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ENVIRONMENTAL BEHAVIOUR OF HEAVY METALS IN GARDEN SOILS MODIFIED BY ANTHROPOGENIC ACTIVITIES IN THE CASE OF SZEGED

Theses of Dissertation

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INTRODUCTION AND AIMS OF THE RESEARCH

The intensive growth of urban areas and the anthropogenic activities being present there result in the physical and chemical modification, the transformation at different rate, and the contamination of urban soils. The cumulative effects of concentrated busy traffic that is characteristic of cities, domestic heating, uncontrolled dumping of domestic and industrial waste, and industrial emission cause the heavy metal content of these soils to increase. As these materials do not decompose naturally, and, as a result, they are able to accumulate in soils, heavy metals become excellent indicators of environmental impact. However, urban soils are not only the recipients of anthropogenic heavy metals, these soils can easily become the sources of these toxic and potentially toxic materials as well since these heavy metals are able to enter the human body system of urban residents either directly (inhaling contaminated dust, ingesting soil, or the metals being absorbed through the skin) or indirectly (consuming vegetables and fruits grown in contaminated soils) from these soils. Due to their being cultivated, the soils of urban orchards and vegetable gardens need special attention because they can become contaminated through their cultivation too (using pesticides containing metals, mixing compost as well as organic and artificial fertilizers into the soil, irrigating with contaminated water). Therefore, during the course of my doctoral research I aimed at studying the garden soils located in the transition zone (i.e. “urban buffer zone”) of downtown technogenic soils and natural soils surrounding the cities comprehensively; especially emphasizing the heavy metal contamination of these soils and the possible harmful effects arising therefrom.

The study area of my research is Szeged, the third most populated city of Hungary, where the soils with garden cultivation function can be found on the outskirts of the city, further from the downtown area, quite similarly to other Hungarian and European cities; therefore, Szeged represents other Hungarian and European cities of similar size and without heavy industry very well.

The aims of my doctoral research are as follows:

- I aimed at measuring to what extent the cumulative effects of urbanization and garden cultivation modify the physical and chemical properties as well as the pedologic classification characteristics of garden soils with cultivation function.
- I also aimed at classifying the soils profiles exposed in the studied gardens into the international soil classification system (Word Reference Base for Soil Resources; WRB).

- I aimed at studying the heavy metal contamination of garden soils as well as separating the group of anthropogenic metals in these soils by employing enrichment factors, simple and multivariate statistical methods, and the vertical and horizontal distribution of metal concentrations; furthermore, I aimed at identifying the sources of these metals in order to assess both the extent of urban environmental impact, and the extent of the cumulative effect of heavy metal contamination which was induced by garden cultivation.
- I aimed at sorting the gardens with similar heavy metal load by employing multivariate statistical methods so that I could study these groups more thoroughly in order to gain more accurate information about the factors influencing the heavy metal load of garden soils.
- I aimed at studying the heavy metal buffering capacity of garden soils modified by anthropogenic activities by analyzing and evaluating soils properties that exert great influence on the mobility of heavy metals and, therefrom, their bioavailability for plants.
- I aimed at estimating the mobilizable (i.e. easily obtainable for plants) and potentially mobilizable metal proportions of certain elements using sequential extraction; moreover, I aimed at revealing the differences between anthropogenic and geogenic metals within this particular aspect.
- Finally, I aimed at measuring the heavy metal content of vegetables often grown in urban garden soils in order to see to what extent the different vegetables are able to accumulate certain elements from urban garden soils; also, by employing bioaccumulation indices I aimed at evaluating the actual mobility of metals in the soil-plant system.

SAMPLES AND METHODS

Sampling

In order to study urban garden soils, I collected composite topsoil samples (0–10 cm) and control samples (80–100 cm) from 51 gardens (31 vegetable gardens, 9 orchards, and 11 flower gardens) of 50 houses in Baktó, a district on the outskirts of Szeged, in 2010. In 9 gardens, full soil profiles were exposed and analyzed on the spot, and more soil samples were taken from each of the genetic horizons and soil layers of these profiles for laboratory analysis. I also collected different vegetables (lettuce, sorrel, spinach, carrot, and onion) from 20 of the studied gardens, so the total laboratory analysis involved 134 soil samples and 35 plant samples altogether. Besides collecting soil samples and plant samples, I also asked the residents to fill in a questionnaire in order to collect information about garden soil-use methods, the past of the garden in question, the use of pesticides and other soil improvers, and possible infills.

