

Variability in chemical composition of waters in the Zoloushka gypsum cave (Ukraine-Moldova) as a consequence of anthropogenic degradation of a karst aquifer

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The Zoloushka Cave, with passages >90 km long and a volume of ~0.65 million m³, is among the largest gypsum caves in the world. The cave was opened in the course of gypsum excavation in a quarry in the village of Criva (Moldova) located just near the border with Ukraine. During the quarry exploitation, with the accompanying pumping of water, the groundwater table was lowered to the bottom part of the gypsum layer. As a result of the pumping, the karst aquifer within the cave labyrinth was fragmented into separate underground reservoirs controlled by the morphology of the karst system and its content of clay deposits. Currently, there are several dozen lakes in the cave with a varied hydrodynamic regime (relict lakes, lakes with direct and indirect hydraulic connection with the aquifer). Research was carried out in February 2020 to determine the degree of, and reasons for, the hydrogeochemical diversity of 10 selected lakes of various hydrodynamic types present in the cave. The degree of variability of the hydrogeochemical parameters of these lakes was found to depend on a number of factors, mainly: the hydrodynamic type of the cave lake resulting from the degree of its hydraulic connection with the aquifer; the geochemical environment of the lake; and anthropogenic influence. The autonomizing role of these factors is the modification (within individual lakes) of the hydrogeochemical context of the transit waters flowing through the cave system to the quarry.

Key words: karst aquifer degradation, gypsum karst, water geochemistry, Zoloushka Cave.

INTRODUCTION

Mining activity is a key element of anthropopression influencing groundwater, including its circulation. The quarrying of mineral resources has a great impact in this regard. When mining of mineral resources occurs below the water table it is necessary to pump out the groundwater, which severely changes its flow and chemistry.

The impact of these changes is especially apparent in aquifers located in karstic rocks, such as gypsum, limestone, dolomite,

potassium salts and other rocks that are vulnerable to dissolution. In such cases, the changes influence not only the groundwater (hydrodynamic conditions, chemistry and groundwater quality) but also the host rock environment (rock dissolution, formation of cavities, creation of sinkholes etc.).

The subject of quarry exploitation as a factor influencing groundwater, including in the karst environment, has been widely researched. Thematically varied publications describe different aspects of this topic: the influence of exploitation on engineering and construction conditions in the vicinity of quarries (e.g., Andreychouk, 1999; Yilmaz, 2001; Brunetti et al., 2013; Sadeghiamirshahidi and Vitton, 2019); water hazards during quarrying, including exploitation of gypsum (Banzato et al., 2010; Caselle et al., 2020); the impact of quarry dewatering on hydrodynamic conditions and their monitoring (e.g., Darling et al., 2010; Chambers et al., 2015; Barthelemy et al., 2016; Dubois et al., 2019; Oggeri et al., 2019; Różkowski et al., 2020); activation of karst processes (Andreychouk, 2007; Sprynskyy et al., 2008); utilisation of abandoned groundwater-flooded quarries in pum-

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ped hydro energy storage systems (PHES) (Poulain et al., 2018); changes in water quality and pollution (e.g., Misra, 2013; Adabanija and Oladunjoye, 2014; Eang et al., 2018; Meena and Haritash, 2018); alterations of the hydrogeochemical environment in groundwater (Andreychouk and Klimchouk, 2001; Andreychouk, 2007; Barhoum et al., 2014); quarries and gypsum deposits as a source of water supply (Van der Gaag, 2008); and the impact of gypsum quarrying on the natural environment (e.g., Gorbunova et al., 1990; Mota Poveda et al., 2004; Pulido-Bosch et al., 2004; Margutti, 2009; Pitz et al., 2015).

The present study focuses on the hydrogeochemical effects of circulation changes in karstic aquifers caused by dewatering of the Criva (Kryva in the Ukrainian language) gypsum quarry, located in northern Moldova, near the Ukrainian border (Fig. 1). This quarry is widely featured in the scientific literature due to presence of an enormous karst system, which was discovered during mining. The system is called the Zoloushka Cave with a total length of passages reaching >90 km and a volume of ~0.65 million m³, placing it amongst the largest gypsum caves in the world (Andreychouk and Klimchouk, 2017). It is situated in

the Prut River Valley, close to the Ukrainian, Moldavian and Romanian borders (Fig. 1A). This cave formed within a ~23–26 m thick Badenian (Middle Miocene) gypsum bed (Peryt, 1996), deposited in the border area of the Volhynian-Podolian Plate and the Carpathian Foredeep.

The gypsum is underlain by Lower Badenian marls (4 m thick) and overlain by a thin (0.7–1.5 m) layer of Ratyn Limestone (Peryt and Peryt, 1994; Peryt et al., 2012) and Upper Badenian clays intercalated with sandstones and limestones, and Pleistocene sands, gravels and loesses, with a total thickness of 10–60 m.

The gypsum together with the underlying Lower Badenian marls and Cenomanian limestones (13–18 m thick) form a hydraulically connected hydrogeological fissure-karst system. In the carbonate rocks, situated underneath the gypsum, groundwater fills the fissures, while in the gypsum it resides within the karst cavities. The cavities in the gypsum attain volumes of tens of thousands m³ and, along with the slightly smaller passages, they form a vast maze-like system. The total length of surveyed passages exceeds 90 km.

The karst system described in this paper was artificially exposed during the preparation stage of gypsum exploitation in the Criva Quarry (Fig. 1B). Prior to the gypsum exploitation (late 1940s and early 1950s) both the gypsum and the cave itself were almost completely saturated with water. The Cenomanian-Badenian aquifer, located below the Prut River Valley floor and establishing the local groundwater drainage level, was characterized by confined conditions and slower groundwater circulation. The hydrogeochemical environment was reducing, with aqueous mineralisation of ~3.0–4.0 g/l and levels of dissolved hydrogen sulphide between 100–140 mg/l (Andreychouk, 2007; Fig. 2A).

In the course of gradual gypsum uncovering, quarry exploitation and associated pumping of the groundwater to the surface (at a rate of 10–25 thousands m³/day), the water table was lowered to the bottom of the gypsum bed and the majority of the cave volume was dewatered (Fig. 2B). This allowed speleologists to physically enter the cave in 1977 which resulted in its mapping and the conducting of research studies and observations. Approximately 3–5 m of unexploited gypsum floor remained saturated with water.

