AES BIOFLUX

Advances in Environmental Sciences - International Journal of the Bioflux Society

A study on lead concentration in Haţeg Country soils

Valerica-Letiţia Murgoi[1], Daniela Bratosin[1], Sorin Voia[2], Andrei Osman[2]

[1]"Vasile Goldiş" Western University of Arad, Arad, Romania;
[2]Banat’s University of Agricultural Sciences and Veterinary Medicine "Regele Mihai I al României" of Timișoara, Timișoara, Romania.
Corresponding author: V.-L. Murgoi, vali_ionescu3106@yahoo.com

Abstract. This research focused on determining the concentration of lead in the soil from two hunting areas, 57 Gânţaga (G) and 45 Valea Fierului (F), belonging to Haţeg Country (Romania). The samples were taken at a depth of 20 cm and 40 cm during two consecutive years. The analysis of soil samples was performed by atomic spectrometry with electrothermal atomization. Significant differences ($p<0.05$) were observed between the two hunting areas, at both depth of 20 cm and of 40 cm. Lead concentration in soil decreased in the second year of study at both depths, it ranged between 2.9% and 20% in the second year compared to the first and it was higher in the 57 Gânţaga area.
Key Words: soil, heavy metal ions, lead content, Haţeg Country, pollution.

Introduction. The economic and social development from the last century requires the implementation of measures to prevent the unsustainable exploitation of the soil and subsoil and to protect the air, water, flora and fauna, both at local and global level. Complex contamination of the soil is more and more frequent, negatively affecting the life cycles, and, therefore, the quality control of the environment is necessary, including the determination of the pollution levels (Roman 1994; Burtică et al 2000).

If pollutants remained within the perimeter where they were produced, the pollution problem would be much easier to solve, but, on the field, they spread in the environment, contaminating larger areas, sometimes to a planetary scale (Stugren & Killyen 1975; Tufescu & Tufescu 1981; Vespremeanu 1981; Teuşdea 2000).

The soil is the part of Earth’s crust where the biological processes take place. It is a dynamic and open system, with its own organization, whose functionality depends on the flux of energy it receives from the cosmos, energy processed by the vegetation layer and stored in organic matter and, partly, in the mineral material; the soil is the result of the interaction between the lithosphere and biosphere, is heavily dependent on climatic conditions and it is greatly influenced by its agricultural use (Grainer 1958; Paulette et al 2007, 2009; Oroian et al 2011; Rusu et al 2006, 2009, 2013). The soil has a reciprocal dependence relationship with the atmosphere, the hydrosphere and the biosphere and, as a result, most of the chemicals pass from the soil into the air, water, plants and animals (Mănescu et al 1982; Kühl 1976; Alfani et al 1996). The natural consequence of this phenomenon is the load of water, plants and animals with chemical elements, mainly minerals. The excess or lack in minerals of the soil generated a similar pattern in water and plants, and, further on, in animals and food products obtained from these (Budeanu & Călinescu 1982; Ciararnău 2000).

Heavy metals are placed among high-risk pollutants and lead and cadmium are two contaminants that cause with highly severe damages (Radulescu 2001; Rahman et al 2010). Lead is a still metal, which circulates by means of environmental factors (Davranche & Bollinger 2001). In the air, the maximum permissible limit is of 1.5 µg / m^3 / 90 days, and the animal feed is 10 mg/kg, with some exceptions depending on the feed type (Ord.120 / 16.11.2005).

Lead availability is influenced by soil pH: acid pH leads to loss of lead, while a pH> 6.5 leads to its retention in the soil.

Lead accumulates in living organisms: the lead is taken from the environment by plants and animals and stored in tissues (Ernawati 2014; Sarong et al 2015). Thus, game meat can be contaminated with lead if the animals fed on contaminated lands, such as roads sides.

The present research analyzed the lead concentration in soil samples taken from the depth of 20 cm and of 40 cm, broadening the knowledge on the current situation in Haţeg Country (Romania). The results can contribute in designing the best measures to restore and protect the environment and, especially, the ecosystems affected by the cumulative impacts of anthropogenic stress.

Materials and Method. The work protocol included: soil sampling, locating the prelevation points 57 Gânţaga (G) and 45 Valea Fierului (F) (see Figure 1), transportation and preparation of samples for determination, namely the concentration of lead.

The soil sampling was carried out over two years (2012 to 2013) in two distinct areas with different levels of pollution that correspond to two separate hunting funds, 57 Gânţaga (G) and 45 Valea Fierului (F) in Haţeg Country (see Figure 1). Three soil samples were taken at two depths (20 cm and 40 cm), stored in plastic bags until analysis and labeled with depth and sampling point. The location of the prelevationtion points 57 Gânţaga (G) and 45 Valea Fierului (F) was made using a GPS system - GARMIN GPS 60. The samples were transported and analyzed for the determination of lead concentration at the Institute of Life Sciences, "Vasile Goldiş" Western University of Arad and Banat's University of Agricultural Sciences and Veterinary Medicine "Regele Mihai I al României" of Timișoara.

