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Hydrodynamic and hydrochemical conditions at the groundwater source "Pašino vrelo", with a focus on its development

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ABSTRACT

At the "Pašino vrelo" source, groundwater is exploited by means of wells which tap a carbonate aquifer of Badenian age. The natural quality of groundwater complies with the provisions of the Regulation on health and safety of drinking water. However, anthropogenic impacts in the form of microbiological pollution have been observed. Extensive hydrogeological investigations have been conducted in recent years in the recharge area of the groundwater source with the aim of ensuring additional quantities of drinking water and protection of the source from pollution. The analysis of hydrogeological monitoring results for groundwater levels and discharges at the groundwater source confirmed the existence of a hydraulic connection between the Quaternary alluvial and Badenian carbonate aquifers. Differences in the hydrodynamic conditions between the "Pašino vrelo" spring and "Bojanića vrelo" spring have also been observed, and are related to the influence of pumping on the groundwater discharge regime, but also to drainage conditions at the springs. Hydrochemical indicators also suggest the mixing of groundwater from both aquifers in springs and exploitation wells. Specific hydrogeological conditions at the groundwater source determined the concept of its development. Recent hydrogeological research was carried out in order to explore the possibilities of tapping deeper parts of the carbonate aquifer in order to minimise the inflow of groundwater with anthropogenic impacts from the shallow alluvial aquifer during groundwater abstraction. Preliminary results for groundwater quality in the new well justified the aforementioned investigation approach. Intensive exploitation of the well will show whether these conditions are sustainable in the long term.

Keywords: carbonate/alluvial aquifer, groundwater, hydrodynamics, hydrochemistry, isotopes, groundwater quality protection, groundwater pollution

1. INTRODUCTION

The "Pašino vrelo" source of drinking water is located in the Sunja river valley, between the settlements of Borojevići and Mečenčani in the Sisak-Moslavina county, in the municipality of Hrvatska Kostajnica (Fig. 1). It is named after the "Pašino vrelo" spring, which is the most important hydrogeological phenomenon in the region. There is another spring at the groundwater source – "Bojanića vrelo", as well as pumping site facilities comprising four abstraction wells (PVB-1, PVB-2, PVB-3, and SPBPv-1/06) and several observation wells. The "Davidovića vrelo" and "Grabovac" springs occur in the vicinity of the groundwater source. The former is periodic and the latter a perennial spring. With respect to surface waters, the Sunja river is the most prominent watercourse, but there are also a few smaller streams – e.g. the Bekej stream in the south-eastern part of the groundwater source.

The pumping site has been active since the 1970s, when two wells were drilled, based on favourable results of hydrogeological and geophysical investigation works. Today, three active wells abstract groundwater from the carbonate aquifer of Badenian age which underlies the Quaternary alluvial aquifer. Both aquifers form the "Pašino vrelo" aquifer system, the hydrodynamic and hydrochemical characteristics of which had not previously been extensively explored. The nominal yield of the pumping site is 38.4 l/s, however, in practice about 20 l/s are abstracted on average, due to the limited flow rate in the distribution network. The natural quality of groundwater complies with the provisions of the Regulation on health and safety of drinking water (OG 47/08). However, specific hydrogeological conditions in the aquifer together with the occurrence of polluters in the immediate vicinity result in occasional microbiological pollution of groundwater. Such circumstances were important considerations in determining the concept of groundwater source protection, and in the investigative works carried out in recent years in order to ensure additional quantities of drinking water. In recent times there is a renewed need for abstraction of larger quantities of water at the pumping site, since the conceptual design of the water supply system anticipates, in its final stage, a maximum daily water consumption of 108 l/s.

The objective of this study was to increase the level of understanding of hydrogeological model of the "Pašino vrelo" groundwater source. This was accomplished by conducting analyses of the hydrodynamic and hydrochemical characteristics of both the Quaternary alluvial aquifer and Badenian carbonate aquifer.

Research was undertaken between 2005–2007. A groundwater monitoring program was established in order to interpret the hydrodynamics of the aquifer system. It included monitoring of groundwater levels in the alluvial aquifer, water levels in the "Pašino vrelo" spring and discharge of both the "Pašino vrelo" and "Bojanića vrelo" springs. On several occasions, groundwater samples were taken from springs and wells for the purpose of defining the hydrochemical conditions in the aquifer. Besides the measurements of physical and physico-chemical parameters of groundwater *in situ*, analyses were subsequently conducted in laboratories regarding the basic chemical composition and the ratios of stable hydrogen and oxygen isotopes in the groundwater. Application of the mass-balance model facilitated estimation of the proportions of water from carbonate and alluvial aquifers in the wells and springs under different hydrological conditions.

The research results provided the basis for updating the protection zones according to the Regulation on the determination of sanitary protection zones of the source (OG 55/02) and directed the investigations towards deeper parts

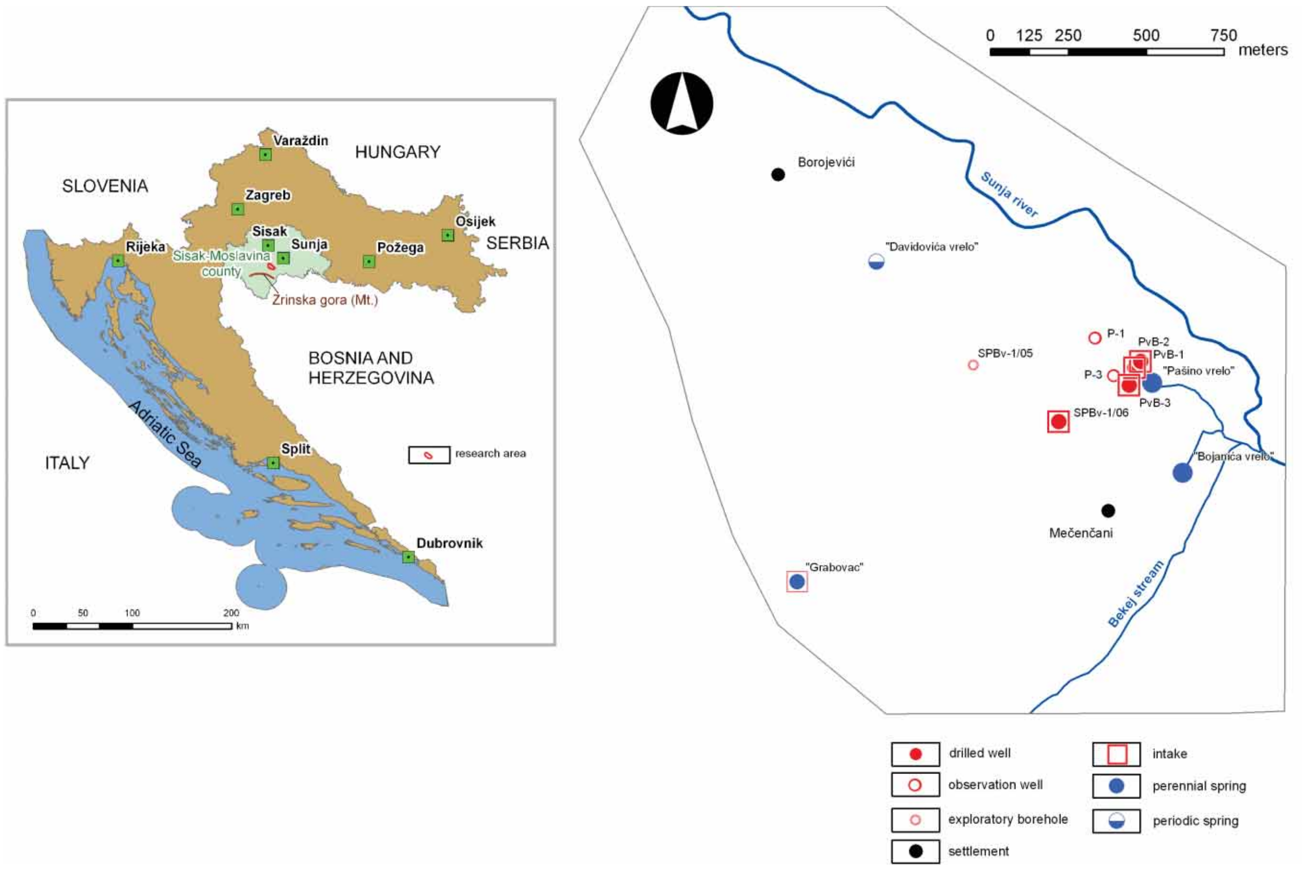

Figure 1: Location map showing the studied springs and wells.

of the carbonate aquifer with the aim of abstracting additional groundwater quantities without anthropogenic contamination. Thus, in 2005, an exploratory borehole SPBPv -1/05, and a year later a test exploitation well SPBPv-1/06 were drilled west of the pumping site. The results of the pumping test as well as of chemical analyses of groundwater from the well are promising with respect of both groundwater abstraction quantity and quality.

