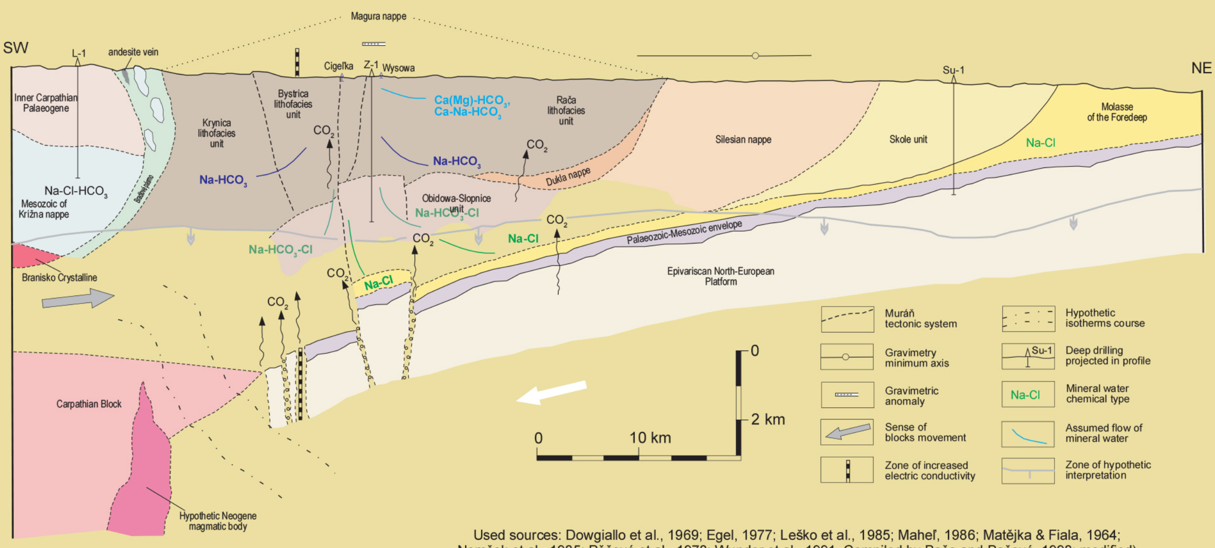
SLOVAK GEOLOGICAL MAGAZINE

VOLUME 16 NO 2 ISSN 1335-096X

MINERAL WATERS OF SLOVAKIA



Used sources: Dowgiallo et al., 1969; Egel, 1977; Leško et al., 1985; Maheľ, 1986; Matějka & Fiala, 1964; Nemčok,et al., 1985; Pěčová et al., 1978; Wunder et al., 1991. Compiled by Bačo and Bačová, 1998; modified).

State Geological Institute of Dionýz Štúr, Bratislava

2/2016

SLOVAK GEOLOGICAL MAGAZINE

Periodical journal of the State Geological Institute of Dionýz Štúr is a biyearly presenting the results of investigation and researches in wide range of topics:

- regional geology and geological maps
- lithology and stratigraphy
- petrology and mineralogy
- palaeontology
- geochemistry and isotope geology
- geophysics and deep structure
- tectonics and structural geology
- geology of raw minerals deposits
- hydrogeology and geothermal energy
- environmental geochemistry
- engineering geology and geotechnology
- geological hazards and risks
- geoinformatics
- geotourism

The journal is thematically focused in the issues of the Alpine-Carpathian region.

Bratislava, December 2016

Address of Editorial Office: State Geological Institute of Dionýz Štúr, Mlynská dolina 1, 817 04 Bratislava, Slovak Republic, IČO 31753604. The journal is indexed in the list of periodicals of the Ministry of Culture of the Slovak Republic under registration number EV 5006/14.
Printed at State Geological Institute of Dionýz Štúr Bratislava, Slovak Republic.
Online: www.geology.sk/new/sk/sgm

ISSN 1335-096X

SLOVAK GEOLOGICAL MAGAZINE

VOLUME 16 NO 2 ISSN 1335-096X

MINERAL WATERS OF SLOVAKIA

State Geological Institute of Dionýz Štúr Bratislava

2/2016

Edited by:

RNDr. Dušan Bodiš, CSc.

Reviewers:

Assoc. Prof. Mgr. Renáta Fľaková, PhD.

Dr. Hab. Ing. Józef Chowaniec, Prof. Nadzw. PIG-PIB

Prof. Ing. Jozef Kriš, PhD.

RNDr. Peter Malík, CSc.

MUDr. Janka Zálešáková

Prof. RNDr. Zlatica Ženišová, PhD.

ISSN 1335-096X

Preface

"*Why the waters have different taste and flavour?*

Since the taste and flavour are the secondary qualities, originating from blending of four elements, it is certain, that neither water nor any other element, while it is in its original condition, cannot have the same characteristics. Therefore, they must come from elsewhere.

The waters get their taste in the way, that mixed with some earth, they take from it something by temperature, or they flow through soil owning any distinct flavour, or stone, metal or thicken juice. In this way those that pass through alum deposit, become bitter, those that flow through soda, are acidic, again those which pass through the iron ore, are ferrous, etc. In the same way smell of water is created. When water is flowing through a stinking soil, or they receiving exhalations or some fragrant juice, or they contain a mixed proportion of soil and mixed something like this they take over by underground fires, or they rot enclosed in the hollow places".

Szentivány Martin (1689): On wondrous power and properties of water. From the Latin original *Curiosiora et selectiora variarum scientiarum miscellanea in tres partes divisa* translated by Augustín Rebro (1981).

Martin Szentiványi (born at Szentiván (Liptovský Ján), 20 October 1633; died at Nagyszombat (Trnava), 5 March 1708) was a polymathic Hungarian or Slovak.

This excerpt from the work of M. Szentivány suggests that people in the past were intensely interested in the composition and properties of mineral waters. Of course every era brings its own view on the issue, which is subject to the relevant knowledge. It can be stated that even today in the 21st century we are still not fully familiar with the genesis and properties of mineral waters and many of them have not been even discovered yet. According to the last inventory (as of 2016) there are 1,782 sources of mineral waters in Slovakia.

This SGM issue represents an effort to create a picture of the mineral waters of Slovakia from the regional perspective, through the characterisation of isotopic and chemical composition, legislation and local studies of the evaluated spa sites and mineral water sources.

Due to the existing technical information, which has high scientific value even at international level, we hope that have managed to offer by this issue a step forward and shift the knowledge about the mineral waters Slovakia a bit higher, or to look at things from a different angle of view. That little piece of value added are the regional characteristics of mineral water according to the rock environ and its properties; and, in addition, a complete summary of the isotopic composition of mineral waters. For the professional geological journal is somewhat unusual a legislative view of the mineral waters, but it is vital in terms of their use and protection. Many countries do not adopt this system and spa resorts tend to focus on wellness and entertainment instead of utilization of this natural heritage for health care. Novelty is also an attempt to score the Sliač Spa using the method of Rapid Impact Assessment Matrix. In case of a positive response this could be used for the evaluation of other spa resort.

Slovak Spa school has a rich tradition and excellence, which are based on the use of natural medicinal resources. Taking care of the natural environment is a team concern and we have no doubts that the geological community has relevantly contributed to discovering new sources, as well as to their use and protection.

Dušan Bodiš

LIST OF ACRONYMS

BE	Biological-Ecological Components
CDT	Canyon Diablo Troilite
CIS	Central Information System
DIC	Dissolved Inorganic Carbon
EIA	Environmental Impact Assessment
EO	Economic-Operation Components
EU	European Union
EC	European Community
EEC	European Economic Community
FCE SUT	Faculty of Civil Engineering, Slovak University of Technology
FMFI	Faculty of Mathematics, Physics and Informatics
GMWL	Global Meteoric Water Line
GNIP	Global Network of Isotopes in Precipitation
GNIR	Global Network of Isotopes in Rivers
GSSR	Geological Survey of the Slovak Republic
ISS MoH	Inspectorate of Spas and Springs, Ministry of Health SR
LIS	Local Information System
MoE	Ministry of Environment
MRT	Mean Residence Time
NHS	Natural Healing Source
NHW	Natural Healing Water
NHIC	National Health Information Centre
NMS	Natural Mineral Source
NMW	Natural Mineral Water
NWRL WRI	National Water Reference Laboratory of Water Research Institute
PC	Physical-Chemical Components
PDB	Pee Dee Belemnite
RIAM	Rapid Impact Assessment Matrix
S	Sustainability Score
SC	Social-Cultural Components
SEA	Strategic Environmental Assessment
SGIDŠ	Slovak Geological Institute of Dionýz Štúr
SGO	Slovak Geological Office
SMOW	Standard Mean Ocean Water
SSC	State Spa Commission
SSR	Slovak Socialist Republic
TDS	Total Dissolved Solids
ÚÚG	Central Geological Institute (*Ústřední ústav geologický*)
VES	Vertical Electrical Sounding

