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Taking Stock Of Heavy Metals In Agricultural Lands In Vitia And Obiliq Areas In Kosovo

Besim Zejnullahu[1], Fatos Harizaj[2]
[1, 2]Department of Plant Production, Agricultural University of Tirana, 1029, Kodër-Kamëz, Tirana, Albania
Corresponding Author: Besim Zejnullahu

ABSTRACT:- The purpose of this study is to establish the content of heavy metals in agricultural lands in the Obiliq and Vitia municipalities in Kosovo. The study was carried out within the span of 2015. Sampling was done on agricultural lands in Vitia and Obiliq areas, which were under cultivation with *Capsicum Annum* culture. Elements subject to analysis included: As, Cr, Ni, Pb and Zn. Heavy metals were analyzed according to Atomic Absorber Spectrophotometry (AAS) at Technologies Transfer Center in Fushë-Kruje. The analysis have demonstrated lower values of As with a minimum and maximum values set at 39.88 mg/kg and 53.43 respectively as well as higher values of Zn at a minimum of 107.29 and a maximum of 736.35 mg/kg. The average content of heavy metals appears in this order: Zn> Cr> Ni>Pb>As. Considering the perennial cultivation of these lands with *Capsicum Annum* and the enduring impact of industrial activities in the area, especially in Obiliq, it is necessary to track down and analyze the content of heavy metals and the quality of vegetables consumed by the population.

KEYWORDS:- Heavy Metals, Soils, *Capsicum Annum*, public health

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I. INTRODUCTION

Generally speaking, the production of agricultural crops in Kosovo is a risky operation, because it is characterized by the following aspects: cultures on small areas (0.5-10 Ha) which are not clustered together but distributed far and wide, intensive use of hand-made, non-stabilized and variable market, lack of suitable technology, inadequate post-harvesting management [2]. Among the most important crops in the area is *Capsicum Annum*, which is used for domestic consumption and for export purposes. Areas cultivated with pepper in Kosovo are about 21.1% of the total area cultivated with vegetables fixed at an area of some 14,656 Ha. The Obiliq Municipality occupies a total area of 105 km^2 of which 48% consists in agricultural land and some 37% of forestry/wooded land. Agricultural land occupies about 5400 Ha, of which 900 Ha are commonly owned and 4500 Ha are privately-owned [2].

In general, the land area is planted with arable crops. The area in and around Obiliq Municipality is very rich in coal reserves that have been used for many decades and have a direct impact upon agricultural lands because of the wide-scale contamination, which goes uncurbed. The municipality of Vitia has an area of 300 km2 and lies in the southeast of the Republic of Kosovo. The area is mainly a relatively flat one with fertile soil and considerable forestry area. This municipality is at the mercy of heavy industries and the area under cultivation is at about 53%, while 39.1% are mostly forests [2]. The Obiliq area has been for a number of years under the influence of industrial operations and, hence it is considered to be an area of high risk-based contamination by heavy metals. The heavy metals are heavily present in the area and constitute mainly environmental pollutants like Lead, Cadmium, Mercury and Arsenic [7].

One hand the heavy metal in plants, as in all living organisms, is essential because they act as structural components or catalysts of biochemical processes in organisms.

Human activities do exerts an impact by adding such elements to the soil and water in considerable amounts leading thus to excesses in the accumulation of Pb, Cd metals, Hg, Ni and arsenic, affecting plants and other organisms, and ending up bringing toxicity to ecosystems, [9]. Heavy metals such as Pb, Ni, Cd, Mg, Hg, As, Cr are present in irrigation water. They can build up in land through irrigation water proving to be quite hazardous possessing their non-biodegradable character, with a high degree of toxicity in crops and their [1], [3], [5], [10].

The aim of our study was to evaluate the content of heavy metals in the Obiliq area affected by the industrial activity, the extraction and processing of coal in the Vitia area of Kosovo.

II. MATERIAL AND METHODS

For purposes of the current study we utilized soil samples, which were collected in both study areas in each of the subplots of lands (four sub-parcels in total) which were planted under two cultivars *Capsicum annum*, Sambroska and Kërtoska.

Samples were collected at a depth of 0-40 cm, a sample for each sub-parcel equivalent to 500 gr. The samples are homogenized and left to dry naturally for a week. After drying they are pressed and filtered in the sieve with holes the size of 2 mm and were ready for analysis according to ISO Soil Quality. Each sample is analysed for the establishment of heavy metals As, Cr, Ni, Pb and Zn. Analysis of heavy metals has been done at the Centre of Technology Transfer in Fushë Kruja using the Atomic Absorption Spectrophotometer methodology. Data processing is done using SPSS version 23.0 statistical programs and their interpretation was done using the permissible heavy metals limits for vegetable cultivation on soil Directive 86/278 / EE, [8].

III. RESULTS AND DISCUSSION

The mobility of heavy metals in the soil and the consequent absorption by the plants is associated with various metal association mechanisms in the solid phase. In this association factors of influence included soil pH, organic matter content, redox potential, the content of calcium carbonate and iron levels of magnesium [6]. The content of heavy metals in the soil in Plementina area in Obiliq municipality, considered to be the most polluted area, is as follows: Zn> Cr> Ni> Pb> As, (Table 1).

