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ORIGINAL RESEARCH PAPER

COMPARATIVE ANALYSIS OF THE WATER QUALITY AT MUREȘ RIVER BASIN BASED ON MEASURED PARAMETERS AND WATER POLLUTION INDEX

Elena-Violeta Blidar[1, 2], Simona Gavrilaş[2], Claudiu-Ștefan Ursachi[2], Simona Perța-Crișan[2], Florentina-Daniela Munteanu[1,2,*]

[1] *"Aurel Vlaicu" University of Arad, Interdisciplinary School of Doctoral Studies, 2-4 Elena Drăgoi Str., Arad, Romania*
[2] *"Aurel Vlaicu" University of Arad, Faculty of Food Engineering, Tourism and Environmental Protection, 2-4 Elena Drăgoi Str., Arad, Romania*

*Corresponding author: florentina.munteanu@uav.ro

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Abstract: The present study focuses on monitoring water quality in the Mureş River basin, analyzing three sections (Săvârşin, Arad, Nădlac) from 2017 to 2020. Key parameters such as *p*H, electrical conductivity, dissolved oxygen (DO), chemical and biochemical oxygen demand total nitrogen, phosphates, chromium, copper, zinc, arsenic, and phenol were evaluated using statistical analysis and a global pollution index. The findings confirm the null hypothesis, showing that parameter variations across sections are random and have no significant influence from specific industrial or agricultural activities. Statistical results align with the global pollution index, validating the analysis.

Keywords: *aquatic ecosystem, ANOVA parameters, null hypothesis, physicochemical parameters, watercourse*

INTRODUCTION

All ecosystems require clean, high-quality water for their life and development, making it one of the most crucial elements of different habitats [1 – 4]. Their ability to supply society's demands for food, energy, and water, as well as essential commodities and services such as clean air, climate regulation, and biodiversity, has grown increasingly critical in the twenty-first century [5 – 7]. These resources are more stressed due to enhancing economic activity, shifting land use, population growth, and climate change, but freshwater environments are particularly vulnerable. They face threats such as pollution from industrial and agricultural activities, habitat destruction, and over-extraction for human use, which can significantly impact the quality and quantity of water available [2, 8 – 15]. This vulnerability should be a cause for concern and a call to action for their preservation.

With the increasing number of companies and population growth, the demand for clean water has become a global challenge for governments. In response, numerous nations have implemented regulations governing water management, a crucial step in preserving the cleanliness and quality of water. Water security has emerged as a significant challenge, and understanding the quality and quantity of the world's water resources is crucial [16 – 24]. It is worth noting that rivers, a key source of clean water, are essential for irrigation and drinking water, further underscoring the importance of these regulations [25 – 30].

Hydrological, atmospheric, meteorological, topographical, and rock and soil composition characteristics are among the natural elements that impact water quality [31]. Anthropogenic activities have caused long-term physicochemical changes in water [8, 13, 15, 32 – 34].

Creating water quality assessment sections to regulate the discharge of pollutants and monitor pollution sources is a frequently used technique for assessing the water quality in river basins [35 – 37]. A water quality index, which thoroughly assesses water quality, is an essential instrument in environmental monitoring. This index makes categorizing water samples into different safety levels easier by combining several criteria into a single numerical value [38].

As part of the Danube basin, Mureș River has a large human population, several well-known pollution issues, many wastewater treatment plants along the river that use comparable technology, and a diversity of habitats in the watershed, making it attractive for the present study. Moreover, in the Mureș River basin, there are over 300 first-order control sections, of which 65 are in fast, daily information flow, and 250 are in first-order slow international flow, monthly analysis, and other second-order sections.

The water quality assessment in the Mureș River basin aligns with European laws on hydrology, specifically the Water Framework Directive [39] and the Flood Risk Assessment and Management Directive [40]. These directives are crucial in establishing a framework for water protection, ecosystems, and pollution reduction. They emphasize principles such as achieving environmental objectives for water bodies, managing anthropogenic impact, and, most importantly, engaging the population in water management to ensure community participation.

The current interest in the quality of surface water, especially rivers, has led to the development of methods for determining water pollution indexes, which can facilitate the development of strategies for efficient water resource management and pollution control measures.

