SOME METALS (Fe, Mn, Zn, Cu, Pb, Cd) CONTENTS IN VEGETABLES FROM A NONPOLLUTED PLAIN AREA OF CENAD-BANAT (ROMANIA)

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Abstract: *This paper presents original studies about the occurrence of some heavy metals (Fe, Mn, Zn, Cu, Pb and Cd) in soil and different vegetables (pepper, cucumbers, tomatoes. eggplants, green beans, cauliflower, cabbage, dill-leaves, parsley-leaves and roots, celery-leaves and roots, onion, garlic and potatoes) cultivated in nonpolluted plain area in Cenad-Banat County. The accurate determination of toxic heavy metals in vegetables is of importance because of the toxicity of these elements and their compounds. Total heavy metals in vegetable samples were analyzed after wet digestion with mineral acid, and in the soils they were analyzed after digestion in aqua regia. All metals were analyzed using high-resolution continuum source spectrometer ContrAA-300, Analytik-Jena in the acetylene flame (99.99 % purity). In comparison with official imposed limited the average values for heavy metals contents in soil are in the normally interval for **Zn, Cu** and **Pb**, for **Cd** the limit is exceeded, but under warning threshold. The smaller content of total heavy metals (around 2.5 ppm) was identified in cucumbers, cauliflower and cabbage. In pepper, tomatoes, eggplants, green beans, onion and potatoes the total content of heavy metals are between 3-6 ppm. In root of carrot, celery and parsley the total content is between 3-7 ppm with maximum in parsley root. The highest values were identified in leaves of parsley, dill, celery and garlic. For all soil and vegetables samples the average concentrations of all analyzed metals are lower than the limits established by the present Romanian legislation.*

Key words: *heavy metals, toxicity, soil, plants, FAAS*

Introduction

The main route of entry for these toxic elements is the food chain with soil, vegetables, plant feed and livestock all being important ecological strata. Inhalation can also bee a significant pathway. The accessibility of metal-microelements for plants depends of soil reaction, organic matter content, mineral colloids, soil humidity and microbiological activity. Organic matter, especially humus compounds can form organo-metallic compounds with high mobility in soil solution and availability for plants [1,2]. The essential metal microelements for plants and animals: **Fe, Mn, Cu, Zn, Mo, Se**, can will bee toxic in high quantity. Other metal microelements: **Hg, Cd, Cr, Ni, Pb**, is very toxic for green plants and for animals, too. These metal microelements can affect the biological and biochemical processes in plants: nutrition, photosynthesis and respiration, yield of crops. Toxicity degree of heavy metals was estimated in function of critical concentration for a normal development of plant (Table 1). From these data we can see that **Hg, Cr, Cd** and **Pb** have the highest toxicity for plant [3].

Zn and **Cu** in trace quantities are very important for plants and animals metabolism. They are building component of many enzymes. The importance of **Zn** for enzymes was discovered early this century (1986). The biochemistry of **Zn** includes an account of the genetic disorder acrodematitis enterophathica. This was previously fatal for all babies born with it, but can now bee cured with doses of **Zn**. Excessive consumption of alcohol damages the liver and those suffering cirrhosis have lower levels of **Zn** than normal in that vital organ. Again if the damage is not severe then **Zn** supplements can restore the liver's function. Levels of **Zn** are highest in prostate, muscles, kidney and liver; semen is particularly rich in **Zn**. In human nutrition is the daily intake is of about 15 mg, almost the same as **Fe** [4].

Table 1.

Critical concentration of heavy metals in plants [3]

Metal	**Cr**	**Hg**	**Cd**	**Co**	**Pb**	**Cu**	**Ti**	**Ni**	**Zn**	**Mn**	**Fe**
Critical concentration (ppm)	**1**	**2**	**5**	**10**	**10**	**15**	**20**	**20**	**150**	**150**	**200**

Copper is another essential metal for humans but is never lacking in human diet because we only need 2 mg of **Cu** per day. Like **Zn**, copper is required for enzymes especially by those which govern respiration. One disease directly related to **Cu** is Wilson's disease, a genetic disorder in which sufferers accumulate **Cu** in tissues causing damage to liver and brain [4]. In high quantities the two metals have toxic effects on plants and animals. The adjoining of other heavy metals, **Cd** and **Pb**, affects especially the enzymes with thio (-SH) group [4, 5].

