Baltrėnaitė was awarded the Petras Vileišis sculptural portrait, established by the Confederation of Lithuanian Industrialists. Currently Edita Baltrėnaitė is working as an assistant at the Department of Environmental Protection at Vilnius Gediminas Technical University.

SUNKIŲJŲ METALŲ PERNAŠOS IŠ DIRVOŽEMIO Į MEDĮ TYRIMAI IR ĮVERTINIMAS

Problema

Sunkieji metalai (SM) yra gamtinė žemės plutos sudedamoji dalis, tačiau žmogaus veikla drastiškai keičia jų geocheminį ir biocheminį balansą. Intensyvus miestų augimas, pramonės plėtra, transporto intensyvumo didėjimas ir žemės ūkio vystymasis kelia dirvožemio užtaršos SM problemas. Aplinkos tarša SM yra svarbi problema, nes pagal suminį Korte indeksą, kuris rodo pavojingumą gyvybei, sveikatai ir paveldimumui, SM užima vieną iš pirmųjų vietų tarp tokių ekologinių problemų, kaip pesticidai, rūgštūs lietūs, naftos išsiliejimo pasekmės, cheminių trąšų ar triukšmo poveikis. Dideli žemės plotai yra užteršti SM, susidariusiais nuotekose, atliekų deginimo įrenginiuose, žemės ūkyje naudojant trąšas, pesticidus, pramonėje – apdirbant metalus, odą ir kt. SM yra ilgalaikiai teršalai, besikaupiantys dirvožemyje ir augaluose, tačiau gamtiniu būdu negalintys iš jų pasišalinti. Labiausiai pavojingi yra toksiški SM (švinas, chromas, nikelis, varis, cinkas, manganas ir kt.) bei jų tirpūs junginiai. Vieni SM (pvz., cinkas, manganas, nikelis) yra svarbios augalui maistinės medžiagos, kiti (pvz., švinas, kadmis, gyvsidabris) yra labiau kenksmingos negu naudingos augalams medžiagos. SM patekimas į augalą, jų pernaša ir pasiskirstymas augale turi įtakos augalo mitybai. Augalų gebėjimas kaupti SM savo organizme leidžia spręsti dirvožemių užtaršos SM problemą. Kasmet Lietuvoje susikaupia apie 200 tūkst. tonų nuotekų dumblo. Šiuo metu dumblas sandėliuojamas, juo tręšiami laukai, tačiau sandėliuojamo dumblo kiekiai vis didėja, o dėl didelės SM koncentracijos laukų tręšimui dumblą naudoti draudžiama. Reikalingi ekonominiu požiūriu patrauklūs, darnaus vystymosi principais paremti nuotekų dumblo tvarkymo metodai.

