

## Hydrogeological Relationships of the Golubinka Karst Spring in Ljubač Bay, Dalmatia, Croatia

Ante PAVIČIĆ<sup>1</sup>, Josip TERZIĆ<sup>1</sup> and Nicoletta BEROVIĆ<sup>2</sup>

**Key words:** Coastal spring, Karst hydrogeology, Multivariate analysis, Water quality, Monitoring, Ljubač bay, Northern Dalmatia, Croatia.

### Abstract

The Golubinka spring is a typical karst spring situated in northern Dalmatia, Croatia. The catchment area is mostly composed of limestones of the Cretaceous and Palaeogene, with some dolomitic parts. Hydrogeological barriers are composed of flysch or Quaternary sediments, and most of them are “hanging” barriers, so that the karst water can flow underneath. Many speleological features in the vicinity of the spring point to a typical karst conduit flowing under ground. This has been proven by tracer tests, because a connection exists to the periphery of the catchment with an apparent velocity of 8.1 cm/s. The whole area is situated in the Mediterranean climatic belt, so the precipitation distribution is quite unfavourable – summers are long, hot and dry. This is why the summer seasons usually end with sea water intrusion into the aquifer with a significant increase in chloride ion concentration. Since the spring is capped for water supply, there is a bulk monitoring system established. The data obtained were processed by means of multivariate analysis, and three main types of quality deterioration were recognized. The first is connected with pollution from agriculture and inhabited areas without sewage, the second represents occasional sea water intrusions, while the third relates to heavy rainfall events accompanied by turbidity and pollution. Together with the other conclusions, these results should have a practical purpose primarily in the matter of water protection.

### 1. INTRODUCTION

All the water-supply pumping sites of the region of Zadar in Croatia are situated in a complex coastal catchment area (Fig. 1), mostly composed of karstified carbonate rocks. The research area is entirely situated in the Adriatic regional structural unit, which is the first southern unit in the Dinarides, at the contact between the Adriatic microplate to the SW and the Dinaric regional structural unit to the NE; contacts between these structural units are represented by reverse faults (KUK et al., 2000; PRELOGOVIĆ et al., 2003). All structures in the studied area strike northeast–south-

west. The terrain is mostly composed of limestone of Eocene and Cretaceous ages (MAJCEN & KOROLIJA, 1973; VLAHOVIĆ et al., 2005). The rock mass is tectonically fractured and karstified. Morphologically, the whole catchment area is characterized by small hills and karst fields. The highest peak is only 120 m a.s.l. The only surface water flow in the Zadar hinterland, called Miljašić jaruga, is situated south of the Golubinka spring catchment.

Climatically, this area belongs to the Mediterranean climate, the so-called “olive climate” (ŠEGOTA & FILIPČIĆ, 1996). It is known for its dry, hot summers, with most of the precipitation concentrated in the cold part of the year. This rainfall concentration is quite unfavourable considering the lack of water during the summer time, when it is vital for the water supply of the population, tourism and agriculture. Average air temperature in January is between 5 and 6°C, and in July about 24°C.

### 2. GEOLOGICAL SETTING

Most of the Golubinka spring’s catchment area is composed of Upper Cretaceous dolomites and limestones, Palaeogene limestones and clastic rocks (Eocene flysch), as well as some Quaternary deposits (clays, sandy clays and ‘terra rossa’). Upper Cretaceous dolomites form the cores of anticlines and occur as outcrops only in the Bokanjačko blato structure. Dolomites are overlain by well-bedded limestones. Upper Cretaceous limestones and dolomites are over 400 m thick. Palaeogene rocks are transgressive over Upper Cretaceous deposits. Their base is composed of breccias, and conglomerates only occur occasionally. Eocene foraminiferal limestones are well bedded, with an increase in bed thickness from the older to the younger parts, on average from 1 cm to almost 1 m. Their total thickness is about 300 m. Clastic Palaeogene rocks – the Eocene flysch – is composed of siltites, sandstones and sandy limestones. Sandstones are most common in the younger parts. These rocks form the cores of synclines and are usually eroded. The thickness of the flysch rocks in the syncline NE of Poličnik is almost 850 m (MAJCEN & KOROLIJA, 1973). In the terrain considered here, there are two principal types of Quaternary deposits: residual soils in the area near the Boljkovac spring, and the terra rossa covering karstified

<sup>1</sup> Croatian Geological Survey, Sachsova 2, HR-10000 Zagreb, Croatia; e-mail: apavicic@hgi-cgs.hr

<sup>2</sup> Vodovod Ltd., Water Supply Co., Špire Brusine 17, HR-23000 Zadar, Croatia; e-mail: nicoletta.berovic@zd.htnet.hr

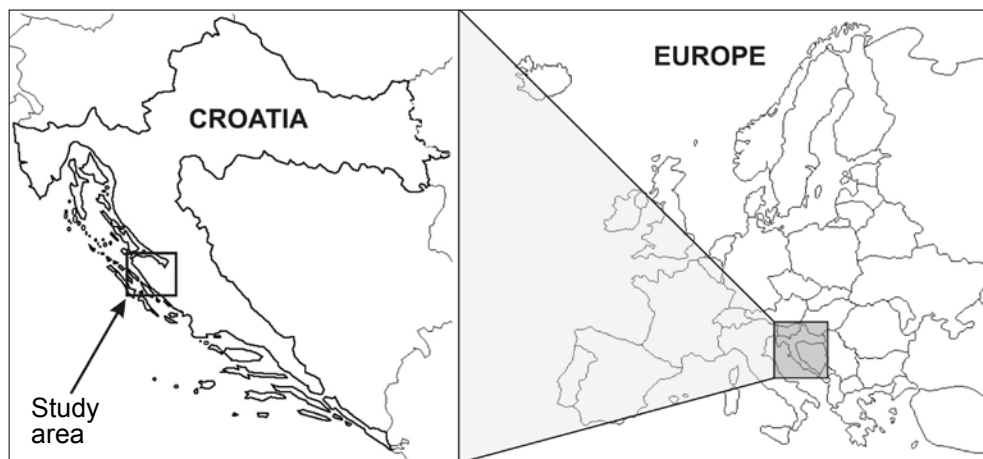


Fig. 1 Situation map of the investigated area.

limestones. The residual soils originate from weathered flysch and have a significant hydrogeological function because of their thickness (over 20 m – FRITZ & PAVIČIĆ, 1991). They act as total or hanging barriers for the karst groundwater. Terra rossa (a ‘modal fersiallitic red soil’ situated on limestones) is a polygenetic type of soil which is widespread in the whole Mediterranean (MIKO et al., 1999; DURIN, 2003). In the Golubinka catchment it is quite thin and discontinuous and with no hydrogeological relevance regarding groundwater flow. However, its influence on the hydrochemical properties and even infiltration should not be neglected.

From the structural-geological point of view the terrain is composed of several anticlines and synclines. These follow the so-called ‘Dinaric’ strike (NW–SE), parallel to the coast and most of the topographic water divides. Some of the folds are significantly tectonically disturbed, mostly by reverse faults and thrusts. Most of them are not visible at outcrops and cannot be traced even morphologically. They have been discovered by a number of boreholes (57) drilled during investigations completed for the purpose of construction of the injection curtain in the late 1960’s (FRITZ, 1976<sup>3</sup>). Maximal displacements amount to 100 m, and the average is between 10–40 m.

### 3. SPECIFIC KARST FEATURES

There are two basic facts indicating typical karst flow conditions in the Golubinka spring catchment:

- very high groundwater velocity, even from far inland, proven by the tracer test;
- visible channels and caves at the spring location of the Golubinka and nearby springs (Pod Gredom and Šušnjarka). Presence of deep vertical caves (pits) in the near hinterland.

Close to the Golubinka spring, there are two other springs called Pod Gredom to the east, and Šušnjarka to the west. There are also three caves: two of them called Šušnjarka and one called Golubinka, as well as springs closely adjoining them. All the springs have been

investigated by scuba divers, but only for a few tens of metres, close to the entrances (Fig. 2, and BOŽIČEVIĆ, 1975<sup>4</sup>). Because of the strong water current and/or muddy water (turbidity), the divers were not able to progress very far. Investigations were stopped and, unfortunately, never continued.