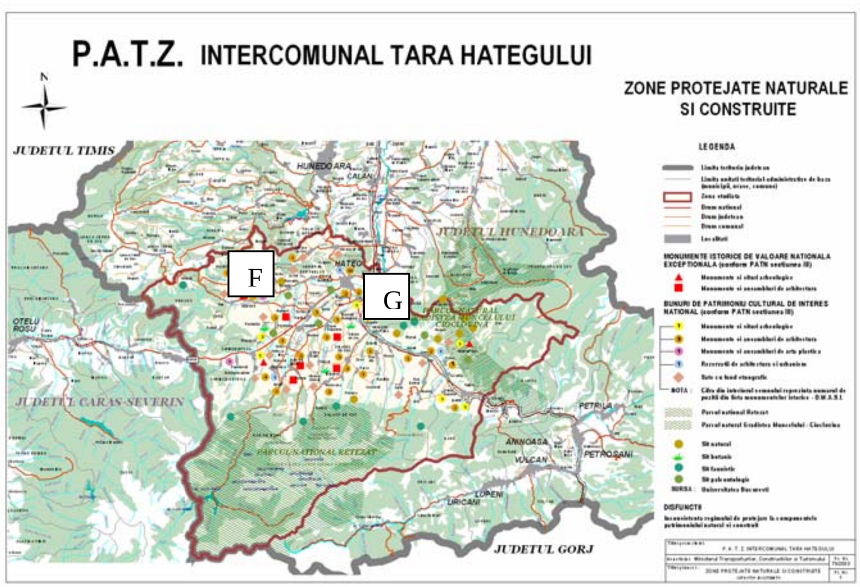

Figure 1. Localization on the sampling areas: 57 Gânţaga (G) and 45 Valea Fierului (F) on Romania map.

The determination of heavy metals was made by electrothermal atomic spectrometry. The method consists of the following steps: the sample is placed in a graphite tube which can be heated quickly and in a controlled manner up to over 2,800^{0}C. The gradual increase of temperature generates processes of drying, thermal decomposition of the matrix and thermal dissociation in free atoms. The resulting (peak) signal is, in optimal conditions, symmetrically sharp and with a narrow medium height. In most cases, the height is proportional to the content of the element in solution, although for some elements, it is best to operate with peak area. The measurements were made at the wavelengths given in Table 1.

Table 1

General conditions for electrothermal absorption spectrometry

Element	*Wavelength (nm)*	*Recommended atomization conditions*	*Recommended techniques for background correction*
Lead	217.0	Platform	Zeeman, Deuterium

The atomic absorption spectrometer should be equipped with: electrothermal atomizer, hollow cathode lamp or electrodeless discharge lamp suitable for the element under analysis, automatic device for background correction, computerized registration system, autosampler introduction system (able to enter the fixed volumes of up to 70 μL).

For electrometric spectrometry, a background correction with accepted minimum technical specification (below 350 nm wavelength) based on deuterium must be used. Background correction with deuterium is appropriate for cadmium, zinc and lead, if not exceeded the capacity to implement the background correction, which is limited to an absorbance of between 0.6 and 0.8 for some instruments.

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

A pyrolytic graphite tube with pyrolytic platform is used together with a matrix modifier, such as ammonium hydrogen phosphate $(NH_4)_2HPO_4$ or reduced palladium, to increase the ratio analytical signal / background signal in the case of highly acidic samples and overloaded matrices. Pyrolytic graphite has the additional advantage that the transfer (contamination) in the sample is strongly reduced for most 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 Mann-Whitney U test.

Results and Discussion. The levels of lead concentrations for the two zones, G and F, studied at two levels of sampling in two different years, were within the normal ranges, according to MAPPDR Order no. 756/97 and presented in Table 2.

Table 2

The reference values for lead traces in soil (ppm dried substance)

Element	*Normal values*	*Alert threshold*		*Intervention threshold*	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Pb	20	50	250	100	1000

The lead concentration values are presented in Table 3 and Table 4.

The lead concentration is significantly higher ($p < 0.01$), in the 45 Valea Fierului (F), area compared to the 57 Gânţaga (G) area, in 2012, at both depths: with 2.7 ppm for the samples taken at the depth of 20 cm in soil and with 0.17 ppm at the depth of 40 cm.

There is a 14 times decrease in the concentration of lead at the 40 cm depth compared to the 20 cm depth in 57 Gânţaga (G) area. The decrease is stronger in the 45 Valea Fierului (F) area: 15.45 times at the 40 cm depth compared to the 20 cm depth.

