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TREND ANALYSIS OF WATER QUALITY PARAMETERS FOR THE NISAVA RIVER*

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Abstract. *The data of 12 water quality parameters have been daily monitored at the Nis station on the Nisava River during 2000-2004. The trend analysis was performed on monthly, seasonal and annual time series using the Mann-Kendall test, the Spearman's Rho test and the linear regression at the 5% significance level. The monthly results showed that significant trends were found only in pH, total hardness, Ca and* SO_4 *data. The results in seasonal series indicated that the significant trends were detected in pH, total hardness, Cl, Ca and* SO_4 *data. In annual series, the trends were insignificant at the 5% significance level*.

Key words: *trend analysis, water quality parameters, Mann-Kendall test, Spearman's Rho test, linear regression, Nisava River.*

1. INTRODUCTION

The trend analysis of water quality data is an important task in hydrology for understanding the changes of water quality parameters, planning streams and monitoring water quality. According to Liebetrau (1979), understanding long-term variations in selected water quality parameters represents one of four necessities of water quality monitoring. Besides, the trend analysis determines the measured values of a water quality parameter increase or decrease during a time period (Antonopoulos et al. 2001).

In recent years, various studies have been done for detecting water quality trends and changes across the world. Antonopoulos et al. (2001) analyzed the time series of monthly measured values of nine water quality variables and the discharge at the Sidirokastro station of the transboundary Strymon River in its Greek part using statistical and trend analysis methods for the period 1980-1997. They found that majority of the water quality parameters showed remarkable seasonal variations. Ferrier et al. (2001) identified spatial

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and temporal trends in water quality for the rivers of Scotland from 1974 to 1995. Besides, they investigated the relationships between nitrate and orthophosphate.

Simeonova et al. (2003) studied long-term trends of seventeen chemical indicators at nineteen sampling sites along the Struma River (Bulgaria) over the period 1989-1998. Their results indicated a lack of statistically significant trends for many of the sites. Gupta et al. (2005) performed a long-term study of temperature, pH, turbidity, suspended solid, salinity, dissolved oxygen, biochemical oxygen demand and ammonia nitrogen in a port and harbor region in India from December 1996 to November 2000. They presented the annual, seasonal and monthly variations of water quality parameters, followed by the correlation and factor analysis and showed that marine water quality results had no regular trend. Naddafi et al. (2007) tested the monthly measurements of 15 water quality parameters and the discharge at the Gatvand and Khorramshahr stations of the Karoon River. They used the Kolmogorov–Smirnov test to select the theoretical distribution which best fitted the data and found positive trends for the majority of water quality parameters.

Chang (2008) detected water quality trends for 118 sites in the Han River basin of South Korea for eight parameters between 1993 and 2002. He used a non-parametric seasonal Mann-Kendall's test and found that there were no significant trends in temperature, but total nitrogen concentrations increased for the majority of the monitoring stations. Moreover, approximately half of the stations exhibited no trends for dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, pH, suspended sediment and total phosphorus. Bouza-Deano et al. (2008) analysed 34 physical–chemical and chemical variables in surface water samples collected every month from thirteen sampling stations located along the Spanish Ebro River during the 1981–2004 period. The trend study was performed using the Mann–Kendall seasonal test and the Sen's slope estimator. Their results revealed parameter variation over time due mainly to the reduction in phosphate concentration and increasing pH levels.

Matsubara et al. (2009) tested pH monitoring data in central Japan using the Mann–Kendall method and reported a significant long-term declining trend in river water pH in several watersheds in Niigata and Gifu prefectures.

Awadallah et al. (2011) analysed total dissolved salts series on two main drains in the Eastern Nile Delta (Bahr Hadus and Bahr El Baqar drains) from 1984 to 2004. They used and compared both seasonal adjustment time series analysis and statistical trend detection tests and showed lower salinity levels in the Bahr Hadus Drain.

