Research Article

The Study of Absorption of Heavy Metals from the Soil at Some Vegetables in Anadrinia Region in Kosovo

Ilir Shehu[1], Naser Bajraktari[1], Skender Demaku*[1], Arton Bekolli[2], Avni Malsiu[2]
[1]University of Pristina "Hasan Prishtina", Faculty of Mathematical and Natural Sciences, Department of Chemistry, Pristina, Kosovo.
[1]University of Peja, "Haxhi Zeka", Str."UÇK-së", Pejë, Kosovo.
[1]University of Pristina "Hasan Prishtina", Faculty of Mathematical and Natural Sciences, Department of Chemistry, Pristina, Kosovo.
[2]University of Pristina "Hasan Prishtina",Faculty of Agriculture and Veterinary, Department of Plowing and vegetable, Pristina, Kosovo.
[2]University of Pristina "Hasan Prishtina", Faculty of Mathematical and Natural Sciences, Department of Chemistry, Pristina, Kosovo.
***Corresponding author's E-mail:** skender.demaku@hotmail.com

Accepted on: 05-07-2016; **Finalized on:** 31-08-2016.

ABSTRACT

Anadrinia agricultural lands include wider region, therefore we are focusing only on some parts of this land fertile, starting from the village: Krusha e Vogel, Krusha e Madhe, Celinë, Rugovë dhe Xërxe. The primary importance of this study in terms of chemical protection of agricultural lands has to do with the calculation of the mass concentrations of heavy metals in trace: Pb (II), Cd (II), Cu (II), Zn (II), Hg (II), and the impact of these metals in pollution of this land and absorption from the some vegetables. Obtained results in the samples of soil and samples of vegetables are done by ICP-OES method. Generally not show contamination with heavy metals, despite the increased level of arsenic where the maximum value reaches up to 50.23 ppm, but also values of iron concentration are at maximum about 15824.26 ppm and manganese 1142.28 ppm. Regarding the level of concentration of heavy metals in vegetables. Generally we do not have any pronounced accumulation of the concentration of heavy metal analyzed. Based on the obtained results, potatoes show a pronounced affinity with the accumulation of heavy metals compared with other types of vegetables. Referring to the European directives for the permissible level of concentration of heavy metals in these vegetables, all of these are at an acceptable level.

Keywords: Absorption, heavy metals, soil, vegetables, anadrinia, Kosovo.

INTRODUCTION

The region of Anadrinia, lie on a large area, which includes three municipalities: Prizren, Gjakova and Rahovec in the state of Kosovo. Region, in which samples are taken, has an altitude of approximately 310-330m. Unlike other regions, this land is very fertile. The largest production is the cultivation of various vegetables and most of them are peppers that distributed throughout Kosovo. Anadrinia agricultural lands include wider region, we are focusing only on some parts of this land fertile starting from the village: Krusha e Vogel, Krusha e Madhe, Celinë, Rugovë dhe Xërxe. The primary importance of this study in terms of chemical protection of agricultural lands and has to do with the calculation of the mass concentrations of heavy metals in trace: Pb (II), Cd (II), Cu (II), Zn (II), Hg (II), and their impact of those metals in pollution of this land and absorption from the some vegetables.

Furthermore we take the samples of vegetables in the same land that are cultivated those vegetables. Also, our main focus has been to analyze and assess the level of contamination of these agricultural soils with heavy metals and absorption from kind sort of vegetables. Heavy metals are conventionally defined as elements with metallic properties and an atomic number >20. The most common heavy metal contaminants are Cd, Cr, Cu, Hg, Pb, and Zn. Metals are natural components in soil[1]. Some of these metals are micronutrients necessary for plant growth, such as Zn, Cu, Mn, Ni, and Co, while others have unknown biological function, such as Cd, Pb, and Hg[2]. Toxic heavy metals such as Pb, Co, Cd can be differentiated from other pollutants, since they cannot be biodegraded but can be accumulated in living organisms, thus causing various diseases and disorders even in relatively lower concentrations[3]. Heavy metals, with soil residence times of thousands of years, pose numerous health dangers to higher organisms. They are also known to have effect on plant growth, ground cover and have a negative impact on soil micro flora[4]. Vegetables are rich sources of vitamins, minerals, and fibers, and also have beneficial ant oxidative effects. However, intake of heavy metal-contaminated vegetables may pose a risk to the human health. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance[5,6,7]. Some heavy metals such as Cu, Zn, Mn, Co and Mo act as micronutrients for the growth of animals and human beings when present in trace quantities, whereas others such as Cd, As, and Cr act as carcinogens[8,9]. Potentially harmful metal contents in soils may come not only from the bedrock itself, but also from anthropogenic sources like solid or liquid waste deposits, agricultural inputs, and fallout of industrial and urban emissions[10]. Excessive accumulation in agricultural soils may result not only in soil contamination, but has also consequences for food quality and safety. So, it is essential to monitor food quality, given that plant uptake is one of the main pathways through which heavy metals