2. HYDROGEOLOGICAL CHARACTERISTICS OF THE GROUNDWATER SOURCE

In the greater area of the groundwater source, deposits range in age from the Palaeogene to the Quaternary (Fig. 2). The Palaeogene is represented by Eocene flysch sediments (E), which are characterized by both vertical and lateral exchange of sandstones, shales, siltites and conglomerates. Weathering of these resulted in materials which formed younger sediments. The possibility of groundwater accumulation in them is slight, but they are therefore characterized by a developed surface hydrographic network. The springs in these deposits have low yields, of 0.1 l/s or less.

Ottnangian clastites (M_3) discordantly overlie the Eocene deposits. They appear as erosion remnants in Eocene flysch, and consist predominantly of alternations of clayey sands and clays.

Badenian deposits (M_4) transgressively overlie the Ottnangian sediments. The basal part of these mostly consists of loosely cemented conglomerates or breccias, with fragments of older bedrock. They are overlain by carbonate rocks represented by lithothamnium limestone. These rocks are porous, and thus enable infiltration of surface waters and circulation of groundwater. Besides the porosity, the Badenian rocks are often also characterized by karst phenomena - sinkholes, smaller caves and conduits with significant local influence on the hydraulic characteristics of the deposits.

_Sarmatian and Pannonian sediments (M_5 and M_6) are predominantly represented by marls, and Plio-Pleistocene clastites (Pl, Q) are mostly clays, clayey sands and sometimes gravels.

The youngest deposits are Quaternary alluvial sediments (al, Q_2), which are found in the Sunja river valley. They are represented by gravels, sands, clays and clayey gravels with boulders of older rocks, and originate from the weathering and resedimentation of older rocks. The deeper parts mostly consist of coarser, prolluvial deposit, with subsequent sedimentation of river sediment. The Sunja river frequently changed its course in the past, which caused vertical and lateral

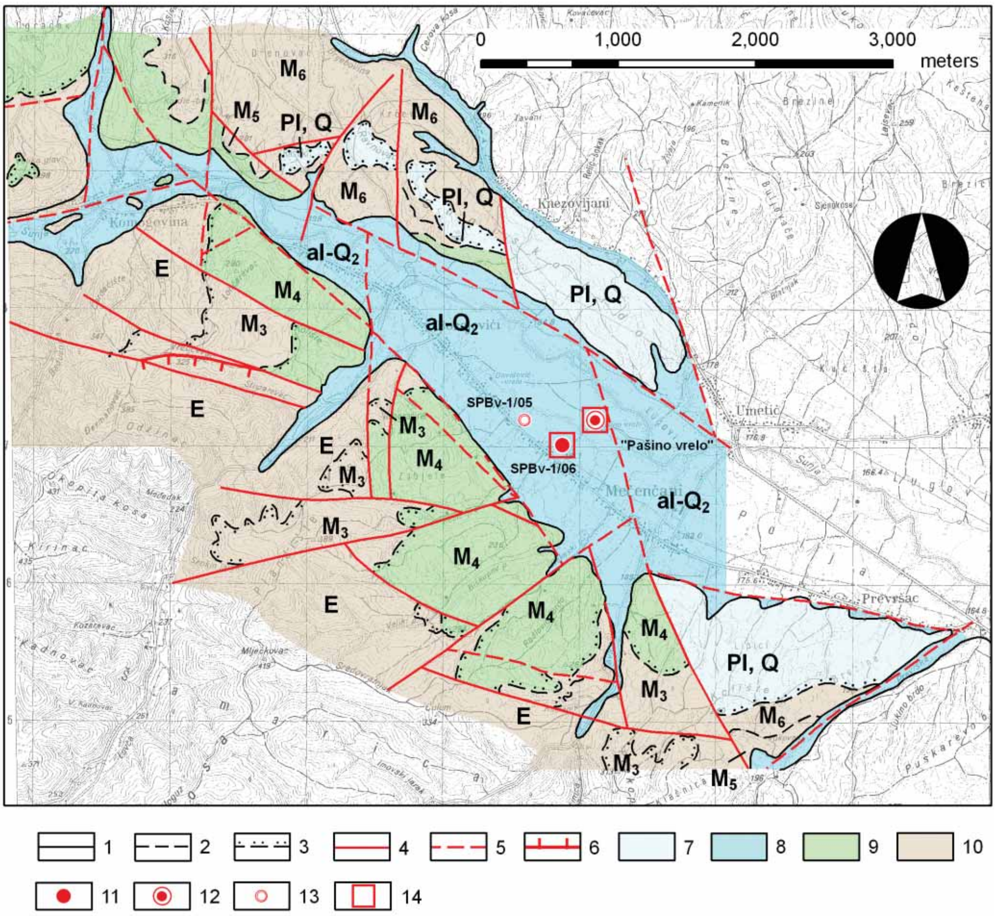

Figure 2: Hydrogeological map. 1 – geological boundary; 2 – supposed geological boundary; 3 – supposed transgressive boundary; 4 – fault; 5 – supposed fault; 6 – reverse fault; 7 – Plio-Pleistocene clastic sediments, Pl, Q – poorly permeable rocks; 8 – Quaternary alluvial sediments, al-Q2 – dominantly very permeable rocks; 9 – Badenian lithothamnium limestone, M4 – permeable rocks; 10 – Eocene, Ottnangian, Sarmatian and Pannonian clastic sediments, E, M3, M5, M6 – dominantly impermeable rocks; 11 – drilled well; 12 – dug well; 13 – exploratory borehole; 14 – intake.

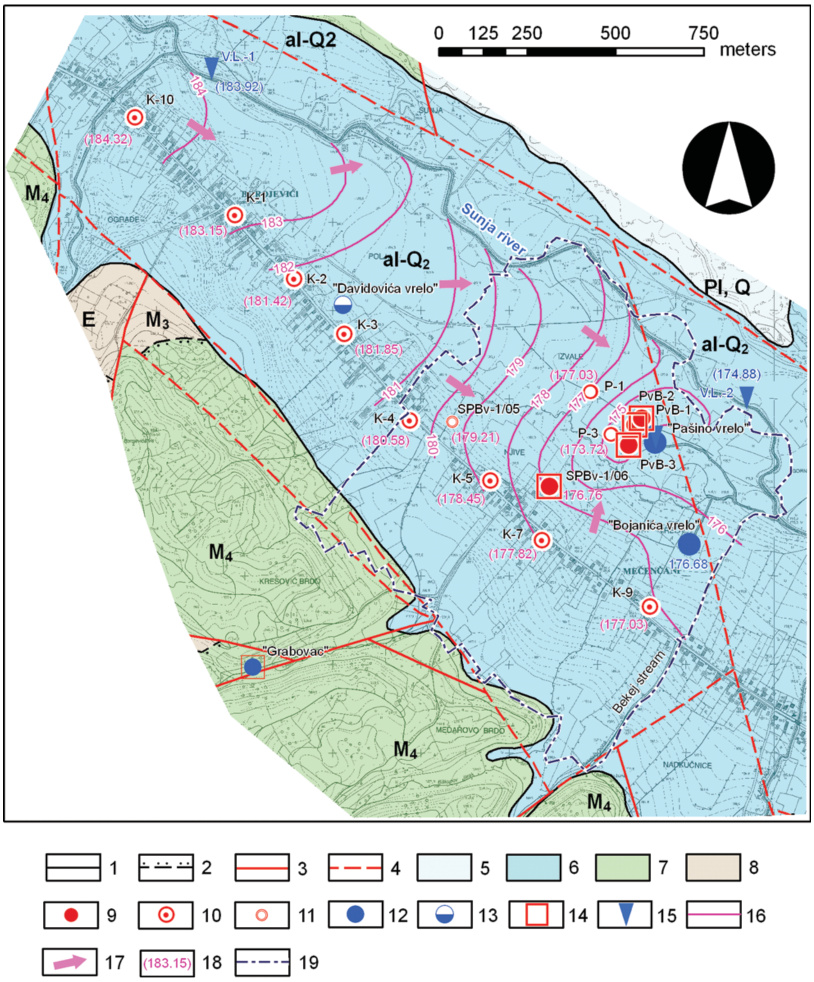

Figure 3: Equipotential map with groundwater flow direction and outer boundary of the II. protection zone. 1 – geological boundary; 2 – supposed transgressive boundary; 3 – fault; 4 – supposed fault; 5 – Plio-Pleistocene clastic sediments, Pl. Q – poorly permeable rocks; 6 – Quaternary alluvial sediments, al-Q2 – dominantly very permeable rocks; 7 – Badenian lithothamnium limestone, M4 – permeable rocks; 8 – Eocene, Ottnangian, Sarmatian and Pannonian clastic sediments, E, M3, M5, M6 – impermeable rocks; 9 – drilled well; 10 – dug well; 11 – exploratory borehole; 12 – perennial spring; 13 - periodic spring; 14 – intake; 15 – staff gauge; 16 – equipotential line; 17 – groundwater flow direction; 18 – piezometric head; 19 – outer boundary of the II. protection zone

interfingering of coarse-grained gravel, sand and sandy and gravelly clay. The whole Sunja alluvium is approximately 10 m thick, unconsolidated to poorly consolidated sediment, which in its coarse-grained parts, enables infiltration and circulation of groundwater.

