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

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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 pollution 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 and 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); Zlaștă 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 - 2.44 µg/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.

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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 Cinciș, passes through the city of Hunedoara and flows into the Mureș 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**

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling point</th>
<th>Geographical coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerna River at the confluence with Mureș River</td>
<td>P1</td>
<td>45°87'11.32&quot; 22°95'63.96&quot;</td>
</tr>
<tr>
<td>Cerna River in place Sântuhalm</td>
<td>P2</td>
<td>45°85'57.00&quot; 22°95'67.36&quot;</td>
</tr>
<tr>
<td>Teliucul inferior River</td>
<td>P3</td>
<td>45°71'55.00&quot; 22°88'78.35&quot;</td>
</tr>
<tr>
<td>Toplița River</td>
<td>P4</td>
<td>45°68'61.70&quot; 22°78'36.41&quot;</td>
</tr>
<tr>
<td>Cristur River</td>
<td>P5</td>
<td>45°82'52.21&quot; 22°94'16.68&quot;</td>
</tr>
<tr>
<td>Peștiș River</td>
<td>P6</td>
<td>45°79'55.98&quot; 22°92'88.59&quot;</td>
</tr>
<tr>
<td>Petac River</td>
<td>P7</td>
<td>45°79'68.54&quot; 22°92'25.83&quot;</td>
</tr>
<tr>
<td>Zlaști River</td>
<td>P8</td>
<td>45°74'90.88&quot; 22°89'10.08&quot;</td>
</tr>
<tr>
<td>Govâjdia River</td>
<td>P9</td>
<td>45°70'65.64&quot; 22°88'03.93&quot;</td>
</tr>
<tr>
<td>Vălarița River</td>
<td>P10</td>
<td>45°68'31.58&quot; 22°70'11.01&quot;</td>
</tr>
</tbody>
</table>

**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 bottles. The bottles 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 (HNO₃ 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 Equipment 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).

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

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

* Maximum Allowable Concentrations. \(\text{\textendash}\) 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.
The results obtained in our study are smaller than the results found by (Kim 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.

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