Regional Hydrogeological Characteristics of Mineral Water Aquifers in Slovakia

Daniel Marcin, Katarína Benková

State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Mlynská dolina 1, 817 04 Bratislava, Slovakia; daniel.marcin@geology.sk

Abstract: During inventory of mineral water sources in 1997-2000 1,687 sources were documented on the Slovak territory, 111 were not found, 297 disappeared and 30 were destroyed. Mineral water sources in Slovakia are characterized by quite a varied representation of chemical water types with a wide range of TDS, temperature and yield. The largest representation of mineral water in Slovakia is located within the Central Western Carpathians (43 %), of which account for most of the resources Inner Carpathian Palaeogene (24.1 %) and Mesozoic sediments of the Central Western Carpathians (15.2 %). The smallest number of sources accounted for metamorphic rocks (3.2 %) and magmatic rocks (1.5 %). The second most numerous sources of mineral water are from Neogene sediments (31.7 %). This structural-geological facies has the largest representation of mineral water sources that have been acquired through technical work (the number of wells far outscores the springs). The third and fourth most numerous sources of mineral water fall within Flysch Zone (13.3 %) and Neovolcanites (6.8 %). The lowest representation of mineral water falls on Klippen Belt (4.2 %). The territory of Slovakia is explored by a number of deep geological wells to verify the presence of mineral waters. Only a small part of them has set the hydraulic parameters of the aquifers. The most important aquifers from the viewpoint of formation of mineral waters in Slovakia are the Mesozoic sediments of the central zone of the Western Carpathian and the Neogene sediments, which fill up the basins. The Mesozoic aquifers (limestones and dolomites) of mineral waters have been verified by 79 hydrogeological boreholes (56 pumping tests) and the value of the geometric mean of transmissivity coefficient G(T) = 9.08 . 10^{-4} m^2 . s^{-1}. The drillings carried out in the Mesozoic carbonates are also reported for relatively large yield (Md Q = 12.4 l . s^{-1}/ Mn Q = 19.4 l . s^{-1}). Neogene sedimentary aquifers (sands, sandstones, conglomerates) of mineral waters have been verified by 58 hydrogeological boreholes (49 pumping tests) and the geometric mean value of the coefficient of transmissivity G(T) = 5.35 . 10^{-4} m^2 . s^{-1}. Drillings carried out in an environment of the Neogene sediments have achieved balanced yields (Md Q = 10.0 l . s^{-1}/ Mn Q = 10 . 5 l . s^{-1}).

Keywords: sources of mineral waters, coefficient of transmissivity, deep borehole, chemical type of water, Western Carpathians

1.1 Introduction

By 1999, 1,687 mineral water sources were registered in Slovakia. These sources are characteristic either of the content of 1,000 mg . l^{-1} of dissolved solids or dissolved gases, CO_2 included (≥ 1,000 mg . l^{-1}), H_2S (≥ 1,0 mg . l^{-1}) or they reach the ground surface temperature of more than 20 °C. The occurrence of mineral waters on the territory between the Tatras and the Danube and Tisza rivers reflects its geological and tectonic evolution. The presence of major regional aquifers of mineral waters that are affected tectonics of alpine or German types created the conditions for the formation of the mineral waters in the hydrogeological structure. In the past the ideas about the formation of mineral waters in the space of hydrogeological structures largely depended on knowledge of geological and tectonic structure, chemical composition of mineral waters and later of the isotopic composition of mineral waters. It has been the isotopic composition of mineral water that has contributed to the fact that the view of the nature of the hydrogeological structure of mineral water as such has changed from the hypothetical viewpoint to the real one. Determination of the isotopic composition of mineral waters in the hydrogeological structures provides information about the nature of the aquifer, where its chemical composition is formed over time. In some cases it is possible to determine the hydrogeological structures in which mixing of waters from multiple aquifers occurs. The knowledge of the geological and tectonic settings of the hydrogeological structure of the Western Carpathians, including the hydraulic parameters of aquifers and character of mineral water in terms of the chemical and isotopic composition, creates a closer correlation to define the conditions of formation of mineral waters. The data gained from deep boreholes in different parts of the hydrogeological structure provides valuable material that documents the evolution of monitored parameters towards the depth.

1.2 Geological and tectonic conditions of mineral waters genesis

The territory of Slovakia is situated within the Western Carpathians, which are part of the Alpine-Himalayan system with folded-Nappe structure. Formation of mineral waters takes place in the rock environment, which is liable to concentrate them, which is reflected in the quantity and quality. As the mineral waters are affiliated to the geological environment, which reflects the geological and tectonic setting of the area, we will describe these in relation to the structural-facies zone, which were earmarked by Andrusov (1958). In Slovakia there are these zones: 1. Flysch Zone, 2. Klippen Belt, 3. Central Western Carpathians, 4. Internal Neogene depressions, plains and volcanic rocks (Fig. 1.1).

The conditions favourable for the formation of mineral waters were outlined by Maheľ (1952) and supplemented by Franko (1975) as follows:

- the presence of large amounts of Mesozoic sediments, mainly the Middle and Late Triassic carbonates (limestone and dolomite) and evaporites in the Permian, Early and Late Triassic;

- Extensive Tertiary (Palaeogene and Neogene) marine and freshwater sediments, mostly pelites with aquifer layers of psephites and psammites. In the Miocene evaporites occurred;
- Tectonics of Alpine type within the Mesozoic formations created far reaching folds plunging from the mountain slopes into larger depths below the internal basins and lowlands;
- Tertiary sediments have tectonics of Alpine and German types;
- Longitudinal and transverse young faults;
- Deep faults among the blocks of the Earth's crust (CO_2);
- Young Tertiary volcanism (CO_2, favourable geothermal conditions);
- Favourable geothermal conditions (average geothermal gradient of 39 °C . km^{-1}, the average heat flow density – 82 mW . m^{-2}).

1.3 Distribution of mineral waters in structural-facies zones

Geological setting of the Western Carpathians, which build particularly the territory of Slovakia, is reflected in the abundance of mineral waters (Tab. 1.1, 1.2) and the diversity of their chemical types (Tab. 1.3). During the inventory of mineral water sources in the years 1997-2000 1,687 sources were documented in Slovakia. Of this number, there were 1,249 sources, 111 were not found, 297 disappeared and 30 were destroyed. Among the lacking sources there were 80 springs, 4 dug wells and 27 wells, of which there is no information on their destruction.

Affiliation of mineral water to the individual zones of the Western Carpathians is reflected in the frequency and variability of chemical water types.

1.3.1 Mineral waters of the Flysch Zone

The Flysch Zone is made of Cretaceous and Palaeogene alternating claystones and sandstones of marine origin. Of the total number of mineral waters in Slovakia, this share is 13.3% with five chemical types of waters (Tab. 1.3).

This zone is characterized by abundant representation of small springs of cold sulphane and carbonate, very weakly (up to 1 g . l^{-1}) and weakly mineralized water (1 – 5 g . l^{-1}) of the chemical type Ca-Mg-HCO_3, Na-HCO_3 with yield do 0.1 l . s^{-1}.

The best known are the cold strongly mineralized carbonated water with mixed mineralization from sources Cigeľka (Na-HCO_3-Cl) and Bardejov (Na-HCO_3) with yield up to 4 l . s^{-1}. In the area Bardejov – Stropkov there are important sources in Bardejov – Dlhá Lúka (Na-HCO_3-Cl), Mikulášová (Na-Cl-HCO_3) and Dubová (Na-HCO_3-Cl) with yield do 0.3 l . s^{-1}. Equally, the cold (springs, wells) and the thermal sources (well FPJ-1) of very high TDS strongly mineralized (35 – 50 g . l^{-1}) are iodine-bromine and water with thalassogenic mineralization of chemical type Na-Cl in Oravská Polhora with yield up to 1 l . s^{-1}. Structural-hydrogeological borehole FPJ-1 (Fig. 1.2) reached a depth of 2,417 m and it verified the sediments of Obidowa-Słopnice-Zboj unit in depth interval 1,298 – 2,417 m. The water temperature at the collar was 31.3 °C, available quantity at exploitation with free spill was set at 1.0 l . s^{-1} (Zakovič et al., 1988).

