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REGARDING THE LEVEL OF SOIL POLLUTION WITH HEAVY METALS (I)

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Abstract

As regards the research methodology, this paper used the comparative method between the current legislation in force in the Member States of the European Union on the regulated standards for the content of heavy metals in soil. As we can see, the legislative regulations vary from country to country, and in Romania, the legislation is the most stringent in terms of one heavy metal, in special, Pb content in soil, compared to the other EU Member States. Finland imposes even higher restrictions for heavy metals such as Cd and Zn content. Dutch legislation is more permissive for essential metals than other EU Member States.

Key words: *heavy metals, human health, soil pollution.*

INTRODUCTION

All soil types contain heavy metals in their structure, but their natural concentrations are very low. As a result, in Romania, Order 756/1997 nominates them as "trace elements". Their analytical detection can only be done with high-finesse spectrometric instruments (Căpățână & Gămăneci, 2011; Alloway, 2013; Musteață et al., 2019).

As pollutants, heavy metals persist in soil horizons for a long time, on the order of decades, as chemically stable compounds. In terms of their ability to be involved in biodegradation processes, it is proven that they are not biodegradable but can bioaccumulate in various plant tissues (Mizutani et al., 2016; Miclăușu et al., 2019; Mitra, 2019; Moldovan et al., 2022).

In the environment, currently the sources of heavy metal pollution are very varied, having both natural and anthropogenic origins.

Natural sources are represented by magmatic and sedimentary rocks through intense erosion processes, clogging, fires, etc. and **anthropogenic sources** are represented by various industrial activities, transport, and intensive agricultural works. In all these processes, heavy metals can be emitted to the atmosphere as aerosols, aqueous particulate pollutants, or solid wastes, being diffuse or point, stationary or mobile sources (Bradl, 2005; Căpățână & Gămăneci, 2011; Gautam et al., 2017; Bora & Bunea, 2019).

MATERIALS AND METHODS

From the wealth of data presented in the literature, we have made a rigorous selection, using primarily the criterion of "negative effects of heavy metals on the human body".

A group of 4 heavy metals (Pb, Cd, Cu, Zn) was thus identified for which detailed research was carried out. The following criteria were considered:

a. Regarding effects on the health status of the human body.

b. Regarding the methods used for the determination of heavy metals in soil.

c. Regarding current European legislative regulations.

Next, using specialized software, namely Microsoft Excel var.16.77.1, a modern method of intuitively comparative graphical representation of the maximum limits allowed for this pollutant in different EU member countries has been developed. The working method aims at current applicability in studies of evaluation of the level of heavy metal soil pollution and, in perspective, at the possibility of extrapolation to other categories of pollutants.

Finally, for each selected pollutant (Pb, Cd, Cu, Zn), a set of "radiographic graphs" and maps showing the maximum permitted limits in the different EU Member States was validated, Romania being considered, in this case, as the main subject.

RESULTS AND DISCUSSIONS

a. **Regarding effects on the health status of the human body**

Heavy metals are economically necessary, but heavy metal pollution has been shown to have significant negative effects on the human nervous, respiratory, circulatory, and digestive systems. For example, Pb, Cd and Hg are toxic without having any role in the metabolism of the human body. On the other hand, Cu and Zn, for example, are toxic only at concentrations and doses exceeding the maximum regulatory limits (Ardelean & Maior, 2000; Doroftei et al., 2008; Băbuț et al., 2011; Micu et al., 2016; Țulugea et al., 2019).

Table 1 summarizes the heavy metal pollutants selected for this work, in terms of their source and effects (role-excess-deficiencies) on the health status of the human body.

Table 1. Summary of the effects of some heavy metals on the human body

Critical metal	Source	Role	Excess	Deficiencies	Citation
Pb	Pesticides, paint, smoking, car emissions, extraction of useful minerals	Lack of conclusive data	Developmental delays in children, encephalopathy, congenital paralysis, epilepsy, gastrointestinal disorders	Low IQ Emotional and behavioral problems.	**Oros et al., 2011 NIH, 2014 Gati et al., 2016 Bora et al., 2017 Fisher & Gupta, 2022**
Cd	Galvanizing, welding, fertilizers, pesticides, battery production, smoking	Lack of conclusive data	Kidney dysfunction, osteoporosis, increased blood pressure, bronchitis	Cardiovascular diseases	**ATSDR, 2013 Balali-Mood et al., 2021 Abdel-Rahman, 2022**
Cu	mining, pesticide production, chemical industry	Helps fundamental biological processes	Anaemia, digestive system disorders	Hypochromic anemia	**Iancu & Buzgar, 2008 Romaña et al., 2011 Gad, 2014**
Zn	Rubber industry, paints, dyes, detergents	Helps the immune system and human metabolism.	Cramps, stomach pain, loss of appetite, headaches	Occurrence of various eczemas	**Hussain et al., 2022 Maxfield et al., 2023**