Darbo aktualumas

Iš lokalių ir tolimesnių taršos šaltinių sausomis iškritomis ir su krituliais SM patenka ant dirvožemio, nusėda ant augalų ir tokiu būdu yra įtraukiami į biogeocheminius procesus. Ilgos vegetacijos augaluose, pvz., medžiuose, SM patekdami per šaknis, lapus ir gali kauptis atskirose dalyse. Dėl šios savybės medžiai priskirtini aplinkos užtaršos bioindikatoriams. Aplinkos taršos bioindikatoriais medžiai naudojami stebint SM koncentracijas spygliuose, lapuose, žievėje ir medienos metinėse rievėse. Jei spygliuose aptinkama pastarųjų trejų–ketverių metų SM kiekiai, lapuose – paskutiniųjų metų SM sankaupos, o žievėje – galbūt ir visu vegetacijos laikotarpiu sukaupti SM kiekiai, tai į besiformuojančias rieves patenka tais metais medžiui prieinami dirvožemyje esantys SM. Šiuo atveju medyje sukaupta informacija apie dirvožemio taršą SM praeityje leidžia stebėti taršos kitimo tendencijas, išskirti lokalius taršos šaltinius, o ligotame medyje – nagrinėti konkrečiu laikotarpiu atsiradusių ligos sukėlėjų ir SM sąveiką. Todėl SM nustatymas medienos ėminiuose, sudarytuose iš kuo mažiau metinių rievių tampa vis aktualesnis. Apie 10 % Lietuvoje augančių pušų turi nustatomus pažeidimus dėl grybinių ligų, žmogaus veiklos, abiotinių veiksnių, graužikų ir kt. Beržai yra daug atsparesni šiems pažeidimams, tačiau grybinės ligos yra pažeidusios apie 1,3 % pušynų ir apie 1,2 % beržynų. Labiausiai paplitusi Lietuvoje pušų grybinė liga – šakninė pintis (*Heterobasidion annosum* (Fr.) Bref.). Šiuo metu pasaulyje jau atlikta nemažai tyrimų apie augalų atsparumą biotiniams veiksniams arba pasisavinant SM, tačiau ligos sukėlėjo paveikto augalo keliami signalai ir medžiagų apykaitos pokyčiai dar nėra plačiai ištirti. Šiame darbe pateikta SM koncentracijos kaita grybinio sukėlėjo – šakninės pinties (*Heterobasidion annosum* (Fr.) Bref.) – pažeistos pušies medienoje ir įvertinta SM ir ligos sukėlėjo tarpusavio sąveikos hipotezė. Plačiai tiriami augalai, galintys intensyviai kaupti antžeminėje dalyje SM, tokiu būdu sumažindami SM kiekį dirvožemyje. Nors apskritai medžiai nėra priskiriami tokio tipo augalams, tačiau pavienės rūšys geba iš dirvožemio į kamienus pernešti net apie 60 % dirvožemyje esančių SM. Tokie medžiai gali būti sėkmingai sodinami užterštu dumblu patręštuose dirvožemiuose. Nuotekų dumblo paskleidimas miškų kirtavietėse ir medžių pasodinimas yra viena iš nuotekų dumblo tvarkymo galimybių, tačiau nepakanka informacijos apie SM pernašą į medžius bei skirtingų rūšių medžių kaupimo efektyvumą natūraliomis lauko sąlygomis.

Darbo tikslas ir uždaviniai

Darbo tikslas – nustatant SM koncentraciją skirtingos užtaršos dirvožemiuose ir skirtingų rūšių medžiuose, įvertinti jų pernašą iš dirvožemio į medį.

Darbo uždaviniai:

1. Įvertinti paprastosios pušies (*Pinus sylvestris* L.) ir karpotojo beržo (*Betula pendula* Roth) bioindikatorines savybes pagal SM koncentracijas metinėse rievėse, klimato sąlygas ir tiriamos vietovės aplinkos taršą SM praeityje.
2. Palyginti SM koncentracijas skirtingais metodais paimtuose medienos metinės rievės ėminiuose.
3. Nustatyti ir įvertinti SM pasiskirstymą dirvožemyje po medžių lajomis.
4. Nustatyti ir įvertinti SM koncentracijų pušies medienoje ir puvinio sukėlėjo tarpusavio ryšį.
5. Nustatyti ir įvertinti SM pernašą iš dumblu patręšto dirvožemio į Lietuvoje paplitusių medžių (paprastosios pušies, karpotojo beržo ir juodalksnio) sodinukus.
6. Atlikti SM pernašos iš dirvožemio į medį modeliavimą.

Mokslinis naujumas

Darbo naujumą sudaro kompleksinis SM tyrimas medžiuose, apimantis teorinę SM pernašos iš dirvožemio į medžius analizę, eksperimentinius tyrimus ir SM pernašos iš dirvožemio į medį modeliavimą. Pristatomi kompleksiniai SM pernašos tyrimai siekiant įvertinti SM pernašą iš įvairios užtaršos dirvožemio į skirtingų rūšių, amžiaus ir augimo sąlygų medžius. Darbe pristatomas SM koncentracijos atskiroje metinėje rievėje nustatymo metodas ir aptariami SM ir ligų sukėlėjo tarpusavio ryšiai.

