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HEAVY METALS DISTRIBUTION IN SOIL – WATER – VEGETABLES SYSTEM IN BANAT AREA

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ABSTRACT:

The paper presents the distribution of Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb and Cd at heavy metals in soil, water and vegetables cultivated in Banat area. The analysis was made by atomic absorption spectrometry in acetylene-air flame. Soils and surface waters physicochemical properties and climacteric factors specific for this area favorite the cultivation of the vegetables heaving a normal content of metals. Comparing the concentrations of heavy metals with toxic character or potential toxic character (Cu, Zn, Cd and Pb) from examined vegetables with maximal values admitted by legislation, it can be seen that these are situated under admitted toxicity limits. These experimental data enrich the scientific knowledge about this old traditional vegetables technology in Banat's region. From this point of view these products are ecological character.

KEYWORDS:

Banat, *heavy metals, vegetables, soil, water.*

1. INTRODUCTION

The heavy metal concentration in Banat soils is generally high: some can exceed the average values [1,2]. Researchers have identified cadmium, lead, chrome and cobalt contents 2 or even 5 times higher than for similar soils in other parts of the country.

Even if the soils in Banat do not present high concentrations of heavy metals, some areas have been identified as polluted. This happens due to the lack of major industrial polluters, as well as due to the favorable conditions of depositing these chemical elements in soils (high content of clay and organic matter in the soil, large total capacity of cationic exchange, basicity, etc). However, it is worth taking into consideration that any important addition of heavy metals to the already-existing stock, by means of agricultural or soil amelioration techniques or by means of other industrial activities (various anthropogenic factors), can destroy the fragile balance that for the moment exists: thus the phenomenon of pollution may appear, with one or more heavy metals. From the soil and water, the heavy metals can get into the plant-animal-human food chain, causing severe affections and diseases [3].

The village Cenad is situated in the western part of the Low Plain of Banat. As there are no major industrial polluters in the area, the abiotic toxic affections of heavy metals in the vegetal products cultivated in the area can be the result of the geo-chemical characteristics of the soil, of the water used for irrigations or of improper amelioration works.

In order to prevent the heavy metal pollution of soil, water and vegetal products, a periodic evaluation is recommended of the distribution of such heavy metals in the soil-water-plant system; also, specific soil amelioration works should be conducted, when necessary.

2. MATERIAL AND METODS

The area under research is situated in the western part of the Low Plain of Banat, represented by the area around Cenad village. Samples were collected and analysed from the soil, surface water and various types of vegetables.

To characterize the soils, the main soil physical and chemical properties have been determined and the total and mobile contents of heavy metals (Cd, Cu, Pb and Zn) have been measured. The total content was measured in the solution obtained by soil digestion in aqua regales [4,5]. Mobile forms have been extracted by an EDTA-CH_3COONH_4 solution at 7,0, pH [6]. Heavy metals have been also determined in water and vegetables. All the heavy metals have been determined by means of atomic absorption spectrometry [7, 8].

3. RESULTS AND DISCUTIONS

The climatic conditions of the area under research present a warm and droughty weather. The climatic factors, by Meteo Station Sânnicolau Mare (table 1), ensure conditions for normal plant growth, with heavy metals.

Genetically, the soil in the area was formed on drift deposits with low capacity of heavy metal retention. The main physical and chemical characteristics of the alluvial soil, which is predominant in this area, are presented in table 2. As shown in table 2, the soil is characterized by a neutral reaction to the surface, coarse texture, average to good provision with humus, and good provision with phosphorus and potassium (mobile forms), with a high degree of base saturation. On such a soil, heavy metal mobility is strongly influenced by pH variations, salt content and phosphorus fertilization.

Table 1. Climatic factors (multiannual average) in village Cenad area

Climatic elements	Multiannual average
Temperature ^oC	10,9
Relative humidity (%)	69
Sunshine duration (hours)	2193
Rainfall (mm)	544,7

Table 2. Physico-chemical parameters of soil horizons in village Cenad area

Horizons	Ap	At	Am	A/C	C
Depth (cm)	0 – 15	16- 30	31-52	53-71	72-110
Grainy sand (2,0-0,2 mm) %	19,00	16,10	22,40	27,80	34,40
Fine sand (0,2-0,02 mm) %	38,10	41,00	37,10	36,90	38,80
Dust (0,02-0,002 mm) %	13,40	12,30	12,50	12,80	8,60
Clay 2 (sub 0,002 mm)%	29,50	30,60	28,00	28,00	18,70
Physical clay (sub 0,001mm) %	37,60	37,90	35,10	30,20	22,40
Texture	LL	LL	LL	LL	LN
pH in H_2O	6,65	7,05	7,35	8,25	8,45
Carbonates (Ca CO_3, %)			0,10	0,45	0,42
Humus, %	3,04	2,73			
P mobile, ppm	39,60	32,20			
K mobile, ppm	273	261			
Exchangeable bases (SB, me/100 g soil)	23,50				
Exchangeables Na (me/100 g soil)				0,29	0,18
Exchangeables Na (% of T)I)				1,01	1,22
Exchangeable hydrogen (SH, me/100 g soil)	3,76				
Cation exchange capacity (T, me/100 g soil)	27,24				
Percentage base saturation (V, %)	86,20				
Soluble salts (1:5, mg/100 g soil)				44,21	46,20