Cd is not an essential metal for plant and animal. At very low concentration (0.0001M) is very toxic for germination and primary development of plants. At old plants the toxic effect is low [6].

Pb is also a strong toxic for germination and primary development of plants. At some concentration (0.0001M) **Pb** is more toxic than **Cd**, for young plants. At 4-200 ppm **Cd** in plant tissue, for 22 plant species, the loss of yields was more 10% [3]. The high concentration of **Cd** and **Pb** in soil and culture medium is favorable for their accumulation in plants, more in roots than in leafs [6]. In plants tissue heavy metals have negative influence of the intern transport of major nutrition elements. **Cd** and **Pb** have an inhibitory effect over nitrogen assimilation enzyme [3]. In the presence of high level of **Cd** and **Pb**, the content of protein, calcium and phosphorus in grain of cereals is loss [7]. These metals can influence negatively the photosynthesis (Hill reaction), pigment content, O_2 development, electron transport and oxidative phosphorilation. At high concentration these metals can reduce the reaction from Calvin cycle at C3 plants and at C4 plants can reduce the carboxilation of phospho-enol piruvic acid. **Cd** and **Pb** have an inhibitory effect over the cellular respiration at mitochondrial level. They reduce the reaction of Krebs cycle and glucose oxidation. They reduce the plasticity and elasticity of cellular wall and have an inhibitory effect on cellular division. At high concentration they have a mutagenic effect [3]. The plants, which have high tolerance at **Cd, Cu, Zn** and **Pb**, can synthesize protein rich in cystein. This protein can make chelates with metallic ions. [5].

Lead and Cadmium are toxic metals that accumulate in human tissues. Lead poisoning is of particular concern in children because it results in neurobehavioral defects. Cadmium is carcinogenic when inhaled. The kidney appears to be the sensitive organ following chronic oral exposure. Cadmium affects the resorption function of the proximal tubules, causing an increase in the urinary excretion of low-molecular-weight known as tubular proteinuria [8].

In animal tissue **Cd** and **Pb** have an inhibitory effect over the thiolo-group of enzymes. They interact with other trace elements, **Cu, Zn** and **Fe** and have a toxic effect on Langerhans cells from pancreas and on the cells from kidneys and testicles. **Pb** has a toxic effect on liver and the mobility of spermatozoid especially. The absorption of heavy metals has generally digestive way, followed by different tissue penetrations. The high concentration of heavy metals was identified in kidneys and liver. The excretion is made in general by faecal and urine. The intoxication with these heavy metals can have acute or chronic form. Frequently the visible clinical signs of diseases appear in 2-3 days and are represented by depression and anorexia [9]. Because of high toxicity grade of these metals, their concentrations in soil and food are restricted by legislation.

The studied area, within the village Cenad is located in the North of Banat County, in a plain region settled on the left part of Mures river valley. This area is far away from the industrial zone and has an old tradition in vegetable production. Also the climatic and soil conditions are favourable for ecological vegetables production.

Materials and Methods

Reagents and solutions

The stock standard solutions (1000 mg/L) were analytical grade purchased from Riedel de Haen (Germany). The working solutions were prepared by diluting the stock solutions to appropriate volumes. The hydrochloric acid 32%, nitric acid 65% and H_2O_2 25% solutions used were of ultra pure grade, purchased from Merck (Germany). All reagents were of analytical-reagent grade and all solutions were prepared using deionised water.

Soil samples preparation

For soils, 6 samples were sampled with agrochemical steel probe, from 0-20 cm deep, within the cultivated area. One mixed sample was made from 10 single samples. The soil samples were kept in plastic bags. In laboratory the soil samples were dried in clean air, ground and passed through a 2mm sieve to remove roots, stones and other large particles. The removal out of total metals content from soil to solution, in the purpose of dosage, can be made by wet proceeding which consists in treating the soil sample with mixture of mineral acids (HCl, HNO_3, 3:1 ratio) [10,11]. The soils were analyzed for total contents of heavy metals after digestion in *aqua regia*. 10mL mixture of nitric acid and hydrochloric acid (3:1) was added to 5.0 g of soil samples and heated on a hot plate. Then, the residue was treated with 1N nitric acid, centrifuged and finally we added 25 mL in quoted flask. The mobile forms of **Zn, Cu, Pb** and **Cd** were extracted from soil with a Na_2EDTA 0.1 N solution buffered at pH=7, at 1/5 soil-solution ratio [11,12]. For the determination, standard working solutions were prepared with the same extraction solution.

