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HYDROCHEMICAL RESEARCH OF THE MLINI SPRINGS, ISTRIA

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ABSTRACT

International co-operation is necessary for an efficient study of karst springs with recharge areas that extend in the territory of more than one country. Such example is the Mlini spring, which was studied within the framework of the Slovene-Croatian programme for scientific co-operation. The spring has been included into the network of the national monitoring of Croatian waters since 1996, and in the planned research detailed measurements of physical-chemical parameters of water were carried out in the chosen water wave formed by intensive precipitation after a prolonged dry period. The obtained results confirm the importance of such additional detailed monitoring that enable us to detect, under adequate hydrological conditions, extreme values of certain parameters of water quality, which could not be detected by regular monitoring.

Key words: Mlini karst spring, monitoring, water quality, Istria, Croatia, Slovenia

RICERCA IDROCHIMICA DELLA SORGENTE DI MLINI, ISTRIA

SINTESI

Per una ricerca efficiente delle caratteristiche delle sorgenti carsiche, l'entroterra delle quali si estende nel territorio di più di una nazione, è necessaria una collaborazione internazionale. Un valido esempio ne è la sorgente di Mlini, che è stata studiata nell'ambito del programma di collaborazione scientifica sloveno-croato. Dal 1996 tale sorgente fa parte del programma nazionale di monitoring della qualità delle acque croate. Nella presente ricerca sono state poste in rilievo le misurazioni dei parametri fisico-chimici dell'acqua nell'ondata provocata da forti piogge, a seguito di un lungo periodo di siccità. I risultati hanno confermato l'importanza di tale monitoring aggiuntivo con il quale è possibile, in condizioni idrologiche adeguate, rilevare valori estremi di alcuni parametri di qualità dell'acqua, che non possono venir misurati durante il monitoring abituale.

Parole chiave: sorgente carsica di Mlini, monitoring, qualità dell'acqua, Istria, Croazia, Slovenia

INTRODUCTION

The lack of available water resources, along with the increasing need for water, deterioration of its quality and difficulties owing to the exceptionally high waters and erosion, present the principal problems we are confronted with both in Slovene and Croatian territories. For several decades, the researchers from both sides of the border have been quite successful in their attempts to provide solutions. The results of numerous investigations were consequently published, yet the joint projects, which would in an all-embracing way and in multidisciplinary manner deal with the water systems in the border regions, are still lacking. Owing to the fact that the hydrological division of the water basins usually does not match the political boundaries and considering that the recharge areas of water sources may extend into the territory of two or even more countries, the need for an international co-operation is even greater.

The precondition for a successful managing of water resources is good knowledge of hydrological and hydrogeological characteristics of the area; of significant importance, however, are also the data on the changes in the water quality. Our collective work within the Slovene-Croatian Intergovernmental Programme for Cooperation in Science and Technology from 1999 to 2001, »The Hydrological Analysis of Karst Waters«, was for that reason first directed into gathering basic information. Our objective was to assess the hydrological characteristics of water phenomena in the border area of Slovenia and Croatia, to elaborate the hydrological models of individual karst springs' functioning, as well as to analyse their mutual interconnection and optimal functioning.

It needs to be emphasised that a great deal has already been done as far as protection and ecology are concerned. We used the extant hydrological and hydrogeological data for the initial regional quantitative evaluation of the hydrological and hydrogeological parameters of water sources as well as a basis for the planning of our joint research. Within such framework we consequently conducted, in the autumn of 2001, a detailed two-month monitoring of the water quality at the karst spring Mlini, which has been included in the network of national monitoring of the Croatian waters since 1996. We embraced the short period of low water level, which was followed by short yet intensive precipitation forming the water waves, as well as the prolonged period of recession and the establishment of stable conditions. The aim was to compare the results of such detailed observation of water waves under specific hydrological conditions with the data gathered through monitoring with regular sampling at longer intervals. Our supposition was that such additional survey could detect extreme values of certain parameters of water quality, which could not be detected by regular monitoring, and in this way provides important additional information.

Geological composition and hydrogeological characteristics

The Mlini spring is situated in the belt of the reverse fault, by means of which the carbonate massif of Čičarija is thrust onto the flysch strata. This geologically highly interesting structure, which in its geo-tectonic sense belongs to the Adriatic carbonate platform or Adriatic (Herak, 1991) is formed in the NE by the folded Cretaceous carbonate layers, whereas in the SW by the thrust and scale-like composition structure of Paleogene limestones (Pleničar *et al.*, 1969). The basic structure is traversed by Dinaric faults, whose presence has an effect on the specific hydrogeological relations and karst peculiarities.

The imbricate structure of the Čičarija has originated due to pressures from NE towards SW. The same pressures are demonstrated in the thrust of the High Karst (Trnovski gozd, Nanos, Hrušica, Snežniško pogorje) in the territory of Eocene clastic rock of the Vipava and Reka basins. In the High Karst unit, real thrust may be present, whereas in the unit of Čičarija real thrust is predominantly not to be found; what predominates is the forming of scale-like structures. The terrain in this area is built up by well permeable foraminiferal limestones and by less permeable to impermeable flysch layers. These flysch strata, which occur in the synclinal parts of isoclinal and tectonically reduced folds, are relatively close to the surface and have the function of hanging barriers. Such conditions were also indicated by the tracing test results (Fig. 1).

The region of Istria covers the edge of the Adriatic carbonate platform with a special impact on the formation of the karst aquifer and the quality of water within it. On the basis of the hydrogeological research conducted till now, we may estimate that rocks have various permeability, which ranges from high to low, depending on the content of dolomite in the lithological composition of individual stratigraphic sections.

