SZENT ISTVÁN EGYETEM UNIVERSITY

ENVIRONMENTAL SCIENCES PhD SCHOOL

EXAMINATION OF THE AFTER-EFFECTS OF HEAVY METAL CONTAMINATION ON BROWN FOREST SOIL

Theses of doctoral (PhD) dissertation

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1. ANTECEDENTS AND AIMS OF THE WORK

1.1. Antecedents

In the last decades human activity has been effecting its' environment in ways that often cause irreversible changes. Air- and water pollution and soil contamination, furthermore unfavourable impact on living organism can be considered global problems, thus pollution, as it is today, endangers the bases of life on earth. Chemical environmental load, especially the accumulation of microelements and toxic heavy metals bears considerable health, biological and ecological importance (KÁDÁR 1991, 1995, 2001b; CSATHÓ 1994a; SIMON 1999a, 2006a).

Soil contaminated with heavy metal raise a fundamental environmental problem. Soil is capable of fixing and storing heavy metals that were released to nature. Above a certain level of loading, and with the changes in equilibrium process, the fixed toxic heavy metals may be mobilized thus endangering more sensitive species and humanity itself by getting into the ecosystem through water systems and the food chain. (SIMON, 1999a, FODOR, 2002, KÁDÁR, 1995, 1996ab, 2001b; KÁDÁR et al., 1998; CSATHÓ, 1994b).

In regions of different ecological relations (pedological, hydrological and climatic) tendencies and regularities of heavy metal contamination appear differently. For the changes come across only in the long run and the effects can be traced only after years, thus the analysis of the phenomena and the exploration of regularities may be reliable when applying long-term freeland experiment with load. Long-term experiments show qualitative and quantitative changes of cultivated plants, and also the usability of food and fodder as primary material. (KÁDÁR, 1995, 1996ab).

Research priorities regarding the heavy metal load of soils have to be defined according to local pedological conditions. On the basis of these results the movement of heavy metals in soil-plant systems can be judged and contamination limits can be determined. In favour of these a research program called „Analysis of the Heavy Metal Load of our Environment" has been started at the Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences (RISSAC) in 1991. This program examined the behaviour of heavy metals and other potential toxic elements in soil-plant and food systems with freeland / hardy, small plot, long-term experiments in the most important local types of soil.

As part of the research program, a heavy metal loading long-term experiment has been started in brown chernozem forest soil on the Tass-puszta model farm of the Károly Róbert College in autumn 1994. In the course of the research data has been collected, correlations and tendencies have been concluded regarding soil-plant-micro element relations.

In my doctoral dissertation I am going to process and summarize examination datas regarding soil and plant indicatos cultivated between 1999 and 2007, I am also going to analyse behaviour of heavy metals in soil and soil-plant systems, their plant accumulation and phytotoxic effects.

1.2. Objectives

1. Examination of the (in soil) behaviour of heavy metals (Al, As, Cd, Cr, Cu, Hg, Pb, Zn) brought to the ploughed layers of the soil.
    1.1. Examination of the back-testing of toxic heavy metals with chemical methods (by dissolving cc. HNO_3 + cc. H_2O_2 és NH_4-acetate + EDTA) and the changes in temporal back-testing.
    1.2. The determination of the solubility order of toxic heavy metals and the temporal change of solubility order
    1.3. Examination of abyssal shifts (erosion) of toxic heavy metals.
2. Examination of the toxic heavy metals' mobility and phitotoxicity (Al, As, Cd, Cr, Cu, Hg, Pb, Zn) regarding plant-soil systems in the ploughed layers of the soil.

