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Correlation analysis of physicochemical parameters of the ecological status: a case study of Ibar River (Serbia)

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The aim of this work is to determine the mutual dependence of selected physicochemical and geochemical parameters using correlation analysis and to assess the ecological status of water quality. The goal of this method is the faster and more precise interpretation of monitoring data, identification of pollution sources, and assessment of river water quality. In this regard, we used the water quality parameters of river Ibar from the monitoring station "Raška". This station is the most representative one for determining water quality, because it is located in the middle course of the Ibar River and is under the heaviest pollutant loads. Comparative analysis showed a deviation of the measured values of biochemical oxygen demand (BOD_5), total organic carbon (TOC), NH_4^+ and PO_4^{3-} from the prescribed reference values, which indicates the presence of organic matters in the river Ibar. This water body was attributed moderate ecological status (class III), while the comparison with the limit values of priority and priority hazardous substances indicated the lack of good chemical status. Based on correlation analysis, it can be concluded that there is pluvial erosion and that oxygen regime is influenced by changes in atmospheric temperature rather than by organic pollutants.

Keywords: Correlation analysis, Ibar River, Ecological status, Chemical status

INTRODUCTION

Current problems of pollution of watercourses in the Republic of Serbia require an ecological status assessment, stressing on the significance of achieving sustainable water management principles set by the Directive 2000/60EC and preserving the environment [1]. Surface water quality is determined by natural processes (atmospheric conditions, level of precipitation and soil erosion), human activities (urbanization, industrial and agricultural activities) and increased exploitation of water resources [2, 3]. Discharges of industrial and municipal wastewater, as well as agricultural effluents are considered persistent sources of pollution [4]. The quality of surface waters faithfully reflects the impact of human activities, particularly in terms of impaired quality of watercourses and characteristics of aquatic ecosystems. According to the ranking of eighteen major river flows, the Ibar River has been classified as one of the most polluted surface waters in Serbia [5]. The Ibar River springs under Hajla Mountain in eastern Montenegro. Being 280 km long and with basin surface of 8060 km^2, it is the longest and the most important tributary of the Western Morava River [6]. In its middle course, the Ibar River becomes the recipient of unpurified industrial wastewater from the power plant "Obilic", the fertilizer factory in Kosovska Mitrovica and Mining, Metallurgical and Chemical conglomerate (MMCC) "Trepca". In this area, water quality of the Ibar River is also influenced by the factory “Leposavic” (processing of zinc and lead) and large number of flotation tailing dumps [7]. Ibar gorge is naturally predisposed to develop erosion and torrent processes that are conditioned by geomorphological conditions of the terrain (steep reliefs, steep slopes), geological conditions of the terrain (high erodibility rocks, intensive sediment yield) and poor protection of hillside cliff vegetation (poorly afforested area, bare land).

The Republic Hydrometeorological Service of Serbia (RHSS) monitors the water quality of the Ibar River at the measuring stations “Batrage”, “Raška” and “Kraljevo”. Monitoring station “Raška” is the most representative one in terms of determining water quality due to the fact that it is located in the middle course of the Ibar River, with the highest pollutant loads.

The aim of this paper is to assess water quality of the Ibar River at the monitoring station “Raška” by determining ecological and chemical status and to identify pollution on the basis of correlations between water quality parameters with the aid of multivariate statistical analysis.

EXPERIMENTAL

The enactment of the Regulation on establishment of surface and groundwater bodies

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and the Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of groundwaters enabled the conditions for RHSS monitoring in accordance with the requirements of the EU Water Framework Directive [8-10].

Ecological status indicates the quality of the structure and functioning of an aquatic ecosystem joined to surface waters and classification in line with the special Regulation [8]. Ecological status of the river is classified as Excellent (Class I), Very good (Class II), Good (Class III), Poor (Class IV) and Very poor (Class V) according to chemical and physicochemical quality elements which are significant for biological elements of a given surface water and surface water body [9]. According to the Regulation on establishment of surface and groundwater bodies, the Ibar River is classified as aquatic water body of the Type-2 (large rivers, dominance of middle layers). Current regulation defines target allowable concentrations of certain parameters for given classes of ecological status of surface waters (Table 1).

For the purpose of assessment of the current water quality of the Ibar River at the monitoring station "Raška", the ecological and chemical status was determined in accordance with the Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of groundwaters and regulation on limit values for priority hazardous substances which pollute surface water and the deadlines for achieving them [10, 11]. The paper analyzes the latest available data by RHSS for 13 water quality parameters, those being: the flow rate (Q), water temperature (T), pH, suspended matter (SM), dissolved oxygen (DO), BOD_5, TOC, chemical oxygen demand (COD), NH_4^+, PO_4^{3-}, Cl^- and P [12].