The quantitative management of the basin's surface water resource is guided by principles that ensure fairness, sustainability, and efficiency. These principles include cost recovery, the user pays, equal access to water resources, and the rational use of water resources. These principles play a significant role in the comprehensive management of the basin's water resources.

The Mures River provides water for agriculture, aquaculture, human consumption, industrial activities and aquatic organism habitat. However, the excessive urbanization of the region, intensive agricultural practices, and the discharge of industrial and domestic wastewater have all impacted the river's waters. In this regard, the current study set out to assess the overall quality of the water in three different river sections over four years and to compare the findings of the statistical analysis with a suggested global pollution index that was applied to the measured parameters in Mures River.

MATERIALS AND METHODS

Study areas

The Mureş river basin is located in the center and west of Romania. It is flanked on the north by the Criş and Someş river basins, on the south by the Banat river basin (Jiu and Olt), on the west by Siret, and on the east by the Hungarian border. It is bounded by the Eastern, Southern, and Western Carpathians, and the lower part is located in the center of the Tisza plain (Figure 1**)**.

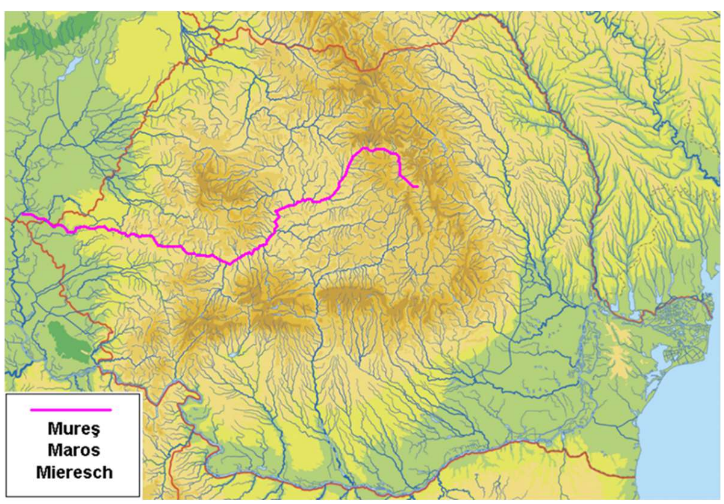

Figure 1. *Map of Mureș river (https://ro.m.wikipedia.org/wiki/R%C3%A2ul_Mure%C8%99)*

The Mureș River basin covers an area of 28,540 km^2, including the Ier Canal, the main watercourse with a length of 761 km, and the coded hydrographic network (798 cadastral rivers of which 59 have areas less than 10 km^2), covering a distance of 10,861 km and a density of 0.39 km·km^{-2}. This basin represents 11.97 % of Romanian territory and has various phenomena monitored in the information system (ABA Mureș, 2021).

Data collection

This study assessed samples from three sections of Mures River water for the following parameters: *p*H, electrical conductivity, dissolved oxygen (DO), chemical and biochemical oxygen demand (BOD5 and COD-Cr), total nitrogen, phosphates, chromium, copper, zinc, arsenic, and phenol. The sampling was performed according to the rules mentioned in the Romanian legislation [41].The four-year sampling period, from 2017 to 2020, involved yearly values. All analyses were performed in accredited laboratories according to national legislation requirements [42].
The study focused on determining the statistically significant differences in the data recorded for the considered parameters for the collected water samples from three sections of the Mureș River. The areas are upstream (Săvârșin) and downstream (Nădlac) compared to Arad city. The selected sections of the Mureș River present interest as the watercourse could be a source of irrigation water, while the possible polluters along the way may impose special treatments. Another important element relates to the fact that the stream is a transfrontier one, and it has to respect the specific legislation, considering that it could be used for agricultural purposes and/or drinking by the communities subsequently situated.

Data analysis

The statistical Fisher test (F test, ANOVA: Single Factor) was used. In this context, the H0 and H1 hypotheses were formulated.
- H0 - the data series do not differ, the differences being random, which indicates that each zone's specific industrial and agriculture activity did not influence the variation of the targeted parameters during the analyzed period.
- H1 - the data series differ, meaning some anthropic operations might impact the considered parameters.

The series variance ratio (Table 1) was compared using the data statistical analysis in the MS Excel package.