    2.2. Examination of vegetal-accumulation and translocations of toxic heavy metals in case of pea, autumn barley, white mustard, fiber hemp, medic and sorghum experimental plants.
    2.2. Examination of the utility of experimental plants for foraging and human consumption and the examination of the adequacy of soil contamination limiting values on the basis of the concerning provisions of law.
    2.3. Examination of the, phitotoxicity, the crop- and quality spoiling effects of toxic heavy metals in case of experimental plants such as pea, autumn barley and white mustard.
3. The determination of the extent that the estimated (with NH_4-acetate + EDTA dissolution) toxic heavy metal content of the ploughed layer of the soil -in case of experimental plants - fits to actual vegetal element uptakes and to the content of elements uptaken by experimental plants.
4. Examination of the correlations between phitometers and the toxic heavy metal content of the ploughed layer of the soil; determination of oil contamination limiting values at certain experimental plants on the basis of the data from the correlation examination.

2. MATTER AND METHOD

2.1. Introduction of the Experiment

The freeland / hardy , small plot heavy metal loading long-term experiment is located at the A-14 plot of the Károly Róbert College Tasspuszta Model Farm. Geographically speaking it is situated in Mátraalja region - the northern border of the Northern-Great Plain's alluvial cone plain - of the North Hungarian Mountains. Its's soil is brown chernozem forest soil evolved on basic sediments.

The experiment was set in with 8 elements (Al, As, Cd, Cr, Cu, Hg, Pb, Zn), on 3 load levels (30, 90 and 270 kg element/hectares), in 3 repetitons and on 35 m^2 area (3,5 m x 10 m) plots. In the split-plot arranged experiment, the 8 elements meant the main plots and the 3 load levels the sub-plots. Numbers of treatments were 24, and the total numbers of plots were 72. The applied metal treatments were modelling such soil contamination conditions that do or may occur in industrial units and in contaminated surroundings of highways, human settlements and urban gardens. High dose loads served the modelling of soil contamination levels.

Treatments happened on one occasion with the water soluble salts of the elements when the experiment was set in. The doses to be dispersed were mixed with dry sand after the preliminary measurement and were then dispersed by hand on the plots. The salts were worked 8-10 cm deep into the soil by a combinator after dispersion.

The plant succession in the experiment was the following: autumn wheat (1995), corn (1996), sunflower (1997), sorghum (1999), white mustard (2002), fibre hemp (2003) and medic (2005-2008) In my doctoral dissertation I examined, the development of the heavy metal content of the soil and effects on experimental plants in the cases of pea, sorghum, autumn barley, white mustard, fibre hemp and medic as plant indicators. Soilworks, fertilising, sowing and cultivation happens every year according to general operative agricultural engineering. Neither soil disinfection nor chemical weed control was applied so that effects of pesticides could not disturb the experiment.

2.2. Soil sampling, soil analysis

During the course of the experiment in the years 1995, 1996, 1997, 200, 2001, 2005 and 2005 soil analysis were made in order to follow up the fate (transformation, erosion) of heavy metals placed in. In 1996 an abyssal sampling happened. The soil sample taking was done with a manual core driller. One average sample was represented by 20 sample points (from a 0.5 m radius distance from plot borders) per net plots. In the case of abyssal sampling, 5 drillings per plot represented one average sample.

From these average samples the soluble („absorbable") content of element was determined by dissolution of NH_4-acetate + EDTA as suggested by LAKANEN-ERVIÖ (1971), while „total" content of elements was determined by cc. HNO_3 + cc. H_2O_2 digestion as recorded by VÁRALLYAY (1995). The element analysis of the soil extracts (MSZ-08-1722/1-1989) was executed with ICP- AES plasm emmission spectrophotometer in the laboratory of the Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences (RISSAC) and in the laboratory of Károly Róbert College in 2007.

2.2. Plant sampling, plant analysis

Plant sampling occurred mostly in phenophases that determine the state of nurturition of the plants to the largest extent. According to KÁDÁR (1992) this is the beginning of blooming in the cases of pea and medic, the end of stooling (green bud) and earing (leaf under the ear) in the case of autumn barley, while in the case of mustard it is the green bud state and the state before harvesting. In the cases of hemp and sorghum sampling happened at full ripening state. Because of the drought at the ripening of the mustard the ripening of the silique was forced, thus opened up and the dry seeds bled, which is why seed saving was impossible during the course of the experiment. In the cases of pea and autumn barley for the determination of native elements and for the examination of certain plant organs we measured and analysed the stalk, the pod and the seedcrop too.

