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A study on cadmium concentration in the Haţeg Country soils

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Abstract. The present study focused on determining the soil cadmium concentration from two hunting areas, 57 Gânţaga (G) and 45 Valea Fierului (F) which belong to the Haţeg Country. The samples were taken at a depth of 20 cm and 40 cm, respectively, over two consecutive years. Analysis of soil samples was performed by atomic spectrometry with electrothermal atomization. Authors found statistically significant diferences ($p < 0.01$) regarding the 20 cm of depth between 57 Gânţaga (G) and 45 Valea Fierului (F) hunting areas and no statistically significant difference ($p > 0.05$) for the 40 cm of depth. In the second year of study, an increased concentration of cadmium was found at both depth-levels, of 37.93% to 746%, more evident in the 57 Gânţaga (G) area.
Key Words: soil, heavy metal ions, cadmium, the Haţeg Country.

Introduction. From chemical point of view, it can be said, without too much wrong, that the soil contains all known chemicals. The amount in which these substances are widespread in soil can be highly variable from one soil to another. Soil is the part of Earth's crust where all biological processes occur. Soil is a dynamic, open system with its own organization, whose functionality depends on the flux of energy it receives from the cosmos, energy which is processed by vegetation cover and stored in the organic matter and, partly in the altered mineral material, being a result of the interaction between the lithosphere and biosphere, highly dependent on climatic conditions and to a large extent influenced by its use in the agricultural economy (Grainer 1958; Oroian et al 2011; Paulette et al 2007, 2009; Rusu et al 2006, 2009, 2013).

Soil is interdependent with the atmosphere, hydrosphere and biosphere and, as a result, most of these chemicals pass from the soil into the air and, especially in water and plants (Kuhl 1976; Mănescu et al 1982; Alfani et al 1996; Sarong et al 2015).

Among the high-risk pollutants, there are the heavy metals and, among them lead and cadmium are considered having particularly severe effects (Rădulescu 2001; Podar 2010). Once it arrives in the environment, cadmium is accumulated mostly in microorganisms and plants but also in animals, especially in tissues which are subject to human consumption (Popek et al 2009; Podar 2010; Rahman et al 2010; Ernawati 2014). Unfortunately, the path of cadmium in the organism is very slow in the case of mammals, making the tissue to increase over time. It is plausible that the persistence of cadmium in the body, is due to fixed binding cadmium protein such as metallothionein.

The organism does not have homeostatic mechanisms to regulate tissue concentrations of cadmium to different inputs, so the overall level of cadmium in the body is directly dependent of the intake (Badora et al 1997; Kayser et al 1999).

Cadmium is a strong enzyme inhibitor, in particular of sulfhydryl enzymes.

Binding cadmium to metallothionein, partially prevents free cadmium ions to produce toxic effects. As a result of the degradation of metallothionein, cadmium ion appears once again within the cell. It initiates the emergence of a new metallothionein, which connects then with cadmium, thus protecting the cell against its toxic effect. When metallothionin binding capacity is saturated, the toxicity of cadmium begins to manifest (Blazka & Shaikh 1991).

Acute cadmium poisoning in humans with doses from 1500 up to 8900 mg (20-30 mg·kg^{-1} body weight) had as consequence the death, but generally lethal cadmium poisoning are rare.

The present research focuses on the concentration of cadmium in soil samples taken from the depth of 20 cm and 40 cm, respectively, bringing valuable information in the field. Not least, data obtained will help a better knowledge of the environment *status quo* of the Haţeg Country. Therefore, the present results may become a useful tool for restoring and protecting the environment, restoring the degraded ecosystems, particularly due to cumulative impacts of anthropogenic stress.

