CONCENTRATIONS OF HEAVY METALS OF IN APPLE FRUITS AROUND THE INDUSTERIAL AREA OF MITROVICA , KOSOVO

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ABSTRACT

The aim of this study is to measure the levels of heavy metals lead (Pb), cadmium (Cd), chrome (Cr), nickel (Ni), arsenic (As), zinc (Zn), copper (Cu) and iron (Fe) in apple fruits with some selected rootstock from the Mitrovica region, Kosovo. The concentrations of heavy metals in soil and apple tissue plants were determined by using atomic absorption spectrometry (AAS). Compared with the reference site in contaminated areas, soil and plant contents of all analyzed metals are higher. The results of this study showed that different types of rootstock have different affinities for heavy metals. The average concentrations ranged from 1.85, 0.37, 6.88, 8.03, 0.05, 2.03, 4.36, 5.09 mg/kg for Pb, Cd, Cr, Ni, As, Zn, Cu and Fe with rootstock mm106. In rootstock m26 concentrations ranged from 1.91, 0.22, 6.31, 7.06, 0.05, 3.28, 3.62, 4.35 mg/kg for Pb, Cd, Cr, Ni, As, Zn, Cu, Fe. While in m9 rootstock these values were found 1.67, 0.24, 5.36, 5.49, 0.03, 2.07, 2.39, 5.16 mg/kg for Pb, Cd, Cr, Ni, As, Zn, Cu and Fe. The highest mean levels of Cd, Cr and Ni were detected in apple fruits with mm106 rootstock. The results of this study showed that continuous industrial production of heavy metals over the years in the study area and permanent pollution were responsible for environmental pollution and particularly soil contamination resulting in high bioaccumulation of heavy metals in fruits.

Keywords: heavy metals, atomic absorption spectrometry, apple fruits, Kosovo

تراكيز العناصر الثقيلة في ثمار التفاح حول المنطقة الصناعية في ميتروفيكا كوسوفو

رسميجي ايميري اندريت كيلاج ادموند دهاني لندم ميلكو
باحث استاذ مشارك باحث مدرس

المستخلص

ان الهدف من هذة الدراسة هو لقياس مستويات العناصر الثقيلة كل من الرصاص الكادميوم والكروم والنيكل والزرنيخ والزنك والنحاس والحديد في ثمار التفاح وبعض الاجزاء الخضرية في اقليم ميتروفيكا، كوسوفو وكذلك قياس مستويات العناصر الثقيلة في التربة مقارنة بالموقع ضمن المنطقة الملوثة وقد اظهرت النتائج ارتفاع مستويات تلك العناصر في التربة والنبات. كما بينت النتائج ان اختلاف المجموع الخضري ادى الى اختلاف قابلية النبات على التلوث، وان معدل تراكيز تلك العناصر كان (0.85، 0.37، 6.88، 8.03، 0.05، 2.03، 4.36، 5.09 ملغم. كغم$^{-1}$) لكل من الرصاص الكادميوم والكروم والنيكل والزرنيخ والزنك والنحاس والحديد ضمن المجموع الخضري 106ملم، في حين تراوحت التراكيز بين (1.91، 0.22، 6.31، 7.06، 0.05، 3.28، 3.62، 4.35 ملغم. كغم$^{-1}$) ولعناصر الرصاص الكادميوم والكروم والنيكل والزرنيخ والزنك والنحاس والحديد ضمن المجموع الخضري 26 ملم. اما في المجموع الخضري 9 ملم فقد فوجد تلك التراكيز بمعدل (1.67، 0.24، 5.36، 5.49، 0.03، 2.07، 2.39، 5.16 ملغم. كغم$^{-1}$) لكل من الرصاص الكادميوم والكروم والنيكل والزرنيخ والزنك والنحاس والحديد. وكانت اعلى معدلات العناصر الكادميوم الكروم النيكل قد وجدت في ثمار التفاح للمجموع الخضري 106 ملم. وقد بينت النتائج الدراسة الحالية ان عملية استمرار انتاج التلوث الصناعي بالعناصر الثقيلة ولسنوات عديدة كانت هي المسؤولة عن التلوث الدائمي للبيئة وخاصةً تلوث التربة والذي ادى الى التراكم الحيوي للعناصر الثقيلة في الثمار.

الكلمات المفتاحية: الاجزاء الخضرية، المناطق الملوثة، تلوث، محتويات التربة والنبات