In every case, the plant sampling (gathering the entire part of the plant above-ground) occurred on net plots and from an incidentally chosen linear metre in a 0.5 m radius distance from the borders of the plots. The determination of the content of elements happened after weighting, drying and grinding the plant samples. Following the digestion of the cc HNO_3 + H_2O_2 the element analysis occurred in the laboratory of the Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences (RISSAC) and in the laboratory of Károly Róbert College in 2007 with a plasm emmission spectrophotometer.

2.3. Data procession and the method of evaluation

The examination of the effects of heavy metal treatments on soil, plant organs and cultivated plants has happened by one elemen tat once and on load levels. The aim was to explore tendency-like changes, statistically demonstrable differences that undergo in the heavy metal content of the soil, plant and plant organs due to loadings. I examined he temporal changes in the effects of treatment too (the uptakeable content of elements, phitotoxic effects ofheavy metal loadings).

In the case of split-plot experiments the mathematical and statisctical evaluation of the data happened with the use of analysis of variance and I performed the correlational anaylsis with the use of regression analysis (SVÁB, 1981). The SD values refer to P=5% significance level. To characterize the standard deviations the determination of the value of the variational coefficients (CV) was also performed beside the regression analysis. On the basis of this, the function that describes the regressive relations can be applied as a mathematical model.

3. RESULTS

3.1. Results of soil analysis

The soil examinations executed during the course of the experiment aimed to study the solubility relations of toxic heavy metals, to examin the accumulation of heavy metals in ploughed layers and also to estimate their leaching. According to local and international experiences what is determinant from an environmental, physiological and agronomic viewpoint is the soluble, toxic hevay metal faction that is uptakable for plants. It's amount - in the case of certain elements -may refer to extreme vegetal uptake, perhaps to erosion (contamination of water base) or to binding in the soil.

Apart from the „soluble" (NH_4-acetate + EDTA soluble) content of elements in the soil samples, in most of the cases the total content of elements (estimated by cc. HNO_3 + cc. H_2O_2 dissolution) was also determined. Although from a physiological viewpoint what bears with significance is the soluble, uptakable (for plants) content of elements, however from an environmental approach the total content of elements bears importance too, because with changes in the environment (e.g. soil acidification) the total content of elements, or a part o fit, may become uptakable for plants. With these results we can answer the question: to what rate can the heavy metal loadings (contaminations) be back tested with the applied analytical methods?

Major results of soil analysis:

1. By the third year of the experiment the „soluble" (NH_4-acetate + EDTA soluble) fraction of heavy metals emitted in the form of water soluble salts had significantly decreased in the schernozem brown forest soil; later on, following the eight year of the experiment, further binding of the elements has occured and only smaller fluctuation was notable. Unequivocal and drastic decreas was to be observed int he cases of rsenic, chromium and mercury. The „soluble" content of elemt of chromium and mercury had practically dissapeared from the ploughed layer after the third year following their emission, while the „soluble" concentration of arsenic had decreased to a fraction of its original value.
2. After twelve years passing, Cd and Pb showed a medium (30-60%), Cu and Zn a weak (10-30%) back testablity, while with both of the methods As, Cr and Hg proved to be hardly or practically non back-testable (under 10%). Among the back tesability averages of As, Cu, Cr, Zn the different methods didn't show ignificant deviations. When classifying contaminations, the age ofthe contamination is determinant, for fresh contaminants can better be revealed in „soluble" fractions.
3. Cadmium and lead are well traceable both by cc. HNO_3 + cc. H_2O_2 digestion and NH_4-acetate + EDTA dissolution, their values determined by the average of measured „total" and „soluble" concentration treatments showed good conformity during the experiment. Thus for the post-classification of lead- and cadmium-contamination (both can be considered significant pollutants) the determination of the „soluble" concentrations is enough.