1 factor (BOD5/COD-Cr/DO/Salinity/alkalinity/total phenols/Dissolved Cr/Dissolved Cu) on 3 sectors;
4 replies (2017-2020).

Table 1. *Variables considered in the statistical analysis*

Independent variable	Dependent variable	Constant elements
Săvârșin	BOD5/COD-Cr/DO/salinity/alkalinity/total phenols/Dissolved Cr/Dissolved Cu	Zone position
Arad		Temperature periodicity
Nădlac		Precipitation regime periodicity

Another essential aspect considered in this study was the calculation of the overall pollution index based on the methods described by Zaharia [42].
The calculation of the overall pollution index is based on the methods described by Zaharia [43, 44].
Initially, the quality index was determined using the subsequent formula:

$$EQ_i = \frac{C_i}{MACi} \quad (1)$$

where EQ_i denotes the parameter's quality index, C_i is the parameter's measured value, and MAC_i is its maximum allowable value for the parameter *i*.
Following the EQ_i calculation, each parameter was given an Evaluation Score (ES_i), determined using the values shown in Table 2.

Table 2. *The quality index (EQ_i), evaluation score (ES_i), and environmental impact on pollution level for the River Mureş Basin sampling sites*

Quality index (EQ_i)	**Evaluation score (ES_i)**	**Impact on the environment**
$EQ_i = 0$	*10*	*A body of water untouched by the human activities*
$0.00 < EQ_i \leq 0.20$	*9*	*Industrial activities impact the water body, albeit this impact cannot be measured.*
$0.20 < EQ_i \leq 0.70$	*8*	*Industrial activity impacts water bodies, but not to the same extent as level 1, the highest authorized limit. Alertness level: potential repercussions*
$0.70 < EQ_i \leq 1.00$	*7*	*Industrial activity impacts water bodies, but only to the degree allowed under level 2 maximum allowable limits. Possible outcomes at this level of intervention*
$1.00 < EQ_i \leq 2.00$	*6*	*Industrial activity impacts the water body to an extent that exceeds the maximum allowable limit, or level 1. The effects are strong.*
$2.00 < EQ_i \leq 4.00$	*5*	*Industrial activity impacts water bodies to an extent that exceeds the maximum permissible limit, or level 2. The outcomes are adverse.*
$4.00 < EQ_i \leq 8.00$	*4*	*Water bodies are impacted by industrial activity, which goes beyond the permissible level 3. Adverse effects are evident.*
$8.00 < EQ_i \leq 12.00$	*3*	*The water body is at level 1 degradation. The consequences are lethal at typical exposure times.*
$12.00 < EQ_i \leq 20.0$	*2*	*The water body is degraded to level 2. Generally, effects take a short time to become lethal after exposure.*
$EQ_i > 20.00$	*1*	*The body of water has been so severely impacted by industrial activity that it is no longer fit for life*

Equation (2) was used to determine the overall pollution index for each sample in this investigation after the assessment score was assigned.

$$I_{GP}^{*} = \frac{100 * n}{ES_1 * ES_n + \sum_{i=1}^{n-1} ES_i * ES_{i+1}} \quad (2)$$

Where, I_{GP}^{*} is the Global Pollution Index, n is the number of parameters, and ES is the attributed evaluation score.

RESULTS AND DISCUSSION

In general, human activities impact the river's water quality. The remark is grounded on previously published research results, which proposed that human activity and water flows from upstream to downstream are the leading causes of rising water pollution. Different human activities have various water demands. Water is required in vast volumes for several industrial operations at different stages. Nevertheless, this process will generate other types of trash, depending on the procedures employed [10, 15, 23, 24, 37, 45 – 47].

Table 3 summarizes the parameters obtained after applying ANOVA single-factor analysis on the data series characteristics for the three sectors since the two-by-two individual comparisons do not prove statistically significant variances.