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INTRODUCTION

The high amount of heavy metals on earth may possibly be considered the most harmful pollutants due to their non-biodegradable nature and their high potential to cause undesirable effects to the living world. Heavy metals are released from various anthropogenic activities, such as industrial activities for energy production, mining and transportation. Environmental pollution due to these toxic pollutants is an important issue in recent times. Heavy metals are such a dangerous pollutant that poses serious threats to the environment and human health (23). The term "heavy metals" refers to any metallic element that has a relatively high atomic weight, high density (those having a specific weight higher than 5 g cm^{-3}) and is toxic or poisonous even at low concentration (19). Heavy metals accumulate in the ecological food chain through receiving at the level of the primary producer and then through consumption at customer level. Agricultural crops obtained from contaminated heavy metals represent an important global challenge for the health of the living world, attributable to both industrial and mining activities. Food security is a major public concern around the world and food consumption has been identified as the main route for human exposure to certain environmental pollutants. In recent years, increased food safety has stimulated research into the risk associated with the consumption of heavy metals contaminated foods (10). Plant nutrition depends on the contamination of arable land which is related to anthropogenic activities such as mining and ore and metal processing. Food contamination with heavy metals can also occur due to irrigation with polluted water, the addition of fertilizers and pesticides with metal base, industrial emissions, transportation, harvesting process, storage, transportation and marketing. Accumulation of heavy metals in plant parts used as food may have a detrimental effect on the health of the inhabitants living there and the surrounding areas (13). The excessive amount of these metals in food is related to the origin of a variety of diseases, particularly with cardiovascular diseases, kidney, nerve, and bone diseases. Also, food insects containing heavy metals can cause carcinogenesis, mutogenesis and teratogenesis. Studies have shown that fruit and vegetable consumption is the primary pathway of human exposure to heavy metals (2). Therefore, it is of practical significance to assess the extent of heavy metal accumulation from soil into plants such as fruits and vegetables, and relevant research has gained increasing attentions. Adamsa (1) and Cairns (1980) defined biological monitoring as the regular application of biological assessment techniques and methods to obtain information about the quality and condition of a biological system. Thus, living organisms provide monitoring capabilities which take into account the actual responses of organisms or populations to environmental variables including pollutants. Wagner and Miiller (28) concluded that the accumulation of pollutants in plants or their reaction to them was a better indication of a system's pollution stress than direct pollution measurement, provided that enough is known about the system itself. Heavy metals may be leached, absorbed by vegetation or retained by the soil and their toxicity depends on factors such as concentration, speciation (the form in which they are present in the soil) and bioavailability (the ease with which they pass into the soil solution and thereby into the trophic chain).

Generally, heavy metals are not biodegradable, have long biological life and have high potential for accumulating in different plant tissues - fruits and food chains to be deposited in various body organs leading to unwanted side effects (12). Fruit consumption is beneficial to human health, however these foods may contain levels of lead, cadmium, nickel, etc., so it is important to monitor the levels of these toxic metals in these foods.

This study aims to assess the current state of soil contamination taking into account the sources of oil pollution and the most exposed areas in the region of Mitrovica region. The Mitrovica area is affected by the presence of a bullet foundry near the residential areas. The fruit trees growing around this area are exposed to the wind and groundwater of landfills that carry heavy metals. This paper aims to investigate the content of heavy metals in the soil and the various apple tissues in the Mitrovica area and analyze their transfer factors in plants as a "real" indicator of soil contamination

MATERIALS AND METHODS

Description of the Study area

The city of Mitrovica lies in the north of Kosovo, at the joining of the Ibar and Sitnica rivers. The region's economy has been dominated by the metallurgical industries, associated with the "Trepça" Combine. The "Trepça" Combine was referring to a conglomerate of metallurgical industries operating in the northern part of Kosovo, including mining, flotation, melting and processing of Pb minerals. The study area contains significant polymetallic deposits of Pb, Zn, Mn, Cr and significant deposits of Pb and Zn (11). Environmental pollution in Mitrovica and its surroundings as an ecological problem began in 1925, when an English company bought the rights to use heavy metal reserves (19). The main sources of industrial pollution have in the past been the starting point for different technological units (smelter, refinery, flotation, battery factory and sulfuric acid factory), the "Trepça" Combine, and the Superfosfate Fertilizer Plant. The work of these wards caused the city of Mitrovica (with its surroundings) to be one of the most polluted cities in Europe. From the high smoke plant in Zvecan, within the year, about 1,500 tons of dust was emitted into the atmosphere, which contained up to 60% of the bullet.

Figure 1. View from the studied area – Mitrovica

According to the data of Shllaku (26), 70% of the lead values, recorded by the measurements made in the city of Mitrovica in 1989, (January to May) exceed the maximum allowed values. This enormous pollution of the atmosphere in this region resulted in contamination of the soil, water, and therefore the contamination of plants, animals and humans. Large amounts of lead and zinc are deposited on the ground. Although, in most cases, lead is bound to the soil as a form of soil, yet there remains an amount that the plants receive through the root system. High concentrations of lead were also found in spinach - 145.8 μg/g of dry mass, onion - 17.35 μg/g, in potatoes - 16.2 μg/g (6).

Sample collection

Individual soil samples were collected from each plant to assess metal content in the immediate plant environment. Samples of fruit, leaf, shoot and soil have been analysed for eight heavy metals (Pb, Cd, As, Ni, Zn, Cu, Cr and Fe). 20 samples of soil and 90 apple samples were collected in the Mitrovica region and reference area during September–November 2017 (Fig 1). Three kinds of apple tree tissues were collected during the harvest period, including fruit, leaf and shoot. To reduce the effect of other agro environmental factors on the issue analysed, the experiment included a row of fruit trees with the same age (6 years), grafted on the same rootstock (mm106, m26, m9). Soil samples were taken from the surface layer (0–20 cm). All samples were sealed in polyethylene bags and transported to the laboratory within 6 h of collection. The soil samples were air-dried at room temperature, with impurities manually removed. Then, the soils were ground and sieved through 80 meshes (0.2 mm). For all samples, the decay and withered tissues were removed and the edible parts were washed with tap water to remove surface dirt. The edible parts of fruits or leaf were repeatedly rinsed with deionised water and dried at 60 °C to a constant weight.