Laboratory Analyses

After laboratory preparation (drying, pulverizing, and sieving), the following analyses were performed in the case of soil samples: mechanical composition was specified on the basis of the Arany yarn number (K_A). The pH of soil samples was measured potentiometrically in H_2O and as well as in KCl soil suspension [pH(H_2O), pH(KCl)]; the Scheibler calcimetric method was used to measure the carbonate content ($CaCO_3$% given in mass percentage) of the soil samples. Humus content (H%) was measured with colorimetric method after having performed oxidization with concentrated acidic and potassium dichromate solutions; the quality of humus was also analyzed with an optical method, without fractionation, and the process was based on the method of Hargitai; in addition, I characterized the quality of humus with the humus stability coefficient value (K). I analyzed the total water-soluble salt content of the soil samples (total salt %) with a conductivity tester by measuring the electric conductivity of a saturated soil paste.

In order to determine the “total” heavy metal content, the soil samples were digested with aqua regia in a microwave oven, and then the concentrations of heavy metals (Ni, Co, Cr, Cu, Pb, Zn, Cd), As, and Ti as reference element were measured by inductively coupled plasma optical emission spectrometer (ICP-OES). Metal fractions of different mobility were also measured (ICP-OES) with the help of the “modified version of the BCR” three-step sequential extraction procedure in the case of some selected soil samples.

Measuring the heavy metal content of the plant samples was also performed by using the ICP optical emission spectrometer after the plant samples were prepared for laboratory analysis and exposed to concentrated acidic solution (cc. HNO_3) in a microwave oven.

Calculating Enrichment Factors and Bioaccumulation Indices

The extent of surface enrichment of the studied elements was estimated with the help of enrichment factors (EF). I calculated two enrichment factors. One of them is the "*Top Enrichment Factor*" (TEF) which shows the proportion of metal concentrations measurable in the topsoil and the control soil samples. The other enrichment factor is the "*Pedologic Enrichment Factor*" (EFP) which shows the proportion of a studied element and that of a carefully chosen reference element (which is Ti in my research) in the topsoil compared to the parent material instead of the real concentrations of these elements. The above mentioned factors were calculated as follows:

$$TEF = \frac{[E]_{SH}}{[E]_{RH}}\ ;\ EFP_{Ti} = \frac{[E]_{SH}/[Ti]_{SH}}{[E]_{RH}/[Ti]_{RH}}$$

where "*E*" represents the concentration of the studied element in the surface soil horizon (SH) (0–10 cm) as well as in the reference horizon (RH) (80–100 cm) at the same sampling spot.

The mobility of the studied metals in the soil–plant system was analyzed by calculating and assessing bioaccumulation indices (BAI). This index represents the proportion of the accumulated metal content of a certain plant (or part of a plant) and the metal content of the soil in which that particular plant grew:

$$BAI = \frac{[E]_{Plant}}{[E]_{Soil}},$$

where "*E*" represents the concentration of the selected metal (mg/kg) in the studied plant (of dry weight) and in the soil ("total", aqua regia-extractable concentration of the same element).

Methods of Evaluating Results and Statistical Approaches

Processing and evaluating survey results were performed using the Microsoft Office Excel 2003 and the IBM SPSS Statistics 20 software. Evaluating survey results and calculated data were performed using multivariate statistical methods (correlation analysis, principal component analysis, cluster analysis), and parametric and non-parametric statistical tests (paired samples t-test, independent samples t-test, analysis of variance (ANOVA), Mann-Whitney *U* test, Kruskall–Wallis test). Geoinformation methods were used to study the spatial distribution of measured or calculated data. Spatial analysing of the data and creating various maps (heavy metal distribution maps, enrichment factors map, cluster map) were done with using the ArcMap 10 software.

SUMMARY OF RESULTS, THESES

1. Due to the cumulative effects of urbanization and garden cultivation, suburban garden soils are modified; this modification is manifested in the quantitative and qualitative changes of the organic matter, the modification of the mechanical composition, and the quantitative change of the carbonate content of these soils the most.