The concentration of heavy metals in the soil – total form (table 3) in the analyzed soil is not uniform. We can notice high and very high values of the content in Fe (25000 ppm) and Mn (685 ppm), as compared to the rest of the elements, determined in concentrations of tens of ppm (Zn, Cr, Ni, Cu, Co and Pb), or even units of ppm. The extreme values were recorded for Fe (macro element for the soil), which presents the highest concentration, and Cd (highly toxic microelement), present in a concentration of only 1,85 ppm.

Table 3. Heavy metals content - total forms, in the soil horizon 0-20 cm, in village Cenad area

Experimental values	Metal content (ppm)								
	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
Average values	25000	685	81,0	34,5	23,5	30,0	46,5	21,0	1,85

When comparing the experimental results with the reference values for heavy metal contents in the soil, it is easy to notice that, from this point of view, the soil in the area under research is to be placed in the category of normal soils [9].

Still, we notice higher contents in Cd (1,85 ppm), Cr (46,5ppm), Cu (34,5 ppm), Ni (30 ppm) and Pb (21 ppm) values which are characteristic for this area, which are under the warning level.

The concentration of heavy metals in mobile form generally emphasizes the degree of their accumulation in plants. In this case also, we can see that the distribution is not uniform (table 4), but this lack of uniformity is not as deep as in the case of the total forms. The highest concentrations were determined for Fe (46,9ppm) and Mn (45,1ppm). It is not difficult to notice that these values are quite close to one another. The

Zn, Cu and Pb concentrations were lower, but still much alike, between 2,17 and 4,10 ppm. The lowest concentrations were determined for Ni (0,88 ppm), Co (0,58 ppm), Cr (0,45 ppm) and Cd (0,12 ppm).

Table 4. Heavy metals content - mobile forms, of the soil horizon 0-20 cm in village Cenad area

Experimental values	**Metal content (ppm)**								
	Fe	**Mn**	**Zn**	**Cu**	**Co**	**Ni**	**Cr**	**Pb**	**Cd**
Average values	46,9	45,1	4,10	3,25	0,58	0,88	0,45	2,17	0,12

Comparing the experimental values of the contents in toxic heavy metals or potential toxic ones, with the recommended values (extracted by an EDTA-CH_3COONH_4 solution at 7 pH), we find that in this case also no maximum limits of toxicity were exceeded [10].

From all of the above, the conclusion can be drawn that the physical and chemical characteristics of the soil in the researched area and the climatic conditions specific to it do not favor excessive accumulations of heavy metals in the plants cultivated on such a soil. Even if total forms of some heavy metals (Cu, Ni, Cr, Pb and Cd) were found to be present in higher concentrations than the normal limit values (but still under the intervention threshold), the physical and chemical characteristics of the soil (pH and texture especially) do not allow of changing into mobile forms, nor of their concentrating in plants.

The phreatic level in this area is high, mineralized, which has as a result the accumulation of salts at the basis of the analyzed profile (table 2). The heavy metal concentration in the surface water used for irrigations (table 5) stands between the normal limits characteristic for the area in question. The same can be noticed about the pH, the average value of which being pH□7,75; the variation limits are in-between 7,60 and 8,00.

Table 5. Heavy metal contents in surface water in village Cenad area

Experimental values	**Metal content (mg/l)**							
	Fe	**Mn**	**Zn**	**Cu**	**Ni**	**Cr**	**Pb**	**Cd**
Average values	0,800	0,155	0,110	0,162	0,055	0,025	0,01	0,002

By comparing the values of the heavy metal concentrations obtained experimentally with the maximum values imposed by legislation, we can notice that no maximum limits are exceeded. Therefore, the surface water falls in the category of type I of waters used for irrigation [11].

The use of this type of water for irrigation purposes, even for a longer period of time, does not have significant effect where the addition of heavy metals to the soil is concerned.