Tab. 1.1 Status of mineral water sources as of inventory 1997 – 2000 (Zeman et al., 2000)

	N	% representation	Spring	Piscine	Dug well	Borehole
exist	1,249	74.0	690	7	138	414
not found	111	6.6	80		4	27
disappeared	297	17.6	188	3	40	66
liquidated	30	1.8	17		3	10
∑	1,687	100.0	975	10	185	517

Tab. 1.2 Representation of mineral waters sources in structure-geological facies

No.	Structure-geological facies	N	% representation	Spring	Piscina	Dug well	Borehole
1.	Flysch Zone	225	**13.3**	158	0	20	47
2.	Klippen Belt	71	4.2	53	0	4	14
3.	Magmatic rocks	26	1.5	18	0	1	7
	Metamorphic rocks – Early Palaeozoic	30	1.8	30	0	0	0
	Metamorphic rocks – Late Palaeozoic	23	1.4	22	0	0	1
	Mesozoic sediments of Central Carpathians	256	**15.2**	159	1	14	82
	Inner Carpathians Palaeogene	406	**24.1**	305	0	31	70
4.	Neogene	535	**31.7**	169	8	99	259
	Neovolcanites	115	6.8	61	1	16	37
∑		**1,687**	**100**	**975**	**10**	**185**	**517**

Note: N – count of sources

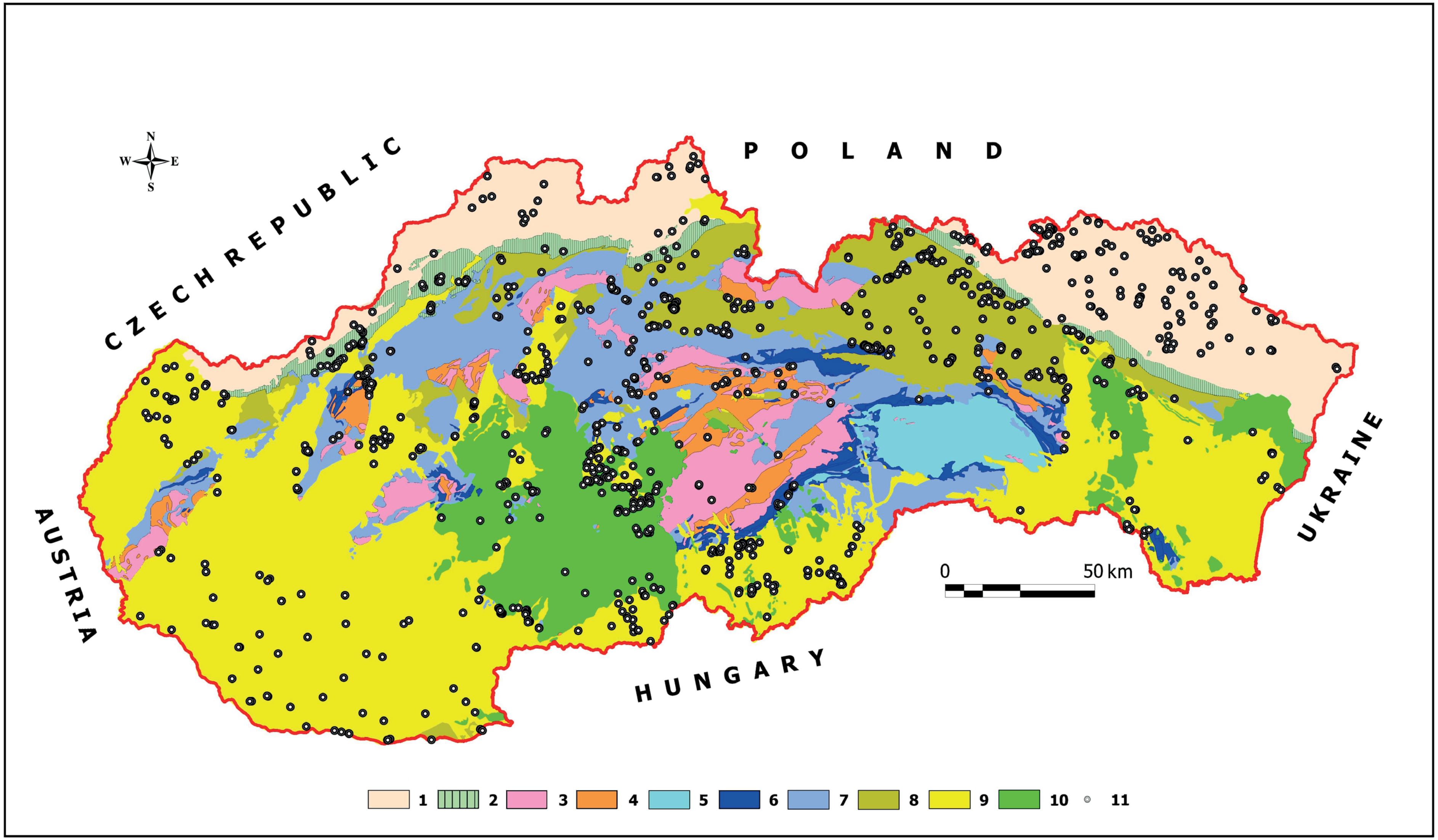


Fig. 1.1 Mineral waters sources in structure – facies zones of Slovakia (based on Zeman et al., 2000; Biely et al., 1996)
Explanation: 1 – Flysch Zone, 2 – Klippen Belt, 3 – Crystalline/magmatic rock, 4 – Crystalline/metamorphic rock (phyllites to mica schists with metavolcanic intercalations, locally gneisses), 5 – Metamorphic rocks – Early Palaeozoic (metasandstones, paraconglomerates, phyllites), 6 – Metamorphic rocks – Late Palaeozoic (metamorphosed clastic sediments, mafic volcanics and volcanoclastics, scarce ultramafic fragments), 7 – Mesozoic sediments (predominantly carbonate rocks – limestones, dolomites), 8 – Inner Carpathians Palaeogene (sandstones, claystones, conglomerates, breccias), 9 – Neogene sediments (clay, sand, sandstones, claystones, conglomerates), 10 – Neovolcanites (volcanic and volcanoclastic rocks), 11 – sources of mineral waters

Better known are sources with hydrosilicatogenic mineralization; they are mainly medium-mineralized, carbonic (5 – 10 g . l^{-1}) waters in Šarišský Štiavnik (Na-Ca-HCO_3) and Malý Sulín (Na-Ca-HCO_3).

Source of mineral water with polygenic mineralization of the chemical type Mg-SO_4-HCO_3 represents cold strongly mineralized water in Zbudzský Rokytov with the yield of up to 0.1 l . s^{-1}.

Fig. 1.2 Wellhead of borehole FPJ-1 Oravská Polhora – Slaná voda (Photo: Teťák, 2012, in Teťák et al., 2016)

1.3.2 Mineral waters of the Klippen Belt

The Klippen Belt is formed by numerous carbonate blocks of Triassic, Jurassic and Early Cretaceous age, which are encompassed within the marly Cretaceous and Palaeogene layers. The best known are the cold carbonic sources of weakly mineralized water in Nimnica (Na-HCO_3) with yield around 2 l . s^{-1}. Sources of thermal and cold (21 °C) weakly mineralized waters are known in Belušské Slatiny (Ca-Mg-HCO_3-SO_4) with yield up to 10 l . s^{-1}. In addition to these better-known water sources there occur occasional cold sources of carbonated and sulphane very weakly to weakly mineralized waters of chemical type Ca-Mg-HCO_3, Ca-Na-HCO_3, Ca-Mg-Na-SO_4 with yield up to 0.1 l . s^{-1}.

1.3.3 Mineral waters of the Central Western Carpathians

Zone of the Central Western Carpathians is built of crystalline fundament cropping out in the Core mountains and envelope. The Core mountains are split from each other by intermountain Young Tertiary basin. Volcanic mountains and lowlands are located in the southern part of the territory of Slovakia. The mineral and thermal waters are the most abundant in this zone.

To Crystalline there are mainly bound cold carbonic very weakly mineralized waters of the chemical type Ca-Mg-HCO_3 with yield up to 0.1 l . s^{-1}. Among the well-known we can state Starý Smokovec (Ca-Na-HCO_3), Mýto pod Ďumbierom (Na-HCO_3-Cl) and Jasenie (Ca-HCO_3). In the Crystalline the wells GVL-1 (Vlachovo) and RS-1 (Čučma) with depth of 1,201.3 m/1,379.6 m documented water of chemical type Na-HCO_3 with a temperature of 19 °C or 25 °C (Franko & Snopko, 1979).

To the *Triassic carbonates* (limestone and dolomite) of different tectonic units there are bound almost all significant sources of cold and thermal waters, which are used for spa treatment, recreation or for filling in consumer packaging.

On *sedimentary Tatricum envelope* are bound weakly mineralized thermal water with sulphatogenic mineralization in Piešťany (Ca-SO_4-HCO_3) and Trenčianske Teplice (Ca-SO_4). The yield of these sources is ranging within 20 – 40 l . s^{-1} and water temperature is in the range 40 – 68 °C. The source Trajan in Piešťany (Fig. 1.3) is a dug well with a depth of 8.4 meters, which is deepened by two hydrogeological wells with ø 400 mm to a depth of 11.2 meters (Krahulec et al., 1977). The maximum yield by pumping equals to 1,200 m^3 . day^{-1} (13.9 l . s^{-1}). The Triassic carbonates of the Tatricum envelope binds also cold carbonated weakly mineralized waters in Baldovce (Ca-Na-Mg-HCO_3-SO_4), Slatina (Ca-Mg-Na-HCO_3-SO_4, Ca-Mg-Na-HCO_3-Cl-SO_4) and Korytnica (Ca-Mg-SO_4-HCO_3). Their yield is ranging within 1 – 4 l . s^{-1} and water temperature in the range 4.5 – 16.5 °C (Franko & Melioris, 2000).