Analysing the soil profiles and the soil samples of the gardens in the buffer zone of Szeged has revealed that due to the effects of various human activities affecting urban garden soils certain properties of these soils (mechanical composition, humus content, humus quality, carbonate content) have been modified partly by garden cultivation (such as using different organic fertilizers as well as kitchen and garden waste turned into compost, mixing different layers of soil, etc.), partly by other human activities not closely related to garden cultivation (such as infilling garden soils, mixing in foreign soil matter):

i. The former activities can be detected in both the quantitative and qualitative changes of the humus state of garden soils; the total humus content of garden topsoils increases while, at the same time, the amount of raw humus matter of less quality also increases as opposed to the humus conditions of the original soil of the area.
ii. The latter activities can be detected in the modification of the mechanical composition of garden soils first of all as using soil with more coarse texture for infilling results in the increased appearance of coarser particle size fractions in the mechanical composition of topsoils, which also causes the value of the Arany yarn number to reduce.
iii. The carbonate content of the topsoil of garden soils is also affected by quantitative changes (it means that the carbonate content of topsoils does not change in each and every garden, and when it does so, the increase is of different rate) which is the collective result of garden cultivation and infilling.

2. The anthropogenic effects affecting suburban gardens and the extent of soil modification therefrom are much smaller and of different nature than those of downtown and heavily technogenic soils.

The prevalence of soils of almost natural status in the buffer zone of Szeged is dominant, these soils are only modified (mixing of topsoil layers, increased humus content) to an extent that does not make it necessary to have them re-classified as anthropogenic soils (WRB). At the same time, the diversity of urban garden soils is well reflected in the presence of partly or totally anthropogenic soils infilled with soil-like materials. Examples of suburban garden soils include Chernozems of almost natural status (Vermic, Calcic Chernozems), young Cambisols with anthropogenic topsoil layer (Hortic Cambisol), and Anthrosol with thick, man-made topsoil layer (Terric Anthrosol) too.

3. Using only enrichment factors (EF), or analysing the vertical and horizontal distribution of metal concentrations, or employing multivariate statistical methods separately is not sufficient to distinguish anthropogenic metals from geogenic metals. However, employing all these methods together enables us to separate anthropogenic metals with great certainty even in the case of suburban garden soils, which are loaded with such metals only to a small extent.

Analysing the concentration of the aqua regia extractable (“total”) content of As, Zn, Cd, Pb, Ni, Co, Cr, and Cu of topsoils has revealed that only 18% of these suburban garden soils can be considered as metal (especially Cu) contaminated soils, and the metal load of these soils (concerning most of the studied elements) is more moderate than that of the downtown Technosols in Szeged. Despite this fact, there are such elements besides copper of which concentration detected in garden soils is induced by human activities. By employing enrichment factors, simple and multivariate statistical methods, and the vertical and horizontal distribution of metal concentrations, I could separate two groups of metals, one having exclusively geogenic sources, the other having both geogenic and anthropogenic sources.

4. Enrichment factors, namely *Top Enrichment Factor* (TEF) and *Pedologic Enrichment Factor* calculated using Ti as reference element (EFP_{Ti}) can both be applied very well when separating metals which have considerably been accumulated in topsoils as these two enrichment factors (EF) provide statistically corresponding results.

Based on these findings, Ni, Co, Cr, and As do not accumulate from anthropogenic source in garden topsoils (EF~1), the development of their concentration is due to the lithogenic background and pedogenic processes. Whereas Cu (EF~4,2), Zn (EF~2,7), Pb (EF~2,5), and Cd (EF~1,5) accumulate considerably in garden topsoils, which is not only due to pedogenic processes, but partly to human activities as well.

By employing principal component analysis (PCA), which also separated the group of elements of geogenic origins (PC2: Ni, Co, Cr, As), I could separate two groups of metals (PC1: Pb, Zn, Cd and PC3: Cu) accumulating from anthropogenic sources, which means that these groups of anthropogenic metals have different sources:

1. The human induced enrichment of Cd from the elements of PC1 (Pb, Zn, and Cd) affects only some of the gardens, mainly due to point sources, but the concentration of this toxic element exceeds even the „B” limit value in the topsoil of two gardens. However, Pb and Zn enrich from anthropogenic sources in a significant number of the gardens, their main source being atmospheric deposition caused by traffic emissions.
2. The second group of elements accumulating from anthropogenic sources (PC3) is represented by Cu alone, of which concentration exceeds the „B” limit value in numerous gardens; moreover, the anthropogenic enrichment of this metal has the greatest extent on the basis of the enrichment factors. The anthropogenic accumulation of Cu being present almost in every garden is not induced by atmospheric deposition caused by traffic emissions though, rather by copper-bearing pesticides often used in garden cultivation.

5. Gardens with similar heavy metal load are well distributed spatially too, which confirms that the two main sources of anthropogenic metal load of suburban garden soils are traffic emissions (through atmospheric deposition) and using pesticides.