Table 3

Lead concentration in soil, year 2012 (ppm)

Depth	*Sampling area*						*Differences*
	57 Gânţaga (G)			45 Valea Fierului (F)			
	X	SD	Confidence level 95 %	X	SD	Confidence level 95 %	
20	0.7	0.02	0.02	3.4	0.13	0.03	2.7**
40	0.05	0.01	0.01	0.22	0.35	0.32	0.17**

Notes: **p<0.01; X - arithmetic mean; SD - standard deviation.

The lead concentration is significantly higher (p <0.01) in the 45 Valea Fierului (F) area compared to 57 Gânţaga (G) area, in 2013, at both depths: with 2.7 ppm for the samples taken at the depth of 20 cm in soil and with 0.16 ppm at the depth of 40 cm.

There is a 15 times decrease in the concentration of lead at the 40 cm depth compared to the 20 cm depth in 57 Gânţaga (G) area. The decrease is again stronger in the Valea Fierului (F) area: 16.5 times at the 40 cm depth compared to the 20 cm depth.

Table 4

Lead concentration in soil in 2013 (ppm)

Depth	*Sampling area*						*Differences*
	57 Gânţaga (G)			45 Valea Fierului (F)			
	X	SD	Confidence level 95 %	X	SD	Confidence level 95 %	
20	0.6	0.01	0.03	3.3	0.05	0.03	2.7**
40	0.04	0.01	0.03	0.20	0.06	0.03	0.16**

Notes: **p<0.01; X - arithmetic mean; SD - standard deviation.

There is a decrease in lead concentration by 14.28% at the depth of 20 cm and by 20% at the depth of 40 cm, between 2012 and 2013 in 57 Gânţaga (G) area. The concentration of lead decreased by 2.9% at the depth of 20 cm and by 9.9% at the depth of 40 cm in 45 Valea Fierului (F) area.

The toxicity of lead and lead compounds is less harmful than that of arsenic and mercury, but they all cause chronic poisoning. Daily ingestion of 0.5 mg of Pb leads to chronic intoxication (Hernandez et al 1987; Alfani et al 1996).

Lead exposure was associated with aggressive behavior, delinquency and attention disorders. In Romania, the 1992 study from Baia Mare, stressed that workers at the lead smelter had blood lead levels of 77.4 $\mu g \cdot dL^{-1}$, and children living in this area had an average of lead in the blood of 63.3 $\mu g \cdot dL^{-1}$. Basic rocks contain an average of 8 ppm and the acidic ones 20 ppm. In regions where lead does naturally occur in the ground, its concentration in the soil should be lower than 5 ppm.

Conclusions. The analysis of soil samples from Haţeg Country showed a significant increase (p <0.01) with 2.7 ppm of lead concentration at a depth of 20 in 45 Valea Fierului (F) area compared to 57 Gânţaga (G) area in both years, 2012 and 2013.

Increase in the concentration of lead was significant (p<0.01) also at the depth of 40 cm in 45 Valea Fierului (F) area compared to 57 Gânţaga (G) area: by 0.17 ppm in 2012, and by 0.16 ppm in 2013.

A decreased of lead concentration at both depths and for both zones was observed in the second year of study.

Acknowledgements. This work was supported by Structural Funds "Doctoral Scholarships complex training in ecoeconomy and bioecoeconomy for safety, food security and feed safety from anthropic ecosystems" - Project POSDRU/CPP107/1.5/S/77082.

References

Alfani A., Batroli G., Rutigliano F. A., Maisto G., Virzo De Santo A., 1996 Trace metal biomonitoring in the soil and the leaves of *Quercus ilex* in the urban area of Naples. Biol Trace Element Res 1:51.

Budeanu C., Călinescu E., 1982 Elemente de ecologie umană. Editura Ştiinţifică şi Enciclopedică, Bucureşti, pp 43.

Burtică G., Pode R., Vlaicu I., Pode V., Negrea A., Mincu D., 2000 Tehnologii de tratare a efluenţilor reziduali. Editura Politehnica, Timişoara, pp 7-11.

Ciorarnău R., 2000 Ecologie şi protecţia mediului. Editura Economică Preuniversitaria, Bucureşti, pp 14.

Davranche M., Bollinger J. C., 2001 A desorption-dissolution model for metal release from polluted soil under reductive conditions. J Environ Qual 30(5):1581-1586.

Ernawati Y., 2014 The analysis of the concentration of heavy metals cadmium, mercury and lead in the flesh of suckermouth catfish (*Pterygoplichthys pardalis*) in Ciliwung River, Indonesia. AACL Bioflux 7(1):33-42.