Fig. 1.3 Dug well Trajan in Piešťany Spa (Photo: Marcin, 2008)

On the *Krížna Nappe* there are bound mainly thermal weakly mineralized waters with prevailing sulphatogenic mineralization. They are extended at the northern edge and amidst the Central Slovak neovolcanites. The best known are waters of chemical type Ca-Mg-SO_4-HCO_3 in Sliač, Kováčová, Sklené Teplice, Kremnica and Chalmová. In Turčianske Teplice the water is of chemical type Ca-Mg-HCO_3-SO_4. Yield of the above sites is ranging

Tab. 1.3 Mineral waters of Slovakia in structure-facies zones of the Western Carpathians (Franko & Melioris, 2000)

Structure-facies zones	RU	TU	MWO	TDS [g . l^{-1}]		CO_2 [g . l^{-1}]		H_2S [g . l^{-1}]		Q [l . s^{-1}]		t [°C]	Chemical type water prevailing > 20 meq . l^{-1} %
				min	max	min	max	min	max	min	max	max	
1. Flysch Zone			CM	0.5	2.6	0.2	1.2	0.0	16.0	0.02	0.5	14	Ca-Mg-HCO_3 Ca-HCO_3
			HSiM	0.4	25.0	0.02	2.5	0.0	30.4	0.01	0.3		Na-Ca-HCO_3 Ca-Na-HCO_3
			TM	14.0	47.0	0.0	0.0	0.0	0.0	0.01	2.5	47	Na-Cl
2. Klippen Belt			CM	0.5	3.2	0.0	1.7	0.0	4.4	0.07	10.0	21.5	Ca-Mg-HCO_3-SO_4
			CM							0.01	2.1	11.0	Na-HCO_3
3. Inner Carpathian Palaeogene	CR		SiM	0.1	9.6	0.0	1.6	0.0	8.5	0.01	2.4	10.4	Ca-Mg-HCO_3 Na-HCO_3
	MS	TCU	CM	3.1	8.4	2.0	2.2	**St.	**St.	0.4	1.5	16.5	Ca-Na-Mg-HCO_3-SO_4, Ca-Na-Mg-HCO_3
			SuM	2.7	3.6	0.2	2.9	0.0	12.0	1.0	56.6	69.5	Ca-Na-Mg-SO_4-HCO_3
		KN	CM	1.5	3.9	0.01	1.7	0.0	4.0	0.9	47.5	45.0	Ca-Mg-HCO_3-SO_4
			SuM	0.5	3.9	0.1	1.4	<0.6	<0.6	7.1	37.0	53.0	Ca-Mg-SO_4-HCO_3
		ChN	CM	0.7	3.5	0.07	2.2	0.0	1.7	0.5	71.2	48.0	Ca-Mg-HCO_3, Ca-Mg-HCO_3-SO_4
	CPg		CM	0.5	2.6	0.04	1.2	0.0	11	0.01	10.0	10.5	Ca-Mg-HCO_3
			HSiM	0.6	0.7	0.02	0.03	3.2	16.6	0.04	0.2		Ca-Na-Mg-HCO_3, Na-HCO_3
			TM	8.7	12.4	0.0	1.27	0.0	0.0	0.2	0.6		Na-Cl-HCO_3
4. Neogene, Neovolcanites			CM	0.2	2.7	0.7	2.5	0.0	0.0	0.01	0.2	13.5	Ca-Mg-HCO_3
			SiM	0.12	9.6	0.0	2.0	0.0	2.61	0.1	5.1	36.6	Ca-Mg-Na-HCO_3, Na-HCO_3
			TM	1.9	41.6	0.0	0.5	0.0	0.0	0.08	25.0	91.5	Na-Cl-HCO_3, Na-Cl
			HM	9.5	292.0	0.04	0.8	0.0	0.0	0.2	2.0	16.8	Na-Cl
Western Carpathians*			MM	0.8	28.8	0.04	2.5	0.0	10.8	0.25	5.0	54.0	Na-Ca-Mg-HCO_3-Cl-SO_4, Na-HCO_3-Cl
			PM	1.6	25.0	0.0	0.4	0.2	700	0.2	2.2	21.5	Na-Ca-Mg-SO_4-HCO_3-Cl, Na-Ca-Mg-SO_4-HCO_3 Na-Mg-SO_4

*Note: **Rock units /RU/:** CR – Crystalline rock, MS – Mesozoic sediments of Central Carpathians, CPg – Central Carpathians Palaeogene,*
***Tectonic units /TU/:** TCU – Tatricum Cover Unit, KN – Krížna Nappe, ChN – Choč Nappe,*
Mineral waters accordance origin of chemical composition /MWO/: petrogenic mineralization** (CM – carbonatogenic dissolved solids, SuM – sulphatogenic dissolved solids, SiM – silicatogenic dissolved solids, HSiM – hydrosilicatogenic dissolved solids, HM – halitogenic dissolved solids, PM – polygenetic dissolved solids), TM **– thalassogenic mineralization**, MM – **mixed mineralization
** – sources with mixed and polygenetic mineralization are distributed across the entire Western Carpathians, ** – traces of H_2S.*

within 4 – 40 l . s^{-1} and water temperature in the range of 33 – 53 °C.

The carbonates of this Nappe bind thermal carbonic weakly mineralized water of chemical type Ca-Mg-HCO_3-SO_4 in Liptovský Ján, Vyšné Ružbachy, Banská Bystrica. The value of the yield of each site is within the range of 20 to 50 l . s^{-1} and water temperature in the range of 20 – 45 °C. Source Kráter (Crater, Fig. 1.4) in Vyšné Ružbachy despite its name, has nothing to do with volcanic activity, but it is a karst-fissure spring. It has the character of a lake with travertine rim with a diameter of 20 m and a depth of 3 m. The yield reaches the value of 7.8 l . s^{-1} (Krahulec et al., 1977).

In the basement of the Inner Carpathian Palaeogene in the northern Slovakia the wells Oravice OZ-1 and OZ-2 (Fig. 1.5), Plavnica PI-2, Poloma Šariš-1, Lipany L-1 and L-2 documented the presence of mineral water in the Mesozoic sediments of the Krížna Nappe close to the Klippen Belt. Drillings OZ-1 and OZ-2 were carried out to verify the presence of geothermal waters and wells (PI-2, Šariš-1, L-1 and L-2) in the north-eastern part of Slovakia aimed to verify the hydrocarbon potential of the area. The mentioned wells have documented the presence of both polygenetic mineral waters with mineralization in the Oravice area and also strongly carbonated mineral water mixed with mineralization in the north-eastern part

Fig. 1.4 Karst-fissure spring "Kráter" in Spa Vyšné Ružbachy (Photo: Marcin, 2008)

of Slovakia. Different chemical composition of water in these areas is due to nature of groundwater circulation and the remoteness of the remote catchment. While in the case of Oravice the infiltration area is close (about 2 km – NE slopes of the altitudinal point Osobitá), for the north-eastern part of Slovakia the aquifers do not crop out directly onto the surface of the potential catchment, but they are covered by sediments of Palaeogene. For potential area may be assumed the slopes of the Branisko Mts., which are located at a distance of approximately 10 – 15 kilometres.

Mineral waters of the Choč Nappe and higher units are typical of acratotherms presence (water with a very weak TDS and temperatures above 20 °C) of chemical type $Ca\text{-}Mg\text{-}HCO_3$. Well-known sources of this chemical type are in Rajecké Teplice, Bojnice, Malé Bielice. The Choč Nappe binds also thermal mineral waters with polygenetic mineralization of chemical type $Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$ in Kalinčiakovo and Vyhne. The yield of the sources in these areas reaches a value of 50 l . s^{-1} and 10 l . s^{-1}. The water temperature ranges from 26 °C to 35 °C (Krahulec et al., 1977).

Besides the above waters the carbonates of the above units bind also carbonated weakly mineralized waters, e.g. in Trenčianske Mitice ($Ca\text{-}Mg\text{-}HCO_3$), Gánovce ($Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$) and Lipovce ($Ca\text{-}Mg\text{-}HCO_3$), Santovka ($Ca\text{-}Mg\text{-}HCO_3$) and Šafárikovo ($Ca\text{-}Mg\text{-}HCO_3$, Silica Nappe). Yield of the above waters is ranging within 1 – 15 l . s^{-1} and water temperature in the range of 10 – 27 °C.

On carbonates of the Hungarian Central Highlands are bound waters of the sources in Patince ($Ca\text{-}Mg\text{-}HCO_3$) and Štúrovo ($Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$). The yield of the sources of these areas is ranging within 29 – 70 l . s^{-1} and water temperature is in the range of 20 – 40 °C.

