How to cite: Simo I.M., Herghelegiu M. C., Roșian G., Beldean-Galea M. S. (2024) Assessment of Heavy Metal Pollution in Cerna River Basin, Hunedoara County. *2024 "Air and Water – Components of the Environment" Conference Proceedings*, Cluj-Napoca, Romania, p. 173-180, DOI: 10.24193/AWC2024_16.

ASSESSMENT OF HEAVY METAL POLLUTION IN CERNA RIVER BASIN, HUNEDOARA COUNTY

IRINA MONICA SIMO[1], MIHAELA-CĂTĂLINA HERGHELEGIU[1], GHEORGHE ROȘIAN[1], MIHAIL SIMION BELDEAN-GALEA[1]

DOI: 10.24193/AWC2024_16

ABSTRACT. Assessment of Heavy Metal Pollution in Cerna River Basin, Hunedoara County. The purpose of this study is to assess the presence of the heavy metals like Cu, Cd, Cr, Pb, Ni, As and Zn, in the surface water samples, collected from Cerna River and it's main tributary, from Hunedoara county.
The main sources of heavy metals is the Hidrografic Reservoir are represented by the industrial activities (especially steel industry) improperly storage of waste, diffuse polution and atmospheric depositions.
The heavy metal content was determined by atomic absorption spectrophotometry with atomization in graphite furnace. Before de analysis, the water samples were treated with nitric acid for heavy metal's mineralization.
Ten water samples were collected from Cerna River and it's main tributary as it follows: Cerna River flowing in Mureș River, Cerna River in Sântuhalm, Cristur River, Pestis River, Petac River, Zlaști River, Teliucul Inferior River, Govâjdia River, Toplița River and Vălarița River.
Depending on the sampling point, the measurable results are as the following: Cerna River flowing in the Mureş River (Cu - 10.1 µg/L, Cd - 0.09 µg/L, Cr - 1.44 µg/L, Pb - 4.67 µg/L. Ni - 1.38 µg/L, As - 2.43 µg/L); Cerna River in Sântuhalm (Cu - 24,9 µg/L, Cr - 16,2 µg/L. Zn - 0.04 µg/L și As - 1.05 µg/L); Cristur River (Cu - 0.74 µg/L, Cd - 0.03 µg /L, Pb - 0.65 µg /L, Ni - 0.51 µg /L); Peștiș River (Cu - 2,78 µg /L, Cr - 0.68 µg /L, Pb - 0.54 µg /L, Ni - 8.03 µg /L); Petac River (Cu - 1.61 µg /L, Pb - 0.12 µg /L, Ni - 0.65 µg /L, As - 1.73 µg /L); Zlaști River (Cu - 3.0 µg /L, Cd - 0.06 µg /L, Cr - 0.64 µg /L, Pb - 0.37 µg /L, Ni - 0,85 µg /L, As - 1.31 µg /L); Teliucul Inferior River (Cu - 3.68 µg/L, Cd - 0.25 µg /L, Pb - 5.3 µg /L, As - 1.82 µg /L); Govâjdia River (Cu - 3.26 µg /L, Cr - 0.55 µg/L, Pb - 0.66 µg/L, Ni - 0.92 µg /L); Toplița River (Cu - 2.07 µg/L, Pb - 0.12 µg/L, Ni - 0.63 µg/L, As - 1.25 µg/L; Vălarița River (Cu - 1.06 µg/L, Cd - 2.44 µg/L, Cr - 1.97 µg/L, Pb - 0.76 µg /L, As - 2.68 µg/L, Ni - 5.05 µg/L, Zn - 2.44µg/L).
The results show that in the analyzed water samples there are exceedances for heavy metals as follows: Cu, one exceedance; Cd, three exceedance; Pb, two exceedance; and Ni, two exceedance.

Keywords: surface water, heavy metals, Cerna River.

[1] Babeș-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fântânele street, 400294 Cluj Napoca, Romania. Iri17_na@yahoo.com, mihaela.herghelegiu@ubbcluj.ro, gheorghe.rosian@ubbcluj.ro, simion.beldean@ubbcluj.ro.

1. INTRODUCTION

Water quality is a main and essential factor for humans, animals, plants and ecosystems (Eze et al., 2023). Surface water pollution occurs when environmental components are either damaged or replaced by dangerous chemicals which can represent a threat to both nature and humans. The water pollution itself represents the physical, chemical, and biological alteration of water which is produced naturally or anthropically, becoming therefore improper for use (Szollosi-Moţa and Sârbu, 2014).

