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Accumulation of Heavy Metals in Vegetables from Agricultural Soils

ELJAN KASA[1*], MARCO CONTIN[2], FRAN GJOKA[1]

[1]Department of Agroenvironment and Ecology, Agricultural University of Tirana, Tirana, Albania

[2]University of Udine, Italy

Abstract

This study analyzed the heavy metals in vegetables cultivated in private gardens in Bregu i Matit, an important agricultural area in the NW Albania.The plant and soil samples taken from irrigated and non-irrigated fields in this area were analyzed for the concentrations of Cd, Cu, Zn, Pb and Ni using atomic absorption spectroscopy (AAS), after extraction by HNO_3 and H_2O_2.The transfer factors (TF) were used to evaluate the risk of metal transfer from soil to plant and the FAO/WHO safe limits to assess the potential hazards of heavy metals to human health. The ranges of heavy metal concentrations ± standard deviation in vegetable samples were (mg kg^{-1}): Cu 2.98-12.90 (±3.08), Ni 4.82-35.79 (±7.68), Zn <1-81.67 (±24.41), Cd 0.05-0.60 (±0.16) and Pb 0.03-0.44 (±0.11). The maximum contents of Cu, Cd, Zn and Pb were found in salad samples taken from the intensively irrigated fields and Ni in a salad sample from a moderately irrigated field, suggesting that the irrigation with polluted waterled to accumulation of heavy metals in plants. The TF was of the order Cd > Zn > Cu > Ni > Pb. The TF values indicate that only Cd was accumulated in plants.The contents of Cd in three vegetable samples, Pb in four samples, and Cu in one sample were above the safe limits set by the FAO/WHO for heavy metals in foods and vegetables indicating that consumption of vegetables grown in the studied soils could be dangerous to human health.

Keywords: contamination, irrigated soils, safe limits, toxic metals,transfer factor.

1. Introduction

The presence of heavy metalsin agricultural soils poses a potential risk to human health due to contamination of the food chain. This is because consumption of products originating from plants that accumulate large amounts of heavy metals like vegetables is increasing rapidly due to their highnutritional value. Oti Wilberforce & Nwabue[19] noted that the elevated levels of heavy metals in soils may lead to uptake by native and agronomic plants. The accumulation of heavy metals by food plants grown in contaminated soils in amounts that can cause health problems has been reported by several authors [11, 5,14, 1). The main sources of heavy metal contamination in agricultural soils include fertilizers, agricultural chemicals, and liquid and solid waste [21]. The soilscontaminatedwithheavymetalsinAlbania are foundnearindustrial sites, in areastreatedwith pesticides andfertilizersand wastewaters, and soilsnaturally high in heavy metals. Our previous studies have shown high contents of Cr, Ni and Cu extracted with aqua regia[15] and high proportions of Cd, Cu and Pb extracted with EDTA [7]in agricultural soils of Bregu i Matit. This study aimed to analyze concentrations of heavy metals Cd, Cu, Zn, Pb and Ni in vegetables cultivated in soils of this areain order to assess the transfer ratio of heavy metals from soil to plant and the potential health risk to local population through the food chain.

2. Materials ans methods

2.1 The study area

The study area (Bregu i Matit) extends in the latitude of 41°42'47" N and longitude of 19°39'16" E, and is located about 46 km north-west of Tirana (Figure 1). This is an important producing area of food crops for Lezha region. The climate is characterized by cold and rainy winters and hotanddry summers.The mean annual rainfall, potential evapotranspiration and temperature are 1461 mm, 1005 mm and 15.5°C, respectively [2, 20]. The predominant soils are alluvial and meadow grey cinnamon soils after the National Soil Classification System (1954) or Calcaric and Gleyic Fluvisol and

*Corresponding author: Name Surname; E-mail: kasaelian@hotmail.com
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Gleyic and Fluvic Cambisol, respectively, after the World Reference Base for Soil Resources [10]. The main food crops are maize, wheat, vegetables, and forages. The main sources of metal contamination for soils of Bregu i Matit were irrigation with polluted water from Mati River, agrochemicals use, etc. The irrigation is applied for a long time (1966-1995) and the amount of water used for irrigation has been 600-800 m^3/ha. Four locations (villages) were selected for this study (Figure 1). It is expected that these locations differ by their degree of metal contamination. The location 1 (L1-Pllane) is considered as a control and wasplantedwithalfalfa; location 2 (L2-Gajush) and location 3 (L3-Shenkoll) are intensively irrigated locations (6-8 irrigationin ayear) and were planted with maize and vegetables; location 4 (L4-Rrile) is a moderately irrigated location (3-4 irrigationin ayear) and was generally planted with wheat, sunflower, maize and fodder.