Palaeogene sediments of the Inner Carpathian Palaeogene overlay the older tectonic units of the Western Carpathians. These rocks of marine facies have a character of flysch turbidites, which constitute both the filling of Intermountain depressions, but also they build up mountains close to the Klippen Belt: Súľovské vrchy, Skorušinské vrchy, Levočské vrchy, Spišská Magura, Bachureň, Šarišská vrchovina Mts.

Mineral waters of the Inner Carpathian Palaeogene are linked to conglomerates and sandstones, and are similar to

Fig. 1.5 Wellhead of borehole OZ-1 (left) and OZ-2 (right) Oravice (Photo: Marcin, 2013)

waters of the Flysch Zone. Cold hydrogen sulphide very weakly mineralized waters of chemical type Ca-Mg-HCO_3 and Na-HCO_3 are in prevail, with yield up to 0.1 l . s^{-1}. In smaller quantities there are present cold carbonated low-mineralized water chemical type Ca-Mg-HCO_3 with similar yield. The most famous sources include Nová Ľubovňa (Ca-Mg-HCO_3, Ca-Mg-Na-HCO_3) with yield 10 l . s^{-1}. Also known are the sources of mineral water in Konská (Na-HCO_3), Slatvina (Ca-Mg-Na-HCO_3-Cl) and Vojkovce (Na-Mg-Ca-HCO_3-Cl) with yield do 0.1 l . s^{-1}.

1.3.4 Mineral waters of sedimentary Neogene

Neogene sediments fill up intermountain depressions and the Vienna, Danube, Southern and the East Slovakian Basins. Neogene mineral waters are tied to the position of the basal clastic rocks, sand and sandstone which alternate with pelites. Neogene mineral water sources are of the highest yield (10 – 20 l . s^{-1}) and the water temperature ranges from 40 to 90 °C. The waters are bound to sandy sediments of Dacian, Pontian and Pannonian of the Central Depression of the Danube Basin (Franko & Bodiš, 1989).

Depressions in Slovakia filled with Neogene sediments are characterized by hydrogeochemical zonation of mineral water in vertical and horizontal directions. In the near-surface zone and on the edges of the depressions there are present cold and thermal very weakly to weakly mineralized waters of chemical type Ca-Mg-HCO_3 (e.g. Diakovce borehole – Di-3, Dubové – Spring at Municipality Office, Hodejov – Kúpeľný prameň, Trubín – Medokýš, Horné Plachtince – Medokýš), Na-HCO_3 (e.g. Diakovce – borehole Di-1, Dolná Strehová – borehole M-4, Valaliky – KAH-5) and the same is valid also for chemical types Na-Ca-HCO_3, which attain a temperature of 22 °C and TDS 0.3 g . l^{-1} (e.g. Dolná Strehová-Hámor – borehole S-107) or temperature of merely 12 °C and high TDS 8.5 g . l^{-1} (Martin-Záturčie – Fatra). Change in the nature of mineral waters from Neogene depends on the depth and position of aquifers and their distance from the edge of the basin, but also on the presence of CO_2. Depthwards and more distant from the edge of the basin occur thermal moderately to strongly mineralized water of chemical type Na-Cl (Gbely – borehole at the swimming pool, Báhoň – borehole B-1, Dunajská Streda – borehole DS-1, Nesvady – borehole K-3, Nová Vieska – borehole NV-1, Číž – well Hygiea, Buzica – Slaný vrt). Sources with the highest yield (10 – 20 l . s^{-1}) and temperature (40 – 90 °C) have open sections in the sands of Dacian, Pontian and Late Pannonian of the Central Depression of the Danube Basin (Franko et al., 1989).

Sources of mineral waters of the sedimentary Neogene with halitogenic mineralization reach a value of TDS from 1.3 to 292 g . l^{-1} (Plavecký Peter – sources Vajcovka, Prešov-Solivar – Leopold Shaft). The largest representation of mineral water with this kind of mine- ralization is located in the East Slovakian Basin, where Karpatian and Badenian sediments contain halite.

1.3.5 Mineral waters of neovolcanites

Complex of neovolcanic rocks builds up central part of Slovakia (Štiavnica, Stratovolcano, Stratovolcano in the Kremnické vrchy Mts., stratovolcanoes Poľana, Javorie, Lysec, Čelovce, eroded stratovolcanic relics from the area of Tisovec and Rimavská kotlina Basin) and in the eastern part of Slovakia it is a line of stratovolcanoes of the Slanské vrchy Mts. (stratovolcanoes Šebastovka, Zlatá Baňa, Makovica, Strechov, Bogota, Milič and Bradlo) and Vihorlat (stratovolcanoes Kyjov, Sokolský potok, Morské oko, Diel and Popriečny). Neovolcanite rocks complex is also involved in the sedimentary infill of the Žiarska kotlina Basin, Danube Basin and the East Slovakian Basin. In terms of abundance of mineral water the neovolcanites have the largest representation of resources from the central regions of Slovakia.

Mineral waters of Neovolcanites (Badenian andesites) were explored by deep wells in the Danube Basin (Rusovce – HGB-1, Šurany – S-1) with documented presence of mineral water of chemical type Na-Cl, TDS with 18.6 g . l^{-1} and water temperature of 28 °C. Yield at the collar was 0.1 l . s^{-1} (Bondarenková et al., 1977). Geological exploration well S-1 in Šurany reached the andesite tuffs and andesites at a depth of 1,750 – 2,700 m and documented the presence of mineral water of chemical type Na-Cl with TDS 32.5 g . l^{-1}.

In the Banská Štiavnica the 910 m deep borehole documented flow of mineral water of chemical type Na-Ca-SO_4-HCO_3, which had the TDS of 2.4 g . l^{-1} and water temperature of 46 °C (Remšík et al., 2007). Inflow of mineral water occurred from altered vein filling in andesites.

On the western outskirts of Žiarska kotlina Basin and the Vtáčnik mountain range with a presence of faults of the N-S direction 8 carbonic mineral water springs have been documented. In Bukovina there are three springs of mineral water of chemical type Ca-Mg-HCO_3 with TDS of 1.4 g . l^{-1} to 3.4 g . l^{-1}. North of the village Dolná Ždaňa surges mineral water of chemical type Ca-Mg-Na-HCO_3 in four springs and one well. The TDS of the water amounts to 0.6 g . l^{-1} to 0.9 g . l^{-1}. West of Zvolen is spring Červený medokýš whose carbonated mineral water is of chemical type Na-Ca-Mg-HCO_3 with TDS of 2.7 g . l^{-1} and CO_2 content of 2.5 g . l^{-1}. Yield of mineral springs is usually up to 0.1 to 0.2 l . s^{-1}, rarely as in the case of the resources in the Medokýš in Dolná Ždaňa it can reach 0.5 l . s^{-1} (Krahulec et al., 1978).

1.4 Characteristics of mineral waters aquifers

Aquifers of mineral waters in Slovakia are characterized by lithological and age diversity, reflecting the geological and tectonic setting of the Western Carpathians.

In the individual structural-facies zones of the Western Carpathians in Slovakia there are aquifers, which are located in such a position and having a hydraulic characteristics that are favourable conditions for the accumulation of mineral waters. The amount of mineral waters concentrated in the accumulation area of individual structures of mineral waters is, firstly, depending upon the very nature of the hydrogeological structure (open, closed), secondly it also depends on the extent of the aquifers, the thickness and depth of the deposit.

1.4.1 Aquifers of mineral waters in the Flysch Zone

The Flysch Zone is characterized by the presence of aquifers with dominant fissure permeability. The lowermost unit, whose aquifer has been documented by means of boreholes, was Obidowa-Słopnice-Zboj unit which in the territory of Slovakia was encountered in four wells Oravská Polhora FPJ-1, Zborov Z-1, Smilno S-1, Zboj-1 in the basement of the Magura Nappe. Zboj tectonic breccias and sandstones constitute the principal aquifer of the mineral waters which have been documented in this unit. Hydraulic parameters of this aquifer were obtained only from the well-FTJ 1 where the value of transmissivity coefficient T = 3.87 . 10^{-7} m^2 . s^{-1} (Zakovič et al., 2009).

In the Magura Nappe the most important aquifers of mineral water are Magura formation of the Krynica lithofacies-tectonic unit, Tvarožec Sandstone in the subsoil of Bialowieza Fm. of the Bystrica lithofacies-tectonic unit and Zlín Fm. (Makovica sandstone) of the Rača lithofacies-tectonic unit.

