## WATER QUALITY OF THE PANNONIAN BASIN RIVERS DANUBE, SAVA, AND TISA AND ITS CORRELATION WITH AIR TEMPERATURE IN SERBIA

## by

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The rivers Danube, Sava and Tisa belong to the Black Sea river basin and they flow through many European countries, while in Serbia they flow through the Pannonian flatland. The water quality of these rivers, which is affected by complex anthropogenic activities and natural factors, is one of important factors that are taken into account in the evaluation of development sustainability of this region. Using the correlation analysis in this paper we tested the impact of air temperature as a natural factor on certain parameters indicating the water quality. A significant correlation was found between air temperature and total nitrogen oxides in the Danube of up to -0.744, namely of -0.740 on the Tisa, and -0.299 on the Sava. A significant correlation was found in electrical conductivity - up to -0.793 on the Danube, -0.226 on the Tisa, and 0.380 on the Sava. Correlation links were found between air temperature and oxygen, Biochemical oxygen demand, as well as suspended matters saturation percentage, but their correlation values are significantly lower. Based on the results of the research it was concluded that air temperature had low effect on changes in water quality during the year and that anthropogenic *impact was far more dominant.* 

Key words: air temperature, water quality, Danube, Sava, Tisa, Serbia

### Introduction

Water is essential for the survival of all living things. Part of this resource is stored in rivers, lakes, and reservoirs, which are freshwater resources used to satisfy environmental and human needs. Unfortunately, water quality of these resources is degraded [1].

Preservation and rational use of water resources, which are considered the most important segment of the environment and foundation of sustainable development, represents one of the most important issues in the 21<sup>st</sup> century. Water as resource is valued by quantity, quality, and status, whereby the quality implies the condition of the aquatic system expressed via physical-chemical, chemical, and biological indicators. In many settlements, rivers are the main

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sources of water for industry, agriculture, and water supply of households. Water quality is one of the most significant factors that have to be taken into account in the evaluation of sustainability of a particular region [2].

Water environment deterioration is a prominent issue in river basin management throughout the world, which has become a serious threat to water security. Surface water was gradually polluted due to natural and anthropogenic activities [3], such as water-rock interactions [4], industrial and municipal wastewater emissions [5], and nutrient losses [6].

Effects of climate change on the hydrologic cycle and water quality of a watershed are associated with large uncertainty from both the climate projections and the hydrologic modelling approaches. The interaction between climatic variables and hydrologic components involves multiple competing processes [7].

Climate change includes changes in precipitation, wind speed, incoming solar radiation, and air temperature, which directly influence rivers, lakes and reservoirs water quality by altering changes in stream flow and river water temperatures [8]. Increasing concern with potential impacts of climate change on river environmental problems has prompted some researchers [9, 10] to formulate theories and numerical models that simulate lake water quality elements. Most of the chemical and bacteriological processes are dependent on temperature, increasing the growth rates, which motivated some authors to focus on possible effects of global warming on stream temperatures [11-13]. Increasing the air and water temperatures may cause undesired occurrence of eutrophication, or overproduction of biomass. After the passage of the growing season for algae, they will become a substrate for microorganisms and passing through the food chain will result in an additional increase in silt in the stream and oxygen consumption [14].

The results of the analyses of climatic conditions in Serbia indicate that discussions on climate changes raise justified attention of general public, media and scientific circles [15]. Based on multi-annual researches, the Intergovernmental Panel on Climate Change (IPCC) concluded in its 4<sup>th</sup> report (2007) that climate changes in the second half of the 20<sup>th</sup> century were dominantly affected by anthropogenic influences [16]. The results of numeric climate modelling according to some of the IPCC scenarios were used in papers analysing forecasts of values of basic climate elements for our country in the forthcoming decades. These papers contain the assessment that by the end of the century, the average annual air temperature for the territory of Serbia will be 2.6 °C higher. The warming is not going to be equal throughout the year so that summer will be warmer by 3.5 °C, autumn by 2.2 °C, winter by 2.3 °C, and spring by 2.5 °C [17, 18].

The increase of rivers, lakes and reservoirs water temperature results in the increased biological activity and reduced diluted oxygen concentration [19]. Due to this, the water quality is usually poorer during the warmer period of the year, namely during spring and summer compared to autumn and winter. Many researchers have confirmed such a trend [20-22].