From the hydrogeological standpoint, these sediments can be categorized as either impermeable or permeable rocks. Eocene, Ottnangian, Sarmatian and Pannonian clastites are impermeable rocks, whereas the group of permeable rocks includes the carbonate deposits of Badenian age and Plio-Pleistocene and Quaternary alluvial sediments.

In the lithological cross-section in the greater area of the “Pašino vrelo“groundwater source, the Quaternary alluvial aquifer is located immediately above the Badenian carbonate aquifer. The appearance of the springs was enabled by favourable structural-tectonic relationships. These are characterized by the Dinaric strike of the main structural units and tectonic elements. Along the faults, there appears to be a gradual lowering of Neogene deposits towards the northeast. Repeated tectonic movements caused fracturing of hard carbonate rocks, thus creating conditions for infiltration and circulation of water below ground. The appearance of the “Pašino vrelo” and “Bojanića vrelo” springs are consequences of a pronounced diagonal fault in the Sunja valley, which brought into direct contact permeable lithothamnium limestones and impermeable Pannonian marls. Impermeable marls caused the appearance of upward springs in this part of the Sunja river valley, thus forming the “Pašino vrelo” groundwater source.

3. HYDRODYNAMIC CONDITIONS AT THE GROUNDWATER SOURCE

The first known data on yields at the “Pašino vrelo” groundwater source date back to 1970-1974 (MAGDALENIĆ et al., 1976). The characteristic values of daily discharges at the “Pašino vrelo” spring at that time were: Qmax = 115 l/s; Qmin = 52 l/s; Qmean = 75 l/s. The authors state that the minimum discharge of the “Pašino vrelo” spring group, which also includes the “Bojanića vrelo” spring, exceeds 80 l/s.

At the end of 2005, hydrogeological monitoring was again established in the greater area of the pumping site. Groundwater levels were monitored in dug wells, piezometers and an exploratory borehole (Fig. 3). The dug wells tap the Quaternary alluvial deposits of the Sunja River, whereas the piezometers, exploratory well and drilled wells tap the Badenian carbonate aquifer. Water levels were monitored at the “Pašino vrelo” spring, while spring yields were estimated at “Pašino vrelo” spring and “Bojanića vrelo” spring using weirs. Upstream and downstream of the pumping site, staff gauges were installed in the Sunja River.

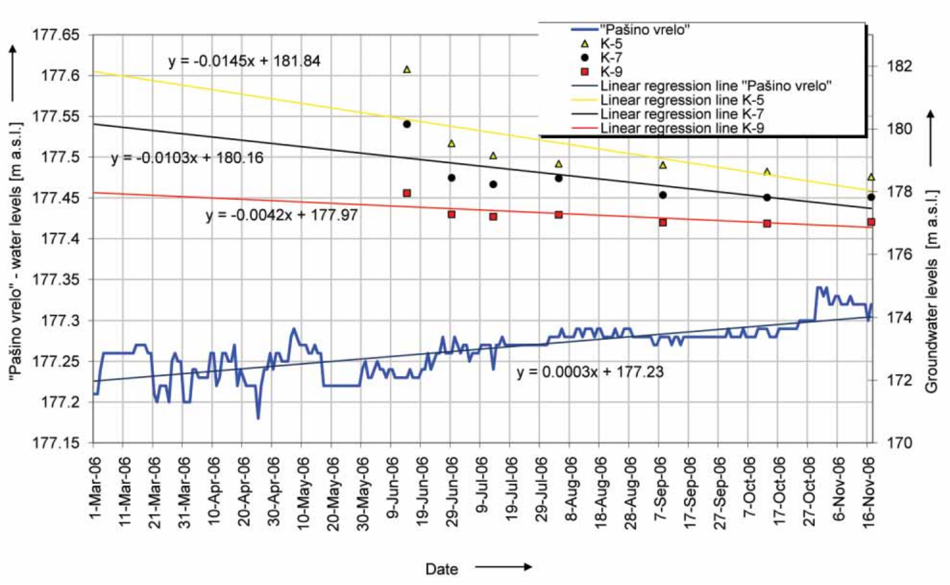

Figure 4 : Groundwater levels in dug wells and the "Pašino vrelo" spring with linear regression lines.

Interpolation of groundwater levels in the monitored facilities and the water levels between the staff gauges in the Sunja River allowed construction of a groundwater equipotential map for low water levels conditions on 17 November 2006 (Fig. 3). Groundwater flow has a general south-east direction. The drainage influence of the river is observed as well as a cone of depression caused by groundwater abstraction at the pumping site.

Hydrodynamic conditions in the Badenian carbonate and Quaternary alluvial aquifers were investigated by analysing a groundwater level time series at the pumping site and in its recharge area as well as through the yields of the "Pašino vrelo" and "Bojanića vrelo" springs.

Oscillations of groundwater levels in the Quaternary alluvial aquifer and the water levels in the spring "Pašino vrelo", revealed opposite trends (Fig. 4). In the Quaternary alluvial aquifer, groundwater levels show a trend of lowering from the beginning of June to mid-November 2006. Conversely, the "Pašino vrelo" spring showed a trend of rising water levels over a slightly longer monitoring period from the beginning of March to mid-November 2006.

The yields of the "Pašino vrelo" and "Bojanića vrelo" springs show different dynamics from November 2005 to December 2007 (Fig. 5). The values registered at the "Pašino vrelo" spring range from 6.7 l/s in January 2006 to 25 l/s in February and April 2007. On the other hand, the "Bojanića vrelo" spring shows greater oscillations in yield, ranging from 3.5 l/s in August 2007 to 50 l/s in December 2007. When the yields of the "Pašino vrelo" groundwater source between 2005−2008 are compared to the yields of the same spring between 1970−1974, a substantial decrease is quite obvious.

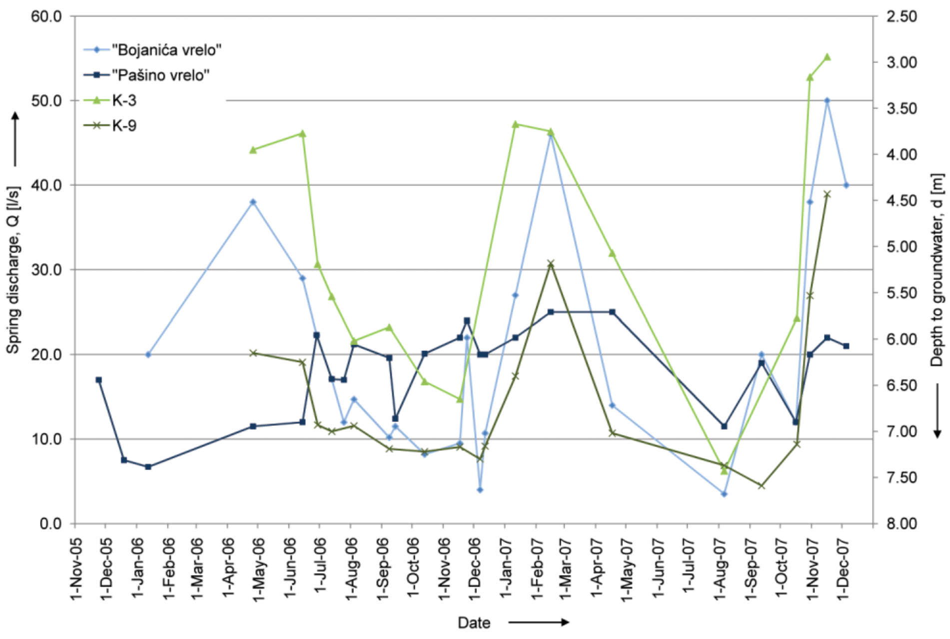

Figure 5: Depths to groundwater in dug wells and springs disc charge.