From the data presented in Table 1 we can conclude that pollution caused by heavy metals deserves more attention because most of them are not found in soluble form, or if they exist, they are complexed with organic or inorganic ligands, which increases their toxicity (Coman et al., 2010a; Țulugea et al., 2019; Briffa et al., 2020; Timothy et al., 2019).

b. **Regarding the methods used for the determination of heavy metals in soil**

Based on the research carried out, instrumental analysis methods have evolved from single-element spectroscopic techniques such as flame atomic absorption spectrometry (AAS) to multi-element techniques such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled atomic emission spectrometry (ICP-AES) and inductively coupled plasma optical emission spectrometry (ICP-OES).

From the above, AAS and ICP-MS are standardized methods for the determination of heavy metal samples in soil at EU level. AAS is an analytical method that is standardized in several countries, not only in EU Member States, due to its high sensitivity, which gives precision and accuracy.

Different methods of analysis, and therefore different standards, are used in EU Member States to assess the impact of these pollutants. For example, for Romania - the standard method is flame atomic absorption spectrometry (FAAS), for Germany - the standard method is Aqua regia (AR) and X-ray Fluorescence (XRF), for Finland – the standard method is Aqua regia (AR) (Dobra et al., 2006; Damian et al., 2008; Berar et al., 2010; Oros et al., 2011; Voica et al., 2012; Damian et al., 2013; Lăcătușu et al., 2014; Mizutani et al., 2016)

c. Regarding current European legislative regulations

Table 2 gives an overview of EU regulations and transposition into legislation in some Member States, with Romania being the central element in this overview. Official regulations have been used as bibliographical resources, i.e., European Council Directive 86/278/EEC 1986, MEF, 2007. Government Decree on the Assessment of Soil Contamination and remediation needs - Ministry of Environment, Finland, Order no. 756/1997.

Table 2. Maximum limits of heavy metals in soil in some European countries (mg/kg)

C. E.	*ROM*	*EU*	*NETH*	*AUST*	*POL*	*GER*	*FIN*
Pb	50	300	150	100	100	500	60
Cd	3	3	5	5	3	2	1
Cu	100	140	250	100	100	50	100
Zn	300	300	500	300	300	300	200
Citations	**Order no. 756/ 1997**	**E.C.D.C. 86/278/ CEE 1986**	**Dehelean et al., 2019**	**Dehelean et al., 2019**	**Dehelean et al., 2019**	**Dehelean et al., 2019**	**MEF, 2007**

*C.E.-chemical element; ROM-Romania, NL-Netherlands, AUST-Austria, POL- Polonia GER-Germany; FIN-Finland

Please note that the values in Table 2 refer to the total pollutant content in the soil and not to the mobile fraction.

As regards the maximum permissible limits for **Pb -** as a soil pollutant, the following extreme values can be found in the legislative reference package:

Minimum value - 50 mg/kg in Romania

Maximum value - 500 mg/kg in Germany

**Maximum permitted limit in Romania - 50 mg/kg dry substance*

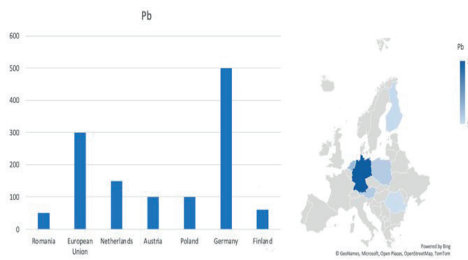

Figure 1. Maximum permissible soil limits for Pb

Figure 1 shows that most European countries have values below 150 mg/kg dry matter, which are lower than those required by the EU Directive.

An average value would not be relevant in such an approach, but it would be about 180 mg/kg, more than 3 times higher than the Romanian legislation and well below the provisions of the EU Directive. A final verdict cannot be expressed, but it is possible, in conjunction with the other heavy metals, to reach a reasonably economically and ecologically human justified conclusion.

