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## PREFACE

On behalf of the Scientific and Organizational Committee, it is my honor and great pleasure to present the Proceedings of the 3rd EUROSA International Conference, held on 14-17 May 2025 in Vrnjačka Banja, Serbia.

The papers contained in this Proceedings represent current scientific and professional informations in the field of *Engineering and Occupational Safety Management, Environmental Engineering and Management; Fire Protection Engineerig and Management, Engineering and Management of Disaster and Emerency Protection*, *Good use of practice in protection* and represent a mix of scientific research and professional opinion, shared with us by participants from academia and industry professionals.

We sincerely thank all the conference participants for their contribution, ensuring the success of the conference. Special thanks to all the participants of the round tables and panel discussions, keynote speakers, chairmen of the sessions and of course the reviewers for their invaluable contribution.

Last but not least, I would like to express my sincere gratitude to all members of the Scientific and Organizing Committee, whose efforts and work led to the successful realization of the EUROSA 2025 conference.

Vrnjačka Banja, May 2025

Chairman of the International Scientific Committee

Dr Miodrag Višković, Associate Professor

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# ASSESSMENT OF SURFACE WATER POLLUTION BY HEAVY METALS IN SERBIA

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**Abstract:** The quality of surface waters in Serbia is systematically monitored by the Environmental Protection Agency as a competent authority. For the purposes of this publication, data on lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr) and cadmium (Cd) concentrations of the all monitored water bodies (2016-2022) were selected as indicators of the trends in surface water quality. Evaluation of the water quality was based on the limit values for priority and priority hazardous substances (Pb, Ni, Cd) in surface waters (Environmental Quality Standards - EQS) which are established by the "Official Gazette of RS", No. 24/2014 and "Official Gazette of RS", No. 50/2012 (for the Cu, Zn and Cr). Considering all metals, only a few percent of the values exceeded the MDK values, while over 90 % of the results indicate low pollution and good ecological status of the water bodies. The most polluted water samples were detected on the profiles Srpski Itebej (river Begej), Kraljevo and Raska (river Ibar) Novi Sad (channel DTD), Hetin (river Stari Begej), Jasa Tomic (river Tamis), Markovicevo (river Brzava), and Novi Becej (river Tisa). The highest levels of contamination were observed on the Vrbica profile (river Zlatica) in April 2019, with peak concentrations of Zn (9530 μg/L), Cu (3221 μg/L), and Cr (55.3 μg/L). In summary, elevated concentrations of heavy metals do exist but overall trends suggest relatively low pollution levels in the majority of monitored water bodies.

**Keywords:** *Heavy metals; Surface water pollution; Environmental Quality Standards; Serbia*

## INTRODUCTION

Heavy metal pollution in the water resources has been a global ecological issue due to their high toxicity, persistence, tendency to accumulate and inability to degrade naturally. Sources of heavy metal pollution include natural processes, such as the breakdown of metal-containing rocks and volcanic eruptions, as well as human activities like urbanization, industrial development, agriculture and domestic activities through surface runoff, sewage, effluent discharge, mine drains, etc. These anthropogenic activities, disrupt existing biogeochemical cycles in both terrestrial and aquatic ecosystems and pose severe environmental hazards to the food chain due to their enduring presence in the environment. The accumulation of toxic heavy metals (metaloids) such as Cu, Ni, As, Pb, and Cd in organisms causes significant health risks across transferring between trophic levels and negatively impacting the health of living beings (Pujari & Kapoor, 2021).

Heavy metals are non-biodegradable and tend to accumulate and magnify within surface waters ecosystems posing serious health risks to consumers and to human health through the food chain. Their heightened toxicity leads to numerous negative impacts, such as the loss of microbial and aquatic ecosystems, chlorosis, inhibited germination and growth, reduced biomass production, impaired photosynthesis, decreased nutrient uptake, and the generation of free radicals that damage membranes and weaken cell structures in aquatic plants. In humans, heavy metal toxicity can result in neurological disorders, nervous system damage, multiple organ failures, Alzheimer's disease, cancer, and more. While the human body requires trace amounts of metals like Cu, Zn, and Fe for cellular and DNA-binding functions, elements such as Pb, Ni, Hg, As, Cr, and Cd can be dangerous due to their high atomic weights and densities, exceeding 5 $g/cm^3$ (Pandey & Kumari, 2023).

