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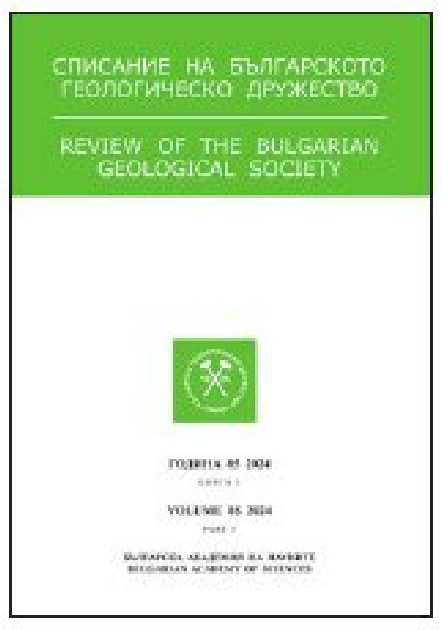

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REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY

Comparative analysis of karst water quality parameters of the Banja spring near Valjevo (Republic of Serbia)

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Сравнителен анализ на качествените параметри на карстовите води на извора Баня край Валево (Република Сърбия)

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Abstract. The monitoring of karst spring release regimes is becoming more and more relevant due to the fact that karst waters are of exceptional quality and most often it is only necessary to chlorinate these waters in order to use them for water supply. In addition to monitoring the discharge regime, it is certainly necessary to establish monitoring of quality parameters that are generally observed sporadically (seasonally or monthly). An example of a well-designed monitoring of quantitative and qualitative parameters is Banja spring (western Serbia). The paper presents the analysis of time series pH values, electrical conductivity, turbidity, suspended sediment, total number of bacteria (TNB), discharge (D) and precipitation (P) using autocorrelation and cross-correlation analyses.

Keywords: pH, Ec, turbitity, disharges, karst spring.

Introduction

Due to the inaccessibility and long distance, it is generally difficult to establish daily monitoring of parameters of the groundwater regime at karst springs. If possible, continuous monitoring of quantitative parameters (discharge, water level) is established, while when it comes to monitoring qualitative parameters, they are mostly monitored sporadically (seasonally or monthly). With the advent of multi-parameter probes and solar panels, it is possible to automatically record changes in parameters such as pH, Ec, turbidity, water level and groundwater level, which is done on an hourly basis and even more often. The Lelić karst area represents the largest zone of open karst terrain within the Internal Dinarides of western Serbia, and some of the most important springs are the Gradačka springs and the Petnica spring. The spring of the Banja river, also known as the Petnica spring, is located 7 km southeast of Valjevo, not far from the Petnica research station (ISP) (Fig. 1a). The spring emerges from the Petnica cave (181 masl), and the very appearance of the spring is conditioned by the existence of a barrier of Miocene sediments. In the watershed with a total area of about 19 km^2 (Lončar et al., 2024), there are two surface streams (Zlatarski and Bukovik) that plunge into the Pećurina ponor (Ristić Vakanjac et al., 2015).

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These waters occur at the Petnica spring, and the connection between the ponor and the spring has been proven several times by tracing test (Ristić Vakanjac et al., 2000). Since ISP has its own chemical laboratory, in the period up to 1990 measurements of parameters of the quality and quantity of the water of the Petnica spring were carried out sporadically, several times a year, with the idea of monitoring the concentrations of nitrates, phosphates and sulfates. The results of these occasional analyzes showed that, in the period from 1982 to 1990, the concentrations of the mentioned parameters were increasing. For this reason, in 1990, the idea was reached to establish continuous monitoring of 11 quality parameters (SO_4^{2-}, NO_3^-, HCO_3^-, Cl^-, Mg^{2+}, Ca^{2+}, pH, turbidity, suspended sediment, electrical conductivity and total number of bacteria), as well as monitoring the amount of runoff water and monitoring the amount of precipitation at the newly installed rain gauge station within the ISP. Of the mentioned parameters, the paper will present the monitoring results of pH value, electrical conductivity (Ec), suspended sediment (SS), turbidity (T), total number of bacteria (TNB), discharge (D) and precipitation (P), as and the results of autocorrelation and cross-correlation analyzes of the same parameters. The period from 1991–1995 was analyzed.