Figure 1. The study area and sampling points

The general soil properties (pH, organic matter - OM and clay contents and cation exchange capacity - CEC) and total metals content (Cd, Cr, Ni, Pb, As, Cu and Zn) of the studied soils were described in detail by Kasa et al.[15], and mobile metals content of these soils by Kasa et al. [7]. The soil reaction is slightly acid to neutral ($pHCaCl_2$6.2-7.4), organic matter content was low to medium (0.97-1.81%), clay content was low to high (14.3-48.7%), and cation exchange capacity (CECpot) was medium to high (17.46-34.70 cmol(+) kg^{-1}).Figure 2 presents the total contents of heavy metals in surface of the studied soils.

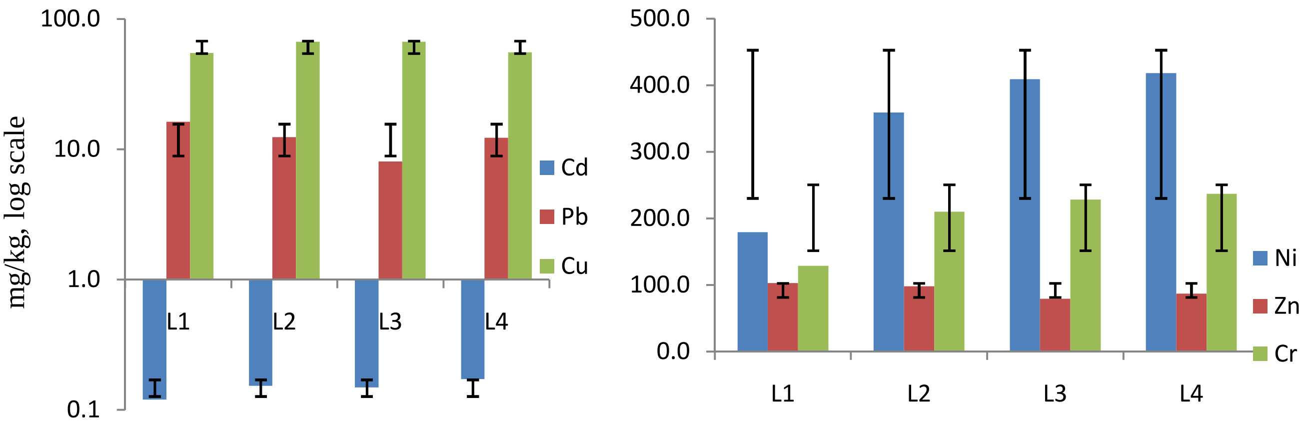

Figure 2. Concentrations of metals in soil samples

The total contents of Cr, Ni and Cu exceeded the critical values of the Federal Soil Protection and Contaminated Sites Ordinance [6]. According to geo-accumulation index (*I*geo) the soils were unpolluted to moderately polluted with Cd, Cr and Zn and moderately to strongly polluted with Ni and As. The NH_4NO_3content of heavy metals in all the studied soils lies under trigger and actionvalues of theBBodSchV[6], indicating that there is no actual harmful pollution ofsoils with these metals. However,Narimanidze et al., [18] found accumulations of Cu, Zn and Cd in food crops despite of a low concentration of these heavy metals in the NH_4NO_3 extract. This suggests the need for analysing the heavy metal contents in vegetables grown in these soils.

2.2 Soil and plant sampling

The composite soil samples were taken from family farms in twelve locations (L1 - non-irrigated, L2, L3, L4 – irrigated) at a depth 0-25 cm. Air-dried samples were passed through a stainless steel sieve with a 2- mm mesh. Finely ground samples were prepared by grinding a subsample of < 2-mm soil to a fine powder in a ball mill. The vegetable samples including cabbage, salad and dill were taken at the same locations.The samples after washing in distilled water were air-dried and put in the thermostat at 65°C during the night. The plant material was ground, sieved through a 2-mm sieve and stored in the glassy vessels.