Increased Zn levels in water bodies is often consequence from the use of pesticides and fertilizers, along with waste from industries such as alloy production, dry batteries, printing, and mining. Cu is commonly used in electrical wiring, plumbing, alloy production, and heat exchangers, leading to higher environmental levels which affects water bodies. Cd is linked to industrial waste and solid waste (such as batteries, paints, and plastics) and is also released through the use of phosphate fertilizers. Its presence in the environment can vary, as it exists in different forms, including free ions and bound to organic material or sediments. Ni is used in alloys, batteries, and as a catalyst in chemical reactions (Stanojevic-Nikolic, 2024). Pb is one of the most toxic elements in surface waters and around 98% of Pb pollution is caused by anthropogenic activities. Dissolved Pb is potentially mobile, bio-accumulative and toxic and it has no biological function in living organism (Wei et al, 2023).

Heavy metals can accumulate in sediments, serving as persistent pollution reservoirs over time. Changes in environmental conditions, like variations in pH or redox potential, can cause these contaminants to be remobilized and reintroduced into the water column, presenting renewed threats (Sunjog et al, 2016). Therefore, there is an urgent need to investigate metal content in water and to implement relevant regulations.

Evaluating surface water quality is a crucial component of environmental monitoring and management overall. The Water Framework Directive (WFD) provides a strategic framework for future water policy initiatives within the European Union and candidate countries seeking EU membership (like Serbia). As the primary legislative tool in water management, the WFD has necessitated the adaptation of surface water monitoring programs which are one of the WFD's goals, with the primary aim to achieve good water quality (good ecological status) across all European waters.

Officially implemented on December 22nd, 2000, the WFD marked a new era in European water management by establishing a unique, coordinated framework for water protection throughout Europe. European waters are organized into large river basins managed collaboratively by the relevant member states. Effective cross-border river basin management requires strong cooperation and partnership among all member states. Consequently, the WFD seeks to harmonize water protection regulations. Continuous monitoring and reliable data are fundamental for identifying pollution sources, tracking changes over time and implementing

effective remediation strategies for improving water status generally. In Serbia, the Environmental Protection Agency has been aligning its surface water status monitoring with WFD requirements since 2012.
For this research Pb, Ni, Cd, Zn, Cu and Cr concentrations were applied to assess whether the quality class of the observed water bodies meets the standards for good ecological status which provide conditions for the functioning of ecosystems, the life and protection of fish (cyprinids) and can be used for the following purposes: supplying drinking water with prior treatment of filtration and disinfection, bathing and recreation, irrigation, industrial use (process and cooling water).

## MATERIALS AND METHODS

This article presents the surface water quality results derived from reports on the results of the quality assessment of surface and groundwater from 2016-2022 (Environmental Protection Agency, 2022). It includes organized data collected during the examination of biological quality elements used to evaluate ecological status and potential, along with physicochemical, chemical, and microbiological indicators of water quality in rivers, reservoirs, and groundwater across the Republic of Serbia. The assessment of surface water quality was conducted at 79 profiles across 47 watercourses, as well as at 6 profiles within the canal network and 2 reservoirs.
Typically, the water quality assessment is determined by comparing the measured results of various parameters against established water quality standards or guidelines. For this work, the results of the Cu, Zn, and Cr concentrations of surface water samples were compared with the threshold values (TV) of quality classes prescribed by the Regulation on Threshold Values for Pollutants in Surface and Ground Waters and Sediments and the deadlines for achieving them (Official Gazette of RS No. 50/2012). Threshold value is the EQS expressed as the concentration of an individual pollutant or a group of pollutants or pollution indicators in surface and groundwater which must not be exceeded in order to protect the environment and human health (Table 1). This regulation expresses limit values (TV) for Zn and Cu according to water hardness. After reviewing the results, it was determined that the water hardness in 95% of the samples ranged between 100 and 300 mg $CaCO_3$/L, and the limit values of 2000 µg/L for Zn and 112 µg/L for Cu were adopted.
The values of the priority and priority hazardous substances (Pb, Ni and Cd) were compared with the EQS values which are linked to the maximum allowed concentration (MDK) and to the values of average annual concentrations (PGK) of priority substances (Table 1). PGK is the average value of concentrations measured over the course of a year for individual pollutants or groups of pollutants in surface that must not be exceeded to prevent serious irreversible long-term consequences for ecosystems and the MDK is the maximum concentration of an individual pollutant or a group of pollutants in surface waters that must not be exceeded in order to prevent serious irreversible consequences for ecosystems. Both are prescribed by the Regulation on