Methodology

In the period 1991–1995, the water sampling of the Petnica spring was carried out every day at 7:00 a.m. The water level of the overflow at the time of sampling was comparatively observed and recorded. Using the overflow equation, the discharge values of the Petnica spring were calculated. For measuring total daily precipitation, a rain gauge was installed within the ISP. Analysis of the considered parameters (Ec, pH, SS, T and TNB) was performed daily on water samples from the spring. The parameters were determined using a pH-meter, a conductometer and a spectrophotometer. Suspended sediment was determined by filtering and drying, after which the mass of the sample was measured on an analytical balance. The total number of bacteria was determined by microbiological analysis, using the agar plate method (Lončar et al., 2024). Autocorrelation and cross-correlation analyze were performed for the analysis of the considered time series of parameters of the quality of the Banja spring, which are theoretically detailed in several available literature sources (Krešić, Stevanović, 2010; Ristić Vakanjac, 2015). The threshold of the autocorrelation coefficient r = 0.2 (Mangin, 1984) was taken as the limit value of the autocorrelation of the series.

Results

Based on the obtained results of chemical analyses, a comparative diagram of changes in the water quality parameters regime of the karst Petnica spring was made (pH, Ec, T and SS; see Fig. 1b), while Table 1 shows the matrix of correlation coefficients between all analyzed parameters. The results of the autocorrelation analysis of the total analyzed period are given on the autocorrelogram (Fig. 1c), while the crosscorrelograms are given in Figure 1d.

Discussion with conclusion

The comparative diagram of quality parameters (Fig. 1b) indicates that the turbidity and suspended solids regimes show high accordance; the increases and decreases of these parameters occur almost simultaneously, resulting in a high correlation between the two parameters (r = 0.949). The total number of bacteria also has a relatively good correlation with turbidity (r = 0.385) and suspended solids (r = 0.250). Increases in these three parameters mainly appear in the first part of the year and are the result of spring precipitation and/or sudden snowmelt. Peaks during the summer and autumn seasons are generally absent, and if they are recorded, they are the result of heavy rain events.

This is supported by the peak of suspended solids recorded on August 14, 1991, at a level of 179 mg/dm^3,

Table 1. Matrix of correlation coefficients between the analyzed parameters

	Q	P	Ec	M	B	SN	pH
Q	1	0.143	–0.325	0.478	0.513	0.320	–0.084
P		1	–0.005	0.024	–0.007	0.042	0.001
Ec			1	–0.622	–0.571	–0.452	–0.100
M				1	0.385	0.949	–0.011
B					1	0.250	–0.002
SN						1	–0.030
pH							1

Legend: Q – the flow of the Petnica spring (m^3/s), P – precipitation (mm), Ec – electrical conductivity, (µS/cm), B – total number of bacteria, M – turbidity (NTU), SN – suspended sediment