Regarding the maximum permissible limits for **Cd-** as a soil pollutant, the following extreme values are recorded:

Minimum value - 1 mg/kg in Finland

Maximum value - 5 mg/kg in Austria and the Netherlands

**Maximum permitted limit in Romania - 3 mg/kg dry substance.*

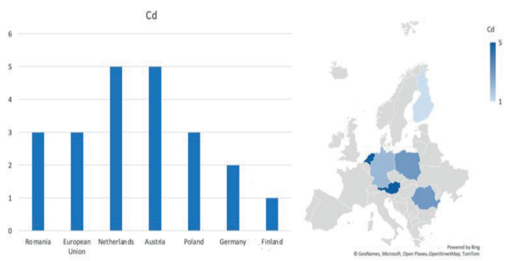

Figure 2. Maximum permissible soil limits for Cd

Figure 2. shows a Romania-Poland tandem, but also, at a maximum level, the Netherlands-Austria. An average value could be estimated at 3.14 mg/kg dry matter, the reference level for Romania.

As regards the maximum permissible limits for **Cu-** as a soil pollutant, the following values were recorded:

Minimum value - 50 mg/kg in Germany

Maximum value - 250 mg/kg in the Netherlands

**Maximum permitted limit in Romania - 100 mg/kg dry substance*

Figure 3 shows that most of the EU Member States, i.e., Romania, Austria, Poland, and Finland have the same regulated value, while at EU level values 1.4 times higher are allowed. An average value would be approx. 120 mg/kg dry matter, close to that of most EU Member States.

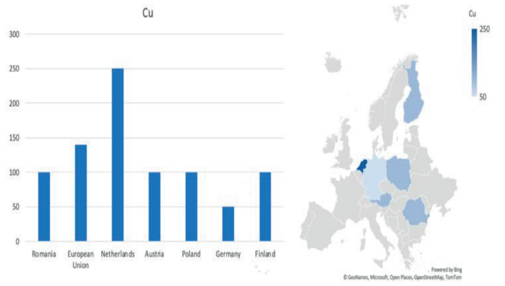

Figure 3. Maximum permissible soil limits for Cu

As regards the maximum permissible limits for **Zn-** as a soil pollutant, the following values were recorded:

Minimum value - 200 mg/kg in Finland

Maximum value - 500 mg/kg in the Netherlands

**Maximum permitted limit in Romania - 300 mg/kg dry substance*

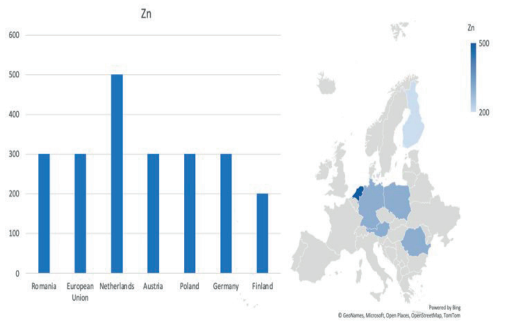

Figure 4. Maximum permissible soil limits for Zn

Figure 4. shows roughly similar benchmarks, with 5 out of 7 countries having the same benchmarks, while the Netherlands is more permissive, and Finland is more restrictive. An average value would be ca. 314 mg/kg dry matter, the most widely accepted value, but data on how to determine it are lacking.

CONCLUSIONS

From an economic point of view, heavy metals are necessary, but it is unanimously accepted that exceeding certain doses and concentrations in environmental factors have significant negative effects on the human body (Iancu & Buzgar, 2008; Coman et al., 2010a; Oros et al., 2011; Romaña et al., 2011; Gad et al., 2014; Bora et al., 2017; Fisher & Gupta, 2022; Hussain et al., 2022; Maxfield et al., 2023).

The detection capability of measuring devices is becoming increasingly accurate, and methods of analysis and reporting for these pollutants are also evolving in parallel.

Data processing for land cover has a pronounced regional specificity.

From the point of view of environmental protection, and hence human health, legislative regulation is necessary. In this context, it is noted that for Europe, Dutch legislation is much more permissive regarding the presence of heavy metals in total form in soil than the rest of the EU Member States. Romanian legislation is the most stringent in the EU regarding Pb content in soil while Finnish legislation is more stringent for Cd, Ni and Zn.

Obviously, knowledge of legislative particularities does not solve the problem of heavy metal pollution in soils, but a comparative representation can contribute to the formulation of more effective public policies of a summative and preventive nature.