(HMs) enter the food chain[11]. A number of studies have drawn attention and found to be higher than the allowable maximum limits in soil to the heavy metals accumulation in plants[12-17]. Thus knowing the content of heavy metals in soil is very useful for determining the degree of pollution in an area and the possible that can be taken to help diminish the effects of pollution and to evaluate the needed rehabilitation of the affected areas[18]. In this regard it will be useful to analyze the ability of accumulation of heavy metals (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) in soil and absorption from vegetables. The largest production is the cultivation of various vegetables and most of them are peppers[22].

MATERIALS AND METHODS

Study Area Description

KrUsha e Vogel, Krusha e Madhe, Celina, Rugova and Xërxe, are located in the region of Prizren, Gjakova and Rahovec and they villages are positioned near of highway Prizren –Gjakovë.

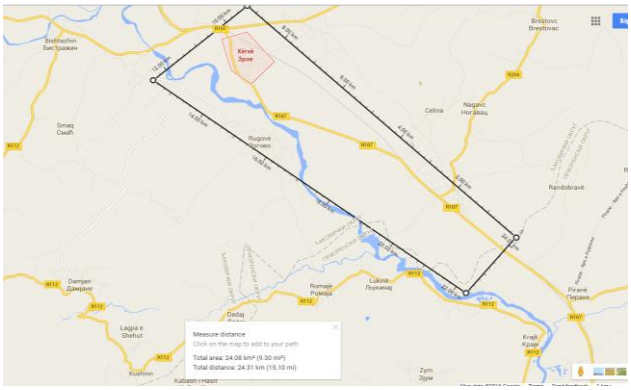

Figure 1: The Map of Study Area and the Sampling Point

Sample Collection

Sample places are selected, taking into account the characteristic countries in which we expected contamination by various actions such as traffic, use large and without control of pesticides, herbicides and chemical fertilizers (Figure 1). In this map, we have represented local area that includes about 24.08 km^2, while the X and Y represent the coordinates. Sampling of agricultural lands Anadrinia is made in summer season. The number of sampling points in our paper is five, sampling points which are defined by GPS coordinates. Our work has been the determination of heavy metals in soil and vegetables to be able to conclude about mass of absorption of heavy metals such as: (potatoes, tomatoes, peppers, cucumbers and cabbage), these samples have listed: M_1 – village Celinë, M_2 – village Rogovë, M_3 - village Krushë Vogël, M_4 - village Krushë e Madhe and M_5-village Xërxe.

Procedure, Reagents and Apparatus

Soil samples were taken in 5 villages (sampling points) and represent the average sample which was prepared from 3 separate samples 0-30cm depth at any point through marked GPS coordinates. Samples were brought to the laboratory where they are undergoing preparation (cleaning, drying, milling and extraction/analysis of chemical composition, namely heavy metals in soil and vegetables.

Cleaning the Sample

The samples of vegetables are purified from roots, organic waste and skeleton and are rinsed twice with distilled water.

Drying of Sample

Sample at the beginning is drayed at room temperature about one month then in the dryer oven at temperatures 105 °C for 3 hours. *Grinding sample*- realized at the mill of spheres of particles about 75 microns.