Tabari et al. (2011) analyzed sixteen water quality parameters at four stations along the Maroon River using the Mann–Kendall test, the Sen's slope estimator and the linear regression for the period 1989–2008. Their results indicated that significant trends were found only in Ca, Mg, SAR, pH and turbidity series.

In this study, water quality data from Nis station located at the Nisava River for the period 2000-2004 were used to analyse the existence of monthly, seasonal and annual trends of 16 water quality parameters. For this purpose, the Mann-Kendall test, the Spearman's Rho test and the linear regression at the 5% significance level were applied.

2. MATERIALS AND METHODS

2.1. Study areas

In the present study, the water quality parameters of the Nisava River (Serbia, South-east Europe) were analyzed. The spring of this river is located in Bulgaria, and the length of its course through Serbia is 195 km. It is a tributary of the South Morava River (Fig. 1) and its confluence is at Trupale village. The surface area of the river basin is 3,950 km^2 in total of which 2,713 km^2 belong to Serbia. Significant tributaries of the Nisava are: Kutinska, Crvena, Koritnicka, Jerma, Visocica and Temstica rivers. In the Nisava River valley there are the following towns and cities: Dimitrovgrad, Pirot, Bela Palanka and Nis. The water of the Nisava River, at the territory of the city of Nis, is used for drinking water supply, local irrigation on a small surface area, and for recreational fishing.

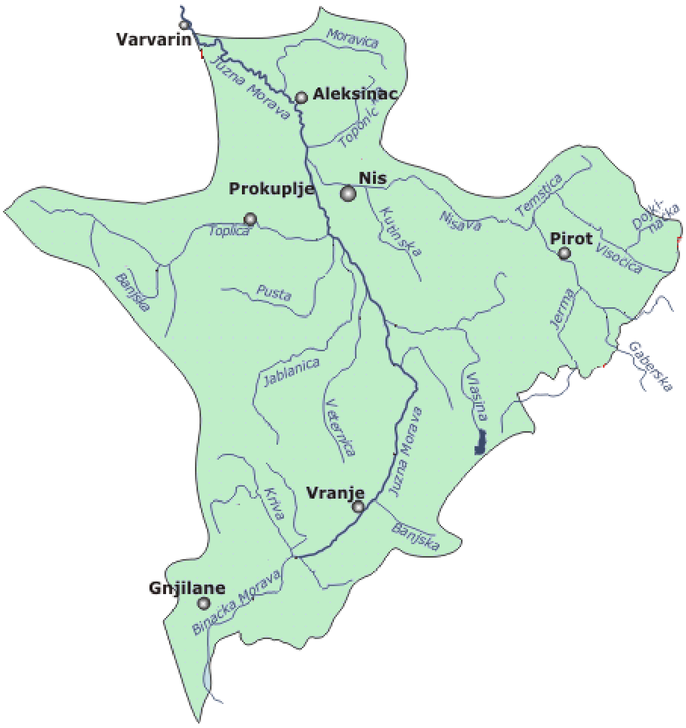

Fig. 1 South Morava basin

2.2. Water quality data

In the present study, series of daily water temperature (*T*, ^{o}C), electrical conductivity (*EC*, μS/cm), pH, biochemical oxygen demand (*BOD*, mg/l), dissolved oxygen (*DO*, mg/l), total hardness (^{o}dH), chlorides (Cl^-, mg/l), calcium (Ca^{2+}, mg/l), magnesium (Mg^{2+}, mg/l), nitrate (NO_3^-, mg/l), nitrite (NO_2^-, mg/l) and sulfates (SO_4^{2-}, mg/l) were analyzed.

The datasets were collected from Nis station from the period 2000 to 2004 and were obtained from the Public Utilities Company Naissus.

Statistical parameters of the time series of daily values of water quality parameters of the Nisava River at Nis hydrological station during 2000-2004 are summarized in Table 1, while the time series of the water quality parameters are illustrated in Fig. 2.