During the groundwater table drop and formation of the cone of depression, a formerly continuous karst aquifer, part of the cave labyrinth, started to split into individual aquifers controlled by the morphology of the karst system. As the water table was lowered, the aquifers shrank and more isolated mini-aquifers have formed. In the 1960s degradation of the aquifer led to the formation of dozens of lakes, located in the lowermost part of the cave.

After reaching stabilisation of the water table and maintaining it at a depth allowing gypsum quarrying at two production levels, set in the bottom of the gypsum bed, the hydrodynamic situation in the cave has stabilised. The passages, formed in the upper parts of the gypsum, have been completely dewatered with small lakes remaining in the passage depressions and in the lowermost areas.

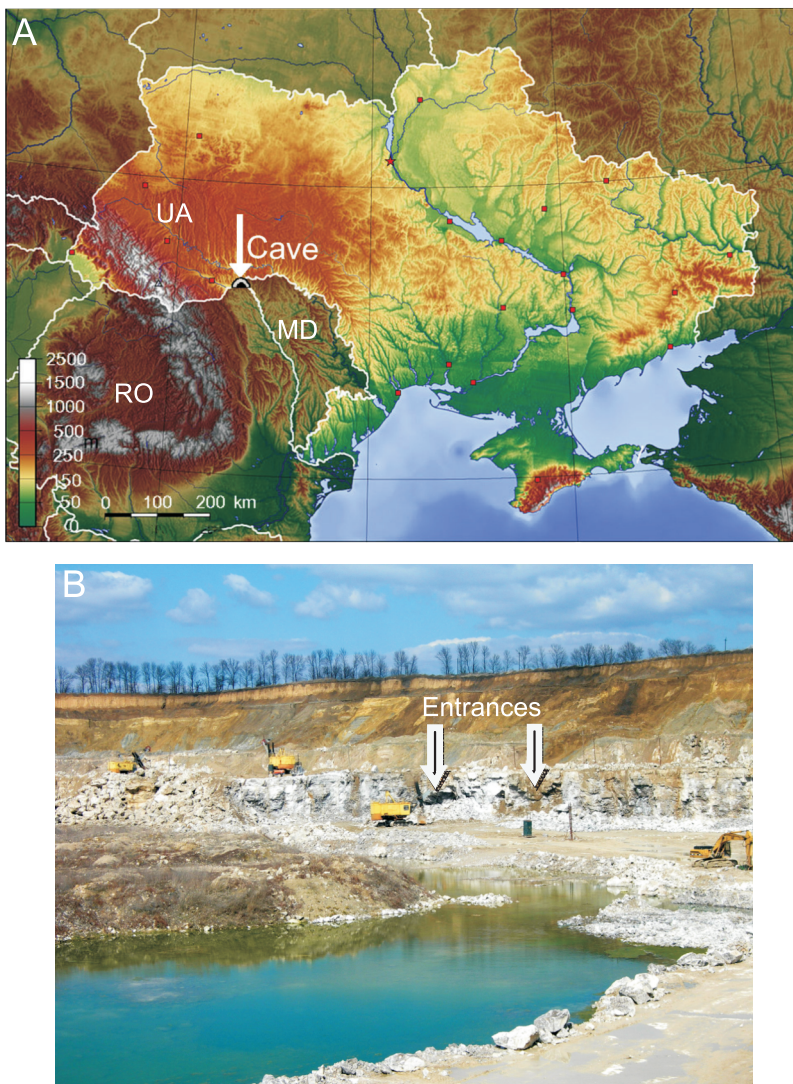


Fig. 1A – Zoloushka Cave location on the map of Ukraine; B – Criva gypsum quarry with “fresh” entrances to the cave system

