

Differences in temporal changes of selected water quality parameters on Jasovská Planina Plateau (Slovak Karst, Slovakia)

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Abstract: *Our study presents the hydrochemical data obtained from seven perennial springs located on the Jasov Plateau – Slovak Karst. It is part of the most heavily karstified area in Slovakia extending into northern Hungary. Monthly observations of discharge, temperature and the calcium content have been carried out on perennial springs for 19 months. Since November 2013 the seasonal changes of the basic hydrochemical parameters (water temperature, electric conductivity, pH and major ions), the stable isotope composition and tritium content have been measured on a regular basis. Except for water temperature, no other parameter showed a clear seasonal signal. Statistically significant relationships were discovered between some springs concerning the fluctuation of the various parameters. The stable isotope analyses of the water samples showed that the springs are of meteoric origin, their stable isotope composition varied between -74.9‰ to -62.1‰ and from -10.5‰ to -9.5‰ for δD and $\delta^{18}O$, respectively. The mean residence time of the water varies between 3,5 and 6 years (tritium concentration).*

Keywords: *Slovak Karst, karstic springs, hydrochemical parameters, tritium analyses*

Introduction

Karst is a vulnerable type of environment. In comparison with other landscapes it reacts to changes faster and more significantly because of its geological characteristics. The Slovak Karst is the largest and most typical karst area in Slovakia and contains abundant karstic springs. Some of them have been captured in the East-Slovakian water management system and others have been systematically monitored.

The aim of this paper is to present a set of results about the hydrochemical characteristics of seven selected springs located on the easternmost plateau of the Slovak Karst, Jasov Plateau. Even though some locations were described in details in the inventory of karst objects by Lešínský (2002), studies in this area were scarce until now. The basic hydrological and hydrogeological research of some springs was carried out in the 1950s and 1960s (Homola 1951, Himmel 1963). In the next two decades studies highlighted the problems of drinking water supply. Mostly, springs on the easternmost part of the plateau (Medzev Hills) were examined (e.g., Orvan 1964). Nowadays a hydrogeological survey is in progress under the leadership State Geological Institute of Dionýz Štúr (Malík et al. 2013) and Slovak Cave Administration. Recent studies of Jasov Plateau have concentrated mostly on geology (Vass et al. 1994, Mello et al. 1997, Čílek 2000, Bónová et al. 2008), hydrogeology, hydrochemistry and hydrology (Homola 1951, Orvan 1977, Hochmuth and Barabas 2001, Barabas 2005, Barabas and Haviarová 2003, Malík et al. 2010, Malík et al. 2013), speleology (Seneš 1950, Hochmuth 1992, 2000, Kladiiva et al. 1999, Zacharov 2013, Petrvalská and Hochmuth 2013) or geomorphology (e.g., Zacharov 2009, 2013, Petrvalská 2008, 2014, Barabas et al. 2010, Malík et al. 2010, Hochmuth and Petrvalská 2010).

The study area

Slovak Karst

The Slovak Karst is situated in the eastern part of southern Slovakia. It forms the largest continuous karst area in Slovakia, extending over 800 km², extending into northern Hungary (Aggtelek Karst). It is characterized by a uniform pediplanation surface that has a complex geological structure with five tectonic units (nappes): Silicicum, Gemicum, Bôrka Nappe, Meliaticum and Turnaicum. The bottom parts of these nappes are built up by Lower Triassic non-karstifying rocks overlain by dominant light grey and white Wetterstein Limestone, Wetterstein Dolomite, Gutenstein Limestone and Dachstein Limestone (Mello et al. 1997).

Canyon- and gorge-like valleys divide the area into several plateaus: Koniar, Plešivec, Silica, Horný vrch, Dolný vrch, Bôrka, Zádiel and Jasov. The altitude difference between the valley and the plateau surfaces is 400 m on average. On the plateau surfaces, karst forms (exokarst) are well-developed, for instance numerous abysses can be found there. Interestingly caves with active water flow are known only from the edge of the Slovak Karst.

After Šuba et al. (1984) we include the investigated area into the region MQ 129 – Mesozoicum of the central and east part of the Slovak karst and subregion SA50. Šuba (1973) delineated here Hačava-Jasov hydrogeological structure typical by massive middle-Triassic carbonates with distinctive karst joints and porosity. Karstification is here connected to faults of the N-S directions. More details on hydrogeology and hydrochemistry of this area is provided in the hydrogeological map of Slovak karst 1:50 000 (Malík et al. 2013).

Jasov Plateau and Medzev Hills

Jasov Plateau and Medzev Hills are situated on the eastern border of Slovak Karst. Even if Jasov Plateau and the neighbouring Medzev Hills are defined as two different geomorphological areas, they represent one compact hydrogeological unit (Šuba 1979). Therefore four of the investigated springs (Skalistý Potok, Teplica, Drienovecká Cave and Kozia Studňa) are to be found on Jasov Plateau, one (Svätý Ján Spring) on Medzev Hills and two (Pekná Dievčina Spring and Hatiny) in between these two areas (Fig. 1).

The northern and the southern parts of Jasov Plateau drain to Hačava-Jasov partial structure and to Silica-Turňa partial structure, respectively. The northern part consists of a layer sequence from Lower to Upper Triassic and due to tectonic activities it is divided into more aquifers. The most important springs (Teplica and Drienovecká Cave) with the highest discharge are present due to non-karstic bedrock. The southern part is made up by a limestone-dolomitic complex bedded on lower Triassic rocks. The most important spring of this structure is Skalistý Potok Spring (Orvan 1988).

From a geologic point of view, Jasov Plateau represents a Mesozoic rock complex; most of the area is built up by Wetterstein limestones. Pre-Mesozoic rocks are situated only in the north-western and in the northern parts of the plateau (Mello et al. 1997). Miglinc Valley along the Rožňava fault leading from NW to SE divides the plateau into two separate tectonic units. The eastern part of the research area (Medzev Hills) is covered by Poltár Formation from Miocene age (Pontian), which is typical for the presence of gravels, sand and clay. These sediments cover the central part of this eastern area, where the slopes are also covered by deluvial Pleistocene-Holocene slope sediments.