Table 1 Statistical parameters of the time series of daily values of water quality parameters of the Nisava River at Nis station during 2000-2004

Water quality parameter	Mean	Standard deviation	CV (%)	Skewness	Kurtosis	A	B
T (°C)	11.50	23.29	202.48	0.033	0.011	-	-
EC (μS/cm)	383.90	66.85	17.41	0.036	0.012	-	-
pH	8.27	7.58	91.69	$-2.319*10^{-6}$	$3.070*10^{-8}$	5	0.4%
BOD (mg/l)	1.99	1.13	56.75	-0.307	0.207	16	2%
DO (mg/l)	8.53	1.34	15.66	0.003	0.0004	1	0.1%
Total hardness (°dH)	11.98	2.03	16.91	0.856	0.813	-	-
Cl (mg/l)	6.68	2.41	36.10	-0.023	0.006	0	0%
Ca (mg/l)	78.65	250.06	317.96	$-6.888*10^{-5}$	$2.822*10^{-6}$	0	0%
Mg (mg/l)	8.80	4.31	49.05	12.469	28.906	2	0.2%
NO_3 (mg/l)	6.31	1.99	31.64	-0.016	0.004	41	5%
NO_2 (mg/l)	0.04	0.15	341.40	0.004	0.0006	276	23%
SO_4 (mg/l)	42.73	10.51	24.59	0.036	0.012	0	0%

CV: coefficient of variation; A: number of analyses whose result does not comply with regulations; B: percentage of analyses whose result does not comply with regulations

The statistic data analysis showed that a large majority of the results of analyses of almost all the water quality parameters is within predicted limits (Brankovic and Trajkovic 2007). There are numerous examples corroborating this assertion. Out of 952 analyses of the dissolved oxygen, only the results of one analysis do not comply with regulations. Only 2% of the analyses of biochemical oxygen demand do not comply with the regulations. Analyses of one parameter significantly does not satisfy the required quality, ie. nitrite (23% analyses whose result does not comply with regulations). The higher concentration of nitrites indicates occurrence of organic pollution. Microbiological pollution of the Nisava was not reduced by closing down the industrial facilities, because the main sources are sanitary waste waters. In the Nisava River, there is a high presence of pathogenic bacteria, protozoa, viruses and intestinal parasites. The received microbiological pollution obviously significantly exceeds the capacity of self-purification of the river.

The datasets were investigated for randomness, homogeneity and absence of trends. The Kendall autocorrelation test and the homogeneity tests of Mann–Whitney for the mean and the variance, were used for this purpose.

