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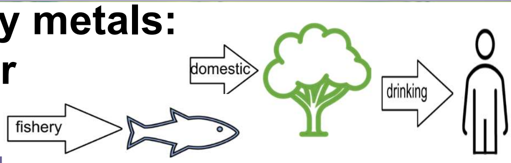
Assessment of the anthropogenic load levels of heavy metals: a case study on the example of the Styr River

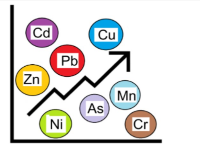


Olha Biedunkova[1], Pavlo Kuznietsov[1], Yuliia Trach[1,2]

1 Affiliation: National University of Water and Environmental Engineering, Ukraine

2 Affiliation: Institute of Civil Engineering, Warsaw University of Life Sciences, Warsaw, Poland

INTRODUCTION & AIM



The predominantly adverse effects of heavy metals on organisms, including their toxicity, persistence and bioaccumulation, have been the subject of global public concern in recent years. Heavy metal pollution in the environment is increasing. Traces of heavy metals, such as zinc (Zn), cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), manganese (Mn), arsenic (As), and chromium (Cr), in surface waters may increase due to anthropogenic activities. Cooling water systems power plant are produced by various industries and district cooling facilities contains high concentrations of different chemicals. **The purpose** of this study is to analyze the temporal distribution of eight heavy metals (Zn, Cd, Pb, Cu, Ni, Mn, As, Cr) in the waters of the Styr River, within the impact zone of the cooling water blowdown from the Rivne Nuclear Power Plant (Ukraine).

METHOD

The Styr River is located in the north-western Ukraine. The sample campaign was organized in every month of 2018-2022.

The sampling was performed according to procedural standards [1, 2]. An inductively coupled plasma optical emission spectroscopy (Fig. 1) was used for analyzing the metal concentrations, following [3]. The statistical processing of the research results JASP software package (Version 0.14.3) was used.

Figure 1. An inductively coupled plasma optical emission spectroscopy ICAP 7400 Duo device.

RESULTS AND DISCUSSION

The arithmetic mean concentration (M ± SD) of eight heavy metals in the water of the Styr River within the influence zone of the cooling water discharge from the Rivne Nuclear Power Plant (NPP) decreases in the following order: Cu (6.43 ± 1.82 ppb), As (5.1 ± 0.2 ppb), Zn (4.67 ± 1.14 ppb), Mn (4.03 ± 2.81 ppb), Ni (3.3 ± 0.8 ppb), Cr (1.06 ± 0.22 ppb), Pb (1.05 ± 0.11 ppb), Cd (1.01 ± 0.03 ppb). The concentrations of As, Cd, Pb, and Cr during the monitoring period corresponded to the lower limit of detection (5.0, 1.0, 1.0, and 1.0 ppb, respectively), with only a few samples exceeding the lower measurement threshold (Fig. 2). During the summer, increased concentrations of Pb and Cr were recorded. Conversely, Cu and Zn concentrations decreased during the summer.

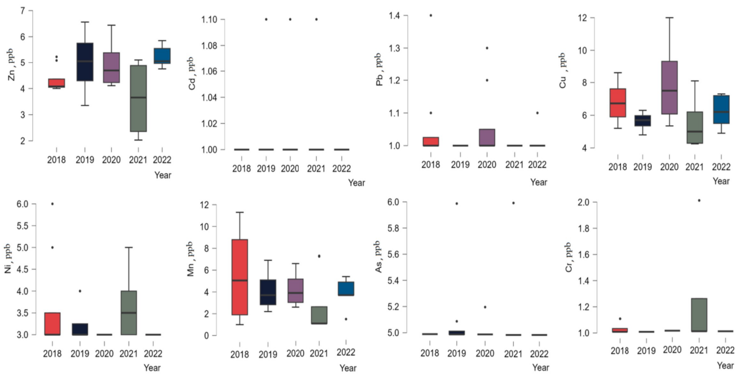


Figure 2. Distribution of concentrations by years of 8 heavy metals.

Seasonal variations in the concentrations of heavy metals are significantly influenced by water flow rates. In this region, water flow peaks during winter and spring (due to snowmelt, floods, and water dilution) and reaches a minimum during summer and autumn (due to evaporation caused by higher temperatures). However, concurrent processes such as sedimentation and bioaccumulation of heavy metals by aquatic organisms complicate this relationship. As a result, no clear seasonal patterns were observed for Mn, Cd, and Cu concentrations. During the summer, increased concentrations of Pb (M = 0.21 ppb) and Cr (M = 0.31 ppb) were recorded. It is known that Pb and Cr pollution sources are predominantly anthropogenic, and their concentration increases during the warm season due to water evaporation in rivers. Conversely, Cu and Zn concentrations decreased during the summer. It is also known that these elements are bioaccumulated by aquatic organisms, and their reduced concentration in the warmer months may be explained by biological uptake processes. Moreover, some metals can be extremely toxic to biota (e.g., Hg, Pb, As, Cd), while others are essential for the proper functioning of organisms; for instance, Zn and Cu play a vital role in phytoplankton growth. The study revealed that while the concentrations of heavy metals remained below the parametric thresholds for water quality as per Council Directive 98/83/EC, their patterns and relationships indicate complex interactions between natural and anthropogenic factors. The observed ranking of heavy metal concentrations suggests that Cu, As, and Zn are the dominant pollutants in the study area. The correlation matrix revealed significant relationships among certain heavy metals, suggesting shared origins or common influencing factors.