Extraction of samples -is done by EPA method 3052. The same procedure is also used for soil samples except soil samples are not rinsed with distilled water. 0.200-0.250g sample weighed, and transferred to Teflon container where reagents are added: 9ml HNO_3 65%, 3 ml HCl 35%, 3ml HF 38-40%, 2ml H_2O_2 30%. Teflon containers placed in microwave oven and selected the program. After the complete mineralization, the data collected is stored in database. Then Teflon containers leave from microwave oven and placed in normal container, where the filtered and leveled with the distilled water. The total amount of heavy metals in the samples analyzed is determined by standard EPA method 6010 C. The concentration of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn in soil and vegetable samples, were determined by ICP-OES, Perkin Elmer Optima 2100 DV type.

RESULTS AND DISCUSSION

Total Concentration of Heavy Metals in Soil and Vegetables

This article presents the heavy metal contents from some agricultural soils and various numbers of vegetables which were taken heavy metals from the soil in this region Anadrinia. Obtained results by analyzing number of 10 samples, taken from soil samples and vegetable samples show quality of soil and some vegetables on this region.

(Table 2) Soil samples and samples of cabbage were taken in the village of Celine.

Based on the results obtained in Table 2, we can come to these conclusions:

More of soil samples that are taken are umbric gleysols. Gleysols lands, have neutral character at alkaline pH around 7.3-8.2 and the presence of $CaCO_3$ with medium exchange cations capacity to (14 to 24 cmol/kg of soil) and are classified as land arsenic, umbric and limestone[21].

Based on this we can see that this sampling point, soil samples indicate a high concentration of arsenic but sample of cabbage do not have higher factor of absorption.

The highest values of absorption are observed in the sample of cabbage to the chromium element, with a percentage of absorption that ranges from 49.43%.

Cabbage samples indicate an average absorption of the nickel element, which not exceed 27.14% of the mass absorption.

The accumulation of lead concentration at the cabbage samples were at mass 39.21 %. At the zinc element, we have no real correlation of the concentration of this element between soil sampling and sample of the cabbage.

Table 1: Coordinates, Altitude and Type of Soils in the Sample Places

Sample Places	Coordinates			Type of Soil
	X	Y	Altitude	
Krushë e vogël	471047	4683744	311 m	Umbric Gleysols
Celinë	469035	4686075	326 m	Umbric Gleysols
Rogovë	465821	4687176	321 m	Umbric Gleysols
Xërxë	464740	4688122	324 m	Stagnic Podzolsuviso
Krushë e Madhe	469551	4685440	315 m	Calcaric Fluvisols

Table 2: Sample M1 - Village Celinë, Concentration of heavy metals (mg/kg) in soil and vegetables

Heavy metals	Units	St. Methods	Soil Sample	Cabbage Sample
As			46.44	< 2 pbb
Cd			0.16	< 0.1 pbb
Co			12.25	0.08
Cr		EPA-6010 C	63.38	31.33
Cu	mg/kg	BS EN 13804	23.44	2.9
Fe		BS EN 13805	11874.83	347.51
Hg		BS EN 13806	<1 pbb	< 1 pbb
Mn		BS EN 13807	585.62	2.53
Ni			81.23	22.05
Pb			16.27	6.38
Zn			47.67	77.74

Table 3: Sample M2 - Village Rogovë, concentration of heavy metals (mg/kg) in soil and vegetables

Heavy Metals	Units	St. Methods	Soil Sample	Peppers Sample
As			62.44	< 2 pbb
Cd			0.23	< 0.1 pbb
Co			21.66	< 0.2 pbb
Cr		EPA-6010 C	166.79	27.75
Cu	mg/kg	BS EN 13804	37.97	24.61
Fe		BS EN 13805	15824.26	363.18
Hg		BS EN 13806	<1 pbb	<1 pbb
Mn		BS EN 13807	799.37	1.35
Ni			284.08	33.12
Pb			19.69	6.85
Zn			63.85	74.01

Table 4: Sample M3 - Village Krushë e Vogël, concentration of heavy metals (mg/kg) in soil and vegetables