In this paper, we studied the effects of natural factors on water quality of the rivers Danube, Sava, and Tisa . The objective of the paper is to establish the impact of air temperature on certain parameters indicating the water quality based on a particular statistical method.

## Main characteristics of the studied area

Three most significant rivers in the Pannonian part of Serbia are the rivers Danube, Sava, and Tisa (fig. 1). The Danube river basin represents the most important non-oceanic water body which discharges into the Black Sea through a wide delta. Around 588 km of its length belongs to Serbia. The largest tributaries on the territory of Serbia are the rivers Tisa, Tamis, and the Danube-Tisa-Danube canal on the left and the rivers Drava, Sava, and Velika Morava on the right side. When it comes to the Danube section that flows through Serbia, it starts at Bezdan and flows to Prahovo. The Danube course through Serbia is 588 km long - 137.6 km are the shared sector with Croatia and 299.35 km with Romania [23]. Data from seven Danube river stations and five weather stations at part of the Serbian Pannonian basin were used for determining changes in water quality parameters. River stations are: Bezdan (CPD1), Bogojevo (CPD2), Novi Sad (CPD3), Slankamen (CPD4), Zemun (CPD5), Smederevo (CPD6), and

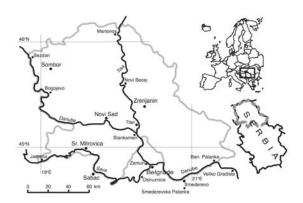


Figure 1. Studied rivers in the Pannonian part of Serbia

Banatska Palanka (CPD7). Weather stations are Sombor (MD1), Novi Sad (MD2), Belgrade (MD3), Smederevska Palanka (MD4), and Veliko Gradiste (MD5) (fig. 1).

The Sava river stretches 940 kilometres along the South-Eastern Europe. The surface of the basin is 95,720 km<sup>2</sup>. It is made of two spring branches, Sava Dolinka and Sava Bohinjka [24]. The Sava river enters Serbia near the village of Jamena, and after 204 km flows into the Danube river in Belgrade. On the Sava river, data were obtained from the three river stations, Jamena (CPS1), Sabac (CPS2), and Ostruznica (CPS3) and from two weather stations Sremska Mitrovica (MS1) and Sabac (MS2) (fig. 1).

The Tisa river basin occupies about 157,220 km<sup>2</sup> with the length of 966 km; it is the largest tributary of the Danube river. The basin of this river lies in the territories of five countries: Romania (47%), Hungary (29%), Slovakia (10%), Ukraine (8%), and Serbia (6%). Regulation works which were conducted during the 19<sup>th</sup> and 20<sup>th</sup> centuries, primarily in the middle and lower parts of the Tisa river, shortened the river by as much as 453 km, or from the former 1,419 km to the current 966 km [25]. The Serbian part is 164 km long. It enters Serbia to the south of the Hungarian city of Szeged and flows into the Danube river near the town of Slankamen. The Tisa river is one of the largest and economically and environmentally most important watercourses in Serbia. In fact, thanks to its favourable location and good navigational characteristics it has a potentially to be far more frequent passenger-cargo and nautical tourism traffic route [23, 25, 26,]. The biggest tributaries are Keres, Cik, Jegricka, and Budzak on the right and Zlatica and Begej to the left. On the Tisa river, data were obtained from the three river stations, Martonos (CPT1), Novi Becej (CPT2), and Titel (CPT3) and from Zrenjanin (MT1) weather station (fig. 1).

#### **Research material and methods**

The present paper uses the data of the Republic Hydrometeorological Institute of Serbia for the period 2004-2013 [27]. The results have been presented based on correlation analysis that was used to establish whether there is a corresponding intensity (level) of correlation and statistical significance between the dependent variables (parameters: conductivity,  $O_2$  saturation, biochemical oxygen demand – BOD, suspended matters, and total nitrogen oxides) and independent variables (air temperature).

The correlation analysis has been conducted between each hydrological and its closest weather station. The analysis and overview of impacts of air temperature that could affect water quality in that part of the Pannonian flow of the rivers Danube, Sava, and Tisa in Serbia is based on the results of system meteorological measurements carried out on the major (synoptic) weather station Sombor, Novi Sad, Zrenjanin, Sremska Mitrovica, Sabac, Beograd, Smederevska Palanka, and Veliko Gradiste.