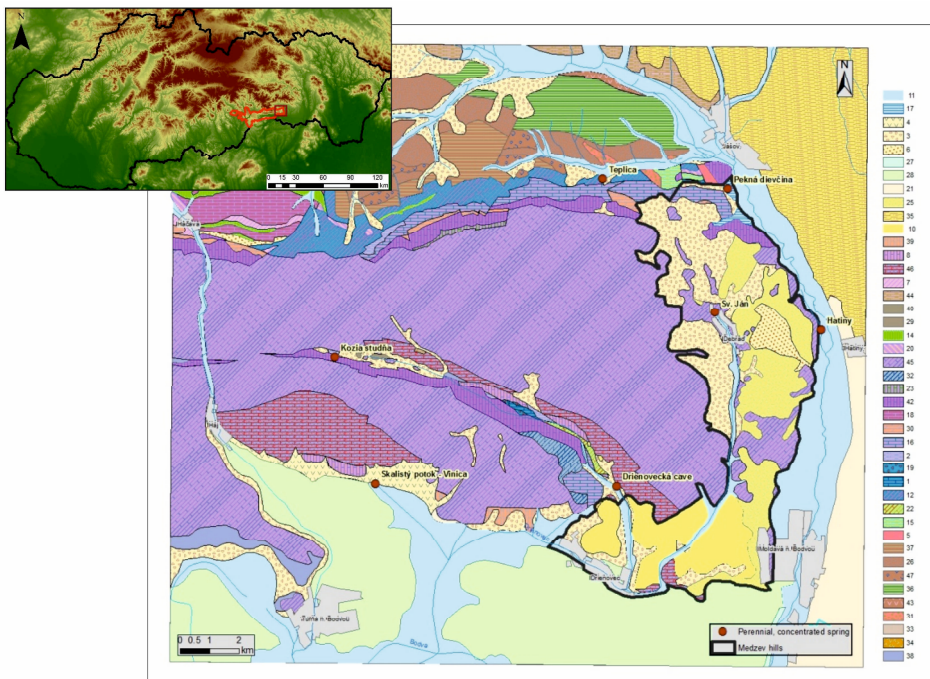


Fig. 1. Small situation map of Slovakia with the research area and geology of Jasov Plateau with position of selected springs (after Mello et al 1997). **Legend:** QUATERNARY: Holocene: 11 – fluvial sediments of alluvial plains – loamy, loamy-sandy, clayey; Younger Pleistocene – Holocene: 4 – deluvial-proluvial sediments; Pleistocene/Holocene: 3 – deluvial sediments; 6 – deluvial sediments: loamy and loamy-gravelous; Pleistocene: 17 – proluvial sediments; 21 – deluvial-eolian sediments: loessic loams and loess. NEOGENE: Miocene-Pontian: 25 – Poltár Formation: variegated clays, gravels, sands; Pannonian: 35 – Sečov Formation. PALEOGENE: 10 – Drienovec Conglomerates: carbonatic conglomerates; Šomody formation: 39 – gray laminated or massive fresh-water limestones. MESOZOIC: Triassic-Upper Triassic: 8 – Dachstein reef and lagoonal limestones; 46 – Waxeneck (Tisovec) limestones; 7 – Dvorníky Beds: shales, phyllites with intercalations of sandstones, silicites, limestones and basic volcanoclastic rocks; 44 – Wetterstein dolomites; 40 – serpentinites; 29 – metabasic rocks; 20 – grey-green and light shaly crystalline limestones; 14 – Dúbrava Formation: chlorite-sericite phyllites with intercalations of marbels and metabasic rocks; 45 – Wetterstein limestones, lagoonal; 32 – Reifling and "Pseudoreifling" limestones; Middle Triassic: Schreyeralms limestones; 23 – Nádaska limestones; 42 – Steinalm limestones; 30 – Gutenstein dolomites, hematite-bearing at places; 18 – marbles; 13 – Gutenstein dolomites; 16 – Gutenstein limestones; Lower Triassic: 38 – Szin Beds: shales, marlstones, limestones; 2 – Bódvaszilás Beds: variegated sandstones and shales. Jurassic-Upper Triassic?-Lower Jurassic: 12 – dark and black phyllites, with laminae of metasiltstones and metasandstones at places; Lower Jurassic: 19 – Adnet and Hierlatz limestones, variegated basal breccias; 1 – Allgäu Beds: dark marly liemstones and marls, spotty at places. Creaceous-Upper Cretaceous: 22 – Miglinc limestones: white massive limestones; 15 – Gombasek Beds: dark shales and sandstones. PALEOZOIC: Upper Permian-Permian: 5 – polymict conglomerates; Lower Permian?: meta-tyholites, metadacites and their volcanoclastics; 37 – sericite and chlorite-sericite phyllites, with chloritoid; 26 – meta-sandstones; 47 – metamorphosed oligomictic conglomerates; Upper Devonian?-Lower Carboniferous?: 36 – laminated seritic-chloritic phyllites; Lower Devon: 43 – quartz meta-greywackers with local intercalations of quartz phyllites

Selected springs

Skalistý Potok Spring is a permanent spring on the southern foothill of Jasov Plateau in the altitude of 210 m a.s.l. (Fig. 1). Water emerges from the contact zone of deluvial-proluvial sediments and fluvial sediments of a river plain.

Drienovecká Cave Spring is situated on the same slope. It flows out from the entrance of a 1.5 km long fluviokarstic cave in the altitude of 254 m a.s.l. under a 10 m high rock wall (Fig. 1). The cave is located in Waxeneck limestone. It is situated only 300 m to the north from former spa. In the 1950's some articles were published about the origin of this water. Water may come from the Drienovec River (the spring is in Debrad' Village) and there is a theory that there is also a small contribution from allogenic catchment of Bodva River (Homola 1951, Orvan 1988, Orvan & Tometz 1999). These theories were not proved by trace experiment.

