Available online at http://journal-of-agroalimentary.ro

Journal of Agroalimentary Processes and Technologies 2011, *17*(3), 246-252

Journal of Agroalimentary Processes and Technologies

The traceability of copper and zinc in some vegetables from old mining area in Baia Mare, NW Romania

Gabriela Oprea[1*], Cristina Mihali[1], Angela Michnea[2], Marin Şenilă[3], Lucia Mihalescu[1], Oana Mare[1]

[1]*North University of Baia Mare, 430083 Baia Mare, 62/A dr. V. Babes Street, Romania*
[2]*Environmental Protection Agency Maramureş, 430073 Baia Mare, 1A Iza Street, Romania*
[3]*INCDO-INOE 2000-Research Institute for Analytical Instrumentation, 400293 Cluj-Napoca, 67 Donath Street, Romania*

Received: 12 August 2011; Accepted: 14 September 2011

Abstract

The study follows the assessment of Cu and Zn concentrations in some vegetables and soil in the main districts of Baia Mare, affected by the historical anthropogenic pollution. These elements were analyzed by atomic inductively coupled plasma atomic emission spectrometry (ICP-AES). Copper content in soil varied between 6.5 and 2968 mg·kg^{-1} (normal value 20 mg·kg^{-1}), while zinc content in soil ranged between 58 and 3791 mg kg^{-1} (normal value 100 mg·kg^{-1}). In plant, copper concentration varied between 0.35 and 33.6 mg kg^{-1}, and zinc concentration between 2.3 and ·199 mg kg^{-1}. The paper discusses about the transfer of metal ions (Cu and Zn) from contaminated soils to plants in terms of transfer factors (TF). The knowledge of these transfer factors for a given element should enable for prediction, whether a given soil is suitable for the cultivation of plants for consumption purposes.

Keywords: Soil–plant transfer factors, vegetables, copper, zinc

1. Introduction

The soils in Baia Mare mining basin have been affected by the contamination with nonferrous metals especially lead, copper, zinc, cadmium. Among these trace metals, copper and zinc have a special place regarding their effects upon the plants growing on the soil. Depending on the soil content, copper and zinc could be either essential microelements or plants contaminants.

Soil pollution is due to the emission and dispersion from pollutant sources during over 100 years with a strong increase in the last 50 years. The main soil pollution sources are: mine entrances (mine openings), waste dumps, tailing ponds, ore processing plants, metallurgical plants.

Copper and zinc from these sources arrive on and in the soil from where they could be uptaken by plants entering in the food chain.

The bioaccumulation of these metals in plants has hazardous effects on the environment and human health.

Previous studies about the soil pollution with heavy metals in Baia Mare area showed that majority of content of copper or zinc in soil (about 70-80%) was in the mobile form that can be easily uptaken by plants [1].

Many studies were carried out in various areas affected by anthropogenic metallurgical [2-4] and mining activities [5-6] aiming the investigation of the level of soil and plants contamination.

The soil to plants transfer factors (TF) of different heavy metals including Cu and Zn were calculated in numerous studies and research papers [2-3,6-9].

Corresponding author: *e-mail:* opreag@yahoo.com

The formula for the TF is the same whatever is the intended purpose in research:

$$TF = \frac{\text{Concentration of heavy metals in plants (mg} \cdot \text{kg}^{-1})}{\text{Concentration of heavy metals in soils (mg} \cdot \text{kg}^{-1})}$$

Transfer factors are used in various evaluation models for predicting the concentration of a given element in particular plants specie at an anticipated level of soil contamination [7]. Soil to plant transfer of metals is the major way of human exposure to soil contamination [2].

Cu and Zn are accumulated more intensively in crops grown on peat bog soils, Zn accumulation being higher than Cu one [8-9]. Plants with high bioaccumulation of heavy metals are clover [8-9] and spinach [10,11].

The conclusion is unanimous and researchers recommend that soils affected by anthropogenic pollution with heavy metals from industrial activities should be neither used for growing plants consumed by humans nor for growing grass for grazing [3,6].

This paper aims to investigate the contents of Cu and Zn in soils and plants in Baia Mare area and to establish the transfer factors of these microelements as “true” indicators of the soil pollution.