Surface water sources ensure the sustainability and balance of aquatic ecosystems and the water supply of human communities. River water is used for various domestic, urban, agricultural, and industrial purposes (Le et al., 2024).

Heavy metals poses a threat to human health due to their toxicity, persistence in the environment, and bioaccumulative nature (Dey et al., 2021). Sources of heavy metal pollution can be anthropogenic: industrial and wastewater treatment plant effluents, use of chemical fertilizers and natural like rock erosion (Kumar et al., 2021).

Effects of heavy metals on human health even at low concentrations can lead to various diseases (cardiovascular, renal, nervous and bone), carcinogenesis, mutagenesis and teratogenesis (Dey et al., 2021). For fish, there are potent neurotoxins which can cause significant tissue deformities and histopathological changes (Morabet et al., 2024; Wu Z. et al., 2021). These harmful consequences have attracted global attention by being subjected to continuous research (Dey et al., 2021; Kumar et al., 2021). According to research, most heavy metals end up accumulating in sediment and significantly in water (Mostafa et al., 2023).

The presence of heavy metals has had a significantly contribution to the deterioration of water quality. Water quality assessment and improvement are the main objectives of the Water framework directive (Okeke et al., 2024; Debnath et al., 2024).

In this study, heavy metal pollution of the Cerna River and its main tributary in Hunedoara County was investigated by sampling water samples from different points of the river. The heavy metals of interest in this analysis were: Cu, Cd, Cr, Pb, Ni, As, and Zn.

2. MATERIALS AND METHODES

2.1. General description of the area

Cerna River (Fig. 1) is one of the most important tributaries of the Mureş River in Hunedoara County.

The city of Hunedoara is the most important human settlement which uses this river as its main source of water. Hunedoara is also the largest city of Hunedoara County, being situated in center of the county, and has a large history in the steel and mining industry, being attested as a technological development in the time of Austro-Hungarian Empire at the end of the 19th century. After 1920 until the abolishment of communism in 1989, the iron and steel plant from Hunedoara represented the most important producers of steel and iron, having a mining and steel complex, who owned a significant operating fund from the iron ore mining from the nearby surroundings (Ardelean et al. 2015).

Cerna River rises in the Poiana Ruscă Mountains, crosses the Land of Pădurenilor, feeds Lake Cinciş, passes through the city of Hunedoara and flows into the Mureş River.

The name of the sampling point, assigned number and the geographical coordinates are given in Table 1, and in the map of the studied watershed (Fig. 1).

Table 1. Sampling points, abbreviation and the geographical coordinates

Location	Sampling point	Geographical coordinates	
		Latitude (N)	Longitude (E)
Cerna River at the confluence with Mureș River	P1	45°87'11.32"	22°95'63.96"
Cerna River in place Sântuhalm	P2	45°85'57.00"	22°95'67.36"
Teliucul inferior River	P3	45°71'55.00"	22°88'78.35"
Toplița River	P4	45°68'61.70"	22°78'36.41"
Cristur River	P5	45°82'52.21"	22°94'16.68"
Peștiș River	P6	45°79'55.98"	22°92'88.59"
Petac River	P7	45°79'68.54"	22°92'25.83"
Zlaști River	P8	45°74'90.88"	22°89'10.08"
Govâjdia River	P9	45°70'65.64"	22°88'03.93"
Vălarița River	P10	45°68'31.58"	22°70'11.01"