Table 3. *Representative ANOVA parameters resulted after comparing the different characteristic series values of the three Mureș sectors*

Characteristic evaluated	Source of Variation	SS	df	MS	F	P-value	F crit
BOD5	Between Groups	1.350366	2	0.675183	0.884144	0.446099	4.256495
COD-Cr		266.2279	2	133.1139	1.68091	0.239729	4.256495
DO		0.07067	2	0.035335	0.056319	0.945568	4.256495
Conductivity		6607.005	2	3303.503	0.81316	0.473553	4.256495
*p*H		0.019717	2	0.009858	0.738298	0.504778	4.256495
Total phenols		9.942917	2	4.971458	2.297317	0.156292	4.256495
Dissolved chromium		8.550122	2	4.275061	1.267298	0.327401	4.256495
Dissolved copper		5.746754	2	2.873377	0.160497	0.854105	4.256495
Dissolved Zn		32.66667	2	16.33333	1.266559	0.32759	4.256495

Increased BOD5 values were observed in 2017, with slight stabilization for the following three years for the Săvârșin section (Figure 2). A slightly different behavior was encountered for the Nădlac section, where the values follow a different dynamic than the ones for the Arad section.

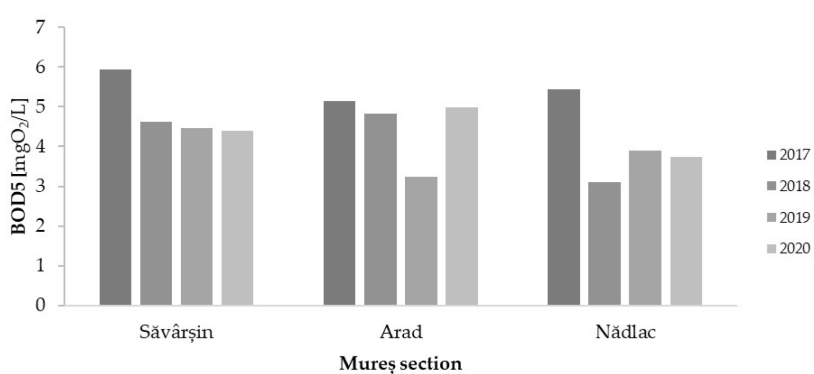

Figure 2. *Variation of biochemical oxygen demand in the Mureș sectors*

As in the case of two individual comparisons, neither of the three series could be observed to have significant differences. As P = 0.45 and $F < F_{crit}$ (0.88 < 4.26) (Table 3), the zero presumption is accepted, meaning that for the sections considered along the watercourse, there are no punctual possible anthropic or natural factors that could determine the statistically significant meaning of this parameter.

The data obtained for BOD5 and COD contrast the manifested behavior. In the case of BOD5, there are similar values in the three control points between 2018 and 2020 and comparable to 2017, where it was the highest of the studied interval. Instead, the tendency levels encountered for the COD are similar for the Arad and Nădlac sections, only in the last two years of the interval and a sizeable decrease compared to 2017. These findings reveal a constant level of biological oxidable compounds in the analyzed samples but a decreasing slope tendency of the inorganic ones.

For the Arad and Nădlac sections, the control points follow a similar pattern, with the COD-Cr values lower compared to the Săvârșin section (Figure 3). Such results reveal a decreased quantity of biotic and abiotic oxidizable material.

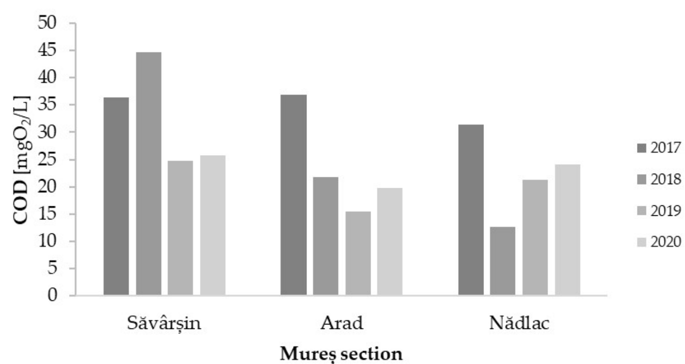

Figure 3. *Variation of chemical oxygen demand in the Mureș sectors*

Considering that P = 0.24 and $F < F_{crit}$ (1.68 < 4.26) (Table 3), it can be sustained that the situation proved to be similar also in the case of chemical oxygen demand, meaning the acceptance of H_0.