Heavy Metals	Units	St. Methods	Soil Sample	Potatoes Sample
As			42.77	< 2 pbb
Cd			0.31	< 0.1 pbb
Co			13.79	< 0.2 pbb
Cr		EPA-6010 C	55.99	30.44
Cu	mg/kg	BS EN 13804	34.04	20.93
Fe		BS EN 13805	12421.57	352.17
Hg		BS EN 13806	<1 pbb	< 1 pbb
Mn		BS EN 13807	1142.28	1.98
Ni			59.65	25.30
Pb			27.29	15.22
Zn			80.18	79.72

Table 5: Sample M4 - Village Krushë e Madhe, concentration of heavy metals (mg/kg) in soil and vegetables

Heavy Metals	Units	St. Methods	Soil Sample	Cucumbers Sample
As			16.49	< 2 pbb
Cd			9.36	< 0.1 pbb
Co			6.14	0.07
Cr		EPA-6010 C	73.65	12.5
Cu	mg/kg	BS EN 13804	21.74	17.64
Fe		BS EN 13805	11484.46	103.24
Hg		BS EN 13806	<1 pbb	< 1 pbb
Mn		BS EN 13807	486	2.34
Ni			74.03	6.55
Pb			42.58	< 0.1 pbb
Zn			49.48	22.94

Table 6: Sample M4 - Village Xërxe, concentration of heavy metals (mg/kg) in soil and vegetables

Heavy Metals	Units	St. Methods	Soil Sample	Tomatoes Sample
As			50.23	< 2 pbb
Cd			0.17	< 0.1 pbb
Co			21.29	< 0.2 pbb
Cr		EPA-6010 C	117.49	21.24
Cu	mg/kg	BS EN 13804	40.02	27.1
Fe		BS EN 13805	14942.1	121.78
Hg		BS EN 13806	<1 pbb	< 1 pbb
Mn		BS EN 13807	978.26	0.62
Ni			181.92	6.55
Pb			20.83	9.87
Zn			72.37	46.17

We believe that this discrepancy may have come as a result of an acute soil contamination, which the cabbages that are cultivated in this location have absorbed in this time.

(Table 3) In the Rugova village, we take soil samples and peppers samples, to see total concentration of elements in these samples and their absorption by the peppers that have been cultivated at this location. All of the analyzed samples of peppers, show an lower values of metal concentration. It shows that peppers have low absorption factor of these metals.

Even in this samplingpoint, we have an irregular correlation in terms of zinc concentration in the soil sample and peppers sample. At the soil samples, concentration of zinc is 63.85 mg/kg but in the pepper sample, concentraion of zinc are 74.01 mg/kg. However there is not any major change in the concentration, but increased of the concentration may comes as an accidental, used compound with high content of zinc.

Obtained results from the samples (Table 4) that are taken in the village: Krushë e Vogël, noted, that the soil samples have high values of some heavy metals, especially arsenic. Based on the results obtained during the analysis of vegetables such as potatoes, appears exceptionally small value of this toxic metal and below 2 ppb of Arsenic and cobalt. Plants take iron in the form of Fe^{2+}, Fe^{3+}, but basis on the obtained results of concentration in the potatoes samples and concentration of this element in the soil sample, we can conclude that this sort of vegetables do not have high factor of absorption, expressed as a percentage is 2.83%. If we compare concentration of Chromium in the soil sample and potatoes sample, then we have a much greater absorption of this element about 54.36%. Zinc element is absorbed more by potatoes which can be seen from results expressed in percentage ranges and up to 98.75%. The absorption of copper element in the sample of potatoes is relatively high and ranges in the mass 61.48%. The Absorption of the nickel element in the sample of potato based on obtained results, ranges in the mass 61.48%. Although absorption of lead is in the amount of 55.71%, we have a large concentration of this element in the potatoes sample.

Competition to connect with iron show copper, cobalt, nickel, zinc, chromium and manganese while at high pH inhibit Ca^{2+} and phosphate ions. The concentration of iron in plants is usually within the limits of 50 to 1000 ppm, in our samples have concentrations of iron in about 347.51 ppm cabbage, pepper 363.18 ppm, 352 ppm potatoes, cucumbers and tomatoes 121.78 ppm 103 ppm. Gleysols lands, have neutral character at alkaline pH around 7.3-8.2 and the presence of $CaCO_3$ with medium exchange cations capacity to (14 to 24 cmol/kg of soil) and are classified as land arsenic, umbric and limestone[21].