The Magura Fm. (Čergov Mb. – mostly sandstone facies) builds bulk of the Čergov Mts. and there were realized 23 hydrogeological wells here. Of these, 4 hydrogeological drillings verified the near-surface zone of disintegration (depth of wells up to 50 meters). Estimated coefficient of transmissivity T reached 1.28 . 10^{-5} to 2.84 . 10^{-4} m^2 . s^{-1}. Hydrogeological massif was documented by 19 wells. The depth of these wells ranged from 100 to 205 meters. The length of the open sections ranged from 38.1 m to 165 m. The lower part of the open section of wells was located at a depth of 75 m to 187 m from the ground surface. The upper part of the open section was located at a depth of 5.9 m to 20 m from the ground surface. Estimates of the coefficient of transmissivity T reached 5.64 . 10^{-5} to 1.59 . 10^{-3} m^2 . s^{-1}. The estimate of the coefficient of transmissivity for the near-surface zone of the hydrogeological massif Čergov has lower values compared to the hydrogeological massif. In the drillings verifying the hydrogeological massif decline was observed in measuring the yield of individual wells with their increasing depth and increasing length of the open section (Marcin et al., 2005).

Makovica and Tvarožec sandstones are characterized by the fact that the hydrogeological drillings carried out in these complexes have the highest transmissivity coefficient T in a zone of intense disturbance along the tectonic lines and near-surface zone of disintegration of sandstone complexes up to a depth of 100 m. The geological environment of this nature reaches a value of T 9.8 . 10^{-4} m^2 . s^{-1} to 9.1 . 10^{-3} m^2 . s^{-1}. With increasing depth of wells the disturbance of hydrogeological massif fades out along with the value of transmissivity coefficient (Zakovič in Nemčok et al., 1990).

1.4.2 Aquifers of mineral waters in the Klippen Belt

The Klippen Belt is characterized by the occurrence of more resistant, especially limestone cliffs – klippens, protruding from the generally less resistant marly flysch strata forming Klippen envelope. The Klippen Belt consists of several units that were thrust over each other and from the North these are: Czorsztyń unit, Kysucká unit, Pruské unit, Klapy unit, Orava unit, Manín unit.

Aquifers of mineral waters in this zone are Jurassic limestones (Czorsztyń radiolarian limestone) and limestones of Jurassic to Cretaceous (crinoidal limestone, Pieniny limestone, Rogoznica Mb. Gregorian breccia). In the Klippen Belt of the Ľubovnianska vrchovina Highlands these sediments were assessed using hydro-chemical method on 12 in descending sources at estimated aquifer thickness of the near-surface zone of 50 m. Due to the nature of the ground (karst-fissure permeability) this estimate of the average coefficient of transmissivity should be taken only indicatively. According to this analogy, the interval of estimated coefficient of transmissivity T is from 1 . 10^{-4} m^2 . s^{-1} to 3 . 10^{-4} m^2 . s^{-1} (Jetel, 1999).

Sedimentary envelope of the Klippen Belt in the Čergov Mts. was evaluated based on seven hydrogeological wells. Of these wells three wells have verified Proč and Jarmuta Palaeogene formations in near-surface zone of disintegration (within 50 meters) and four wells the hydrogeological massif. Estimates of the coefficient of transmissivity for the near-surface zone of disintegration reached T from 1.58 . 10^{-5} to 1.74 . 10^{-4} m^2 . s^{-1}. The depth of exploration wells verifying the hydrogeological massif ranged from 100 m to 133 m. The length of the open section ranged from 81.30 m to 123 m. The lower part of the open section of the wells was located at a depth of 100 m to 133 m from the ground surface. The upper part of the open section was located at a depth of 7.0 m to 10 m from the ground surface. Estimates of the coefficient of transmissivity reached from T 1.11 . 10^{-5} to 2.60 . 10^{-4} m^2 . s^{-1} (Marcin et al., 2005).

The Upohlava Fm. of the Klapy unit of the Klippen Belt made up of calcareous sandstones, marlstones and claystones of Albian to Cenomanian was documented by shallow wells in the area of Nosice – Nimnica. The estimated coefficient of transmissivity of these wells was of the order T = 2.8.10^{-7} m^2 . s^{-1}. Hydrogeological wells with a depth of 160-662 meters verify faulted zones of the Upohlava Fm with mineral water, the value of TDS ranged from 3,741 to 3,960 mg . l^{-1} and water temperature was from 11 °C to 12 °C. The coefficient of transmissivity in these wells T reached from 4.7 . 10^{-6} to 9.38 . 10^{-5} m^2 . s^{-1}. During hydrodynamic tests the following yields/drawdowns were documented: Q = 0.15 l . s^{-1}/s = 54 m; 1.0 l . s^{-1}/s = 32 m; 2.3 l . s^{-1}/s = 34 m (Urban et al., 1962; Rebro et al., 1978; Rebro et al., 1989).

1.4.3 Aquifers of mineral waters in zone of the Central Western Carpathians

Central Western Carpathians zone is made up of aquifers, which are located in the crystalline, Triassic carbonates of the tectonic units and Inner Carpathian Palaeogene.

The *crystalline rocks* do not contain significant mineral water aquifers although at several sites their sources are present. The most favourable conditions for accumulation of cold mineral water can be found on the tectonic zones of regional character (e.g. Sub-Tatric Fault, Čertovica Line).

For the crystalline rocks of the Central Western Carpathians the presence of mineral water with temperatures exceeding 20 °C is not typical, so it was a little surprise when the implementation of structural geological wells in Spiš-Gemer Ore Mountains detected their presence. During the implementation of wells GVL-1 (Vlachovo) and RS-1 (Čučma) with depth of 1,201.3/1,379.6 meters waters were documented of chemical type Na-HCO_3 with a temperature of 19 °C or 25 °C. Inflows of thermal nitrogen poorly mineralized water into the well GVL-1 were located at depths of 701 m, 723 m in the zone of metasomatic limestone surrounded by phyllites of the Gelnica Series. In the borehole RS-1 the inflows of very weakly mineralized water were met in the depth interval of 565-647 m in the contact of greisen zone with the phyllites of the Gelnica Series underlain by a granitoid body. Yield at the collar of the borehole GVL-1 stabilized at 2.15 l . s^{-1} and at the borehole RS-1 at 1 l . s^{-1}. Static water pressure at the well head GVL-1 reached the value 0.6 MPa and in the borehole RS-1 it was 0.3 MPa. Based on these results a new hydrogeochemical province of mineral water – nitrogen acratotherms of the Spiš-Gemer Ore Mts. (Franko & Snopko, 1979) has been allocated in the Central Western Carpathians. Metasomatic limestones surrounded by phyllites of the Gelnica Series documented in the borehole GVL-1 had a value of transmissivity coefficient T = 1.15 . 10^{-3} m^2 . s^{-1}.

Triassic carbonates (limestone and dolomite) of different tectonic units represent significant aquifers, to which cold and thermal waters are bound. Mineral water sources identified in these rock complexes achieved relatively high yield and belong along with the sources documented in the Neogene sediments among the most important in terms of productivity. Given the nature of the Triassic sediments (limestones and dolomites) in each nappe the following aquifers can be distinguished.

In the sedimentary envelope of the Tatricum unit major aquifers are Gutenstein and Ramsau Dolomites. *In the Krížna Nappe* the most *important* aquifers are Gutenstein Limestone, Ramsau Dolomite and Haupt Dolomite in the overlying Lunz Mb. The aquifers *of the Choč Nappe and higher units* are represented by Gutenstein Limestone, Ramsau Dolomite, Reifling Limestone, Wetterstein Limestone, Haupt Dolomite in the overlying Lunz Mb., Dachstein Limestone. *The Silica Nappe* as one of the higher units contains the aquifers represented Guteinstein Limestone, Steinalm Limestone, Schreyeralm Limestone, Wetterstein Limestone, Tisovec Limestone, Hallstatt Limestone, Dachstein Limestone. Hydraulic parameters of hydrogeological units in Slovakia have been processed through the wells database. Of this database 25,323 hydrogeological boreholes were involved, which enabled to obtain data on the reinterpretation 16,729 pumping tests. Group of the Mesozoic sediments contained 767 pumping tests (Malík et al., 2007). The values of the coefficient of transmissivity and filtration of the Triassic carbonates, without distinction of tectonic affiliation documents Tab. 1.4. Among those assessed drillings were mostly shallow wells and fewer consisted of data from deep wells.

Transmissivity coefficient values were obtained from the hydrodynamic tests in deep wells in promising geothermal areas of Slovakia. Documented aquifers parameters for mineral waters are listed in the Tab. 1.5. The total number of wells was 147 and 141 of them identified presence of mineral waters and provided information on the nature of the hydrogeological aquifer. Of these, data are available from 77 wells documenting Mesozoic sediments, 58 wells of Neogene sediments and two wells of Neovolcanites complexes. Transmissivity coefficient values were available from 56 wells verifying the Mesozoic sediments, the 49 Neogene sediments and 2 the Neovolcanites complexes.