Hydrological characteristics

The zone of Mlini karst springs is located in the middle part of the surface stream of Bračana, which is the most important tributary of the river Mirna (Fig. 1). It comprises one permanent spring, which bursts out at an altitude of 90 m, and two springs at an altitude of 110 m, which are active only during high waters. During more intensive precipitation some water outflows in them also from the Jama pod Krogom Cave, which intersects the Slovene-Croatian border. In the cave, there is a permanent water stream that during higher water levels flows over the entrance at an altitude of 144-m a.s.l.

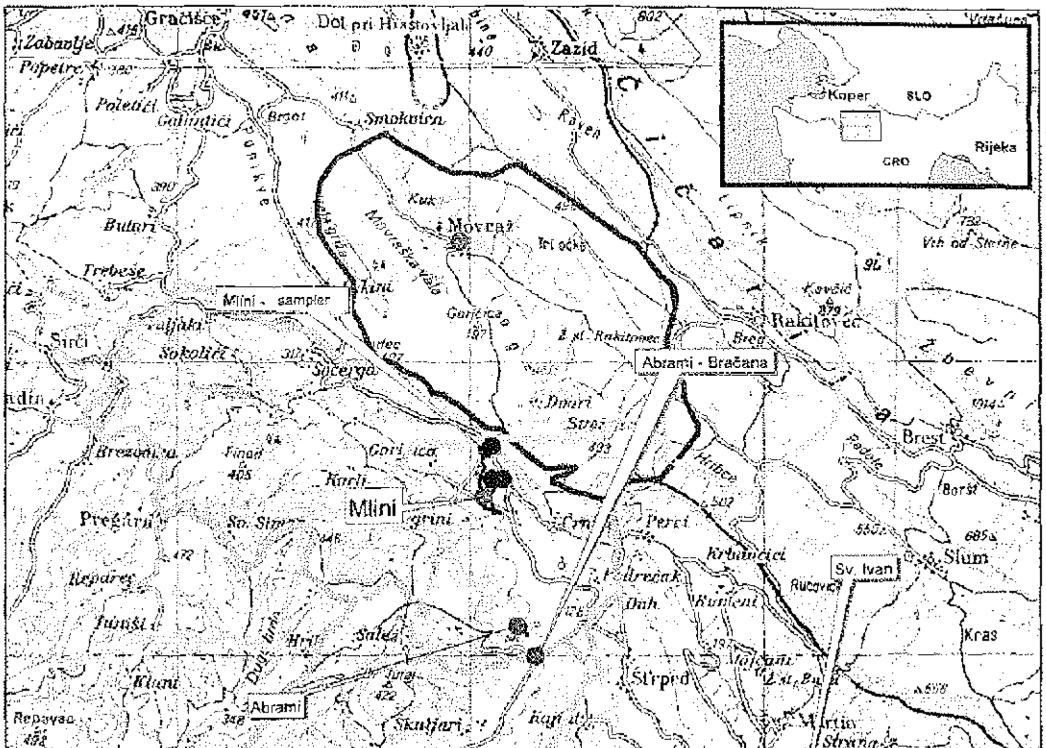

Fig. 1: Location map and the presentation of results of tracing tests in the wider area of Mlini springs: 1 – state border; 2 – automatic water sampler; 3 – spring; 4 – precipitation station; 5 – hydrological station; 6 – hydrographic network; 7 – surface watershed of the Bračana; 8 – hydrogeological watershed of Mlini spring; 9 – surface watershed of the Bračana – Abrami station.

Sl. 1: Pregledna karta in prikaz rezultatov sledenja na širšem območju izvirov Mlini: 1 – državna meja; 2 – avtomatski zajemalnik; 3 – izvir; 4 – padavinska postaja; 5 – hidrološka postaja; 6 – hidrografska mreža; 7 – površinska razvodnica Bračane; 8 – hidrogeološka razvodnica izvira Mlini; 9 – površinska razvodnica Bračane – postaja Abrami.

Tab. 1: Characteristic hydrological parameters of the Bračana surface stream at Abrami station and of the Mlini springs.
Tab. 1: Karakteristični hidrološki parametri površinskega toka Bračane na postaji Abrami in izvirov Mlini.

Param.	Month												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	annual mean
Hydrological station ABRAMI – BRAČANA (discharges in m^3/s) Period of measurement: 1985-1998													
Q_{mean}	0.92	0.72	0.62	0.66	0.46	0.42	0.14	0.09	0.21	0.78	0.98	0.85	0.57
S	0.77	0.61	0.54	0.32	0.50	0.54	0.12	0.07	0.24	1.02	0.69	0.73	0.18
Cv	0.84	0.85	0.87	0.48	1.07	1.27	0.91	0.80	1.13	1.31	0.70	0.85	0.32
Q_{m-min}	0.04	0.03	0.06	0.21	0.11	0.04	0.02	0.01	0.01	0.03	0.05	0.09	0.37
Q_{m-max}	2.52	2.30	1.74	1.34	2.03	2.11	0.45	0.24	0.77	2.97	2.42	2.18	1.01
Q_{min}	0.04	0.02	0.01	0.06	0.02	0.02	0.002	0.002	0.01	0.01	0.02	0.04	0.002
Q_{max}	21.80	15.30	17.60	15.30	20.00	29.70	7.98	5.50	16.30	49.90	25.60	25.90	49.90
Hydrological station ABRAMI – BRAČANA (discharges in m^3/s) Period of measurement: hydrological year 1986/1987													
Q_{mean}	0.06	0.17	0.40	0.76	0.99	0.25	0.50	0.79	0.25	0.08	0.23	0.07	0.38
Q_{min}	0.03	0.03	0.05	0.06	0.16	0.11	0.19	0.13	0.16	0.05	0.05	0.03	0.03
Q_{max}	0.41	6.20	9.30	8.45	6.48	2.32	3.54	7.47	0.99	0.16	4.00	0.81	9.30
Hydrological station MLINI SPRING (discharges in m^3/s) Period of measurement: hydrological year 1986/1987													
Q_{mean}	0.02	0.14	0.31	0.26	0.65	0.12	0.25	0.45	0.03	0.02	0.16	0.02	0.20
Q_{min}	0.02	0.03	0.03	0.02	0.13	0.02	0.07	0.03	0.02	0.02	0.02	0.02	0.02
Q_{max}	0.12	2.80	3.29	1.49	3.29	1.49	2.57	2.57	0.04	0.02	2.34	0.02	3.29

Tab. 2: Mean monthly and annual precipitation at the Abrami and Movraž stations.
Tab. 2: Srednje mesečne in letne padavine na postajah Abrami in Movraž.