Threshold Values of Priority and Priority Hazardous Substances Polluting Surface Waters and the Deadlines for Achieving Them (Official Gazette of RS No. 24/2014). Similar to Zn and Cu, the limit values for Cd are also dependent of the water hardness and the results are categorized into appropriate classes based on the water hardness values, and the corresponding criteria have been applied.

## RESULTS AND DISCUSSION

The distribution of total metal concentrations is depicted in the box plots shown in Figure 1, while the descriptive statistics is presented in Table 1.

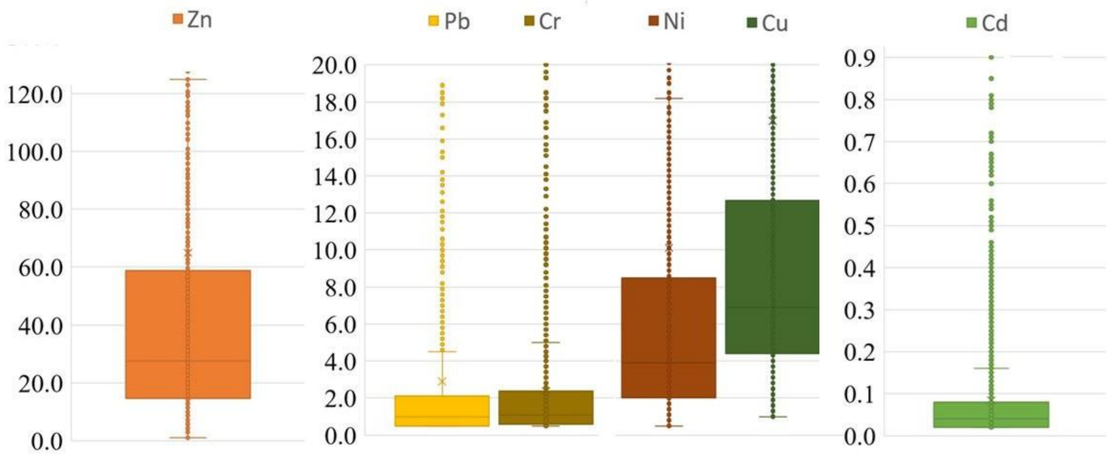


**Figure 1**. Box-plots (not all outliers and extreme values included) of the total metal concentrations detected in the surface waters from 2016-2022 in the Republic of Serbia.

Zn and Cu exhibited biggest values range followed by Ni. The profile with the highest Zn concentration was Vrbica, recording 9530 µg/L in 2019 (river Zlatica in the Tisa catchment area) (Table 1). However, this value was noted only once, and it may have resulted from localized one-time pollution since subsequent measurements were much lower. A similar trend was observed at the Markovicevo profile (river Brzava in the Danube-Tisa-Danube catchment area), which had a concentration of 2412 µg/L in 2022, and at Hetin (river Stari Begej in the Tisa catchment area), which measured 2305 µg/L in 2019.

For Cu, the profiles with the highest contamination were also Vrbica (3221 µg/L in 2019) (Table 1) and Markovicevo (842.1 µg/L in 2022), both identified only once. The highest total Ni concentrations were found at Novi Sad (555.1 µg/L in 2020 from the river Danube) and Markovicevo (428.5 µg/L in 2022) while the highest content of dissolved Ni was found in river Tamis on profile Jasa Tomic (225.2 µg/L in 2019). It was also evident that during 2019-2020 all dissolved Ni concentrations on this profile were among the highest of all measured at the same period in the country.