Mesozoic carbonates in Slovakia are the most important aquifers of mineral waters, delivering a geometric mean of transmissivity coefficient G(T) = 9.08 . 10^{-4} m^2 . s^{-1} at standard deviation of log value σ log T = 0.90 (Tab. 1.6). In terms of classification Krásný (1993) these aquifers attain a moderate transmissivity (Class III) and very high variability (Class E), which represents very significantly non-uniform geological environment. Drillings carried out in the environment of Mesozoic carbonates are also reported to reach relatively large yields (Md Q = 12.4 l . s^{-1}/Mn Q = 19.4 l . s^{-1}); the most productive is the borehole OZ-2 in *Oravice* (Q = 100 l . s^{-1} Tab. 1.5).

The highest value of transmissivity coefficient T for Mesozoic carbonates in terms of wells has been documented in the Upper Nitra Basin (Chalmová – HCH-1), Rimavská kotlina Basin (Tornaľa – HM-5) and Žilinská kotlina Basin (Stráňavy – HZK-1). In evaluating the aquifers of each prospective geothermal areas of Slovakia based on the value T among the all wells of the areas (condition over 3 wells in the area) as Upper Nitra Basin, Komárno high block and Rimavská kotlina Basin appear to be the most favourable. Drillings carried out within these areas are mainly located in the discharge areas of the hydrogeological structures and the obtained data of the of the transmissivity coefficient T exhibit considerable variability. Their depth ranged from 158 m to 600 m (Tab. 1.7).

The lowest value of the transmissivity coefficient T for Mesozoic carbonates in terms of wells has been documented in the Topoľčany Embayment and Bánovská kotlina Basin (Topo*ľč*any – FGTz-1) of the Central Neovolcanites – NW part (Lukavica – LKC-4) and Liptovská kotlina Basin (Pavčina Lehota – FGL-1). In evaluating the aquifers of each prospective geothermal area of Slovakia on the basis of available data of the transmissivity coefficient T of all the wells the least favourable appears the Komárno marginal block, Liptovská kotlina Basin, Topoľčany Embayment and Bánovská kotlina Basin (Tab. 1.7). Drillings carried out in these areas were located mainly in the accumulation zones of the hydrogeological structures, except for Bešeňová boreholes, Malé and Veľké Bielice.

Inner Carpathian Palaeogene sediments in Slovakia are located around the Klippen Belt area; from the west, they comprise Myjava-Hričov Group. Its sedimentation was followed by Sub-Tatric Group. Aquifers of mineral waters in the Myjava-Hričov Group is the Súľov Fm. In the Sub-Tatric Group – Orava-Podhale section there are

Tab. 1.4 Values of standard specific capacities and geometric means ***G(T)*** and ***G(K)*** of derived values of transmissivity and hydraulic conductivity coefficients, calculated for different aquifer types in Slovakia (Malík et al., 2007)

No.	Description	Origin and classification	Group	n	M[^{1}q]	Md[^{1}q]	G[T]	σ log T	G[K]
83	Cellular dolomites, dolomitic breccias, rauhwackes	Tectonically reduced carbonate rocks	MZ	6	0.309	0.372	$5.53 \cdot 10^{-4}$	0.51	$4.05 \cdot 10^{-6}$
84	Metamorphic limestones, carbonates	Metamorphic sediments of Triassic	MZ	5	0.603	0.331	$9.32 \cdot 10^{-4}$	0.66	$8.47 \cdot 10^{-6}$
85	Limestones, quartzitic limestones, nodular limestones, limestones with cherts	Sediments of Middle and Late Triassic	MZ	34	1.622	3.236	$3.52 \cdot 10^{-3}$	0.81	$1.91 \cdot 10^{-4}$
86	Sandstones, shales, variably beds or intercalations of limestones, dolomites, evaporites, metatuffs, silicites	Sediments of Middle and Late Triassic	MZ	20	0.234	0.182	$3.41 \cdot 10^{-4}$	0.93	$1.34 \cdot 10^{-5}$
87	Limestones	Sediments of Middle and Late Triassic	MZ	238	0.339	0.407	$6.19 \cdot 10^{-4}$	1.06	$1.06 \cdot 10^{-5}$
88	Limestones and dolomitic limestones, dolomites	Sediments of Middle and Late Triassic	MZ	3	24.547	40.738	$4.64 \cdot 10^{-2}$	0.47	$6.00 \cdot 10^{-4}$
89	Dolomites	Sediments of Middle and Late Triassic	MZ	438	0.575	0.589	$1.04 \cdot 10^{-3}$	0.86	$2.37 \cdot 10^{-5}$
90	Dolomites with intercalations of shales	Sediments of Middle and Late Triassic	MZ	23	0.724	0.676	$1.43 \cdot 10^{-3}$	0.71	$2.57 \cdot 10^{-5}$

Explanation of abbreviations: ***n*** *– number of interpreted hydraulic tests on hydrogeological boreholes and wells;* ***M(¹q)*** *– arithmetic mean of the standard specific capacity* ***¹q*** *[l . s⁻¹ . m⁻¹];* ***Md(¹q)*** *– median value of the standard specific capacity* ***¹q****;* ***G(T)*** *– geometrical mean of the transmissivity coefficient* ***T*** *[m² . s⁻¹];* ***σ log T*** *– standard deviation of the transmissivity coefficient logarithm values;* ***G(K)*** *– geometrical mean of the hydraulic conductivity coefficient* ***K*** *[m . s⁻¹];* ***MZ*** *– group of Mesozoic sediments.*

Borové and Biely Potok formations and in the Spiš-Šariš section it is Šambron Mb. In southern Slovakia, between Kravany and Štúrovo extend the Palaeogene sediments of Buda facies protrude from the south, which overlay the carbonates of the Hungarian Central Highlands. These sediments together with Cretaceous sediments form an insulator for Triassic carbonate aquifers of the Komárno block (Brodňan & Nemsilová, 1960).

Hydraulic parameters of the aquifers Inner Carpathian Palaeogene and Buda Palaeogene were evaluated in the Slovak territory through the database of hydrogeological wells, from which data were available on the pumping tests. Group sediments of the Inner Carpathian and Buda Palaeogene involved 703 pumping tests (Malík et al., 2007). The transmissivity coefficient and coefficient of hydraulic conductivity values of the above sediments documents Tab. 1.8. Among those assessments were used mostly shallow wells and fewer were obtained from deep wells.

Most famous sources of mineral waters are in the Inner Carpathian Palaeogene of the Ľubovňa Spa at Nová Ľubovňa and in Malé and Veľké Bielice near Partizánske. Originally, in the Ľubovňa Spa there were located 5 sources of mineral carbonic water that reached yield of 0.1 l . s^{-1} (Krahulec, 1978). Larger quantities of mineral water have been obtained by realization of hydrogeological well LZ-6 in the area of the spring (Zakovič et al., 1993). The borehole reached a depth of 176.1 m and verified inflows of mineral water from graded-bedded coarse-grained sandstones of the Šambron Mb. in the interval from 17.0 to 21.0 m – Q = 1.0 to 1.5 l . s^{-1}, and in the interval from 96.0 to 111.0 m – Q = 22 l . s^{-1}. After the final incorporation of the borehole there followed a three-month trial, which documented an average yield of 11.4 l . s^{-1} with a water temperature of 9 °C. Water from this source started to be bottled (Zakovič et al., 2006).

Hydrogeological drillings MB-1 (Malé Bielice) and VB-3 (Veľké Bielice) encountered the thermal water in the discharge area in the elevation of the fundament. Wells with a depth of 160 m and 102 m verified Palaeogene breccias of the Borové Fm. The value of transmissivity coefficient T in these sediments was $2.81 \cdot 10^{-3}$ $m^2 \cdot s^{-1}$ and $3.11 \cdot 10^{-3}$ $m^2 \cdot s^{-1}$, which significantly exceeds the value of G (T) = $3.58 \cdot 10^{-4}$ $m^2 \cdot s^{-1}$ obtained from the evaluation of 60 pumping tests.

1.4.4 Aquifers of mineral waters in sedimentary Neogene

Neogene sediments in Slovakia are significant aquifers, delivering a geometric mean of the transmissivity coefficient G (T) = $5.35 \cdot 10^{-4}$ $m^2 \cdot s^{-1}$ at standard deviation σ log T = 0.51 (Tab. 1.9). In terms of classification by Krásný (1993) the aquifers are of moderate transmissivity (Class III) and higher variability (Class C), which represents rather inhomogeneous geological environment. Drillings carried out in an environment in Neogene sediments achieved relatively balanced yields (10.0 l . s^{-1} – Mn Q = 10.5 l . s^{-1}), the most productive are the wells FGG-2 and FGG-3 in Galanta (Q = 25 l . s^{-1}).