Pekná Dievčina Spring is situated on the eastern foothill of Jasov plateau in altitude of 268 m a.s.l., only 5 meters above Bodva River plain (Fig. 1). Water emerges where the Gutenstein dolomite complex meets proluvial sediments. Water of the Pekná dievčina spring appears in a pond and flows from there.

Teplica Spring appears on the northern foothill of the plateau in the altitude of 325 m a.s.l., in the contact zone of deluvial debris accumulation and Gutenstein Dolomite (Fig. 1). Teplica Spring is not isolated. Spring consists of several partial groundwater outlets, two ephemeral springs on the right and left from the main perennial spring plus group of 8 diffuse groundwater outlets active only at high water stages.

Sv. Ján Spring is situated on a fluvial planation surface in Debrad' Village, 80 m above the Bodva River plain in the contact zone of Poltár Formation and Wetterstein limestones (Fig. 1).

Kozia studňa Spring is situated in the upper part of Miglinc Valley (Fig. 1). By containing nonkarstic series and being defined by a huge fault heading from SE to the NW and continuing across other plateaus on the west. The area is considered to be rather variegated in geological composition.

Hatiny is situated on the foothill of the Jasov Plateau on the contact with Bodva River basin. Water appears in the large pond with more outlets; the largest one was captured into building and monitored as potential water supply.

Methods

Monthly observations of discharge, temperature, alkalinity and the calcium content of water have been carried out in situ for 19 months from November 2013 to May 2015, once a month. Spring discharge measurements were performed by digital water velocity meter (FP 111, Global water) while a MERCK kit (Aquamerck Calcium Test 1.11110.0001, Aquamerck Alkalinity Test 1.11109.0001) was used to determine the in situ Ca^{2+} content and the alkalinity of water. For 17 months only the basic hydrochemical parameters (water temperature, electric conductivity, pH and Ca^{2+}) and the stable isotope composition (δD and $\delta^{18}\text{O}$) of water have been measured on a regular basis. Samples for tritium content were also collected every month. The first samples for groundwater age estimation based on the tritium (^3H) content of water were also collected from the end of December 2013. Water samples for tritium have been analyzed using the ^3He -ingrowth method (Palcsu et al. 2010). Due to the principle of the method, the samples had to be stored for a couple of months so that ^3He is produced from the tritium decay. The tritium concentrations in the table are expressed in tritium units (TU) which represents a $^3\text{H}/^1\text{H}$ ratio of 10-18. In case of water, 1 TU equals to 0.119 Bq/L activity concentrations.

Major ion concentrations (we presents Ca^{2+} content) were measured on a Shimadzu UV-2600 UV-VIS spectrophotometer and on a Metrohm TitrIC 7 ion chromatograph. Stable isotope measurements for water were performed on a Thermo Finnigan DeltaPLUS XP isotope ratio mass spectrometer (Vodila et al. 2010). The delta notation is used for stable isotope ratios. The δ -value is defined as a relative difference of the isotope ratios between the sample and an international reference: $\delta = (\text{Rs}/\text{Rr}-1)*1000\%$, where Rs and Rr is the isotope

ratios for the sample and the reference, respectively. Routine precision better than 2‰ and 0.2‰ was established for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively. All analyses were provided in the Laboratory of environmental studies, Institute of Nuclear Research, Hungarian Academy of Sciences in Debrecen.

Pearson correlation accessible via Microsoft Office Excel 2013 was used to describe the strength of the linear relationship between the parameters that were monitored for a year (water temperature, electric conductivity, pH, discharge, Ca^{2+} content and alkalinity). Statistical analyses were performed by SPSS software.

Results and discussion

As we mentioned above monthly observations have been carried on for 19 months. Although our number of data is limited, discharge, alkalinity, electric conductivity, pH, water temperature and Ca^{2+} content of water were statistically analysed in order to investigate the relationship between the different physicochemical parameters of water, as well as the 7 springs (Tab. 1).

Tab. 1. Measured water parameters overview

| | | temperature (°C) | EC ($\mu\text{S}/\text{cm}$) | pH | Ca^{2+} (mg/l) | isotope composition | | tritium (^3H) | Discharge (l/s) |
|-------------------------|---------|---------------------|-----------------------------------|-------|----------------------------|------------------------|-----------------------|-----------------------------|--------------------|
| | | | | | | δD | $\delta^{18}\text{O}$ | | |
| <i>Skalistý Potok</i> | Min. | 9,0 | 228 | 7,18 | 111,27 | -70,93 | -10,11 | 6,63 | 40,90 |
| | Max. | 12,5 | 638 | 8,31 | 140,00 | -61,19 | -9,10 | 7,53 | 221,00 |
| | Average | 10,7 | 574 | 7,46 | 129,71 | -66,14 | -9,82 | 7,07 | 111,10 |
| <i>Drienovecká Cave</i> | Min. | 7,99 | 556 | 7,39 | 91,20 | -69,89 | -10,28 | 5,05 | 7,80 |
| | Max. | 11,0 | 699 | 12,10 | 148,00 | -62,05 | -9,71 | 7,60 | 109,00 |
| | Average | 9,2 | 625 | 8,10 | 129,07 | -66,13 | -10,07 | 6,87 | 32,11 |
| <i>Pekná Dievčina</i> | Min. | 4,5 | 576 | 7,30 | 92,42 | -67,98 | -10,02 | 6,17 | 0,00 |
| | Max. | 13,9 | 663 | 8,34 | 137,00 | -60,09 | -9,21 | 7,12 | 7,00 |
| | Average | 10,3 | 607 | 7,72 | 114,44 | -65,27 | -9,55 | 6,83 | 1,75 |
| <i>Teplica</i> | Min. | 7,68 | 484 | 7,42 | 91,98 | -70,34 | -10,48 | 6,67 | 0,60 |
| | Max. | 12,40 | 750 | 8,43 | 135,00 | -63,70 | -9,70 | 7,22 | 192,00 |
| | Average | 9,8 | 588 | 7,88 | 117,94 | -66,25 | -10,21 | 6,89 | 35,20 |
| <i>Sv. Ján</i> | Min. | 8,3 | 586 | 7,14 | 103,96 | -69,93 | -10,04 | 6,52 | 10,00 |
| | Max. | 12,9 | 693 | 8,10 | 148,00 | -61,10 | -9,58 | 7,15 | 52,00 |
| | Average | 10,2 | 636 | 7,54 | 132,49 | -66,45 | -9,84 | 6,74 | 21,97 |
| <i>Kozia studňa</i> | Min. | 4,0 | 573 | 7,28 | 79,77 | -74,90 | -10,87 | 6,45 | 0,00 |
| | Max. | 11,9 | 737 | 10,10 | 130,00 | -64,86 | -9,47 | 6,87 | 0,50 |
| | Average | 8,0 | 618 | 7,89 | 102,57 | -68,75 | -10,38 | 6,71 | 0,28 |
| <i>Hatiny</i> | Min. | 8,5 | 416 | 7,42 | 64,14 | -78,98 | -10,33 | 5,66 | - |
| | Max. | 13,6 | 470 | 8,70 | 121,40 | -61,15 | -9,67 | 6,22 | - |
| | Average | 10,2 | 437 | 7,86 | 76,11 | -67,02 | -9,89 | 5,93 | - |