The Golubinka cave is formed in the Eocene foraminiferal limestones about 400 m from the Golubinka spring and water supply plant (Fig. 3, detail). The cave has been speleologically investigated, including speleological diving research below groundwater level. The pit’s entrance is situated 39 m a.s.l. The groundwater level in the cave has been measured approximately and comes to less than 1 m a.s.l. At the bottom of the cave there are three mutually connected water basins. The diving exploration revealed some 22 m of water depth. The two Šušnjarka vertical caves situated west of the Golubinka spring are also formed in Eocene limestones. They are only 9 m deep. The distance between them is 14 m, and they are connected below ground. At the bottom there is water of unknown depth. East of the Golubinka spring there are two karst springs Pod Gredom, most probably connected with the other karst features (Šušnjarka, the Golubinka spring, the Golubinka pit, etc.) with underground conduits.

The main outflow site of Golubinka is now canalized with a channel 1.5 to 3 m wide. The water level in the channel varies from 1 to 2 m. The first Pod Gredom spring is situated under a cliff, and there are three karst channels from which the groundwater springs. Close under ground these three channels connect in one karst conduit, about 80 m from the coast. Diving could be performed only up to 27 m in the karst channels from

<sup>3</sup> FRITZ, F. (1976): Ravni kotari–Bukovica, Hidrogeološka studija [Ravni Kotari–Bukovica, Hydrogeological study – in Croatian]. – Unpublished report, Archive of the Croatian Geological Survey, Zagreb, 134 p.

<sup>4</sup> BOŽIČEVIĆ, S. (1975): Izvorište Golubinka – Ljubački zaljev, speleološko istraživanje [The Golubinka spring – speleological diving investigations – in Croatian]. – Unpublished report, Archive of the Croatian Geological Survey, Zagreb, 7 p.

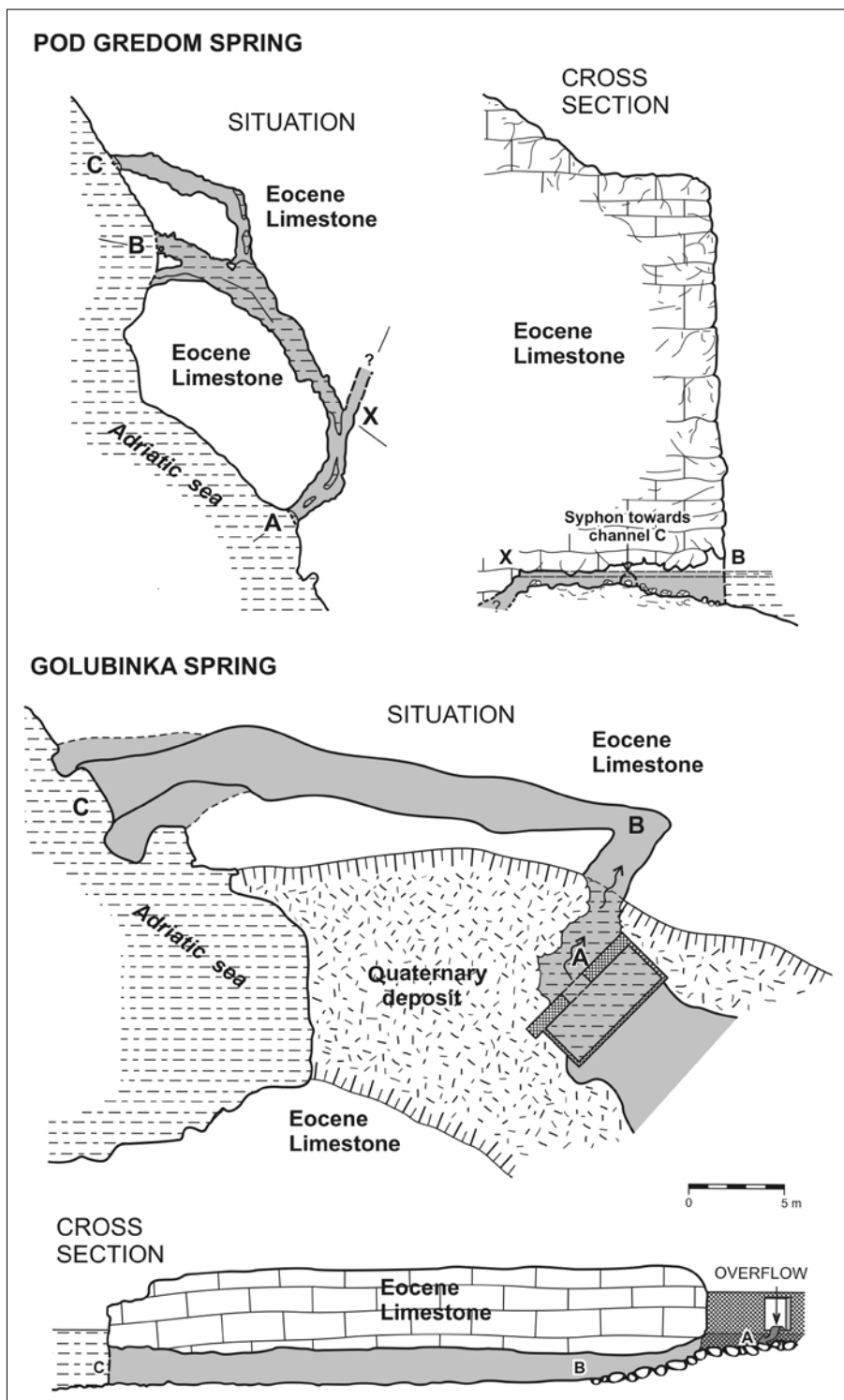


Fig. 2 Spelaeological scheme of the Golubinka and Pod Gredom coastal karst springs entrances (cave mouths) (after BOŽIČEVIĆ, 1975<sup>4</sup>).

the cave entrance. The second Pod Gredom spring is similar to the first, but here there are two channels connecting in one main karst conduit about 50 m from the cave mouth (the entrance).

These diving investigations were never performed as was desired, mainly because of the high turbidity caused by fine-grained material. It was presumed that the channels (after a few tens of metres) continue deeper below ground, and that they are mutually connected as one karst hydrogeological system.

#### 4. HYDROGEOLOGICAL RELATIONSHIPS

The hydrogeological relationships are mostly a consequence of the geological circumstances. The mean elevation of the terrain (relief) is low, close to the recent base of erosion – sea level. It is significant that sea level is now about 100 m higher than that during the last glaciations (Würm; ŠEGOTA, 1982; BENAC & JURAIĆ, 1998; MASSE & MONTAGGIONI, 2001). In the last 6000 years sea level has stabilized (BENAC