2.3 Soil and plant analyses

The soil pH was determined on a 1:2.5 soil:0.01M $CaCl_2$ suspension by pH-meter (DIN ISO 10390); total carbon were determined by the gas chromatography using a CNS element analyzer (HERAEUS); cation exchange capacity (CECpot) as the sum of exchangeable cations was measured according to Mehlich [16], in buffered $BaCl_2$-TEA solution (0.1 M, pH 8.2), percolation for 8 h, by atomic adsorptionspectrometer (Varian AA240FS); soil texture was determined bysieving and pipetting method (DIN 19683); total (at aqua regia extract) (DIN ISO 11466, 1995), and mobile contents (at 0.025 M NH_4EDTA and 1 M NH_4NO_3 extracts DIN 19730, 2009) of heavy metals were measured with an inductively coupled plasma optical emission spectrometry (ICP-OES). Precision of the analyses was checked by analysing a certified reference sample (CRS). 0.3 gram of prepared plant sample was weighed into a 50 ml Teflon vessel. After addition of 8 mL of 69% HNO_3 and 2 mL of 33% H_2O_2, samples were gently homogenized in the reagents and digested in a microwave digestion system. Plant samples were digested at 180^{o}C. After cooling, the solution was made up to a final volume of 50 ml with distilled water. The metal concentrations were measured by atomic absorption spectroscopy, equipped with ETA/GFAAS System (model novAA-400).

The obtained data were reported in mg/kg (on a dry matter basis). The transfer factor was calculated for each heavy metal according to formula: TF = Mplant/Msoil, where Mplantis the metal content in the plant; and Msoilis the total metal content in the soil.

The evaluation of heavy metal levelsin plant samples was carried out with the international standards set by WHO/FAO [8, 9] for heavy metals in plants and vegetables, respectively. Statistical analysis was performed using Microsoft Office Excel 2010.

3. Results and discussion

3.1 Heavy metal contents in plants

The results of plant analysis were presented in Figure 3. The ranges (± SD) of heavy metal contents were as follows: Cu 2.98-55.13 (±3.08) mg kg^{-1}, Ni 4.82-35.79 (±7.68) mg kg^{-1}, Zn <1-81.67 (±24.41) mg kg^{-1}, Cd 0.05-0.60 (±0.16) mg kg^{-1}, and Pb 0.03-0.44 (±0.11) mg kg^{-1}, while Cr was not detected. The maximum contents of heavy metals were found for Cu and Cd in one salad sample taken from a vegetable plot in Gajush village, Zn in two salad samples taken from two vegetable plots in Gajush and Shenkoll villages, Pb in one salad sample taken from a vegetable plot in Shenkoll village, and Ni in one salad sample taken from a vegetable plot in Rrile village. The soils in Gajush and Shenkoll villages have been intensively irrigated for a long time, while the soils in Rrile village was moderately irrigated. The low values of standard deviation indicated relatively homogeneous distribution patterns of metals in the studied soils, suggesting a low variability of soil parameters that control the transfer of metals from soil to plant.These parameters are given below. Considering the mean values, the order of metal contents in plant samples from non-irrigated soil was Ni > Cu > Zn > Cd > Pb, while in plant samples from irrigated soils was Zn > Cu > Ni > Cd > Pb, corresponding to the sequence of metal amounts extracted with aqua regia only for Ni in non-irrigated soil[15].While the order of metal accummulation in the studied vegetables were salad >cabbage.