The highest values have been found for the Zn element which has resulted in very high values in SM_2, SM_3 and SM_4 with a maximum value of 736.35 mg/kg in SM_4, (Table 1). The same trend was observed for all other elements analysed Cr, Ni and As with maximum values at 393.67, 179.98 and at 53.43 mg/kg respectively, (Table 1).

This trend was not observed for the Pb element which resulted in higher value in $S\text{-}M_4$, with a value of 110.2 mg/kg. Among the heavy elements analysed the lowest values were observed for As at 39.88 mg/kg in KM1 and the maximum value at 53.43 mg/kg was found in the SM_4. The biggest problem is Pb which is found to be much higher than the acceptable values for a healthy diet (20 mg/kg) according to [4]. In 37.5% of the analysed samples, the values of Pb exceeded the levels considered as phytotoxic (100 mg/kg).

Heavy Metals mg/kg	**K-M $_1$**	**K-M $_2$**	**K-M $_3$**	**K- M $_4$**	**S- M $_1$**	**S-M $_2$**	**S- M $_3$**	**S-M $_4$**
As	39.88	39.49	42.85	38.36	45.38	45.22	47.71	53.43
Cr	291.69	314.26	322.43	292.74	343.05	339.42	358.79	393.67
Ni	100.02	148.6	148.67	132.52	154.57	154.8	168.37	179.98
Pb	102.36	95.15	87.11	101.96	97.07	96.83	99.48	110.2
Zn	118.43	620.77	653.09	569.8	639.96	725.76	701.87	736.35

Table 1: Content of heavy metals in soil samples (mg/kg), Plementine, Obiliq (Spotted area).

Although the metal content in soil has been relatively high the metals exploited from the ground have resulted at very low values. The only exception is Zn which has resulted in very high values as a expendable element at a maximum of 45.88 mg/kg, (Table 2) in the first sample and the third sample of 44.41 mg/kg in Kërtoska cultivar which were also at the maximum assimilated values, while the lowest assimilated value resulted in cultivated land under the Sambroska cultivar, sub parcel 2. The highest values of assimilated Cr have resulted in the first sub-parcel cultivated under the Sambroska cultivar at 0.06 mg / kg and the lowest in the sub parcel 3 and 1 cultivated under the cultivars Kërkoska and Sambroska respectively. The Pb element has resulted in all cases in values less than 1 ppb, Nickel <0.5 and As <2ppb, (Table 2) very low values without causing problems for the consumption of pepper by the population in the area. Values of heavy metals assimilated by *Capsicum annum* resulted in the following order: Zn> Cr> As> Pb> Ni.

Heavy Metals mg/kg	**K-M $_1$**	**K-M $_2$**	**K-M $_3$**	**K- M $_4$**	**S- M $_1$**	**S-M $_2$**	**S- M $_3$**	**S-M $_4$**
As	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb
Cr	0.05	0.05	0.04	0.05	0.06	0.04	0.05	0.04
Ni	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb
Pb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
Zn	45.88	33.04	41.02	44.41	33.74	32.89	38.82	39.22

Table 2: Content of heavy metals (usable) in soil samples Plementine, Obiliq, (mg/kg).

The content of heavy metals has also been high in Mogilla, Vitia Municipality, despite being considered as an unpolluted area. It has resulted in a minimum value of 35.67 mg/kg in the third sub-parcel cultivated under Kërkoska cultivar (KM_3) and with a maximum value of 49.53 mg/kg in SM_4, (Table 3). In the case of arsenic no apparent upward trend of its content has been observed, but the content has resulted in significant differences from one sub plot to the other. Cr content has been found to be much lower than the corresponding figure in Obiliq area with a maximum value of 145.36 mg/kg in S-M_4 (Table 3) and a minimum value of 102.19 K-M_3.

The average content of Cr has been at 121.53 mg/kg and nickel at 156.93 mg/kg. Nickel has resulted in approximate values in the Obiliq area, with values that have inched up in the region of 134.44 mg/kg to 180.18 mg/kg, (Table 3), the maximum values were found in the fourth sub-parcel cultivated under the Sambroska cultivar. The content of Pb has been very small in the Vitia area with an average value of 56.80 mg/kg while the average content in the Obiliq area is at 98.77 mg/kg.

Heavy Metals mg/kg	K-M 1	K-M 2	K-M 3	K- M 4	S- M 1	S-M 2	S- M 3	S-M 4
As	43.51	40.01	35.67	41.4	41.15	43.33	42.58	49.53
Cr	127.12	114.04	102.19	121.96	115.93	118.33	127.32	145.36
Ni	167.09	147.83	134.44	162.64	150.88	150.3	162.05	180.18
Pb	57.61	54.82	56.85	49.96	57.82	57.59	61.47	58.27
Zn	107.29	104.72	96.38	114.39	112.45	117.56	122.82	138.16

Table 3: Content of heavy metals in soil samples (mg / kg) Mogilla.