Vegetable samples preparation

Heavy metals in vegetable samples were analyzed after wet digestion with mineral acid [13]. For the vegetables' analysis we selected 100 g (or 3 pieces of bulky vegetables) from different location until 1000 g for one sample. After having been washed with deionised water the vegetables were homogenized by mincing. After homogenization, 100 g materials was transferred into a quartz capsule, dried at 105^0 C and after cooling the samples were homogenized by mincing. 1g of each dry sample was submitted to digestion with 10 mL pure HNO_3 and 10 mL H_2O_2 at 170 ^{0}C in a digesting device Digestion System 6-1007 Digester, provided by Tecator. After complete digestion the sample solutions were filtered, made up to 50 mL with deionised water. This solution was used for heavy metal **Zn, Cu, Pb** and **Cd** analysis by FASS in air/acetylene flame using an aqueous standard calibration curve. All analyses were made in triplicate and the mean values were reported.

Sample analysis

The most data referring to the abundance of these metals in soil, water and food were obtained by atomic absorption spectrometry methods, which suit best for routine determination. Atomic absorption spectrometry in air-acetylene flame presents a sufficient sensibility for the direct determination in the acid solution resulted after digestion [14-16]. The analysis of heavy metals (Zn, Cu, Pb, Cd) was made by ContrAA-300, Analytik-Jena device, by flame atomic absorption spectrometry (FASS) in air/acetylene flame. The device working parameters are presented in Table 2.

Table 2

The working parameters for spectrometer ContrAA 300, Analytik-Jena

Nr.crt.	Element	Wave length (nm)	Acetylene flow (L/h)	Air flow (L/h)	Concentration range (mg/L)	Correlation coefficient
1	Zn	213.9	60	400	0.010-1.600	0.991
2	Cu	324.8	60	400	0.025-3.000	0.975
3	Pb	217.0	60	400	0.025-5.000	0.980
4	Cd	228.8	60	400	0.015-2.000	0.992

All metals were analyzed using high-resolution continuum source spectrometer ContrAA-300, Analytik-Jena and the acetylene was of 99.99 % purity. The characteristics of working parameters and metal calibration are presented in Table 2. Under the optimum established parameters, the standard calibration curves for metals were constructed by plotting absorbency against concentration. In a definite range of each metal, good linearity was observed (Table 2).

Results and Discussion

The experimental data of heavy metal total content in soil around the village Cenad are presented in Table 3. We can observe a large variation of content, especially for **Cu** and **Cd**. In comparison with the official imposed limited, presented in Table 4, the average values for heavy metals contents in soil are in the normally interval for **Zn, Cu** and **Pb**, for **Cd** the limit is exceeded, but under warning threshold. Our experimental data are in agreement with literature data, this hill area have acid soils with small content of clay and mineral underground poor in heavy metals [17-19]. In this area other sources of pollution with heavy metals are absent.

Table 3

Heavy metals content, in total forms, in the soil horizon 0-20 cm, in village Cenad area

Metal (mg/Kg)	Zn	Cu	Pb	Cd
Minimum values	75.0	25.5	15.6	1.00
Maximum values	101	40.0	29.0	3.00
Average values	81.00	34.5	21.0	1.85

Table 4

Excerpt from Romanian Agriculture Ministry Ordinance 756/1997, standard values for trace elements in soil [20]

Experimental values mg/Kg	Zn	Cu	Pb	Cd
Normal values	100	20	20	1
Warning threshold	300	100	50	3
Intervention threshold	600	200	100	5

Table 5

Heavy metals content - mobile forms- of the soil horizon 0-20 cm in village Cenad area

	Zn	Cu	Pb	Cd
Minimum values	1.87	2.07	1.68	0.05
Maximum values	4.38	4.10	3.05	0.20
Average values	4.10	3.25	2.17	0.12