Sample analysis

For the research needs of the metal content: Lead (Pb), Cadmium (Cd), Chromium (Cr), Nickel (Ni), Arsenic (As), Zinc (Zn), Copper (Cu), Iron (Fe) field samples were obtained in accordance with the respective protocols and consisted in sampling soil from apple planted surfaces within the respective localities. Samples received are labelled with all relevant data (locality, sampling date, and other notes). Concentration of metals in soil samples was determined by the Atomic Spectrometer Absorber (AAS) of the Perkin-Elmer model 1200 mark. Work samples (2.0 gr of soil sample) were treated with a 1:3 aqueous regia mixture (4 ml HNO_3 + 12 ml of concentrated HCl) in an electrical reso at a temperature of 200°C for 60 minutes. Prior to mineralization with aqua regia, the organic matter was disintegrated with hydrogen peroxide concentrated (35% H_2O_2). Then the mineralized samples were mixed with distilled water and filtered with Watman 0.45 µm filtration paper. The filter is placed on a volumetric balloon of 50 cm^3 and is levelled up to the mark with distilled water. Such samples are read with AAS and spectrophotometer. The AAS calibration is done with the standard reference material of 1000 ppm (mg/kg) from which the respective metal standards are prepared.

Statistical analysis

The data were statistically analyzed using GraphPad Prism - version 7.05, and Microsoft Excel, 2010, computer packages. The level of significance was set at $p < 0.05$.

RESULTS AND DISCUSSION

Concentrations of heavy metals in plant tissue samples (fruit, leaf, shoot) of apple trees in the Mitrovica region and control zone, expressed as milligrams per kilogram of dry weight (DW), are shown in Table 1 and Table 2. The obtained results showed that the content of heavy metals in fruit were generally above the EU's maximum allowable concentrations in foods. The main sources of heavy metals for plants are their growing environments or the lands where they are cultivated (14). Ph values in all analyzed soil samples were distributed from 5.8 to 7.6, indicating that the soil analyzed was neutral and basically weak. The general concentrations of metals in soils between the two analyzed regions (Mitrovica and the reference site) showed significant differences in scale.

Table 1. Heavy metal concentration (mg kg^{-1}) in soil, shoot, leaf and fruit of apple species depending on rootstocks type from Mitrovica region.

Rootstock	Tissues	Level	Heavy metals (mg/kg^{-1}) Pb	Cd	Cr	Ni	As	Zn	Cu	Fe
M106	Shoot	Mean	8.43	0.67	2.39	1.36	0.18	35.1	19.5	47.6
		SD (±)	1.35	0.11	0.19	0.14	0.03	1.84	1.67	2.87
		CV (%)	16.1	16.4	7.04	10.2	16.7	5.24	8.56	6.02
	Leaf	Mean	3.91	0.51	5.78	2.07	0.25	43.7	11.6	72.1
		SD (±)	0.37	0.08	0.56	0.31	0.06	2.04	1.51	1.96
		CV (%)	9.46	15.6	9.68	14.9	24.1	4.66	13.1	2.71
	Fruit	Mean	1.85	0.37	6.88	8.03	0.05	2.03	4.36	5.09
		SD (±)	0.77	0.17	1.63	1.91	0.02	0.79	1.16	1.17
		CV (%)	41.6	45.9	23.7	23.7	40.2	38.9	26.6	22.9
M26	Shoot	Mean	10.6	0.52	2.47	1.82	0.27	56.7	23.2	56.1
		SD (±)	1.56	0.15	0.33	0.21	0.09	2.45	1.49	3.34
		CV (%)	14.7	28.8	13.3	11.5	33.3	4.32	6.42	5.95
	Leaf	Mean	4.43	0.48	4.61	2.41	0.51	49.9	16.7	98.1
		SD (±)	0.58	0.07	0.44	0.35	0.11	3.88	1.13	2.64
		CV (%)	13.1	14.5	9.54	14.5	21.5	7.78	6.76	2.69
	Fruit	Mean	1.91	0.22	6.31	7.06	0.05	3.28	3.62	4.35
		SD (±)	0.61	0.11	1.25	1.77	0.01	0.85	1.09	0.93
		CV (%)	32.3	50.1	19.8	25.1	20.4	25.9	30.1	21.7
M9	Shoot	Mean	5.89	0.36	2.12	0.88	0.08	60.5	17.5	54.2
		SD (±)	0.67	0.07	0.28	0.11	0.01	4.43	1.81	3.26
		CV (%)	11.3	19.5	13.2	12.5	12.6	7.33	10.3	6.12
	Leaf	Mean	2.78	0.31	4.62	1.81	0.09	53.8	15.5	91.3
		SD (±)	0.23	0.06	0.47	0.19	0.03	3.14	1.62	7.11
		CV (%)	8.28	19.3	10.1	10.4	33.3	5.84	10.4	7.79
	Fruit	Mean	1.67	0.24	5.36	5.49	0.03	2.07	2.39	5.16
		SD (±)	0.58	0.07	0.91	1.28	0.01	1.05	1.12	1.15
		CV (%)	34.8	29.1	16.9	23.3	33.3	50.7	46.9	22.3
Soil		Mean	3.32	0.79	18.8	16.5	0.009	40.3	10.7	12.7
		SD (±)	0.79	0.32	1.81	2.51	0.003	3.71	1.51	1.95
		CV (%)	23.7	40.5	9.63	15.2	33.3	9.21	14.1	15.3

Note: Values are expressed as means X and ± SD.