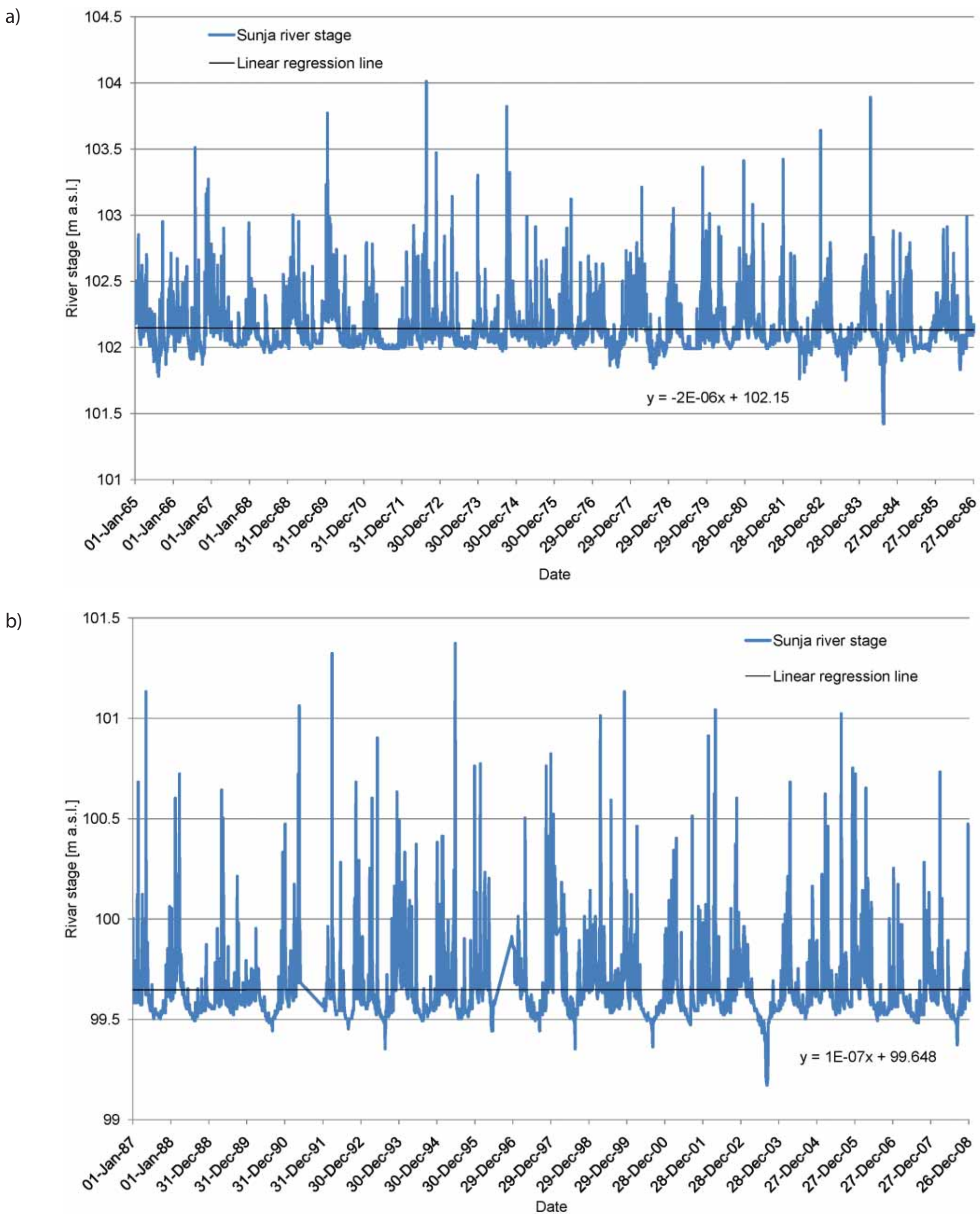

Figure 6: Sunja river stages at the gauging station in Sunja with a linear regression line for a) 1965–1987 and for b) 1987–2009.

In order to assess the hydrological conditions in the region and their possible influence on the reduction in spring yields, the following data were analyzed:

- A time series of stage data on the Sunja River from 1965–2009. The gauging station is located in Sunja (Fig. 1). The stage data were analyzed separately for the periods 1965-1987 and 1987–2009 because the gauging station was moved from its original position to a new location at the beginning of 1987.
- A time series of precipitation data for 1965–2009 at the main meteorological station at Sisak (Fig. 1), located approximately 20 km to the north of the investigated area.

Analysis of the stage data on the Sunja River shows no meaningful trend (Figs. 6a, b). However, the precipitation data shows a definite increasing trend (Fig. 7). Total annual precipitation ranges from 590 to 1160 mm. The lowest and the highest amounts of precipitation were registered in 1971 and 2002 respectively. In the 44-year period, mean annual precipitation was 893 mm. These hydrological conditions could not lead to the observed reduction of spring yield. Based on performed analyses, it could be concluded that the lowered yields in recent years are mostly a consequence of groundwater exploitation over a long time.

In addition to the observed differences in the ratios of maximum to minimum yields in the "Pašino vrelo" and "Bojanića vrelo" springs, occasional variation in trends were also apparent (Fig. 5). Thus, for instance, in the period from 26 April to 28 June 2006, the yield of the "Pašino vrelo" spring increased from 11.5 l/s to 22.3 l/s. At the same time, the yield of the "Bojanića vrelo" spring decreased from 38

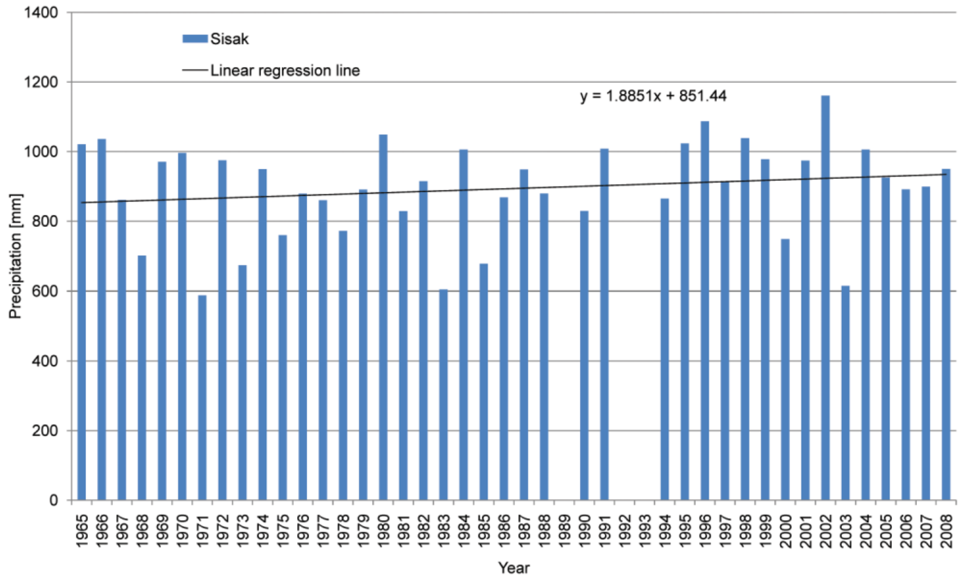

Figure 7: Total annual precipitation at the Sisak meteorological station with linear regression line for 1965–2009.

l/s to 22.3 l/s. These circumstances are partly related to the impact of pumping on the discharge regime at the "Pašino vrelo" spring, but above all to the different hydrodynamic characteristics of the two springs. Corresponding yield trends of the "Bojanića vrelo" spring and hydrographs of groundwater in wells K-3 and K-9 are also significant. In the periods marked by a decrease in groundwater levels in the wells, the yield of the "Bojanića vrelo" spring also decreased, and vice versa – an increase in the yield of the "Bojanića vrelo" spring is followed by increased water levels in the wells. Conversely, yields of the "Pašino vrelo" spring do not show such correlation with water levels in the Quaternary alluvial aquifer.

In November 2006, a pumping test was conducted on the SPB-Pv-1/06 well. During the continuous pumping rate of 21.9 l/s, it was noticed that discharge from the "Pašino vrelo" spring remained relatively unaltered at 20 l/s whereas discharge from the "Bojanića vrelo" spring was only 4 l/s. Although the spring yields were not controlled immediately prior to the start of pumping test, measurement data 13 days prior to pumping may serve for orientation purposes when discharge from the "Pašino vrelo" spring was 24 l/s, and 22 l/s from "Bojanića vrelo" . About ten hours after the pumping test was completed, the yield of the "Pašino vrelo" spring remained at 20 l/s, whereas the yield of the spring "Bojanića vrelo" increased from 4 l/s to 10.7 l/s.