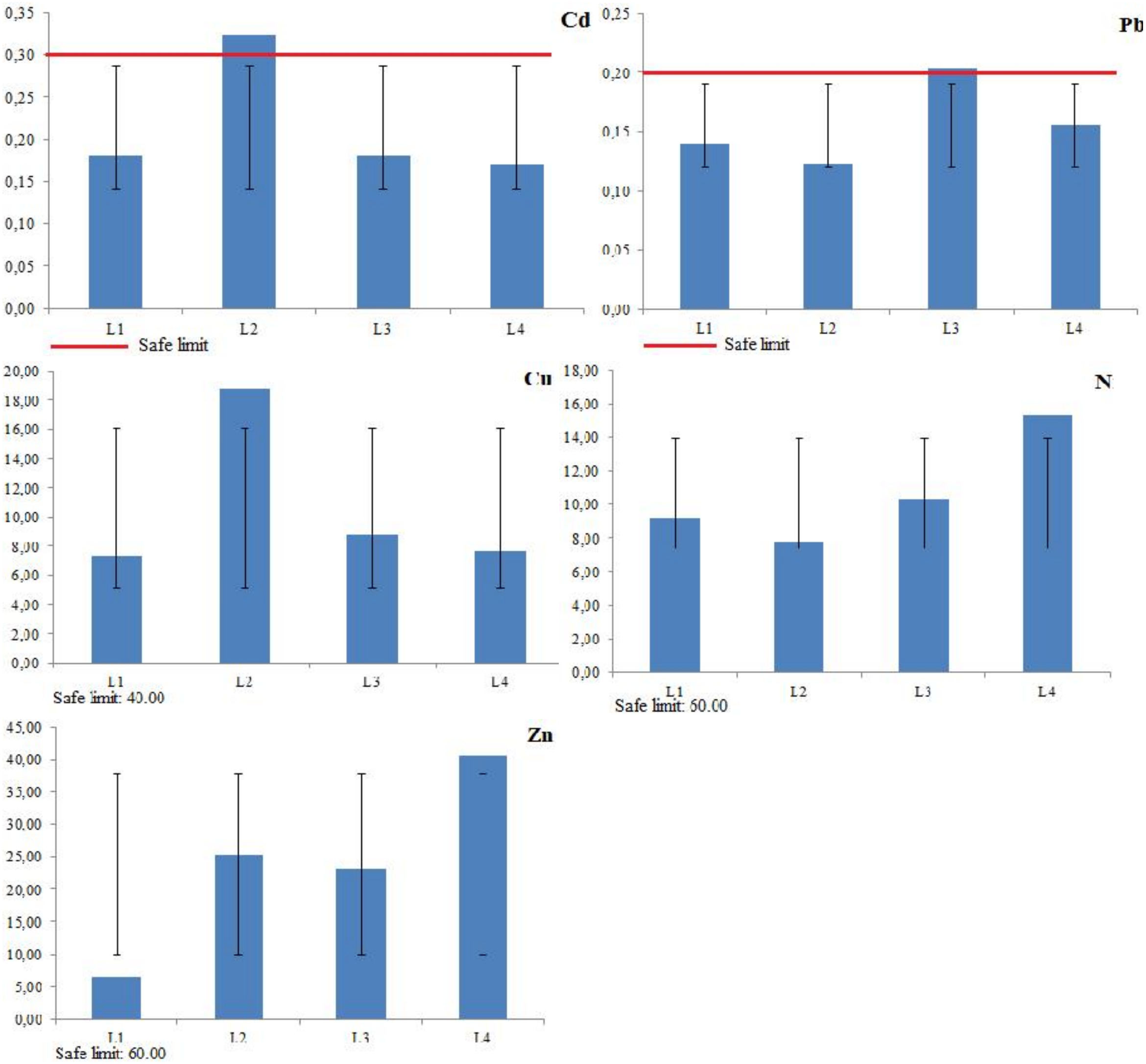

Figure 3. Concentrations *of heavy metals in the vegetable samples* (mg kg^{-1})

3.2 Origin of heavy metals in plants

In this study, the correlation is used as a statistical tool to identify the origin of metals in the analyzed plant samples. The results of correlation analysis presented in Table 1 indicated that there was the significantly positive correlation between Cu and Cd (r=0,779**; p<0.001) and among Zn and Ni (r=0,681**; p<0.01), suggesting that these metals have the same origin in the studied vegetables.

Table 1. Pearson correlation between heavy metals in vegetables

Metal	Cu	Zn	Ni	Pb	Cd
Cu	1.000				
Zn	-0.155	1.000			
Ni	0.010	0.681**	1.000		
Pb	0.424	-0.246	0.311	1.000	
Cd	0.779**	-0.024	-0.078	0.123	1.000

***Correlation is significant at the 0.001 level (2-tails); **Correlation is significant at the 0.01 level (2-tails)

The correlation revealed no significant relationships between the contents of other heavy metals in plants, indicating a different originof these metals.In order to determine whether metals in plants come from the soil, the correlation coefficients between total and mobile contents of metals in soil and their contents in plants are calculated (Table 2). On the other hand, the existence of a significant relationship between the contents of metals in soil and plants canserve as prerequisite for the soil–plant transfer factor concept [Bunzl et al., 2000, quoted by 13]. The results of this study indicated no significantly positive relationships between the total and mobile contents of heavy metals in soil and heavy metals in plants, except for Zn, Pb, Ni (in NH_4NO_3 soil extract) and Cd (in aqua regia soil extract) that showed negative relationships. No significantly positive relationships were also found between heavy metal contents in plants and plant available phosphorous in soil. This indicate that the presence of heavy metals in plant can be attributed to the other sources than the soil and fosphatic fertilizers.Therefore, additional investigtion has to be done to *explore these sources (probably water*, animal manure *or air) of metals* in order to guarantee both the soil quality and food security.Low correlation between metal contents in plants and soil pH indicates that the pH did not influence metal uptake by plants in the studied soils. This can be explained by high pH values (6.15-7.44).