REFERENCES

Abel-Rahman, G. N. (2022). Heavy metals, definition, sources Heavy metals, definition, sources of food contamination, indice, impacts and remediation. A literature review with recent updates, *Egyptian Journal of Chemistry*, 65(1), 419-437.

Alloway, B. J., (2013). Heavy Metals in soils: trace metals and metalloids in Soils and their Bioavailability, *Environment Pollution*, 22, 11-50.

Ardelean, A., Maior, C., (2000). Management ecologic, ISBN: 973-9442-12-9, Arad, RO: Servo-Sat

ATSDR, 2013. (Internet) https://www.atsdr.cdc.gov/csem/cadmium/Chronic-Effects.html. Cited 15.08.2023.

Băbuț, C. S., Micle, V., Potra, A. F. (2011). Considerații asupra remedierii solurilor poluate cu metale grele prin bioremediere, *Analele Universității „Constantin Brâncuși*” din Târgu Jiu, Seria, Inginerie, 3, 368-378.

Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M. R., Sadeghi, M. (2021). Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic, *Front. Pharmacol*., 12:643972.

Berar (Sur), I. M., Micle ,V., Oros, V., Cociorhan, C. S., Urs (Nedelcu), A. M., (2010). Studii și cercetări privind evaluarea calității solurilor din zona SC. Romplumb S.A. Baia Mare în vederea remedierii terenurilor poluate, *ProEnvironment*, 3, 472-476.

Bora, D. F., Bunea, C., (2019). Bioacumularea metalelor în vița-de-vie, Cluj-Napoca, RO: Bioflux

Bora, F. D., Donici, A., Calugar, A., Mag, I. V. P., Gal, E., Bunea, C. I., (2017). Determination of heavy metals and lead-strontium isotope characterization from merlot soil samples, Dealu Bujorului Vineyard, *Studia Universitatis Babes-Bolay Chemia*, 62(4), 317-332.

Bradl, H. B., (2005). Heavy metals in the environment: origin, interaction, and remediation", *Elsevier Academic Press*, 1-2.

Briffa, J., Sinagra, E., Blundell, R., (2020). Heavy metals pollution in the environment and their toxicological effect on humans, Helyon., (9):e04691, PMID:32964150.

Căpățână, C., Gămăneci, G., (2011). Studiul poluării solului cu metale grele în localitatea Motru, *Analele Universității „Constantin Brâncuși" din Târgu Jiu,* Seria, Inginerie, 3, 358-367.

Coman, M., Oros ,V., Făluș, B., Pop, R. (2010a). Poluarea solurilor cu metale grele – probleme specifice pentru zona Baia Mare, *ProEnviroment*, 3, 155-158.

Damian, F., Damian, G., Lăcătușu, R., Iepure, G. (2008). Heavy metals concentrations of the soil around Zlatna and Copșa Mică smelters Romania, *Carpth. J. of Earth and Environ. Sci*., 3(2), 65-82.

Damian, F., Damian, G., Lăcătușu, R., Postolache, C., Iepure, G., Jelea, M., Năsui, D. (2013). The heavy metals immobilization in polluted soils from Romania by the natural zeolite use, *Carpth. J. of Earth and Environ. Sci.*, 8(4), 231-250.

Dehelean, A., Magdaș, D. A., Cristea, G. (2013). Investigation of Trace Metals Content and Carbon Isotopic Composition on the Soil Leaf-Fruit Chain from some Transylvanian Areas, *Analytical Letters*, 46(3), 498-507.

Dobra, M., Viman, V., (2006). Determination of concentration of air and soil polluant heavy metals by ICP-AES, *Revista de Chimie*, 57(12), 1283-1286.

Doroftei, E., Rotaru-Stanciuc, M., Dobrinas, S., Mandalopol, D. (2008). Relationships between metals extent and cytological charachteristics at *Prunus persica L.* pollen, *Environmental Engineering and Management Journal*, 7(2), 97-101.

Fisher, R. M., Gupta, V. (2022). Heavy Metals, StatPearls (Internet), PMID: 32491738.

Gad, S. C. (2014). Encyclopedia of Toxicology, 3rd Edition, Reference Module in Biomedical Science, 1034 – 1036.

Gati, G., Pop, C., Brudasca, F., Gurzau, A. E., Spinu, M. (2016). The ecological risk of heavy metals in sediment from the Danube Delta, *Ecotoxicology*, 25, 688-696.