2. Materials and Method

Selection of study areas. Based on previous studies about soils pollution and plants contamination with Zn and Cu in Baia Mare mining and metallurgical area [1,9,12,13], three study areas have been selected: Ferneziu district, Săsar district and Central zone of the city named in the present paper as Center.

The main pollution sources of the soil are two metallurgical factories: a lead processing factory, located in the North-East side of the Baia Mare city in Ferneziu district and a copper processing factory, located in the South-East side of Baia Mare. Săsar district is located along the preferential direction of the wind that transports and deposes on the soil the dust emissions form the metallurgical factories. Central zone of the municipality is close to the copper metallurgical factory. Dura zone, located in the west side of the city in a hilly area is sufficiently far from the pollution sources and was considered as reference zone.

Soil and plants sampling. A random soil sampling had been taken during July-August 2009 from the surface soil (depth of 0-10 cm) aimed to cover the entire surface of selected areas. In the same time, there had been collected plants growing in the locations from where the soil samples had been drawn. The soil samples were collected from several locations in gardens, in residential areas and squares. Vegetables like onion (*Allium Cepa*) and dill (*Anethum graveolens*) were collected in Ferneziu district while in Săsar district, in Center area as well in the reference Dura area, plants form spontaneous flora were collected: bent grass (Agrostis), clover (*Trifolium repens*), and nettle (*Urtica dioica*).

A GPS was used to get the location of each sampling point. The samples were conditioned and prepared in laboratory for the determination of copper and zinc content. The soil samples were crushed and dried at room temperature for 48 hours, then passed through a 2 mm sieve. A sub-sample of 100 g was obtained through the method of quarters which was ground to a fine powder in a Fritsch PM100 mill for 3 min and passed through a sieve of 150 microns. From this sub-sample, 2.5 g of soil were taken and subjected to mineralization with aqua regia according to ISO 11466: 1999.

The plant samples were washed with tap water and than with distilled water in order to remove the dust and then were oven dried. The dried samples were ground and passed through a 100 μm sieve. A portion of 1.0 g plant sample was subjected to mineralization with aqua regia and hydrogen peroxide following the method from ISO 11466: 1999. Blank extractions with quartz sand were carried out for each set of analyses.

Cu and Zn determination. The determination of Cu and Zn in soils and plants samples was done using the inductively coupled plasma atomic emission spectrometer, ICP-AES, with simultaneous detection Optima 5300 DV (Perkin Elmer), with axial and radial dual vision. All reagents used (65 % HNO_3, 32 % HCl) were purris p.a. quality (Merck). For external calibration, multielemental stock solutions of 1000 μg mL^{-1} (Merck) were used. All dilutions were made with 2 % (v/v) HNO_3. A certified soil CRM (SRM 2709, San Joaquin Soil, NIST) was used to evaluate the accuracy of metal extraction procedures.The quantification limit (in mg/kg of dry soil) was 0.5 mg kg^{-1} both for Cu and Zn. In the case of plants the quantification limit was 0.03 mg kg^{-1} of dry matter.

Statistical analysis of data. In order to assess the level of soil pollution with Cu and Zn in the studied areas, pollution load indexes were calculated [5].

The correlation of data was statistically analyzed using the statistical package Statgraphics. Box plot diagrams were used to compare the data (Cu and Zn in soil, Cu and Zn in plant and transfer factors) in the studied areas related to data from the reference area. The maps of metal soil iso-contents were drawn using Origin 6.1 package.

3. Results and Discussion

The quantification of the level of soils pollution and plants contamination in the selected areas of Baia Mare was done by using the pollution load index [5]. The pollution load index (PLI) was calculated as the nth root of the product of the n CF [5]:

$$PLI = (CF1 \times CF2 \times \ldots\ldots \times CFn)^{1/n},$$

where n is the number of samples, and CF is the contamination factor expressed as the ratio obtained by dividing the concentration of each metal (in soil or in plant) by the baseline or background value. In our study background values are the metal concentrations from Dura area. Figure 1 shows the pollution load index (PLI) of the soils.