The multiple sources (traffic emissions, garden cultivation) of anthropogenic metals (Cu, Pb, Zn, Cd) as well as the non-equal extent of enrichment of these metals in certain gardens rendered it necessary to classify the sampling units (the gardens) into more homogenous units on the basis of heavy metal load, and I chose the method of cluster analysis. By employing cluster analysis, I could identify three sampling plots with either extremely high or extremely low metal concentrations that are not characteristic of all the studied garden soils, and after excluding these conspicuous cases (6% of the studied gardens), the rest of the gardens could be classified into three different groups according to their heavy metal load, furthermore, the spatial distribution of these groups is also clear:

1. The 1st cluster involves *gardens free from anthropogenic metals* (18% of the studied gardens), where even the otherwise anthropogenic metals [(Pb, Zn, and Cd); (Cu)] do not accumulate in their topsoils. The elements of this cluster are represented by flower gardens first of all, which are usually located the furthest from the busy main road on the northern and north-western parts of the study area.

ii. The 2nd cluster involves *gardens heavily loaded with anthropogenic metals* (51% of the studied gardens), where each of the anthropogenic metals (Pb and Zn of traffic origin, and Cu of pesticide origin) accumulates in the topsoil to a certain extent. These gardens cover a significant part of the study area, but gardens situated just beside the busy main road are also represented here. Orchards, vegetable and flower gardens alike can be found among the elements of this cluster, which indicates very well that metal load may occur anywhere independently from the type of garden use.

iii. The 3rd cluster involves *gardens heavily loaded with copper* (25% of the studied gardens), where only Cu originates from anthropogenic sources from all the anthropogenic metals found in the topsoil. These gardens are situated in the middle of the study area, and almost all of them are orchards and vegetable gardens, where the anthropogenic enrichment of copper is due to past and present garden cultivation.

6. Anthropogenic activities affecting urban garden soils exert different influence on the heavy metal buffering capacity of these garden soils (they either increase or reduce it).

After analysing the metal load of garden soils, I evaluated the heavy metal buffering capacity of these soils, which is extremely important in the case of soils which are used for growing vegetables for human consumption. It was ascertained that the heavy metal buffering capacity of urban garden soils slightly modified by anthropogenic activities is good, which is due to the slightly alkaline pH of garden topsoils which by itself prevents the metals from getting mobilised. In addition, the anthropogenic carbonate content of topsoils increases the heavy metal buffering capacity of urban garden soils by preventing them from acidification; whereas infilling these soils with soil matter of poor organic and mineral colloids reduces the heavy metal buffering capacity of the same soils. Although the total amount of the humus content, which has a great role in binding heavy metals, increases as a result of mixing different types of organic matter (organic fertilizers, compost, etc.) into the soils, it is not the amount of good quality humus that increases but that of the raw, poorly humificated humus fraction, therefore it does not contribute to increasing the heavy metal buffering capacity of garden soils.

7. The potential mobility of geogenic elements (Ni, Co, Cr, As) found in urban garden soils is of small extent, while the potential mobility of anthropogenic elements increases as follows: Cd < Cu < Zn < Pb.

As ”total” metal content does not provide any information about the bioavailability or mobility of the individual elements, I also analysed the mobile (i. e. easily obtainable for plants) and the potentially mobilizable fractions of the elements in selected garden soil samples by employing the modified version of the BCR three-step sequential extraction procedure. Based on these results it can be stated that the potential mobility of the geogenic elements (Ni, Co, Cr, As) found in the garden soils is low, the highest proportion of the “total” amount of these elements can be found in the residue (inert) fraction and they are strongly bound to (the lattice system of) minerals. However, the potential mobility of anthropogenic metals increases as follows: Cd < Cu < Zn < Pb, and in the case of the previously mentioned elements the mobilizable and potentially mobilizable fractions are predominant in the “total” metal content. The proportion of the easily mobilizable fraction, which is also easily obtainable for plants, is not significant even in the case of anthropogenic metals which are mainly due to the good heavy metal buffering capacity of these garden soils.

8. The metal uptake of vegetables often grown in gardens is not of the same extent; leafy vegetables accumulate more zinc, cadmium, and arsenic than root vegetables, but each of the analysed vegetables is suitable for human consumption.