Results that are show in the Table 5, are taken in the village Krusha e Madhe.

If we compare the concentrations of elements in soil samples but also in the vegetables, noted that this sampling points have lower values of the concentration of metals. The reduce metals concentration at the sample point in this location, is justified given that we are dealing with a different kind of land known as Calcaric Fluvisols.

Also absorption factor of metals from the samples of cucumbers seem to be very small if you refer to the results in Table 5.

Cucumbers also known as the vegetables which contain more than 95% water, and this can also be an indication of small absorption of the metals from the soil. A higher absorption is observed in zinc metal, in which we have 46.36%.

(Table 6) In the village Xërxa, we have another type of soil, known as land Stagnic Podzolsuviso.

As seen from the table 6, the content of heavy metals in samples of potatoes are not high, they range in acceptable value if compared with European Directive standards[19].

Content of heavy metals in soil samples there is not high, unless at manganese and nickel. If we compare content of samples of potato, we have no large accumulation of heavy metals concentration in these samples except zinc, although zinc is at acceptable values.

Usually, for analyzing samples of potato, measurements made in two ways: measurement of content in the peel of potatoes as well as measuring the content of heavy metals in complete potato.

We have made this sample in the measurement of the complete potato.

CONCLUSION

Based on the obtained results during the analysis of soil and vegetables samples on the content of heavy metals in these samples and metal accumulation by some vegetables, we can come to these conclusions:

1. Based on the results obtained in Table 2, at this sample point, soil samples that are taken are umbric gleysols. Gleysols lands, have neutral character at alkaline pH around 7.3-8.2 and the presence of $CaCO_3$ with medium exchange cations capacity to (14 to 24 cmol/kg of soil) and are classified as land arsenic, umbric and limestone. When we have analyzing the samples of cabbage, noted that the accumulation of heavy metals from the soil to the cabbage is specific to certain types of metals like: Accumulation of heavy metals in cabbage samples ranges: cromium at mass 79.34% for nickel, accumulation in cabbage samples is 27.14% and for lead, accumulation is 39.21%. Although the soil samples have high values of the content of metals like arsenic and iron, their accumulation of cabbage is not stressed, even it is in very low value. The anomaly which has appeared on the content of zinc in soil samples and samples of cabbage, is explained in the discussion of the results.
2. In thes sample point also we have the Umbric Gleysols land that cultivatet a lot of kind vegetables but we analysed the peppers samples in acumulation of those metals.

The obtained results in Table 3, show that even though we have the highest value of content of heavy metals in the soil samples, the accumulation of heavy metals from the peppers is not significant in either element.

And here is a disproportion in terms of zinc metal content in soil samples and in samples of peppers.

We think that there should be an analysis of other research in a particular.

3. During the analysis of the samples at the sampling point in the village of Krusha e Vogël, Table 4, we have noticed a light reduction of the content of heavy metals in the soil sample.

But if we analyze the accumulation of these metals from samples of potato, then we can conclude that the potatoes have a great affinity on accumulation of metals.

If we express in percentages, then we have: for zinc accumulation by the potato, brought extent 98.75%, lead 55.77%, nickel42.41%, copper 61.48%, chromium 54.36% and iron 2.83%.

If we compare with other vegetables, it is noted that the potatoes have a great affinity of the accumulation.

4. According to the results obtained in the sampling point in the village Krushë e Madhe, we have decline highlighted the content of heavy metals.

This region, known as the fertile agricultural land, also noticed something that according to the obtained results for the content of heavy metals in the soil sample in this locality. Given the fact that cucumbers contain more than 95% water, and then the possibility of accumulation of heavy metals in this type of vegetables is smaller. Accumulation of heavy metals in samples of cucumbers is very small in all sorts of elements analyzed.

5. According to the results obtained in the sampling point in the village Xerxe, we have a highlighted value of the content of heavy metals, especially arsenic, manganese and iron.