Hydrochemical results

Water temperature (Fig. 2) shows a seasonal pattern reflecting the variation in air temperature, being higher in summer and lower in winter. Due to the moderating effect of the karst aquifer the month amplitude of changes were 3.5°C, 4.6°C, 3.0°C, 4.5°C, at Skalistý Potok, Sv. Ján, Drienovecká Cave and Teplica Spring, respectively. Pecná Dievčina and Kozia Studňa springs were characterized by higher variation, 7.7°C and 7.9°C due to the influence of the air temperature that we will wider discuss in next parts of this article. So water temperature of springs is in two cases strong influenced by air temperature (Fig. 2). The amplitude of the temperature is 7.7°C (Pecná Dievčina) and 7.9 °C (Kozia Studňa Spring). The lowest elevated value

measured at Kozia Studňa was 4.0°C on 12/12/2013 and reflects strong decreasing of the air temperature from 8.1°C (21/11/2013) to minus temperatures. Other low value 4.5°C was measured by Pekná Dievčina on 1/2/2014 (but not at Kozia Studňa). We supposed that the low temperature is effect of low minus temperatures in previous period (-3 to -11°C) affected by inversion of temperature because Pekná Dievčina is situated on the foothill of the plateau. Another peak appears on 19/9/2014 by Pekná Dievčina, 13.9°C. That situation is affected by spring outlet character, small pond that concentrates air temperature from longer period (summer months). Cooling effect is slow. Anyway, both springs reflect the influence of air temperature. As Pekná Dievčina spring has no specific resurgence, water appears in a pond, and therefore, it starts to equilibrate with surface temperature. Regarding Kozia Studňa spring, the lowest temperature was recorded when the spring was almost dry and had a water discharge of 0.01 l s⁻¹. These last two springs seem to be debris springs of the shallow groundwater circulation.

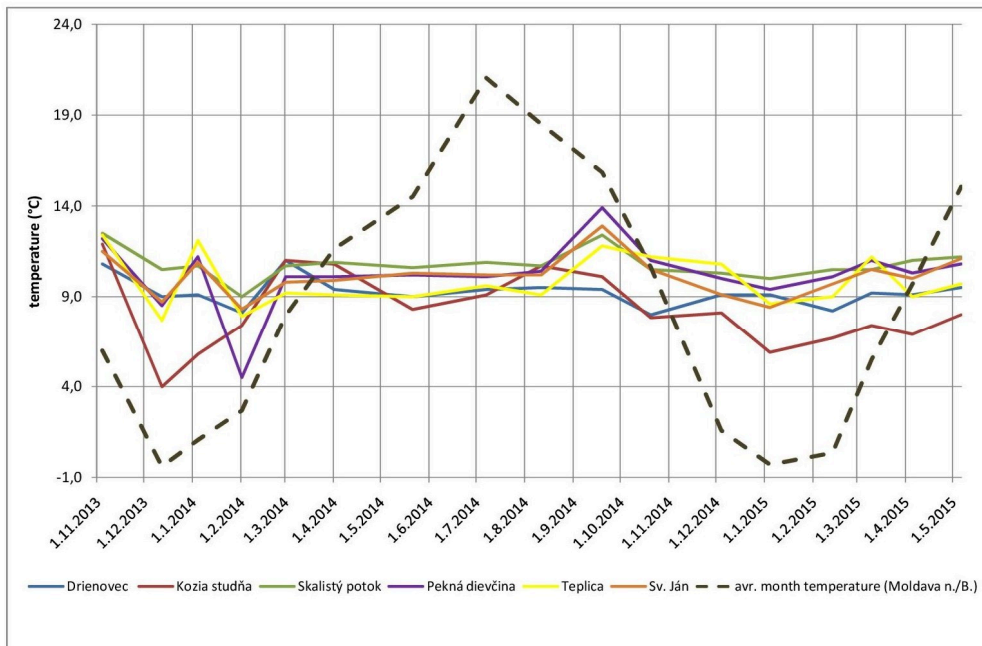


Fig. 2. Relation between water temperature and average month temperature at the springs