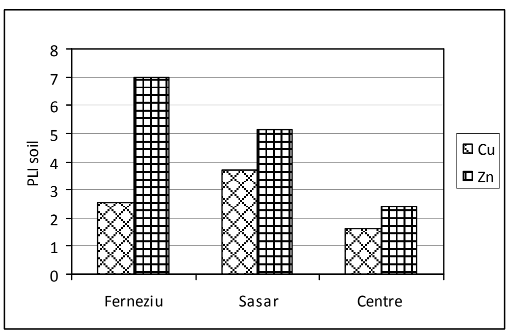

Figure 1. Pollution load index for soil from investigated areas in Baia Mare

Based on the CF value, the contamination levels may be classified on a scale ranging from 1 to 6 having the following meaning: 0 = none, 1 = none to medium, 2 = moderate, 3 = moderate to strong, 4 = strong, 5 = strong to very strong, 6 = very strong [5]. The highest copper concentrations in soil have been found in Săsar district, where the contamination factors ranged from 1.31 to 36.63, defined as a very strongly polluted area.

The same was concluded for Ferneziu district, where the highest zinc concentrations have been found and the contamination factors for Zn ranged from 1.06 to 40.18. Soil in Centre area seems to be less polluted, the maximum CF for Cu is 3.09 (moderate to strong polluted) and for Zn is 4.52 (strong polluted).

Figure 2 shows the pollution load index (PLI) for plants. Regarding the plants, the highest copper concentration have been found in Ferneziu district where the contamination factors ranged from 0.10 to 9.71 and the highest Zn concentration have been found in Săsar district where the contamination factors ranged from 0.98 to 13.85. In Center, the maximum contamination factor was 1.90 for Cu and 2.89 for Zn.

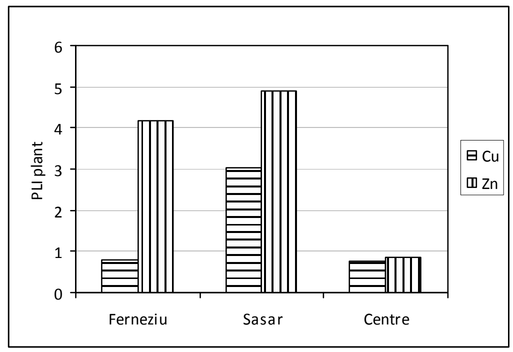

Figure 2. Pollution load index for plants from investigated areas in Baia Mare

Figures 3 and 4 shows the range of Cu and Zn content in soil samples in the studied areas as Box plot diagrams compared with Dura reference area where the average value of Cu in soil was 81.02±33.89 mg/kg of dry matter (expressed as mean value ± standard deviation) while the average value of Zn in soil was a little higher: 94.35±21.69 mg/kg.

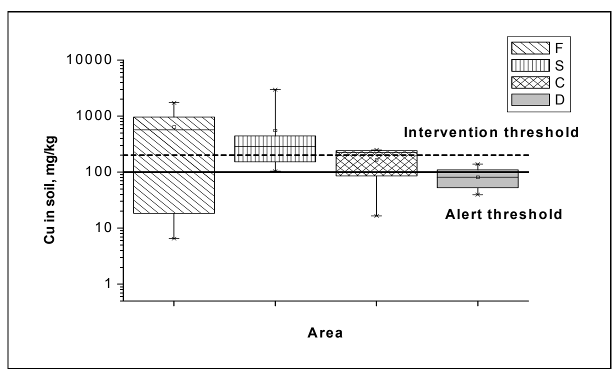

Figure 3. Box plot diagram of Cu content in soil in some district of Baia Mare: F-Ferneziu; S-Săsar; C-Center; D-Dura reference area

The average Cu content in soil in Săsar area is 6.83 times higher than in Dura reference area while in Ferneziu area is 6.78 times higher and in Center area is 2 times higher.

The average Zn content in soil in Ferneziu area is 11.5 times higher than in Dura reference area while in Săsar area is 6.1 times higher and in Center area is 2.7 times higher indicating a non-uniform spreading of these pollutants in Baia Mare area.

These findings are in good agreement with the pollution load index previously calculated.