Photo by V. Andreychouk

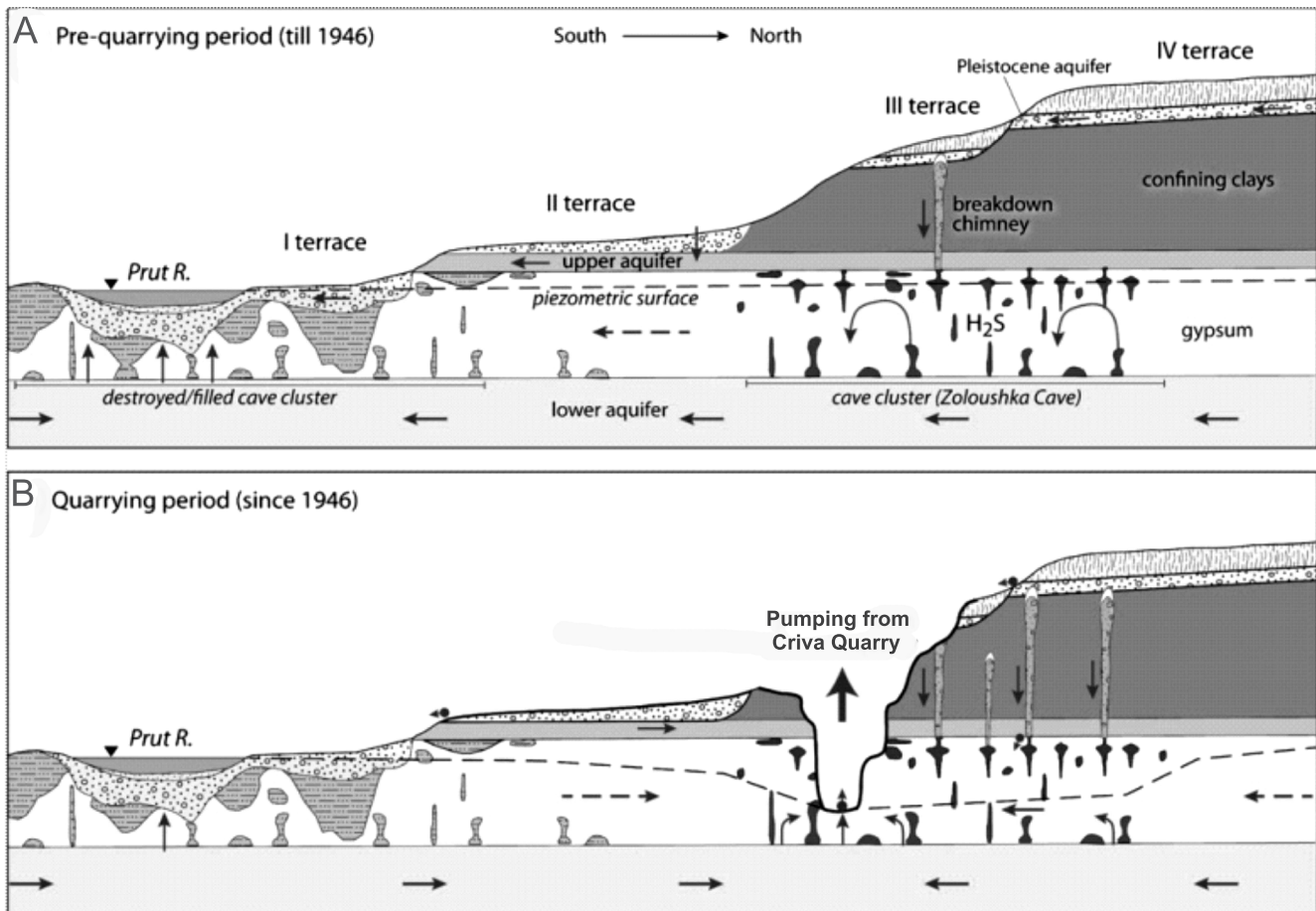


Fig. 2. Hydrogeological conditions in the Zoloushka Cave area in the pre-quarrying period (A) and their changes due to quarrying (B)

Arrows indicate direction of groundwater flow, dotted-line arrows show sluggish forced flow, curved arrows indicate natural convection (Andreychouk and Klimchouk, 2017)

In the first few years of cave exploration, speleologists already noticed variation in water levels in lakes located in different parts of the cave labyrinth, an observation supported by subsequent measurements. The differences in water elevation could be as high as several metres, although they usually ranged between a few and tens of centimetres. The cause of this phenomenon was sedimentation of clay material at the bottom of the passages, the clay originating from the overburden and being redeposited in the cave as a result of cave-in processes (Andreychouk, 2007). This led to storing of water, during degradation of the aquifer, in the morphologically conductive sections: in the upper parts. As a result, “hanging” lakes (i.e. situated above the water table level) were formed. Over time most of these lakes have gradually shrunk, with only a few surviving (in morphological traps) to this day. The preservation of water in these lakes is facilitated by 100% humidity levels prevailing within the cave, which limits evaporation. They represent a distinct (relic) type of among the aquifers studied.

A more prevalent hydrodynamic type is represented by cave lakes hydraulically connected with the current karst aquifer. Amongst these are lakes linked directly through hydrogeological windows or indirectly through a sedimentary layer of

varying permeability. In the first type the lake’s water table reacts immediately to the aquifer’s water table fluctuations, in the second type there is a delay, dependent on the level of hydraulic connection to the aquifer.

Occasionally “ephemeral” lakes can be formed within the cave, which are linked to groundwater table fluctuations of significant amplitude and these disappear quickly as the groundwater table drops. In the course of our research these were not encountered. Small lakes fed by infiltration water inflow from the overburden emerge in places of sudden cave-ins. They are extremely rare and water lingers in them only for a couple of days.

This research focuses exclusively on the permanent lakes currently present in the cave: hanging lakes (type 1), lakes well-connected to the aquifer (type 2) and lakes with poor connection to the aquifer (type 3; Appendix 1*).

The goals of this study were:

1. Determining the degree of hydrogeochemical diversity in various hydrodynamic lake types present in the cave.
2. Explaining the reasons for the hydrogeochemical diversity through analysis of the factors influencing the chemical composition of the lake waters.

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1610

METHODOLOGY

In February 2020, 10 water samples were collected from the cave (Fig. 3), with simultaneous measurement of water temperature, pH and air temperature. The waters' chemical composition was determined at the laboratory. The data acquired was subsequently analysed using statistical methods and modelling. When selecting the number of samples and place of its collection, the following rules were taken into consideration:

1. The sample number should be large enough to adequately represent the cave. The samples collected represent >60% of the lakes present in the cave during the winter season. Contrasts observable in the chemical composition during winter are important methodologically, because they allow for more precise investigation of the factors influencing the chemical composition of the lake waters. During the summer season, water levels rise and the number of lakes can increase. This can reduce the variability in the chemical composition due to lake mixing and dilution caused by water inflow from the aquifer.

2. Sample collection sites should be evenly distributed throughout the cave to adequately characterize the research subject. This condition has been met. However, ideal uniformity was not achieved as the layout of lakes is determined by the cave morphology.

3. The cave lakes sampled should represent the entire spectrum of conditions shaping their hydrogeochemical composition. Thus, the samples were collected from lakes with different hydrodynamic conditions, as noted above.

All of the samples were filtered through a standard membrane filter (pore size 0.45 μm). Filtered samples were placed into two polyethylene containers. Samples for cation analysis were acidified with nitric acid down to pH <2.

In the course of fieldwork, cave air CO₂ values were estimated. The Zoloushka Cave exhibits high concentrations of this gas, reaching 5%, a result of poor air circulation in the cave, which has only one entrance (Andreychouk, 2007; Andreychouk et al., 2011). CO₂ concentration increases farther into the cave and fluctuates between 0.1–0.5% in the section near the cave opening, up to 2.0% in the central section and 4–5% in the deepest section. Measurements were conducted due to the possibility of CO₂ having an influence on the lake water chemistry, especially on the HCO₃ concentrations.

Samples collected in cave conditions were simultaneously tested for pH and temperature. Water was placed in plastic 0.2 l containers and transported and stored at low temperatures (2–7°C) until analysis (3 days after sample collection).

The chemical composition of the water, including macro- and microelements, was determined by two *Perkin Elmer* spectrometers located at the certified Hydrogeochemical Laboratory at the University of Science and Technology in Kraków; *Elan 6100 ICP-MS* (Inductively Coupled Plasma – Mass Spectrometer), *Plasma 40 ICP-OES* (Inductively Coupled Plasma – Optical Emission Spectrometer). The sulphur concentration was converted into the SO₄ concentration. The concentrations of HCO₃ and Cl were determined by titration.