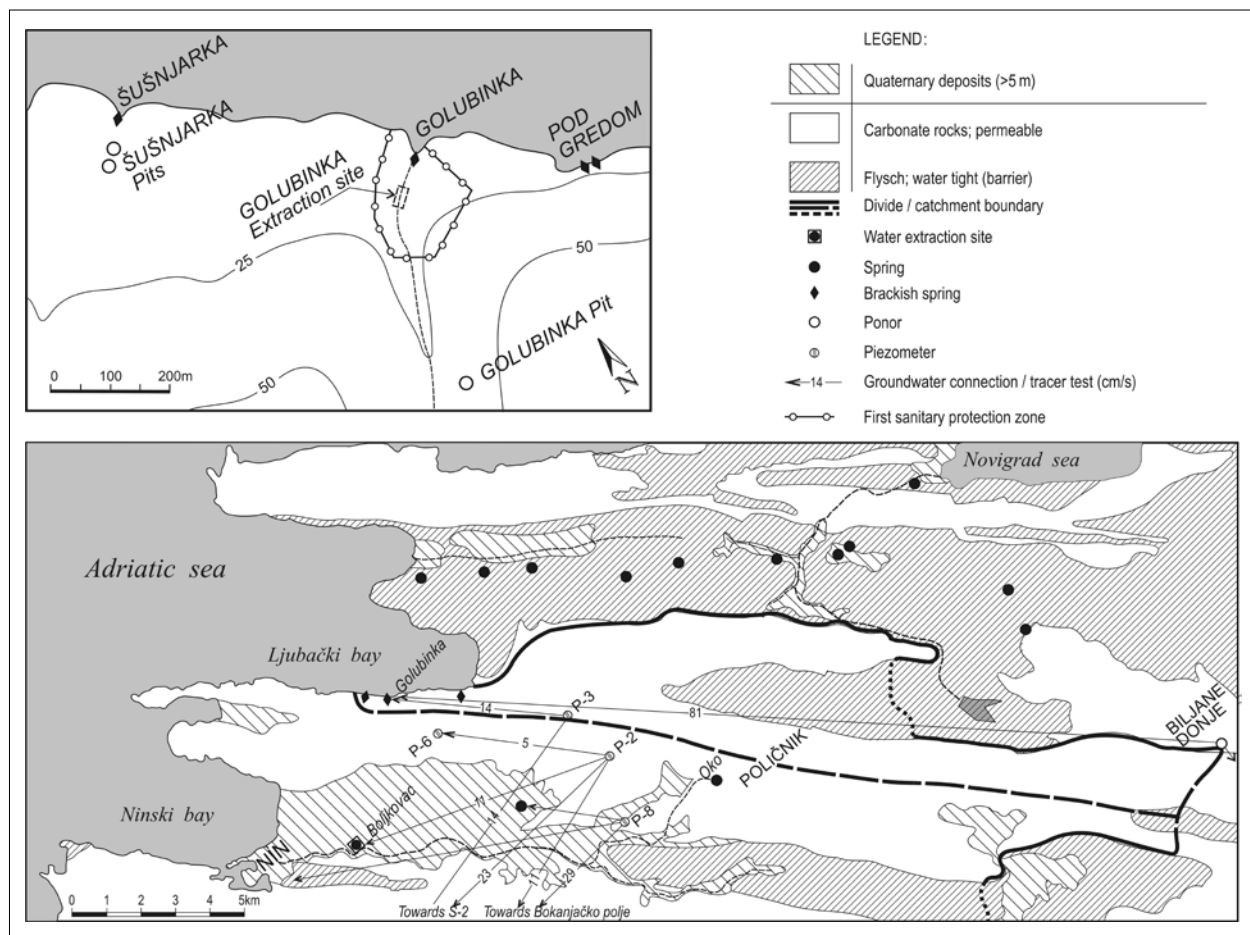


Fig. 3 Schematic hydrogeological map of the Golubinka spring catchment area.

et al., 2004; PIRAZZOLI, 2005). Still, the large sea level rise in the Holocene caused much deeper karstification than would be expected with the recent sea level. Limestones are considered permeable, dolomitic rocks decrease permeability; so if they prevail in some sections, carbonate rocks behave in a less permeable manner. Flysch represents impermeable rocks, sometimes acting as a hydrogeological barrier. Occasionally, the flysch is not thick enough to stop the flow of groundwater completely. In these cases the groundwater can flow through deep karst conduits under impermeable flysch, and the flysch in those situations behaves as a “hanging barrier”.

The catchment area of the Golubinka spring (Fig. 3) is the northern part of a wider karst catchment called the “Bokanjac–Poličnik”. This wider catchment covers the whole of the Zadar hinterland in NW Dalmatia, and most of the well-known karst springs and pit wells are situated within that area. Some of these water sources are exploited for water supply. The local catchment of the Golubinka spring could be separated from the rest of the terrain by a zonal underground water divide. The flysch rocks in Ljubački bay represent an undersea barrier, so the karstified carbonate rocks are in contact with the sea water in quite a narrow area close to the coastline. This circumstance is positive from the hydro-

geological point of view, because the groundwater flow from the aquifer can suppress the intruding sea water; thus the Golubinka spring water stays fresh until the end of the summer dry periods when the groundwater level in the aquifer drops, together with the discharge, and sea water intrudes.

Effective infiltration in the whole catchment area formed by carbonate rocks is very high. Precipitation falling on the impermeable flysch rocks usually forms short temporary surface streams, which often end in ponors, a specific karst phenomenon. The greater part of the rainfall onto impermeable parts of the terrain is also infiltrated into the karst aquifer through ponors. This primarily applies to the catchment periphery, where the well-known ponor in Biljane Donje is located. An underground connection between the ponor in Biljane Donje and the Golubinka spring has been proven by a tracer test, and it has a very high groundwater velocity of 8.1 cm/s (FRITZ, 1976<sup>3</sup>). Over the whole area, the greater part of the groundwater typically flows parallel to geological structures, towards the NW. Southwest of the Golubinka spring, residual soils, over 5 m thick, act as a groundwater barrier (FRITZ & PAVIČIĆ, 1991). This barrier is partly “hanging”, so some of the groundwater probably flows underneath it, towards the Boljkovac spring. Groundwater levels in distant parts of

the catchment area (from the coast) are about or above 60 m a.s.l., as is demonstrated by the Oko spring (60 m a.s.l.). Such elevation causes a significant groundwater gradient and high velocities towards the springs of Golubinka or Boljkovac. Part of the groundwater from this part of the catchment flows through deep karst sumps (siphons) and conduits under the flysch barriers to the Bokanjačko polje area. These phenomena have been demonstrated by a few tracer tests from boreholes and the ponor in Biljane Donje (FRITZ, 1976<sup>3</sup>) (Fig. 3). Mean velocities parallel to the geological structures were 1.4, 1.4, 1.0, 3.3, and 8.1 cm/s (average 3 cm/s). Mean velocities at right angles and diagonal to the geological structures were 1.4, 2.2, 2.9, 2.3 and 5.0 cm/s (average 2.8 cm/s). High velocities diagonal to the structure are caused by faults. Shallow zones are highly karstified, and in deeper zones there is a rock mass of lower permeability, but with a network of karst conduits. That is why sometimes the groundwater velocities were higher to distant boreholes than to ones closer to where the tracer fluid was poured in. These kinds of karst conduits were probably developed during the last 15,000 years when the sea levels were about 70 m lower than today (BENAC & JURAČIĆ, 1998). The placement of the water divide which separates the Golubinka spring catchment from other catchments in the hydrogeological system is only known approximately, based on knowledge of some minor geological units and features in the area. Since it is a zonal divide, it can move significantly according to hydrological conditions.

The spring itself is developed in karst conduits which form cave systems at the place where the groundwater surfaces (Fig. 2). This occurs some 15 m from the coast, at an elevation of less than 1 m. Such proximity to the sea causes occasional saline intrusions in the karst aquifer near the spring site. During the summer dry periods, the groundwater level in the karst aquifer decreases, the Golubinka spring discharge also decreases, and water becomes slightly brackish (Table 2). The intensity of this phenomenon varies from year to year, according to the annual amount of precipitation. The sensitive karst environment reacts very quickly, and soon after the first significant rains, usually in September, the discharge increases, the chloride level drops and the water becomes fresh again.

Near the Golubinka spring there are also some similar karst springs called Pod Gredom and Šušnjarka. They are also spelaeological formations but their discharge is lower. Access is very difficult and this is the main reason why the Golubinka was capped for water supply in 1993. The Golubinka water supply facility was very important during the war for Croatian independence, when most of the other water supply sources were occupied until the liberation in 1995. During that time the facility at the Golubinka spring was renovated, and a small dam construction was built at the site where the water springs from the cave. This construction achieved some positive results regarding water quality. By increasing the groundwater levels in the

nearby karst underground, saline intrusions in the dry periods were decreased to some extent. Unfortunately, there are no relevant data for a parametric description of that decrease. Today, the Golubinka pumping site is part of the wider water supply system. It usually uses about 100 l/s. When the concentration of the chloride ion becomes exaggerated, the water from the Golubinka spring is mixed with water from other pumping sites. When sea water intrusion becomes excessive at the end of the summer dry periods, pumping has to be stopped. Experience indicates that this usually happens when the discharge decreases to some 60 l/s.