4. In the ploughed layers of the soil, the solubility order of the elements in the experiment has not fundamentally been changed throughout the years. On the basis of the experimental results the contaminants can be seperated such as mobile (cadmium, lead, copper), less mobile (arsenic, zinc) and quickly binding (turns to insoluble form) non-mobile (mercury, chrome).
5. Toxic heavy metals placed during the course of soil loading stayed mostly at their place; they accumulated in the ploughed layer of the soil. Abyssal shifts were produced by arsenic, chrome and lead according to the examination performed in the third year of the experiment.

3.2. Results of plant analysis

The determination of the extent of the heavy metal accumulation due to soil loading happened in the case of each experimental plant; with the element analysis of plant samples taken from different phenophase it was also possible to examin the heavy metal accumultaion dynamics of autumn barley, mustard and hemp. During the growth season of the plant indicators pea, autumn barley and mustard, phenological observations, measurments occurred in order to judge the phitotoxic effetcs of heavy metal accumulation. By knowing the heavy metal content of the soil and the plants, the mobility of the examined elements can be followed in the soil-plant system; the results can be ompared to the hevay metals' solubility in soil, furthermore it can also be examined whether the accumulation of heavy metals in plants cause phitotoxic symptoms when their value exceed the limits.

Major results of plant analysis:

1. In the case of pea, the elements arsenic, cadmium and mercury showed significant concentration in the vegetative organs. In the case of single (shelled) peas only cadmium was concentrated.
2. In the case of autumn barley arsenic and cadmium in the vegetative organs, while cadmium in the grains showed significant concentration.
3. In the vegetative organs of mustard, significant cadmium and moderate zinc concentration was notable compared to the control.
4. Cadmium and zinc showed significant concentration in sorghum. Accumulation of other elements were not statistically demonstrable (P=5%).
5. In young hemp there was insignificant, but statistically demonstrable concentration (P=5%) following arsenic and chrome loading. The other examined elements had a low level of significance which is statistically undemondstrable on a P=5% level of significance.
6. 14 years after the soil treatment in the case of medic the elements arsenic and cadmium showed moderate statistically demonstrable (P=5%) concentration.
7. On the basis of the heavy metal content of air-dry plants, the mobility order of the examined heavy metals in plant-soil system is the following: Zn > Cu > Cd > Cr >As > Pb > Hg.
8. Three or four years after the contamination the depressive effect of toxic elements on the growth of the plants ended or significantly lessened, however heavy metal accumulation in plants still remained to extents that depend on the plant organs.

9. Concentration of toxic elements in plants is more explicit in the beginning phase of their development than at the end of the vegetation season.
10. Grains are defended against the majority of the examined heavy metals, only cadmium, chrome and lead appeared in them.

3.3. Results of the comparison of heavy metal content of plants and the ploughed layer of soil

The concentration and uptakability of the single heavy metals can also be elvaluated by determining the soil-plant transfer coefficents. The value of soil-plant coefficient is given by the fraction of heavy metal content of the plants and the „total" (cc. HNO_3 + cc. H_2O_2 soluble) content of elemnts in soil. The calculations of soil-plant transfer coeffitient could happen in those experimental years (2001, 2002, 2007) when the „total" content of elements in soil were also determined.

Significant heavy metal uptake was observable at essential elements (copper and zinc) and cadmium. The highest accumulation was shown by zinc; experimental plants took up an average of 68% „total" element content from the soil. Mustard accumulated sesquialter amount of the „total" zinc content of the soil. Transfer coefficients of copper and cadmium showed nearly equal values (0.23 and 0.31). Transfer coefficient of copper in the experimental plants fluctuating around the average value, while in the case of cadmium the 0.86 transfer coefficient value calculated for mustard plant influenced largely the average value calculated for cadmium. According to soil-plant transfer coefficient values, the mobility order of the examined heavy metals in soil-plant system is the following: Zn > Cu > Cd > Cr > As > Pb > Hg.