Period	Month												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	annual mean
Precipitation station: ABRAMI (precipitation in mm)													
1961-98	88	71	83	91	96	106	82	101	115	119	129	93	1174
1986/87	59	61	74	97	108	24	70	137	95	61	89	62	937
Precipitation station: MOVRAŽ (precipitation in mm)													
1961-90	117	143	110	108	85	105	106	100	108	87	115	116	1300
1986/87	64	67	84	101	113	48	62	129	82	84	128	133	1095

(Habič *et al.*, 1983). The minimal flow rate of springs is 0.015 m^3/s, yet with their average common discharge of 0.2 m^3/s they contribute, in place where they flow into it, around 50% of the Bračana's entire water volume. The spring is captured for the water supply of the Mlini village.

The data on discharges of the Mlini springs are rare and related to the short-term periods of measurements or temporary observations. According to the available data, the first monitoring of the spring results are linked to the period 1971/72, when the flow rate ranged between 0.032 m^3/s and 2.2 m^3/s. For the annual monitoring with the staff gauge in the hydrological year 1986/87 the measured mean annual discharge amounts to 0.199 m^3/s, with the fluctuation of daily discharges between 0.019 m^3/s and 3.293 m^3/s. During the temporary observation in the 1994/95 interval, the discharge ranged between 0.013 m^3/s and 3.244 m^3/s. In the period from 11 September to 12 December 2001, however, the discharges measured within the framework of the joint Slovene-Croatian project ranged between 0.020 m^3/s and 2.199 m^3/s.

The closest permanent limnigraph station on the Bračana surface stream is Abrami station, towards which 19.4 km^2 of the flysch recharge area and a part of the karst aquifer, which is discharged through the spring

Mlini, is being drained. If Bračana's mean discharge of 0.570 m^3/s is taken into account for the 1985-1998 period, the average annual precipitation volume measured at the precipitation station Movraž and Abrami, which is equal to 1165 mm, and the mean annual evapotranspiration for the region of Istria, which is 725 mm (Pristov, 1998), we may estimate the total extent of the Bračana's recharge area at approximately 41 km^2, which would signify that the share of the karst recharge area amounts to around 21.6 km^2.

The comparison of the measured discharges of the Bračana stream and Mlini springs is demonstrated in Table 1, whereas in Table 2 we inserted the mean monthly and annual precipitation measured at the precipitation stations Abrami and Movraž.

Both hydrological and precipitation data indicate that the hydrological year 1986/87 was relatively dry. For the hydrological station Abrami, the yearly runoff coefficient of 0.29 was calculated for the year 1986/87. The monthly runoff coefficients range between 0.09 (September and October) and 0.67 (January). With regard to the hydrological conditions, these values prove to be in accordance with the regionally determined values of the runoff coefficient (Žugaj, 1995).

In the period from 1 September to 12 November 2001, the gauging station Mlini was temporarily restored and we were able to measure the total discharges of permanent and intermittent springs. For this period, figure 2 displays mean daily discharges of the Mlini spring and of the Bračana surface stream at the Abrami station as well as mean daily precipitation at Movraž and Abrami stations.

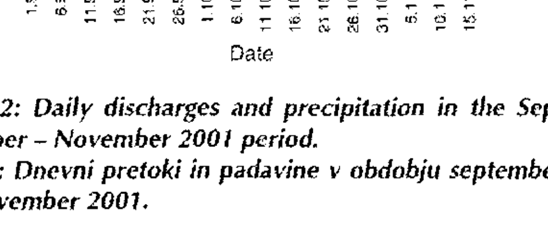

Fig. 2: Daily discharges and precipitation in the September – November 2001 period.
Sl. 2: Dnevni pretoki in padavine v obdobju september – november 2001.

The previous period of summer 2001 was exceptionally dry and for that reason the first rainfall in the beginning of September, which exceeded 20 mm, was not reflected in the increase of the discharge. Due to the interception on the vegetation cover, enlarged evapotranspiration and the filling in of soil moisture deficit the effective infiltration proved to be practically negligible. Only more intensive precipitation on 15 September (68.4 mm at Abrami and 84.6 mm at Movraž station) resulted in a significant increase of discharges. Within the next days the rainy period continued and in September of 2001 the rainfall quantity amounted to a double average quantity common for this month. Characteristically higher were also the average discharges. Precipitation in October and November were, however, once again below the average values.

The analysis of interrelations between daily precipitation at Abrami and Movraž stations indicated a high correlation (R^2=0.96):

$$H_{MOVRAŽ} = 1.173 \cdot H_{ABRAMI} - 0.45 \quad \text{(mm)}$$

We also compared daily values of discharges at the Mlini springs and Bračana stream. Subsequent to the two-month observations discharges of the former ranged between 0.020 m^3/s and 2.199 m^3/s having an average value of 0.243 m^3/s, whereas the latter ranged between 0.032 m^3/s and 6.44 m^3/s with an average of 0.530 m^3/s. The share of water from the Mlini springs in the Bračana surface stream at Abrami station was thus around 44%. Within the analysed scope of discharges, the level of correlation proved to be very high (R^2=0.968), whereas the determined linear dependence does not apply to the discharges larger than approximately 2 m^3/s in case of Mlini and 4-5 m^3/s in case of Bračana, since due to the restrained outflow of the underground waters the discharge of Mlini springs does not follow the rise in the surface Bračana stream.