Analysis of the hydrodynamic characteristics of the Badenian carbonate and the Quaternary alluvial aquifers in the greater area of the groundwater source, indicate a hydraulic connection between the genetically distinct aquifers and different groundwater discharge conditions at the "Pašino vrelo" and "Bojanića vrelo" springs. The "Pašino vrelo" spring shows greater yield stability and is more strongly influenced by inflow from the carbonate aquifer when compared to the spring "Bojanića vrelo". Conversely, the "Bojanića vrelo" spring is more directly influenced by the hydrodynamic conditions in the alluvial aquifer, as confirmed by a very good positive correlation of yields of the "Bojanića vrelo" spring and groundwater levels in the Quaternary alluvial aquifer.

4. HYDROCHEMICAL CHARACTERISTICS OF GROUNDWATER

During June and September 2006 as well as April, September and October 2007, groundwater samples were taken from the wells (PVB-1, PVB-2 and PVB-3) and from the springs (the "Pašino vrelo" and "Bojanića vrelo") at the groundwater source "Pašino vrelo", as well as from the "Grabovac" spring, which drains the groundwater from the lithothamnium limestones. Water samples were also taken from the Sunja River. Prior to sampling, the following parameters were measured ''in situ'' by probes of the WTW company: electrolytic conductivity (EC), total dissolved solids (TDS), temperature (T), pH and oxygen content in waters to be sampled. At the Hydrochemical Laboratory of the Department of Hydrogeology and Engineering Geology at the Croatian Geological Survey, the concentrations of basic anions: chlorides, sulphates and nitrates were measured by ion chromatograph (by the LabAlliance Co.), whereas the concentrations of orthophosphates and ammonium were measured by spectrophotometer DL/2010 (by the HACH Co.). Concentrations of the basic cations: calcium, manganese, sodium and potassium were measured by atomic adsorber (Perkin Elmer Co.). The content of HCO_3^- was determined by titration. Ratios of the stable isotopes of hydrogen (δD, δ^2H) and oxygen ($\delta^{18}O$) in sampled water were measured at the JOANNEUM RESEARCH Forschungsgesellschaft mbH, Institute of Water Resources Management (WRM) Hydrogeology and Geophysics in Graz, Austria.

Water temperatures ranged from 10.7 to 21.2^{o}C (Table 1), the smallest variations being observed in springs and wells (11 to 12^{o}C). This indicates the mean annual temperature in their recharge area. However, water temperatures in

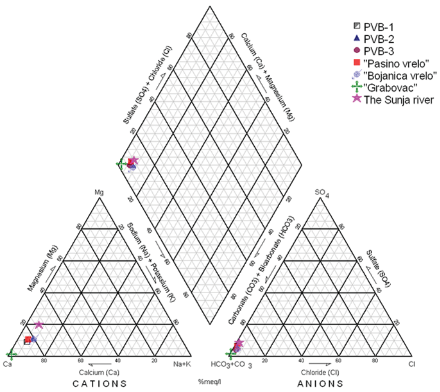

Figure 8: Piper diagram of sampled waters from the study area.

the surface flow of the Sunja indicate differences in temperatures during colder and warmer months as a consequence of cooling and warming of the watercourse. It has long been observed that temperatures in surface water bodies show diurnal and annual oscillations, related to weather conditions, particularly atmospheric temperature (KEERY et al., 2007). The pH-values range from 7.02 to 8.26, thus the waters are neutral to mildly alkaline (Table 1). The water from the springs is well saturated with oxygen, whereas the water from the wells is poorly saturated with oxygen (Table 1). Poorer oxygen saturation of well waters is a consequence of the consumption of oxygen in the alluvial aquifer for different chemical reactions, such as the oxidation of organic matter, mineral wear, nitrogen transformation processes, etc. The measured EC values range from 222 to 581 μS/cm (Table 1). Higher EC values and total dissolved solids (TDS) were measured in the water of the "Grabovac" and "Bojanića vrelo" springs as well as well PVB-3. Slightly lower values were measured in the other wells (PVB-1 and PVB-2) and in the "Pašino vrelo" spring and the lowest values were measured in the Sunja watercourse itself (Table 1). The EC and TDS values of the measured waters indicate a grouping of springs and wells according to the proportion of waters from lithothamnium limestones and alluvium, depending on hydrological conditions. During wet months (maximum and medium waters), a significant influence of waters from the alluvial aquifer was observed in the wells PVB-1 and PVB-2 and in the springs "Bojanića vrelo" and "Pašino vrelo", whereas in the drier period (minimum waters) there is a stronger influence from the lithothamnium limestones. In the PVB-3 well, water from the lithothamnium limestones was the dominant influence observed throughout the hydrological year.

According to the basic ionic composition (Piper diagram), the analyzed groundwater belongs to the Ca-HCO_3 water type, while the water sampled from the Sunja river belongs to the CaMg-HCO_3 water type (Fig. 8). Such hydrochemical facies of water is a consequence of the dissolution of carbonate minerals in the recharge area of the springs, wells and the river.

The quantity of dissolved carbonate minerals depends on the partial pressure of CO_2, i.e. the solubility of CO_2 in water, since its solubility increases simultaneously with the increase of partial pressure of carbon dioxide leading to increased quantities of carbonic acid and greater solubility of carbonate minerals (STUMM & MORGAN, 1996; HEM, 1989). If, however, for some reason, the partial pressure of CO_2 is reduced, there is a reduction in its solubility, and the opposite reaction becomes possible – precipitation of carbonate minerals (GARRELS & CHRIST, 1965; MACPHERSON et al., 2008). The saturation index of water is a measure which serves as an indicator of changes in balance between the solid phase (carbonate minerals) and liquid phase (groundwater).

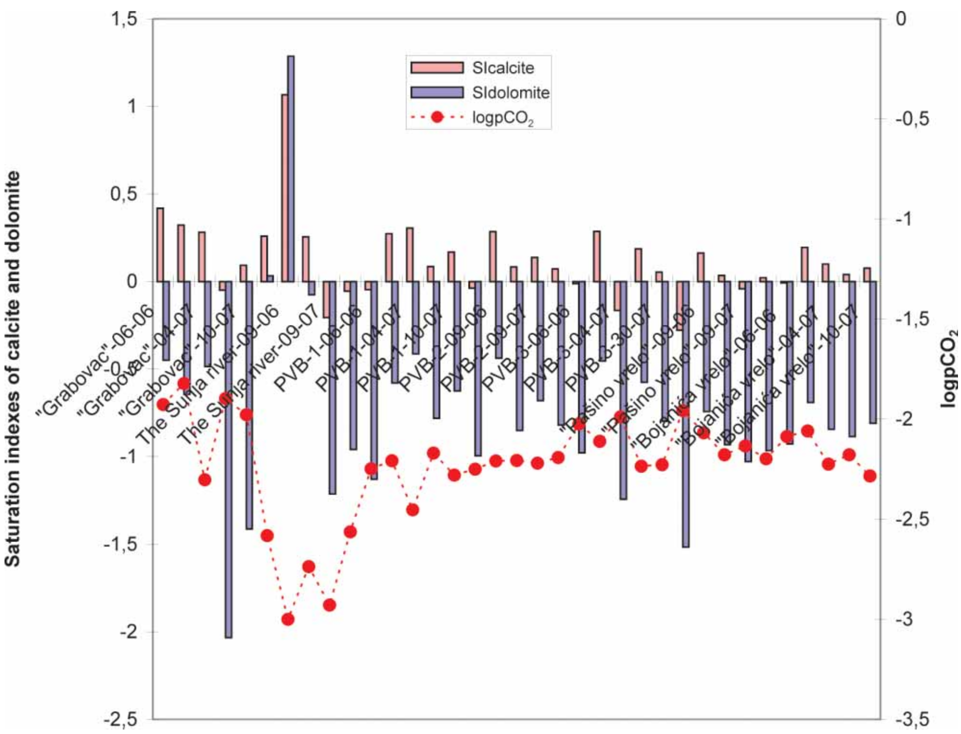

Figure 9: Distribution of calculated saturation indices of calcite and dolomite and logCO_2 of sampled waters.