The correlation matrix revealed significant relationships among certain heavy metals, suggesting shared origins or common influencing factors. For example, the strong positive correlation between Cu and Pb, and between Zn and Mn, indicates potential common sources such as urban runoff or industrial discharges. Conversely, the weak negative correlations between Mn and Ni, and Cr and Zn, highlight divergent origins or environmental processes governing their mobility and distribution. Cluster analysis (Fig. 3) further refined these interpretations by grouping metals with similar sources. Notably, Pb, Cr, and Ni clustered together, implicating industrial emissions, whereas Cd and As exhibited more isolated clustering, likely linked to specific industrial or agricultural inputs.

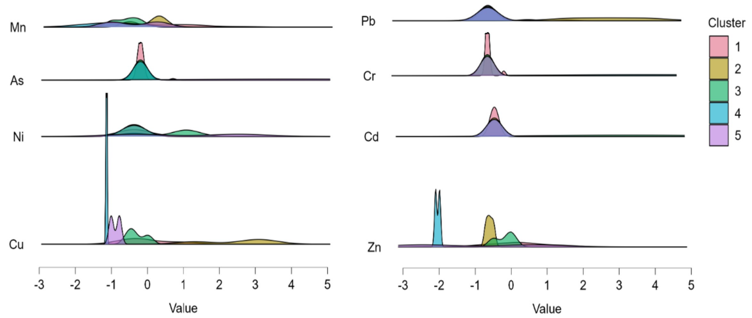


Figure 3. Cluster analysis of 8 heavy metals.

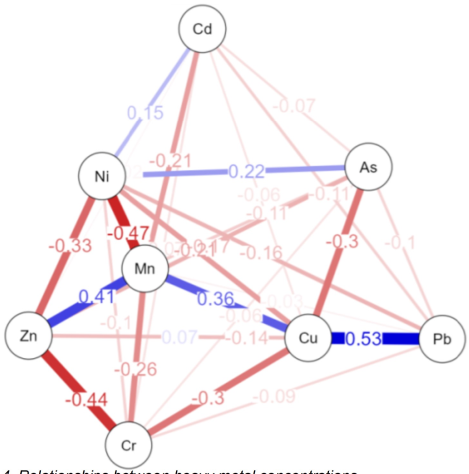
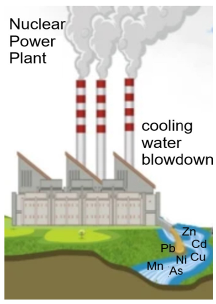


Figure 4. Relationships between heavy metal concentrations.

A moderate positive correlation correlation was observed between Zn and Mn (r = 0.41), suggesting that these metals may share common sources or environmental pathways that lead to simultaneous increases in their concentrations (Fig. 4). Similarly, Cu and Pb; Cu and Mn exhibited a moderate positive correlation (r = 0.53; r = 0.36). For example, Mn and Ni exhibited a significant negative correlation (r = -0.47), indicating that factors increasing Mn concentrations may simultaneously decrease Ni concentrations. Furthermore, Zn and Cr (r = -0.44) and Mn and Cr (r = -0.44) also showed negative correlations, suggesting inverse relationships between these metals.

Despite the concentrations of all studied heavy metals falling below the thresholds established for potable water, their persistent presence raises environmental concerns. Long-term exposure, even at low concentrations, can have detrimental effects on aquatic ecosystems and human health. Additionally, exploring the synergistic toxic effects of metal mixtures on aquatic organisms could provide a more comprehensive understanding of ecological risks.

CONCLUSION



The study of heavy metal concentrations in the Styr River, within the zone influenced by the Rivne Nuclear Power Plant's cooling water discharge, revealed that none of the eight monitored metals (Zn, Cd, Pb, Cu, Ni, Mn, As, Cr) exceeded the parametric values established by Council Directive 98/83/EC, ensuring that the water remains suitable for human consumption. Temporal and seasonal variations in metal concentrations were observed, with some fluctuations in 2021 attributed to localized anthropogenic activities. While the presence of Cu and Zn suggests possible corrosion from industrial equipment (MNZh-5 alloy), this introduction remains within permissible limits. Cluster analysis indicated a complex interaction of natural and anthropogenic sources, particularly for metals like Pb, As, Cd, and Cr, which show clear signs of pollution from human activities. In contrast, Mn, Cu, Ni, and Zn display more variability, suggesting both natural and industrial sources. Overall, the study highlights the need for continued monitoring to manage environmental risks effectively.

FUTURE WORK / REFERENCES

Future studies should focus on high-resolution temporal and spatial monitoring to capture subtle variations and identify emerging pollution sources.

Reference 1. ISO 5667-23:2011. Water quality - Sampling - Part 23: Guidance on passive sampling in surface wates. Available online: https://www.iso.org/standard/50679.html; **2.** ISO 5667-3:2024. Water quality - Sampling - Part 3: Preservation and handling of water samples. Available online: https://www.iso.org/standard/82273.html; **3**. ISO 11885:2007 Water quality —Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). Available online: https://www.iso.org/standard/36250.html