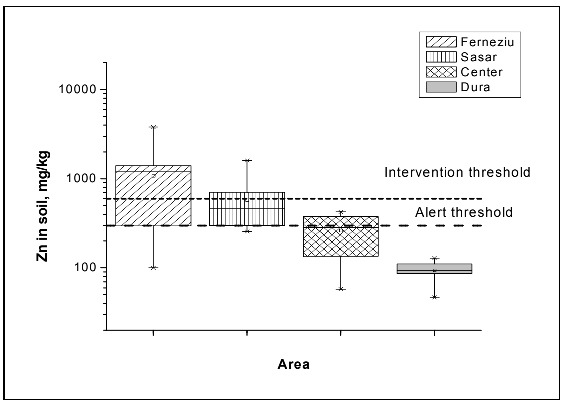

Figure 4. Box plot diagram of Zn content in soil in some district of Baia Mare: F-Ferneziu; S- Săsar; C-Center; D- Dura reference area

The iso-contents maps for Cu and Zn in soil in Baia Mare are plotted in figures 5 and 6 (the sampling points are marked with black quadrates and the dispersion stacks of the metallurgical plants are marked with black circles).

The Cu distribution shows a hot spot with more than 2000 mg/kg in Săsar district soil, near the centre of the city. This is the result of the dust emissions from the copper metallurgical plant located in the south-east side of the city, running for almost 80 years but closed since 2008.

The soil quality assessment according the Order no. 756/1997 issued by the ministry of the environment highlights the severe pollution with Cu.

In Săsar district as well as in the whole east side of the city, the Cu content in soil exceeds the intervention threshold value (>200 mg/kg) for sensitive use of the land and in the Centre of the city the Cu content in soil exceeds the alert threshold value (>100 mg/kg).

The hot spot for Zn has been found in Săsar district but also near the lead processing plant that is running for more than 150 years in Ferneziu district. The raw material used to contain Zn along with lead. The soil in Săsar district contains Zn that exceeds the alert threshold value (> 300 mg/kg) while in Ferneziu district the Zn content exceeds the intervention threshold value (> 600 mg/kg).

The distribution of both metals in soil is in agreement with the specific movements of air currents due to the local geographic characteristics of the site. Baia Mare depression is opened only in its western and south-western side, and on the other sides being surrounded by mountains. For both metals the historical pollution is of great concern and comes mainly from the atmospheric deposition of the dust emitted from the two sources resulting in the accumulation of the metals in the soil from the investigated areas.

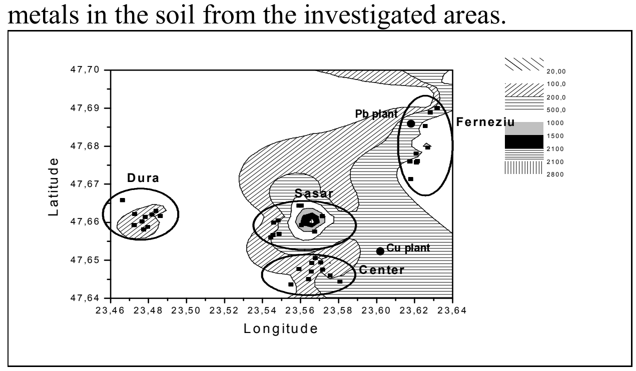

Figure 5. Iso-contents for Cu in soil from Baia Mare city

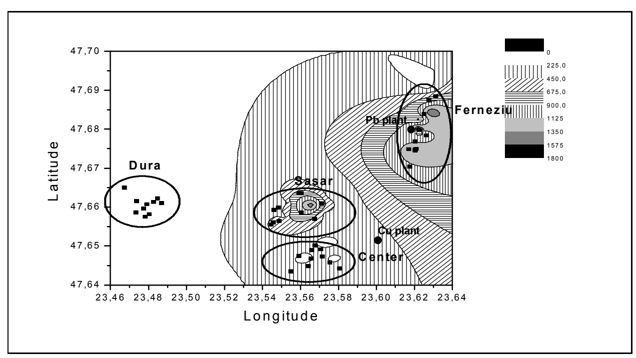

Figure 6. Iso-contents for Zn in soil from Baia Mare city

Box plot diagrams indicating the range of Cu and Zn content in plants in the studied areas compared with Dura reference area are shown in Figures 7 and 8. The average Cu content in plants in Dura area was 3.46±4.07 mg/kg of dry matter while the average Zn content was higher being 19.7±4.84 mg /kg.