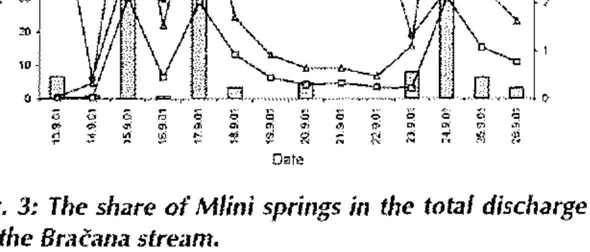

Fig. 3: The share of Mlini springs in the total discharge of the Bračana stream.
Sl. 3: Delež izvirov Mlini v skupnem pretoku Bračane.

A comparison of shares of discharge of the Mlini springs in the total discharge of the Bračana at the Abrami station is also interesting. In figure 3, these shares are represented during both most intensive precipitation events. The considerable decrease in the share of the Mlini spring just before the rise of discharges indicates that the surface Bračana stream with its flysch recharge area reacts characteristically faster to precipitation than the Mlini karst spring. We may also find out that within a longer period of dry weather the Mlini spring represents the principal source of water in the Bračana stream (around 50%).

We may thus conclude that the selected two-month period of monitoring physical and chemical characteristics of the Mlini spring proves to be of hydrological interest primarily due to the possibility of observing the reactions of the spring and the surface stream to the first precipitation after the prolonged period of dry weather.

MATERIAL AND METHODS

At the Mlini karst spring we also conducted, between 11 September and 14 November 2001, a two-month detailed monitoring of the composition of its water. Thus we covered a short period of low waters that was followed by a brief yet intensive precipitation forming water waves, as well as longer period of recession and a longer period of reestablishment of stable conditions.

Tab. 3: The applied methods of analyses are ISO methods (10253:1994; 7888:1985; 5813:1983; 5815:1989; 9963-1:1994) (APHA, 1995), and DIN 38409 H18 method.
Tab. 3: Uporabljene ISO metode (10253:1994; 7888:1985; 5813:1983; 5815:1989; 9963-1:1994) (APHA, 1995) in DIN 38409 H18 metoda.

Indicator	Method	Detection limit
temperature	*St.Meth. 2550 B.	
pH	ISO 10253:1994.	
Conductivity – SEC	ISO 7888:1985	1 µS/cm
turbidity	turbidimetrical	5 mgSiO_2/l
dissolved oxygen	ISO 5813:1983	0.01 mgO_2/l
BOD_5	ISO 5815:1989	0.01 mgO_2/l
COD – permanganate	method according to Kubel Tiemann	0.01 mgO_2/l
alkalinity	ISO 9963-1:1994	0.002 mmol $CaCO_3$/l
chlorides	St. Meth.4500-Cl B. argentometric	0.1 mg/l
sulphates	St. Meth. 400-SO_4 E. turbidimetric	1 mg/l
hardness – total	St. Meth. 2340 C. complexometric (EDTA)	0.002 mmol $CaCO_3$/l
total solids dried at 105 °C	St. Meth. 2540 B. gravimetric	0.001 mg/l
total suspended solids dried at 105 °C	St. Meth. 2540 D. filtration through GF 45 µm, gravimetric	0.001 mg/l
ammonia	spectrophotometric with fenolate hypochloritome	0.001 mgN/l
nitrites	St. Meth. 44500-NO_2 B. spectrophotometric with α-naftilamine and sulfinic acid	0.001 mgN/l
nitrates	St. Meth. 4500-NO_3 B.	0.01 mgN/l
organic nitrogen	St. Meth. 4500-N_{org}. B. digering in the acid media, spectrophotometrical as ammonia	0.001 mgN/l
ortho-phosphates	St. Meth. 4500-P E. spectrophotometrical with ammonia-molibdate and ascorbic acid	0.005 mgP/l
total phosphorus	digering, followed by a procedure as with ortho-phosphates	0.005 mgP/l
oil and grease, mineral oils	DIN 38409 H18	0.002 mg/l
Mn, Cu, Cr, Pb	AAS – flameless technique (graphite)	1 µg/l
Cd	AAS – flameless technique (graphite)	0.1 µg/l
K, Na, Ca, Mg	AAS – flame technique	0.1 mg/l
Zn	AAS – flame technique	5 µg/l
Fe	AAS – flame technique	10 µg/l
TC, FC, FS	MF technique, selective bases, number/100ml	
aerobic mesophile bacteria N/37	nutrient agar 37 °C, number /ml	

The measurements of discharge, temperature, pH and the specific electrical conductivity (SEC) were carried out by means of YSI 600 probe at 5-minute intervals and were then saved in a datalogger with ISCO 6700 portable sampler. At the same time and within the set interval (every 6 hours at the beginning and three times per week later on), water samples were also collected. Parallel with the sampling we manually measured temperature of the spring water by means of a quicksilver thermometer and also manually, gathered some samples to determine the quantity of dissolved oxygen, oil and grease, mineral oils and heavy metals (cadmium, copper, zinc, iron, manganese, total amount of chromium and lead). In the laboratory, the samples taken by automatic sampler were analysed on pH, SEC, turbidity, presence of suspended solids, total solids, alkalinity, total hardness, chlorides, sulphates and indicators of nutrient substances: ammonia, nitrites, nitrates and organic nitrogen. We also determined the phosphates, total phosphorus, sodium, potassium, calcium, magnesium, COD-permanganate and BOD_5, UV absorption and bacteriological analyses (total coliform bacteria, faecal coliform bacteria, faecal streptococci and the number of aerobic mezophile bacteria at 37 °C – N/37). The analyses were conducted in the Institute for Public Health of the Istrian region in Pula, whereas the methods used in determination are to be found in Table 3.