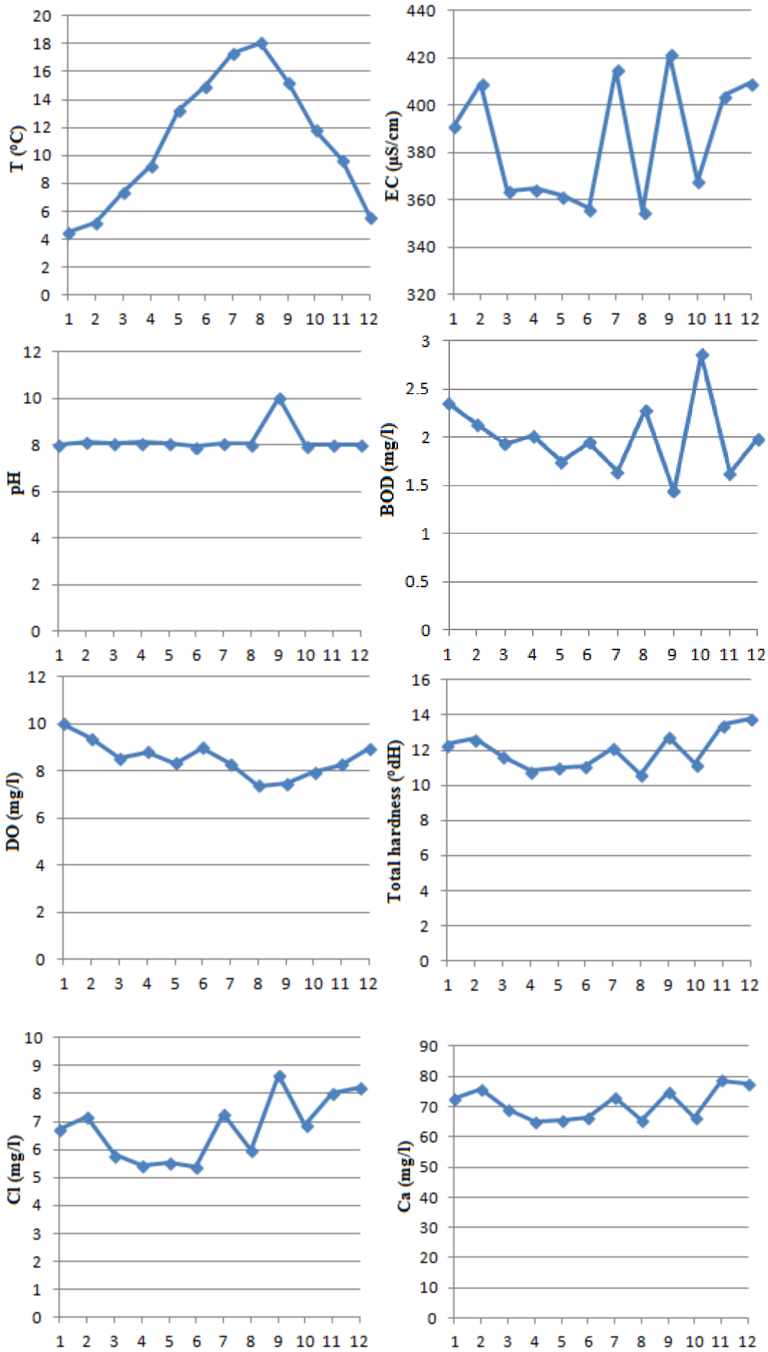

Fig. 2 Time series of the water quality parameters

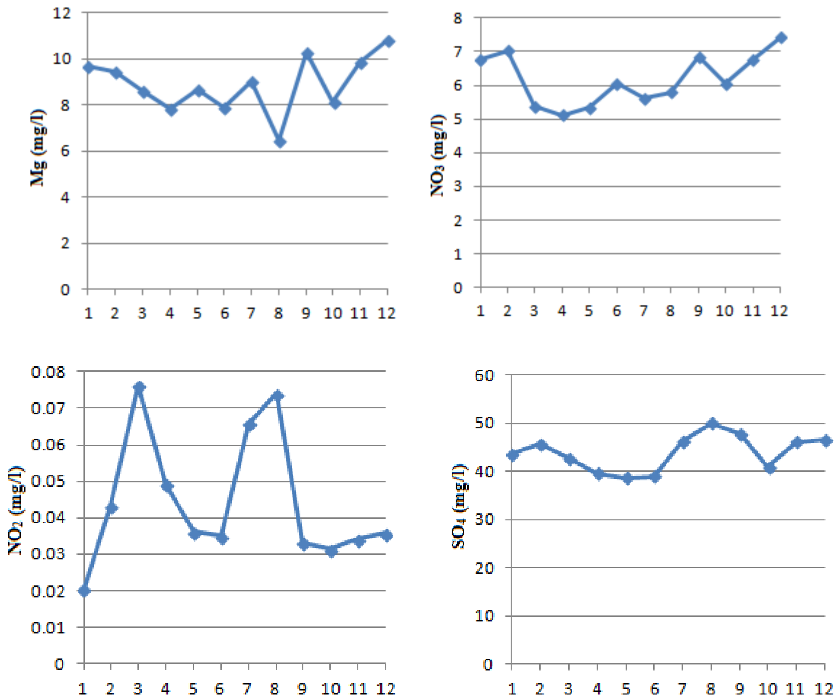

Fig. 2 (continued)

2.3. Trend analysis methods

Many statistical techniques have been developed to detect trends within time series such as Bayesian procedure, Spearman's Rho test, Mann-Kendall test, Sen's slope estimator. In this study, two non-parametric methods (Mann-Kendall and Spearman's Rho) and one parametric method (linear regression) were used to detect trends in the water quality parameters.