Concentrations of heavy metals vary widely between the Mitrovica area and the control area. While significant differences in concentrations of metals in plant tissues mean that different apple rootstock had different abilities and capacities to take up and accumulate different metals. The average values of Pb, Cd, Cr, Ni, As, Zn, Cu, Fe in apple plant tissues with different rootstock in the Mitrovica area are given in Figures 1, 2, 3. Concentrations of heavy metals in the fruit of the apple with the rootstock mm106 were quite different as: 1.85 mg / kg dw for Pb, 0.37 mg/kg dw for Cd, 6.88 mg/kg dw for Cr, 8.03 mg/kg dw for Ni, 0.05 mg/kg dw for As, 2.03 mg/kg dw for Zn, 4.36 mg/kg dw for Cu, 5.09 mg/kg dw for Fe. The heavy concentrations of metals in apple with rootstock m26 were: 1.91 mg/kg dw for Pb, 0.22 mg/kg dw for Cd, 6.31 mg/kg dw for Cr, 7.06 mg/kg dw for Ni, 0.05 mg/kg dw for As, 3.28 mg/kg dw for Zn, 3.62 mg/kg dw for Cu, 4.35 mg/kg dw for Fe.

Table 2. Heavy metal concentration (mg kg^{-1}) in soil, shoot, leaf and fruits of apple species depending on rootstocks type from Reference site

Rootstock	Tissues	Level	Heavy metals (mg/kg^{-1}) Pb	Cd	Cr	Ni	As	Zn	Cu	Fe
M106	Shoot	Mean	3.23	0.23	0.26	3.76	nd	56.17	5.12	34.05
		SD (±)	1.09	0.17	0.18	0.54		10.3	0.91	4.16
		CV (%)	33.7	73.9	69.2	14.3		18.3	17.7	12.2
	Leaf	Mean	1.69	0.16	1.13	0.93	nd	23.2	8.55	79.14
		SD (±)	0.81	0.15	0.19	0.47		4.67	2.63	4.51
		CV (%)	47.9	93.7	16.8	50.5		20.1	30.7	5.69
	Fruit	Mean	0.51	0.009	1.27	0.28	nd	0.88	0.98	3.36
		SD (±)	0.34	0.001	0.63	0.07		0.44	0.32	1.79
		CV (%)	66.6	11.1	49.6	25		50	32.6	53.2
M26	Shoot	Mean	2.65	0.17	0.18	2.44	nd	48.02	6.31	41.03
		SD (±)	1.69	0.24	0.11	1.08		11.03	1.41	4.37
		CV (%)	63.7	141.1	61.1	44.2		22.9	22.3	10.6
	Leaf	Mean	1.38	0.19	1.06	0.41	nd	41.15	11.7	104.3
		SD (±)	0.7	0.16	0.43	0.33		6.66	3.92	9.55
		CV (%)	50.7	84.2	40.5	80.4		16.1	33.5	9.15
	Fruit	Mean	0.38	0.08	0.99	0.18	nd	0.74	0.78	3.23
		SD (±)	0.26	0.05	0.58	0.17		0.36	0.56	0.74
		CV (%)	68.4	62.5	58.5	94.4		48.6	71.7	22.9
M9	Shoot	Mean	2.12	0.13	0.42	3.33	nd	62.11	4.97	36.14
		SD (±)	1.05	0.09	0.14	1.38		12.17	1.65	6.09
		CV (%)	49.5	69.2	33.3	41.4		19.5	33.1	16.8
	Leaf	Mean	0.85	0.06	0.86	0.31	nd	29.2	9.84	94.9
		SD (±)	0.82	0.04	0.28	0.28		6.96	2.93	11.24
		CV (%)	96.4	66.6	32.5	90.3		23.8	29.7	11.8
	Fruit	Mean	0.31	0.003	0.49	0.19	nd	0.31	0.93	4.13
		SD (±)	0.21	0.001	1.37	0.27		0.13	0.87	2.59
		CV (%)	67.7	33.3	279.5	142.1		41.9	93.5	62.7
Soil		Mean	1.03	0.05	0.39	1.99	nd	4.72	1.92	9.22
		SD (±)	0.66	0.009	0.31	1.43		1.14	0.39	3.58
		CV (%)	64.1	18	79.4	71.8		24.1	20.3	38.8

Note: Values are expressed as means X and ± SD. nd- not detected.

The heavy concentrations of metals in apple with rootstock m9 were: 1.67 mg/kg dw for Pb, 0.24 mg/kg dw for Cd, 5.36 mg/kg dw for Cr, 5.49 mg/kg dw for Ni, 0.03 mg/kg dw for As, 2.07 mg/kg dw for Zn, 3.62 mg/kg dw for Cu, 4.35 mg/kg dw for Fe. At the reference site, the amount of the heavy metals concentration was the lowest and the pollution rate was also very low. Therefore, to determine the amount of accumulation of heavy metals in selected plant tissues, the transfer factor (TF) was determined. TF is an index for estimating the possible transfer of a metal from soil to plants versus the ability of fruit trees to accumulate a particular metal with respect to its concentration on the substrate of the earth (Adamo et al., 2014).