RESULTS AND DISCUSSION

Temperature, pH, specific electrical conductivity – SEC and total suspended solids

Measurements of temperature, SEC and pH by means of YSI 600 probe were until 11 October unfortunately absent for an unknown reason. In the period until 23 October, we occasionally detected some difficulties in measuring SEC and pH, most probably due to the fallen leaves carried by water and accumulated around the probe. The temperature measurements were performed with no problems at all. The entire period of monitoring proved to be very stable, *i.e.* from 12.7 to 12.8 °C, which was also confirmed by the manual measurements with quicksilver thermometer during every manual sampling.

By means of YSI 600 probe, we measured the pH values within the interval from 7.0 to 7.4 and the average value 7.2. The pH measurements of the collected samples performed in the laboratory demonstrated higher values ranging from 7.2 to 8.0 and the average value of 7.7, which is probably a consequence of the heating and airing of samples in the automatic sampler, since they remained closed in it for up to 5 days, and due to the transport to the laboratory.

The measurements of SEC by means of YSI 600 probe after 11 October, provided to eliminate greater variations due to the given difficulties, displayed an even increase of values between 478 and 510 µS/cm with an average value of 489 µS/cm. In the period from 18 October until 6 November 2001, these values matched very well with the SEC measurements conducted in the laboratory, which yielded slightly lower values (Fig. 4). However, we have no reasonable explanation for the measurement differences occurring after 6 November.

At the time of the first two water waves, the SEC decreased (laboratory measurement), as actually expected. From 14 to 19 September 2001, the SEC decreased from 436 µS/cm to 409 µS/cm, and then rose to 461 µS/cm. Simultaneously, with the increase of discharge and decrease of SEC, the turbidity markedly increased as well, whereas the quantity of total suspended solids increased to a lesser degree (Fig. 4), which indicates a greater transfer of small, solid particles and the lower quantity of dissolved substances due to the inflow of less mineralised water. This was additionally corroborated by the measurements of alkalinity, calcium and total hardness. During the next water wave on 24 and 25 September, however, we detected no decrease in SEC and no decrease in calcium and alkalinity. This perhaps reflected the inflow of water from different parts of the aquifer.

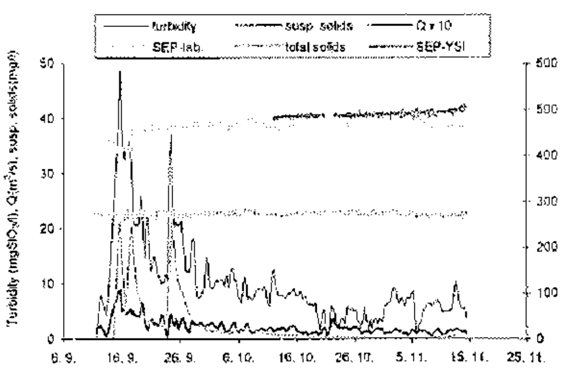

Fig. 4: Mlini spring: measurements of turbidity, total suspended solids, total solids and conductivity – SEC in autumn 2001 (5-term smoothing used for the measuring of turbidity and suspended matter).
Sl. 4: Izvir Mlini: meritve motnosti, suspendiranih snovi, suhega ostanka in specifične električne prevodnosti – SEP jeseni 2001 (meritve motnosti in suspendiranih snovi so glajene 5 v 1).

The water present in the Mlini springs contains mostly calcium and hydrogen-carbonates. During the time of measurements it contained from 4 to 8.5% magnesium and from 2 to 7% of non-carbonates. The alkalinity ranged from 284 to 317 mg HCO_3^-/l, the total hardness from 242 to 272 mg $CaCO_3$/l, the share of calcium from 91 to 103 mg Ca^{2+}/l. The quantity of potassium fluctuated between 0.5 and 1.1 mg K^+/l, whereas the share of sodium oscillated more markedly between 1.9 and 4.8 mg Na^+/l. During the rise of the discharge at the time of water waves the quantity of sodium perceptibly decreased.

Dissolved oxygen, COD–Mn, BOD_5 and UV absorption

The water in the Mlini springs is well saturated with oxygen, *i.e.* from 87 to 104%. COD measurements showed values from 0.6 to 1.9 mg O_2/l, and BOD_5 measurements from 0.3 to 1.1 mg O_2/l (Fig. 5). The dilution effect in the period of the first two water waves resulted in a decrease of the physical-chemical parameters, and a simultaneous increase of the transfer of tiny, solid particles, also signified a slightly enlarged input of organic oxidizable substances. The largest increase of COD was registered during the water waves, although we detected a similar oscillation of this parameter later on as well.

Some organic substances, which usually emerge in the water, e.g. lignin, tannin, humic acids and various aromatic compounds, possess the manifested absorption within the UV area of λ=254 nm. The measured value of absorption denotes presence of these organic compounds and not an individual component. The increased values of organic burdening were detected after the rainfall and during the increased discharge of the spring (Fig. 5).