The average content of Cu in the plants was highest in Săsar area and was 3.26 higher than in reference area.

In Ferneziu area the average Cu in plants was 6.70, being 1.93 higher than in Dura reference area while in Center the average Cu content was almost equal to those from the reference area. Regarding the Zn content in plants, the highest average was found also in Săsar area exceeding 6.05 the average value of Zn in plants in Dura reference area while in Ferneziu area it was 4.74 times higher and in Center only 1.36 times.

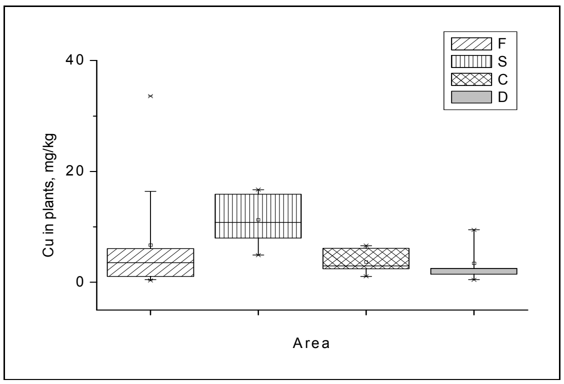

Figure 7. Box plot diagram of Cu content in plants in some district of Baia Mare: F-Ferneziu; S- Săsar; C-Center; D- Dura reference area

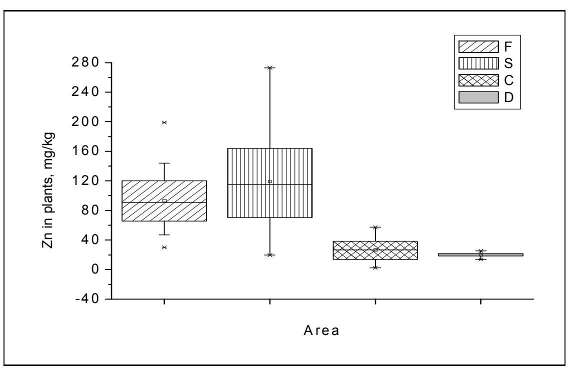

Figure 8. Box plot diagram of Zn content in plants in some district of Baia Mare: F-Ferneziu; S- Săsar; C-Center; D- Dura reference area

These findings showed that the uptake of these metals by plants depends on the soil content but there is a complex relation including more factors related both with the soil and with the plant genotype like the mobility of the chemical specie of the metal, the pH of the soil, climate factors etc.

Among the plants samples are also vegetables (onion and dill) grown in the garden from Ferneziu area. The average Cu content in vegetables was 4.08±5.18 mg/kg (between 0.35 and 16.4) while Zn content was 77.82±33.62 (between 30.1 and 139).

Maxim allowed values for the vegetables used in human consumption are: 50 mg Cu/kg and 50 mg Zn/kg for dehydrated vegetables and fruit considering Romanian legislation (Order 975/1998 issued by the ministry of the health). None of the collected samples of vegetables exceeded the maxim allowed value for Cu but Zn content in vegetables exceeded the maxim allowed content for 70 % of the samples.

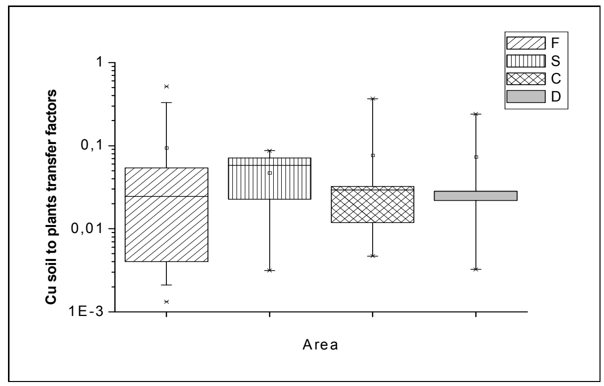

Figure 9. Box plot diagram of Cu soil to plant transfer factors in some district of Baia Mare: F-Ferneziu; S- Săsar; C- Center; D- Dura reference area