The unfavorable distribution of rainfall throughout the year in the catchment of the Golubinka spring causes large differences in the spring's discharge from minimum to maximum. The average monthly discharge at the Golubinka spring as well as the amount of precipitation at the nearby Poličnik measuring site are shown in Fig. 4.

The data from 1961–1990 are divided into two separate sets, because in 1980–1990 there was a dry period in the research area. Average monthly precipitation was 87 mm/m<sup>2</sup> in the 1961–1980 period and 74 mm/m<sup>2</sup> in the 1980–1990 period. During the same time intervals, average monthly discharge at the Golubinka spring was 446 and 358 l/s, respectively. The largest discharge occurs in February, and the average for that month is almost 1 m<sup>3</sup>/s. The lowest discharge is in July (average lower than 100 l/s; ŽUGAJ, 1995). For the complete time period the average yearly precipitation was 992 mm/m<sup>2</sup> and the average discharge of the Golubinka spring was about 417 l/s.

## 5. HYDROGEOCHEMICAL DATA

### 5.1. Hydrogeochemical facies, basic relations and seawater intrusion

For determination of the hydrogeochemical facies the data from June 2004 (Table 1, Fig. 5) were used for the Golubinka spring, as well as the Oko and Boljkovac springs (Fig. 3).

Although samples were taken in June 2004, there were no high chloride concentrations, and water at the two sites was of the Ca–HCO<sub>3</sub> type. However, the sample at the Boljkovac spring (well) showed the Na–Cl type, which means that this spring was already subject to sea water intrusion (FRITZ & PAVIČIĆ, 1991). This is most probably a consequence of the extensive pumping for water supply that was being done during the period when sampling took place. Water extraction lowered the water level and gradient so that sea water intruded from the western side, or from the lower levels (“upwelling” of the sea water). This situation also indicates that it is justifiable to locate the groundwater divide between the Golubinka and Boljkovac springs – these are most probably two quite distinct groundwater systems. In contrast, samples at the Oko and Golu-

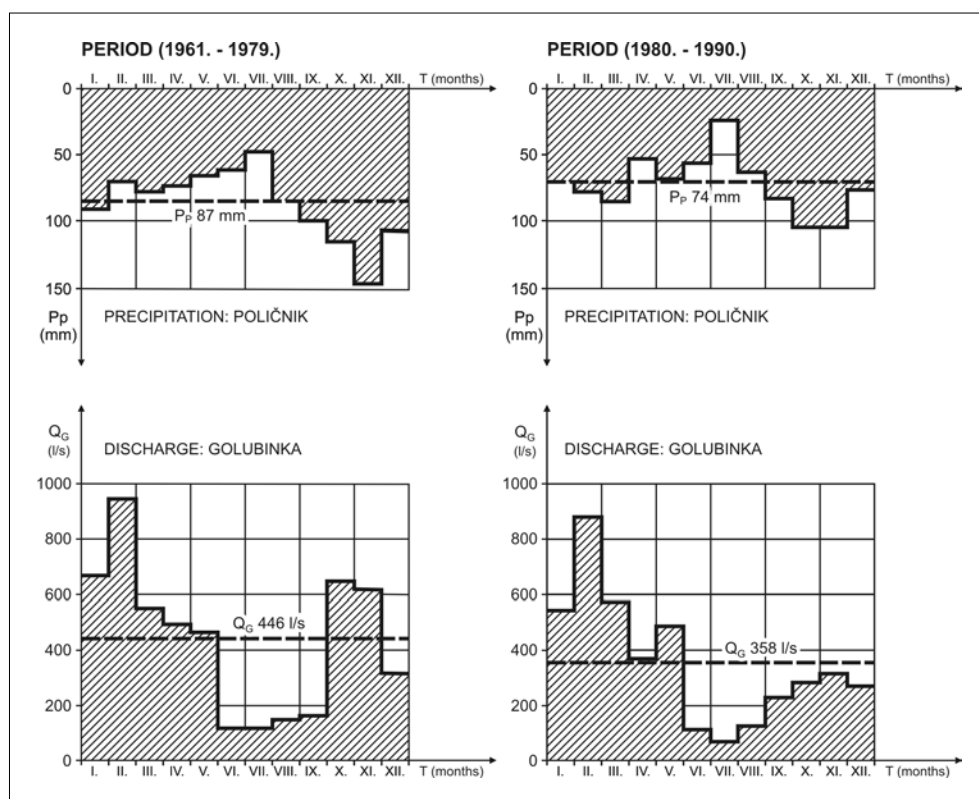


Fig. 4 Average monthly discharge of the Golubinka karst spring and average monthly precipitation at the Poličnik measuring site (ŽUGAJ, 1995).

binka show very similar ionic composition. The spatial position of the Oko spring, half way between the ponor in Biljane Donje and the Golubinka spring, implies that this water probably belongs to the same karst aquifer.

In the climatic belt under discussion the dry season begins in June, and the karstified underground aquifer begins to discharge water accumulated during the rainy half of the year. The result of that discharge is the lowering of the groundwater table, so the springs in coastal zones, such as Golubinka, could suffer intrusion by sea water. The main indicator (and result) of such mixing of salt and fresh water is a higher concentration of chlorides, as shown by levels up to 1630 mg/l in September 2003 (Table 2) in the research period. It can be seen that during the late part of every summer season there is an increase in the chloride concentration (Fig. 6). The amount of that increase varies from year to year, depending on the hydrological conditions.

## 5.2. Quality monitoring: data acquisition

The Zadar water supply company has established permanent monitoring of the water quality at the Golubinka spring. Data for the period 2003–2006 (Table 2) have been statistically analyzed, by means of correlation and multivariate factor analysis.

In the basic analysis for the purpose of monitoring the water quality, 20 parameters are periodically measured. Besides the 14 analyzed parameters (Table 2), others noted include smell, taste, oxidativity, free residual chlorine, free ammonia and nitrite concentration. The measurement of these parameters is within the so-called “basic analysis” and it is determined by current legislation in Croatia (NARODNE NOVINE, 2004). The 6 parameters that are not analyzed either (1) were not measured, (2) are just descriptive, or (3) relate to treated water. The 14 parameters (Table 2) are suitable and sufficient for a basic estimation of water quality. The main goal of further statistical and mathematical analysis was to describe the relationships between some of the parameters, and to group parameters into factors

	CND ( $\mu\text{S/cm}$ )	T ( $^{\circ}\text{C}$ )	pH	$\text{HCO}_3$ (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	$\text{SO}_4$ (mg/l)	Cl (mg/l)	$\text{NO}_3$ (mg/l)
Golubinka	781	14.8	7	271	17.9	1.8	80	7.5	14.9	33	7.4
Oko	786	14.5	6.92	280	18.5	1.3	85	5.2	15	33.8	7.5
Boljkovac	4170	14.6	6.91	281	628	22	104	69	230	1050	8.5

Table 1 Basic ion composition for samples at the Golubinka, Oko and Boljkovac springs, June 2004.