The reference condition indirectly defines the goal that aquatic body must achieve. Therefore, the values of these parameters are compared with reference values which define the condition of a water body in which changes of physicochemical and biological parameters are considered negligible, i. e., there is a low level of changes in the natural water quality of the Ibar River [13].

Multivariate statistical methods were used to characterize and evaluate water quality and they are a useful tool for determination of weather and seasonal variations due to natural and anthropogenic impacts. Correlation analysis explains the connection of parameters by monitoring the basic factors that are not directly visible. High correlation of data in the analysis (positive or negative) represents a high possibility that the data are influenced by the same factors, while relatively non-correlated data are influenced by different factors, which is the axiom of the analysis. The software package *Statistica7.0* is applied.

The indicators of the water quality are mutually correlated, and Pearson's correlation coefficient was used for measurement of the intensity of their stochastic connection. Pearson's correlation coefficient is the measurement of the intensity and direction of linear connection of the two parameters [14]. The obtained matrix of Pearson's correlation coefficient enables identification of dependence, that is, strength and direction of connections between variables [15].

Table 1. Chemical limits of the classes of ecological status for aquatic bodies of Type 2.

Parameter	Units	I-II	II-III	III-IV	IV-V
pH	-	6.5-8.5	6.5-8.5	6.5-8.5	<6.5/>8.5
DO	[mg L^{-1}]	8.5	7.0	5.0	4.0
BOD_5	[mg L^{-1}]	1.8	4.5	6.0	20.0
TOC	[mg L^{-1}]	2.0	5.0	7.0	23.0
NH_4^+	[mg L^{-1}]	0.05	0.1	0.8	1.0
NO_3^-	[mg L^{-1}]	1.5	3.0	6.0	15.0
PO_4^{3-}	[mg L^{-1}]	0.02	0.1	0.2	0.5
P	[mg L^{-1}]	0.05	0.2	0.4	1.0
Cl^-	[mg L^{-1}]	50.0	100	-	-

Basic characteristics of Pearson's correlation coefficient (r) are as follows:

- The value of the coefficient is within the interval from -1 to 1. If r is negative, the connection between variables is also negative (high values of one variable correspond to low values of the second variable); if r is positive, the connection between variables is positive (high values of one variable correspond to high values of the second variable; low values of one variable correspond to low values of the second variable).
- If $r = \pm 1$, there is a complete linear connection between two variables.
- If the variable is in correlation with itself, then $r = 1$.
- If $r = 0$, two variables are uncorrelated, which does not mean that they are independent.
- If two variables are independent, then $r = 0$ [14].

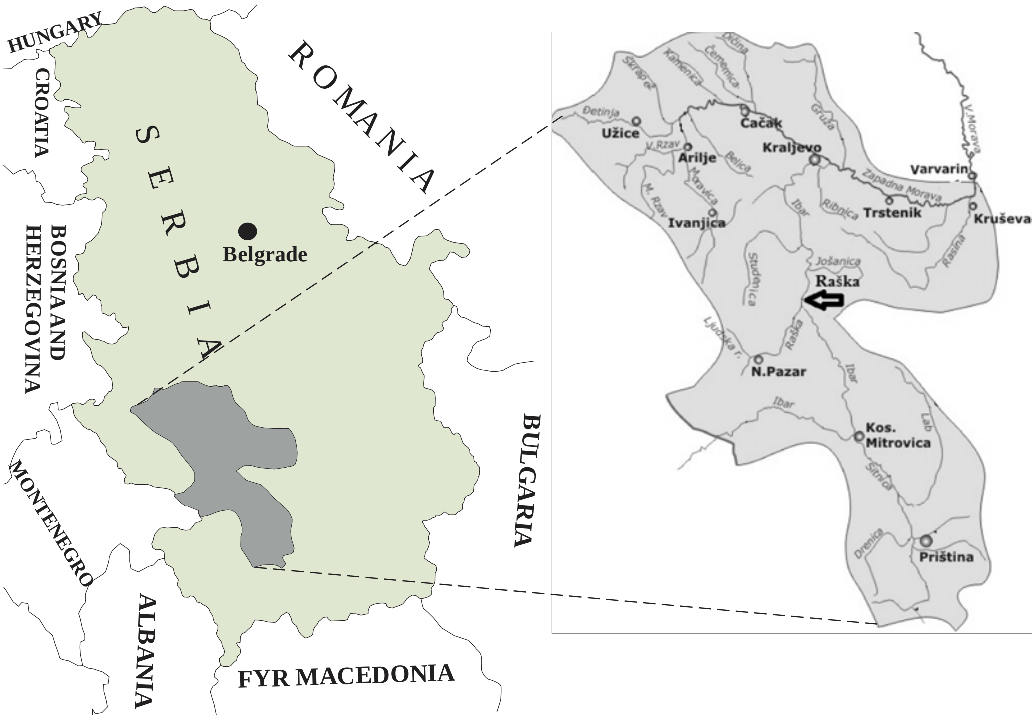

Figure 1. Location of the monitoring station „Raška“.