Praktinė vertė

Pagal SM koncentracijas medžio rievėse gaunama informacija apie aplinkos taršą jais konkrečioje vietoje ir konkrečiais praeities metais. Tokiu būdu galima nustatyti taršos SM šaltinių intensyvumą praeityje ir įvertinti apkrovos šiais teršalais dinamiką praeityje, o taip pat nustatyti lokalinių taršos šaltinių emisijos kaitą. Pagal darbe pasiūlytus ir patobulintus metinės rievės ėminių paėmimo būdus galima paimti medienos metinių rievių ėminius iš nukirstų medžių arba tiksliau paimti ėminius iš augančių medžių, jų nenukertant. SM pernašos iš nuotekų dumblo į trijų rūšių Lietuvos medžius rezultatai suteikia praktinės informacijos apie skirtingų medžių gebėjimą kaupti SM, todėl gali būti panaudoti, parenkant dumblo tvarkymo alternatyvas, parenkant medžių rūšį.

Ginamieji teiginiai

1. Dirvožemiuose po medžių laja ir priklausomai nuo taršos pobūdžio kinta SM ir jų cheminių formų pasiskirstymas.
2. Ant dirvožemio paskleistam dumblui valyti nuo SM tinka ir pušies, beržo ir juodalksnio sodinukai.

Darbo apimtis

Darbą sudaro bendra darbo charakteristika, 5 skyriai, išvados ir rekomendacijos, literatūros sąrašas, publikacijų ir pranešimų mokslinėse konferencijose sąrašai. Bendra disertacijos apimtis – 153 puslapiai, 54 iliustracijos ir 25 lentelės.

Pirmame disertacijos skyriuje analizuojama literatūra apie SM kaitą dirvožemyje, medžiuose ir SM pernašos iš dirvožemio procesus bei juos veikiančius veiksnius.

Antrame disertacijos skyriuje pateikiama eksperimentinių tyrimų metodika (SM nustatymas dirvožemyje, medienoje, dirvožemio savybių nustatymas), naudoti statistiniai metodai, SM pernašos iš dirvožemio į medžius koeficientų skaičiavimas.

Trečiame disertacijos skyriuje aptariami eksperimentinių tyrimų metu gauti rezultatai apie: SM pernašą į medžius, augusius potencialiai užterštose teritorijose ir į grybų pažeistą pušį, SM pernašą iš nuotekų dumblu patręšto dirvožemio į pušies, beržo ir juodalksnio sodinukus; SM koncentracijų ir judrių bei potencialiai judrių formų kaitą dirvožemyje po medžių laja. Šiame skyriuje palyginamos SM koncentracijos skirtingais metodais paimtuose metinių rievių ėminiuose ir aptariami palyginamųjų matavimų, nustatant SM koncentracijas medienoje, rezultatai.

Ketvirtame disertacijos skyriuje pateikta SM pernašos iš dirvožemio į medį modeliavimo metodika ir rezultatai.

Penktame disertacijos skyriuje aprašomi patobulinti metodai ir panaudoti įrenginiai, skirti imti metinės rievės ėminius ir juose nustatyti SM koncentracijas.

Rezultatų aprobavimas

Darbo rezultatai paskelbti 13 mokslinių publikacijų: 2 moksliniai straipsniai žurnaluose, įtrauktuose į Mokslinės informacijos instituto (MII) duomenų bazės pagrindinį sąrašą (ISI Master Journal List); 1 – konferencijos pranešimų medžiagoje, referuotoje Mokslinės informacijos instituto (MII) duomenų bazėje (ISI Proceedings); 2 moksliniai straipsniai recenzuojamuose užsienio leidiniuose; 2 mokslo straipsniai žurnaluose; 5 mokslo straipsniai kitoje Lietuvos spaudoje, gautas Lietuvos patentas LT 5325 B. Disertacijos rezultatai aptarti 6 tarptautinės konferencijose ir moksliniuose susitikimuose bei

5 respublikinėse mokslinėse konferencijose. 7 mokslinės publikacijos išspausdintos konferencijų pranešimų medžiagoje, o 3 mokslinių publikacijų santraukos – konferencijų santraukų knygose.

