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Researches regarding the soil contamination with heavy metals in the Banat mountains

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Abstract

In this paper we studied the distribution of some heavy metals (iron, nickel, cadmium, manganese, lead, zinc, cooper) in soil samples derived from mountain area of Banat region, Ruschita village. The soils from research area is characterized as a hilly relief and belong to the following types of soil: cambisols, rendzinas, luthisols.

The experimental results indicate that the analysed soil in research area in frame in soil natural rich in heavy metals, especially with zinc, manganese, cadmium and lead. The heavy metals distribution in researched soil horizon is variable, those concentration is situate in a very large interval, being between 4,5 ppm (for Cadmium) and 26150 ppm (for iron). In much lower concentration, than iron, have been determinate manganese (1710 ppm) and zinc (1150 ppm). The rest of the metals have been determinate in lower concentration (Chromium 74 ppm, Nickel - 43,5 ppm, Lead - 42,5 ppm, Cooper - 40,5 ppm) or (Cadmium - 4,5 ppm), normal limits for this area.

Keywords: heavy metals, iron, nickel, cadmium, manganese, lead, zinc.

1. Introduction

From an agro-chemical point of view, heavy metals are those electropositive chemical elements that have, in their elementary state, a density higher than 5 g/cm^3. In biochemistry and biology, they are considered heavy metals, chemical elements of the periodic table of chemical elements with metal features and high atomic mass (Alexa, 2008). From a physiological point of view, metals, among which some are heavy metals, ensure growth, development and balance of the living matter. There is almost no biological phenomenon without direct or indirect involvement of these chemical elements. Their presence in insufficient amounts or in amounts above certain limits, considered normal, can result in metabolic unbalance with extremely serious consequences (EPA, 2000). Thus, together with metal chemical elements that are essential to the human body such as iron, copper, zinc, cobalt, manganese, molybdenum, chromium, etc., agricultural produce also contain such mineral chemical elements as mercury, lead, cadmium, etc., which are toxic even in very small amounts (Lacatus, 1996).

Depending on their toxic character, heavy metals present in the human body can be classified as micro-elements with no toxic impact (Fe, Mn, Co, Cr, and Ni), potentially toxic micro-elements (Cu, Zn, and Sn), and toxic micro-elements (Hg, Cd, and Pb). This classification is not a very strict one, since it is well-known that, in general, almost all chemical elements in amounts above certain limits are toxic to the human body (Florea, 2000).

The main source of contamination of the environment and of vegetables with heavy metals is genetic inheritance from the rocks

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and parental materials on which soils formed and developed, i.e. a geogenous origin. Some areas are naturally rich in heavy metals as a result of some specific geological processes (Gergen, 2000).

Depending on the physical and chemical properties of the soil (particularly pH and redox potential), heavy metals are mobilised in the soil solution and are adsorbed by the plants. Some heavy metals reach the soil directly, under the form of fertilisers used as a supplement for plant nutrition or indirectly, as a result of amendaments or other chemical substance applications (herbicides, insecticides, etc.) that contain heavy metals. In the terrestrial food chain, plants take over the most important amount of heavy metals directly from the soil or indirectly, from irrigation works or from foliar treatments. Humans also take over heavy metals from the plants that they eat fresh or processed. Heavy metals from plant debris and from human and animal wastes (including cadavers) are then recycled into the soil. This process is mainly a geo-bio-chemical cycle of heavy metals on the earth ecosystem (Gogoasa, 2004).

2. Materials and Method

The area we studied from the point of view of heavy metal charge of the soil is located in a mountain area characterized by a cool and moist landscape. The area around Ruşchiţa is characterized by an uneven land and by different types of cambosoils, lithosoils, regosoils, and rendzines. They are characterized by the massive presence of the skeleton (parental rock), variable pH (from acid to alkaline), variable contents of humus, general poor or very poor supply of phosphorus and poor supply of potassium.

Soil sampling was done according to the recommendations of the Ministry of Agriculture, Food, and Forests Order nr. 223, updated and published in Romania’s Official Monitor nr. 598/13 August 2002. Agro- chemical samples were harvested with the help of agro-chemical probes at 0 - 20 cm and 20 - 40 cm horizontes. Each medium soil sample was made up of 15-20 individual samples evenly distributed over the studied plots.