In this paper, we have monitored the value of Pearson's correlation coefficient that is higher or equal to 0.8, which corresponds to strong and significant mutual dependence between the parameters. Monitoring station "Raška", 93 km away from the mouth of the West Morava River, is the most exemplary one for the assessment of the Ibar River water quality taking into account its undeniable pollutant loads and its status of the major hydrological station (Figure 1).

RESULTS AND DISCUSSION

The values of hydrological, chemical and physicochemical parameters of Ibar River water quality at the monitoring station "Raška", as well as their mean values are presented in Table 2. Measured pH values show the basic character of the Ibar River water, whereas parameters with the highest variability are Q, SM, BOD_5 and COD. High volume discharge of the Ibar River from January to April (Q >50 m^3 s^{-1}) was conditioned by precipitation or snow melting (Table 2).

Table 2. Values of hydrological, physicochemical, and chemical [mg L^{-1}**]** parameters for monitoring station "Raška"

Parameter	Sampling date											Average
	16.01.	14.02.	09.03.	08.05	18.06.	08.07.	19.08.	02.09.	08.10.	07.11.	16.12.	
Q [m^3 s^{-1}]	42.4	32	40.1	35.3	53.9	15.9	11.4	14.7	17.6	14.7	19.4	27.0
T [°C]	4.2	5.2	8.0	14.0	14.0	17.6	18.0	15.2	10.4	10.8	3.0	10.9
pH	8.4	8.4	8.4	8.5	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
SM	1.9	14.0	47.0	55.0	11.0	7.0	24.0	11.0	23.0	4.0	3.0	19.8
DO	11.0	10.7	10.9	8.8	9.9	8.3	7.7	9.5	8.8	9.0	12.6	9.7
BOD_5	nd	2.8	2.6	3.4	2.9	1.4	3.1	1.7	3.1	2.0	2.4	2.5
TOC	7.3	5.2	4.7	4.3	3.7	3	3.7	3.2	4.1	4.2	3.1	4.2
HPK	nd		12.4	11.0	nd	11.2	nd	3.5	10.0	6.0	8.0	8.9
NH_4^+	0.8	0.4	0.4	0.1	0.2	0.3	0.2	0.5	0.1	0.1	1.0	0.3
NO_3^-	1.5	1.8	1.6	0.6	1.1	1.4	2.0	0.2	1.0	0.4	0.7	1.1
PO_4^{3-}	0.4	0.1	0.2	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1
TP	0.4	0.2	0.2	0.5	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Cl^-	10.0	9.0	8.0	9.0	7.0	15.0	20.0	16.0	10.0	16.0	12.0	12.0

Nd:-not detected

Table 3. The comparison between the measured values of physicochemical parameters and their reference values.

Physicochemical parameters	Comparison
pH	within the limits
DO	within the limits
BOD_5	deviates
TOC	deviates
NH_4^+	deviates
NO_3^-	within the limits
PO_4^{3-}	deviates

By comparing the values of the physicochemical parameters with their reference values, the deviation of BOD_5, TOC, NH_4^+ and PO_4^{3-} from the allowed limits was determined (Table 3). Organic matter and nutrients loading in the middle course of the Ibar River is attributed to the inflow of a large number of untreated municipal and industrial wastewater as well as to coastal erosion. Ecological status, according to the European Water Framework Directive, is an expression of the quality of the structure and functioning of aquatic systems associated with a surface water body [9]. The results of ecological status assessment in terms of physicochemical parameters of the water quality at the monitoring station "Raska" are presented in Table 4.

Table 4. Ecological status of the Ibar River at the monitoring station "Raška".

Physicochemical parameters	Ecological status
pH	I
DO	I
BOD_5	II
TOC	II
NH_4^+	III
NO_3^-	I
PO_4^{3-}	III

The ecological status of the Ibar River water quality at the monitoring station "Raška" is classified as Moderate (class III), due to exceeding values of parameters that define good status NH_4^+, PO_4^{3-} and TP.