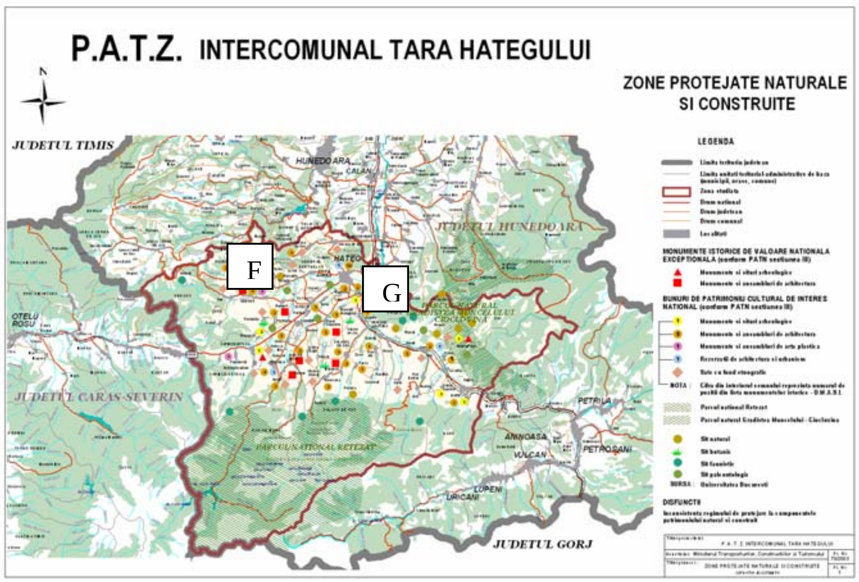

Figure 1. Localization on the sampling areas: 57 Gânţaga (G) and 45 Valea Fierului (F) on Romania map.

Material and Method. The research protocol included: soil sampling, locating the prelevation points, transportation of samples, preparation of samples for determination, namely, the determination of cadmium concentration.

The soil sampling was carried out over two years (2012 and 2013) in two distinct areas with different levels of pollution that correspond to the two separate hunting areas, 57 Gânţaga (G) and 45 Valea Fierului (F) from Haţeg Country (see Figure 1). Three samples of soil from two depths (20 cm and 40 cm) were taken, plastic bags were used, labeled / depth / sampling point.

A GPS - GARMIN GPS 60 was used to locate the prelevation points.

Samples were transported and analyzed at the Institute of Life Sciences, "Vasile Goldiş" Western University of Arad where they were submitted to this protocol in order to determine cadmium concentrations.

Determination of heavy metals was done by atomic spectrometry with electrothermal atomization. By this method, the sample is placed in a graphite tube which can be heated quickly and in a controlled manner over 2,800^{0}C. By gradually increasing the temperature, processes of drying, matrix thermal decomposition and thermal dissociation in free atoms take place. The resulted (peak) signal is in optimal conditions, symmetrical sharp and with a narrow medium height.

For most of the elements, the height is proportional to the content of the element in solution, although for certain elements it is preferred to operate with the peak area.

The measurements are made at the wavelengths given in Table 1.

Table 1

General requirements for electro-absorption spectrometry

Element	*Wavelength (nm)*	*Recommended atomisation conditions*	*Recommended techniques for background correction*
Cadmium	228.8	Platform	Zeeman, Deuterium

The atomic absorption spectrometer should be equipped with: electrothermal atomiser; hollow cathode lamp or discharge lamp without electrodes suitable for the item of interest; automatic device for background correction; computerized recorder; automatic system for sample introduction, capable of introducing fixed amounts of up to 70 μL.

For electrometric spectrometry, the background correction should be used, for which the minimum accepted technical specification (below 350 nm wavelength) is that based on deuterium. The background correction with deuterium is suitable for cadmium, zinc and lead, if it not exceeded the capacity to apply background correction, which for some instruments is limited to an absorbance between 0.6 and 0.8.

The correction Smith-Hieftje or Zeeman is necessary for all the heavy metals, if the background signal is high.

In order to increase the ratio analytical signal / background signal, at highly acidic samples and the charged matrix, it is used a graphite tube with pyrolytic platform together with matrix modifiers such as ammonium hydrogen phosphate $(NH_4)_2HPO_4$, or reduced palladium.

Pyrolytic graphite has the additional advantage that transfer (contamination) in the sample is strongly reduced for most of the heavy metals, as compared with the non-pyrolytic graphite.

All decisions regarding the acceptance or rejection of statistical hypothesis were performed at the 0.05 level of significance, using the Mann-Whitney U test.

Results and Discussion. The levels of cadmium concentration for the two sampling sites, 57 Gânţaga (G) and 45 Valea Fierului (F), at two different depth sampling levels, in two different years, were within the normal values established by MAPPDR Order no. 756/97, as they are presented in Table 2.

Table 2

Reference values for cadmium traces in soil (ppm dry matter)

Element	*Normal values*	*Alert threshold*		*Intervention thresholds*	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Cd	1	3	5	5	10

The values of cadmium concentration in soil are listed in Table 3 and Table 4.