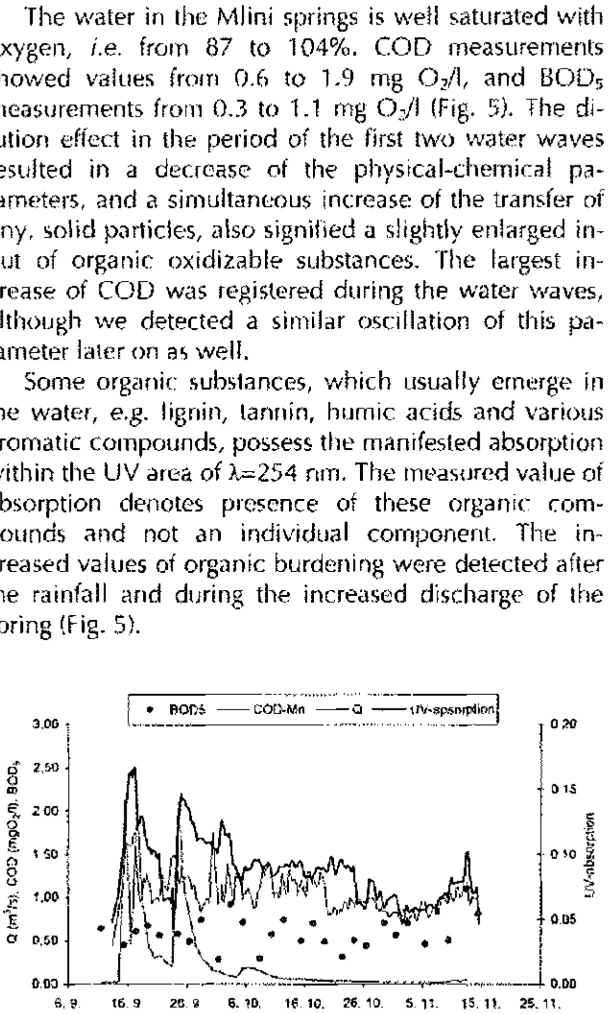

Fig. 5: Mlini spring: measurements of BOD_5, COD-Mn and UV-absorption conditioned by the water discharge in autumn 2001 (5-term smoothing used for values of UV absorption and KPK).
Sl. 5: Izvir Mlini: nihanje BPK_5, KPK-Mn in UV-absorbcije v odvisnosti od pretoka jeseni 2001 (vrednosti UV absorbcije in KPK so glajene 5 v 1).

Nutrient substances

Nutrient substances represent the compounds of nitrogen and phosphor. Various nitrogen compounds, which are apart of the nitrogen cycle or the compounds of differently valenced nitrogen, are created in nature by means of microorganisms. This cycle is one of the most important dynamic processes in nature and represents, together with the string of other bio-chemical reactions, the basis of bio-disintegration, which is taking place in nature. What occurs at this point is the process of exchange of nitrogen between the atmosphere, organic substance and inorganic compounds. The presence of ammonia and nitrites in water indicates organic pollution, since ammonia is generated through the microbiological disintegration of amino groups out of the proteins.

The analyses carried out at the Mlini springs indicated the quantity of the ammonia (present as NH_4^+) ranging between <0.001 and 0.080 mg N/l, whereas the concentration of nitrites was constantly below 0.001 mg N/l. The share of the organically bound nitrogen amounted up to 0.677 mg N/l. Nitrate is the final inorganic product of the mineralisation of the organic matter. During the water wave, we registered a noticeable decrease of nitrates, which we ascribe to the diluting process. The quantity of nitrates in the observed period oscillated between 0.10 and 1.48 mg N/l. At the same time there were no visible changes of other N-components, which signifies that at the time of the greater discharge the increased transfer of these components occurred.

The analyses of ortho-phosphates yielded values between 0.007 and 0.046 mg P/l, and in one case even 0.079 mg P/l. Some greater changes were detected in the total phosphorus, whereby during the water waves we registered some moderate oscillations, whereas larger increases were noticed only 25 to 30 days after the precipitation. Subsequent to this followed the period of the lowest values ranging from 0.020 to 0.060 mg P/l (Fig. 6).

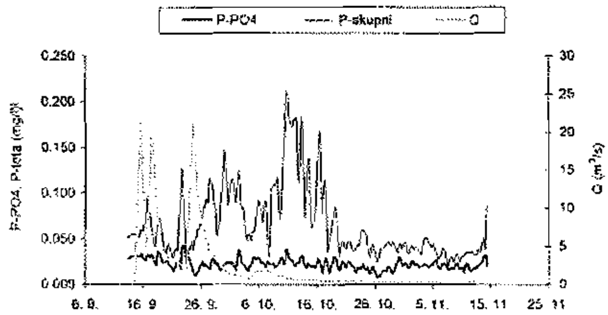

Fig. 6: Mlini spring: measurements of phosphates and total phosphorus (5-term smoothing used).
Sl. 6: Izvir Mlini: nihanje fosfatov in celokupnega fosforja ob nihanjih pretoka jeseni 2001 (vrednosti so glajene 5 v 1).

Organic compounds

In the water from the Mlini springs we also determined the quantity of total lipophilic substances and mineral oils. During the water waves after the precipitation there also occurred, in addition to the increased inflow of the suspended matter and organic pollution, an increase of the quantity of oil and grease or lipophilic substances, which were extracted in the strong organic solvent.

Subsequent to the first less intensive precipitation on 12 and 13 September, when the discharge of the Mlini spring did not yet significantly increase, besides the increase of the turbidity and oil and grease, a brief upsurge in the concentration of mineral oils (0.01 mg/l) also occurred. In the stable hydrological conditions, prior to the rainfall, their concentration was below 0.006 mg/l. During the water waves up to the middle of October their concentration, parallel to the decreasing discharge, oscillated around 0.0045 mg/l. In the stable conditions, during the further slow decrease of discharge below 0.6 m^3/s, a renewed rise of the concentration of mineral oils up to 0.0147 mg/l occurred. This pattern of the occurrence of mineral oils was recorded in all springs in the region of Istria: an increase in the share of mineral oils immediately after the precipitation due to the rise in the presence of suspended substances and the later increase of them in stabilised conditions, in transparent and clear samples. Here we are probably witnessing the initial washing out during the minimal increase of discharge and the later outflow of lighter oils, which were washed by rainfall through the vadose zone and along the connected channels reached the spring only during the lowering of the water level in the underground.

The quantity of oil and grease most markedly rose at the time of the first water wave (0.054 mg/l). During the second water wave it was below 0.012 mg/l, while later on, in the recession period, it again ranged from 0.013 to 0.031 mg/l.

Heavy metals

The water samples were analysed with regard to the concentrations of cadmium, copper, zinc, iron, manganese, total chromium and lead. The total content of metals was also determined both of the part dissolved in water and the part bound to the suspended particles. Cadmium concentration in the spring water is below the detection limit of 0.1 μg/l. Other metals occur occasionally in measurable concentrations. At the time of the first water wave the amount of metals increased.