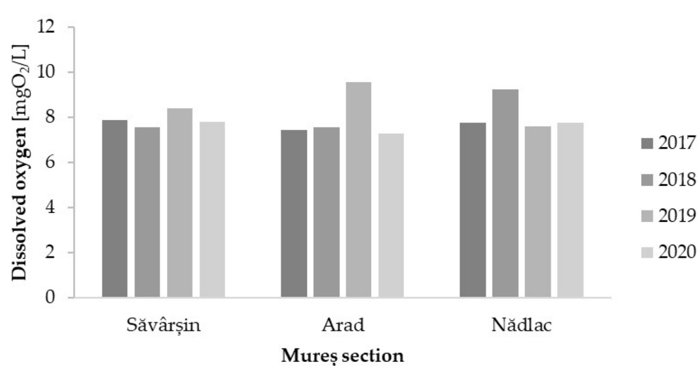

Figure 4. *Variation of dissolved oxygen in the Mureș sectors*

The tendency of the dissolved oxygen level determined in all the monitoring points, Figure 4, shows a constant behavior. Such results supported the data obtained for COD (Figure 3). Corroborating these findings, we can underline the capacity of the river supplies to maintain good aquatic life form development. Table 3 shows a good similarity of the serious values for dissolved oxygen, with a P = 0.94 instead of a significant variance.

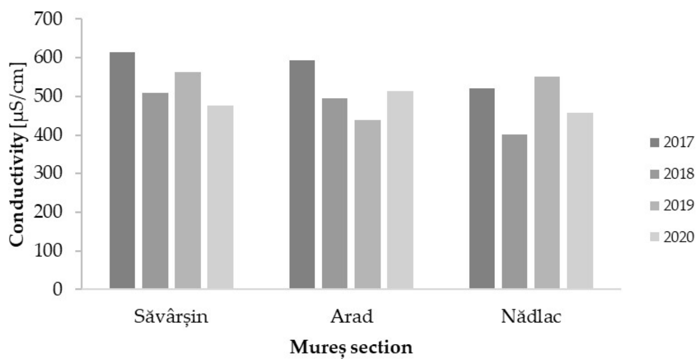

Figure 5. *Variation of conductivity in the Mureș sectors*

There are minimum differences between the Mures sampling points over 2017 and 2020, observing the results for conductivity presented in Figure 5. These findings are also sustained by the statistical Fisher test applied, which revealed a P = 0.47 and an $F < F_{crit}$ (0.81 < 4.26) (Table 3).

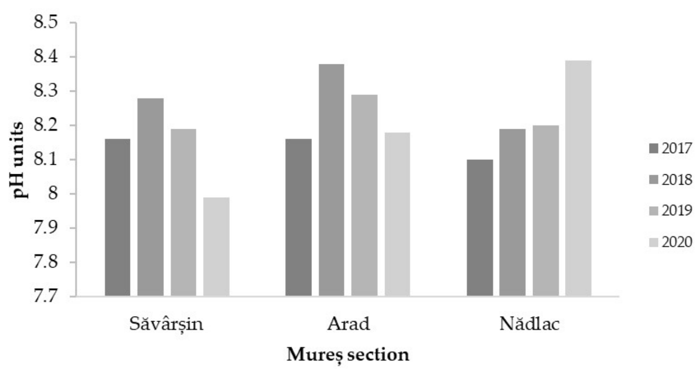

Figure 6. *Variation of pH in the Mureș sectors*

As shown in Figure 4, a constant tendency of the dissolved oxygen level was determined in all monitoring points in correlation with data obtained for COD (Figure 3). Corroborating these findings, we can underline the capacity of the river supplies to maintain good aquatic life form development. The trends have similarities in the case of Arad and Nădlac monitoring points for the total phenols content, Figure 7. Their average values for the periods analyzed are approximately half that of the Săvărșin. The observation completed the information highlighted by the BOD5, Figure 2, where these parameter values are higher in the Săvărșin section, knowing that an increased level of organic aquatic material after possible decomposition could determine the rise of the phenolic quantity.