The data obtained were statistically analysed by calculating the deviation of individual values from the mean value and the

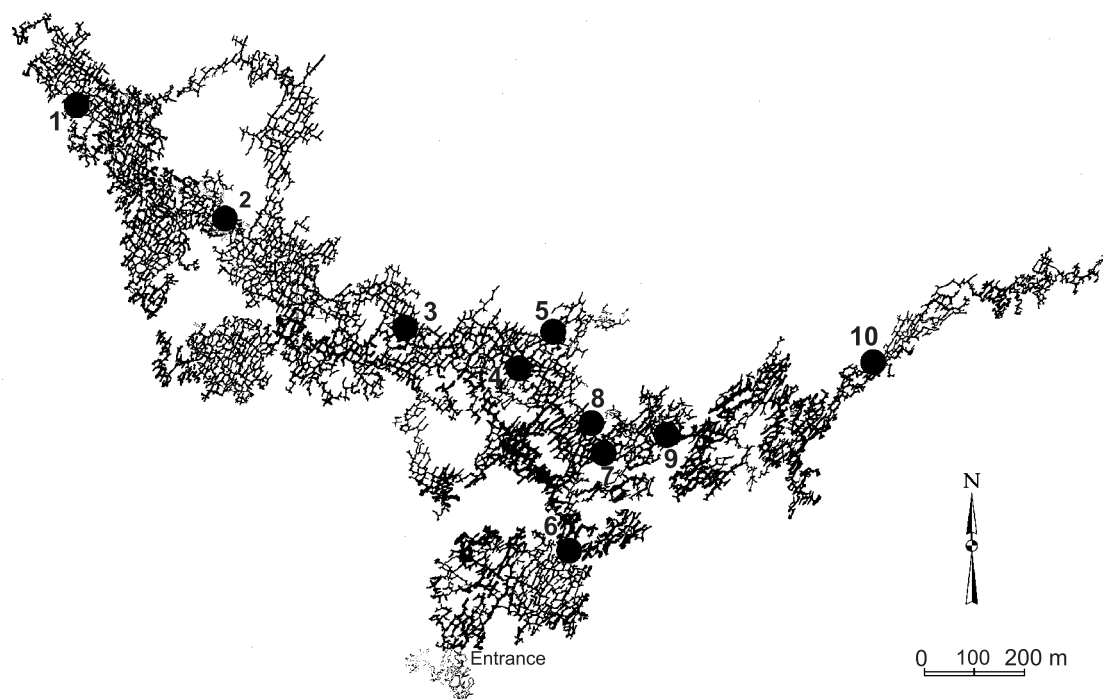


Fig. 3. A plan of Zoloushka Cave with sampling sites (underground lakes): 1 – Bukovina, 2 – Basements, 3 – Spelunca, 4 – Siphon, 5 – Venice, 6 – Filipcovo, 7 – Fragment, 8 – Green Labyrinth, 9 – Crocodile, 10 – Four

standard deviation. This allowed for comparison of water chemical composition, its character and range of variation.

Geochemical modelling was applied to estimate the distribution of speciation and saturation index values of the lake waters studied, as well as the factors that affect them. *PHREEQC* software, version 3.1.7.9213 was used for modelling. Calculations were performed using the *wateq4f.dat* database (several reactions were rewritten to better suit the environment studied). The saturation index (SI) towards a particular phase was calculated to evaluate mineral and gas equilibrium in aqueous solution. The SI was calculated according to the following formula:

$$SI = IAP/KT$$

where: IAP is the ion activity product of the dissociated chemical species in solution, KT is the equilibrium solubility product for the chemical involved at the same temperature. If $SI = 0 \pm 5\% \log k$ then phase/solution equilibrium is assumed (with the margin of error taken in account).

As a result of these calculations, the phase speciation and saturation index of the aqueous solution towards selected mineral phases were estimated. The system described can be classified as a hydrogeochemical reactor. The main factors controlling water chemical composition in this reactor were as follows: reactions of mineral dissolution/precipitation, ion exchange, presence of gas phases, redox processes and effects of changes in temperature.

In accordance with the water cycle recognized within the cave, it was assumed that water samples collected from the near-surface layer (0–20 cm) of the cave lakes and the cave air were in a state close to equilibrium. To test this hypothesis, carbon dioxide and oxygen concentrations were measured in the cave air. In the outermost parts of the cave (Fig. 3, site 6) the CO₂ content is ~1.0%, while in the innermost sampled points (sites 1 and 2) it reaches 4.0–5.0%. The oxygen content equals 20% and 14.5% at the sites number 1 and 2 respectively. The thesis that water is in equilibrium with oxygen and carbon dioxide present in cave air is supported by the fact that after water equilibration, the pH value increased by a maximum of 0.1 units.

RESULTS

After examining the hydrodynamic situation of the lakes studied, it was concluded that the only lake belonging to the hanging ("relic") group is the Green Labyrinth Lake (Appendix 1, site number 8; Fig. 3). The remaining lakes show hydraulic connection to the aquifer, which is documented by seasonal fluctuations of the water table. In the case of the Siphon, Spelunca and Basements lakes this linkage is almost direct, while in the other lakes it is indirect (delayed water table reaction and asynchronous fluctuations).

The hydrogeochemical results and the statistical analysis of groundwater chemical composition are shown in Appendix 1. The air temperature in the cave is stable and ranges between 11.0–11.2°C. The seasonal temperature fluctuations occur only in the section near the cave opening. The temperature of the cave water is equally constant, oscillating in the range of 10.9–11.2°C (within measurement error). All of the sampled waters are slightly basic; the pH value ranges from 7.48 (Spelunca Lake) to 7.93 (Bukovina Lake). The average value for 10 lakes amounts to 7.65 with a standard deviation of 0.17. The deviation of individual values from the mean value ranges

between –2.2 and +3.66%. The Eh value falls within a range of 231–243 mV, documenting the transitional and oxidising character of the environment. The cave waters exhibit high total hardness (1320–1740 mg CaCO₃/l with a mean value of 1572.5 mg CaCO₃/l), with non-carbonate hardness prevailing (20.88–28.0 mval/l).