The experimental results obtained in the characterization of the main factors which encourage the accumulation of heavy metals in plants: the physical and chemical characteristics of the soil, the climatic conditions and the quality of water (pH and heavy metal content), show the fact that this area does not present major risks of contaminating the vegetal products with toxic or potentially toxic metals. Although some heavy metals were identified in higher total concentrations, but still characteristic for the area, the soil and climatic conditions do not allow of their entering neither the soil solution, nor their translocation into the plant.

Heavy metal concentrations in vegetables. The facts presented so far show that the area around Cenad village does not bring any foreseeable risk of contamination with toxic or potentially toxic heavy metals for the vegetables grown on its soil. The experimental data obtained from the analysis of heavy metals in the vegetables grown on the soils in the area around Cenad are presented in table 6.

From the data presented in table 6 we can see that the heavy metal distribution in the vegetables grown in this area is not uniform, the concentration levels depending not only on the nature of the heavy metal, but also on the type of vegetable product analyzed.

Iron, an essential bio-element for the living organisms, is the best represented metal of all the heavy metals analyzed. The iron concentration limits are between 2,1 ppm in cucumbers and 114 ppm in celery leaves. On groups of vegetables, some representatives from the group of the leafy and the leguminous vegetables are the richest in iron. The lowest iron content has been found in some vegetables from the group of the fruity vegetables (cucumbers, tomatoes and egg plants), bulbous vegetables (onion), cabbages and tuberculates (potatoes).

Table 6. Heavy metal content (average values) in some vegetable cultivated within village Cenad area

Vegetables	**Metal content (mg/kg fresh edible product)**								
	Fe	**Mn**	**Zn**	**Cu**	**Co**	**Ni**	**Cr**	**Pb**	**Cd**
Pepper	4,90	0,43	6,40	0,11	0,11	0,22	0,09	0,33	0,02
Cucumbers	2,10	0,27	2,11	0,22	0.17	0,10	0,05	0,25	0,02
Tomatoes	2,20	0,35	2,91	0,12	011	0,25	0,04	0,40	0,02
Eggplants	3,21	0,85	4,04	0,81	0,21	0,11	0,08	0,15	0,02
Green beans	35,5	10,39	4,33	0,85	0,57	0,02	0,10	0,23	0,09
Cauliflower	3,80	1,30	1,70	0,51	0,22	0,02	0,10	0,08	0,02
Cabbage	4,10	1,11	1,20	0,57	0,18	0,51	0,02	0,36	0,02
Dill – leaves	18,3	4,11	8,40	1,12	0,61	0,50	0,15	0,46	0.06
Parsley - leaves	47,6	6,90	21,0	1,40	1,50	0,62	0,10	0,40	0,08
Celery – leaves	114,0	9,90	6,50	1,40	0,59	0,65	0,11	0,38	0,11
Carrots – root	5,57	1,30	2,10	0,19	0,21	0,11	0,21	0,01	0,03
Parsley – root	8,20	2,55	5,90	1,10	0,47	0,69	0,43	0,01	0,04
Celery – root	4,60	1,50	3,10	0,47	0,19	0,25	0,13	0,01	0,04
Onion	3,70	1,11	4,60	0,75	0,15	0,11	0,06	0,18	0,03
Garlic	12,20	1,70	11,0	1,50	0,21	0,25	0,31	0,21	0,04
Potatoes	5,60	1,70	2,10	0,71	0,26	0,28	0,07	0,11	0,05

Manganese was found in sensibly lower concentrations than iron, the manganese content having values between 0,27 ppm (tomatoes) and 10,4 ppm (string beans). The highest manganese values were found in string beans and in the leaves of celery, parsley and dill. The fruity vegetables are among the poorest in manganese content; the values there do not exceed 1 ppm Mn.

Although *zinc* is an essential microelement for the organisms, it can become toxic when it exceeds certain concentration levels. Its concentration is limited to maximum values of 10 ppm in potatoes and 15 ppm in the rest of the vegetables, with the exception of the leafy vegetables [12].

Experimentally, zinc has been determined in concentrations between 1,2 ppm (in cabbage) and 21 ppm (in parsley leaves), under the limit accepted by legislation. On groups of vegetable products, zinc is best represented in the vegetables with leaves and the tuberculates. As they concentrate the greatest quantities of zinc, these vegetables run the risk of getting contaminated with zinc.

Copper, as well as zinc, is an essential micro-element for the organism, but it becomes toxic if it exceeds certain concentration limits. The maximum concentration limits admitted for copper are 3 ppm – for potatoes and 5 ppm – for the rest of the vegetables, with the exception of the vegetables with leaves, where the concentration of copper is not limited by legislation [12]. If compared to manganese and zinc, copper was identifies in the experiment as having lower concentrations, between 0,75 and 1,5 ppm, thus much under the maximum limit permitted by law. On groups of vegetable products, copper is best represented in the group of the bulbous vegetables and the leafy ones. As they concentrate greater quantities of copper, these vegetables can be contaminated by this heavy metal. The smallest quantities of copper were identified in pepper, tomatoes, carrot root and cucumbers.

