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Research Article

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Heavy metals in soil and vegetables in anadrinia region as a result of the use of pesticides, herbicides and fertilizers

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ABSTRACT

In our work, results show that the area where the analysis of soil samples 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. Regarding the level of concentration of heavy metals in vegetables, generally we do not have any pronounced deviation of the concentration of heavy metal analyzed, concern are the high values of lead concentration, where the analysis of cabbage are found values up to 6.38 ppm. Samples of pepper, taken on land planted with this species, indicate the raised value of chromium and lead, as well as the concentration of other metals analyzed are present in the average value. In the analyzed sample of potatoes, show a tendency of the increase of concentration of lead where the maximum values go to 15.22 ppm, at potatoes, we have two types of standards, in the potatoes and peel of the potatoes, but also we have a high values of lead. Cucumbers generally show low values of the concentration of heavy metals. In tomatoes, we have normal values of concentration of heavy metals, apart from a deviation of the concentration of lead in the maximum level of 9.87 ppm at Xërxe village.

Keywords: Heavy metals, vegetables, pesticides, herbicides, fertilizers, Anadrinia

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INTRODUCTION

Agricultural lands Anadrini, lie on a large area, which includes three municipalities: Prizren, Gjakova and Rahovec. 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. 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, analytical, 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 other metals, so together with pesticides, herbicides and chemical fertilizers, using in excess can affect negatively. Also, our main focus has been to analyze and assess the level of contamination of these agricultural soils with heavy metals, as well as the impact of this pollution on flora and fauna. 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 (Shallari et al, 1998; Yoon et al, 2006; Salah & Barrington, 2006; Klavrouziotis et al, 2007a; Kalavrouziotis et al, 2007b; Jamali et al, 2009). 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(Iancu & Buzgar, 2008. 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 various numbers of vegetables.

Figure 1. Some vegetables that are used for analysis

EXPERIEMNTAL SECTION

Study Area Description

Krysha 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.

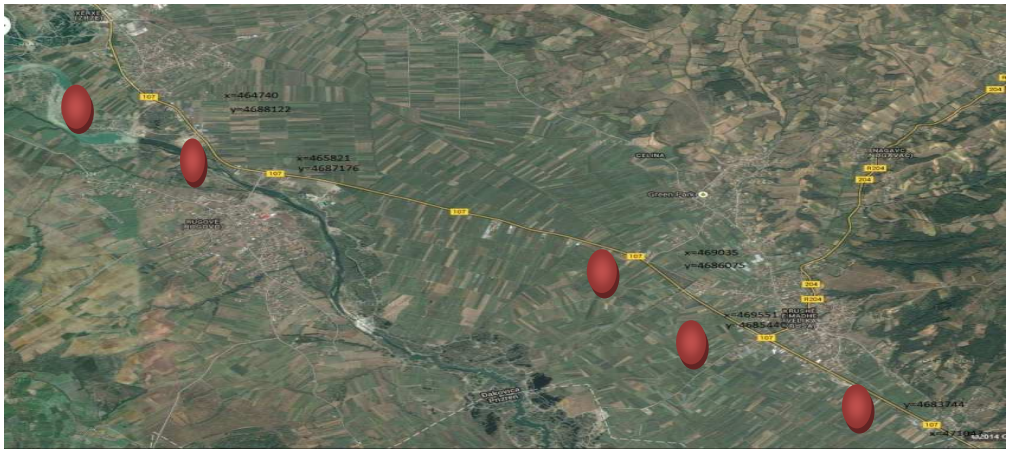

Figure 2.The map of study area and the sampling point

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 2). In this map, red points represent the village, while the X and Y represent the coordinates. Sampling of agricultural lands Anadrinia is made in summer season of year 2013. 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 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.

Table1. 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

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 - samples purified from roots, organic waste and skeleton.
Drying of sample-sample at the beginning dry at room temperature then in the dryer 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. 0.200-0.250g sample weighed, and transferred to Teflon container where reagents are added: 9ml HNO_3 65%, 3ml 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

This article presents the heavy metal contents from some agricultural soils and various numbers of vegetables in this region Anadrinia, obtained by analyzing a number of 10 samples taken from soil samples and vegetable samples.

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

On the basis of results obtained in samples taken in villages: Celinë, Rugova, Krushë e Vogël, Krushë e Madhe and Xërxë, 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 cabbage, peppers, potatoes, cucumbers and tomatoes, appears exceptionally small value of this toxic metal and below 2 ppb. Plants take iron in the form of Fe^{2+}, Fe^{3+}. 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, www.iao-florence.it.