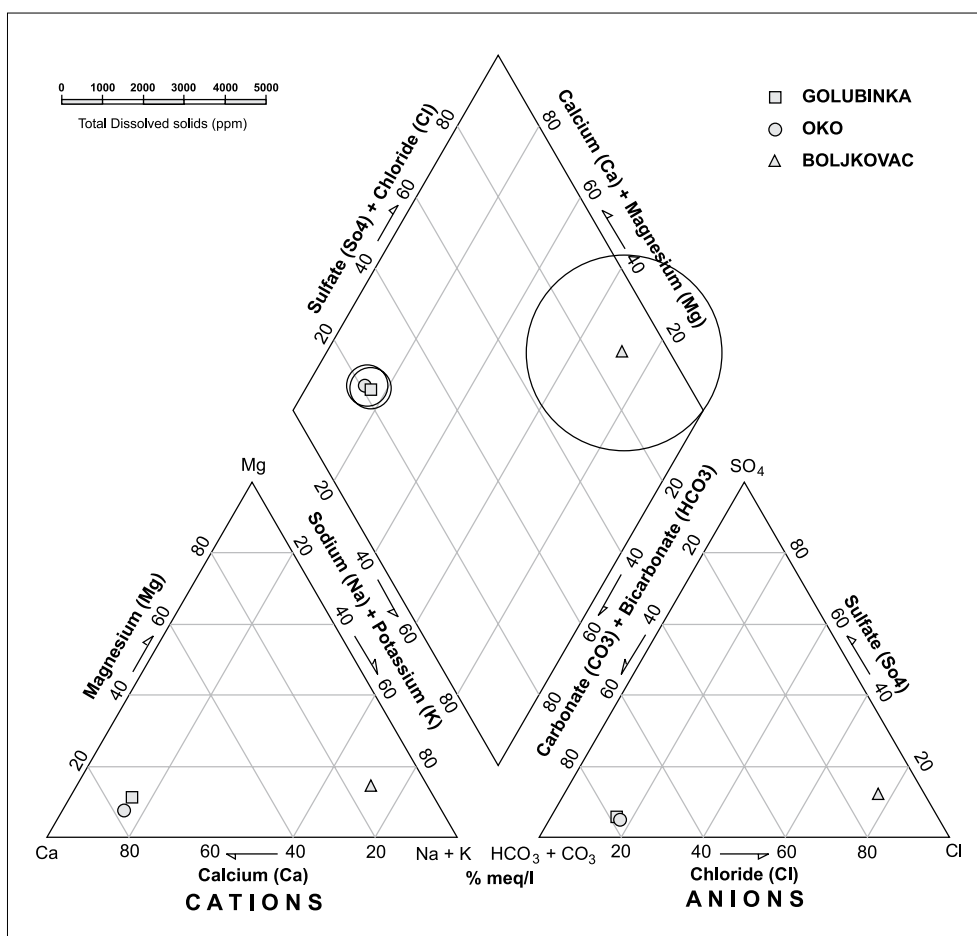


Fig. 5 Basic ionic composition presented by Piper diagram.

which can be attributed to natural processes (basically, describing the origin of possible pollution).

### 5.3. Mathematical and statistical analysis of results

#### 5.3.1. Statistical correlation

There are only a few statistical correlations (regressions) that are really worth considering. The most important relationship is between chlorides and electrolytic conductivity (Fig. 7). It is important to point out that this is a correlation matrix (Table 3) without colour measurements. Measurement of colour began at the end of 2005, so it was better not to calculate it together with the other parameters in such a matrix. Nevertheless, there is an interesting connection between colour and turbidity ( $r=0.98$ ). Those two relationships could be shown by linear equations (1) and (2):

$$[Cl] = 0.31 \cdot EC - 200.6 \quad (1)$$

$$TB = 0.6 \cdot CO + 0.18 \quad (2)$$

where:  $[Cl]$  – chloride concentration (mg/l);  $EC$  – electrolytic conductivity ( $\mu S/cm$ );  $TB$  – turbidity (NTU units), and  $CO$  – colour (mg/l Pt/Co scale). There are also connections between the other parameters, but not as high as these two.

#### 5.3.2. R mode multivariate factor analysis

More interesting data were achieved by means of the multivariate exploratory technique – factor analysis (Table 4, Fig. 8). In this calculation some parameters were grouped in the factors, and colour was also put into the calculation. The main purpose of such analysis is to express variables as groups of variables (factors). In this manner the number of variables is reduced, and groups of variables (calculated factors) in a “factor space” could be presented as processes in a real environment. The data structure that is hidden from direct observation or measurement is recognized (DAVIS, 1986; PEH, 1992, 1994). Such analysis is often used in similar studies, especially for estimating the source of pollution (AHMED et al., 2005; SINGH et al., 2005; SHRESTHA & KAZAMA, 2007). The data (Table 2) were subjected to multivariate factor analysis and five factors were extracted (Table 4). Processing was done by the Statistica software, using the extraction by principal components and ‘varimax’ rotation. Only factors with Eigen values above 1.0 are emphasized. The eigenvalue of the 1st factor is 26% of the total variance, for the 2nd factor it is 16%, and for the 3rd 12%. The interpretation of the 4th and 5th factors is much lower and they can hardly be attributed to natural processes, since they are described with low eigenvalues and only one or two (which are actually one) variables. When a fac-

	Colour (mg/l Pt/Co scale)	Turbidity (NTU units)	Temperature (°C)	pH	EC (µS/cm)	Cl (mg/l)	NO <sub>3</sub> (mg/l)	T. coliforms (No/100ml)	F. coliforms (No/100ml)	F. streptococci (No/100ml)	Clostridium perf. (No/100ml)	Aerobic bacteria 22°C (No/100ml)	Aerobic bacteria 37°C (No/100ml)	Pseudomonas aer. (No/100ml)
28.02.2003.	1.4	13	6.9	890	44	5.72	0	0	2	0	60	30	0	
10.04.2003.	1.1	14	6.8	1011	105	8.36	240	240	0	0	64	280	0	
21.05.2003.	1.7	20	6.7	1360	260	7.92	15	5	0	0	42	24	0	
30.05.2003.	1.35	19	6.8	1670	323	8.36	15	2	0	0	20	60	0	
27.08.2003.	1.1	18	7.1	4040	1030	9.24	5	5	0	0	120	30	0	
04.09.2003.	1.3	18	7	5530	1630	6.95	5	2	0	0	10	20	0	
10.10.2003.	3.5	18	7	4115	1029	3.52	96	2	0	0	20	10	0	
22.10.2003.	4.5	16.5	7	5400	1477	8.36	240	240	16	0	52	26	0	
03.11.2003.	0.8		7.1	3130	775	7.92	240	240	0	0	410	150	0	
10.11.2003.	0.98	16.5	7	2700	740	9.24	240	240	38	0	320	210	0	
21.11.2003.	2.7	15	6.9	3330	795	15.84	240	240	9	1	100	90	0	
26.02.2004.	3.1		7	760	36	9.68	240	240	15	1	5950	3500	0	
04.03.2004.	3	13.5	7	790	92	8.36	38	2	5	1	440	60	0	
15.04.2004.	11.5	15	7.3	700	32	8.668	240	240	38	0	2050	560	0	
02.06.2004.	1	19	7.2	770	40	9.94	38	38	2	0	56	4	0	
16.06.2004.	1.5	17	6.8	930	81	10.60	240	4	16	2	64	32	0	
09.07.2004.	1.2	24.5	6.9	1420	255	9.55	12	0	2	0	41	24	0	
30.07.2004.	1.7	22	6.9	2030	462	8.32	240	8	5	0	122	50	0	
17.08.2004.	1	15.5	7	3140	604	8.67	240	9	0	0	212	80	0	
01.09.2004.	1.7		7	2990	780	8.8	15	0	0	0	29	20	0	
14.09.2004.	0.9	16.5	6.8	2690	600	8.40	9	2	0	0	28	30	0	
01.10.2004.	0.8		6.9	3040	746	7.48	38	9	2	0	114	83	0	
20.10.2004.	1.5	15	6.6	2760	640	8.27	15	15	0	0	36	32	0	
15.12.2004.	2.4	14	6.8	740	34	10.56	27	9	9	0	770	164	0	
16.02.2005.	1.34	15	6.9	765	31	8.8	9	9	0	0	27	160	0	
07.04.2005.	3.4	16	6.7	780	45	8.36	240	240	2	0	326	42	0	
06.05.2005.	1.5	17	6.7	762	40	7.92	38	38	16	2	678	310	0	
19.07.2005.	1.4	20	6.9	1850	362	8.67	38	38	0	0	68	58	0	
12.08.2005.	0.4	18	7	2240	485	8.36	96	15	2	0	246	6500	0	
06.09.2005.	1.8	20.5	6.9	2120	447	8.89	240	240	16	0	68	10	0	
14.09.2005.	0.6	16	7	2300	505	9.77	240	240	16	2	1300	62	0	
06.10.2005.	0.9	15	6.9	1580	250	10.12	38	38	1	0	131	62	0	
17.10.2005.	1.2		6.9	3530	850	14.26	240	240	16	2	3140	820	2	
11.11.2005.	3	1.6	15	720	27	10.03	240	240	16	0	193	86	0	
29.11.2005.	10	5.5	14	690	25	9.37	240	240	2	0	990	540	0	
07.12.2005.	30	20.6	14	785	46	10.12	240	240	16	0	6500	120	0	
09.12.2005.	30	16.7		820	50	7.92	240	240	216	2	133	78	0	
12.12.2005.	8	5.4	13.5	830	53	7.39	38	38	16	0	253	84	0	
13.01.2006.	3	1.9	13.5	780	40	8.8	240	240	9	2	79	53	0	
03.02.2006.	0	0.63	13.5	3360	765	8.54	5	5	0	0	60	120	0	
03.03.2006.	3	2.4	13.3	760	37	7.39	15	9	2	0	3600	4500	0	
10.03.2006.	3	1.92	13	765	35	7.44								
17.03.2006.	3	2.8	14	760	35	7.26	38	38	9	0	110	440	0	
07.04.2006.	3	2.1	14.5	820	35	8.67	38	38	2	0	77	46	0	
12.04.2006.	3	1.6	15	740	30	7.79	15	15	3	0	1	25	0	
21.04.2006.	3	1.9	14.5	750	34	8.8								
05.05.2006.	10	4.1	15.5	775	39	6.6	240	240	16	1	1200	1700	0	
15.05.2006.	5	2.8	17	760	35	8.36	240	240	0	2	3620	960	0	
19.05.2006.	3	1.9	15.5	760	36	8.01	38	9	2	0	210	110	2	
02.06.2006.	0	1.4	16.5	780	34	6.38	38	5	2	0	400	280	8	