Knowing the soil-plant coefficient of the heavy metals it is possible to examine the extent to which the „soluble" content of elements determined by LAKANEN-ERVIÖ (1971) method corresponds to effective uptake of elements of plants. For this congruence examination distribution rate values of heavy metals were determined as fraction of „soluble" (NH_4-acetate + EDTA soluble) and „total" (cc. HNO_3 + cc. H_2O_2 soluble) contents of elements of the soil. By comparing values soil-plant transfer coefficiens and the distribution rates it an be decided that to what extent does NH_4-acetate + EDTA soluble content of element corresponds to the content of elements plants can uptake.

The averages of distributional rates significantly exceeded the value of soil-plant coefficients in the cases of most elements. Mercury, chrome and zinc were exceptions of these. In the cases of mercury, chrome, cadmium and copper the NH_4-acetate + EDTA soluble content of elements came near to the content of elements plants can uptake. However, we have to mention that emitted mercury and chrome salts had turned to insoluble forms within a short time, thus mercury wasn not demonstrable at all, while chrome was only moderatly demonstrable in examinational plants. In the case of zinc the distributional rate was one-fifth of the rate of transfer coefficient. This shows that soil might have such reserves of zinc that are uptakable for plants, but can not be demonstrated by the LAKANEN-ERVIÖ (1971) method.

3.4. Examinational results of relations between the heavy metal contents of plants and the ploughed layer of soil

In 2001, 2002 and 2007 „soluble" and „total" content of elements were determined in the ploughed layer of the soil. On the basis of the results the examination of the relationship between plant heavy metal content and soil heavy metal content in the ploughed layer could also occur. I executed the correlation examination with regression analysis and with the determination of the values of coefficients of variation (CV). Function relationships and the consequenses derived are mostly of inromatory nature, for the correlation examination could be expanded only to 4 average results of the mensuration in each case due to the particularity of the experiment.

In the cases of lead and mercury, accumulations in plants were under the demontrability level; the effects of treatments with copper and chrome (with the exception of mustrad) were not demonstrable. The correlation examinations showed linear and logarithmic function relationship between „soluble" and „total" As-, Cd- and Zn- content of autumn barely, mustard and medic. On the basis of the values of the determined coefficients of variation, most of the function relationships can be considered mathematic models. With results of correlation examination we can define the level of „soluble" and „total"heavy metal content of soil when the heavy metal accumulation in plants exceed the limit values.

3.5. New scientific results

1. In the average of the experimental years, the solubility order derived from percentage of NH_4-acetate + EDTA soluble and cc. HNO_3 + cc. H_2O_2 soluble content of elements in the ploughed layers of chernozem brown forest soil was: Cd > Pb > Cu > As > Zn > Hg > Cr. During the experiment the groups of the most soluble and the least soluble elements had not changed. In the ploughed layer of the soil Cd, Pb, Cu, and Zn stay soluble for a lon time, while Cr and Hg turns insoluble very fast.
2. In the case of pea (*Pisum sativum L.*), grown on chernozem brown forest soil, arsenic, cadmium and mercury showed significant concentration in the vegetative organs compared to controll. In single peas only cadmium concentration was to be observed. In the fourth year of the experiment, only chrom effected pea with mild toxicity. Depressive effects of As, Cd, Cr, Cu, Hg, Pb, Zn on the characteristics of crop was not demonstrable. Arsenic-, cadmium- and mercury accumulation happened in plants without any visible symptoms or decrease in crop.
3. In the case of autumn barley (*Hordeum vulgare L.*) grown on chernozem bron forest soil, cadmium and arsenic showed significant concentration compared to control. In the grain cadmium was significantly, while chrome tendentially concentrated. According to plan examinations, non of the heavy metals proved to be toxic to autumn barley. Treatments didn't hinder the growth and yielding of the plants. Depressive effect of As, Cd, Cr, Cu, Hg, Pb, Zn on the development of crop characteristics. Arsenic and cadmium concentration took place in the plants without visible symptoms and decrease in crop.
4. In the case of white mustard seed grown on brown chernozem forest soil, cadmium showed significant concentration in plant organs, while zinc showed a moderate one. In young mustard plant cadmium and