Copper rose from the initial value of <1.0 μg/l to 31.7 μg/l, whereas later on it oscillated only up to the maximum concentration of 6.6 μg/l. The quantity of chromium in the first water wave increased to 11.8 μg/l and in the ensuing twenty days fell back to <0.1 μg/l. The concentration of lead increased in similar way from <0.1μg/l to 6.3 μg/l, then started to decline and fluctuate around the value of 1 μg/l, and fell under 0.1 μg/l only in the stabilised hydrological conditions in November. Manganese, too, rose significantly during the first water wave from its initial value of 0.1 to 105 μg/l, yet later its concentration rapidly declined and subsequently oscillated around the concentration of 2 μg/l.

The quantity of iron deviates from the pattern of the already mentioned metals. From the initial concentration of 26.3 μg/l it increased during the first water wave to 105 μg/l; during the second wave it increased to 126 μg/l and during the third wave to 146 μg/l. There followed a decline to the value of 24.4 μg/l reached by the end of October, with a subsequent upsurge to 179 μg/l after a minor discharge increase. The quantity of zinc slightly increased during the water waves, yet it reached its highest values in the recession period (Fig. 7).

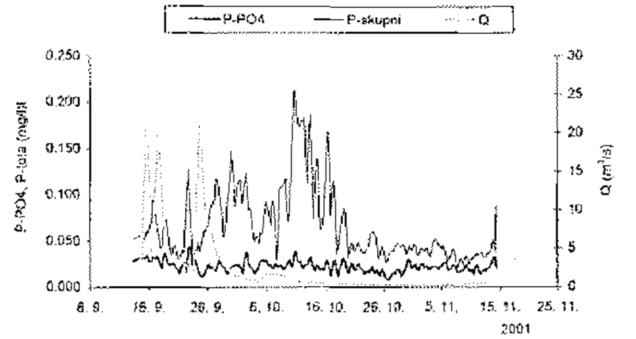

Fig. 7: Mlini spring: measurements of zinc, lead and iron in autumn 2001.
Sl. 7: Izvir Mlini: vsebnost cinka, svinca in železa jeseni 2001.

Bacteriological indicators

In the collected samples we analysed the following: total coliform bacteria (TC), faecal coliform bacteria (FC), faecal streptococci (FS), and aerobic mezophile bacteria (N/37) (Figs. 8 and 9).

Larger inflow of water from the surface layers during the water wave caused an increased microbiological pollution which, however, quite rapidly declined. In the second half of October and in November the bacteriological burdening of water was relatively low, yet it still did not fulfil the criteria required for the potable water.

The process of changes in the quantity of overall coliform bacteria (TC) and faecal coliform bacteria (FC) proved to be very similar (Fig. 8), except that the latter reached lower values. There were two maximums, the first on 13 September in the morning, when the discharge was only beginning to grow, and the other simultaneously with the highest discharge of the first wave. In the period of the second water wave, the TC and FC gradually decreased and reached the lowest values during the third water wave. More markedly they increased on 7 October during the decrease of the discharge after its slight increase.

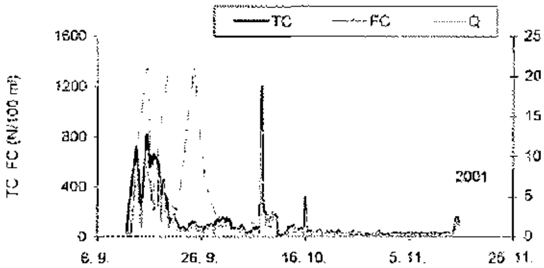

Fig. 8: Mlini spring: total coliform bacteria (TC) and faecal coliform bacteria (FC) in autumn 2001.
Sl. 8: Izvir Mlini: skupne koliformne bakterije (TC) in fekalne koliformne bakterije (FC) jeseni 2001.

Aerobic mezophile bacteria (N/37) increased slightly later than TC and FC, *i.e.* during the increase and decrease of the discharge in the 1st and 2nd water wave, as if a dilution effect occurred at the peak of the water wave. The quantity of faecal streptococci (FS) rose later than already mentioned bacteria and reached their maximal value with a slight delay after the peak of the first water wave; later, however, they gradually declined, yet they reached their initial value prior to the precipitation only in the middle of October, whereas later on their concentration fell even lower. The renewed rises were registered by the end of our observations, when the discharge increased once again (Fig. 9).

Comparison of the results with the measurements carried out within the framework of the national monitoring of the Republic of Croatia

The Mlini spring has been included in the Croatian national monitoring network since 1996. Since then the monitoring has changed a great deal, both in the extent of parameters and in the frequency of measurements and analyses. As far as the springs on the Istrian peninsula are concerned, there has been an increase in the number of parameters by means of which the samples of water were analysed, whereas the number of sample collection has fallen.

If we compare the minimal, maximal and mean values for the year 2000, when most sample collections were carried out (12), with the frequent sampling conducted from September to November 2001, we can notice that the majority of the parameter values from the detailed observations of the autumn 2001 actually fall into the range of measured values in the year 2000. Larger values were detected for SEC, alkalinity, total hardness, calcium and magnesium, which is a reflection of the increased dissolving of carbonate rocks in the autumn period. We also established an increased turbidity and larger shares of suspended solids, manganese, total chromium and especially an increased presence of all kinds of bacteria, as well as an occasional rise in the organic nitrogen, total phosphorus and phosphates. The majority of the increases were related to the rise in the discharge of the Mlini springs after precipitation, washing out of the aquifer and the enlarged transport power of water.