Table 2 Hydrochemical, physical and microbiological parameters from 2003 to 2006.



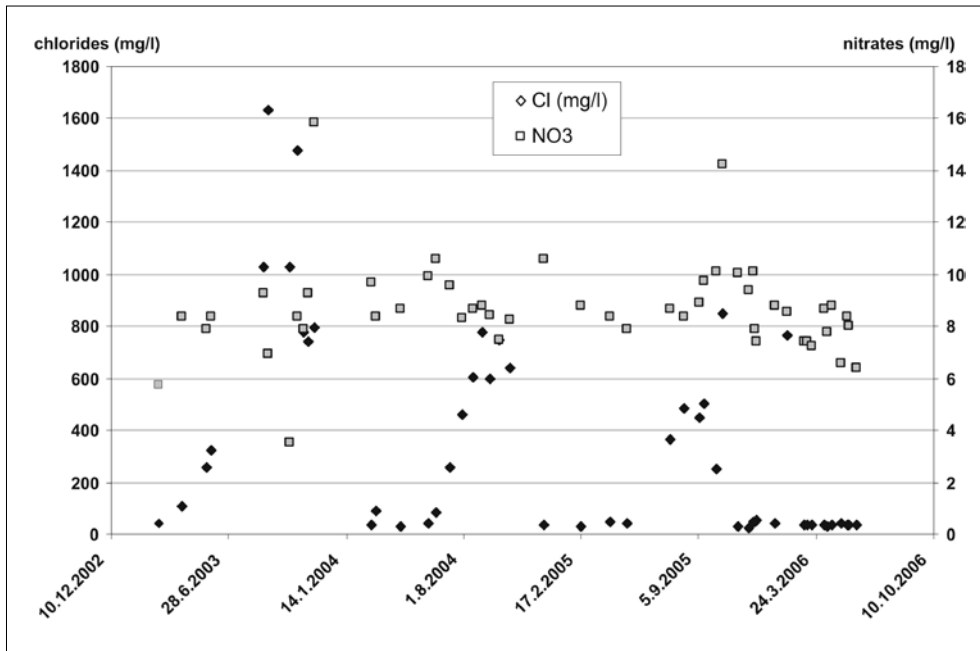


Fig. 6 Chlorides and nitrates concentration during the investigation time.

tor is expressed only with one variable, it can be taken as a boundary (the eigenvalue can be ignored), and no further extraction is needed.

Factors 4 and 5 are less important because they are connected with only one or two parameters, so the interpretation is limited. Their eigenvalues are smaller, as well as their interpretative connection with the natural systems. Although the calculation shown indicates three main types of water quality deterioration, this does not mean that these are the only polluting processes in the system. They are merely the processes that could be rec-

ognized by the parameters monitored, and the purpose of monitoring is connected with pollution. If there were more parameters continually measured, there would possibly be more important processes recognized in the system. For example, dissolution of carbonates would probably be recognized, and calcium and carbonate ion in that potential factor would be loaded. This presumption is justified because the Golubinka spring water is of the Ca-HCO<sub>3</sub> facies (Table 1, Fig. 5). The three most important factors which could indicate natural processes are:

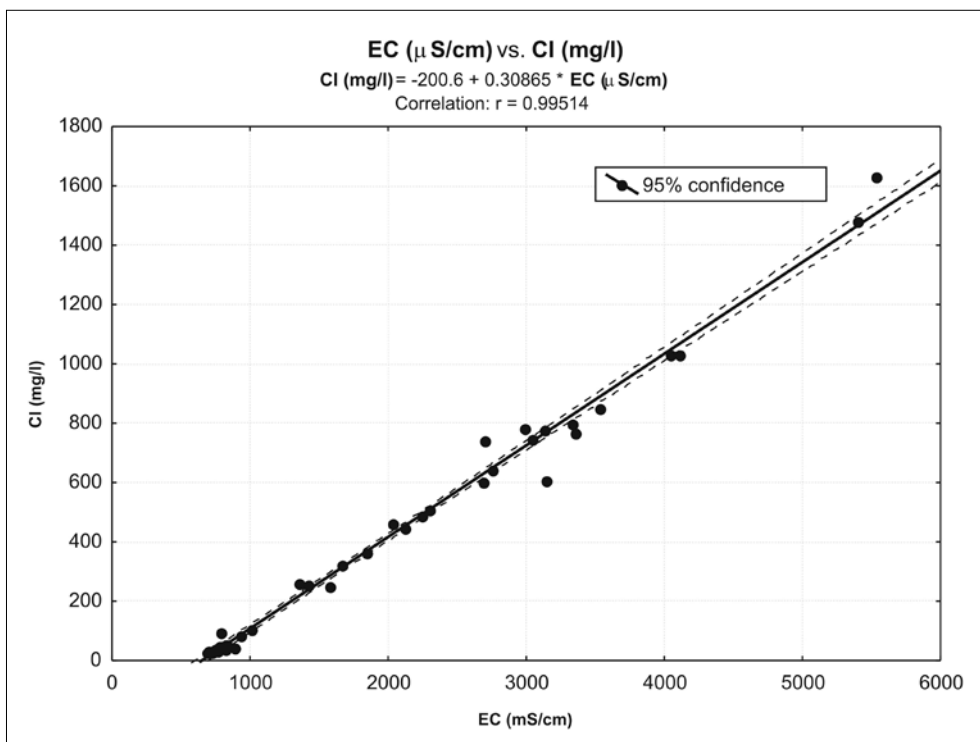


Fig. 7 Correlation between chlorides and electrolytic conductivity at the Golubinka spring.