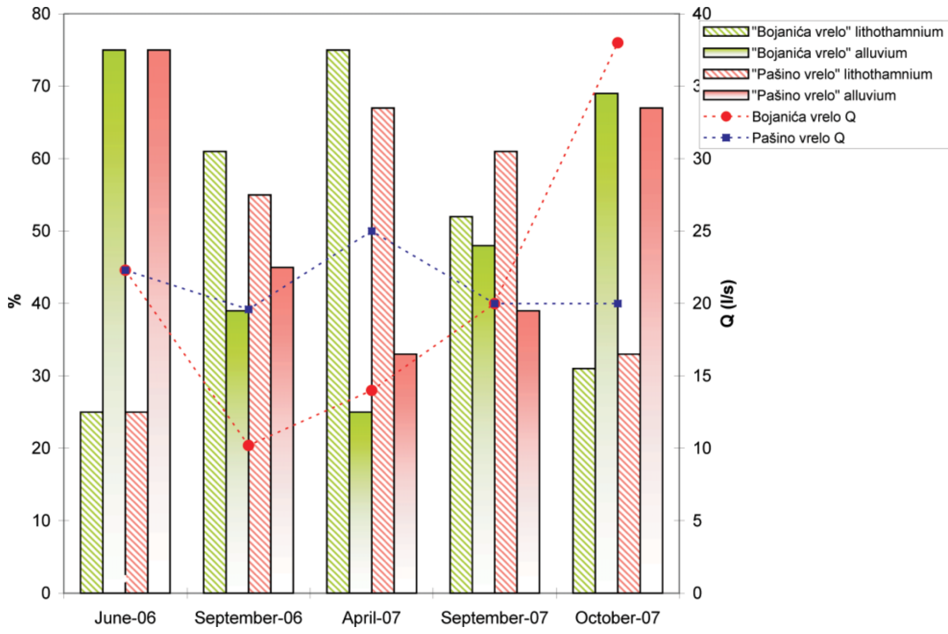

Figure 10: Plot of calculated mixing portions of waters from "Bojanića vrelo" and "Pašino vrelo".

Based on the results obtained by chemical analyses, partial pressure of CO_2, indices of saturation of calcite and dolomite are calculated by application of the geochemical mass-balance model NETPATH (PLUMMER et al., 1994). It is evident that the sampled waters are mostly saturated with respect to calcite, and unsaturated in respect of dolomite (Fig. 9). A higher (positive) partial pressure of CO_2 is observed during the colder months compared to warmer months (Fig. 9). A higher partial pressure of CO_2 during colder months is a consequence of the transport of organic matter from the surface of the terrain into the underground, under conditions of low soil and air temperatures, so that CO_2 is not released from the soil, but dissolves in the water. In addition, there is higher precipitation (snow and rain) in the colder months, dissolving CO_2 and infiltrating it below ground. Conversely, in the warmer months, with less precipitation and higher air and soil temperature, CO_2 is released from the soil, thus creating a lower partial pressure of CO_2 in groundwater. Due to a higher partial pressure of CO_2 carbonate rocks dissolve, thus the values of calcite saturation index are lower, or in some cases, water is unsaturated with regard to calcite (e.g. "Grabovac"/09/07). Lithothamnium limestones are more soluble than carbonate boulders which comprise the Quaternary alluvial aquifer, thus the EC values of water from the lithothamnium aquifer are higher in relation to waters from the alluvial aquifer. Similarly, understanding changes in the balance between the solid phases (carbonate minerals, i.e. calcites and dolomites) and the liquid phase (groundwater) is important for the natural control of groundwater quality. Heavy metals which show an affinity for the carbonate min-

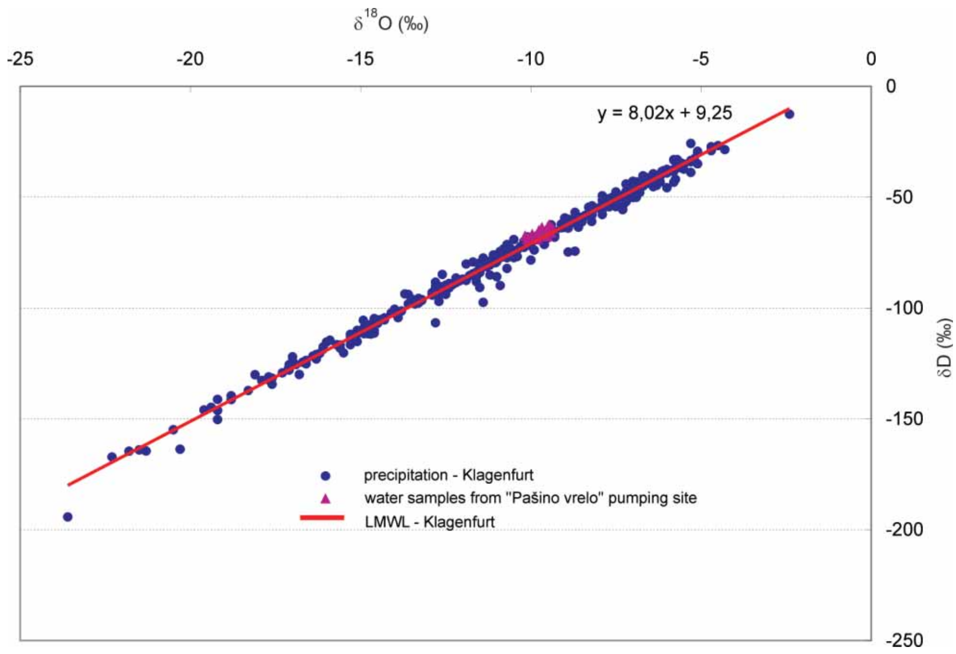

Figure 11: Stable isotopic composition of water samples collected from the spring and wells at the "Pašino vrelo" groundwater source relative to the meteoric water line from Klagenfurt.

eral phase tend to be deposited together with calcite, mostly in the form of coatings, and leach out from water (HERRERA et al., 2008; CURKOV et al., 2008; LAKSHTANOV & STIPP, 2007; ZACHARA et al., 1988, 1991).

Estimation of the proportions of water from the lithothamnium and alluvial aquifers in the "Pašino vrelo" and "Bojanića vrelo" springs, and wells PVB-1, PVB-2 and PVB-3 was carried out using the NETPATH software (PLUMMER et al., 1994). This program was used to interpret net geochemical mass-balance reactions between the initial waters that mix and the final waters along real flow paths in aquifers or other hydrologic systems. The program uses geochemical modelling techniques (PLUMMER et al., 1983; PLUMMER, 1985; PARKHURST & PLUMMER, 1993; GLYNN & BROWN, 1996; NORDSTROM, 2007) to construct geochemical reaction models, using chemical and isotopic data for waters from the hydrochemical system. The model is a set of mixing fractions and mole transfers that precisely account for the changes in concentration of elements in the waters (PLUMMER et al., 1994). Models between selected evolutionary waters are found for every possible combination of the plausible phases that can account for the composition of a selected set of chemical and isotopic constraints in the system (PLUMMER et al., 1994).

Simultaneous water drainage was observed at springs from both aquifers (Fig 10). However, the proportions change depending on hydrological conditions. Thus, in the conditions of lower and medium waters (September 2006, April 2007 and September 2007), the prevailing groundwater component is from the carbonate aquifer. Conversely, during high waters, groundwater from the alluvial aquifer prevails (June 2006 and October 2007).

From the measured ratios of stable oxygen and hydrogen isotopes, it is evident that the waters from the "Pašino vrelo", "Bojanića vrelo" and "Grabovac" springs, and the wells PVB-1, PVB-2 and PVB-3, are directly influenced by renewal from recent precipitation, since the values are evenly dispersed along the local meteoric water line (LMWL) – Klagenfurt (Fig. 11).