zinc concentrated significantly, as the plant was growing older the concentration became tendencial. Arsenic, mercury and lead were not demonstrable in plant organs. The mustard was highly responsive to cadmium, chrome and copper treatments of the soil; the toxic effects of cadmium and chrome were also demonstrated in the phenological qualities of mustard.

5. In chernozem brown forest soil, the NH_4-acetate + EDTA soluble heavy metal content of the ploughed layer of the soil in the cases of Hg, Cr, Cu and Cd came near, while in the cases of As and Pb significantly exceeded the actual heavy metal uptake of the plants. In the case of Zn, the actual Zn uptake of the plants was fivefold of the NH_4-acetate + EDTA soluble Zn content in the ploughed layer of the soil.
6. According to values of soil-plant transfer coefficients in chernozem brown forest soil, the mobility order of the examined heavy metals in soil-plant system was the following: Zn > Cu > Cd > Cr >As > Pb > Hg. Int he case of certain plants zinc was followed by cadmium or chrome in the mobility order. Lead and mercury got accumulated the least in the plants; the degree of accumulation was –in most cases- under the demonstrability level.
7. In chernozem brown forst soil, in the examined heavy metal territory of the ploughed layer
   - As- and Cd-content of the ploughed layer of soil showed a linear logaritmic relation with plant As- and Cd- content, while in the case of autumn barley grain this relationship was logarhyitmic,
   - in the cases of autumn barely, medic and white mustard, the Zn content of the ploughed layer showd linear relationship with plant Zn content,
   - In the case of arsenic, cadmium and zinc a close relationship was demonstrable between the arsenic-, cadmium- and zinc content of the soil and the plant.

4. CONCLUSIONS AND SUGGESTIONS

4.1. Conclusions

Conclusions regarding the solubility relations and accumulation (in soil) of the examined heavy metals.

1. The Al loading increased the „soluble"Al content of the ploughed layer of the soil and it is statistically demonstrable (P=5%). However concentration did not happen, because Al-silicates are the main soil generators, thus the 270 kg/ha dose Al loading proved to be nsignificant when compared to their weight.
2. The „soluble" As content of the ploughed layer of the soil had decrease to a fifth of its' original by the third and to a twentieth by the fourth year of the experiment. In the following years the „soluble" As content varied between 0.5-7.2 mg/kg depending on the treatment levels.Ion the basis of the reults of experiment it can be proved that the mobility of arsenic in soil is quite difficult and it is not getting leached.
3. The „soluble" Cd content of the ploughed layer of soil had decreased to the four-fifth of its' original in the third year and two-fifth o fit by the following year, from then on it's amount decreased slowly. In the following years of the experiment the „soluble" fraction varied between 4.2 and 35 mg/kg end values dependingh on treatment levels. Cadmium proved to be the most soluble element in the ploughed layer

of the soil during the course of the experiment. Cd treatment remained in the same zone it was placed, its' abyssal mobility and it resists to leaching can be considered impossible.