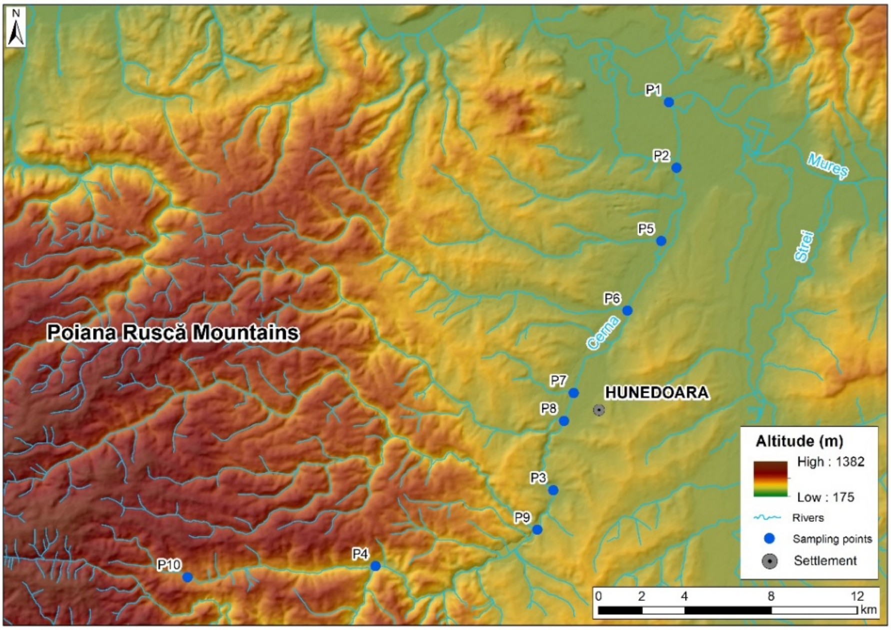

Fig. 1. Map of Cerna River and sampling points in Google Earth

Ten water samples were collected from different sections of the Cerna River using polypropylene botles. The botles were precleaned in the laboratory and rinsed with distilled water before sample collection. Afterwards, they were transported in a lid-covered crate with ice patrons inside, as the water sample must be kept at 4°C until it is fixed with acid (HNO_3 from Merck with VWR-certificate of Analysis).

2.2. Methods and materials

The heavy metal content of the samples was analysed using atomic absorption spectrophotometry with atomization in graphite furnace (SYSTEM GF 3000, GBS Scientific Equioment Australia). The standardized SR ISO 8288:2001 was used as analytical method for the detection of elements. Working standard solutions were prepared by diluting the concentrated standard solutions of fresh metals for each series of sample to be analyzed according to STAS (SR EN ISO 15586-2008).

Standard solutions of metals (ICP standard) in concentration of 1000 mg/L each compound were acquire from Sigma Aldrich (Merck, Darmstadt, Germany).

Fig.2. Graphite Furnace Atomic Absorption Spectrophotometer

3. RESULTS AND DISCUSSION

In the ten analyzed surface water samples, heavy metal concentration values ranged between not detected (nd) to 24.90 µg/L. Cu was the most prevalent, being found in all ten samples and ranging from 0.74–24.9 µg/L. Pb were second prevalent metals, being found in 9 samples and ranging from 0.12–5.30 µg/L. Ni was found in 8 samples in concentration range of 0.51–8.03 µg/L. As and Cr were found in 7 samples, with Cr ranging between 0.55–16.2 µg/L and As between 1.05–2.68 µg/L. Cd was found in 5 samples, with values from 0.03–2.44 µg/L, and Zn was the least one detected, being found only in 2 samples with values of 0.04 and 2.44 µg/L respectively (Table 2).

Table 2. Concentrations of analysed heavy metals

Sample	Cu (µg/L)	Zn (µg/L)	Cd (µg/L)	Pb (µg/L)	Ni (µg/L)	Cr (µg/L)	As (µg/L)
P1	10.10	-	0.09	4.67	1.38	1.44	2.43
P2	24.90	0.04	-	-	-	16.20	1.05
P3	0.74	-	0.03	0.65	0.51	-	-
P4	2.78	-	-	0.54	8.03	0.68	-
P5	1.61	-	-	0.12	0.65	-	1.73
P6	3.00	-	0.06	0.37	0.85	0.64	1.31
P7	3.68	-	0.25	5.30	-	-	1.82
P8	3.26	-	-	0.66	0.92	0.55	-
P9	2.07	-	-	0.12	0.63	-	1.25
P10	1.06	2.44	2.44	0.76	5.05	1.97	2.68
MAC*	**20**	**500**	**0.08**	**1.2**	**4**	**50**	**10**

* Maximum Allowable Concentrations. „-„ not detected

Analyzing the values obtained in the collected water samples, and comparing these values with the Maximum Allowable Concentrations (MAC), stipulated by Water Framework Directive, NTPA-001/002 norm and the legislation according to Order 161/2006; GD 100/2002; GD 570/2016; GD 1038/2020 (Surface waters), it can be observed that there are exceedance for the analysed heavy metals in the water samples as it follows: Cu, one exceedance; Cd, three exceedance; Pb, two exceedance; Ni, two exceedance (Fig. 3 and Fig. 4). For a better presentation, the MAC of Zn, was divided by ten.