The Pearson correlation test was applied to establish the variables with significant differences.

The correlation means the connection between variables while correlation coefficient means the measure based on which it can be concluded about the extent of their connection. The correlation coefficient indicates the extent up to which the changes in the value of one variable are accompanied by changes in the value of another variable [28]. The correlation coefficient between two accidental variables x and y, with the mean values  $\bar{x}$  and  $\bar{y}$  and standard deviations  $\sigma_x$  and  $\sigma_y$ , is defined by means of the formula:

$$r_{xy} = \frac{\sigma_{xy}^2}{\sqrt{\sigma_{xx}^2 \sigma_{yy}^2}} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}}$$
(1)

The correlation coefficient shows the rate of linear dependence between variables. If the values of r are closer to 1 or -1, the correlation between the analysed variables is higher. In case the value is equal to or it makes approximately zero, the variables are independent one from another, but the opposite case is not always exclusively true (namely, if two variables are mutually dependent their correlation coefficient can be 0) because the correlation coefficient defines only the linear dependence between variables.

The square correlation coefficient ( $r^2$ ), which is defined by identical formula that is squared, is used in the analysis of linear dependence between two variables:

$$r_{xy}^{2} = \frac{\sigma_{xy}^{4}}{\sigma_{xx}^{2}\sigma_{yy}^{2}} = \frac{\left[\sum_{i=1}^{\infty} (x_{i} - \bar{x})(y_{i} - \bar{y})\right]^{2}}{\sum_{i=1}^{n} (x_{i} - \bar{x})^{2} \sum_{i=1}^{n} (y_{i} - \bar{y})^{2}}$$
(2)

In this case, the value of  $r^2$  between two variables has to be positive in all cases [29].

## Results of correlation analysis and discussion

Values of the annual mean temperatures in the research period showed substantial increase compared to current climate normal period (1961-1990), defined by World Meteorological Organisation (www.wmo.int). Annual mean temperatures on all stations were higher in the range 0.8-1.4 °C in the period 2004-2013. Furthermore, temperatures trends in the research period (from 0.100 °C per year to 0.165 °C per year) showed increase compared to current climate normal period (from -0.012 °C per year to 0.010 °C per year). Registered temperatures increase have direct influence on the water quality (see *Conclusions*).

Electrical conductivity is the amount of total soluble salts, or total amount of diluted ions in water. The increase of air temperature in the Pannonian Basin results in more intensive water evaporation, which in turn increases the concentration of diluted salts in the remaining water that causes the increase of electrical conductivity [30]. Based on the aforementioned, electrical conductivity is the parameter that should be linked with air temperature, if set in positive

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correlation, namely the increase of air temperature should result in the increase of electrical conductivity of water. The results of the study show the correlation connection between low intensity on all profiles of the Sava river. The correlation rates (tab. 1) are lower than 0.4 and they have a positive denominator.

River	Control point		Conductivity	O <sub>2</sub> saturation	BOD	Suspended solids	Total nitrogen oxides
Danube	Bezdan (CPD1)	k	-0.640	0.199	0.002	0.256	-0.336
		р	0.000**	0.033*	0.980	0.005**	0.000**
	Bogojevo (CPD2)	k	-0.793	0.365	0.271	0.286	-0.697
		р	0.000**	0.000**	0.005**	0.003**	0.000**
	Novi Sad (CPD3)	k	-0.754	0.202	0.297	0.201	-0.744
		р	0.000**	0.028*	0.001**	0.028*	0.000**
	Slankamen (CPD4)	k	-0.652	0.201	0.229	0.180	0.144
		р	0.000**	0.036*	0.019*	0.060	0.410
	Zemun (CPD5)	k	-0.384	-0.075	0.154	0.110	-0.310
		р	0.000**	0.419	0.120	0.250	0.003**
	Smedervo (CPD6)	k	-0.199	-0.038	0.093	-0.045	-0.268
		р	0.030*	0.679	0.333	0.644	0.003**
	Banatska Palanka (CPD7)	k	-0.591	-0.064	-0.179	-0.235	-0.662
		р	$0.000^{**}$	0.512	0.065	0.015*	0.000**
Sava	Jamena (CPS1)	k	0.300	0.048	0.258	-0.116	-0.280
		р	0.001**	0.610	0.005**	0.212	0.004**
	Sabac (CPS2)	k	0.380	0.170	0.203	-0.186	-0.299
		р	$0.000^{**}$	0.066	0.029*	0.043*	0.002**
	Ostruznica (CPS3)	k	0.193	-0.076	-0.002	-0.131	-0.171
		р	0.035*	0.409	0.985	0.158	0.087
Tisa	Martonos (CPT1)	k	-0.226	-0.008	0.174	-0.065	-0.740
		р	0.014*	0.930	0.067	0.486	0.000**
	Novi Becej (CPT2)	k	-0.032	-0.205	0.110	-0.109	-0.509
		р	0.734	0.029*	0.243	0.249	0.000**
	Titel (CPT3)	k	-0.103	-0.014	-0.048	-0.098	-0.406
		р	0.276	0.880	0.613	0.303	0.000**