Electric conductivity (EC) (Fig. 3) varies by springs with different amplitude. Biggest differences in electric conductivity between summer (August-September) and winter time (February) present Teplica Spring (266 $\mu\text{S}/\text{cm}$), the lowest Pekná dievčina (87 $\mu\text{S}/\text{cm}$). EC values show two strong responses. Firstly, we notice the decrease of values, which is caused by winter period, hence snow precipitation. Followed by spring warm weather and snow melting, we observed the increase of EC values, which originated in water that was stored underground during winter. This trend is clearly atypical, since typically there is a opposite trend, during which the conductivity decreases as a result of mixing groundwater with low mineralized precipitations. The observed trend appears to be the result of a generally low water level in the second half of 2014. During that time water mineralisation was increasing and after snow melting it was flushed out from underground. In the following summer period we observe no big changes in chemograph, until end of summer. The next autumn period is interesting for us. In chemograph we can see two dominant peaks, which represent Kozia Studňa and Teplica Spring. Kozia Studňa is reacting very fast on a rainy conditions and EC – values are increasing already in august. Other springs do not have such a fast response and need some time to reach

their maximum volume. Second peak (purple) is representing Teplica Spring, which is in connection with the Teplica Cave nearby. The maximum of aquifer was reached, and water stored underground was flushed out. Responses of other 6 springs are also increasing, but the run is moderate and we see no strong correlations to Kozia Studňa or Teplica. Kozia Studňa spring is showing us another strong increasing during the period from November 2014 until February 2015. This again, is a sign that spring is reacting really fast to any type of precipitation; hence we categorized it as a debris type of spring (Fig. 3).

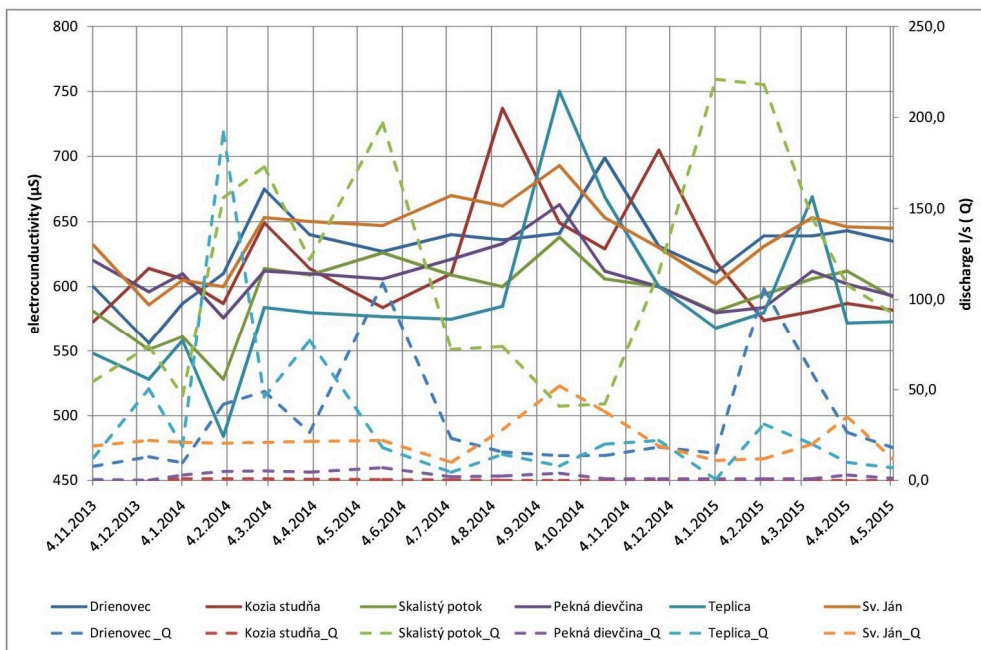


Fig. 3. Electric conductivity and discharge relationship

The *pH* value (Fig. 4) of the investigated springs is slightly alkaline and usually ranges from 7.2 to 8.4. The highest were recorded at Drienovecká Cave, while Skalístý Potok and Sv. Ján in springs were characterized by the lowest values during our measurement period. All sampling sites showed the highest levels during the last two measurements in April and May 2015 (8.0 to 8.4), lowest in the winter period during February 2015 (7.1 to 7.5).

Time changes of *pH* values by monitoring springs are good visible. Interesting are values during May and June 2014, when *pH* change and response on springs is identical. Similar rates along whole measuring period show Teplica and Pekná Dievčina springs, their neighbouring catchment areas are situated in the north part of the plateau. Kozia Studňa reacts similar as by temperature, changes in water and air temperature or rainfall reflects quickly spring water parameters. One negative peak by Skalístý Potok is complicated to explain. There is inverse running of *pH* opposite to other springs in the period between October 2014 and January 2015.

During the measurement period there was a flood event from March to May 2014 and from January 2015 to March 2015 having peaks in May and January (Fig. 5). The highest amplitudes in the case of *discharge* were observed at Skalístý Potok with peak above 220 l s^{-1} and lowest discharge around 40 l/s in dry period, so the maximum discharge is 2 times higher than the average value. Similar peak is visible for Teplica Spring in February 2014 and is related to the snow melting period.