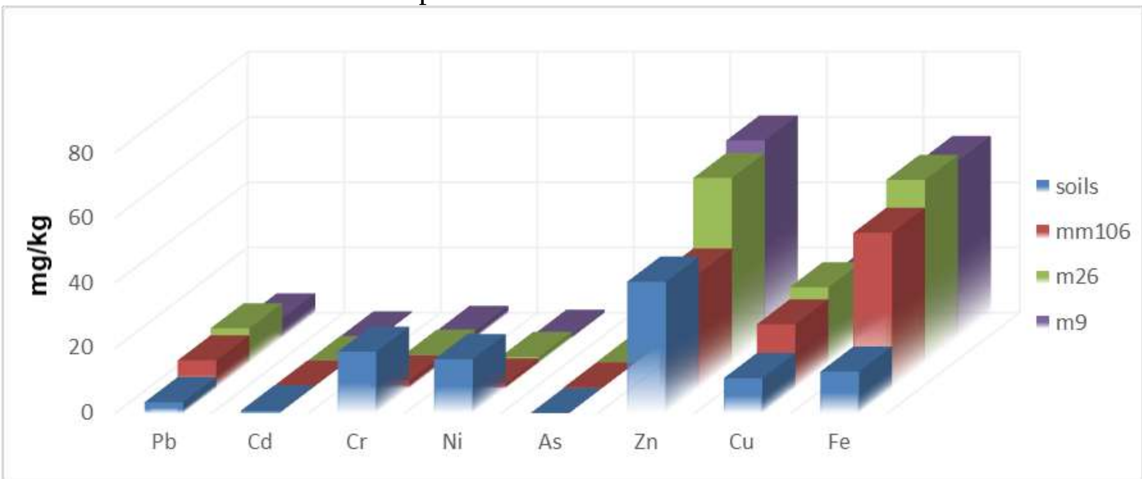

Figure 2. Average concentrations of heavy metals in apple shoot and soil in three different rootstocks at Mitrovica region

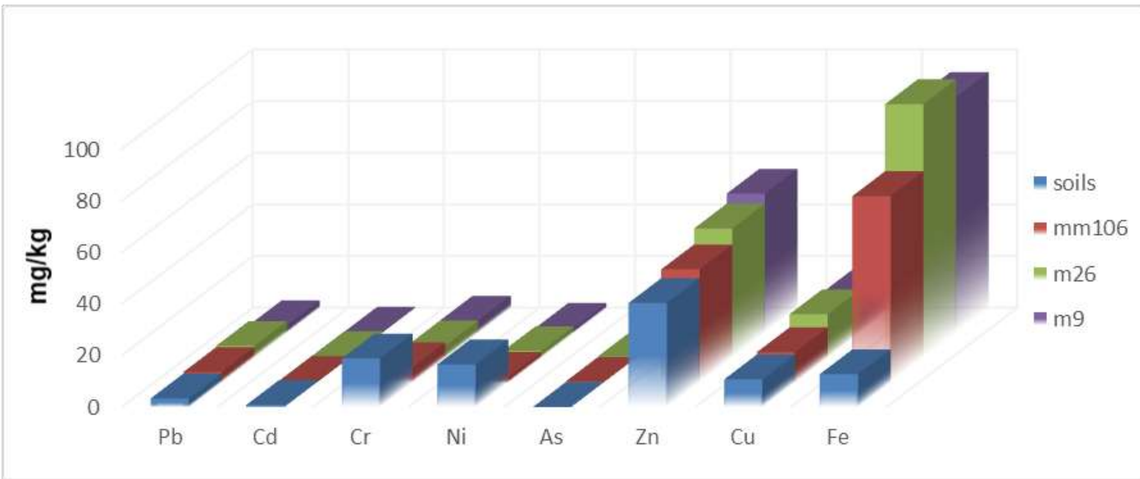

Figure 3. Average concentrations of heavy metals in apple leaf and soil in three different rootstocks at Mitrovica region.

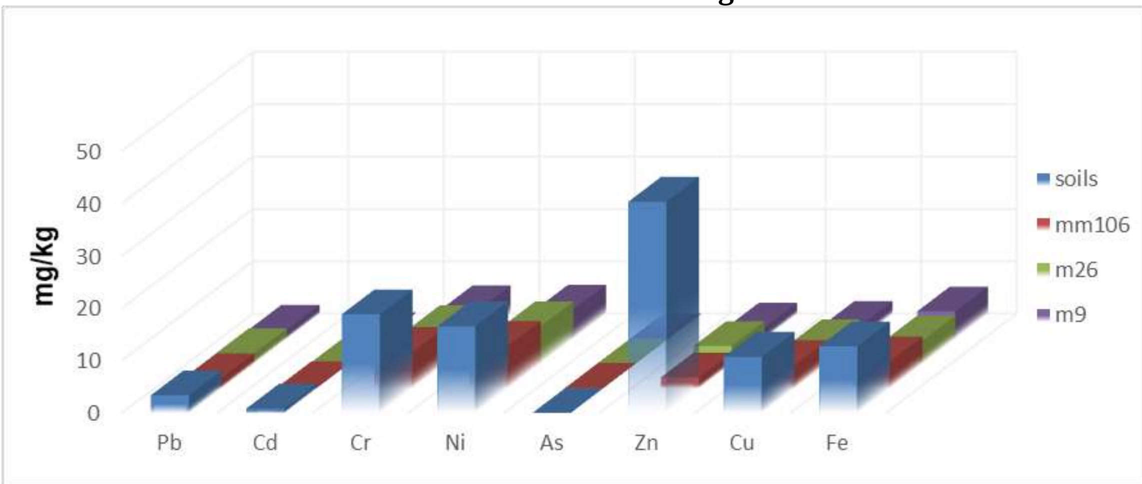

Figure 4. Average concentrations of heavy metals in apple fruit and soil in three different rootstocks at Mitrovica region.