Zn is the element that has resulted in higher values compared to all the other heavy elements analyzed in both study areas Obiliq and Vitia. The maximum value of Zn has resulted in sub parcel 4 planted under Sambroska cultivar with 138.16 mg/kg, while the lowest resulted in KM_4 at 96.38 mg/kg. Even in the Vitia area, the content of usable metals has been very low, excluding zinc which is available for plants in almost half of its contents. The highest usable value resulted in the third sub-plot planted with Kërkoska cultivar 57 mg/kg and in the fourth sub-parcel planted with the Sambroska cultivar 44.36 mg/kg.

Heavy Metals mg/kg	K-M 1	K-M 2	K-M 3	K- M 4	S- M 1	S-M 2	S- M 3	S-M 4
As	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb	< 2 ppb
Cr	0.06	0.05	0.05	0.1	0.1	0.05	0.07	0.08
Ni	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb	< 0.5 ppb
Pb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
Zn	42.59	39.61	57.7	45.1	38.63	39.15	42.99	44.36

Table 4: Content of heavy metals (usable) in soil samples (mg/kg) Mogilla.

Other elements like As, Cr and Pb have resulted in very low values. As has been found to be in higher values compared to Pb, Nickel and Chrome with the latter values being very low compared to the content of Zinc.

Arsenic in all cases resulted in values <2ppb, Pb <1ppb, Ni <0.5mg/kg, while Cr has resulted in higher values in the fourth sub-parcel cultivated under Kërkoska cultivar and the first sub-parcel cultivated with under the Sambroska cultivar with a value of 0.1 mg/kg.

The different value of the content of Zn and its usable content, with a high variability, proves to be a characteristic of the lands in this area. By comparing both areas it turns out that the highest content of heavy elements was found in the Obiliq area, which is also an Industrial zone, (Fig.1).

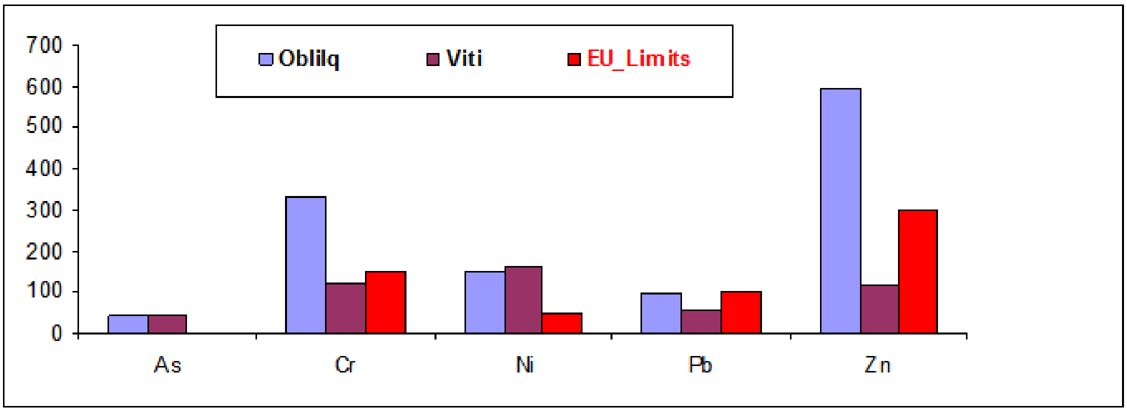

Fig.1: The mean values of the heavy elements found in the soils of Vitia and Obiliq area.

The average values of heavy metal content have resulted very high in the Obiliq Industrial Zone as a result of the power station activity, but also because of the content of such elements embedded in the soil, a fact established by the high content of metals such as Ni, As and Cr in Vitia's unpolluted zone (Figure 1).The content of Cr, Pb and Zn has resulted much higher in Obiliq, while this trend has not resulted as such for Ni and As. Nickel has resulted in the highest values in Vitia with an average of 156.93 mg/kg. Cr, Ni and Zn values in Obiliq have resulted to be higher than the values set by European Community Directive 86/278 / EEC on the content of heavy metals in soil, while Pb has resulted to be very close to the permitted limit of 100 mg/kg.
This Directive does not specify the maximum permissible values for As, but in our study this element has resulted in values of assimilability from the culture of *Capsicum annum* very low.

IV. CONCLUSIONS

Based on the results of our study, we conclude that the heavy metal content is higher in the Obiliq area, which has been for decades under the influence of industrial activity, coal exploitation. The highest values are found for zinc, chromium and nickel, values well beyond the limits set by Directive 86/278 / EEC. The findings did not show the same trend in Vitia area. The content of heavy metals in this area has resulted within the limits set by Directive 86/278 / EEC, excluding Nickel, which has resulted in permissible norms. With the exception of the element of Zn with its content being very high, other elements have resulted in a low usability.

Based on the results of our study and in previous studies concerning the content of these elements in *Capsicum annum* [11], we conclude that despite the very high content of these elements in the two study areas, the passage of such elements to the *Capsicum Annum* plant from the soil becomes difficult due to the characteristics of this plant. It is necessary to monitor constantly the content of these elements in the soil and plants so that the fruits of *Capsicum annum* are to be of high quality for consumption within the standards.

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