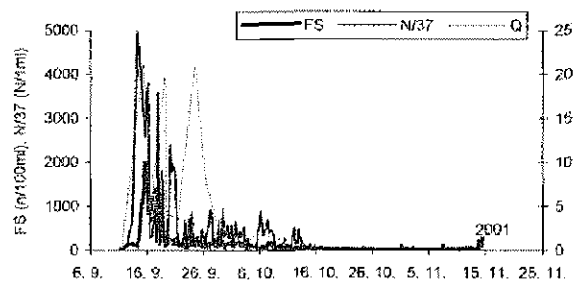

Fig. 9: Mlini spring: faecal streptococci (FS) and aerobic mezophile bacteria (N/37) in autumn 2001.
Sl. 9: Izvir Mlini: fekalni streptokoki (FS) in aerobne mezofilne bakterije (N/37) jeseni 2001.

These findings indicate a great importance of detailed observations of the springs, particularly during the periods of intensive precipitation when greater variations also occur, which cannot be perceived by regular monitoring with less frequent measurements.

CONCLUSIONS

The selected two-month period of observation of physical-chemical characteristics of the Mlini spring is interesting especially because of the possibility of observing the reactions of the spring to the precipitation after prolonged periods of draught. Hydrologically interesting is the response of the spring to the first rainfall at the beginning of September, which during two days exceeded 20 mm. The discharge did not change visibly, since the effective infiltration was due to the interception on the vegetation cover, increased evatranspiration and the filling in of the soil moisture deficit practically negligible. Only more intensive rainfall on September 15 resulted in a significant and rapid increase of the discharge, when we also monitored the changes in the composition of water.

The discharge increase of the Mlini spring subsequent to the precipitation signifies on the one hand dilution, which was reflected in low concentrations of dissolved substances (SEC, alkalinity, total hardness, calcium and magnesium), while on the other hand the precipitation caused intensive washing of the aquifer and also brought into the spring, during the increased discharge and along with enlarged transport power, greater quantities of suspended solids, increased organic pollutants (UV absorption, COD) and particularly bacteriological pollution as well as lager quantities of heavy metals (especially manganese and total chromium) bound to suspended particles. The quantity of mineral oils, which during the initial increased turbidity rose for a brief period, as well as the increase in the quantity of oil and grease during the first increase of the discharge and later in the stabilised hydrological conditions parallel to the slowly decreasing discharge, probably reflects a given manner of the transport of substances, which do not mix with water. This phenomenon was detected in karst springs throughout Istria (Diković & Stipić, 2000; Diković, 2001, 2002).

On the basis of the conducted research we may conclude that in order to obtain more accurate picture of the functioning, sampling would be required at intervals of at least 12 hours, which is due to the rapid changes, especially in the initial part of the water waves, whereas the measurements of temperature, SEC and pH by probes (automatic recording of data by means of dataloggers) should be carried out even more frequently. The described detailed manner of spring monitoring significantly supplements the usual karst spring monitoring, which was in the case of Mlini springs conducted at two-month intervals. The temporal planning of more accurate detailed measurements is subject to hydrological conditions. The performed measurements have shown that the greatest changes in water composition and quality occur during the increase of the spring's discharge after more extensive precipitation, particularly subsequent to a longer period of dry weather.

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POVZETEK

V okviru slovensko-hrvaškega medvladnega programa sodelovanja v znanosti in tehnologiji smo jeseni 2001 dva meseca podrobno spremljali kakovost vode na kraškem izviru Mlini. Izvir, ki je zajet za vodooskrbo vasi Mlini, leži v srednjem delu površinskega toka Bračane, ki je najpomembnejši desni pritok Mirne. Že od leta 1996 je vključen v nacionalni monitoring kakovosti hrvaških voda, v načrtovani raziskavi pa smo posebno pozornost posvetili detajlnemu spremljanju spreminjanja fizikalno-kemijskih parametrov vode v vodnem valu v ekstremnih hidroloških razmerah. Zajeli smo kratko obdobje nizkega vodostaja, ki so mu sledile kratkotrajne, a intenzivne padavine in oblikovale vodne valove ter daljše obdobje iztekanja in vzpostavljanja stabilnih razmer.

Po padavinah povečanje pretoka Mlinov pomeni po eni strani razredčenje, ki se je pokazalo v nižjih koncentracijah raztopljenih snovi (SEP, alkaliteti, celokupni trdoti, kalciju in magneziju). Na drugi strani pa padavine intenzivno spirajo zaledje izvira in ob povečanem pretoku z večjo transportno močjo prenašajo v izvir tudi večje količine *suspendiranih snovi, povečano organsko onesnaženje (UV absorpcija, KPK) in predvsem bakteriološko onesnaženje ter večje količine težkih kovin (predvsem mangan in celokupni krom), vezanih na suspendirane snovi. Vsebnost mineralnih olj, ki se je kratkotrajno zvišala ob začetni povečani motnosti, ter povečanje vsebnosti skupnih maščob ob prvem naraščanju pretoka ter kasneje v stabilnih hidroloških razmerah ob počasi upadajočem pretoku verjetno odseva način prenosa snovi, ki se z vodo ne mešajo. Ta pojav beležijo v kraških izvirih celotne Istre.*

Na osnovi opravljenih raziskav lahko zaključimo, da je zaradi hitrih sprememb, predvsem v začetnem delu vodnih valov, za pridobitev podrobnejše slike dogajanja potrebno vzorčevanje vsaj v intervalu 12 ur, medtem ko je priporočljivo meritve temperature, SEP in pH s sondami (avtomatsko beleženje podatkov z dataloggerji) opravljati pogosteje. Opisani podrobnejši način opazovanja izvirov je pomembna dopolnitev običajnega monitoringa kraškega izvira, ki se v primeru izvira Mlini opravlja v časovnem intervalu dveh mesecev. Časovno načrtovanje podrobnejšega merjenja je vezano na hidrološke razmere. Opravljene meritve so pokazale, da prihaja do največjih sprememb sestave oz. kakovosti vode ob povečanju pretoka izvira po izdatnejših padavinah, predvsem po koncu daljših sušnih obdobij.

Ključne besede: kraški izvir Mlini, monitoring, kakovost vode, Istra, Hrvaška, Slovenija

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