2.2.1. Mann-Kendall test

The Mann-Kendall test statistic *S* (Mann 1945; Kendall 1975) is calculated as

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \operatorname{sgn}(x_j - x_i) \tag{1}$$

where n is the number of data points, x_i and x_j are the data values in time series i and j ($j > i$), respectively and $\operatorname{sgn}(x_j - x_i)$ is the sign function as:

$$\operatorname{sgn}(x_j - x_i) = \begin{cases} +1, if\ x_j - x_i > 0 \\ 0,\ if\ x_j - x_i = 0 \\ -1, if\ x_j - x_i < 0 \end{cases} \tag{2}$$

If $n < 10$, the value of S is compared directly to the theoretical distribution of S derived by Mann and Kendall (Gilbert 1987). The null hypothesis (H_0) is rejected in favor of the alternative hypothesis (H_1) if S is positive and if the probability value in the theoretical distribution of S corresponding to the computed S is less than the a priori specified α significance level of the test. To test H_0 against the alternative hypothesis H_1 of a downward trend, reject H_0 and accept H_1 if S is negative and if the probability value in the theoretical distribution of S corresponding to the absolute value of S is less than the a priori specified α value. In this study, significance level of $\alpha = 0.05$ was applied.

2.3.2. Spearman's Rho test

The Spearman's Rho test is non-parametric method commonly used to verify the absence of trends. The null hypothesis (H_0) is that all the data in the time series are independent and identically distributed, while the alternative hypothesis (H_1) is that increasing or decreasing trends exist. The Spearman's Rho test statistic D and the standardized test statistic Z_D are expressed as follows (Lehmen 1975; Sneyers 1990):

$$D = 1 - \frac{6\sum_{i=1}^{n}(R(X_i) - i)^2}{n(n^2 - 1)} \tag{3}$$

$$Z_D = D\sqrt{\frac{n-2}{1-D^2}} \tag{4}$$

where $R(X_i)$ is the rank of ith observation X_j in the time series and n is the length of the time series and Z_D has Student's t-distribution with $n - 2$ degrees of freedom. The sample size in this study is $n = 5$.

Positive values of Z_D indicate increasing trends while negative Z_D show decreasing trends. At the 5% significance level, the null hypothesis of no trend is rejected if $|Z_D| > 2.571$.

The Spearman's Rho test has been frequently used to quantify the significance of trends in hydrological time series (Antonopoulos et al. 2001; Yue et al. 2002; Dave 2006; Naddafi et al. 2007; Shadmani et al. 2012).

2.3.3. Linear regression method

A linear regression method attempts to explain the relationship between two or more variables using a straight line. Regression refers to the fact that although observed data are variable, they tend to regress towards their mean, while linear refers to the type of equation we use in our models.

3. Results and discussion

3.1. Serial correlation of the water quality parameters

Autocorrelation is also sometimes called "lagged correlation" or "serial correlation", which refers to the correlation between members of a series of numbers arranged in time. Autocorrelation plots for the water quality parameters are presented in Fig. 3. As shown, positive serial correlations were obtained for the SO_4, DO and BOD, while all other water quality parameters had the negative serial correlations. The highest serial correlation of -0.764 was obtained for NO_2.. The lowest serial correlations of -0.764 was detected for NO_2.