Table 3. Transfer factor of heavy metals (Pb, Cd, Cr, Ni, As, Zn, Cu, Fe) in the Mitrovica region

Rootstock	Transfer factor (TF)	Pb	Cd	Cr	Ni	As	Zn	Cu	Fe
	TF=C(shoot)/C(soil)	2.53	1.17	7.86	12.1	0.05	1.14	0.54	0.26
M106	TF=C(leaf)/C(shoot)	0.46	0.76	2.41	1.52	1.38	1.24	0.59	1.51
	TF=C(fruit)/C(leaf)	0.47	0.72	1.19	3.87	0.21	0.04	0.37	0.07
	TF=C(shoot)/C(soil)	3.19	0.65	0.13	0.11	30.2	1.41	2.16	4.41
M26	TF=C(leaf)/C(shoot)	0.41	0.92	1.86	1.32	1.88	0.88	0.71	1.74
	TF=C(fruit)/C(leaf)	0.43	0.45	1.36	2.92	0.09	0.06	0.21	0.04
	TF=C(shoot)/C(soil)	1.77	0.45	0.11	0.05	8.88	1.51	1.63	4.26
M9	TF=C(leaf)/C(shoot)	0.47	0.86	2.17	2.05	1.12	0.88	0.89	1.68
	TF=C(fruit)/C(leaf)	0.61	0.77	1.16	3.03	0.33	0.03	0.15	0.05

Table 4. Transfer factor of heavy metals (Pb, Cd, Cr, Ni, As, Zn, Cu, Fe) to the reference site

Rootstock	Transfer factor (TF)	Pb	Cd	Cr	Ni	As	Zn	Cu	Fe
	TF=C(shoot)/C(soil)	3.13	4.61	0.66	1.88	nd	11.9	2.66	3.69
M106	TF=C(leaf)/C(shoot)	0.52	0.69	4.34	0.24	nd	0.41	1.66	2.31
	TF=C(fruit)/C(leaf)	0.31	0.05	1.12	0.31	nd	0.03	0.11	0.04
	TF=C(shoot)/C(soil)	2.57	3.41	0.46	1.22	nd	10.1	3.28	4.44
M26	TF=C(leaf)/C(shoot)	0.52	1.11	5.88	0.16	nd	0.85	1.85	2.53
	TF=C(fruit)/C(leaf)	0.27	0.42	0.93	0.43	nd	0.01	0.06	0.03
	TF=C(shoot)/C(soil)	2.05	2.63	1.07	1.67	nd	13.1	2.58	3.91
M9	TF=C(leaf)/C(shoot)	0.41	0.46	2.04	0.09	nd	0.47	1.97	2.62
	TF=C(fruit)/C(leaf)	0.36	0.05	0.56	1.18	nd	0.01	0.09	0.04

On average, the transfer of heavy metals from soil to shoot, leaf and fruit of the apple with the rootstock mm106 was in the order: TF=C(shoot)/C(soil) Ni (12.1) > Cr (7.86) > Pb (2.53) > Cd (1.17) > Zn (1.14) > Cu (0.54) > Fe (0.26) > As (0.05). TF=C(leaf)/C(shoot) Cr (2.41) > Ni (1.52) > Fe (1.51) > As (1.38) > Zn (1.24) > Cd (0.76) > Cu (0.59) > Pb (0.46). TF=C(fruit)/C(leaf) Ni (3.87) > Cr (1.19) > Cd (0.72) > Pb (0.47) > Cu (0.37) > As (0.21) > Fe (0.07) > Zn (0.04). Transfer factor to apple tissues with rootstock m26 was in the order: TF=C(shoot)/C(soil) As (30.2) > Fe (4.41) > Pb (3.19) > Cu (2.16) > Zn (1.41) > Cd (0.65) > Cr (0.13) > Ni (0.11); TF=C(leaf)/C(shoot) As (1.88) > Cr (1.86) > Fe (1.74) > Ni (1.32) > Cd (0.92) > Zn (0.88) > Cu (0.71) > Pb (0.41); TF=C(fruit)/C(leaf) Ni (2.92) > Cr (1.36) > Cd (0.45) > Pb (0.43) > Cu (0.21) > As (0.09) > Zn (0.06) > Fe (0.04). Transfer factor to apple tissues with rootstock m9 was in the order: TF=C(shoot)/C(soil) As (8.88) > Fe (4.26) > Pb (1.77) > Cu (1.63) > Zn (1.51) > Cd (0.45) > Cr (0.11) > Ni (0.05); TF=C(leaf)/C(shoot) Cr (2.17) > Ni (2.05) > Fe (1.68) > As (1.12) > Cu (0.89) > Zn (0.88) > Cd (0.86) > Pb (0.47); TF=C(fruit)/C(leaf) Ni (3.03) > Cr (1.16) > Cd (0.77) > Pb (0.61) > As (0.33) > Cu (0.15) > Fe (0.05) > Zn (0.03). The Ph value of the soil all the samples has ranged from 5.8 to 7.6. PH of the soil may be affected also by the sewage and irrigation of Sitnica river which is considered highly polluted. According to SEPA, 2005, the maximum permissible limits for Cd, Cr, Cu, Ni, Pb and Zn for vegetables and fruits are 0.1; 0.2; 0.5; 20; 10; 9 and 100 mg/kg, respectively, in dry weight. Our study analyzes showed that concentrations of heavy metals (Pb, Cd, Cr, Ni, As, Cu, Zn and Fe) in the analyzed tissue samples were higher in areas near the industrial zone of Mitrovica region compared to control area. Our findings are consistent with those reported by Demirezen et al. (7), Kumar et al. 2009, Lacatusu et al. 2008, which in their studies show high metals values. As is known, Cd is accepted as a carcinogen in the first instance.

The obtained results show that the inputs are anthropic (industrial pollution, contaminated water for irrigation, traffic, etc.) in the Mitrovica region have raised the levels of heavy metals in the soil, and as a result, the concentrations of metals in fruit trees have increased. Our study showed that levels of pollution with heavy metals in the soil and fruit were mainly related to local and regional resources. Levels of heavy metal concentrations compared between the contaminated area and the reference area were found to be significantly different. The obtained results showed that the fruits were powerful accumulators of heavy metals, considering that for some types of rootstocks the concentrations of heavy metals in the samples have exceeded the allowed values.