Very high Pb concentrations were recorded in the river Ibar of the Zapadna Morava catchment area, with profiles Kraljevo (169.1 µg/L in 2022) and Raska (236.3 µg/L in 2022) showing very high levels throughout the observed period due to long-term pollution and increased turbidity. Cr and Cd were detected in approximately 70 % of all water samples, with the highest concentrations found in Raska (Cr = 73.3 µg/L in 2016) and Badovinci (Cd = 3.14 µg/L from the river Drina) (Table 1).
Based on the total concentrations of the heavy metals analysed, the most contaminated profiles were Markovicevo, Hetin, Raska, Kraljevo, Jasa Tomic and Vrbica.

**Table 1**. Threshold values and summary statistics of the total and dissolved heavy metal concentrations in the surface waters in Serbia (2016-2022).

| | Pb | Ni | Cd | Zn | Cu | Cr | Pb | Ni | (4) Cd | (5) Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total concentrations | | | | | | Dissolved | | | |
| | µg/L | | | | | | | | | |
| Min | <0.5 | <0.5 | <0.02 | <1 | <1 | <0.5 | <0.5 | <0.5 | <0.02 | |
| (1) $Q_1$ | 0.5 | 2.0 | 0.02 | 14.5 | 4.4 | 0.6 | <0.5 | 1.2 | <0.02 | |
| Median | 1.00 | 3.90 | 0.04 | 27.55 | 6.90 | 1.10 | <0.5 | 2.2 | <0.02 | |
| (1) $Q_3$ | 2.1 | 8.5 | 0.08 | 58.8 | 12.67 | 2.37 | <0.5 | 4.0 | <0.02 | |
| Max | 236.3 | 555.1 | 3.14 | 9530 | 3221 | 73.3 | 9.4 | 225.2 | 2.2 | |
| (1) IQR | 1.6 | 6.5 | 0.06 | 44.3 | 8.27 | 1.77 | <0.5 | 2.8 | <0.02 | |
| Range | 235.8 | 554.6 | 3.12 | 9529 | 3220 | 73.5 | 9.15 | 224.9 | <0.02 | |
| Mean | 2.90 | 10.11 | 0.08 | 65.01 | 16.97 | 2.38 | 0.55 | 4.56 | 0.03 | |
| Count | 2196 | | | | | | 2348 | | | |
| PGK | * | * | * | * | * | * | 1.2 14 | 4 | 0.25 | 0.15 |
| (2) MDK | | | | | | | | 34 | 1.5 | 0.9 |
| (3) TV | * | * | * | 2000 | 112 | 50 | * | * | * | * |

(1) Q1- value under which 25% of data points are found when they are arranged in increasing order. Q3- is the value under which 75% of data points are found when arranged in increasing order. Interquartile Range (IQR): the difference between Q3 and Q1,

(2) Regulation on Threshold Values of Priority and Priority Hazardous Substances Polluting Surface Waters and the Deadlines for Achieving Them (Official Gazette of RS No. 24/2014)

(3) Regulation on Threshold Values for Pollutants in Surface and Ground Waters and Sediments and the deadlines for achieving them (Official Gazette of RS No. 50/2012)

(4) Treshold values (PGK, MDK) for water hardness >200 mg $CaCO_3$/L

(5) Treshold values (PGK, MDK) for water hardness between 100 and 200 mg $CaCO_3$/L

As already mentioned, the total Cu, Zn, and Cr concentrations water samples, were compared with the TV of quality classes prescribed by the Regulation on Threshold Values for Pollutants in Surface and Ground Waters and Sediments and the deadlines for achieving them (Official Gazette of RS No. 50/2012) while the values of the Pb, Ni and Cd dissolved concentrations were compared with the MDK and PGK determined by the Regulation on Threshold Values of Priority and Priority Hazardous Substances Polluting Surface Waters and the Deadlines for Achieving Them (Official Gazette of RS No. 24/2014). Percentage of the total number of samples that meet the limit values regulated by the already mentioned guidelines are presented on the Figure 2.