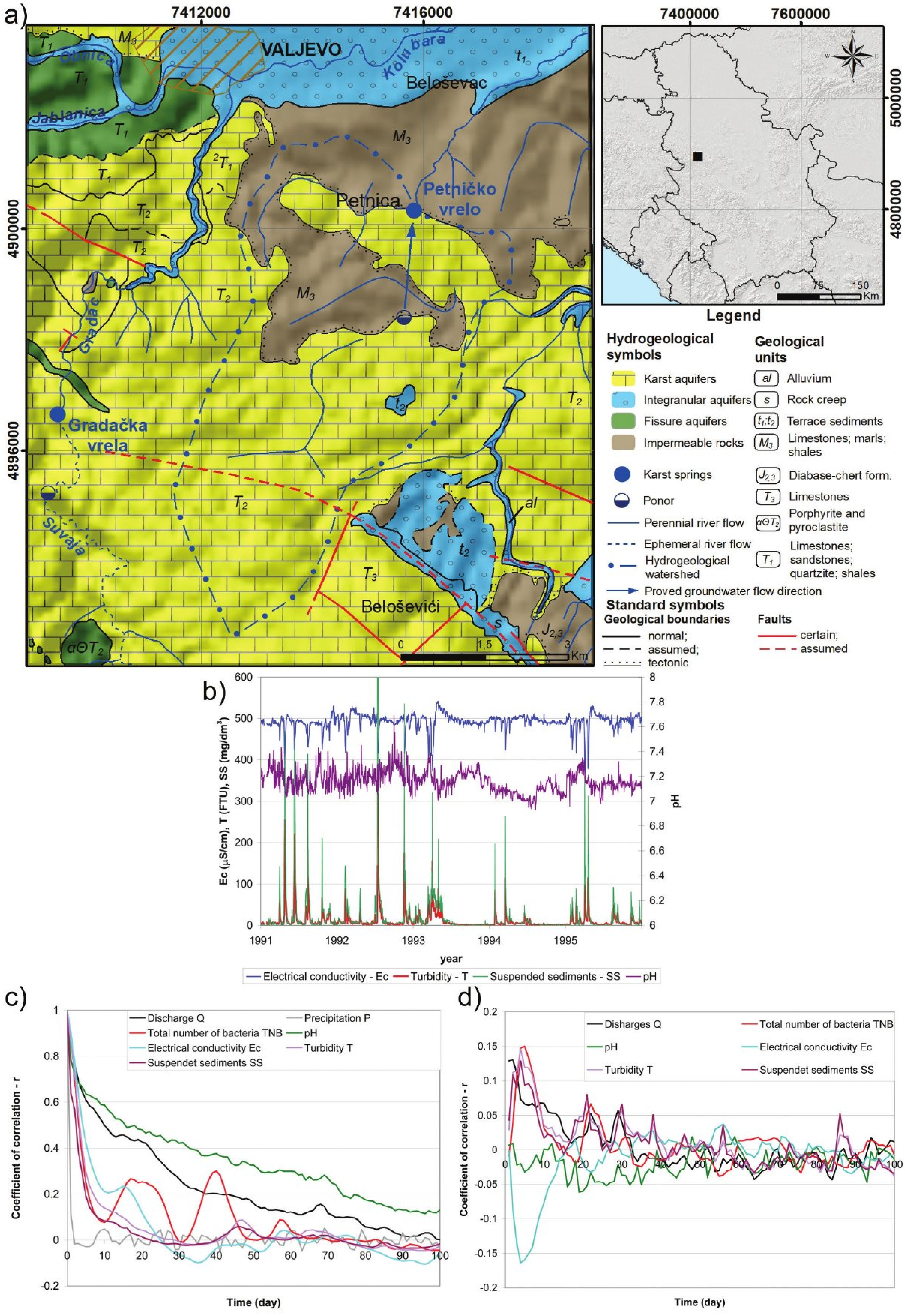

Fig. 1. *a*, hydrogeological map of the wider environment of Petničko Vrelo; *b*, comparative diagram of electrical conductivity, turbidity, suspended solids, and pH values; *c*, autocorrelation of qualitative characteristics and groundwater discharge; *d*, cross-correlation of precipitation time series with groundwater discharge at Petničko Vrelo, bacteria, pH, turbidity, electrical conductivity, and suspended solids

which was caused by precipitation recorded the day before, totaling 48.5 mm. A similar situation was observed on July 14, 1992, when suspended solids were recorded at a level of 1.923 g/dm³. This concentration was the result of a rainy episode with cumulative precipitation of 50 mm that lasted from July 10 to July 14, 1992. On the other hand, July 29, 1993, a daily precipitation total of 45.1 mm was recorded, which caused an increase in suspended solids amounting to 9.1 mg/dm³, measured two days later. This relatively low value is the result of the pluviographic regime observed in the period leading up to the recorded maximum. More precisely, during the spring months of 1993, frequent rains with an intensity of more than 20 mm per day were recorded, which fed the karst aquifer by infiltration and caused the hydrograph to rise. During these periods, there was also rinsing of precipitated micro- and macro-particles in the cavities, fractures, and channels formed during the months when precipitation was not of high intensity (Pešić et al., 2016). Regarding Ec, it can also be noted that there is a relatively good correlation of this parameter with the previously mentioned parameters (TNB, T, and SS), although the obtained correlation coefficients have negative values. More precisely while intense precipitation causes an increase in TNB, T, and SS, at the same time, it leads to a decrease in Ec. This is supported by the comparative diagram in Figure 1b, as well as the correlation coefficients presented in Table 1. Regarding pH values, the obtained correlation coefficients indicate that this parameter is not correlated with any other analyzed parameter (r approximately = 0). The highest obtained value of the correlation coefficient is between pH and Ec, but it also amounts to –0.1, which is still a low correlation. The autocorrelogram indicates that pH has the longest memory of 74 days, then the discharge of karst spring has a memory of 37 days, then Ec (18 days), while the other parameters have a much shorter memory (less than 10 days).

The low memory of the time series is conditioned by intense precipitation, whose autocorrelogram also shows low memory, which is the result of their temporal unevenness. On all autocorrelograms, around the 16th day, a slight increase in the autocorrelation coefficient is noticeable, which is most likely the result of the melting of the snow cover, which doesn't stay long in the watershed due to the relatively low altitude (the maximum elevations of the watershed are about 600 masl). The cross-correlogram indicates that the precipitation that reaches the catchment area requires two days to be recorded on the hydrogram of the examined spring. An increase in turbidity and suspended material occurs during spring with a delay of four days, while the maximum value of the total number of bacteria is observed after five days. The maximum value of Ec also occurs four days after the recorded maximum cumulative precipitation. Additionally, the reciprocal appearance of the cross-correlogram for bacteria and electrical conductivity resembles a mirror image, which directly confirms the conclusions drawn from the autocorrelation analysis. On the other hand, the cross-correlograms of the other qualitative parameters are synchronous, further affirming the findings of the autocorrelation analysis.

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