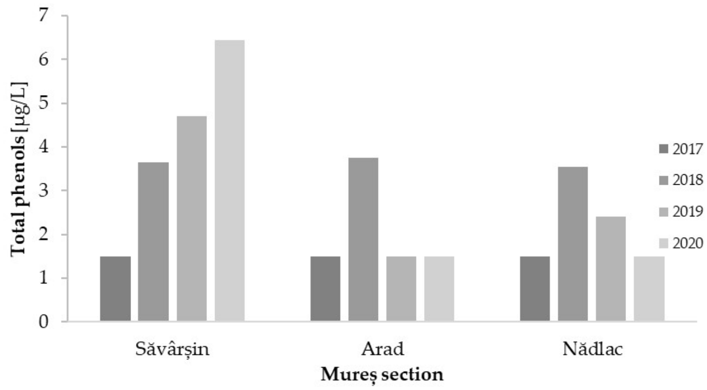

Figure 7. *Variation of total phenols content in the Mureș sectors*

The average quantity of chromium found throughout the surveillance interval is almost at the same levels for Săvârșin and Arad, and there is a slight decrease in the Nădlac case. Maintenance of approximately the exact quantities may be determined by adding supplementary chromium ions from the activities developed in Arad, such as galvanization. Another source could have an indirect path through Mureș contributors that cross a part of a county where various activities are carried out in the leather industry [48].

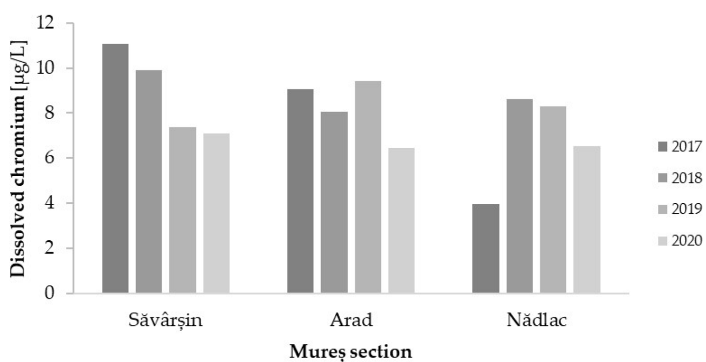

Figure 8. *Variation of dissolved chromium content in the Mureș sectors*

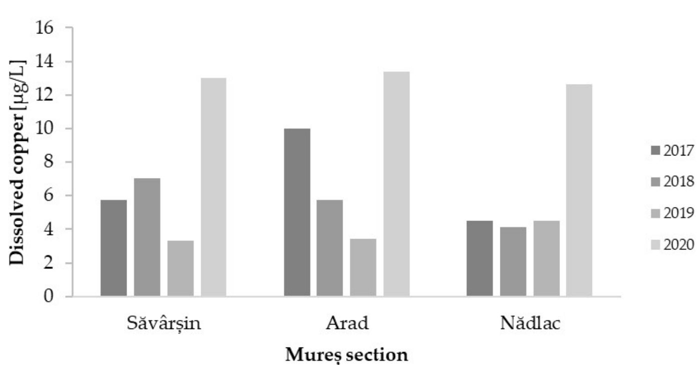

Figure 9. *Variation of dissolved copper content in the Mureș sectors*

The level of copper found in the Mureș control point registered a significant average increase of around 40 % in 2020 compared to the previous three years. Such a situation could be determined by the progress of the railway rehabilitation works located in the vicinity of the Mures Valley, which also required excavation works and implicitly the increase to a certain extent of the degree of soil erosion, respectively the facilitation of the washing by the waters from the precipitation of the former mining dumps in the area. These two situations can significantly contribute to the increase in the content of this mineral in river water [49].

In addition to the above-discussed parameters, the dissolved arsenic ($\mu g \cdot L^{-1}$) (Figure 10) and zinc ($\mu g \cdot L^{-1}$) (Figure 11) were determined. Regarding the arsenic measured concentrations, no modification of the values was determined. The situation is identical and independent of the watercourse sector or the year from the evaluated period. Such a context could be determined by the inactivity of mining exploitations along the river basin. Then, we can assume that the find quantity results from washing tailings heap by rain and/or the constant infiltration of water from the technological water treatment basins of the former mines situated upstream of Săvârșin. The current anthropic activities did not contribute to the variation of this parameter.