Soil sample preparation for analysis consisted in drying the soil, removing foreign bodies, grounding, and sieving.

Based on the soil samples thus prepared, we measured total heavy metal forms through atomic absorbtion spectrophotommetry. The dry sample was extracted with clorhydric acid/nitric acid by maintaining the sample for 16 hours at room temperature followed by backflow boiling for 2 hours. The extract was then cleared and quoted with nitric acid. Heavy metal content of the extract was determined by flame atomic spectrometry. The method is based on metal chemical element absorbance measurement in regal water extract at a specific wave length (SR ISO:11047) using Varian atomic absorption mono-beam spectrometer of the AA-110 type, with four lamps (HCL), PC controlled. Functional characteristics of the optical component are: Wave length: 185-900 nm; Czerni Turner Monocromator 0.25 m; Automated selection cleavage set for 0.2 nm, 0.5 nm, and 1 nm; Holographic diffraction network with 1,200 lines/mm. The performance characteristic of the apparatus is as follows: for an absorbance higher than 0.75, the lowest precision is 0.5% RDS for a copper solution containing 5 mg/l copper.

Analysis methods were validated for the following chemical elements: iron, nickel, cadmium, manganese, lead, zinc, cooper, for which we established linearity domain, standard abatement, precision, and calibration curve regression coefficient over the range of concentrations se used.

Metal content was determined with the help of the following formula:

$$\mathbf{C\ (mg/kg\ or\ ppm) = a \times f / m}$$

where:
f – dilution factor;
a–chemical element content reading in mg/l;
m – soil volume under study.

Mobile forms of heavy metals were determined using as common extractor a solution of EDTA-ammonia acetate with a pH = 7.0. The method is base on the absorption spectrometry measurement of a chemical element in a neuter solution of EDTA-ammonia acetate, at wave lengths characteristic to each metal chemical element la (Lacatusu, 1996).

3. Results and Discussion

Total form heavy metal concentrations in the soil in the studied area are shown in Table 1. Experimental results show a varied distribution of heavy metals in the studied soil horizon, their concentration ranging over a very wide range between 4.5 ppm (for Cd) and 26,150 ppm (for Fe). Iron is the best represented of the heavy metals and is, therefore, considered a macro-element of the soil. Concentrations below that of the iron were in manganese (1,710 ppm) and zinc (1,150 ppm). The rest of the heavy metals had concentrations in the range of tens of ppm (Cr – 74 ppm, Ni – 43.5 ppm, Pb – 42.5 ppm, Cu – 40.5 ppm, and Co – 12.2 ppm) or of ppm units (Cd – 4.5 ppm), but within normal limits for the area. Comparing experimental values with reference values recommended in literature (Figures 1 and 2), we can see that, except for the zinc, heavy metal concentration is below intervention limit. Since mobile forms of heavy metals in the soil are, in general, responsible for the amount of metal that can accumulate in the plants we also determined mobile forms of heavy metals in an EDTA – ammonia acetate extract (Lăcătuşu, 1987). The optained values are presented in Table 2.

In this case also there is an uneven distribution of heavy metals over the soil horizon between 0 and 40 cm, but the values of heavy metal concentrations are much diminished.

This can be explained by the fact that we extracted, in the EDTA-ammonia acetate solution pH = 7.00 only heavy metal amounts that are available for plants, i.e. mobile forms existing in the soil solution. The best represented of the metals are manganese, iron, and zinc, with concentrations between 10.47 ppm (Zn) and 51.1 ppm (Fe). The other chemical elements had low values (Cu and Pb) or very low values (Co, Ni, Cr, and Cd) between 0.31 and 0.94 ppm.

Comparing experimental values with limit values recommended in literature for some toxic metals (Figure 3), we can notice that they are all below the toxicity limit.

Though some heavy metals (Co, Cr, Pb, Zn, and Cd) were determined in rather high concentrations as total forms in the soil, the physical and chemical features of the soil, particularly pH and texture, as well as the relatively high humus content do not allow the passage of these chemical elements in their mobile form and, therefore, their concentration in plants (fruits and vegetables) cultivated in the studied area.

