RESEARCH ARTICLE (Open Access)

The Contents of Heavy Metals in Soils Around the Industrial Area of Obiliq, Kosovo

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Abstract

The objective of this study was to determine the contents of heavy metals in agricultural land of the Obiliq municipality, Kosovo. The study was carried out during 2015. Sampling was administered in agricultural lands of Obiliq area, which was cultivated with *Capsicum Annum*. Elements analyzed included: As, Cr, Ni, Pb and Zn. Heavy metals were analyzed using Atomic Absorber Spectrophotometry (AAS) at Technology Transfer Center in Fushe-Kruje. The analyses have demonstrated lower values of As with a minimum and maximum of 39.88 mg/kg and 53.43 respectively and higher values of Zn with a minimum of 107.29 and a maximum of 736.35 mg/kg. The average contents of heavy metals has been esablished in this order: Zn>Cr>Ni>Pb>As. Considering the perennial cultivation with *Capsicum Annum* of these lands and the continuing impact of industrial activities in the area, especially in Obiliq, it is necessary to track and analyze the content of heavy metals and the quality of vegetables consumed by the population.

Keywords: Heavy metals, agricultural land, *Capsicum Annum*, soils.

1. Introduction

The Municipality of Obiliq lies in the northern part of Kosovo plain, 10 km north-west of Pristina, Kosovo. It is an area of 105 km² and occupies a space equal to 1% of Kosovo's territory. It features a mountainous terrain, combined with flat plains with fertile soil. Obiliq Municipality occupies a total area of 105 km2 consisting of 48% of agricultural land and 37% woodland. Agricultural land occupies about 5400 Ha, of which 900 Ha are commonly owned among the local population with yet another 4500 Ha of land being privately-owned [2].

The Obiliq municipality has a population of 26.000. The municipality is characterized by the exploitation of lignite (about 100 years) and operations of TEC built in two phases (from 1962 to 1964 and from 1970 to 1975). TCB has 2 blocks that were built from 1983 to 1984. Two power plants differ in terms of environmental impacts due to age factors and technology differentiation. Quite close to TCA lies an abandoned industrial area where coal and nitrogen gasification plants were in operation several years ago. All these industrial activities contribute to the pollution of the lands around them.

Generally speaking, the land area is under arable crops. The land around Obiliq Municipality is very rich in coal reserves which in turn have been exploited for a number of years causing a wide-scale contamination of agricultural lands. On one hand, it could be stated that heavy metals in plants, as is the case with all other living organisms, are demed essential because they act as structural components or catalysts of biochemical processes in organisms. On the other hand, human activities do exerts an impact by adding such elements to the soil and water in considerable amounts leading excesses of accumulation of Pb, Cd metals, Hg, Ni and arsenic, affecting plants and other organisms ending up in bringing toxicity to ecosystems, [9; 12]. The most common heavy metal contaminants are Cd, Cr, Cu, Hg, Pb, and Zn which are to be found in inirrigation water as well, [4]. They can build up in land through irrigation water proving to be quite hazardous bacause they possess non-biodegradable traits, with a high degree of toxicity in crops [8;1;5].

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The objective of our study was to evaluate the contents of heavy metals in the Obiliq area affected by the industrial activity, both by the extraction and processing of coal.

2. Material and Methods

For purposes of the current study we utilized soil samples which were collected in Obiliq area in each of the sub-plots 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 were homogenized and left to dry in the open for a week. After drying they were pressed and filtered in the sieve with holes the size of 2 mm and were subjected to analysis according to ISO Soil Quality. Each sample is analyzed for the evaluation of heavy metals As, Cr, Ni, Pb and Zn. Analysis of heavy metals were conducted at the Center 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 on vegetable cultivation in soil laid down in Directive 86/278 / EU, [8].

3. Results and Discussion

The mobility of heavy metals in soil and the consequent absorption by plants is associated with various metal association mechanisms in the solid phase. In this association factors of influence included soil pH, organic matter contents, redox potential, the contents of calcium carbonate and iron levels of magnesium, [6]. The contents of heavy metals in soil in Plementina area in Obiliq municipality were considered to be the most significant following this order: Zn>Cr>Ni>Pb>As, (Figure 1). The highest values have been found for Zn element which 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, (Figure 1). The same trend was observed for all other elements analyzed Cr, Ni and As with maximum values established at 393.67, 179.98 and at 53.43 mg/kg respectively, (Figure 1).

Among the heavy elements analyzed the lowest values were observed for As at 39.88 mg/kg in KM_1 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 permissible values for a healthy diet (20 mg/kg) according to [3; 11]. In 37.5% of the analyzed samples, the values of Pb exceeded the levels considered as phytotoxic (100 mg/kg).