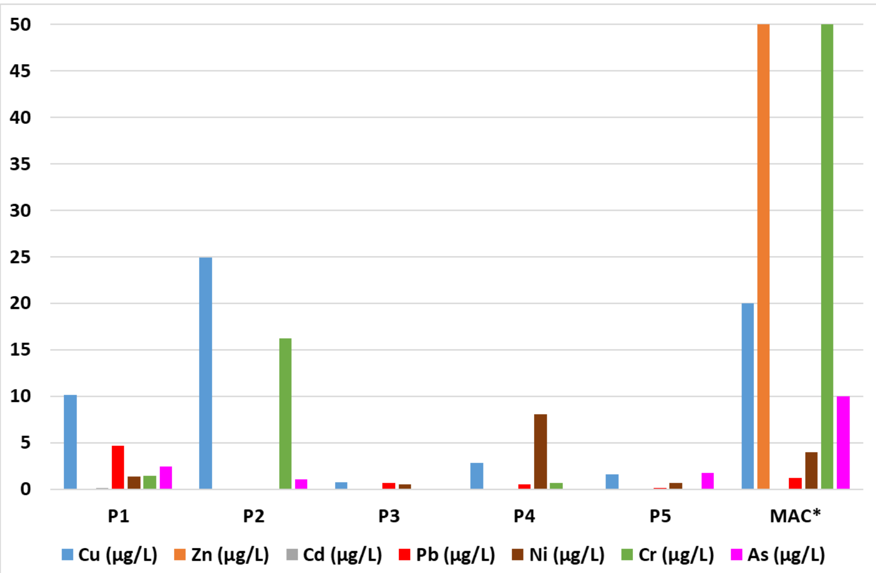

Fig.3. Comparison of heavy metals concentration in water samples with MAC

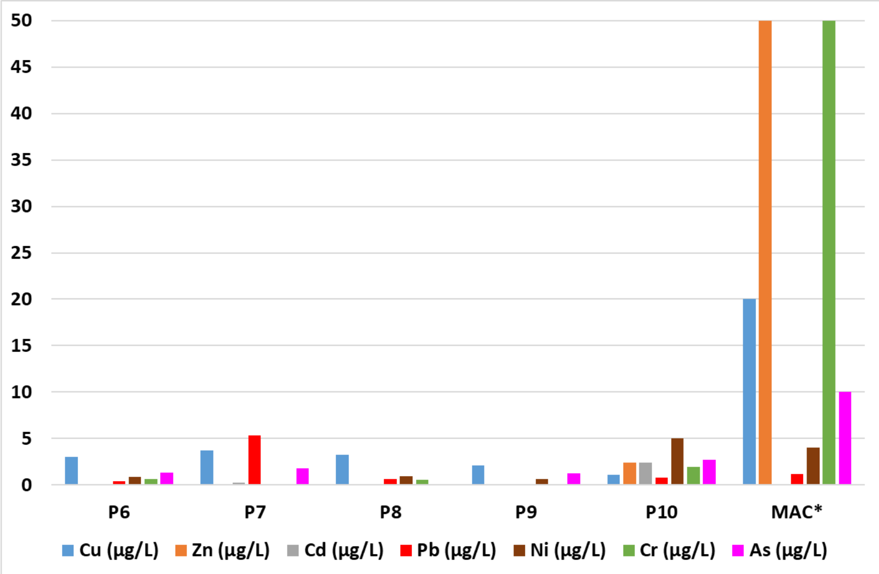

Fig.4. Comparison of heavy metals concentration in water samples with MAC

The results obtained in our study are smaller than the results found by (Kim et et al., 2016) in Hunedoara county, which has found the following concentrations: As (nd–1070 µg/L), Cd (170–1206 µg/L), Cr (14.1–96.8 µg/L), Cu (399–3319 µg/L), Ni (548–1550 µg/L), Pb (nd–27.2 µg/L).

4. CONCLUSIONS

This study explores the quality of surface waters collected from the Cerna River and its main tributaries, in terms of heavy metals, in Hunedoara County, an area with a long history of mining and processing activities.

The results show that in the analyzed water samples there are exceedances for heavy metals as follows: Cu, one exceedance; Cd, three exceedance; Pb, two exceedance; and Ni, two exceedance.

Due to these exceedances, further research should be done for the regular monitoring of heavy metals in the Cerna River and its main tributary in order to identify the sources of pollution and to minimize their negative effects on the environment as much as possible.

Acknowledgements

This research was performed in the framework of doctoral studies from the Babeş-Bolyai University, Doctoral School of Environmental Science. The authors are grateful to the Water Quality Laboratory within the Romanian Water Management System Târgu-Mureş for the technical support provided.