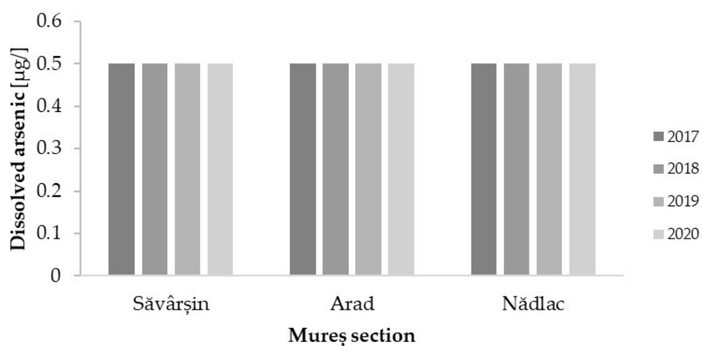

Figure 10. *Variation of dissolved arsenic in the Mureș sectors*

The obtained values are constant for the considered period, except for the first year (2017) when Zn in the Săvârșin section presented an increased level by almost 50 % compared to the following years (2018 - 2020) and nearly four times higher reported to Arad and Nădlac sections in the same year. For Arad and Nădlac, the differences between 2017 and 2018 - 2020 are 2.5 higher, but constant values were observed, beginning with 2018 (Figure 11).

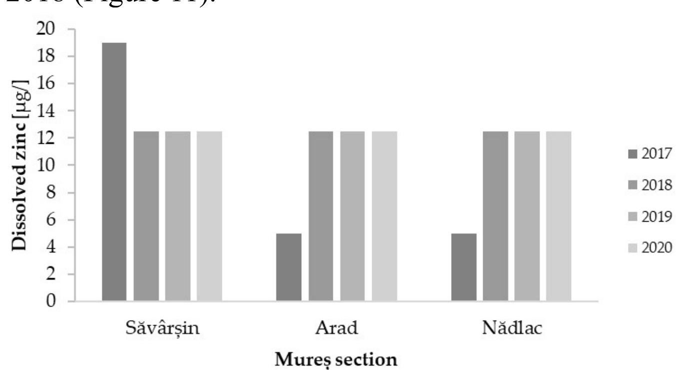

Figure 11. *Variation of dissolved zinc in the Mureș sectors*

The results obtained by applying the F test confirm the H_0 hypothesis with a P = 0.33 and $F < F_{crit}$ (1.27 < 4.26), Table 3. The three series that were compared are not significantly different, and arbitrary factors influence the parameter variation from the first year relative to the following three (2018 - 2020) included in the investigated interval.

Considering the method for the calculation of the overall pollution index based on the methodology described by Zaharia [42], the variation of the calculated general pollution indexes over the studied period for the Nădlac, Arad, Săvârșin sections is presented in Figure 12.

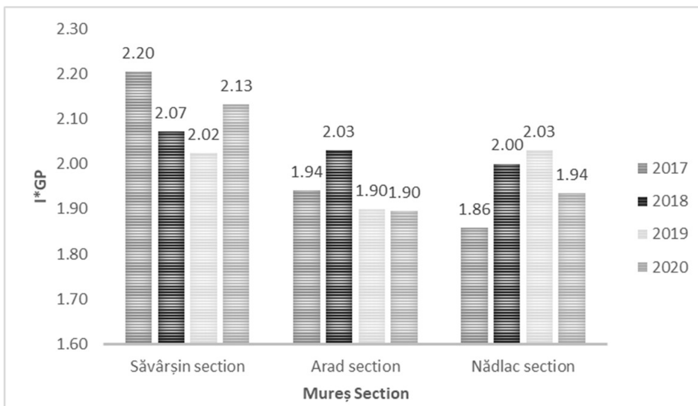

Figure 12. *Variation of the general polluting index for the Săvârșin, Arad, Nădlac sampling point sof Mureș River Basin*

For each of the considered sections of the Mureș River, the situations when the global pollution index had a value that indicated any discomfort to any forms of life from the water body were counted. Therefore, Table 4 summarizes this situation, showing that the most frequent is for the Săvârșin section, in agreement with the results from the statistical analysis.