Table 1. Correlation analysis of the impact of air temperature on certain chemical water parameters

Note: k – correlation coefficient obtained based on the Pearson correlation test; \* p < 0.05; \*\* p < 0.01

The results of the analysis for the Danube river show entirely opposite results. The connection between these two parameters is highly emphasised, as shown in tab. 1 (correlation rates range from -0.199 CPD6 to even -0.793 CPD2). The correlation denominator is negative on all tested profiles. This situation can be explained by the significantly higher rate of

anthropogenic pollution in certain periods of a year. The main sources of anthropogenic pollution that have a strong impact at certain measuring points include waste water discharge from industrial plants, communal waste water discharge from settlements, drainage from agricultural land and municipal storm water [29]. An intensive anthropogenic impact is clearly seen on CPD1-CPD4. Downstream Slankamen (CPD4) the anthropogenic impact decreases, namely the values of electrical conductivity get lower. The results of the analysis for the Tisa river also show a negative correlation rate between air temperature and electrical conductivity, but the significance level on all CPT is very low. In the case of the river Tisa river, just as in the case of the Danube river, the anthropogenic impact of pollution is more dominant than that of natural factors such as climate change.

Oxygen is very important in maintaining the quality of aquatic ecosystems and is essential for the respiration of aquatic organisms [31]. Seasonal changes affect the diluted oxygen concentration. Higher temperatures result in faster photosynthesis and plant decomposition. At the end of the vegetation period, the decomposition of plant residues causes large oxygen consumption. Cold water can sustain more gas than hot water. As water is getting warmer it keeps less and less of diluted oxygen, which means that during the summer period the amount of diluted oxygen is limited by temperature.

If we analyse the mutual connection between the  $O_2$  saturation percentage and air temperature we see that there is a relatively low statistically significant connection between them (tab. 1). The correlation coefficient between these two parameters in the Danube river is very low at all control points. The correlation denominator is positive at CPD1-CPD4 control points, which is contrary to the fact that  $O_2$  saturation percentage reduces with the increase of air temperature, and vice versa. At control points CPD5, CPD6, and CPD7 there is a noted negative correlation rate that is not statistically significant. The reduction in the percentage of diluted  $O_2$  is largely affected by pollutants that reach surface waters by sewer spilling, bank erosion, washing from agricultural land, as well as nutrients that stimulate algae growth [30]. These are the facts that could justify a positive correlation at control points CPD1-CPD4, namely certain sources of anthropogenic pollution have stronger impact than water temperature so that the  $O_2$  saturation percentage is lower in the colder period of a year. When it comes to the Sava river, the correlation coefficient does not show its significance at any control points, while on the Tisa river a low correlation rate is registered only at CPT2. It is the matter of negative correlation, namely the reduction of  $O_2$  saturation percentage with the increase of air temperature.

The BOD is a measure of the amount of oxygen consumed by microorganisms in a water sample in order to oxidise organic carbon, which indirectly determines the amount of organic matter in water itself [32]. The increase in temperature causes the increase of BOD. Sources of organic materials in water can be natural (swamps, ponds, leaves falling, *etc.*), anthropogenic (food industry and waste water treatment) and diffuse (washing off of urban and agricultural areas).