In these sampling points also we have other type of land known as Stagnic Podzolsuviso. Even though we have the highest value content of some metals, we have of low value of heavy metals content on tomatoes samples. Tomatoes also have small affinity on the accumulation of metals.

Referring to the obtained results in samples of vegetables and in samples of soil, we are dealing with a light accumulation of heavy metals by the vegetables that cultivated in this region and as a result, vegetables grown in this region are in a high quality.

REFERENCES

1. Lasat M. M. "Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues."*Journal of Hazardous Substance Research,* 2.5, 2000, 1-25.
2. Gaur, Atimanav, and Alok Adholeya. "Prospects of arbuscular mycorrhizal fungi in phytoremediation of heavy metal contaminated soils." *Curr Sci,* 86.4, 2004, 528-534.
3. Pehlivan, Erol. "Adsorption of Cu 2+ and Pb 2+ ion on dolomite powder." *Journal of Hazardous Materials,* 167.1, 2009, 1044-1049.
4. Roy, Sebastien. "Phytoremediation of heavy metal and PAH-contaminated brownfield sites." *Plant and Soil,* 272.1, 2005, 277-290.
5. Marshall. Enhancing food chain integrity: quality assurance mechanism for air pollution impacts on fruits and vegetables systems. Crop Post Harvest Program, Final Technical Report, 2004, R7530.
6. Radwan and Salama, M.A. Radwan, A.K. Salama. Market basket survey for some heavy metals in Egyptian fruits and vegetables, Food and Chemical Toxicology, 44, 2006, 1273–1278.
7. Khan, S. Khan, Q. Cao, Y.M. Zheng, Y.Z. Huang, Y.G. Zhu, 2008. Health risk of heavy metals in contaminated soils and food crops irrigated with waste water in Beijing, China**,** Environmental Pollution, 152(3), 2008, 686–692.
8. D.I. Feig, T.M. Reid, L.A. Loeb. Reactive oxygen species in tumor genesis. Cancer Research, 54(Suppl.), 1994, 1890–1894.
9. D. Trichopoulos. Epidemiology of cancer V.T. De Vita (Ed.), Cancer, Principles and Practice of Oncology, Lippincott Company, Philadelphia, 1997, 231–258.
10. Wilson B.; Pyatt F.B. Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey, UK. Ecotoxicology and Environmental Safety, 66, 2007, 224-231.
11. Antonious G.; Kochhar T. Mobility of heavy metals from soil into hot pepper fruits: a field study. Bulletin of Environmental Contamination and Toxicology, 82, 2009, 59-63.
12. S Shallar, C Schwart, A Hasko, JL Morel, *Sci. Total Environ*. 209, 1998, 133-18.
13. J Yoon, Cao X, Zhou Q, Ma LQ *Sci. Total Environ*., 386, 2006, 456-464.
14. SA, Salah, SF Barrington, *Agricultural Water Management*, 82, 2006, 979-985.
15. IK Kalavrouziotis, J Carter, SP Varnavas, Mehra A, Drakatos PA *Int. J. Environ. & Pollut.*, 30(3/4), 2007a, 576-592.
16. IK Kalavrouziotis, P Jones, J Carter, SP Varnavas, *Fre. Environ. Bull.*, 16, 2007b, 133-139.
17. MK Jamali, TG Kazi, MB Arian, HI Afridi, N Jalbani, GA Kandhro, AQ Shah, JA Baig *J. Hazard. Mat*., 164(2-3), 2009, 1386-1391.
18. CV Secu, OG Iancu, N Buzgar, *Carpathian J. Earth & Environ. Sci.* 3, 2008, 131-144.
19. Directive 86/278/EEC.
20. VI Vukadinovic, Z Loncaric"Ishrana bilja", Poljoprivredni Fakultet u Osijeku, Osijek. 1998, 107-118.
21. www.iao-florence.it.
22. Shehu, Ilir. "Heavy Metals in Soil and Vegetables in Anadrinia Region as a Result of the use of Pesticides, Herbicides and Fertilizers." *Journal Of International Environmental Application And Science.* 15.1, 2015, 191-196.

Source of Support: Nil, **Conflict of Interest:** None.