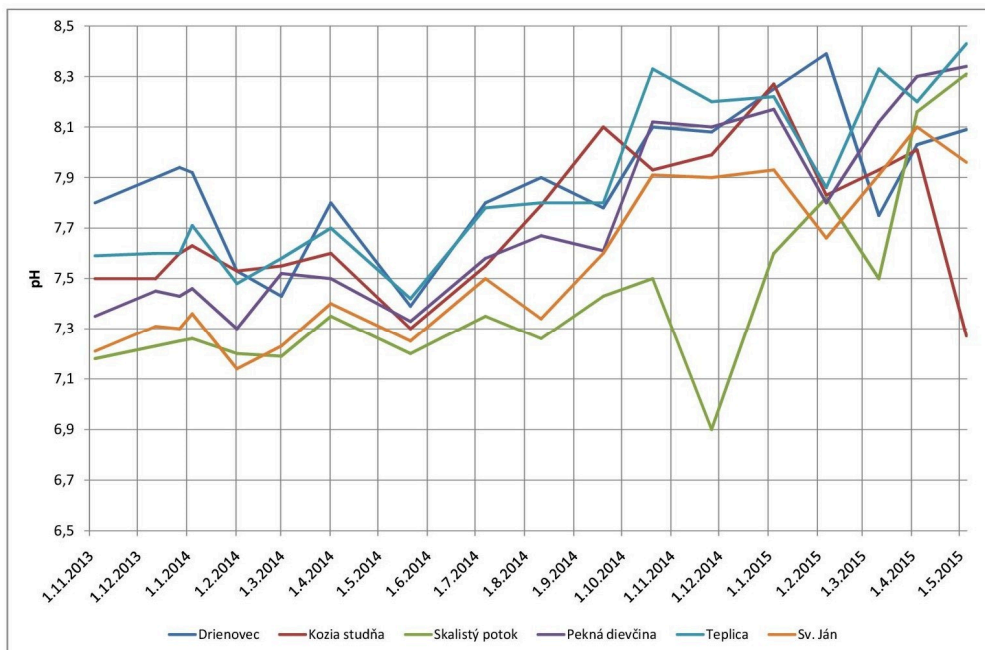


Fig. 4. pH values during the study period

Similar fluctuations in the *water flow* were discovered between Skalístý Potok and Drienovec springs, Drienovecká Cave and Sv. Ján springs, while a statistically still significant but weaker relationship was detected between Skalístý Potok and Sv. Ján springs. The changes in discharge of Sv. Ján spring showed similarities to the values measured at Teplica Spring (Table 2). For this comparison data from Moldava meteorological station were used.

Tab. 2. Auto correlation coefficients for discharge between monitored springs

| | Skalístý potok | Pekná dievčina | Teplica | Drienovec cave | Sv. Ján | Kozia studňa |
|----------------|----------------|----------------|---------|----------------|---------|--------------|
| Skalístý potok | 1 | | | | | |
| Pekná dievčina | 0.902** | 1 | | | | |
| Teplica | 0.603 | 0.686* | 1 | | | |
| Drienovec Cave | 0.593 | 0.535 | 0.476 | 1 | | |
| Sv. Ján | 0.798** | 0.860** | 0.826* | 0.351 | 1 | |
| Kozia studňa | 0.532 | 0.369 | 0.341 | 0.617 | 0.401 | 1 |

Note: * and ** mark correlation on 0.01 and 0.05 significance levels, respectively

From the Fig. 5 we can see later response to the rainfall at the Teplica or Pekná Dievčina springs. Both of them have their probable recharge area in the north part of the Jasov plateau and this is related to the higher altitude and microclimate (longer snow period, slower snow melting). High peak on Teplica and Skalístý Potok is connected to rapid warming during the end of the January and quickly snow melting; Skalístý Potok response is the fastest from all springs.