The values of the indicators of surface water pollution by organic matter (BOD_5 and TOC) exceed the reference values for an excellent ecological status and, therefore, correspond to a good ecological status. NH_4^+ occurs due to bacterial decomposition of dissolved organic matter that comes into the recipient by municipal water discharge or rinsing of agricultural land [4, 16]. If the pH is greater than 9, ammonia in the molecular form is toxic to the living world [16, 17]. The largest part of the phosphorus pollution of surface water appears as a consequence of municipal and industrial wastewater treatment [4].

The assessment of the chemical status based on the comparison between the concentration of priority and priority hazardous substances and their allowed average year concentrations (PGK) and maximum allowable concentration (MDK), in accordance to the Resolution, is presented in Table 5.

When assessing chemical status, the first and the second group of environmental quality standards (EQS) were taken into account; therefore, EQS implies the concentration of individual priority substance or group of priority substances in surface waters that should not be exceeded with the aim to protect the environment and human health. The concentrations of priority substances such as Cd, Pb and Hg and their compounds exceed the limits prescribed by EQS, which makes us conclude that a good chemical status of the Ibar River was not achieved. Increased concentrations of heavy metals in this part of the Ibar River are the result of the confluence of mining and industrial wastewater, as well as wastewater from flotation and metallurgical dumps.

Heavy metals dissolved in surface waters are less stable and extremely toxic due to their ability to accumulate in the aquatic organisms, thus reaching the food chain [18-20]. The matrix of Pearson's coefficients of water quality parameters of the Ibar River at the monitoring station "Raška" is presented in Table 6. A strong negative correlation between DO and T ($r = -0.86$) confirms the theory which claims that oxygen becomes more soluble in water at low temperatures, while a strong positive correlation between DO and NH_4-N ($r = 0.9$) is explained by ammonification of nitrogen circulation cycle which indicates the organic origin of nitrogen compounds in the aquatic ecosystem [21]. Low correlation of DO with BOD_5 and COD indicates that the oxygen regime is under a greater influence of atmospheric conditions rather than the presence of organic pollutants in water. The matrix shows a strong positive correlation between Q, pH and SM ($r = 0.97$, $r = 0.91$, respectively), as expected, because the content of suspended matter increases in case of higher flows due to erosion and sediment resuspension [14]. Great number of phosphorus transformations occur in the fresh waters, and for this reason organic and inorganic forms dissolved in water make the total phosphorus. It is important that both high and low pH values can influence the complexation of

Table 5. Assessment of chemical status according to the concentration of priority and priority hazardous substances

Substances	PGK [μg L^{-1}]	MDK[μg L^{-1}]	Chemical status
	Organic		
Alachlor	$<2\times10^{-3}$	$<2\times10^{-3}$	good
Anthracen	$<5\times10^{-4}$	$<5\times10^{-4}$	good
Atrazine	$<1\times10^{-3}$	$<1\times10^{-3}$	good
Chlorfenvinphos	$<1\times10^{-2}$	$<1\times10^{-2}$	good
Chlorpyrifos	$<5\times10^{-3}$	$<5\times10^{-3}$	good
Cyclodiene pesticides	$<1\times10^{-2}$	-	good
Total DDT	$<1\times10^{-3}$	-	good
p, p'-DDT	$<1\times10^{-3}$	-	good
Diuron	$<2\times10^{-3}$	$<2\times10^{-3}$	good
Endosulfan	$<5\times10^{-3}$	$<5\times10^{-3}$	good
Fluoranthene	$<5\times10^{-4}$	$<5\times10^{-4}$	good
Hexachlorbenzene	nd	$<1\times10^{-3}$	good
Hexachlorobutadiene	nd	$<1\times10^{-3}$	good
Hexachlorocyclohexane	$<1\times10^{-3}$	$<1\times10^{-3}$	good
Isoproturon	$<1\times10^{-3}$	$<1\times10^{-3}$	good
Octylphenol	$<1\times10^{-3}$	-	good
4 - (1,1, 3,3 - Tetramethylbutyl)	nd	6.1×10^{1}	good
Phenol	$<5\times10^{-4}$	$<5\times10^{-4}$	good
Naphthalene	$<1\times10^{-3}$	$<1\times10^{-3}$	good
(4- (para) Nonylphenol)	$<1\times10^{-3}$	$<1\times10^{-3}$	good
Pentachlorobenzene	$<1\times10^{-3}$	-	good
Pentachlorophenol	3×10^{-2}	3×10^{-2}	good
Terbutryne	nd	3×10^{-1}	good
	Inorganic		
Ni	2×10^{1}	3.4×10^{1}	good
Pb	7×10^{o}	2.4×10^{1}	good
Cd	4×10^{-1}	1.4×10^{0}	good is not achieved
Hg	5×10^{-2}	1.0×10^{-1}	good

nd-not detected

Table 6. Correlation matrix of water quality parameters at the monitoring station "Raška"