REFERENCES

1. Ardelean M., Ardelean E., Vilceanu L., Josan A. (2015). Environmental impact of brown fields sites in Hunedoara Area. *Review of Air Force Academy*, The Scientific Informative Review, Vol XIII, 2(29), 107-112, Brasov, Romania, ISSN: 1842-9238.
2. Debnath A., Singh P.K., Sharma Y.C. (2024), Spatial distribution of heavy metals in the sediments of River Ganges, India: Occurrence, contamination, source identification, seasonal variations, mapping, and ecological risk evaluation. *Marine pollution bulletin*, 198, 115910. https://doi.org/10.1016/j.marpolbul.2023.115910.
3. Dey M., Akter A., Islam S., Dey S.C., Choudhury T.R., Fatema K.J., Begum B.A. (2021), Assessment of contamination level, pollution risk and source apportionment of heavy metals in the Halda River water, Bangladesh. *Heliyon*, 7, e08625. https://doi.org/10.1016/j.heliyon.2021.e08625.
4. Eze V.C., Onwukeme V.I., Ogbuagu J.O., Okechukwu V.C., Aralu C.C. (2023), Distribution of sources of polychlorinated biphenyls in surface waters and sediments of Otamiri River, Imo State. *African Scientific*, 22, e01957. https://doi.org/10.1016/j.sciaf.2023.e01957R.
5. Hao M., Zuo Q., Shi S., Li B., Zhao X. (2022), A comprehensive exploration on distribution, risk assessment and quantification of the source of heavy metals in the multi-media environment of the Shaying River Basin, China. *Ecotoxicology and environmental safety*, 231, 113190. https://doi.org/10.1016/j.ecoenv.2022.113190
6. Kim L., Vasile G. G., Stanescu B., Dinu C., Ene C. (2016), Distribution of trace metals in surface water and streambed sediments in the vicinity of an abandoned gold mine from Hunedoara County, Romania. 67. 1441-1446.
7. Kumar S., Islam A.R.M.T., Islam T.H.M., Hasanuzzaman M., Ongoma V., Khan R., Mallick, J. (2021), Water resources pollution associated with risks of heavy metals from Vatukoula Goldmine region, Fiji. *Journal of Environmental Management*, 293, 112868. htps://doi.org/10.1016/j.jenvman.2021.112868.
8. Le V. T., Nguyen B.T. (2024), Heavy metal pollution in surface water bodies in Khanh Hoa province, Vietnam: Assessment of risks to pollution and human health, quantification of source and implications for sustainable management and development. *Environmental Pollution*, 343, 123216. https://doi.org/10.1016/j.envpol.2023.123216
9. Morabet R.El., Barhazi L., Bouhafa S., Dahim M.A., Khan A.M. (2024), Water quality, heavy metal contamination and health risk assessment of surface water bodies in Mohammedia Prefecture, Morocco. *Environmental chemistry and ecotoxicology*. https://doi.org/10.1016/j.enceco.2023.12.002Z.
10. Mostafa M.G. (2023), Assessment of heavy metals pollution in surface waters of Bangladesh. *Environmental challenges*, 13, 10078. https://doi.org/10.1016/j.envc.2023.10078
11. Norm of 28 February 2002 on setting limits for taxation with pollutants for the discharge of industrial and urban wastewater into natural receivers, NTPA-001/2002 Published in the Official Gazette, Part I nr. 187 of 20 March 2002.
12. Okeke E.D., Enochoghene A., Ezeudoka B. C., Kaka S.D. Chen Y., Mao G. (2024), An overview of heavy metals risks around comparable e-waste sites and municipal landfills in major African cities: recommendations and future perspectives. *Toxicology*, 501, 153711.https://doi.org/10.1016/j.tox.2023.153711.
13. Order 161/2006; GD 100/2002; GD 570/2016; GD 1038/2020 (Surface water).

14. Szollosi-Moţa A., Sârbu R. (2014), Research on heavy metal pollution of the river mureş in hunedoara county due tributaries affected by human activities, industrial and mining. Annals of the „Constantin Brâncuşi" University of Târgu Jiu, Economy Series, *Special Issue-Information society and sustainable development*. http://www.utgjiu.ro/revista/ec/pdf/2014-04.Special/29_Szollosi-Mota.pdf
15. Water Framework Directive 2000/60/EC. https://jiu.rowater.ro/despre-noi/legislatie/directive-europene-in-domeniul/Directive-Framework-Water-2000-60-EC
16. Water quality. Determination of trace elemetes by atomic absorption spectrometry with a graphite furnace – SR EN ISO 15586/2008; SR ISO 8288:2001
17. Wu Z., Ma F., Lai X. (2021), Concentration, distribution and evaluation of heavy metals dissolved in rivers in Lake Chaohu basin, China. *Journal of Environmental Management*, 300, 113744. https://doi.org/10.1016/j.jenvman.2021.1137440.