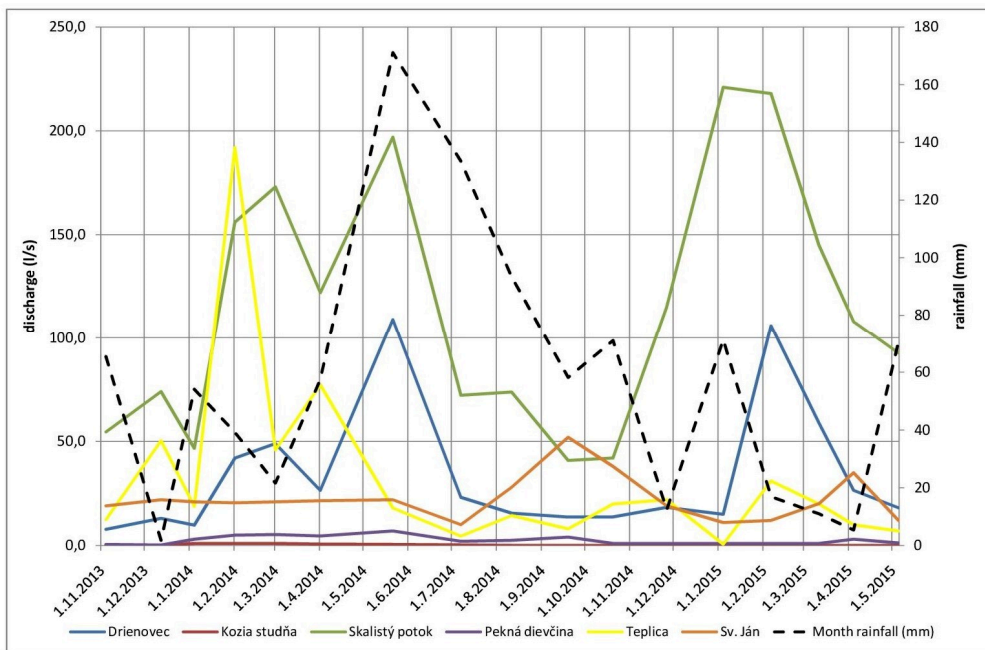


Fig. 5. Rainfall and discharge relationship

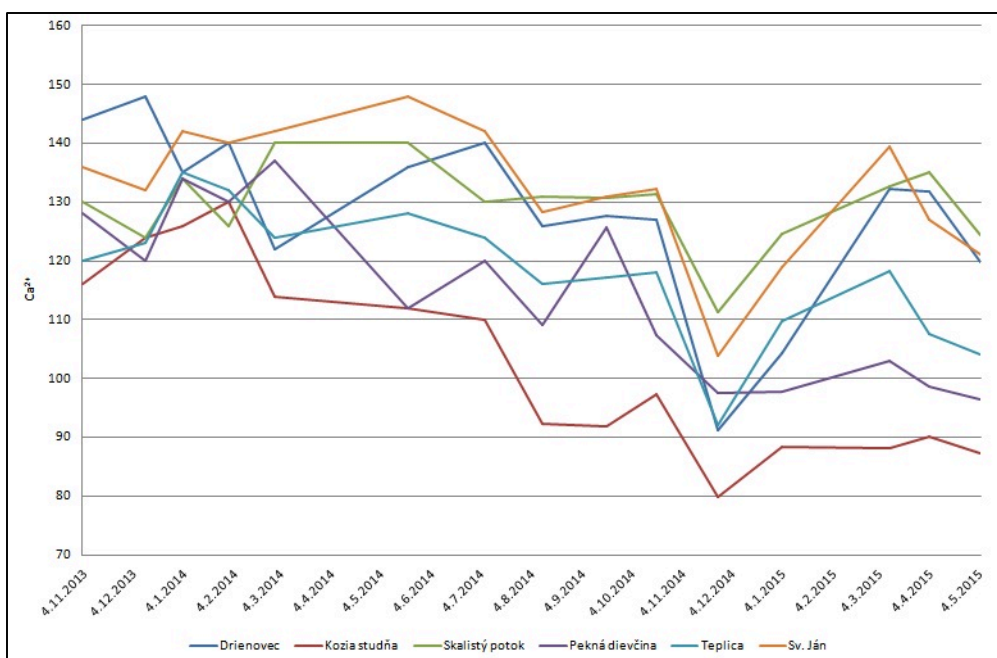


Fig. 6. Ca²⁺ content

The highest Ca^{2+} levels (Fig. 6) were measured at Drienovecká Cave and Sv. Ján springs (variations between 91 and 200 mg/l). Ca^{2+} values show little variation at a given site. Regarding electric conductivity, no significant differences can be observed between the springs, values started to rise in March to the end of the autumn. Opposite fluctuation is visible by Skalistsý Potok Spring.

Apart from alkalinity and Ca^{2+} levels ($R^2=0.358$ on a 0.01 significance level) of water no correlation coefficients were found between the various parameters at different springs.

Concerning each springs separately in the case of Drienovecká Cave spring a negative relationship ($R^2=0.894$ on a 0.05 significance level) was experienced between conductivity and the Ca^{2+} content of water. At Pekná Dievčina spring a large correlation coefficient ($R^2=0.904$ on a 0.05) significance level was found between discharge and the Ca^{2+} values of water. The relationships between temperature and discharge, as well as temperature and electric conductivity were characterized by even stronger correlation coefficients, $R^2=0.933$ and 0.983 on 0.01 significance levels, respectively.

Mean residence time

Since karst water aquifers are vulnerable, the response of the water quality to a potential surface contamination has to be taken into account. As a first approach, the mean residence time of the spring water can be estimated using environmental tracers. Mean residence time in a karst aquifer represents an average age composed of the waters of different residence times contributing of the water discharge in the spring. To constrain the residence time of the waters in the aquifer more samples have to be analysed in a longer time period in order that a sort of seasonal pattern could be observed either in the stable isotope compositions or tritium amounts of the springs. The radioactive isotope of hydrogen, tritium (^3H) has been used to estimate a sort of the mean residence time of the spring waters. Figure 7 shows the tritium time series for the seven springs investigated from December 2013 till February 2015.

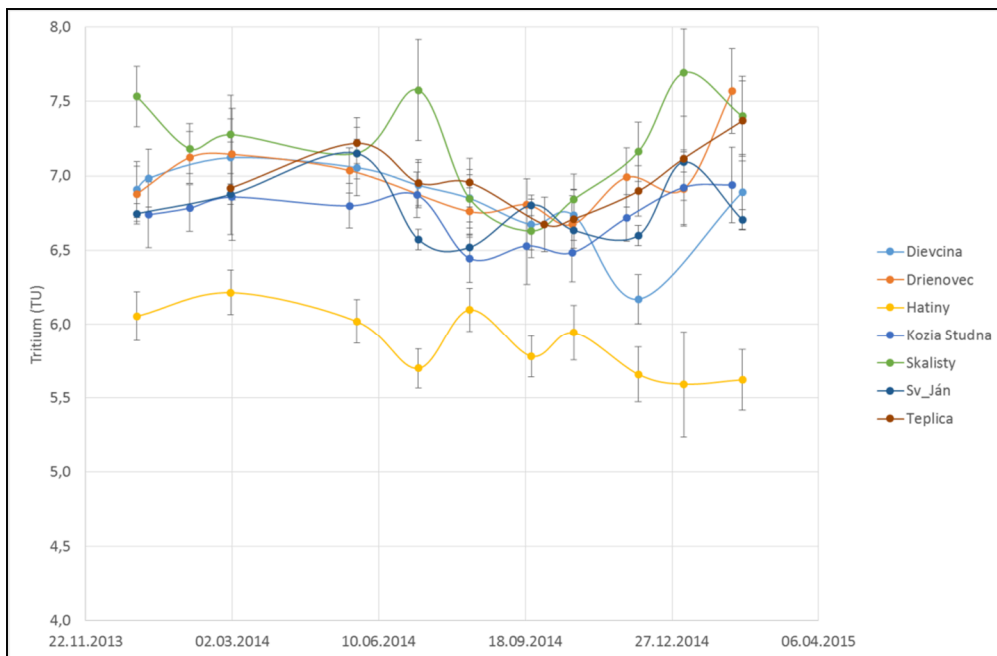


Fig. 7. Tritium concentration at different springs

Almost all the water samples, except for Hatiny, are between 6.2 and 7.7 TU, so their tritium amounts differ slightly from each other. No seasonality could be seen. However, water samples of Hatiny have always significantly lower tritium concentrations between 5.6 and 6.2 TU. A slight decreasing trend can be seen in Hatiny samples during the observation period. Similar trend can be seen in the tritium time series of springs for 2014, but samples taken at the end of 2014 and in the beginning of 2015 seem to have somewhat higher tritium concentrations.