4. The „soluble" fraction of chrome had decreased to a tenth in the ploughed layer of the soil only six months after it was released. Three years ollowing the contamidation, 0.7% of the Cr-contamination was back-testable. In the following years of the experiment, its' „soluble" fraction was demonstrable in a concentration between end values 0.1-0.8 mg/kg depending on the levels of treatment. During the experiment chrome proved to be the least mobile of the elements, the chrome given in „soluble" form presumably got fixed fast in the form of Cr-oxid in the surface soil. Examination of the soil proved the abyssal shift and quick leaching of chrome. Leaching was observable in the whole soil profile.
5. The „soluble" Cu content of the ploughed layer of the soil decreased to the half by the third year and a third by the eight year of experiment. In the following years its' concentration was moving between the end points 8-30 mg/kg depending on treatment levels. Copper can be considered a mobile element in soil; it was the third most soluble one in the order of the examined elements. Copper got fixed in the ploughed layer and turned into forms difficult to solve, its' abyssal shift can be cosnidered impossible.
6. The „soluble" fraction of mercury had decreased to an eight of its' original onesix months after its' release. Three years following the contamination, 07% of the released HG-contamination was ack-testable. In the following years of the experiment, mercury, in its' „soluble" form was not demonstrable. Experimental results showed that salts of mercury get fixed quite fast in the soil; it infiltrates into crystal-lattice and turns into microbiologically volatile compounds. Concentration in the abyssal layers was not demonstrable int he case of mercury.
7. The „soluble" fraction of lead in the ploughed layer of soil had decreased to a third of its original in the third year of the experiment, then it had not changed in the following years, its' value changed depending on the treatment levels between the end values 7-36 mg/kg. According to experimental results lead is among the most mobile elements in the soil. Abysaal soil examination showed mild Pb concentration int he 30-60 cm layer of the soil, this referd to abyssal shift, leaching of lead.
8. The „soluble" fraction of zinc had decreased to its' half in the ploughed layer of the soil by the third year of the experiment. In the following year it decreased to its' fourth then its amount got stabilized (6.5-17 mg/kg). Zinc did not prove to be a mobile element, it did not show abyssal shift, it got fixed in the same place it was released, it resisted to leaching.
9. Comparing our experimental results with contamination limiting values applied to the examined elements in 6/2009. (IV. 14.) KvVM-EüM-FVM joint regulation, it can be found that at maximum load of the soil (270 kg/ha) the measured „total" concentration of elements have significantly exceeded the contamination limiting values in the cases of arsenic, mercury and cadmium 12-14 years after their release.

Conclusions regarding the phitotoxic effects and the accumulation tendencies of the examined heavy metals in soil-plant system:

1. Negative effects of aluminium load did not emerge. Al-concentration of plants and plant organs showed great dispersion. Neither the tendency-like, nor statistically demonstrable (P=5%) Al- concentration could be determined.
2. The depressive effect of arsenic manifested itslef in the fist two years of the experiment, in the following years this effect on the examined plants had reduced and then ceased. Not even at maximum load did the arsenic get concentrated in the plant organs; only the vegetative organs of some plants showed some concentration. The grains of the experimental plants proved to be defended against As pollution.
3. Cadmium showed phitotoxic effect in the second year of the experiment, in the following years this effect on the experimented plants had reduced and then ceased. Cadmium accumulated in every plant organs; it kept its' mobility for a long time in the plant-soil system, however this mobility can be considered moderate due to the insignificant accumulation. Cadmium showed only moderate concentration in every experimental plant. Accumulation in vegetative organs was generally tendential, only the largest treatment (270kg/ha) caused statictically demonstrable (P=5%) effect. From among the examined elements, it was only cadmium that causes statistically demonstrable effect of treatment in grain. In the case of almost every plant and plant organ, the vegetal Cd-accumulation in 270 kg/ha treatmants prevented human or forage purpose utilization.
4. The toxicity of chrome at 270 kg/ha dosage of load was distinctive during the first three years and then it had gradually reduced; Cr(VI) turned into a less toxic Cr(III) compound in the soil. In the case of some plants stimulating effect of chrome was observable. Autumn wheat showed explicit Cr-accumulation in the second year of the experiment. In the following experimental years, Cr showed insignificant concentration in plant organs, thus it can not be classified mobile in the plant-soil system.
5. Explicit depressive effect of copper was revealed in the first two years of the experiment; this depressive effect got reduced in the following years and then ceased. Only in a few cases did Cu accumulation appear at 270 kg/ha load dosage in the experimental plants. Cu content of the individual plant organs showed balanced values. Only the 1995 wheat experiment showed statistically demonstrable (P=5%) effects of copper treatment, no plants had verifiable effects of treatment that could be demonstrated.
6. Signs of phitotoxic effects and significant HG concentration were shown by autumn wheat, the first experimental plant (its' grains, however did not get polluted); neither toxicity, nor substantial concentration occurred in the other plant species that were cultivated later. The mobility of mercury in soil-plant system almost completly ceased two years after the contamination. According to results of the experiment, mercury can not be considered mobile in the soil-plant system.
7. Depresive effect of lead in soil-plant system was not statistically demonstrable (P=5%), stimulative effect of lead was observable in certain cases. Pb load of the soil showed moderate Pb concentration in plant indicators in the first four years of the experiment, however this was not observable in the following years. Effects of treatment was demonstrable only in autumn wheat in the first year of the experiment, this plant has accumulated lead into its grains too. According to the results lead can not be considered a mobile element in the soil-plant system.