Table 6

Maximum accepted limits for some heavy metals in soil, mobile forms in EDTA-ammonium acetate (Lăcătuşu, 1995) [23]

Specification	Metal (mg/kg dry matter)			
	Zn	**Cu**	**Pb**	**Cd**
Maximum limit accepted	43.00	8.00	18.00	1.0

The phytoavailability of trace elements, from soil to plant, is a key factor controlling the quality of plant food and it correlates best with the concentration (total and mobile forms) of elements [3]. For all investigated trace elements the concentrations in soil, both total and mobile form, are below toxic limits. So this area is favourable to ecological vegetables production. The experimental data for heavy metals content in vegetables are presented in Table 7. Similar to soil, the limits of variation in heavy metals contents are very large. In comparison with legal limits presented in Table 8 we can observe that in general the experimental average values are below these limits.

In all analyzed vegetables, the average **Zn** content is included between 1.20-21.0 ppm, with maximum value 21.0 ppm in parsley leaves. In general we can observe that in leaf vegetables (dill, parsley, and celery) the content of all heavy metal are high. For these vegetables in our legislation the maximum limits are absent (Table 8). The average **Cu** content in the analyzed vegetables is included between 0.11- 1.50 ppm, with maximum content in garlic (1.50 ppm). This value is below the accepted limit (5.0 ppm).

The average **Pb** content in the analyzed vegetables is between 0.07-0.46 ppm, also below legal limit (0.5 ppm), with maximum value in dill leaves (0.46 ppm). In humans, approximately 50% of the Pb intake is through food which more than half originates from plants [21]. The rest is inhaled and absorbed depending on the particle size of the **Pb**-contaminated dust. Children however, absorb 50% of ingested **Pb** compared to adults who absorb 10-15%, making **Pb** ingested through hand-to-mouth behaviour or food an exposure source of significant concern [22].

The **Cd** average content in the analyzed vegetables are low (0.02-0.11 ppm) also below the legal limit (0.1 ppm or 0.2 ppm). Maximum value was identified in celery and parsley leaves. Cadmium accumulates gradually in the kidney, especially the renal cortex. Animals over 10 years old showed concentrations of up to 40 mg/kg dry matter, whereas young animals' kidneys showed only trace amounts of 0.5 mg/kg [21]. The liver is the other target organ with levels of 0.08 mg/kg in young animals and up to 10 mg/kg in older ones.

In our study smaller content of total heavy metals (around 2.5 ppm) was identified in cucumbers, cauliflower and cabbage. In peppers, tomatoes, eggplants, green beans, onion and potatoes the total content of heavy metals is between 3-6 ppm. In the root of carrots, celery and parsley the total content is between 3-7 ppm with maximum in parsley root. The highest values were identified in the leaves of parsley, dill, celery and garlic. The high content in root is associated with high content in leaves. Anke and coworkers obtained the same result [24]; in parsley and lettuce they have identified more Pb (0.81ppm) than in cucumbers (0.16 ppm) and potatoes (0.12 ppm)

Table 7

Heavy metals content (mg/kg, ppm) in some vegetables cultivated within village Cenad area

.Metals/ Vegetables	Zn			Cu			Pb			Cd		
	Minimum values	Maximum values	Average values	Minimum values	Maximum values	Average values	Minimum values	Maximum values	Average values	Minimum values	Maximum values	Average values
Pepper	3.00	9.65	6.40	0.05	0.31	0.11	0.05	0.33	0.11	0.01	0.05	0.02
Cucumbers	1.00	4.00	2.11	0.07	0.51	0.22	0.01	0.25	0.08	0.01	0.05	0.02
Tomatoes	0.50	5.00	2.91	0.05	0.31	0.12	0.05	0.40	0.12	0.01	0.08	0.03
Eggplants	2.51	5.20	4.04	0.25	1.69	0.81	0.01	0.15	0.07	0.01	0.05	0.02
Green beans	2.20	7.10	4.33	0.20	2.10	0.85	0.10	0.50	0.23	0.05	0.15	0.09
Cauliflower	0.50	2.50	1.70	0.10	1.00	0.51	0.05	0.40	0.08	0.01	0.05	0.02
Cabbage	0.50	3.00	1.20	0.20	1.82	0.57	0.10	0.95	0.36	0.01	0.05	0.02
Dill - leaves	5.50	12.3	8.40	0.35	2.65	1.12	0.28	0.50	0.46	0.01	0.10	0.06
Parsley - leaves	10.5	32.0	21.0	0.50	3.00	1.40	0.30	0.50	0.40	0.05	0.15	0.08