The *stable isotope composition* of the spring waters varied between -74.9‰ to -62.1‰ and from -10.5‰ to -9.5‰ for δD and $\delta^{18}O$, respectively, during the measurement period (Fig. 9). The springs are of meteoric origin, their stable isotope composition lies above the Global Meteoric Water Line. That means higher latitude and altitude more arid areas. In Debrecen (the closest location where the stable isotope composition of local precipitation is analysed can be found here), the mean annual values for $\delta^{18}O$ and δD of precipitation are -7.6‰ and -56.3‰, respectively (Vodila et al. 2011). The delta values of oxygen and hydrogen are more negative than the annual means of the precipitation, implying a different contribution of summer/winter precipitation in the recharging water. Using stable isotopes ratios of hydrogen and oxygen in water, the seasonality patterns and recharge circumstances can be revealed. The stable isotope composition of precipitation and hence recharge water show seasonality as summer contribution has more positive delta values than winter recharge. When investigating stable isotope time series, seasonal patterns could indicate a contribution of waters with very short residence times. Figure 9 show the stable isotope ratio time series for hydrogen and oxygen for more than 14 months. The stable isotope ratios are hardly changing during the study period; hence no seasonality can be seen. This means that recent recharge has no significant contribution to the discharging karstic spring waters.

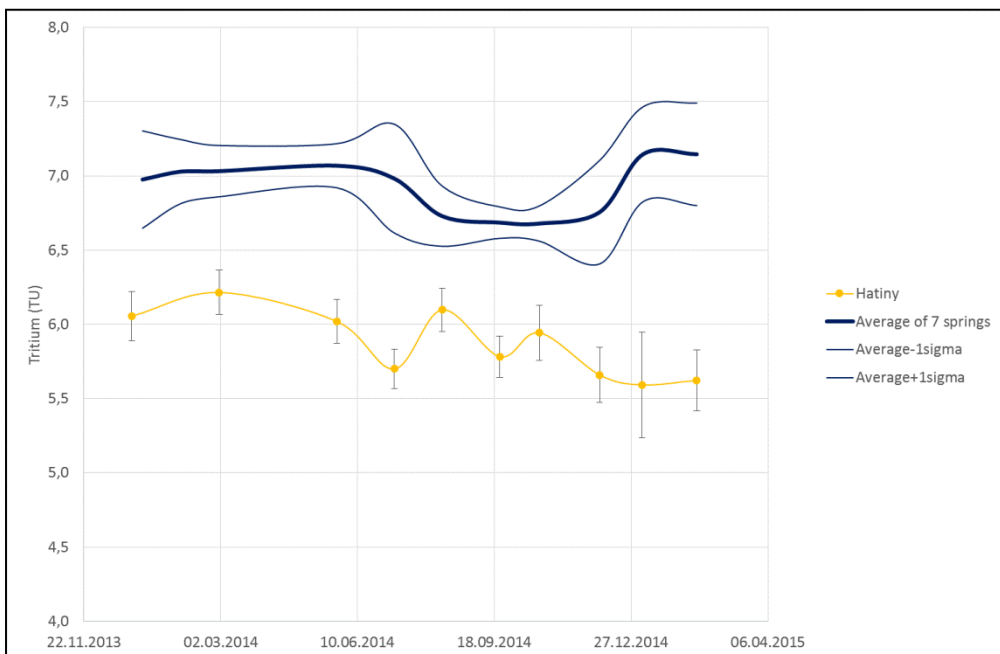


Fig. 8. Average tritium concentrations



Fig. 9. Hydrogen (left) and oxygen (right) isotope ratio time series of the spring water samples

Mean residence time – tritium. The tritium is a good tracer to estimate the time of recharge or the age distribution of discharging water. The average tritium concentrations of the precipitation in Debrecen, Eastern Hungary, and in Krakow, Southern Poland are 11.3 TU (Palcsu et al. 2013) and 10.0 TU (GNIP database, IAEA), respectively. We are aware that the isotope composition of precipitation does not reflect that of infiltrating water, because the summer contribution is smaller than that of the other seasons. It could be seen from the stable isotope composition of the spring water, as well. Hence, the recharge has slightly lower tritium concentration than the average precipitation does. Estimating tritium concentrations of recharge water between 9 and 10 TU, and using the radioactive decay law, the mean residence time is obtained to be between 4.5 and 6.5 years. As Hatiny has significantly lower tritium concentration, the mean residence time is 3 year higher (between 7.5 and 9.5 years) than that of the other springs (Fig. 8).

Conclusions

A seasonal variation of water parameters was observed during the 19 months monitoring period. Except for conductivity and Ca^{2+} the statistical analysis shows no significant relationship between different monitored parameters of water when all data is considered, nevertheless seasonal relationship was discovered between the various springs concerning the fluctuations of water temperature, electric conductivity, pH and Ca^{2+} . Seasonal differences in EC values among springs indicate changes in the position and extent of catchment areas. Clearly we can see a „relationship” between origin of some springs – Kozia studňa/Teplica, Skalístý potok/Dvojičky, Hatiny/Svätý Ján.

The main ion compositions classify Drienovecká Cave, Sv. Ján, Skalístý Potok and Kozia Studňa springs as Ca-HCO_3 -type groundwater. Except for Drienovecká Cave spring, $\log\text{pCO}_2$ values are around or slightly higher than the atmospheric level ranging from -3.4 to -3.1.

The water in springs is of meteoric origin; their stable isotope composition is consistent with the Global Meteoric Water Line. The delta values of oxygen and hydrogen suggest a more pronounced contribution of winter precipitation in the recharging water, most probably as a result of evapotranspiration during the warm season. If we estimate the tritium concentration of infiltrating water to be 9 and 10 TU, the mean residence time of springs on Jasov Plateau is obtained to be between 3 and 6.5 years. This is consistent with the observation that apart from water temperature the various monitored parameters showed no significant seasonal changes during the first year of monitoring.

In regard of mentioned results presented in this work, the most perspective for the following research will be stable isotopes and tritium monitoring (oxygen, hydrogen, let us say sulphur) and continue monitoring of the discharge, EK, temperature, pH. Also, in this area, dye tracing has not yet been done and only stable isotopes could be used for the assessment of the catchment areas. It is because our area of interest is a part of national park with very strict protecting rules. This research, in long-term perspective, is aiming to determine the ratio between snow and rain precipitations, that supply the underground streams (springs) a denudation rate of several areas.

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