	Q	T	pH	SM	DO	BOD_5	HPK	NH_4^+	NO_3^-	PO_4^{3-}	TP
Q	1.00	0.03	0.97	0.91	0.05	0.75	0.52	0.21	0.05	0.34	0.93
T		1.00	0.21	0.26	0.86	0.32	0.11	0.57	0.18	0.05	0.16
pH			1.00	0.93	0.22	0.66	0.43	0.34	0.13	0.32	0.96
SM				1.00	0.36	0.79	0.48	0.47	0.05	0.01	0.97
DO					1.00	0.03	0.26	0.90	0.25	0.16	0.20
BOD_5						1.00	0.44	0.28	0.07	0.14	0.77
HPK							1.00	0.32	0.81	0.44	0.31
NH_4^+								1.00	0.13	0.13	0.34
NO_3^-									1.00	0.31	0.26
PO_4^{3-}										1.00	0.04
TP											1.00

phosphorus with the tendency to accumulate by binding to organic matter. At increased flow, there is positive correlation between pH and TP (r = 0.97), that is, pH and SM (r = 0.93), which indicates that the natural balance of circulating phosphorus significantly depends on the value of these indicators of water quality. Also, the interdependency of matrix parameters DO, T and NH_4^+, as well as PO_4^{3-} and COD is the consequence of water pollution due to agricultural practices, appearance of leachates from farms as well as scattered illegal dumps and industrial wastewater discharges into the Ibar River.

The result of parameter correlation analysis results shows the overall synergistic effect of complex biochemical processes occurring in aquatic ecosystems of the Ibar River due to the above mentioned atmospheric and anthropogenic impacts.

CONCLUSION

The ecological status of water quality of the Ibar River at the monitoring station "Raška" is classified as moderate (class III) which is a sign of deviation from the required water quality. Comparative analysis showed that certain parameters, BOD_5, TOC, NH_4^+ and PO_4^{3-} exceeded their reference values. It was concluded that good chemical status was not achieved, due to the increased concentrations of heavy metals, cadmium, lead and mercury and their compounds which exceed the limits prescribed by EQS.

Multivariate statistical analysis, expressed by the Pearson's coefficients matrix, demonstrates the synergy of correlation between water quality parameters and identifies the pollution sources which have an impact on the ecological status of the Ibar River. The most significant correlations between parameters, i.e. the values of Pearson's coefficient above 0.8, clearly show the cause of impaired water quality and indicate the need to improve the existing monitoring implementation. The importance of preserving and improving the water quality of the Ibar River implies considering the actual quality of water at the monitoring station "Raška", which is affected by the combination of loads due to: weather conditions, catchment pluvial erosion and sediment resuspension, the inflow of mining and industrial wastewater, leachate wastewater from flotation and metallurgical waste damps. The conducted two-stage methodology, the assessment of water quality and correlation analysis suggest the need for operational monitoring with the aim to monitor the improvement of the water quality of the Ibar River after the implementation of anti-pollution programmes.

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КОРЕЛАЦИОНЕН АНАЛИЗ НА ФИЗИКОХИМИЧНИТЕ ПАРАМЕТРИ НА ЕКОЛОГИЧНИЯ СТАТУС: ПРИМЕР С РЕКА ИБАР (СЪРБИЯ)

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(Резюме)

Предмет на настоящата работа е определянето на взаимозависимостта между избрани физикохимични и геохимични параметри с помощта на корелационен анализ и оценката на екологичния статус на качеството на водата. Разработката цели по-бързо и по-точно интерпретиране на мониторинговите данни, идентифициране на източниците на замърсяване и оценка на качеството на речната вода. За целта са използвани данните за качеството на водата от мониторинговата станция „Рашка”. Тази станция е най-представителна за оценка на качеството на водата, тъй като се намира в средното течение на река Ибар и е подложена на най-тежко замърсяване. Сравнителният анализ показва отклонение на измерените стойности за биохимично необходим кислород, тотален органичен въглерод, NH_4^+ и PO_4^3 от предписаните референтни стойности, което сочи за наличие на органична материя в реката Ибар. Водата в тази река е оценена със среден екологичен статус (клас III), а сравнението с граничните стойности за приоритетни и приоритетни вредни вещества свидетелства за отсъствие на добър химичен статус. На основата на корелационния анализ може да се заключи, че е налице плувиална ерозия и режимът на кислорода се влияе повече от промени в атмосферната температура, отколкото от наличие на органични замърсители.