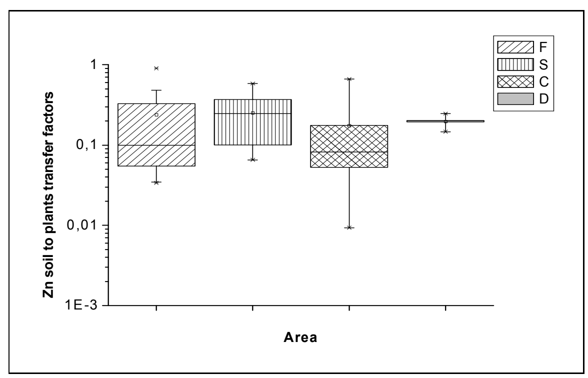

Figure 10 . Box plot diagram of Zn soil to plant transfer factors in some district of Baia Mare: F-Ferneziu; S- Săsar; C- Center, D- Dura reference area

The transfer of metals from soil to plants is of great concern especially in high polluted areas [6]. Box plot diagrams indicating the range of Cu and Zn transfer factors in the studied areas are shown in Figures 9 and 10

The highest Cu transfer factors were found in Ferneziu area with an average value of 0.094 ±0.162 in a large range of values: 0.001-0.513, while in the reference area the average value was 0.073 ± 0.112.

In Săsar area the average Cu transfer factor was 0.047±0.028 and in Center was 0.077±0.142.

The highest Zn transfer factors were found in Săsar area with an average value of 0.253±0.174, while in the reference area the average value was 0.197 ± 0.041.

In Ferneziu area the average Zn transfer factor was 0.239 ±0.267 and in Center was 0.174±0.246. Zn transfer factors are higher than Cu transfer factors in all the studied areas. This tendency is mentioned in literature and is due to the higher mobility of Zn ions [7].

The iso-values maps for the transfer factors were drawn in Figures 11 and 12.

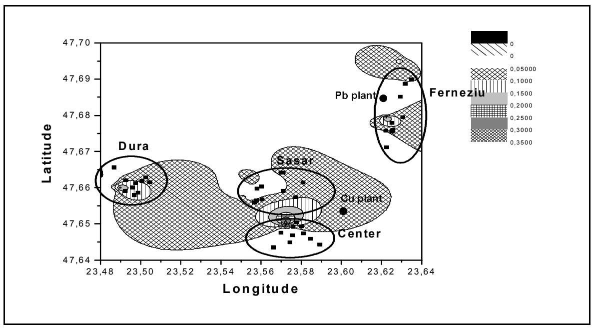

Figure 11. Iso-value map for Cu soil to plants transfer factors, Baia Mare city

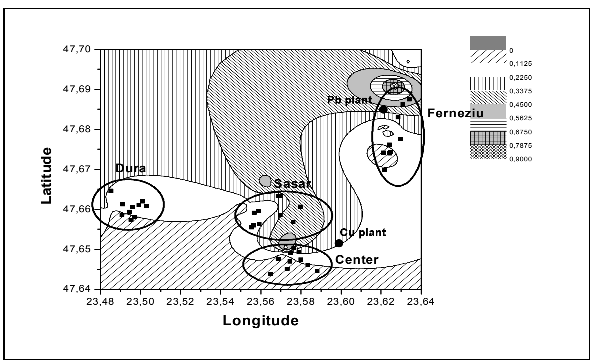

Figure 12. Iso-value map for Zn soil to plants transfer factors, Baia Mare city

Comparing the maps of iso-values of transfer factors for Cu and Zn with corresponding maps of isocontents in soils it can be noticed that there is no similarity between them and the hot spot are in different locations.

This is due to the complex relations in the soil-plant system depending of many factors associated with the chemical species of the metal, soil characteristics, plant species and agronomic management.

Also it is known that many plants have developed mechanisms to limit the translocation of metals across the roots.

4. Conclusion

The soil and plants level of pollution with Cu and Zn was studied in Baia Mare area using pollution load index. The highest value for Cu load index was found in Săsar area both for soil and for plants while the highest Zn load index was found in Ferneziu area also for soil and plants.