8. Zinc showed explicit depressive effect on the growth and development of the first two plant indicators, however it ceased from the fourth year of the experiment. On certain plants Zn treatment had a stimulative effect. Because the soil was well supplied with zinc, plant indicators showed high zinc content. As a result of zinc load the vegetative organs of the experimental plants showed moderate concentration. Outstanding and statistically demonstrable (P=5%) zinc concentration was observable in sunflower (37-80 mg/kg), sorghum (35-81 mg/kg) and mustard (87-158 mg/kg). Zinc as an essential element, can be regarded a mobile element in within the soil-plant system.
9. Aluminium and cadmium accumulates less in plant organs of field crops of human consumption and forage purpose, thus worthful load examination can not be accomplished int he cases of these elements.
10. Although, throughout the examinations of plants, elements that are considered more significant in terms of contamination (Pb, Cd, Hg, Cu, Zn) were toxic in the first years of the experiment, only cadmium proved to be dangerous contaminator.
11. One of the reasons, apart from cthe transformation of the soluble fractions of the elements, for the decrease in the phitotoxic effects of the treatments could be that the anions of the water-soluble salts of the metals (Cl^-, SO_4^{2-}, NO_3^-) got fixed too.

4.2. Suggestions

The following suggestions can be formulated on the basis of the experimental results:

1. The examination of the abyissal mobility of heavy metals happened in the third year of the experiment, samples were taken only from a max 60 cm depth. Because of the temporal and spatial barriers of the sampling the datas of abyssal examinations are only informatory. Leaching is a slow process, thus its act and dynamics can not be determined clearly on the basis of data from the second year of the experiment, to do that, further examinations going also into deeper layers of the soil would be needed.
2. The experimental results in the case of arsenic and cadmium reason for the re-examination of the contamination limiting values declared in 6/2009. (IV. 14.) KvVM-EüM-FVM joint regulation.
3. The soluble content of elements of the soil is more determinant regarding the plant uptake than the „total" content of elements, thus phitotoxicity of a given element can be detter judged on the basis of „soluble" content of elements. Accordingly, it seems appropriate to provide the limiting values of heavy metal soil contamination on the basis of „soluble" content of elements beside „total" content of elements.
4. One of the factors that influences cadmium and zinc uptake of different soils is their pH level, because at a lower pH level, the zinc and cadmium uptake of plants is bigger. Thus the cadmium and zinc content of soils bearing higher background contamination can be reduced by liming. Zinc content can be further diminished by phosphorus-zinc antagonism, phosphorus fertilization of well accumulating plants.
5. According to theexaminations pre-flowering mustard can be a plant suitable forcadmium and zinc phitoremediation.

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