The extent of the possible harmful effects of the metal load of urban garden soils cannot be judged without knowing the heavy metal content of the plants grown in these soils; therefore I analysed the heavy metal content of different vegetables (lettuce, spinach, sorrel, carrot, onion) often cultivated in the studied gardens in addition. These results revealed that the order of magnitude of the metal concentrations measured in the analysed vegetables is much the same as the metal concentrations measured in vegetables cultivated in the various soils of other cities, but the Pb concentration of the vegetables grown in the garden soils of the buffer zone of Szeged is much lower compared to them. The slightly elevated Cu concentrations in the analysed vegetables reflect the anthropogenic Cu load of these suburban garden soils very well though. There is, however, no connection between the “total” metal content of garden soils and the metal concentrations measured in the different vegetables cultivated in these soils, which indicates well that the heavy metal content absorbed by the plants does not depend on the “total” heavy metal content of these soils, it rather depends on the easily mobilizable metal content and the heavy metal buffering capacity of the particular soil as well as plant specific factors. The leafy vegetables of the analysed vegetables (lettuce, sorrel, spinach) accumulate significantly more As, Zn and Cd than the root vegetables (onion, carrot). Nevertheless, none of the vegetables grown in the garden soils that were studied in the buffer zone of Szeged have so high Cd or Pb concentrations which would be above the threshold limit (maximum limit in food products), these vegetables are suitable for human consumption, so consuming root vegetables and leafy vegetables grown in suburban gardens do not pose any threat on human health.

9. Based on the calculated bioaccumulation indices (BAI), the mobility sequence of the elements I analysed in this particular soil-plant system is as follows: Zn > Cd > Cu > Ni > As > Cr > Pb ≈ Co.

I analysed the mobility of the studied elements in the soil-plant system by using bioaccumulation indices (BAI), which describe the metal absorption capability of different plants and the extent of the mobility of the individual elements at the same time. The mobility of the studied elements based on the calculated mean BAI values is as follows: Zn > Cd > Cu > Ni > As > Cr > Pb ≈ Co. I found that the most mobile elements in the studied soil–plant system are Zn and Cd, which means that these metals can be absorbed by the analysed vegetables to the highest degree compared to the “total” metal content of garden soils. However, leafy vegetables (lettuce, sorrel, spinach) can accumulate significantly more of these metals than root vegetables (carrot, onion) often grown in gardens, which is proved not only by the metal concentrations of these plants but by the calculated BAI values as well.

My doctoral research is a good example of the fact that the possible negative effects of human induced changes being present in urban environment cannot be estimated without the complex study of urban environmental components. It is particularly true of soil that does not only receive and store those harmful materials that accumulate in the soil either directly or stem from other components of the environment, but soil itself can be the direct or indirect source of these harmful elements at the same time. The results of the present research also reveal that not only urban environment and its characteristic anthropogenic activities affect urban soils but these soils may also affect urban citizens' quality of life of which life-long consequences must always be considered.

LIST OF PUBLICATIONS RELATED TO THE THESES

Szolnoki, Zs., Farsang, A., Puskás, I., 2013. Cumulative impacts of human activities on urban garden soils: Origin and accumulation of metals. *Environmental Pollution* 177, 106–115. (IF: 3,730 (2012))

Szolnoki, Zs., Farsang, A., 2013. Evaluation of metal mobility and bioaccessibility in soils of urban vegetable gardens using sequential extraction. *Water Air and Soil Pollution* 224, 1737. (IF: 1,748 (2012))

Farsang, A., Puskás, I., **Szolnoki, Zs.**, 2009. Human health risk assessment: A case study of heavy metal contamination of garden soils in Szeged. *AGD Landscape and Environment* 3, 11–27.

Szolnoki, Zs., Farsang, A., 2013. Nehézfémek feldúsulása és mobilitása kertművelés alatt álló talajokban, városi környezetben. *Talajvédelem* (Különszám), 491–502.

Szolnoki, Zs., Farsang, A., Puskás, I., 2011. Szeged külvárosi, kerti talajainak osztályozása. *Talajvédelem* (Különszám), 93–102.

Szolnoki, Zs., Farsang, A., Puskás, I., 2012. Nehézfémek eredetének és feldúsulásának vizsgálata egy külvárosi kertes övezet talajában. In: Galbács, Z. (Ed.) Proceedings of the 17th International Symposium on Analytical and Environmental Problems. JATEPress, Szeged. pp. 38–42.

Szolnoki, Zs., Farsang, A., Puskás, I., 2011. Nehézfém-feldúsulás vizsgálata városi környezetben, kerti talajokon. In: Mócsy, I. et al. (Eds.) VII. Kárpát-medencei Környezettudományi Konferencia I.-II. Ábel Kiadó, Kolozsvár. pp. 653–657.