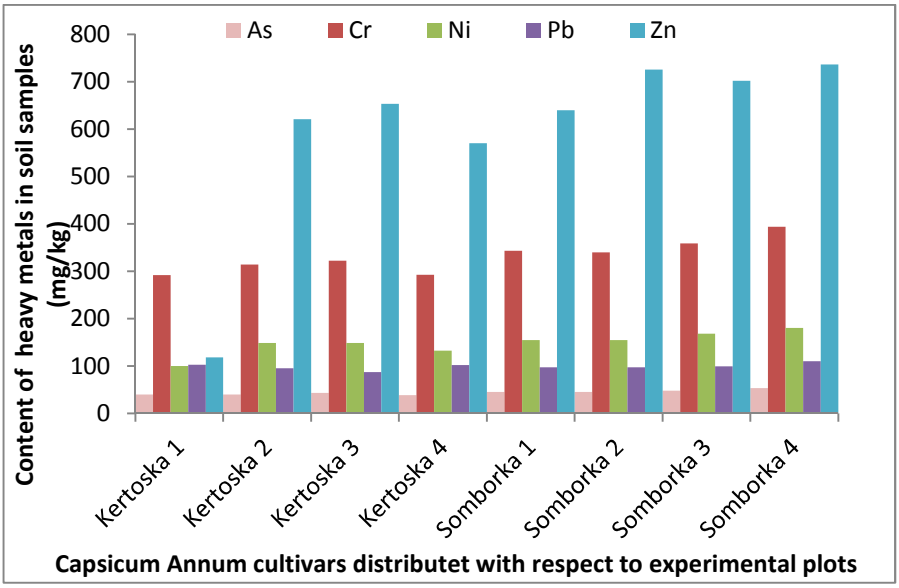

Figure 1. Content of heavy metals in soil samples (mg/kg), Obiliq, with Kërtoska, Sambroska cultivar.

Although the metal contents 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 an expendable element at a maximum of 45.88 mg/kg, (Figure 1) 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, (Figure 1) considered to have very low values stopping short of causing problems in 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.

Table 1. Content of heavy metals (usable) in soil samples Plementine, Obiliq, (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	0.05	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

The average contents 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 areas with the maximum values found in the fourth sub-parcel cultivated under the Sambroska cultivar. The average contents of Pb in the Obiliq area is at 98.77 mg/kg. Pb is an element that has resulted in higher values compared to all the other heavy elements analyzed in areas of Obiliq. The maximum value of Zn has resulted in sub-parcel 4, planted under Sambroska cultivar with 736.35 mg / kg, while the lowest resulted in KM_1 at 118.43 mg/kg. Other elements including As, Cr and Pb have resulted in very low values. Pb has been found to be in higher values compared to As, Nickel and Chrome with the latter having very low values when compared to the contents 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 and the first sub-parcel cultivated with under the Sambroska cultivar with a value of 0.1 mg/kg.

The different value of the contents of Zn prove to be a characteristic of lands in this area, which is also an Industrial zone, (Figure 2).

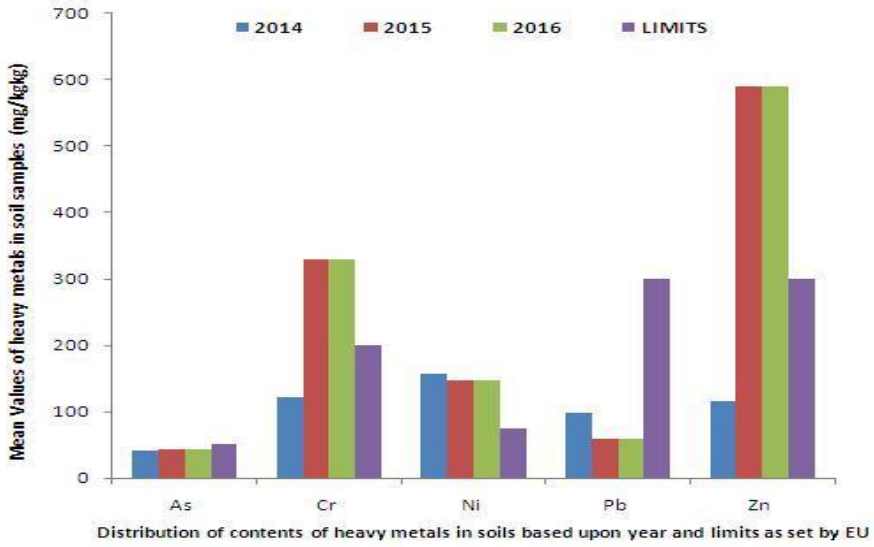

Figure 2.The mean values of the heavy elements found in the soils of Obiliq area during the years 2014-2016

The average values of heavy metal contents have resulted very high in the Obiliq Industrial Zone as a result of the power station operations, but also due to the contents of such elements embedded in the soil, a fact established by the high content of metals. The contents of Cr, Pb and Zn has resulted much higher in Obiliq, while this trend has not resulted as such for Ni and As. Ni and Zn values in Obiliq have resulted to be higher than the values set by European Community Directive 86/278/EEC on the contents of heavy metals in soil, while Pb has resulted to be very close to the permissible limits of 100 mg/kg. This Directive does not specify the maximum permissible values for As, but in our study this element has resulted very low in values of being able to be assimilated from the culture of *Capsicum annum*.

4. Conclusions

Based on the results of our study, we conclude that the heavy metal contents is higher in the Obiliq area, which has been for decades under the influence of industrial activity and intensive coal exploitation. The highest values are found for zinc, chromium and nickel with their respective values proving to be well beyond the limits set by Directive 86/278/EEC. The contents 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 contents being very high, other elements have resulted in a low usability.

Based on the results of our study and in previous studies concerning the contents of these elements in *Capsicum annum*, [10], we conclude that despite the very high contents of these elements in the two study areas, the transmission of such elements to the *Capsicum Annum* plant from the soil is almost impossible due to the characteristics of this plant. It is necessary to constantly monitor the contents of these elements in the soil and plants so that the fruits of *Capsicum annum* are to be fit for consumption within the standards.

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