#### THE PRESENCE OF SOME METALS IN VEGETABLES GROWN ON LAND LOCATED NEAR THE TAILINGS DUMPS

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#### Abstract

In Maramures county a area of the 250 milion of square meters was estimated as historical polluted.

The repossession as owners of land led to the situation in which agriculture is practiced today in the various locations. One of these locations is located near the ponds and waste dumps located in the west part of Baia Mare city. Although these ponds and waste dumps are in conservation, the specific mining activities (which have meanwhile become history) and their performances, is felt even today.

The maize crop is commonly practiced in the areas near these deposits. From the desire to use the land efficiently, between corn are grown various vegetables as: cabbage, zucchini, beans or kohlrabi. These vegetables are intended for human or animal consumption, in own their households.

This study highlights the presence of metals in soil (in total and mobile forms) and in vegetables (the cabbage and the zucchini) taken from the culture of corn. Samples of soil and vegetables were taken in late September 2010 and their analysis was conducted in the period between September and October 2010.

Keywords: dumps, tailings ore, metals, vegetables, maize

#### INTRODUCTION

In the west of Baia Mare city, in the village Sasar and Bozanta Mare, the crops are developed every year, near the triad of mining the tailings ponds. These landfills were born as a result of the practices related to mining for thousands of years in this area of the country.

The maize crops are an usual on this fields; the maize is used as the main food in animal husbandry. In the maize crops are practiced, usual and various vegetable crops: beans, cabbage, zucchini, kohlrabi, etc.

One of the major concerns for human and/or animal health is represented by monitoring the quality of food consumed, knowing the fact that, the different vegetable have different capacity to absorb contaminants from soils that are grown.

For this study were sampled zucchini and cabbage from the corn crops and were determined metals: cadmium, copper and lead.

# PLACE OF RESEARCH

The samples of soils and vegetables were taken from the maize crops, grown upstream and downstream of triad of tailings dams, from the west part of the Baia Mare city: Aurul, Sasar and Remin.

Soil and vegetables samples were taken in September 2010 and their analysis was carried out in period September - October 2010. Geographical coordinates of the sampling points are shown in Table 1.

Place of sampling	Sample code Soil Vegetable	Geographical coordinates
Upstream ponds- Sasar village	S1- soil D 1- zucchini V 1- cabbage	N 47°38'40", E 23°28'47"
Downstream ponds – Bozanta Mare village	S2- soil D 2- zucchini V 2- cabbage	N 47°38'23", E 23°26'52"

## **Table 1** - Geographical coordinates of the sampling points

## MATERIALS AND METHODS

The soil samples were collected in accordance with STAS 7184/1:1984 - "Soils. Sampling for pedologycal and agrochemical investigations", from depth of 0-20 cm, in polyethylene bags, properly labeled and transported in the laboratory.

For determination of metals (cadmium, copper and lead) soil samples were processed according to standard SR ISO 11466:1999 - "Soil quality. Extraction of trace elements soluble in aqua regia", and total form of the metals was determined according to standard SR ISO 11047:1999 - Soil quality. Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil. Flame and electrothermal atomic absorption spectrometric methods.

Interpretation of results was carried out in accordance with the Order 756/1997 - approving the Regulation on the assessment of environmental pollution, table no.1 of the Annex: Reference values for traces of chemical elements in soil, for soils with sensitive use [6].

The soil reaction (pH) was determined in aqueous solution, in report soil/water = 1/2.5, in accordance with standard SR 7184/13:2001: Soils. Determination of pH in water, saline suspensions (mass/volume) and in saturated paste.

To determine the availability of transfer in trophic chains, the concentration of the mobile metals was determined with simultaneous extraction method, with a combined solution of 0.01 M EDTA -  $CH_3COONH_4$  1N at pH = 7.00, according with the Methodology of the elaboration the pedological studies [4].

In both cases, interpretation of data from these analysis was conducted in accordance with the methodology developed by Research Institute for Soil Science and Agrochemistry (ICPA), Bucharest [4].

The collected vegetables - zucchini and cabbage, were washed in doubly distilled water, dried at 105 °C, shredded and homogenized. The powder obtained was subjected to digestion, in accordance with the protocol Millestone DG-AG-02, to quantify the content of the metals, the total form. These values were compared with those stipulated in the European Regulation no. 1881/2006 - laying down maximum levels for certain contaminants in foodstuffs [5].

## **RESULTS. DISCUSSION**

**The soil characteristics**: pH, regim of nitrogen, humus content and metal (cadmium, copper and lead).

a. The soil reaction (pH)

Interpretation of results was carried out in accordance with the limits classification laid down in appreciation of soil reaction, in accordance with the Methodology ICPA, Bucharest [4]. As can be seen in table 2, soil samples are written in the category highly and moderately acidic [3,4].

**Table 2** - Assessment of the soil reaction after pH values

Sample	рН <sub>н20</sub> ,	The interpretation of
code	(units pH)	results
S1	4.94	Highly acidic
S2	5.10	Moderately acidic

So, the crops in the immediate vicinity of tailings dams are practiced on mainly acidic soils in which, the heavy metals are mobilized easily.

b.The regim of nitrogen

To determine the supply level with nitrogen we have determined total nitrogen content by Kjeldahl method and the mineral forms of nitrogen (nitrate and ammonia nitrogen) using spectrophotometric methods and the specific staining reagents.