Our results are in line with the results reported by Zhen et al. (31), Xiao et al. (29) in China. Zhen (2008) reported that cultivated fruits near the Shenyang-Dalian highway were polluted with Pb and Cd with average concentrations of 0.082 and 0.010 mg/kg in apple fruit. Cultivated fruits in the mining areas were prone to contamination with heavy metals (29). The results of the present work exhibited differential distribution of heavy metals in different tissues of apple tree. There are different variations in the ability of to take up heavy metals through their root tissues and transport them to the edible parts of the plants. This variation depends on the physicochemical properties of heavy metals, industrial region, species of crops, cultivation strategy, soil type and growing conditions. Previous studies showed that the higher the concentration of heavy metals on soil, the higher its probability will be in plant cultures (21). Poniedzialek (24) found differences between cultures at the level of accumulation of heavy metals in specific organs. Like lead, cadmium is also known for its toxic and negative effects on human health. Cadmium can accumulate in the human body and can cause kidney dysfunction, skeletal damage and reproductive deficiency. The cadmium content in the literature was reported in the range of and 0.0002 0.527 mg/kg in fruit foods from the Greek market (15). In our study, fruit analysis from all sampling points was contaminated by an excessive amount of Cd compared to the permitted limit (0.05 mg/kg) proposed by FAO / WHO (8). The above results show that Cd has a high capacity to be transferred from soil to edible parts of fruit in agricultural lands of the Mitrovica region. This can be attributed to the competition between Cd^{2+} and Ca^{2+}. It is easier for Ca^{2+} to be replaced by Cd^{2+} than other metals due to their same valence (16). In addition, Ca is an essential element for plants and can enter plant tissues through active transport, while most heavy metals (as non-essential elements) can only be introduced into plant tissues through passive methods (eg, concentration diffusion and permeation) Costa and Morel (5). The concentration of Cr in delicious apple cultivars in three rootstock mm106, m26 and m9 in the contaminated studied fields was greater than in the reference area. The content of chromium in the literature was reported in the range of 1.48 - 6.43 mg/kg in wet weight in various summer fruits from Pakistan (31). There is no information on maximum chromium levels in dried fruit samples (2). Chromium (III) is an essential nutrient that empowers the action of insulin and thus affects the metabolism of carbohydrates, lipids and proteins. However, chromium (VI) is carcinogenic (27). This high concentration of Cr can be dangerous to the local community and fauna of the study area (6). Ni levels in fruit were many times higher than the maximum allowed limit (0.3 mg/kg) (9). The content of nickel in literature was reported in the range of 1.0-8.9 mg/kg in some fruits from Pakistan (30). In the study area, the nickel concentration in plant tissues was observed a few times higher than the reference site. Ni is an important and essential element to plants; however, its excess causes variable symptoms of toxicity (33). The low content of copper in apple fruits is most likely due to the poor movement of copper in plants as well as the high concentration of zinc in soil known to have an antagonistic effect on copper absorption (4). The soil surface is a large reservoir of heavy metals as well as a natural buffer for transporting chemical elements into the biosphere. The most harmful effect of heavy metals is that they can enter the food chain and seriously threaten human health.

Pollution at high levels of land in the Mitrovica region appears as a result of industrial activities, with smelters in this region as potential contributors. The degree of soil contamination where the trees are cultivated is closely related to the emissions released by the founders for years in the past, where all the metals have fallen between the upper layers and the ground layers. This study highlights the potential risk of accumulation of heavy metals, particularly Pb, Cd, Cr and Zn, in fruit growing near the foundry. Further research should be undertaken to analyze the levels of metals present in the atmosphere (quantitative) and the bioaccumulative ratio of metals to the fruit trees of the area

REFERENCES

1. Adamsa, M. L., F. J., Zhao, S. P., McGratha, F. A.,Nicholsonb, and B. J. Chambersb, 2004. Predicting cadmium concentrations in wheat and barley grain using soil properties. Journal of Environmental Quality, 33, 532–541

2. Anonymous. 2002. Regulation of setting maximum levels for certain contaminants in foodstuffs. Official Gazette, Issue 24908, 16 October

3. Cairns, J., 1980. Scenarios on Alternative Futures for Biological Monitoring, 1978-1985. In: D.L. Worf (Ed.), Biological Monitoring for Environmental Effects. Lexington Books, Lexington, pp. 11-21

4. Chaudhry, F. M., M. Sharif, A. Latif, R. H. Qureshi, 1973. Zinc-copper antagonism in the nutrition of rice (Oryza sativa L.). Plant and Soil 38(3): 573-580

5. Costa, G., and J. L. Morel, 1993. Cadmium uptake by Lupinus albus (L): cadmium excretion, a possible mechanism of cadmium tolerance. Journal of Plant Nutrition, 16(10), 1921–1929

6. Deda, Sh., R. Kastrati, XH. Elezi, R., Bakalli, A., Demaj, and V. Konjufca, 1996: Lead Concetracion in Crops from Vicinity of Lead Indystry of “Trepça” plant. Environmental letters. Special issue, pp: 29-32.