Table 4. *Evaluation of the General Pollution Index*

Sampling point	Number of cases with I^*_{GP} higher than 2
	$2 \leq I^*_{GP} < 3$ (Water body subject to human activity, causing discomfort to the forms of life)
Săvârșin section	4
Arad section	1
Nădlac section	1

Considering the results presented in Table 4, the calculated general polluting indexes for the sampling point Săvârșin indicate that in this part of the Mureș River Basin, the impact of human activities determining discomfort for different media, I^*_{GP} between 2 and 3, is significantly increased in case of five parameters, compared with the other sectors. The attention values were registered for chemical and biochemical oxygen demand and total nitrogen. The registered values for the phenolics draw special attention, as this section found the highest values and, therefore, a high contribution to the final values of the calculated I^{*}_{GP}.

The mining operations of the Hunedoara (HD) and Arad (AR) counties are potential sources of remanent contamination. The analysis for the considered period suggests that the Săvârșin section is significantly affected by spills from the washing of tailings and copper (HD) and uranium (AR) ores by rainwater. The presence of heavy metal contaminants in river water, possibly from mining and other industrial activities, has been documented in the literature [50 – 53]. It is a well-known fact that the historical spilling of industrial substances due to massive industrialization has led to the current pollution levels [9, 54]. The lack of comprehensive cleanup efforts in both Counties is a matter of concern and requires urgent measures. Given that phenol does not dissolve in water, these historical industrial discharges likely continue to impact the pollution levels of the three water bodies of Mureș.

The next point of interest of the river course was that of Arad, considering the possible polluters that could be found in an urban area, mainly through the different sewages river discard [55]. These are considered potential vectors for several pollutants, both from industrial and household sources. The parameters that mainly contributed to higher calculated pollution indexes are chemical and biochemical oxygen demand, total nitrogen and, for the year 2018, the determined concentration of phenolics. An aspect that must be highlighted is the index values determined for the period 2017 - 2020. The mean value is 1.94, with a slight increase in 2018 by 0.03 over the limit of the safe zone. The behavior registered might be due to the implementation of the requirement related to the specific parameters of the urban and industrial wastewater discharged into tributaries.

The third control point was in the Nădlac sector. According to the data from Table 4, even though for this area there is only one registered value for the considered period, there is an urgency of implementing sustainable agricultural practices, as without these, the enterprises might represent serious river contaminant sources [56]. The same trend as the Arad point is observed for 2017 - 2020. The media of the General Pollution Index is similar, with the tendency to remain stable intolerance.

As an overview of the considered checking point, the evidenced differences between the Săvârșin and Arad, Nădlac in the period 2017 - 2020 might be highlighted. For these four years, the media of the Total Pollution Index increased by around 8 % in Săvărșin point. However, this situation presents an opportunity for improvement, which might be determined by the possible dilution effect exhibited by the small river tributaries from the area.

The level of annual precipitation further exacerbates these differences in the pollution index. Therefore, appropriate measures must be adopted to reduce the effects of agricultural, industrial, domestic, and residential activities in this section.

The findings of analyzing the quality parameters in the three sections (Săvârșin, Arad, Nădlac) are largely positive. This should provide reassurance, as most of the evaluated parameters fall within acceptable limits, with deviations for the parameters chemical and biochemical oxygen demand, total nitrogen, and phenol indicating a relatively healthy environment that can be maintained with continued vigilance.

CONCLUSIONS

The present study aimed to evaluate the water chemistry and quality of the Mureș River and determine which parameters impact the river's water quality. Using a statistical analysis based on the parameters measured on three sections of the Mureș River and a calculated global pollution index, important conclusions could be drawn, including important findings referring to the river's suitability for irrigation and potability. Over four years, three key locations were sampled and analyzed, comprehensively understanding the river's water quality.

By integrating chemical, physical, and biological indicators into a comprehensive index, stakeholders can better understand the extent of river pollution, identify priority areas for intervention, and track progress over time. Moreover, the use of the global pollution index is sustained by the statistical analysis that leads to similar observations. Developing such an index requires collaboration, standardization, and ongoing data collection and analysis efforts. It also underscores the urgent need for a sustainable water management strategy, which must be strictly enforced, especially for these two locations. Future research should focus on extending the number of sampling points considered along the Mureș River and enhancing the precision of water quality monitoring based on statistical analysis or global pollution indexes by considering other emerging contaminants and climate changes affecting the rivers.

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