The traceability of Cu and Zn in some plants and vegetables was studied using the soil to plant transfer factors. The high mobility of Zn was highlighted, higher than for Cu. According to the high contents of Zn in soil in Ferneziu area, it is assumed that the vegetables grown in this area pose a potential health risk on the consumers.

Acknowledgements

The present researches were supported by the Romanian Ministry of Education and Research, within the PNCDI II Program (Project CISPPA no. 52157/2008). We grateful thank for the financial support.

References

1. Lacatusu, R.; Lacatusu, A. R.; Lungu, M.; Breban I.G., Macro-and microelements abundance in some urban soils from Romania, *Carpth. J. of Earth and Environmental Sciences*, **2008,** *3*(1), 75-83, http://www.ubm.ro/sites/CJEES/upload/2008_1/Lacatusu.pdf
2. Cui, Y.-J.; Zhu, Y.-G.; Zhai, R.-H.; Chen, D.-Y.; Huang, Y.-Z.; Qiu, Y.; Liang, J.-Z., Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China, *Environment International*, **2004**, *30*, 785–791, doi:10.1016/j.envint.2004.01.003
3. Kachenko, A.G.; Singh, B., Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia, *Water, Air, and Soil Pollution*, **2006**, *169*(1-4), 101–123, doi: 10.1007/s11270-006-2027-1
4. Gogoasa, I.; Oprea, G.; Gergen, I.; Alexa, E.; Cozma, A.; Bordean, D-M.; Moigrădean, D.; Alda, L. M., Researches regarding the soil contamination with heavy metals in the Banat mountains, *Journal of Agroalimentary Processes and Technologies*, **2009**, *15*(1), 172-176.
5. Oprea, G.; Michnea, A.; Mihali,C.; Senilă,M.; Roman, C.; Jelea, S.; Butean, C.; Barz, C., Arsenic and Antimony Content in Soil and Plants from Baia Mare Area, Romania, *American Journal of Environmental Sciences*, **2010**, *6* (1), 33-40.

6. Rashed, M.N., Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt, *Journal of Hazardous Materials*, **2010**, *178*(1-3), 739–746, doi:10.1016/j.jhazmat.2010.01.147
7. Chojnacka, K.; Chojnacki, A.; Gorecka, H.; Gorecki, H., Bioavailability of heavy metals from polluted soils to plants, *Science of the Total Environment*, **2005**, *337*(1-3), 175– 182, doi:10.1016/j.scitotenv.2004.06.009
8. Grytsyuk, N.; Arapis, T. G.; Perepelyatnikova, L.; Ivanova, T.; Vynograds'ka, V., Heavy metals effects on forage crops yields and estimation of elements accumulation in plants as affected by soil, *Science of the Total Environment*, **2006**, *354*(2-3), 224– 231, doi:10.1016/j.scitotenv.2005.01.007
9. Intawongse, M.; Dean, J. R., Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract, *Food Additives and Contaminants*, **2006**, *23*(1), 36–48, doi:10.1080/02652030500387554
10. Kashif, S.R.; Akram, M.; Yaseen, M.; Ali, S.; Studies on heavy metals status and their uptake by vegetables in adjoining areas of Hudiara drain in Lahore, *Soil & Environ*., **2009**, *28*(1), 7-12
11. Lacatusu, R.; Lacatusu, A. R., Vegetable and fruits quality within heavy metals polluted areas in Romania, *Carpth. J. of Earth and Environmental Sciences*, **2008**, *3*(2), 115-129.
12. Spurgeon, D.J.; Rowland, P.; Ainsworth, G.; Rothery, P.; Long, S.; Black, H.I.J., Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils, *Environmental Pollution*, **2008**, *153*(2), 273-283, doi:10.1016/j.envpol.2007.08.027
13. Damian, F.; Damian, G.; Lacatusu, R.; Macovei, G.; Iepure, G.; Chira, R.; Kollar, L.; Raţă, L.; Zaharia, D.C., Soils from the Baia Mare zone and the heavy metals pollution, *Carpthian Journal of Earth and Environmental Sciences*, **2008**, *3*(1), 85-98