Celery - leaves	4.50	9.70	6.50	0.50	3.10	1.40	0.26	0.50	0.38	0.05	0.18	0.11
Potatoes	1.10	4.20	2.10	0.10	2.00	0.71	0.05	0.30	0.11	0.01	0.08	0.05
Onion	2.10	7.10	4.60	0.10	2.00	0.75	0.05	0.38	0.18	0.01	0.07	0.03
Garlic	7.50	16.0	11.0	0.50	3.90	1.50	0.05	0.40	0.21	0.01	0.10	0.04
Carrots - root	1.05	3.10	2.10	0.05	0.31	0.19	0.21	0.50	0.41	0.01	0.05	0.03
Parsley - root	2.90	9.80	5.90	0.50	2.90	1.10	0.18	0.46	0.39	0.01	0.10	0.04
Celery – root	2.10	5.70	3.10	0.10	0.95	0.47	0.15	0.31	0.25	0.01	0.10	0.04

Table 8

Excerpt from the ministry of public health ordinance no 975/1998, maximum accepted limits for heavy metal in foods [25]

Food	Metal (mg/kg fresh product, ppm)			
	Zn	Cu	Pb	Cd
Fresh or deep - frozen vegetables except for leaf vegetables	15	5.0	0.5	0.1
Leaf vegetables	-	-	0.5	0.2
Fresh or deep – frozen fruits	5.0	5.0	0.5	0.05

These values of heavy metals concentrations are close to literature data for similar soil and regional condition [26] and smaller than the values identified in polluted area [27].

In humans, about one-third of the total **Cd** burden originates from animal products and two-thirds from plants [21].The FAO/WHO advises provisional tolerable weekly intakes (PTWI) of 25 and 7 μg of **Pb** and **Cd**, respectively, per kg of body weight, corresponding to maximum tolerable daily intakes of 3.6 and 1 μg of **Pb** and **Cd**, respectively. The mean daily intake per kg of body weight in a recent 24-hours total diet study conducted in The Netherlands, was 0.25 μg **Pb** (range 0.05 to 2.17 μg) and 0.15 μg **Cd** (range 0.05 to 0.43 μg). These values were greatly below the limits corresponding to the results of other recent studies [22].

In March 2001 the new Commission Regulation (EC) No.466/2001 in relation to the permitted concentration of **Pb and Cd** in foodstuffs has come into force. The maximum levels are 0.1, 0.5, 0.5 and 0.1-0.3 mg/kg wet weight for **Pb** in meat, liver, kidney and vegetables, respectively. The corresponding figures for **Cd** are 0.05, 0.5, 1.0 and 0.05-0.3 mg/kg wet weight.

Vegetable consumption is very important for human nutrition. However vegetables polluted with high content of heavy metals can be the main way of entry for toxic metals in humans. For a healthy nutrition it is very important to know these contents. Our data come to complete the knowledge in this domain.

Conclusions

This paper presents some original studies concerning Fe, Mn, Zn, Cu, Pb and Cd, distribution in different vegetables (peppers, cucumbers, tomatoes. eggplants, green beans, cauliflower, cabbage, dill-leaves, parsley-leaves and roots, celery-leaves and roots, carrots-roots, onion, garlic and potatoes) from a plain nonpolluted area of Cenad-Banat (Romania).

For all analyzed metals in vegetable samples, the average values are below the legal limits. The legal limit for Zn (15 ppm) is exceeded in garlic and parsley leaves maximum values. The limit for Cu (5 ppm) and Cd (0.2 ppm) is not exceeded but the limit for Pb (0.5 ppm) is reached by green beans, carrot root and leaves of parsley, dill and celery and exceeded by cabbage maximum values. For the other vegetables also the maximum values are below the legal limits. In this area the soil and climatic conditions, agricultural practice, are favourable to ecological vegetables production. The identified contents in heavy metals are in general below the legal limits of investigated toxic metals.

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