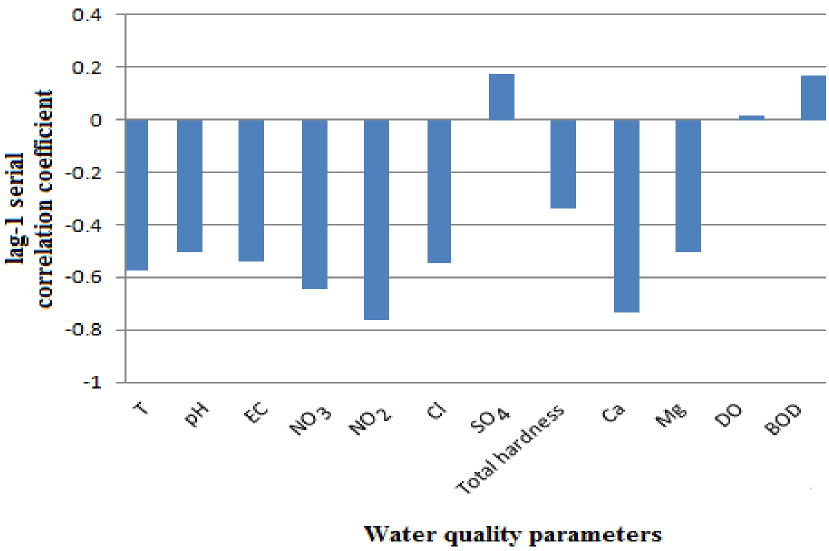

Fig. 3 Lag-1 serial correlation coefficient for the water quality parameters during the period 2000-2004

3.2. Trends of water quality parameters

3.2.1. Monthly analysis

Monthly trends of water quality data obtained by the statistical tests are given in Table 2. As shown, there were significant trends in February, April, May, August and November at the 5% significance level. Significant trends were observed in pH, total hardness, Ca, BOD, DO and SO_4 data. In particular, more than 75% of the significant trends were negative, while the positive significant trends were found in pH data in February and April.

Table 2 Results of the statistical tests for the monthly series of water quality parameters over the period 2000-2004

Water quality parameter	Test	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
		Month											
T (^oC)	Z_S	0.24	0.41	0.59	0.41	0.41	0.41	0.59	0.24	0.12	0.59	0.41	0.41
	Z_D	-1.30	-0.35	0.17	0.55	0.35	0.35	0.17	0.76	2.31	0.17	-0.55	-0.55
EC (µS/cm)	Z_S	0.24	0.12	0.24	0.59	0.41	0.24	0.24	0.24	0.24	0.41	0.41	0.24
	Z_D	1.30	1.70	1.00	-0.17	0.35	-1.30	-1.30	-1.00	0.76	0.55	0.55	0.76
pH	Z_S	0.12	**0.04***	0.12	**0.04***	0.24	0.59	0.59	0.24	0.12	0.41	0.24	0.59
	Z_D	1.70	**3.63***	2.31	**3.58***	0.76	0.17	0.17	-1.30	1.70	0.55	-1.00	0.17
BOD (mg/l)	Z_S	0.41	0.24	0.41	0.59	0.59	0.41	0.12	0.24	0.12	0.24	**0.04***	0.41
	Z_D	-0.55	-1.00	-0.55	-0.17	0.65	-0.55	-1.14	-0.65	-1.14	-0.65	**-3.48**	0.09
DO (mg/l)	Z_S	0.41	0.41	0.59	0.24	0.41	0.41	0.12	0.24	0.12	0.12	**0.04***	0.41
	Z_D	0.55	-0.55	0.17	-1.30	1.14	0.55	-1.14	-0.65	-1.14	-1.14	**-2.88**	-0.09
Total hardness (^{o}dH)	Z_S	0.41	0.41	0.41	0.24	0.59	0.24	0.24	**0.04***	0.41	0.59	0.59	0.41
	Z_D	1.00	0.55	0.55	-1.00	0.17	-1.30	-1.30	**-3.23***	0.55	0.17	0.17	0.55
Cl (mg/l)	Z_S	0.41	0.24	0.24	0.59	0.24	0.24	0.24	0.12	0.59	0.59	0.41	0.41
	Z_D	0.35	1.30	0.76	-0.17	-1.00	-1.30	-1.30	-2.31	0.17	0.17	0.000	0.55
Ca (mg/l)	Z_S	0.41	0.41	0.59	0.24	0.59	0.12	0.41	**0.04***	0.41	0.59	0.41	0.41
	Z_D	1.00	-0.35	0.00	-1.00	0.17	-2.31	-1.00	**-3.58***	0.55	0.17	0.00	-0.35
Mg (mg/l)	Z_S	0.12	0.41	0.41	0.41	0.12	0.59	0.59	0.41	0.24	0.24	0.41	0.41
	Z_D	1.70	0.35	0.35	0.55	-1.70	-0.17	-0.17	-0.55	1.00	0.76	0.55	0.55
NO_3 (mg/l)	Z_S	0.41	0.12	0.12	0.12	0.59	0.41	0.41	0.12	0.41	0.59	0.59	0.41
	Z_D	1.00	1.70	1.70	-1.70	0.17	0.35	-0.55	-2.31	0.35	0.17	0.62	0.29
NO_2 (mg/l)	Z_S	0.24	0.59	0.41	0.41	0.41	0.41	0.59	0.41	0.41	0.24	0.41	0.59
	Z_D	-0.76	-0.17	-0.55	-0.55	0.35	-0.29	-0.65	0.62	0.55	1.30	0.35	0.17
SO_4 (mg/l)	Z_S	0.24	0.24	0.24	**0.01***	**0.04***	0.12	0.24	0.12	0.41	0.41	0.12	0.12
	Z_D	-1.30	-1.30	-1.30	**-3.58***	**-3.33***	-2.31	-1.30	-2.31	-0.55	0.55	-2.31	-2.31