The waters studied are rich in dissolved components. Their TDS (total dissolved solids) level fluctuates from 2174 (Siphon Lake) up to 2985 mg/l (Crocodile Lake) with an average value of 2646 mg/l and a standard deviation of 247 mg/l. The range of deviation of individual values from the mean value spans between –17.9 and +12.8%. The amount of metasilicic acid (H₂SiO₃) in the waters oscillates between 14.43 (Siphon Lake) and 24.70 mg/l (Venice Lake), averaging 18.63 mg/l. The waters investigated can be predominantly categorized as SO₄-Ca type and secondarily as SO₄-Ca-Na type (Venice, Green Labyrinth and Crocodile lakes) according to the hydrochemical classification of Shchukarev-Priklonskiy.

The concentrations of major ions in the water fall within the following ranges (value range; mean value; standard deviation; respectively): SO₄ (1685.5–1239.6; 1439.0; 136.2), HCO₃ (473.0–273.0; 401.4; 65.1), Cl (78.0–14.0; 37.3; 22.6), NO₃ (41.0–0.60; 9.5; 12.2), Ca (592.0–466.30; 543.0; 40.8), Na (64.08–210.30; 122.92; 59.2), Mg (70.82–38.06; 51.80; 9.3), K (15.73–7.87; 11.62; 2.7) (mg/l). High concentrations of SO₄, HCO₃ and Ca ions are typical of karst waters shaped by the sulphate rock environment. There are exceptionally high Mg and Na concentrations and significant fluctuations of the latter.

The concentrations of microelements in the water fluctuate, usually across wide ranges: Sr (7.070–9.600; 8.431; 0.7); Li (0.074–0.163; 0.114; 0.0351); Ba (0.009–0.025; 0.018; 0.0054); Mn (0.001–0.005; 0.003; 0.0012); Cu (0.0008–0.0080; 0.0019; 0.0021); Ni (0.0012–0.0070; 0.0046; 0.00098); Co (0.0010–0.0013; 0.0012; 0.00013); Cr (0.0009–0.0039; 0.0019; 0.0010); Mo (0.0018–0.0064; 0.0035; 0.0015) (mg/l). Among the cations, exclusively in the Bukovina Lake (site 1), the presence of Fe²⁺ (0.009, <0.005 mg/l in others) and Ag (0.0004, <0.0004 mg/l in others) was observed. In the Bukovina (site 1) and Basements (site 2) lakes Zn (0.043 and 0.042 respectively <0.002 mg/l in others) and Cd (0.0008 and 0.0107 respectively, <0.00003 mg/l in others) were detected. The analytical errors for each microelement measured were as follows: Sr – 0.116, Li – 0.022, Ba – 0.001, Mn – 0.0008, Cu – 0.0001, Ni – 0.0001, Co – 0.0001, Cr – 0.0001, Mo – 0.0001 (mg/l). In the Bukovina Lake (site 1), analytical errors for Fe²⁺ was 0.002 and in the Bukovina (site 1) and Basements (site 2) lakes, analytical error for Zn was 0.002 and for Cd was 0.00001 (mg/l). In the cave waters studied the following elements did not exceed detection limits: Al – <0.005, As – <0.00002, Be – <0.00006, Hg – <0.0002, Pb – <0.00002, Sb – <0.0002, Se – <0.01, Ti – <0.00002, W – <0.002 and Zr – <0.0001 (mg/l). Among the anions that fell below the detection limit are: Br – <0.20, I – <0.20, PO₄ – <0.05, CO₃ – <0.5 and NO₂ – <0.020 (mg/l).

The most prevalent forms of dissolved compounds in the groundwaters are simple ionic forms. Ca²⁺ and Mg²⁺ ions account for ~69.5–71.3% of all forms of dissolved compounds; with Na⁺ and K⁺ exceeding 97.4%, and together with Li⁺ summing to 97.8%. Due to the high percentage of these main species, there is no clear tendency towards fluctuation of form concentrations in relation to the location of the sampling points. However, in the part of the cave closest to the quarry, their involvement slightly increases – e.g. Ca²⁺ to 71.2% (Appendix 2). Lower concentrations of simple ionic forms were recorded for strontium (70.5–71.7%) and barium (46.3–47.7%).

The percentage variability of forms is insignificant, but a slight correlation can be observed between divalent forms and

aquifers with definite hydrogeochemical stagnation (types 1 and 2). The sulphate forms – CaSO_4 , MgSO_4 – which occur in the 29.1–30.6% range are most prevalent in the suspended Green Labyrinth Lake. Lakes 5 and 9 (Venice and Crocodile) are characterised by an increased amount of HCO_3^- (>83%) when compared to the peripheral parts of the cave (e.g., site number 1 – 68.9%).

Sulphate forms of sodium and potassium show patterns of change similar to those of calcium and magnesium. Still, the trend of KSO_4 (2.3–2.7%) exceeding that of NaSO_4 (2.0–2.5%) persists. A similar tendency can be observed in other gypsum caves (Jóźwiak et al., 2007; Solovey and Jóźwiak, 2008; Rózkowski et al., 2011).

Bicarbonate forms of calcium and magnesium oscillate in the ranges of 3.1–4.1% (CaHCO_3^+) and 0.5–0.9 (MgHCO_3^+). Silica occurs in form of orthosilicic acid, which in basic waters dissociates into small amounts of the H_3SiO_4^- ion.

In general the following trends are observable in relation to hydrogeochemical variability of the cave waters:

- Domination of simple ionic forms (except for Ba, occurring primarily as BaSO_4 – constituting 50.4–55.7% of all Ba forms in the waters);
- Relatively constant percentage of the sulphate forms (CaSO_4 , MgSO_4);
- Correlation between acidic carbonates and the presence of CO_2 and O_2 in the cave air. As the O_2 level in the cave air increases so does the concentration of calcium bicarbonates and acidic carbonates;
- Increase of HCO_3^- ion share in relation to CO_2 (aq).