Cobalt was found in somewhat lower concentrations than copper, between 0,11 - 1,5 ppm. Comparing the cobalt distribution on groups of vegetables analyzed, we can notice the fact that, in this case also, the richest vegetables in cobalt are the leafy ones. At the other extreme are the fruity vegetables, the bulbous ones, the tuberculates and some root crops (carrot and celery), which present the smallest contents of cobalt.

Nickel was determined in low concentrations; the values of the nickel content in the analyzed vegetables did not exceed 1 ppm. The variation limits of the nickel concentration are situated between 0,02 - 0,91 ppm. It is best represented in the leafy vegetables, but also in some root crops (parsley) and cabbage.

Chrome was identifies in much lower concentrations than the heavy metals presented so far; the chrome content in the analysed vegetables being under 0,5 ppm. The concentration limits are between 0,02 -0,43 ppm. The smallest chrome contents, under 0,1 ppm were identified in the fruity vegetables, onion and cabbage. Some vegetables from the root crops(carrot and parsley) are richer in chrome, as well as some bulbous vegetables (garlic).

Lead is a highly toxic heavy metal, the maximum limits allowed by legislation being of 0,3 ppm – for potatoes and 0,5 ppm – for the rest of the vegetables, whether fresh or frozen [12]. In the analyzed products, lead, as well as chrome, was identified in very low concentrations, between 0,07-0,46 ppm, under the maximum limit allowed. On groups of products, the leafy vegetables and the root crops concentrate the greatest quantities of Pb, sometimes close to the maximum concentration allowed. Therefore, such products can be easily contaminated with Pb. At the other extreme, we find the fruity vegetables and the tuberculates, but also cauliflower, which presented very small quantities of lead.

Cadmium is the most toxic heavy metal of all we analyzed. That is why the maximum concentrations allowed by legislation are very small. Thus, the maximum limit for cadmium concentration is 0,1 ppm in potatoes and fresh or frozen vegetables, with the exception of the leafy vegetables, for which the maximum allowed is of 0,2 ppm [12]. In all types of vegetables analyzed, cadmium was identified in very small quantities (close to the limit of detection of the spectrometer), between 0,02 – 0,11 ppm, under the maximum allowed by legislation. Even if it was identified in extremely low concentrations in most vegetables, we notice higher cadmium contents in the leafy vegetables and in string beans. Therefore, these vegetables concentrate bigger quantities of cadmium, which, if exceeding some limits, can lead to cadmium contamination.

4. CONCLUSION

- The climate factors specific for the area around the village of Cenad create conditions for normally supplying plants with heavy metals.
- The physical and chemical parameters of the soil in the area around Cenad, in the specific climate conditions, do not encourage excessive heavy metal accumulations in the plants grown on such a soil.
- Although they contain some heavy metals (Cu, Ni, Cr, Pb and Cd), they were determined in higher concentrations than the normal limit values, but still under the warning threshold; the physical and chemical properties of the soil (especially pH and texture) do not allow of changing to mobile forms, nor their concentration in plants.
- The results obtained when analyzing the surface water in this area indicate that they fall in the category of type I waters used for irrigation and they do not present any obvious risk of contamination with heavy metals.
- The experimental data obtained while analyzing the heavy metal content of various vegetables grown in the area show an uneven distribution. Still, the distribution stands between the normal limits for the given area and for the given type of food products.
- Of all the metals analyzed, the best represented are iron, zinc, manganese and copper. The lowest contents were those of cadmium and chrome. Cobalt, nickel and lead were found in similar values.
- It is quite difficult to attempt setting a hierarchy of heavy metal abundance in the various groups of vegetables. Still, with small exceptions, the leafy vegetables, the vegetables with pods (string beans), some root crops (especially parsley) and bulbous (garlic), seem to be the richest in this type of metals.
- When comparing the experimental values with the maximum values allowed by legislation for some toxic or potentially toxic metals (Cd, Pb, Cu and Zn), we find that these are below the limits of toxicity. However, we have to note that some values of lead concentration in some leafy vegetables are higher, closer to the maximum value allowed by law.
- Of everything that has been presented so far we can draw the conclusion that there are favourable conditions in the area around Cenad village for obtaining vegetables rich in metallic nutrients. At the

same time, the vegetables grown there present low contents of metallic contaminants.

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