	Turbidity	Temp.	pH	EC	Cl	NO <sub>3</sub>	Total Coliforms	Faecal Coliforms	Faecal Streptococci	Clostridium	Aerobic bacteria 22°C	Aerobic bacteria 37°C	Pseudomonas
<b>Turbidity</b>	1	-0.25	0.16	-0.18	-0.17	0.07	<b>0.32</b>	<b>0.39</b>	0.4	-0.08	<b>0.76</b>	-0.04	-0.07
<b>Temp.</b>		1	-0.08	0.26	0.28	-0.01	-0.05	-0.19	-0.12	-0.09	-0.24	-0.05	0
<b>pH</b>			1	0.16	0.16	-0.02	0.03	0.03	0.29	-0.16	-0.04	0.05	-0.13
<b>EC</b>				1	<b>0.99</b>	-0.02	0	-0.07	-0.09	-0.17	-0.27	-0.08	-0.14
<b>Cl</b>					1	-0.03	-0.01	-0.06	-0.05	-0.17	-0.26	-0.08	-0.14
<b>NO<sub>3</sub></b>						1	<b>0.31</b>	<b>0.32</b>	0.19	0.21	0.07	-0.12	-0.21
<b>Total Coliforms</b>							1	<b>0.83</b>	<b>0.51</b>	<b>0.35</b>	0.28	-0.03	-0.14
<b>Faecal Coliforms</b>								1	<b>0.54</b>	0.28	<b>0.35</b>	-0.06	-0.15
<b>F. Streptococci</b>									1	0.21	0.23	-0.05	-0.1
<b>Clostridium</b>										1	0.16	-0.03	-0.09
<b>Aer. bacteria 22°C</b>											1	0.26	-0.04
<b>Aer. bacteria 37°C</b>												1	-0.03
<b>Pseudomonas</b>													1

Table 3 Correlation between monitored parameters. High correlation coefficient is shown by gray shading, medium correlation only by bold font.

Factor	Eigenvalue	% Total variance	Cumulative Eigenvalue	Cumulative %
1	3.69	26.36	3.69	26.36
2	2.19	15.66	5.88	42.02
3	1.63	11.66	7.51	53.68
4	1.37	9.79	8.88	63.46
5	1.06	7.60	9.95	71.06

Table 4 Eigenvalues and variance percentages for extracted factors.

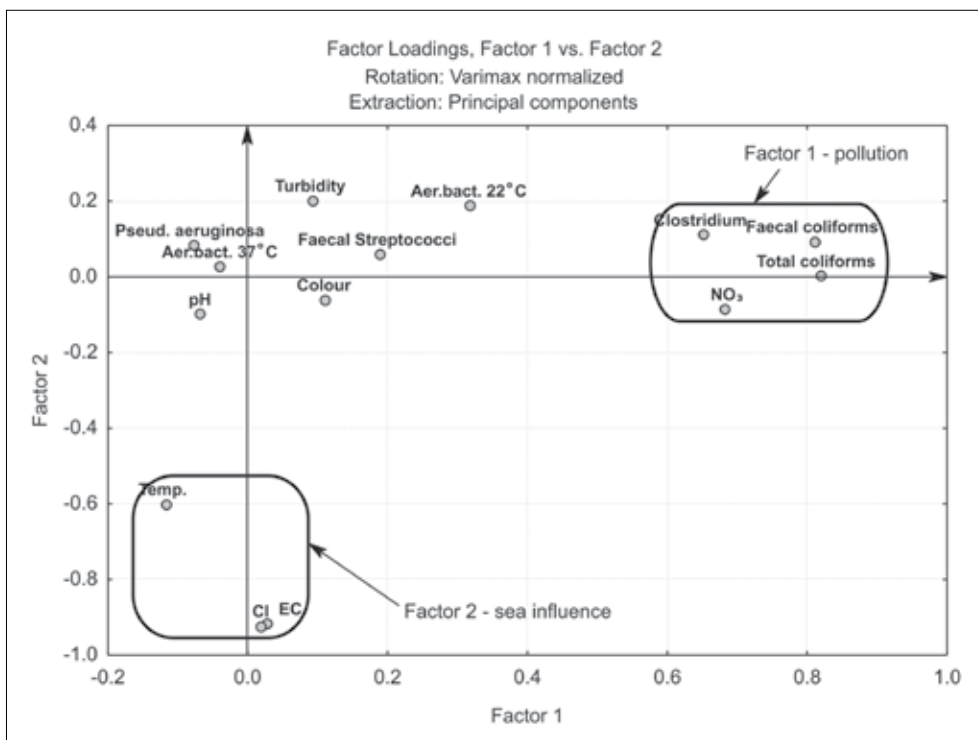


Fig. 8 Multivariate factor analysis diagram. Factor loadings: Factor 1 vs. Factor 2.

- **Factor 1** – nitrates and some biological components indicate pollution caused by agriculture and inhabited places without sewage infrastructure;
- **Factor 2** – chlorides, electrical conductivity and temperature grouped together represent a mixing with sea water either underground (intrusion) or as a consequence of sea water spray scattered on land by wind and infiltrated into the aquifer by precipitation;
- **Factor 3** – also pollution, but this time connected with turbidity and colour – this usually occurs after heavy rains.

## 6. DISCUSSION AND CONCLUSIONS

The Golubinka spring is situated in a rock mass composed of Eocene limestones. These rocks are highly karstified, so that the spring occurs in a cave. In the vicinity of the Golubinka spring, there are more springs, also connected with some vertical caves in the close hinterland (Figs. 2 and 3). High tracer velocities from distant parts of the catchment area indicated karstification in the whole aquifer. The majority of those karst conduits are sumps in the deep underground, usually below the present sea level. Such a karst conduit network could originate from the period before sea level stabilization (6000 years before present – PIRAZZO-LI, 2005), when the mean sea level was about 100 m (25,000 years BP – ŠEGOTA, 1982) or 70 m (15,000 years BP – BENAC & JURAIĆ, 1998) lower than today. Outside these preferential flow directions, there is a fractured rock mass that could be regarded as a continuous medium. It is very important that in such karst environments a high ratio of the precipitation infiltrates very quickly.

The Golubinka spring behaves like a typical karst spring, with a significant difference in its minimum and maximum discharges, as well as a rapid response to precipitation (Fig. 4). Hydrogeological circumstances are additionally complicated by the fact that this is a coastal spring subjected to sea-water intrusions during the dry summer seasons. Since this spring is capped for water supply, continuous monitoring of the water quality had to be carried out (Table 2). When the saline intrusion exceeds the permissible amount, pumping of the water has to be stopped, or the Golubinka water is mixed with water from other pumping sites.

The position of the Oko spring, half way between the ponor in Biljane Donje and the Golubinka spring, indicates that they belong to the same karst aquifer. This is an important conclusion because the Oko spring is about 60 m a.s.l, equating to a hydraulic gradient of approximately 0.006.

The problems with the water supply from these two springs are different. At the end of the summer dry season, the Oko spring significantly lowers its capacity (below the economically justified quantities), while the Golubinka water supply station lowers its extraction

capacity as a result of the sea water intrusion.

Parts of the Golubinka spring catchment are affected by extensive agricultural production, but this does not greatly influence water quality, as shown by the level of nitrates, which is always below 16 mg/l (Fig. 6). Under Croatian legislation, the permitted quantity of nitrates is a maximum of 50 mg/l. Even so, agricultural production near the ponor in Biljane Donje could cause pollution because of the high groundwater velocity, and quite limited purification capacity of the karst underground. Consequently that ponor must be monitored and put under sanitary protection, however far it is from the spring. Besides, some other minor ponor zones in the catchment, together with tectonically preferred flow directions in the vicinity of the Golubinka spring, should also be monitored and protected. There is extensive agricultural production, as well as inhabited places without sewage systems, but despite this the water in the Golubinka spring is able to satisfy regulatory criteria for potable water quality. Determined factors that could cause pollution should be monitored, and sustainable water protection zones ought to be established as soon as possible. If this could be done, there is a good chance of protecting and keeping this important karst groundwater for use as potable water in the future. With regard to the amount of nitrates, it is also important to point out that their amount in the groundwater is not susceptible to classification. That is because the concentration of nitrates depends on many factors, such as the composition of the soil through which water drains, forests, waste materials, agriculture, etc. (CANTER, 1997). Also, below the surface there is no light, restricting the use of all nutrient substances for life support and primary production in the groundwater. All nitrogen compounds (nitrogen gas, ammonium, nitrites, etc.) transform to nitrates (CANTER, 1997). As is recognized by the factor analysis, the three most important sources of pollution are settlements without sewage systems, seawater intrusion and 'washing out' from soil and the shallow epikarst belt by heavy rainfall events. Grouping of variables in factors (Table 5) would not be recognized by statistical regression, but factor analysis recognized it quite clearly, so the interpretation of factor space by natural processes was not difficult. In further monitoring, considering measured variables as parts of factors could increase the level of interpretation concerning pollution sources, even if other variables do not act accordingly in the beginning. For example, increase in colour and turbidity would point to the physical pollution of heavy rainfall (which is quite obvious) but, most importantly, to a possible occurrence of faecal streptococci in the water.