Table 1. Heavy metals content -total forms- in the soil horizon 0-40 cm in village Ruschița area

Experimental values	**Metal content (ppm)**								
	Fe	**Mn**	**Zn**	**Cu**	**Co**	**Ni**	**Cr**	**Pb**	**Cd**
Minimum values	22500	900	500	38,5	10,0	35,0	45,5	20,0	2,50
Maximum values	31000	1750	1500	53,0	19,0	50,0	81,0	55,0	6,50
Average values	26150	1710	1150	40,5	12,2	43,5	74,0	42,5	4,5

Table 2. Heavy metals content, in mobile forms, of the soil horizon: 0-40 cm within Ruschița area

Experimental values	Metal content (ppm)								
	Fe	Mn	Zn	Cu	Co	Ni	Cr	Pb	Cd
Minimum values	15,5	30,5	4,38	1,40	0,10	0,50	0,15	1,75	0,50
Maximum values	45,0	60,0	12,1	5,10	0,55	1,15	0,60	5,00	2,05
Average values	21,5	51,1	1o,4	2,96	0,31	0,82	0,35	2,50	0,94

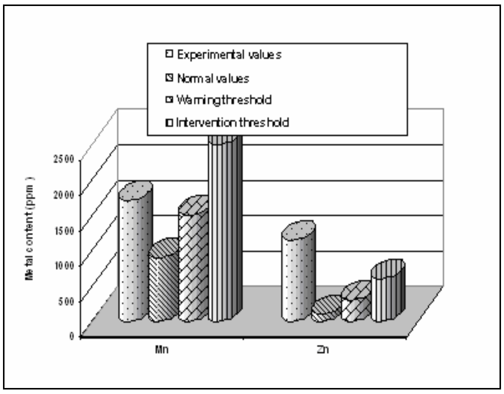

Figure 1. Mn and Zn content –total forms- in the soil horizon 0-40 cm, in Ruschița area, comparative with some reference

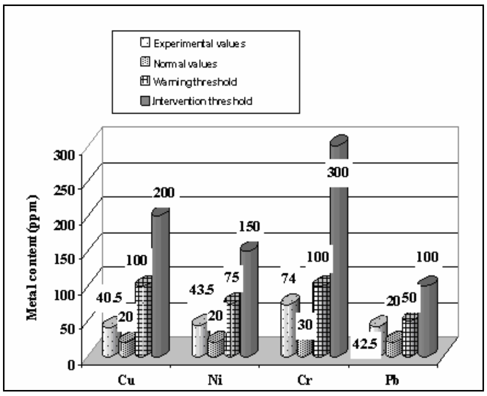

Figure 2. Cu, Ni, Cr and Pb content –total forms- in the soil horizon 0-40 cm in Ruschița area, comparative with some reference

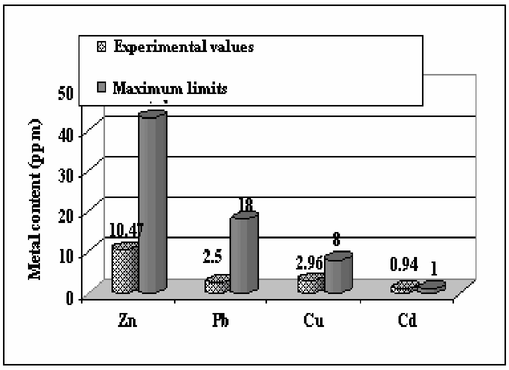

Figure 3. Zn, Cu, Pb and Cd content –total forms- in the soil horizon 0-40 cm in Ruschița area comparative with some references

4. Conclusion

1. Comparing experimental values with reference values recommended in literature, we can see that, except for the zinc, heavy metals (iron, nickel, cadmium, manganese, lead, and cooper) concentration in soil samples from the Banat Mountain area are below intervention limits.
2. Zinc content in some of the samples we analysed is close to the intervention limit. The cause of zinc accumulation in the soil of the studied area is the genetic inheritance from the rocks and parental materials on which formed and developed the soils, hence their geogenous origin.
3. Physical and chemical proprieties of this type of soil (high heavy metal retention capacity, poor alkaline reaction, relatively high loam content, etc.) substantially diminish the transition of heavy metals to mobile forms, accessible to plants.
4. Mobile form heavy metal content accessible to the plants in the analysed soils is low and below toxicity levels in all the heavy metals we studied.

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