Changes in the $\delta^{18}O$ ratio of monitored waters are small, indicating a complex hydrogeological system in the recharge zone of the springs and wells of the "Pašino vrelo" groundwater source. The recharge area of the Sunja river is on Mt. "Zrinska gora" (Fig. 1), where altitudes range from about 178 m a.s.l to about 600 m a.s.l. Depending on the hydrological conditions (precipitation quantity and season), the measured $\delta^{18}O$ values were more negative (-9.96 ‰) when the Sunja is influenced by tributaries from the higher altitudes and colder precipitation, while they were more positive (-9.36 ‰) in reverse conditions (Fig. 12). The Sunja recharges the alluvial aquifer in its valley, and thus influences the isotopic composition of water in wells and springs (Fig. 12). However, at times of low waters, the isotopic composition of spring waters is influenced by groundwater from the lithothamnium limestones. A similar scenario was observed between the waters from the "Grabovac" and "Bojanića vrelo" springs. At times of high waters, both springs have the same recharge area, i.e. the hilly parts of Mt. "Zrinska gora". However, the $\delta^{18}O$ values measured at times of low waters indicate the recharge of these springs from higher altitudes. Furthermore, the measured negative $\delta^{18}O$ values in water samples from the "Pašino vrelo" spring indicated that its recharge area is larger, encompassing not only the hilly parts of the Mt. "Zrinska gora" area but also Mt. "Zrinska gora" itself. At higher altitudes, where the average temperatures are lower, precipitation is isotopically depleted (CLARK & FRITZ, 1997). This altitude effect is useful in hydrogeological studies, as it distinguishes groundwater re-

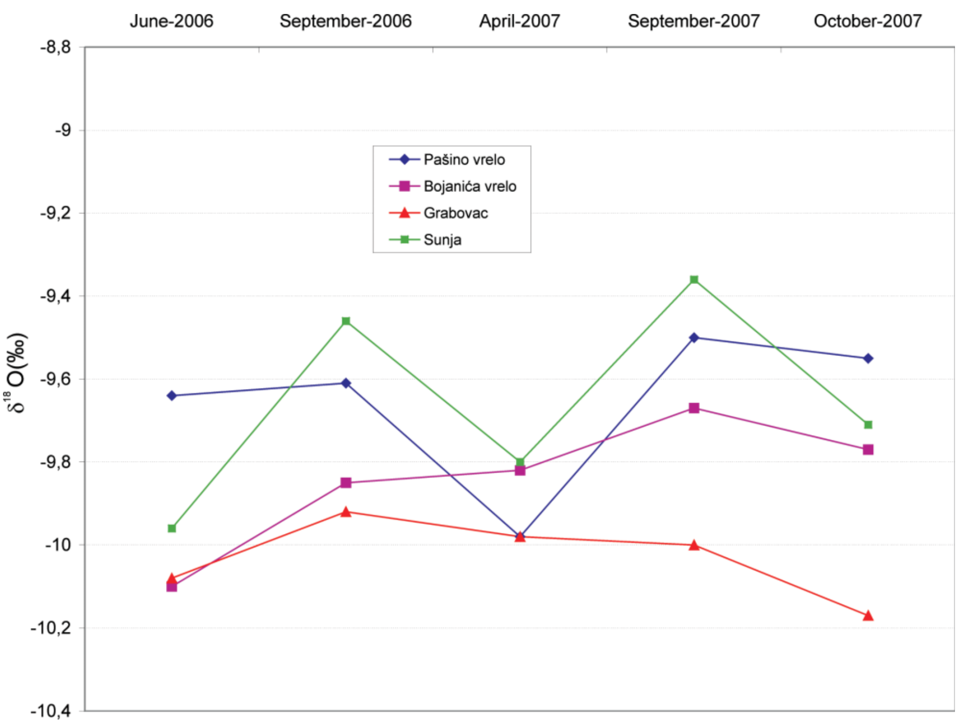

Figure 12: Stable isotopic composition of waters sampled from Grabovac, Sunja, "Bojanića vrelo" and "Pašino vrelo".

Table 1: Results of measured physical, physico-chemical and chemical parameters of the sampled waters.

	EC (µS/cm)	TDS (mg/l)	T (°C)	pH	O_2 (%)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	NH_4^+ (mg/l)	$PO4^{3-}$-P(mg/l)
PVB-1-06-06	367	256	11.4	7.47	55	63.9	4.2	4.1	1.7	203	11.5	1.9	4.9	<0.01	0.03
PVB-1-09-06	361	252	12.5	7.56	60	82	4.2	9.9	3.3	274	11.3	3.2	4.3	<0.01	0.04
PVB-1-04-07	340	238	10.8	7.74	50	69	4.8	12.4	2.1	240	12.7	3.5	4.4	<0.01	0.05
PVB-1-09-07	375	263	12.2	7.48	48	70	5.4	13.2	2.3	248	14.4	4.6	4.8	0.01	0.02
PVB-1-10-07	366	256	12.9	7.59	57	64.2	4.7	13.2	1.9	246	14.4	4.3	4.3	<0.01	0.04
PVB-2-06-06	366	256	11.3	7.47	47	66.1	5.7	6.7	1.7	203	11.8	1.7	4.5	0.07	0.05
PVB-2-09-06	360	252	12.5	7.56	59	85	5.7	9.8	3.3	274	11	2.8	3.9	0.01	0.04
PVB-2-04-07	338	237	11.7	7.5	70	69.5	4.7	12.5	2.1	240	12.7	3.5	4.3	<0.01	0.03
PVB-2-09-07	379	265	12.4	7.53	54	70	5.3	13.1	2.3	248	14.6	4.7	5.0	0.02	0.06
PVB-2-10-07	367	257	12.7	7.5	50	63.8	4.7	13.3	2.1	245	15.9	3.2	4.5	0.01	0.05
PVB-3-06-06	409	286	11.5	7.34	52	77.4	6.1	5.9	1.4	254	9.6	2.9	4.8	0.03	0.05
PVB-3-09-06	407	285	11.8	7.5	60	92	6.1	8.9	2.7	303	9.4	6.8	4.3	<0.01	0.05
PVB-3-04-07	397	277	11.7	7.28	50	64.8	5.6	14.4	1.6	238	9.7	6.2	4.3	<0.01	0.05
PVB-3-09-07	419	293	12.2	7.55	43	74.3	5.8	14.4	2.2	252	10.6	4.7	4.7	0.02	0.06
PVB-3-10-07	400	291	12	7.52	52	61.1	5.3	14.6	1.8	238	11.8	5.6	4.5	0.02	0.05
"Pašino vrelo"-06-06	357	250	11	7.2	72	67.9	5.4	4.4	1.7	214	12	2.3	4.5	<0.01	0.04
"Pašino vrelo"-09-06	355	249	11.8	7.42	57	90	5.4	10	3.3	277	10.7	4.3	3.8	<0.01	0.04
"Pašino vrelo"-04-07	330	231	11.3	7.47	60	67.2	4.8	12.8	2.1	240	12.5	5.6	4.2	<0.01	0.04
"Pašino vrelo"-09-07	375	263	11.8	7.43	50	60.3	4.8	13.4	2.3	240	15.6	2.7	5.3	0.02	0.04
"Pašino vrelo"-10-07	365	256	11.9	7.49	43	61.2	4.2	13.7	2.2	238	17.3	3.4	4.7	<0.01	0.04
"Bojanića vrelo"-06-06	381	266	13.3	7.39	53	68	5.5	7.5	1.7	240	9.6	4.2	5.1	0.08	0.03
"Bojanića vrelo"-09-06	397	278	12	7.42	78	95	5.5	11.1	2.7	283	8.1	8.4	4.1	<0.01	0.05
"Bojanića vrelo"-04-07	375	262	11.3	7.52	66	69.3	4.5	15.8	1.9	242	9.1	9.7	4.9	<0.01	0.05
"Bojanića vrelo"-09-07	402	281	11.4	7.48	55	64.7	5	14.9	2	245	9.5	4.8	4.9	0.01	0.02
"Bojanića vrelo"-10-07	406	284	10.7	7.57	80	60	4.8	15.9	1.9	238	10.1	6.6	4.9	0.02	0.07
"Grabovac"-06-06	581	406	11.3	7.42	84	124	1.1	1.6	0.7	391	5.3	1.3	3.1	0.03	0.01
"Grabovac"-09-06	570	399	11.2	7.32	96	124	0.8	2.6	0.8	396	4.9	2.4	3.3	<0.01	<0.01
"Grabovac"-04-07	552	386	13.2	7.62	95	75.8	1.2	6.2	0.5	250	4.5	1.5	2.7	<0.01	0.04
"Grabovac"-09-07	446	372	12	7.23	80	86.4	0.7	5	0.6	262	4.1	1.2	2.6	<0.01	0.01
"Grabovac"-10-07	550	385	11.3	7.33	78	93.8	1.7	6.5	0.5	278	4.6	1.3	2.9	<0.01	0.07
The Sunja river-06-06	291	203	21.2	7.8	103	49	8	4.6	1.5	178	13.4	1.8	3.4	<0.01	0.01
The Sunja river-09-06	311	218	15.7	8.26	121	74	8	10	2.9	178	11	4.3	3	<0.01	0.01
The Sunja river-04-07	246	172	15.4	7.9	116	49.4	7.8	12.9	1.7	170	14.3	4.3	2.8	<0.01	0.02
The Sunja river-09-07	222	155	13.3	7.86	100	31.7	3.3	12.9	2.1	100	16.2	4.9	8.8	0.03	0.02
The Sunja river-10-07	307	215	12.6	7.69	129	44.8	4.3	14.3	1.9	160	17.9	4.0	3.0	0.02	0.04

charged at high altitudes from that recharged at low altitude (CLARK & FRITZ, 1997; ROZANSKI et al., 1993).