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 5. 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

In soil samples nickel exceeds average values according to Directive 86/278 / EEC, where the sampling points taken, have these values: Celina 81.23 ppm, Rugova 248.08 ppm, Krushë e Vogël 59.65 ppm , Krushë e Madhe 74,03 ppm and 181.92 ppm in Xërxë. So as seen in our sample, the cabbage have an increased amount of this component in the value of about 5.22 ppm, 33.2 ppm paprika, on potatoes 25.30 ppm, 6.55 ppm in cucumbers and in tomatoes 15:39 ppm. Manganese in the soil samples, found in the average value according to standards acceptable to the values of manganese in the soil but have an excess of its values in soil samples in village Krusha e Vogël, 1142.28 ppm. In samples of vegetables, like cabbage, where the concentration of manganese is 2:53 ppm, paprika 1:35 ppm, 1.98 ppm in potatoes, in cucumbers 2.34 ppm and tomatoes 0.62 ppm, well what would be expected when we consider the type of soil in these sample places, neutral towards alkaline. In soil samples, the concentration of chromium found in values allowed, but in plants or vegetables have these values: Cabbage 31.33 ppm, 27.75 ppm pepper, potatoes 30.44 ppm, cucumbers and tomatoes 21:24 12:5 ppm. Copper compounds form complexes with organic acids or organic humid acids, weak plants is achievable. Therefore, the lack of copper occurs in humus soils. The content of copper in the earth revolves on average 5-50 ppm, Vukadinovic,V & Loncaric ,Z, 1998.

In soil samples the concentration of copper is within the standards allowed under Directive 86/278 / EEC and in samples of vegetables amount of copper behaves as follows: Cabbage 2.90 ppm, 24.61 ppm pepper, potatoes 20.93 ppm, 17.64 ppm cucumbers and tomatoes 27.10 ppm and as can be seen from these values, do not have any enormous increase in copper concentration in vegetables. Zinc in all soil samples taken at five sampling points, indicates values below the values permitted under Directive 86/278 / EEC. The normal values of zinc are found in five samples taken,in vegetables behave as: cabbage 77.74 ppm, 74.01 ppm in pepper, potatoes 79.72 ppm, cucumbers 22.94 and tomatoes 46.17 ppm. In soil samples are found high amounts of cobalt, where a part can come from geological structures of the earth, but this amount can contribute greater use of fertilizers where most of them contain cobalt bound, then from pesticides and herbicides. The cobalt concentration in samples of vegetables brought to low values as follows: Cabbage 0.08 ppm, peppery less than 2 ppb, potatoes less than 2 ppb, cucumbers 0.07 ppm and tomatoes less than 2 ppb. In soil samples have low levels of cadmium, deviation observed in the soil sample in the village of Krusha e Madhe, where the value of cadmium concentration ranges up to 9.36 ppm. Cadmium in vegetables behave in very small value, such as: Cabbage less than 0.1 ppb, also peppers less than 0.1 ppb, the potato less than 0.1 ppb, the cucumbers less than 0.1 ppb and tomatoes less than 0.1 ppb. Lead is a heavy metal and one of the most dangerous chemical pollutants to the environment. On soil found in its compounds form, but can also come from anthropogenic factor, especially from mining, then by cars because in gasoline found in associated form of tetraethyl of lead, during the use of pesticides and other forms.

Soil samples were analyzed and found the normal values of concentration of lead, but worrying is the fact that the samples of vegetables have high values of lead as: Cabbage 6.38 ppm, 6.85 ppm pepper, potatoes 15.22 ppm, in small concentration appear at cucumbers, below 1 ppb and 9.87 ppm in tomatoes . Mercury can be found in some

form on earth, but most of the dangerous forms are methyl mercury. Mercury found in some forms of its compounds as HgS, and then in halogenated form, nitrates, sulphates, perchlorates, bound with organic compounds etc. In soil samples, we have very small amount of mercury concentration, all less than 1 ppb. In samples of vegetables are also low values in all of varieties that sampled, in range less than 1 ppb.

CONCLUSION

In general, based on our study regarding impact of fertilizers, pesticides and herbicides on soil and vegetables, we may come to conclusions, as follows:

1. Concentration of heavy metals in analyzed soils is not high with exception of some sample – sites where there are increased values of Arsenic, which may come as a result of contents of the soils being Umbric Gleysols, which is also known as Arsenate soil, there are also increased values in concentration of Iron in all soil-sites in soil samples. Concentration of other metals is at normal levels of contents in soil samples.
2. In samples of vegetables depending on the species, there are different values of concentration of heavy metals but they are found in normal permitted values of contents, with exception of level of increased concentration of Lead almost on all samples of vegetables with exception of cucumbers where the detected level of Lead is less than 1 ppb. Chromium in some samples is found in increased levels but given that it participates in metabolic processes of human organism, thus disintegrating sugars then we may say that the contents of Chromium could be taken as normal in samples of vegetables.
3. The objective of this paper has been achieved by coming to tangent and reliable results as regards to the level of pollution in general with heavy metals in this region, but always taking into account cultivation of agricultural cultures which is progressively increased, therefore there should be conducted frequent controls of contents in terms of these metals but also expansion of their ranges.

We believe that farmers should consult the consulting offices set up within the Ministry of Agriculture in order for them to use fertilizers, pesticides but also herbicides in a more rational way, and this way achieve the best results in producing of agricultural products, but also in reducing of contamination of soil and vegetables.

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