The values obtained for all forms of nitrogen mineral indicate a medium fertility of the both groups, total nitrogen fits in the category with lower content after regulations of ICPA Bucharest [4] and all samples of the soil are clean in terms of nitrogen content (Table 3).

Sample code	Total nitrogen (N <sub>total</sub> ),	(Ntotal), (N-NO <sub>3</sub> ),	
	%	mg N/100 g soil	mg N/100 g soil
S1	0.118	0.831	1.024
S2	0.105	1.034	0.906

Tabel 3 – The nitrogen content of soil samples

#### c. Humus content

The soil fertility depends on the humus content; the humus provide the nutrients for the plants [3]. The analysis of humus content, indicate the poor provision [4] (Table 4).

Sample	Humus content,	Providing the soil with humus
code	%	
S1	1.216	poor
S2	1.696	poor

Tabel 4 – The providing the soils after humus content

d. The metals content

In table 3 are shown the concentrations determined for total form of the metals and values imposed by the Order 756/1997 in Annex 1, for soils with sensitive use [6].

**Table 5** - Values determined and imposed by Romanian legislation

Metal	Concentration, mg kg <sup>-1</sup>			
Sample code	The value	The	The alert	The intervention
	determined	normal	threshold	threshold value
		value	value	
Cadmium				
S1	3.08	1	3	5
S2	1.83			
Copper				
S1	124	20	100	200
S2	61.4			
Lead				
S1	298	20	50	100
S2	56.8			

For both soil samples is distinguished the overtaking from the normal values for all analyzed indicators.

Biggest overtaking is represented by the lead from soil sample taken from upstream of the ponds; the concentration exceeds the intervention value of almost 3 times.

For all samples, cadmium exceed the normal value imposed, but is fits in the threshold value for downstream ponds sample; the upstream sample from ponds exceed with 2.6% the concentration of the threshold value.

The mobile form of metals, was approached like their availability to transfer in trophic chains; so, this form of the metals, was determined by extraction method with a combined solution of EDTA  $0.01M - CH_3COONH_4 1N$ , at pH = 7.00 [4].

Cadmium is strongly retained in moist soil and is easily mobile in the range of pH = 3-5 pH units [1]. In uncontaminated solis, the cadmium concentrations is between 0.06 -1.1 mg kg<sup>-1</sup>, with an average of 0.5 mg kg<sup>-1</sup>

while, in contaminated soils have been reported values in the range 0.22 - 0.51 mg  $kg^{-1}$ [1].

Determined values for the mobile cadmium (0.793 mg kg<sup>-1</sup> for upstream and 0.202 mg kg<sup>-1</sup> for soil downstream) entitle us to say that, the soil is contaminated with cadmium.

The values determined of the mobile copper, assimilable for the plants (18.3 mg kg<sup>-1</sup> in S2 and 36.2 mg kg<sup>-1</sup> in S1), are well above the value considered "high content" (1.5 mg kg<sup>-1</sup>) [1,4].

Because is not a micronutrient for plants, mobile lead is not normalized, but there are average values reported in various studies. Thus, Tiller (in "Urban soil contamination in Australia", Australian Journal Soil Research 30, 1992), cited by Kabata [1] reports an average of 97 mg kg<sup>-1</sup> of a series of 69 samples, with values ranging from 5 - 1450 mg kg<sup>-1</sup>[1]. For S1 soil sample was obtained a value of 71.4 mg kg<sup>-1</sup> and for S2 sample a value of 18.7 mg kg<sup>-1</sup>.

## 2. The vegetables characteristics

Because we found significant overruns of metals in soil samples collected, in vegetables samples we just watched their content. For collected vegetables, the concentrations of the metals considered and the limits imposed of European Regulation no. 1881/2006 [5] are shown in table 4.

<b>Table 6</b> - Determineted values and impose values for metals present in			
vegetables			

Sample code	Concentration, mg kg <sup>-1</sup> wet weight		
	Determined	Impose by Regulation CE no. 1881/2006	
Cadmium			
D 1- zucchini	0.069	0.05	
D 2 - zucchini	<0.03*		
V 1- cabbage	0.116	0.20	
V 2- cabbage	0.044		
Lead			
D 1- zucchini	1.02	0.20	
D 2- zucchini	0.548		
V 1- cabbage	2.02	0.30	
V 2 - cabbage	1.29		

Note: 0.03 represents the laboratory detection limit value for cadmium

It can see that the limits for the lead presents the most serious overruns. For the zucchini grown on the land located downstream of ponds, this limits are overcome almost 2.5 times, while for ones cultivated in field located upstream of the ponds is overcome of 5 times. Identical, cabbage presents overtaking of lead content, of the 4 and 7 times the maximum allowed.

# CONCLUSIONS

The study highlights once again the polluted character, low humus content and low nitrogen supply in the lands in the immediate vicinity of the triad of ponds situated in west part of Baia Mare city.

Would be properly to impose the urgent measures of awareness of the residents on the direct effects about consumption human and/or animals of these vegetables, grown on these soils.

Would be properly to take the urgent measures to correct the pH of soil, by making at least,of amendments; so, it can reduce the mobilization of pollutants.

Some agrochemical studies are necessary to streamline the agricultural potential of these rural areas so, they to be able to give indications about the cultivation of certain plants, that can live in communion with this hostile environment.

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