Gautam, P. K., Gautam, K. R., Banerjee, S., Chattopadhaya, M. C., Pandey, J. D. (2017). Heavy metals in the environment: fate, transport, toxicity, and remediation technologies, ISBN: 978-1-63484-740-7, USA: *Nova Science Publisher*.

Hussain, S., Khan, M., Mahmood ,T. M., Mumtaz, M. Z., Chohan, T., A., Shamim, S., et al. (2022). Zinc Essentiality, Toxicity, and Its Bacterial Bioremediation: A Comprehensive Insight, *Front. Microbiol., Sec. Terrestrial Microbiology*, 13, 900740.

Iancu, G. O., Buzgar, N. (2008). Atlasul geochimic al metalelor grele din solurile municipiului Iași și împrejurimi, Ed. Univ. "Alexandru Ioan Cuza", Iași, RO.

Lăcătușu, R. (2014). Contributions regarding heavy metals flow within soil-plant-animal system in polluted Areas, *Acta Metallomica – Meemb*, 11(1), 73-88.

Maxfield, L., Shukla, S., Crane, J. S. (2023). Zinc Deficiency, Stat Pearls 2023 (Internet) https://pubmed.ncbi.nlm.nih.gov/29630283/ Cited 15.08.2023.

Miclăușu, C., Pop, C., Vâlcan, B., Radu, A., Roșu, C. (2019). Study of soil pollution with heavy metals in the town of Copșa Mică, *Studia UBB Ambientum*, 64(1), 37-54.

Micu, L. M., Petanec, D. I., Iosub-Ciur, M. D., Andrian, S., Popovici, R. A., Porumb, A. (2016). The heavy metals content in leaves of the forest fruits (Hippophae rhamnoides and Rubus fruticosusu) from the Tailings Dumps Mining", *Rev. Chim*., 67(1), 64-68.

Mitra, A. (2019). Heavy Metals Status in the Lower Gangentic Delta, In: Estaurine Pollution in the Lower Gangetic Delta, 113-156, USA: *Springer Cham*

Mizutani, S., Ikegami, M., Sakanakura, H., Kanjo, Y. (2016). Enviromental Remediation Technologies for Metal-Contaminated soils, Chapter 4-Test Methods for the Evaluation of Heavy Metals in contaminated Soil, *Springer*, Tokyo http://doi.org/10.1007/978-4-431-55759-3_4.

Moldovan, A., Torok, I. A., Kovacs ,E., Cadar, O., Mirea, I. C., Micle, V. (2022). Metal contents and pollution indices assessment of surface water, soil land sediment from the Arieș River Basin Mining Area, Romania, *Sustainability*, 14, 8024.

Mustățea, G., Belc, N., Ungureanu, E. L., Lăcătușu, R., Petre, J., Pruteanu, A. (2019). Heavy metals contamination of the soil – water vegetables chain in the Ilfov region, *E3S Web of Conferences*, 112, 03030.

National Institutes of Health (2014). https://www.nih.gov/news-events/nih-research-matters/low-levels-lead-linked-problems-children Cited 10.08.2023.

Oros, V., Roman, S., Coman, M., Oros, D. A. (2011). Lead occurrence in children's biological fluids from Baia Mare Area, Romania, *Springer*.

Romaña, D. L., Olivares, M., Uauy, R., Araya, M. (2011). Risks, and benefits of copper in light of new insights of copper homeostasis, *J. Trace Elem. Med. Biol*., 25(1), 3-13.

Timothy, N., Wiliams, E. T. (2019). Environmental Pollution by Heavy Metal: An Overview, International *Journal of Environmental Chemistry*, 3(2), 72-82.

Țulugea, A., Bulimaga, C., Portărescu, A. (2019). Contribuții la studiul conținutului de metale grele în solurile din ecosistemul urban Bălți, *Revista de Știință, Inovare, Cultură și artă „Akademos"*, 1(60), 57-62. ISSNe 2587-36787.

Voica, C., Dehelean, A., Iordache, A., Geana, I. (2012). Method validation for determination of metals in soils by ICP-MS, Romanian Reports in Physics, 64(1), 221-231.

*** European Council Directive 86/278/CEE 1986.

*** MEF, 2007. Government Decree on the Assessment of Soil Contamination and remediation needs – Ministry of Environment, Finland.

*** Order no. 756/1997, Romania.