Išvados ir rekomendacijos

1. Nustatyta tiesioginė priklausomybė tarp SM koncentracijos medienoje, dirvožemyje ir nepalankių medžių prieaugiui klimato sąlygų.
2. Nustatyta, kad SM koncentracijų pasiskirstymui dirvožemyje po medžių laja turi įtakos vyraujančioji vėjų kryptis: 0–40 cm dirvožemio gylyje pavėjine kryptimi nuo kamieno SM koncentracijos buvo nuo 1,2 karto (Zn) iki 2,5 karto (Mn) mažesnės negu priešvėjine kryptimi nuo kamieno.
3. Nustatyta, kad SM judrių ir potencialiai judrių formų padidėjimas tirtų medžių augimviečių dirvožemyje priklauso nuo: dirvožemio užtaršos pobūdžio (nuotekų dumblu patręštame dirvožemyje judrių ir potencialiai judrių SM formų buvo apie 2 kartus Zn, 4 kartus Ni ir apie 5 kartus Cu ir Pb atvejais daugiau negu kontroliniame dirvožemyje); dirvožemio gylio (išskyrus Mn ir Pb, kitų tirtų SM judrių ir potencialiai judrių formų 20–40 cm gylyje buvo nuo 1,5 iki 2,0 karto daugiau negu vidutiniškai 0–40 cm dirvožemio sluoksnyje); vyraujančios vėjo krypties (pavėjine kryptimi nuo kamieno SM judrių ir potencialiai judrių formų dalis turi tendenciją mažėti lyginant su priešvėjine kryptimi).
4. Pastebėta, kad išilgai kamieno viršūnės link Cr, Ni ir Zn atvejais vyravo koncentracijų mažėjimo, o Pb, Mn ir Cu – didėjimo tendencijos.
5. Pušies medienoje 1959–1960 m. medienos rievėje aptiktas puvinio sukėlėjas *Heterobasidion annosum* lemiamos įtakos Mn, Zn, Cu ir Pb pernašai iš dirvožemio neturėjo, o Ni ir Cr koncentracijos tų metų medienoje padidėjo vidutiniškai 5 kartus.
6. SM koncentracijoms nustatyti medienos rievės ėminiams imti tinka įvairūs metodai: skėlimas „lenktaisiais“ ir „paprastaisiais“ kaltais, obliavimas ir medienos gręžimas Preslerio grąžtu.
7. Pagal palyginamuosius matavimus VGTU Aplinkos apsaugos ir darbo sąlygų laboratorijoje ir Mikkeli politechnikos institute (Suomija) nustatyta, kad medienos ėminius galima ruošti šlapiosios ekstrakcijos ir mineralizavimo būdu, nes statistinio T-tyrimo metu skirtumas tarp vidutinių verčių buvo nereikšmingas (apskaičiuota T kriterijaus vertė buvo mažesnė negu kritinė T vertė).
8. Pritaikius pagal eksperimento sąlygas pakoreguotą Hung ir Muckay teršalų pernašos iš dirvožemio į augalus modelį, modeliavimo rezultatai nuo matavimo rezultatų skyrėsi apie 6 % lapuose, 5 % kamiene ir 8 % šaknyse.

9. Pagal gautą Lietuvos patentą LT 5325 B rekomenduojama SM koncentracijoms nustatyti, medienos rievių ėminius imti Preslerio grąžtu, nes sumažinus ėminio masę iki 0,10 g SM koncentracijos santykinė paklaida vidutiniškai buvo 9 %. Pagal šį metodą tikslinga rievės medieną kruopščiai susmulkinti ir patartina prieš mineralizavimą palaikyti 65 % azoto rūgštyje.
10. SM iš nuotekų dumblo valyti rekomenduojama nuotekų dumblą paskleisti ant dirvožemio ir pasodinti medžių sodinukus. Didžiausi pernašos į pušį faktoriai buvo 0,75 (Ni), į beržą – 0,86 (Zn), į juodalksnį – 0,83 (Ni).

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INVESTIGATION AND EVALUATION OF THE TRANSFER OF HEAVY METALS FROM THE SOIL TO THE TREE

Summary of Doctoral Dissertation
Technological Sciences, Environmental Engineering and Landscape Management (04T)

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