Z_S: Mann-Kendall test, Z_D: Spearman's Rho test
* Statistically significant trends at the 5% significance level.
Bold characters represent trends identified by 2 statistical methods together.

3.2.2. Seasonal and annual analysis

Results of the statistical tests for seasonal and annual series of water quality parameters during the period 2000-2004 are presented in Table 3. The majority of the trends in the spring, autumn and winter series (65% of the trends) were positive. On the contrary, 82% of the trends in summer series were negative.

Table 3 Results of the statistical tests for the seasonal and annual series of water quality parameters over the period 2000-2004

Water quality parameter	Test	Spring	Summer	Autumn	Winter	Annual
T (^{o}c)	Z_S	0.592	0.592	0.592	0.242	0.592
	Z_D	-0.467	-0.071	0.634	-0.959	0.174
	b	1.228	3.724	1.623	0.610	2.324
EC (μs/cm)	Z_S	0.592	0.117	0.408	0.242	0.408
	Z_D	0.945	-1.826	2.092	2.309	0.354
	b	34.306	88.670	68.059	32.646	49.120
pH	Z_S	**0.042***	0.408	0.592	0.242	0.242
	Z_D	**3.795***	0.304	0.448	1.872	0.756
	b	0.559	1.623	1.719	0.546	1.113
BOD (mg/l)	Z_S	0.592	0.242	0.117	0.408	0.242
	Z_D	0.349	-0.614	-1.370	-0.206	-1.299
	b	0.466	0.553	0.727	0.493	0.507
DO (mg/l)	Z_S	0.408	0.117	0.117	0.592	0.408
	Z_D	0.284	-0.181	-1.616	0.574	-1.000
	b	2.044	2.115	2.412	2.085	1.931
Total hardness (^{o}dh)	Z_S	0.592	**0.042***	0.592	0.592	0.408
	Z_D	0.375	**-2.900***	0.910	1.209	0.002
	b	0.885	2.668	1.903	0.996	1.376
Cl (mg/l)	Z_S	0.408	**0.042***	0.408	0.242	0.408
	Z_D	0.772	**-2.642***	1.434	0.777	0.545
	b	0.408	1.510	1.571	0.356	0.750
Ca (mg/l)	Z_S	0.242	**0.042***	0.592	0.592	0.408
	Z_D	-0.206	**-3.099***	0.567	1.239	0.003
	b	5.146	16.350	11.709	5.545	14.673
Mg (mg/l)	Z_S	0.592	0.242	0.242	0.242	0.408
	Z_D	-0.155	-0.187	1.112	1.239	0.354
	b	0.977	2.073	1.272	0.909	1.172
NO_3 (mg/l)	Z_S	0.408	0.408	0.408	0.592	0.592
	Z_D	0.886	-1.068	0.839	1.624	0.174
	B	0.465	1.447	1.360	1.074	0.930
NO_2 (mg/l)	Z_S	0.592	0.408	0.242	0.592	0.242
	Z_D	-0.090	-0.181	0.981	-0.415	-1.000
	b	0.024	0.012	0.011	0.012	0.011
SO_4 (mg/l)	Z_S	**0.042***	**0.042***	0.408	**0.0083***	0.117
	Z_D	**-3.371***	**-3.040***	-0.715	**-2.914***	-2.309
	b	5.343	14.675	6.821	4.668	8.346