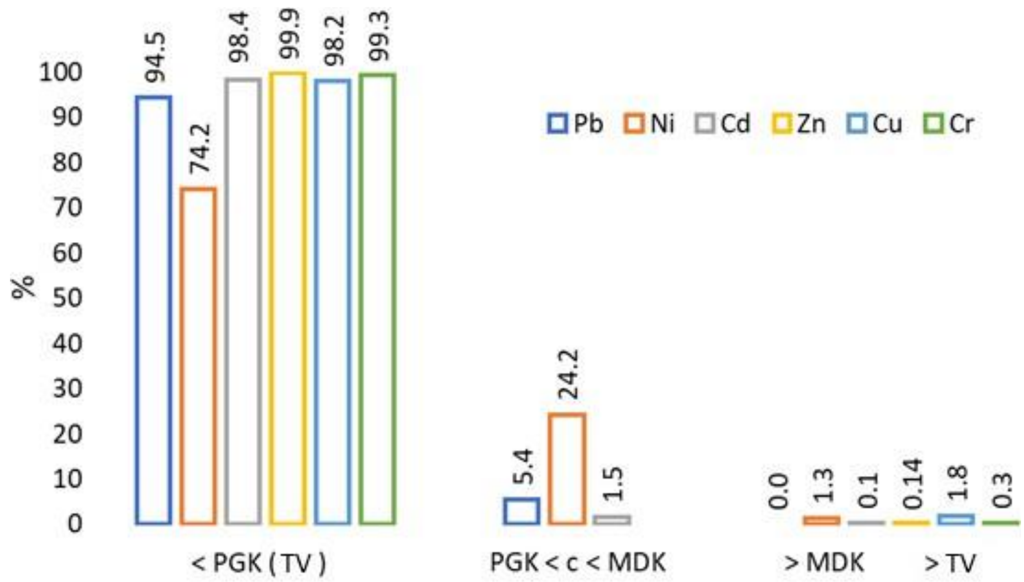


**Figure 2**. Percentage of the total number of samples that meet the limit values for good/moderate/poor/bad ecological status regulated by the Official Gazettes of RS No. 50/2012 (TV) and No. 24/2014 (PGK, MDK).

It illustrates that a very small percentage of all samples, in terms of total concentrations of Zn, Cu, Cr, and dissolved Pb, Ni, and Cd, exceeded the threshold values (TV) for Zn, Cu, and Cr or the maximum allowable concentrations (MDK) for Pb, Ni, and Cd, failing to meet the criteria for good ecological status. Ni was identified as the most problematic metal, with the highest number of samples (569 out of 2,348) exceeding the permissible concentration guideline (PGK), resulting in a classification of moderate to poor ecological status. Additionally, 1.3% of the samples were identified as water bodies with bad ecological status. As mentioned earlier, the Jasa Tomic profile accounted for 1.3% of these occurrences, being recorded four times during 2019-2020, which resulted in a bad ecological status indicating that the surface water cannot be used in any purpose. The same applies to the Hetin profile in 2019 (95.8 and 74.8 µg/L) and 2022 (108.7 and 94.5µg/L).

Compared to Ni, the highest percentage of samples that did not meet the criteria for good ecological status (1.8%), are those based on Cu content (40 samples). Among all profiles, the most problematic included Hetin 5 times, Jasa Tomic, Markovicevo, and Novi Becej 3 times each, and Srpski Itebej 2 times.

## CONCLUSIONS

Based on the concentrations of the observed heavy metals and relevant regulations, several profiles were identified as water bodies which didn't meet the criteria for good ecological status. The most problematic profile was Srpski Itebej (river Begej, Danube catchment), with 7 samples exceeding limits, followed by Novi Sad (Danube-Tisa-Danube canal Savino Selo), Hetin, Jasa Tomic, Markovicevo, and Novi Becej (river Tisa, Danube catchment), each with 6 problematic samples. The most polluted sample was recorded at the Vrbica profile in April 2019, showing the highest concentrations of Zn (9530 µg/L), Cu (3221 µg/L), and Cr (55.3 µg/L). It signifies a severely degraded aquatic ecosystem, with very low possibility of biodiversity and high levels of pollutants. This water body failed to achieve the minimum ecological quality standards. However, these elevated concentrations were observed only once and may result from recent contamination likely linked to anthropogenic activities.

This study highlights that although many monitored water bodies exhibited low heavy metal pollution levels, some water bodies particularly the Ibar, canal DTD, Velika Morava, Tamis and Tisa rivers demonstrated elevated concentrations that require special attention.

In summary, the continuous monitoring of surface water quality in Serbia ensures compliance with regulatory standards aimed safeguarding environmental and human health. While elevated concentrations of heavy metals do exist, overall trends suggest good ecological status in the majority of monitored water bodies.

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