With constant quality monitoring and implementation of sanitary protection, even a karst coastal spring such as this could be included in the water supply system. Although this is a typical and very sensitive karst environment, all of the parameters that indicate pollution are below the permitted limits. All the new information about the behavior of the Golubinka karst spring

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Colour (mg/l Pt/Co scale)	0.11	-0.06	<b>0.93</b>	0.08	0.03
Turbidity (NTU units)	0.09	0.20	<b>0.89</b>	0.15	0.18
Temperature (°C)	-0.12	<b>-0.60</b>	0.04	0.01	-0.41
pH	-0.07	-0.10	-0.12	0.11	<b>0.77</b>
EC (µS/cm)	0.03	<b>-0.92</b>	-0.10	-0.11	0.24
Cl (mg/l)	0.02	<b>-0.92</b>	-0.09	-0.10	0.23
NO <sub>3</sub> (mg/l)	<b>0.68</b>	-0.08	-0.11	0.00	-0.02
Total Coliforms (No/100 ml)	<b>0.82</b>	0.00	0.26	0.10	0.13
Faecal Coliforms (No/100 ml)	<b>0.81</b>	0.09	0.28	0.11	0.21
Faecal Streptococci (No/100 ml)	0.19	0.06	<b>0.80</b>	-0.15	-0.14
Clostridium perfringens (No/100 ml)	<b>0.65</b>	0.11	0.16	0.01	-0.36
Aerobic bacteria 22°C (No/100 ml)	0.32	0.19	0.26	<b>0.75</b>	0.07
Aerobic bacteria 37°C (No/100 ml)	-0.04	0.03	-0.11	<b>0.87</b>	-0.04
Pseudomonas aeruginosa (No/100 ml)	-0.08	0.09	-0.17	0.08	-0.46

Table 5 Multivariate factor analysis. Factor loadings for the five most important factors.

should improve water quality and ensure large quantities of potable water for use in the future.

## 7. REFERENCES

- AHMED, S.M., HUSSAIN, M. & ABDERRAHMAN, W. (2005): Using multivariate factor analysis to assess surface/logged water quality and source of contamination at a large irrigation project at Al-Fadhli, Eastern Province, Saudi Arabia.– *Bull. Eng. Geol. Environ.*, 64, 319–327.
- BENAC, Č. & JURAČIĆ, M. (1998): Geomorphological indicators of sea level changes during upper Pleistocene (Würm) and Holocene in the Kvarner region (NE Adriatic sea).– *Acta Geographica Croatica*, 33, 27–45.
- BENAC, Č., JURAČIĆ, M. & BAKRAN-PETRICIOLI, T. (2004): Submerged tidal notches in the Rijeka bay NE Adriatic Sea: indicators of relative sea-level change and of recent tectonic movements.– *Marine Geology*, 212, 21–33.
- CANTER, L.W. (1997): Nitrates in groundwater.– Lewis publishers, CRC Press, New York, London, Tokyo, Boca Raton, 263 p.
- DAVIS, J.C. (1986): Statistics and data analysis in geology.– John Wiley & Sons, New York, 646 p.
- DURN, G. (2003): Terra rossa in the Mediterranean region: parent materials, composition and origin.– *Geologia Croatica*, 56/1, 83–100.
- FRITZ, F. & PAVIČIĆ, A. (1991): The Boljkovac spring, Croatia – a case of the overexploitation of a karst spring.– XXIII I.A.H. Congress “Aquifer overexploitation”, Proceedings, Canary Islands, Spain, 515–518.
- KUK, V., PRELOGOVIĆ, E. & DRAGIČEVIĆ, I. (2000): Seismotectonically active zones in the Dinarides.– *Geol. Croatica*, 53/2, 295–303.
- MAJCEN, Ž. & KOROLIJA, B. (1973): Osnovna geološka karta SFRJ 1:100.000, List Zadar L33–139 (Basic Geological Map of the SFRY, scale 1:100.000, Zadar Sheet).– Institut za geološka istraživanja Zagreb (1963–1969), Savezni geološki zavod, Beograd.
- MASSE, J.P. & MONTAGGIONI, L.F. (2001): Growth history of shallow-water carbonates: control of accommodation on ecological and depositional processes.– *Int. J. Earth Sciences (Geol. Rundschau)*, 90, 452–469.
- MIKO, S., DURN, G. & PROHIĆ, E. (1999): Evaluation of terra rossa geochemical baselines from Croatian karst regions.– *Journal of Geochemical Exploration*, 66, 173–182.
- NARODNE NOVINE (2004): Pravilnik o zdravstvenoj ispravnosti vode za piće [*Directions on the health propriety for potable water* – in Croatian].– Narodne Novine – Official Bulletin of the Republic of Croatia, 182, 14 p.
- PEH, Z. (1992): Factor model of the geomorphological system of a part of Northwestern Croatia.– *Geol. Croatica*, 45, 163–172.
- PEH, Z. (1994): Faktorski model kao izraz dinamike geoloških procesa na primjeru sjeverozapadnog dijela Hrvatskog zagorja [*The factor model as the expression of dynamics of geological processes in the northwestern Croatia* – in Croatian with English abstract].– Unpubl. PhD Thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, 162 p.
- PIRAZZOLI, P.A. (2005): A review of possible eustatic, isostatic and tectonic contributions in eight late-Holocene relative sea-level histories from the Mediterranean area.– *Quaternary Science Reviews*, 24, 1989–2001.
- PRELOGOVIĆ, E., PRIBIČEVIĆ, B., IVKOVIĆ, Ž., DRAGIČEVIĆ, I., BULJAN, R. & TOMLJENOVIĆ, B. (2003): Recent structural fabric of the Dinarides and tectonically active zones important for petroleum–geological exploration in Croatia.– *Nafta*, 55/4, 155–161, Zagreb.
- SHRESTHA, S. & KAZAMA, F. (2007): Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan.– *Environmental Modeling and Software*, 22, 464–475.

- SINGH, K.P., MALIK, A. & SINHA, S. (2005): Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques – a case study.– *Analytica Chimica Acta*, 538, 355–374.
- ŠEGOTA, T. (1982): Razina mora i vertikalno gibanje dna Jadranskog mora od Ris–Würmskog interglacijala do danas [*The sea level and vertical movements of the Adriatic Sea bottom since Ris–Würm glaciations till today* – in Croatian].– *Geol. vjesnik*, 35, 93–109.
- ŠEGOTA, T. & FILIPČIĆ, A. (1996): Klimatologija za geografte [*Climatology for Geographers* – in Croatian].– Školska knjiga, Zagreb, 471 p.
- VLAHOVIĆ, I., TIŠLJAR, J., VELIĆ, I. & MATIČEC, D. (2005): Evolution of the Adriatic Carbonate Platform: Palaeogeography, main events and depositional dynamics.– *Palaeogeography, Palaeoclimatology, Palaeoecology*, 220, 333–360.
- ŽUGAJ, R. (1995): Regionalna hidrološka analiza u kršu Hrvatske [*Regional Hydrological Analysis in Croatian Karst* – in Croatian].– Croatian Hydrological Society, Zagreb, 139 p.

Manuscript received September 1, 2006.

Revised manuscript accepted November 24, 2006.