Z_S: Mann-Kendall test, Z_D: Spearman's Rho test, b: Slope of linear regression
* Statistically significant trends at the 5% significance level.
Bold characters represent trends identified by 2 statistical methods together.

The statistical tests identified seven significant trends in the seasonal time series. The significant positive trend was observed in pH data in spring. The negative trends were found in total hardness, Cl and Ca in summer, while SO_4 data had the negative trends in spring, summer and winter. On the contrary, no significant trends were found in autumn. Both positive and negative trends were detected by the statistical tests in annual water quality data. However, the trends were insignificant at the 5% significance levels.

The increasing trends in T, Ca and total hardness series obtained in this study are deal with the results in Naddafi et al. (2007) and Tabari et al. (2011). On the contrary, the given decreasing trends in SO_4 and DO are inconsistent with the trends observed in Greece (Antonopoulos et al. 2001), while the trends in Mg, Cl, EC and pH found in this research are inconsistent with the trends found in Iran (Tabari et al. 2011). Meanwhile, the result found for pH is consistent with the increasing trend for pH in Spain (Bouza-Deano et al. 2008) and Iran (Naddafi et al. 2007).

4. CONCLUSIONS

The data of water quality parameters at the Nis station of the Nisava River in its Serbian part were analysed using Mann-Kendall test at the 5% significance level. The time series of daily measured values of 12 water quality parameters (T, EC, pH, BOD, DO, total hardness, Cl, Ca, Mg, NO_3, NO_2 and SO_4) over five years (2000-2004) were used for monthly, seasonal and annual analysis.

The results in monthly series indicated that significant trends were detected in pH, total hardness, Ca and SO_4 data.

The most of the trends were insignificant at the 5% significance levels in the seasonal time series. Meanwhile, the highest numbers of significant trends were detected in the summer series. The significant trends were detected in pH, total hardness, Cl, Ca and SO_4 data. In contrast, no significant positive or negative trends were found in autumn water quality data.

The Mann-Kendall test showed both positive and negative trends in annual water quality data. However, no significant trends were detected at the 5% significance level.

The analyzed results can be helpful for planning and controlling the water supply of the Nisava River.

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ANALIZA TRENDA PARAMETERA ZA KVALITET VODE NA RECI NIŠAVI

Podaci 12 parametara kvaliteta vode su prikupljani na mernoj stanici Niš tokom perioda 2000-2004. Analiza trenda je urađena za mesečne, sezonske i godišnje vremenske serije korišćenjem Mann-Kendall testa, Spearmanovog Rho testa i linearne regresije za 5% nivoa značajnosti. Mesečni rezultati pokazuju da značajni trendovi postoje samo za sledeće podatake: pH, ukupnu čvrstoću, Ca i SO_4. Rezultati sezonskih serija ukazuju das u značajni trendovi detektovani za pH, ukupnu čvrstoću, Cl, Ca i SO_4. Za godišnje serije, trendovi nisu značajni za 5% nivoa značajnosti.

Ključne reči: *analiza trenda, parametri kavaliteta vode, Mann-Kendall test, Spearman's Rho test, linearna regresija, Nišava*