The saturation index values acquired for the main rock-forming minerals building the gypsum massif indicate little ability for further dissolution of the rock framework by the lake waters studied (Appendix 3). In all of the sampled sites the gypsum SI values are relatively high ($-0.14 \div -0.03$), which points to a state of equilibrium. Equilibrium (or a state close to it) is also displayed in baryte, celestine and partly in dolomite. Supersaturation with tendency towards precipitation from solution is typical for the following minerals: calcite (in certain lakes), iron hydroxides, goethite, manganite and quartz. The cave waters exhibit varying degrees of hydrochemical aggressiveness towards brucite, jarosite, siderite, silica and strontianite. In the case of six lakes the concentrations of calcite (CaCO_3) indicate equilibrium in aqueous solution, while in the remaining four lakes, supersaturation with a tendency towards precipitation prevails. A similar trend was observed by Jóźwiak et al. (2012) in the groundwater flow systems within the gypsum of Deshat Korabi Massif (Albania/North Macedonia).

DISCUSSION

The values of the lakes' hydrogeochemical parameters listed in the tables show general patterns concerning all of the samples and also highlight their diversity.

All of the samples are characterized by high TDS (2174–2985 with a mean value of 2646 mg/l and slight deviation between 12–18%) and high hardness. The chemical composi-

tions of the cave waters studied were shaped in similar conditions and the high concentrations of dissolved substances result from the high solubility of the sulphate rocks – in this case chemically pure gypsum (96–98%; Andreychouk, 2007)¹. The high concentration of the sulphate ion (1234–1686 with a mean value of 1439.0 mg/l) is a consequence of the chemical composition of the karstified rock ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The increased, in most cases, HCO_3^- content is a result of the water's chemical composition being influenced by the carbonate host rocks, which are hydraulically connected to the aquifer in the gypsum, and also by the high CO_2 content in the cave air leading to higher carbonate solution capacity. A significant amount of Sr in the chemical composition of the gypsum is reflected in its higher levels in the cave waters (7.1–9.6; with mean value of 8.4 mg/l). The cave-forming gypsum deposits contain 10 times more Sr than the clay-carbonate overburden deposits (Andreychouk, 2007). These common characteristics can be explained by lithological control, meaning the chemical composition of rock environment in which the waters circulate.

In comparison to areas with active groundwater flow, the lakes studied have relatively high concentrations of Mg, Ba, Cl, BO_3 and partially Na (Appendix 1). It is apparent that the groundwater circulation within the cave block and its surroundings is slower. This is caused by gypsum being present below the valley floor drained by the Prut River (Andreychouk, 2007; Andreychouk et al., 2009). As a result, the karst environment is being enriched in the ingredients analysed. A large range of concentrations of Na (64.08–210.30 with a mean value of 122.92 mg/l) and Cl (14.0–78.0 with a mean value of 37.3 mg/l) ions can stem from high NaCl solubility and pollution of some lakes due to speleological activity in the cave (see below).

The hydrogeochemical diversity in the lake population studied correlates with the hydrodynamic situation (see above). The Green Labyrinth hanging lake (type 1) which is disconnected from the current water table, visibly stands out with its high water mineralisation (2979 mg/l), highest SO_4 and BO_3 contents in the water and increased levels of Na, K, Mg, Li, Mo and Sr. Elevated concentrations of these constituents may result from the "residual" character of the lake, prolonging the dissolution period of the surrounding gypsum as well as leaching the clay deposits lining its floor. The accumulation of Fe and Mn hydroxides at its bottom and seasonal emergence of a thin film on the water surface implies a near to saturation state in relation to these solutes. In particular we can observe the oversaturation of lake water with dissolved Fe and Mn compounds (Appendix 3; Fig. 4).

A high TDS content (2602–2985 mg/l), hardness (1415–1739 mg CaCO_3 /l) and elevated concentrations of SO_4 (1336–1635 mg/l) and HCO_3^- (414–453 mg/l) is shown by lakes with poor water circulation (type 3) e.g. Bukovina, Venice, Filipcovo, Fragment, Crocodile and Four lakes (Appendix 1). In contrast, in the lakes with better connection to the groundwater aquifer (type 2) and faster water circulation (Basements, Spelunca and Siphon) we can observe lower, resulting from dilution, TDS content (2171–2513 mg/l), hardness (1320–1576 mg CaCO_3 /l) and concentrations of SO_4 (1240–1351 mg/l) and HCO_3^- (273–421 mg/l).

¹ The main impurities are: CaCO_3 – 0.3–1.0%; SiO_2 – 0.1–0.8%; Fe_2O_3 – 0.02–0.09%; MgO – 0–0.5%; SO_3 ; Na_2O . The following are also present: low-magnesian calcite, brucite, quartz, celestine, organic impurities and clay minerals: montmorillonite, kaolinite. The presence of anhydrite was not identified. Other impurities found include: Fe, Mn and Al oxides and hydroxides, amorphous and cryptocrystalline forms of silica.

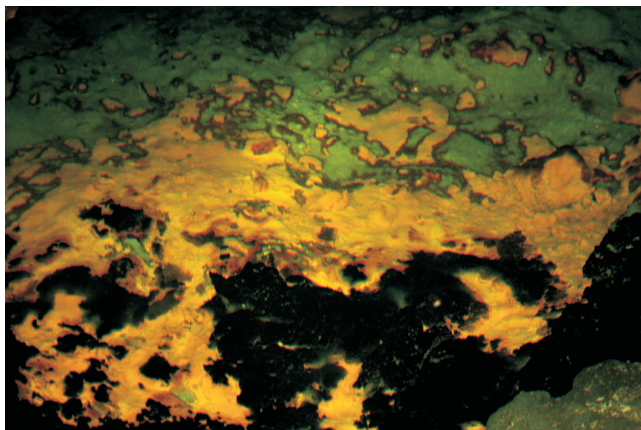


Fig. 4. Bottom of the hanging Green Labyrinth Lake (Colourful)

The name of the cave was derived from its emerald green water and deposited (earlier – under reducing and transition conditions) iron and manganese hydroxides, lining the lake floor with green (Fe^{2+}), orange (Fe^{3+}) and black (Mn^{2+} , Mn^{4+}) sediments (Photo by V. Andreychouk)

Hydrodynamic control of some hydrogeochemical parameters is also demonstrated in the SI analysis — index of water saturation with certain compounds (Appendix 3). Table (Appendix 4) illustrates that lakes characterised by poor water circulation (type 3) (see: Appendix 1) such as Bukovina, Venice, Filipcovo, Fragment, Crocodile and Four lakes, have increased saturation index values for all compounds by comparison with lakes with relatively good circulation. The supersaturation of aqueous solution in relation to CaCO_3 occurs exclusively in these lakes.