Table 2. Pearson correlation between metals in soils and vegetables

	Cu_{PLANT}	Zn_{PLANT}	Ni_{PLANT}	Pb_{PLANT}	Cd_{PLANT}
Cu_{TOTAL}	0.283				
Zn_{TOTAL}		-0.391			
Ni_{TOTAL}			0.292		
Pb_{TOTAL}				-0.336	
Cd_{TOTAL}					-0.039
Cu_{EDTA}	0.130				
Zn_{EDTA}		-0.379			
Ni_{EDTA}			0.086		
Pb_{EDTA}				-0.258	
Cd_{EDTA}					0.149
Cu_{NH4NO3}	0.370				
Zn_{NH4NO3}		-0.435			
Ni_{NH4NO3}			-0.118		
Pb_{NH4NO3}				-0.382	
Cd_{NH4NO3}					0.053
$P_{PLANT-AVAILABLE}$	0.027	-0.137	-0.144	-0.053	-0.175
Soil pH	0.226	0.151	-0.085	-0.153	0.142

3.3 Transfer of heavy metals in plants

The risk of metal transfer from soil to plant is evaluated on the basis of transfer factor (TF). Liang et al. [12] noted that the soil-to-plant transfer factor is one of the key components of human exposure to metals through the food chain. In this study, interpretation of this parameter is done according to Baker [4].

The ranges (±SD) of the TF values were (Table 3): Cu 0.13-0.26 (±0.19), Ni 0.02-0.05 (±00.02), Zn 0.06-0.50 (±0.34), Cd 1.03-2.10(±1.06) and Pb 0.01-0.03 (±0.02), and the trends of TF were in the order of Cd > Zn > Cu > Ni > Pb. The highest values of TF were found in salad. The TF values were lower for all the analyzed metals, except for Cd.This means that Cd was the most soluble and mobile metal in the studied soils.Similar results were reported by Ivasuc & Rusu [17] and Singh et al. [3]. In general, the metals Zn, Cu and Pb have the higher TF values in vegetable samples collected from irrigated soils, suggesting that water or other agricultural inputs (animal manure, etc.) are the main source of these metals in soils.

Table 3. Transfer factor (TF) of metals from soils to investigated vegetables

Sampling location	Soil pH	Soil OM (%)	CEC cmol(+)kg^{-1}	Cu	Ni	Zn	Cd	Pb
L1	6.15	1.23	17.46	0.13	0.05	0.06	1.50	0.01
L2	7.39	1.35	26.51	0.26	0.02	0.28	2.10	0.01
L3	7.10	1.05	24.07	0.13	0.03	0.29	1.38	0.03
L4	6.77	1.51	26.95	0.16	0.04	0.50	1.03	0.01
SD	0.48	0.24	4.49	0.19	0.02	0.34	1.06	0.02

3.4 Metal pollution of vegetables

The contents of Cd in three vegetable samples, Pb in four samples, and Cu in one sample exceeded the safe limits set by the FAO/WHO [8, 9]for heavy metals in foods and vegetables, and within the normal range of metals in plants, except for Cu in all the samples and Ni in three samples (see Figure 2).No Ni and Zn contamination was detected in the studied vegetables samples. These results are consistent with those of a previous study on the mobility of heavy metals in these soils [7].

4. Conclusions

The results of this study indicated the presence of heavy metals in vegetables cultivated in soils of Bregu i Matit Plain, NW Albania. The accumulation of these metals in vegetables analyzed seems to be associated mainly with the use of irrigation water. The concentrations of heavy metals were in the order ofZn>Cu>Ni>Cd>Pb and Ni>Cu>Zn>Cd>Pb in irrigated and non-irrigated soils, respectively. The study revealed that Cd, Pb and Cu in some vegetable samples were higher than the FAO/WHO safe limits and the TF for Cd and Zn were the highest, suggesting that consumption of vegetables grown in the studied soils could be dangerous to human health.

5. Acknowledgements

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