Concentrations of ammonium and orthophosphates in water samples are below the MPC values (Table 1). However, increased concentrations of ammonium and orthophosphates during washing out of upper parts of alluvial deposits were observed in the wells. Increased concentrations of ammonium and orthophosphates indicate the influence of domestic wastewater (DOYLE & PARSONS, 2002; CELEN et al., 2007). A sewerage system in the settlements surrounding the groundwater source has not yet been constructed, so the inhabitants discharge their wastewater into canals along the road and, during precipitation, wastewater from the canals is infiltrated into underground. In the "Grabovac" spring, increased concentrations of ammonium and orthophosphates are occasionally registered. However, their origin is natural, i.e. caused by the decomposition of organic matter (leaves, twigs, etc.) on the forest floor.

Concentrations of nitrates in all water samples are well below the MPC values (Table 1). Agricultural activity is not intensive in the area (mostly meadows and pastures, less fields), thus there is no possibility of groundwater pollution by manure or mineral fertilizers. Similarly, concentrations of sulphates and chlorides are also well below the MPC values (Table 1). The origin of sulphates and chlorides in groundwater is natural, since the aquifers are composed of rocks which contain chloride and sulphate or sulphide bearing minerals.

It can be generally stated that the waters of the "Pašino vrelo" groundwater source are of good quality in terms of chemical indicators. However, microbiological indicators suggest groundwater pollution with domestic wastewater, as confirmed by occasionally raised concentrations of ammonium and orthophosphates.

5. DEVELOPMENT OF THE GROUNDWATER SOURCE

In 2005, an exploratory borehole (SPBPv-1/05) was drilled north-west of the pumping site, followed a year later by a test exploitation well SPBPv-1/06, with the aim of ensuring the availability of additional quantities of groundwater (Fig. 3). The well was 152 m deep, and the aquifer was tapped in the 50−105 m and 120−137 m intervals. During the pumping test with a quantity of 21.9 l/s, a drawdown of 3.95 m was achieved. An exploitation capacity of at least double this is expected, which could not be confirmed during the pumping test, since a pump of adequate capacity was not available. Groundwater samples were taken during testing for chemical analyses in order to determine the proportions of groundwater from different parts of the aquifer system. 83 % of groundwater was from the lithothamnium limestone with only 17% from the alluvial aquifer, which is significantly more favourable in relation to the other facilities at the pumping site. The results proved that tapping deeper parts of the carbonate aquifer was justified. The sustainability of these conditions will be verified in the course of long-term exploitation of the well.

To date, protection of the groundwater source has been carried out through active and passive measures according to the currently unenforced Regulation from 1986 (OG 22/86). The expert maps for update, which also includes the new well SPBPv-1/06, according to the current Regulation in force on the determination of sanitary protection zones of the drinking water source (OG 55/02), is given by MRAZ et al. (2007)[1]. The specific characteristics of the hydrogeological system as previously described, were taken into consideration when defining protection zones. They played an important role in the definition of the II. protection zone, along the external boundary of which, according to the Regulation, groundwater has a minimal travel time of 50 days before it enters groundwater capture. When determining this protection zone, the hydrogeological characteristics of the carbonate aquifer, (which has a primary significance from the water supply standpoint), were not taken into account. The focus was placed on the Quaternary alluvial aquifer, since it was assumed that the values of hydraulic conductivity, and thus also of velocity of groundwater flow in the alluvial aquifer were higher in relation to the carbonate aquifer. Namely, the interpretation of the pumping test results showed that the hydraulic conductivity of the lithothamnium limestone is 3.6 m/day. Based on lithological composition of the Quaternary alluvial aquifer, data from reference sources and analogy with other areas, a hydraulic conductivity of 150 m/day was estimated. According to the hydrogeological model, pollution from the surface of the terrain leaches vertically to the saturated zone of the alluvial aquifer and then, under the influence of the gradient, advances by means of advection towards the well field. Bearing in mind the aforementioned conditions, the gradient achieved during the pumping site operation and an estimated value of alluvial aquifer effective porosity of 0.2, the average flow velocity in horizontal flow was defined as 7.5 m/day. In the course of this, the radial flow of groundwater in the vicinity of the wells was neglected. Given the flow velocity and the minimum permissible groundwater travel time in an area included in the II. protection zone, it was possible to define its external boundary (Fig. 3). It was especially convenient for the part of alluvial aquifer located up-gradient from the pumping site,

[1] MRAZ, V., MARKOVIĆ, T. & LARVA, O. (2007): Izvorište "Pašino vrelo". Zaštitne zone za novi zdenac SPBPV-01/06 i vodocrpilište "Pašino vrelo" [Groundwater source "Pašino vrelo". Protection zones for new well SPBPV-01/06 and groundwater source "Pašino vrelo" – in Croatian].– Unpubl. report, Croatian Geological Survey, Zagreb, 44 p.

where there is no natural boundary to groundwater flow. The external boundary of the II. protection zone was subsequently adjusted in order to correspond to the boundaries of cadastral plots. In the north it follows the Sunja river and the Bekej watercourse in the east and south-east. In the west and south-west it follows the natural boundary of the alluvial aquifer and in the north-west, up-gradient from the pumping site, it is located approximately 450 m from the pumping site which is in accordance with the minimum permissible groundwater travel time.

6. CONCLUSION

The groundwater accumulated in the carbonate aquifer of Badenian age presents an exceptionally valuable natural resource in the municipality of Hrvatska Kostajnica. The focus of the recent investigations of the "Pašino vrelo" aquifer system was placed on the definition of its hydrodynamic and hydrochemical characteristics. The results have increased the level of understanding of the hydrogeological model, which in turn enabled better insights into the possibilities of abstraction of additional drinking water quantities of more favourable quality, and adequate protection of the groundwater source from pollution.

The analysis of oscillation of groundwater levels and spring discharges at the groundwater source enabled conclusions to be drawn about the hydrodynamic conditions in the aquifer system. A positive correlation between oscillations of groundwater levels in the Quaternary alluvial aquifer and the discharge quantities in the "Bojanića vrelo" spring proved the hydraulic connection between the carbonate and alluvial aquifers. This had already been indicated by the bacteriological contamination of groundwater abstracted at the pumping site. At the same time, the difference in trends of groundwater levels in the alluvial aquifer and water levels in the "Pašino vrelo" spring, as well as in trends of yields in the "Pašino vrelo" and "Bojanića vrelo" springs pointed to different discharge conditions at the groundwater source. The same conclusion is indicated by the stable discharge of the "Pašino vrelo" spring, which did not alter even during the pumping test of the SPBPv-1/06 well while, in contrast, the discharge of the "Bojanića vrelo" spring was substantially reduced. Such hydrodynamic indicators are, to a point, a consequence of the influence of exploitation wells (PVB-1, PVB-2 and PVB-3) in operation at the pumping site, but, above all, of a more pronounced groundwater drainage from the carbonate aquifer to the "Pašino vrelo" spring, whereas the "Bojanića vrelo" spring is more strongly influenced by the Quaternary alluvial aquifer. Calculation of the proportions of water from the lithothamnium and alluvial aquifers in the "Pašino vrelo" and "Bojanića vrelo" springs, as well as in the PVB-1, PVB-2, PVB-3 and SPBPv-1/06 wells, indicates larger proportion of water from the lithothamnium aquifer during low and medium water flow at monitored springs and wells, while during high waters there is a larger proportion of water from the alluvial aquifer.

Groundwater quality in the recharge area of the ''Pašino vrelo'' groundwater source is good with regards to its chemical indicators. However, microbiological indicators indicate groundwater pollution with domestic wastewater during high waters as confirmed by occasionally increased concentrations of ammonium and orthophosphates, which are chemical indicators of the impact of domestic wastewater. The mass-balance model confirmed the hydraulic connection of the genetically different aquifers.

Results of the investigations suggested exploration of the possibility of extracting drinking water of adequate quality from the deeper horizons of the Badenian carbonate aquifer. Initial results are promising. Besides the fact that the expected exploitation capacity of the well exceeds water abstraction quantities at the pumping site to date, a favourable ratio of the proportions of water from the carbonate and alluvial aquifers was also determined. If such a ratio remains under conditions of long-term exploitation, a more favourable quality of groundwater in relation to the other wells at the pumping site is guaranteed.

While defining the protection zones for the groundwater source, the specific characteristics of the hydrogeological model were taken into consideration, particularly during definition of the II. zone of sanitary protection. Due to the hydraulic connection between the alluvial and carbonate aquifers, the focus was placed on hydraulic characteristics of the alluvial aquifer when determining the size of the zone. By remedying the anthropogenic influences on groundwater quality in the alluvial aquifer, the existing water quality problems at the pumping site will be resolved.

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