An important role in the creation of the cave waters' geochemistry is the anthropogenic factor. Cave exploration has been going on here since 1977. Thousands of speleologists have visited the cave for almost 45 years. Speleologists from several speleological clubs in Ukraine and Moldova conduct non-stop research in the cave. Over the years, both the technical methods of exploration, the lighting systems used, and the ecological awareness of speleologists, which was not very responsible at the beginning, have changed. These circumstances caused high levels of contamination of the cave. The factor contributing to the accumulation of foreign substances (chemical and biochemical) was and is the filling of the corridor bottoms with a thick layer of cave clays with high absorption capacity (they are composed mainly of montmorillonite).

We suggest that the clear differences in nitrate concentration in the lakes of different types are caused by speleological activity (exploration). Due to the "wild" nature of the cave and its enormous size, speleologists entering the labyrinth, sometimes for a few days, are forced to urinate in the cave. Unfortunately, there are no designated and adapted (for these purposes) places in the cave. Nitrogen compounds reach the lakes directly or enter them during water level fluctuations and flooding of places polluted with nitrates. For this reason, the nitrate contents are chaotic and do not show patterns which could be related to the natural factors which control the chemistry of the cave water.

Apart from hydrodynamic and anthropogenic factors, the variation in the cave lake waters' chemical composition can be also influenced by:

1. Lithological lake environment;
2. CO_2 concentrations in the cave air at the lake locations.

The role of the first factor is related to lakes being in diverse environmental settings. Both the bottom and walls of the lakes can be either made of gypsum or clayey deposits covering the passage floors. The total contact surface of the lake waters with gypsum rock or clayey deposit can have important implications. In the case of increased contact with gypsum the pH, TDS, hardness and concentrations of SO_4 and Ca can be significantly elevated. Cave clays exhibit substantial lithological, mineralogical and geochemical diversity, originating from various sedimentary types overriding the gypsum: carbonate, clayey sandstone and also soil material. Thus, the higher concentrations of certain microelements (Li, Cu, Ni, Co, Cr, Mo, Mn) in selected lakes can be a result of their extraction (leaching) from predominantly clayey surroundings.

However, the comparative analysis of their concentrations in the lake waters (Appendix 1) suggests that the lithological surroundings factor has practically no influence on the amount of microelements in the water. In the lakes studied, increased levels of the following components were identified: Basements (Ni, Co, Cr, Mo), Filipcovo (Ni, Co, Cr, Cu), Bukovina (Li, Cr, Co), Spelunca (Ni, Co), Green Labyrinth (Colorful) (Li, Mo), Venice (Li), Siphon (Ni), Fragment (Mn), Four (Mn) and Crocodile (Li). The contact surface (with gypsums/clays) varies greatly between these individual lakes. Therefore it may be concluded that the microelements analysed were introduced to the groundwater at elevated levels before infiltrating the caves and coming into contact with the clay deposits. This might indicate the influence of an additional transit factor, i.e. that the elements analysed were at similar or closely concentrations in the waters before their arrival into the lakes.

The role of CO_2 concentrations in cave air as a factor controlling levels of certain components (mainly carbonates) should not be unequivocally assessed on the basis of this research. On the one hand, high concentrations of CO_2 in the air and cave water must have a stimulating impact on the dissolved carbonate levels in water, such as CaHCO_3^+ and MgHCO_3^+ . This means that this factor, regardless of carbonate concentrations in individual cave waters, participates in shaping their "carbonate chemistry". However, its influence cannot be quantified because the level of connection between the lakes and the aquifer can have a greater impact on this matter². Thus, comparison of HCO_3^- levels in lake water with the CO_2 concentrations in air shows no significant correlation. The impact of this factor is restricted by the influence of other factors.

In order to clarify or to better understand the role and importance of different factors we conducted statistical research (factor analysis) on the chemical composition data from the lake waters in order to establish the similarity between individual lakes and link them to potential factors. The results of this analysis are shown in graphical form on Figure 5.

It can be seen from Figure 5A that the factors that distinguish lakes 1, 2, 3 and 6 from the others are mainly NO_3^- and Cl^- , while the remaining lakes are mainly grouped by the Na^+ factor. Using the chart, it can be concluded that the subgroups created,

² This matter could be a subject of further study. Unfortunately, the methodology of this research does not allow for appropriate assessment of this factor.