In 2012, at the depth of 20 cm of soil, cadmium concentration is significantly higher ($p < 0.01$) with 0.24 ppm in the Valea Fierului (F) area compared to the 57 Gânţaga (G) sampling site. For the samples taken from 40 cm depth, cadmium concentration is insignificant higher ($p > 0.05$) throughout the area 45 Valea Fierului (F) with 0.008 ppm compared to the 57 Gânţaga (G) area.

Between the two depths in the 57 Gânţaga (G) area, there is a decrease in the concentration of cadmium of 38.46 times at 40 cm depth compared to 20 cm depth and, in the 45 Valea Fierului (F) sampling area, the decrease is less, by 29 times, respectively.

Table 3

The concentration of cadmium in the soil in 2012 (ppm)

Depth (cm)	*Sampling area*						*Differences*
	57 Gânţaga (G)			45 Valea Fierului (F)			
	X	SD	Confidence level 95 %	X	SD	Confidence level 95 %	
20	0.05	0.02	0.01	0.29	0.09	0.01	0.24**
40	0.0013	0.01	0.01	0.01	0.01	0.01	0.008^{nss}

Note ** p<0.01; ^{nss} not statistically significant; X – arithmetic mean; SD – standard deviation.

In 2013, at the depth of 20 cm of soil, cadmium concentration is significantly higher (p <0.01) with 0.26 ppm in the 45 Valea Fierului (F) area compared to the 57 Gânţaga (G) sampling site. For the samples taken from the 40 cm of depth, cadmium concentration is insignificant higher (p >0.05) in the 45 Valea Fierului (F) area with 0.013 ppm compared to the 57 Gânţaga (G) area.

Between the two depths in the 57 Gânţaga (G) area, there is a decrease in the concentration of cadmium of 12.72 times at the 40 cm depth compared to 20 cm depth and, in the 45 Valea Fierului (F) sampling area the decrease is less, by 16.66 times, respectively.

Table 4

The concentration of cadmium in the soil in 2013 (ppm)

Depth (cm)	*Sampling area*						*Differences*
	57 Gânţaga (G)			45 Valea Fierului (F)			
	X	SD	Confidence level 95 %	X	SD	Confidence level 95 %	
20	0.14	0.02	0.01	0.4	0.15	0.01	0.26**
40	0.011	0.01	0.01	0.024	0.01	0.01	0.013^{nss}

Note ** p<0.01; ^{nss} not statistically significant; X – arithmetic mean; SD – standard deviation.

Between 2012 and 2013, in the 57 Gânţaga (G) sampling site, there is an increase of 180% of cadmium concentration at the depth of 20 cm and of 746% at the depth of 40 cm.

In the 45 Valea Fierului (F) area, the increase was of 37.93% at the depth of 20 cm and of 140% at the depth of 40 cm.

In the soil, cadmium can be found in concentration of 0.01 up to 7 ppm.

Natural cadmium content can be increased by administering phosphorus fertilizers and irrigations with wastewater. Cadmium has high mobility, it is poorly retained by the soil and it is easily absorbed by plants.

The content of cadmium in plants is normally between 0.1 and 0.8 ppm, higher values than 1 ppm are considered to be toxic. The toxic effects in animals and humans have been observed after repeated consumption of plants with a cadmium content of around 3 ppm. Cadmium toxicity is manifested by disrupting the enzyme activity, explained by its affinity towards thiolic groups (-SH) of enzymes or proteins. Although, it is not essential to animal organisms (basically being absent at birth), cadmium accumulates in tissues with age. Regarding the total concentration of cadmium in the body, there is significant sexual dimorphism in all species, meaning that male tissues contain more cadmium than female tissues (Davidescu et al 1988; Kühl 1976; Hernandez et al 1987).

Conclusions. The studies developed on the soil samples from the the Haţeg Country showed a significant increase ($p < 0.01$) of 0.24 ppm of the cadmium concentration at a depth of 20cm in the 45 Valea Fierului (F) sampling site compared to the 57 Gânţaga (G) sampling site, both in 2012 and 2013, when the concentration level reached 0.26 ppm.

At a depth of 40 cm, for the 45 Valea Fierului (F) area the increase was not statistically significant ($p > 0.05$) with 0.008 ppm in 2012 and with 0.013 ppm in 2013, compared to the 57 Gânţaga (G) area.

In the second year of study, a cadmium concentration increase was found for the both depths of soil sampling and for the both sampling sites.

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