7. Demirezen D, and A .Aksoy 2006. Heavy metal levels in vegetables in Turkey Is within safe limits for Cu, Zn, Ni and Exceeded For Cd and Pb. Journal of Food Quality 29: 252-265

8. FAO/WHO 1995. Codex General Standard for Contaminants and Toxins in Food and Feed (193-1995), pp. 31-32

9. Fresse, D. S., R., E. and K. Klitgaard, Pedersen, 2004: Environmental Management in Kosovo. Heavy Metal emission from Trepca. TekSam. Linku: http: // dspace. ruc.

Dk / bitstream / 1800 / 210 / 1 / Environmental _ management_in.pdf.

10. Garg, V.K., P.,Yadav, S., Mor, B., Singh, and V. Pulhani, 2014. Heavy metals bioconcentration from soil to vegetables and assessment of health risk caused by their ingestion. Biol. Trace Elem. Res. 157 (3), 256–265. http://dx.doi.org/10.1007/ s12011-014-9892-z, Epub 2014 Jan 25

11. Hyseni, S., B., Durmishaj, B., Fetahaj, F., Shala, A., Berisha, and D. Large, 2010: Trepça Ore Belt and Stan Terg mine – Geological overview and interpretation, Kosovo (SE Europe). GEOLOGIJA 53/1, 87-92, Ljubljana

12. Jarup L. 2003. Hazards of heavy metal contamination. Br Med Bull 68:167_182

13. Järup, L., L., Hellström, T., Alfvén, M.D.,Carlsson, A., Grubb, B., Persson, C., Pettersson, G., Spång, A., Schütz, and C.G., Elinder, 2000. Low level exposure to cadmium and early kidney damage: the OSCAR study. Occup. Environ. Med 57 (10), 668–672Oct 57 (10), 668–672

14. Kabata-Pendias, A. 2011. Trace Elements in Soils and Plants, 4th ed. Taylor & Francis Group, Boca Raton London New York

15. Karavoltsos S, A, Sakellari, M, Dimopoulos M, Dasenakis and M. Scoullos 2002. Cadmium Content in Foodstuffs from the Greek market. Food Additives Contam 19:954962

16. Kim, Y.Y., Y.Y. Yang, and Y., Lee, 2002. Pb and Cd uptake in rice roots. Physiologia Plantarum, (116):368–372

17. Kumar A, I. K, Sharma, A, Sharma, S, Varshney P.S. Verma, 2009. Heavy Metals contamination of vegetable foodstuffs in jaipur (India). Electronic Journal of Environmental, Agricultural and Food Chemistry 8 (2): 96-101

18. Lacatuşu R, A.R. and Lacatuşu 2008. Vegetable and fruits quality within heavy metals polluted areas In Romania Carpth. Journal of Earth and Environmental Sciences 3 (2): 115-129

19. Lenntech Water Treatment and Air Purification. Water Treatment. Published by Lenntech, Rotterdamseweg, Netherlands. http://www.excelwater.com/thp/filters/Water-Purification

20. Liu J, J, Wang, J,Qi, X, Li, Y,Chen. C,Wang, and Y. Wu 2012. Heavy metal contamination in arable soils and vegetables around a sulfuric acid factory, China. Clean Soil Air Water 40:766–772

21. Mapanda F, E N, Mangwayana J, Nyamangara, and K E. Giller, 2007. Uptake of heavy metals by vegetables irrigated using wastewater and the subsequent risks in Harare, Zimbabwe. Physics and Chemistry of the Earth (Parts A/B/C), 32, 1399–1405

22. McLaughlin M. J, D. R. Parker, J.M. 1999. Clarke Metals and micronutrients – food safety issues. Field Crops Research; 60 (1–2): 143–163.

23. Mohanty M, H.K. Patra 2011. Attenuation of chromium toxicity by bioremediation technology. Rev Env Contam Toxicol 210: 1–34

24. Poniedzialek, M., J. Ciura, , E. Stokowska, and A. Sekara, 1999. Control of the contamination of lettuce crop with heavy metals by the selection of a site and a cultivar. Scientific Works of the Lithuanian Institute of Horticulture and Lithuanian University of Agriculture. Hort. Veg. Grow. 18:146-150

25. SEPA. The Limits of Pollutants in Food; GB2762-2005; State Environmental Protection Administration: Beijing, China.

26. Shllaku, L., L. Landner, 1992. : Environmentalin Kosovo – Environmental Problems Related to Mineral Exploitation, Stokholm, Sweden, WHO

27. Tuzen M, M. Soylak 2006. Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108. J Hazard Mater 129:266273

28. Wag.ner, G. and P. Miiller, 1979. Fichten als 'Bioindikatoren' fiir die Immissionsbelastung urbaner Okosysteme unter besonderen Beriicksichtigung yon Schwermetallen. Verh. Ges. ()kolog., VII:307-314

29. Xiao Z L, Q. Cong, and J. Qu 2010. Assessment of heavy metal pollution in orchard soil and its affections to fruit quality around molybdenum mining area. Science Technology and Engineering, 10, 5831–5834

30. Yang Z, LuW, Y. Long, X. Bao, and Q. Yang 2011. Assessment of heavy metals contamination in urban topsoil from Changchun City, China. J Geochem Exp 108:27–38

31. Zahoor A, M, Jafar, and M. Saqib 2003. Elemental distribution in summer fruits of Pakistan. Nutr Food Sci 33:203207

32. Zhen H. 2008. Pollution characteristics of heavy metal in grains and fruits at both sides of Shenyang-Dalian expressway. Journal of Meteorology and Environment, 24, 1–5.

33. Zornoza P, Robles S, and N. Martin 1999. Alleviation of nickel toxicity by ammonium supply to sunflower plants. Plant Soil 208:221– 226.