Grainer C., 1958 Dispersion secondaire du tungstene et de l'arsenic en sol residuel. Bul Soc Fran Min Cest, pp 81.

Hernandez L. M., Rico C., Gonzalez J., Hernan A., 1987 Environmental contamination by lead and cadmium in plants from an urban area of Madrid, Spain. Bull Environ Contam Toxicol 38:203-208.

Kühl U. G., 1976 Toxickologische und biochemische Unterschungen zur Feststellung subklinischer Cadmiumwirkungen bei Schafen, Inaug. Diss., Tierärztl. Hochschule Hannover, pp 43.

Mănescu S., Dumitrescu H., Diaconescu M. L., 1982 Chimia sanitară a mediului, vol II. Editura Medicală, Bucureşti, pp 56, 78.

Ord.120 / 16.11.2005, available at http://www.legex.ro/Ordin-120-2005-49818.aspx

Ord.756/ 03.11.1997, available at http://www.legex.ro/Ordin-756-1997-13758.aspx

Oroian I. G., Brașovean I., Petrescu-Mag I. V., 2011 Compostul și Agricultura Organică. Bioflux, 268p.

Paulette L., Morar G., Oroian I., Neag C., 2009 Protection and conservation of the soils properties influenced by the organic agriculture system. Bulletin of UASVM - Agriculture 66(1):425-432.

Paulette L., Oroian I., Rusu M., Todoran A., 2007 Main ways of soil degradation and pedoameliorative technologies of soil polluted with heavy metals. Lucrări Ştiinţifice - Universitatea de Ştiinţe Agronomice București. Seria A, Agronomie 50:330-336.

Rahman M. M., Rahman M. M., Chongling Y., Islam K. S., 2010 Changes in growth and antioxidant enzymes activities during cadmium stress in the mangrove plant *Kandelia candel* (L.) Druce. AES Bioflux 2(1):15-24.

Rădulescu H., 2001 Poluare şi tehnici de depoluare a mediului. Editura Eurobit, Timişoara, pp 124.

Roman L., 1994 Teste analitice rapide. Editura Tehnică, Bucureşti, pp 43.

Rusu T., Guș P., Bogdan I., Oroian I., Paulette L., 2006 Influence of minimum tillage systems on physical and chemical properties of soil. Journal of Food, Agriculture & Environment 4(3-4):262-265.

Rusu T., Guș P., Bogdan I., Moraru P. I., Pop A. I., Clapa D., Marin D. I., Oroian I., Pop L. I., 2009 Implications of minimum tillage systems on sustainability of agricultural production and soil conservation. Journal of Food, Agriculture & Environment 7(2): 335-338.

Rusu T., Pacurar I., Dirja M., Pacurar H. M., Oroian I., Cosma S. A., Gheres M., 2013 Effect of tillage systems on soil properties, humus and water conservation. Agricultural Sciences 4(5):35.

Sarong M. A., Jihan C., Muchlisin Z. A., Fadli N., Sugianto S., 2015 Cadmium, lead and zinc contamination on the oyster *Crassostrea gigas* muscle harvested from the estuary of Lamnyong River, Banda Aceh City, Indonesia. AACL Bioflux 8(1):1-6.

Stugren B., Killyen H., 1975 Ecologie probleme generale şi tehnologie didactică. Editura Didactică şi Pedagogică, Bucureşti, pp 45.

Teuşdea V., 2000 Protecţia mediului. Editura Fundaţiei ''România de Mâine'', Bucureşti, pp 23.

Tufescu V., Tufescu M., 1981 Ecologie şi activitate umană. Editura Albatros, Bucureşti, pp 34.

Vespremeanu E., 1981 Mediul înconjurător - ocrotirea şi conservarea lui. Editura Ştiinţifică şi Enciclopedică, Bucureşti, pp 102.

Received: 12 August 2015. Accepted: 05 September 2015. Published online: 30 September 2015.

Authors:
Valerica-Letiţia Murgoi, "Vasile Goldiş" Western University of Arad, 94 B-dul Revoluţiei, Arad, Romania, e-mail: vali_ionescu3106@yahoo.com;
Daniela Bratosin, "Vasile Goldiş" Western University of Arad, 94 B-dul Revoluţiei, Arad, Romania;
Sorin Voia, Banat's University of Agricultural Sciences and Veterinary Medicine "Regele Mihai I al României" of Timișoara, 119 Calea Aradului, Timișoara, Romania.
Andrei Osman, Banat's University of Agricultural Sciences and Veterinary Medicine "Regele Mihai I al României" of Timișoara, Timișoara, Romania.

How to cite this article:
Murgoi V.-L., Bratosin D., Voia S., Osman A., 2016 A study on lead concentration in Haţeg Country soils. AES Bioflux 8(1):65-70.