The BOD is the parameter that shows low intensity correlation connection in relation to air temperature. Correlation rates (tab.1) are below 0.4 and they have positive denominator. Based on that, we conclude that BOD value increases with the increase of temperature. If we look at the results that refer to the Danube river, statistical significance can be noted at control points CPD2, CPD3, and CPD4, at control points CPS1 and CPS2 on the Sava river, while no statistical significance of these two parameters was noted on the Tisa river.

Suspended matters are closely related to soil and river bed erosion, with the transport of nutrients (in particular of phosphorus), metal, industrial waste water and chemicals that are used in agriculture [31].

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When it comes to suspended matters we also find a low correlation connection in relation to air temperature (tab. 1). The analysis of data that refer to the Danube river, we find that the correlation denominator is positive at first five control points (CPD1-CPD5), which shows that the amount of suspended matters increases with the increase of air temperature. Statistical significance was registered only at control points CPD1-CPD3. At control points of the Sava river (CPS1-CPS3) and the Tisa river (CPT1-CPT3) negative correlation denominators of these two parameters without statistical significance were found. The results that refer to the Sava and the Tisa rivers point to the increase of suspended matters with air temperature lowering.

Nitrate are of paramount importance due to their effects on aquatic life and the overall environmental health of a river system [33, 34]. Nitrogen substances cause eutrophication of watercourses and they stimulate organic production [35-37].

When it comes to the parameter of total nitrogen oxides, the correlation coefficient indicates that there is a significant correlation between this parameter and air temperature parameter (tab. 1). With regards of the Danube river, the results indicate a high correlation between these two parameters, as well as a negative correlation denominator. Based on these indicators we can conclude that the values of nitrogen oxide decline if the air temperature rises, and vice versa. Similar results have been confirmed in the paper by Raj Paudel *et al.* [38]. The correlation coefficient on the Danube river control points ranges from -0.268 at CPD6 to -0.744 at CPD3. Nitrogen discharge contributes significantly to the pollution of the Danube river in its downstream section. It is estimated that Serbia discharges annually around 14% of the total amount of discharged nitrogen. These values place Serbia at the third position according to the amount of discharged nitrogen among the Danube basin countries. When it comes to the Sava river, a low rate of negative correlation was registered CPS1 and CPS2 that is not statistically significant. On the Tisa river we registered a medium rate of negative correlation that ranges from -0.406 at CPT3 to -0.740 at CPT1.

### Conclusions

The results of the study of air temperature characteristics of the Pannonian basin in Serbia, as well as their correlation with the qualitative characteristics of water courses, show that there is a correlation connection. The correlation between air temperature and water qualitative elements is not permanent and its quantity depends on the period of the year and control points.

The biggest impact of air temperature is seen on nitrogen oxide concentration where the reduction of temperature increases the concentration of that parameter. In the conditions of high concentration of nitrogen in water, algae start pullulating suddenly. Once they die out, a large amount of oxygen is consumed to decompose organic matter. The lack of oxygen affects negatively the aerobic organisms in water, primarily fish. In the waters of the Danube and the Tisa rivers the reduced electrical conductivity was registered and it was in correlation with the increase of air temperature. A positive correlation between these two parameters was noted on the river Sava.

When it comes to other water quality parameters we could also see a certain correlation rate with air temperature, but that link is at a relatively low level. The increase of temperature results in the increase of  $O_2$  saturation percentage at the first three control points on the Danube river, as well as the decrease of  $O_2$  saturation percentage at all control points of the Tisa and the Sava rivers. The increase of BOD concentration on all rivers is directly connected with the increase of air temperature. Suspended matters are another problem since their presence is more significant in the period of lower temperatures on the Sava and the Tisa rivers, while the situation is reverse on the Danube river. Suspended matters fill the river canal with sediments and they are the compounds the oxidation of which requires microorganisms to consume oxygen. That endangers the species in water courses using oxygen. Two negative effects occur due to sedimentation: accumulation-depositing of mud in water courses and ecological damage due to reduced concentration of diluted oxygen that is below biological minimum.

Although the anthropogenic impact on the quality of watercourses is far more intensive based on this study it has been determined that natural factors can also affect up to a certain extent the increase or reduction of water pollution concentration during the year.

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