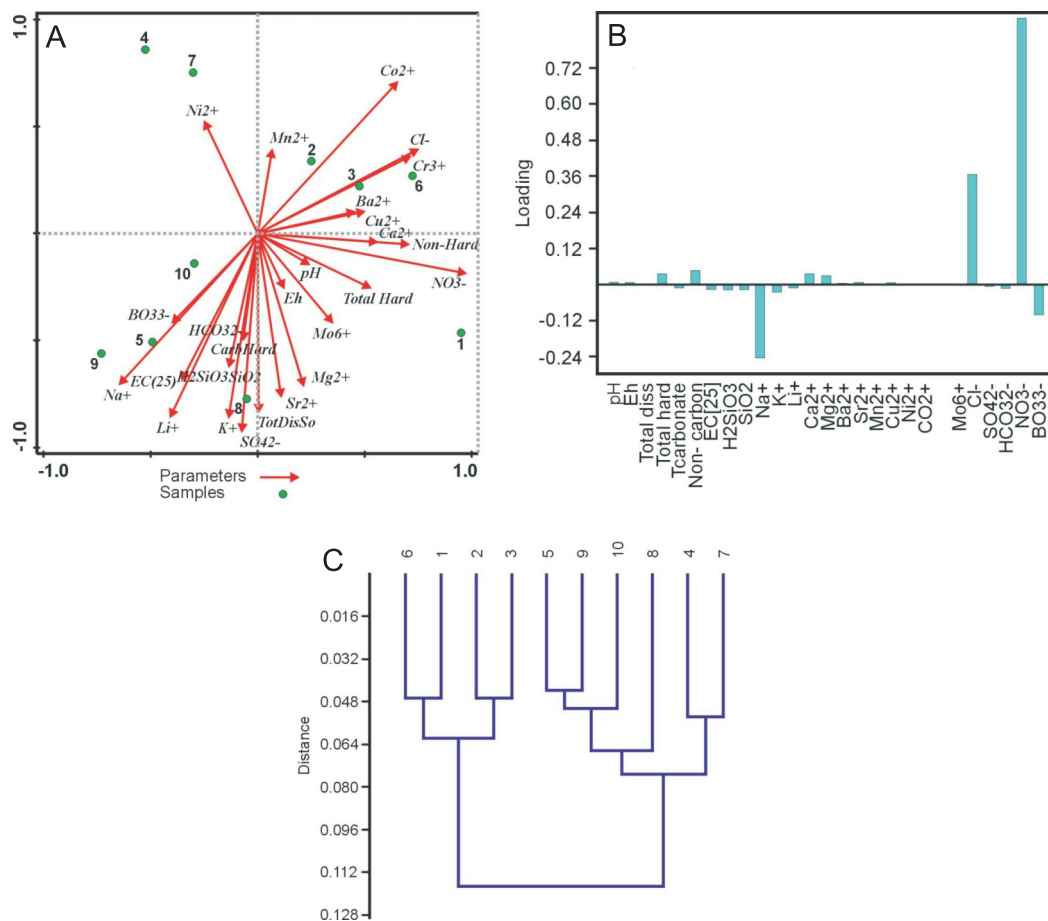


Fig. 5. Graphical results of factor analysis of chemical composition data from Zoloushka Cave lakes

A – biplot showing scattering of the elements analysed due to the factors distinguished, **B** – graph showing the variable environmental loads to PCA, **C** – dendrogram that shows a cluster analysis

due to the positive and negative values of these factors, are: lakes 4 and 7; lakes 5, 8, 9 and 10; lakes 2 and 3; and lake 1. Lakes 1, 2, 3 and 6 can be treated as showing similarities, as can the other six lakes.

On Figure 5B it can also be clearly seen that the dominant grouping factors here are again NO_3^- , Cl^- and Na^+ .

As for graph Figure 5C, the distance shown is calculated using the nearest neighbour method. Assuming the distance between clusters as the grouping criterion, not greater than $d = 0.07$, the set of lakes can be divided into three groups: A = {1, 2, 3, 6}, B = {5, 8, 9, 10}, and C = {4, 7}. Objects from group A are characterized by a high content of NO_3^- and then Cl^- . Objects from group B by Na^+ content, while objects from group C by Ni^{2+} content.

Figure 5 shows that the most important factors grouping lake water samples are NO_3^- , Na^+ and Cl^- . The 1st group (lakes 1–3 and 6, group A) is characterized with relatively high concentrations of NO_3^- . According to previous suggestions, such kinds of compounds may be connected with human (speleological) activity in caves. These lakes are located in the western part of the cave system. During the two last decades, this part of the cave was significantly more frequently visited by cavers. This is because this part of the cave was and still remains the most promising area as far as new discoveries are concerned. Speleological exploration is currently concentrated in this western part of the cave.

CONCLUSIONS

Analysis of the data acquired during hydrogeochemical research conducted in Zoloushka Cave in February 2020, allows the following conclusions:

1. Anthropogenically induced hydrodynamic degradation of the karst aquifer in strongly karstified gypsum in the study area is accompanied by hydrogeochemical degradation triggered by progressing autonomisation of hydrogeochemical parameter values of individual underground lakes, which formed during lowering of the groundwater table.

2. The degree of diversity of hydrogeochemical parameters in lakes is considerable and depends (to varying degrees) on various factors, e.g.: hydrodynamic type of the lake, resulting from its degree of hydraulic connection/disconnection to the groundwater aquifer; geochemical lake environment, anthropogenic pollution due to speleological activity and also the composition of the cave air, particularly the CO_2 content influencing the carbonate capacity of the waters. These factors are responsible for the progressive diversity of hydrogeochemical parameter values of individual lakes. The autonomising role of these factors consists of modification (within individual lakes) of the hydrogeochemical background of the transit waters passing through the cave system and into the quarry, from where they are passed on to the river drainage system.

3. Among all of these factors the one having the most significant impact on the hydrogeochemical autonomisation of the chemical composition of the underground lake waters is the hydrodynamic factor. This is indicated by significant differences in the large number of parameters of lakes belonging to different hydrodynamic groups. The anthropogenic factor is also important, and may be responsible for some compounds entering the water as a result of caving activity. The remaining factors noted above undoubtedly contribute to shaping the water chemistry, but their role is currently difficult to determine. Their quantitative assessment requires the use of research methodology dedicated to each factor, and appropriate equipment.

4. The chemical composition of the lake waters can facilitate the determination of the level of connection between underground lakes and the aquifer. For example, lakes that are not currently associated with the aquifer clearly stand out with high water mineralisation (2979 mg/l), highest SO₄ and BO₃ content and increased levels of Na, K, Mg, Li, Mo and Sr. Thus, when examining the chemical composition of the waters of cave lakes (there are >40 in this cave) in the future, one can initially infer their hydrodynamic features.

5. The cave conditions described can be an excellent basis for hydrogeochemical research designed to determine the role of individual factors controlling groundwater chemical composition. In this respect, the cave studied is an excellent testing ground.

Thus, the research conducted refers to the part of hydrogeology that deals with explaining the influence of both natural

and anthropogenic factors on the formation of groundwater chemistry. It shows the scale (to some extent) and the qualitative nature of the transformation of groundwater geochemistry in a lithologically diverse karst environment. It also provides new information for the speleology department dealing with the circulation, hydrochemistry and quality of water within the caves.

The practical importance of the study is, however, limited because of the water pumped out from the cave (quarry) is highly mineralised and cannot be used for most purposes. Nevertheless, recognizing that groundwater pumped out of quarries exploiting karst rock formations undergoes specific geochemical transformations in a strongly karstified environment may have a certain practical significance. The composition and quality of water pumped out directly from quarries with a developed network of karst cavities may differ from the hydrogeochemical background of the drainage karst aquifer outside the quarry and cave system. This should be kept in mind when planning any use of the pumped water.

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