The highest value of transmissivity coefficient T for the Neogene sediments among the wells has been documented in the Central Depression of the Danube Basin (Veľký Meder – C-2), Diakovce – Di-3, Želiezovce – HGŽ-1). The wells with the highest documented values

Tab. 1.5 Deep boreholes verifying the parameters of mineral water aquifers in Slovakia

Locality	**Borehole**	**Year of realization**	**Deep of borehole [m]**	**Open interval of borehole [m]**	**Age of aquifer**	**Lithology of aquifer**	**Yield [l . s^{-1}]**	**T [m^2 . s^{-1}]**	**Temperature at well head [°C]**	**Heat power [MWt]**	**TDS [g . l^{-1}]**	**Chemical water type**
Central Depression of the Danube Basin												
Rusovce	HGB-1	1974	1,493	1,067-1,493	Badenian	andesites	0.1	$1.14.10^{-5}$	28	-	18.6	Na-Cl
Chorvátsky Grob	FGB-1	1974	1,232	971-1,150	Badenian	base clastics	1.9	$4.17.10^{-5}$	47	0.26	1.9	$Na\text{-}Cl\text{-}HCO_3$
Chorvátsky Grob	FGB-1/A	1975	500	276-299	Pontian	sands	3.5	$1.43.10^{-4}$	24	0.13	0.5	$Na\text{-}Mg\text{-}Ca\text{-}HCO_3$
Kráľová pri Senci	FGS-1	1974	810	430-570	Pontian	sands	0.3	$8.47.10^{-5}$	23	0.01	3.6	$Na\text{-}Mg\text{-}HCO_3$
Kráľová pri Senci	FGS-1/A	1974	1,500	910-1,370	Pontian-Pannonian	sands	13	$3.52.10^{-4}$	52	2.01	7.7	$Na\text{-}HCO_3\text{-}Cl$
Kráľová pri Senci	VMK-1	1992	804.5	439-572.5; 601-784	Pontian	sands	1.2	$1.5.10^{-4}$	30	0.07	2.8	Na-Mg-HCO3
Senec	BS-1	1981	1,350	928-1,181	Pontian	sands	12	$7.88.10^{-4}$	49	1.71	2.5	$Na\text{-}HCO_3\text{-}Cl$
Topoľníky	FGT-1	1975	2,501	1,394-2,487	Pontian	sands	23	$1.6.10^{-3}$	74	5.68	2.2	$Na\text{-}HCO_3\text{-}Cl$
Čilistov	FGČ-1	1979	2,500	1,195-1,549	Pannonian	sandstones	15	$1.99.10^{-3}$	52	2.32	6.9	$Na\text{-}HCO_3\text{-}Cl$
Dvory nad Žitavou	FGDŽ-1	1980	2,500	1,024-1,607	Pontian	sands	7.2	$4.71.10^{-4}$	62	1.42	3.4	$Na\text{-}HCO_3\text{-}Cl$
Sládkovičovo	FGG-1	1975	1,990	1,212-1,670	Pontian	sands	10.8	$5.14.10^{-4}$	62	2.13	3.2	$Na\text{-}HCO_3\text{-}Cl$
Galanta	FGG-2	1983	2,100	1,706-2,032	Pannonian	sands	25	$2.3.10^{-3}$	80	6.8	4.9	$Na\text{-}HCO_3\text{-}Cl$
Galanta	FGG-3	1984	2,102	1,731-1,999	Pannonian	sands	25	$4.85.10^{-4}$	77	6.49	5.9	$Na\text{-}HCO_3\text{-}Cl$
Tvrdošovce	FGTv-1	1978	2,406	1,362-1,637	Pontian	sands	20	$3.79.10^{-4}$	70	4.6	2.5	$Na\text{-}HCO_3$
Horná Potôň	FGHP-1	1978	2,500	1,394-1,804	Pontian	sands	20	$1.2.10^{-3}$	68	4.43	4.7	$Na\text{-}Cl\text{-}HCO_3$
Horná Potôň	VHP-12-R *	1987	2,100	1,380-1,832	Pontian	sands	22.3	$1.7.10^{-3}$	68	4.94	4.3	$Na\text{-}HCO_3\text{-}Cl$
Dunajská Streda	DS-1	1971	2,500	2,183-2,432	Pontian	sands	15.2	$2.42.10^{-4}$	91	5.82	6.9	$Na\text{-}Cl\text{-}HCO_3$
Dunajská Streda	DS-2	1985	1,600	1,190-1,549	Dacian-Pontian	sands	23	$2.83.10^{-3}$	55	3.85	1.6	$Na\text{-}HCO_3$
Čiližská Radvaň	ČR-1	1986	2,513	1,614-2,430	Pontian-Pannonian	sands	6	$3.76.10^{-4}$	82	3.3	1.6	$Na\text{-}HCO_3\text{-}Cl$
Čiližská Radvaň	VČR-16	1990	1,800	1,390-1,745	Pontian	sands	14.5	$1.26.10^{-3}$	64	2.93	0.8	$Na\text{-}HCO_3$
Zlaté Klasy – Eliášovce	VZK-10	1987	1,800	1,331-1,457	Pontian	sands	12.5	$7.72.10^{-4}$	65	2.6	8.3	$Na\text{-}Cl\text{-}HCO_3$
Veľký Meder	Č-1	1972	2,502	1,573-1,791	Pontian	sands	10	$1.11.10^{-4}$	79	2.59	1.1	$Na\text{-}HCO_3$
Veľký Meder	Č-2	1983	1,503	1,037-1,439	Pontian	sands	18.2	$6.93.10^{-3}$	57	3.2	0.9	$Na\text{-}HCO_3$
Šaľa	HTŠ-1	1982	X				0.2 $^+$		22			
Šaľa	HTŠ-2	1983	1,200	880-1,169	Pontian	sands	3.1	$3.0.10^{-4}$	42	0.36	1.5	$Na\text{-}HCO_3$
Šaľa	HTŠ-3	1983	290	73-282	Dacian	sands	5 $^+$	$5.5.10^{-4}$	18	0.06	0.5	$Na\text{-}HCO_3$
Šaľa	GTŠ-1	2010	1,800	1,481-1,786	Pannonian	sands, sandstones	15 $^+$	$6.04.10^{-4}$	69	3.39	4.9	$Na\text{-}HCO_3\text{-}Cl$
Poľný Kesov	BPK-1	1980	847	387-737	Neogene	sands	1	$1.44.10^{-4}$	26	0.15	1.1	$Na\text{-}Ca\text{-}HCO_3$

Locality	Borehole	Year of realization	Deep of borehole [m]	Open interval of borehole [m]	Age of aquifer	Lithology of aquifer	Yield [l . s^{-1}]	T [m^2. s^{-1}]	Temperature at well head [°C]	Heat power [MWt]	TDS [g . l^{-1}]	Chemical water type
Poľný Kesov	BPK-2	1981	1,200	1,089-1,189	Neogene	sands	4	$9.21.10^{-5}$	49	0.6	1.8	$Na-HCO_3$
Lehnice	BL-1	1985	1,500	1,031-1,455	Dacian-Pontian	sands	23.2	$2.1.10^{-3}$	54	3.78	2.2	$Na-HCO_3$
Diakovce	Di-1	1962	3,303	720-810	Pontian-Pannonian	sands	4		38	0.39	0.5	$Na-HCO_3$
Diakovce	Di-2	1982	1,551	1,416-1,536	Pontian-Pannonian	sands	12	$1.7.10^{-3}$	68	2.66	2.1	$Na-HCO_3-Cl$
Diakovce	Di-3	1983	306	215-275	Dacian	sands	15	$5.0.10^{-3}$	19	0.25	0.6	$Ca-Na-HCO_3$
Vlčany	FGV-1	1982	2,500	1,244-1,852	Pontian	sands	10	$1.8.10^{-4}$	68	2.22	2.1	$Na-HCO_3$
Gabčíkovo	FGGa-1	1982	2,582	1,122-1,926	Pontian	sands	10	$2.01.10^{-3}$	52	1.64	1.1	$Na-HCO_3$
Boheľov	GBP-1 **	1982	2,800	-	-	-	-		-	-	-	-
Ňárad (Topoľovec)	VTP-11	1988	2,500	1,533-2,482	Pontian-Pannonian	sands	14.6	$7.50.10^{-4}$	74	3.6	1.2	$Na-HCO_3-Cl$
Zlatná na Ostrove	VZO-13	1990	1,650	1,089-1,625	Pontian-Pannonian	sands	7.5	$2.8.10^{-4}$	51	1.25	7.5	Na-Cl
Zemianska Olča	VZO-14	1990	1,849	1,555-1,839	Pontian	sands	10	$3.2.10^{-4}$	74	2.51	2.7	$Na-HCO_3-Cl$
Dunajský Klátov	VDK-15	1990	2,240	1,425-2,222	Pontian-Pannonian	sands	15.4	$5.80.10^{-4}$	74	3.75	2.4	$Na-HCO_3-Cl$
Nové Zámky	GNZ-1	1983	1,506	1,236-1,473	Pontian	sands	4.5	$2.69.10^{-4}$	59	0.83	3.2	$Na-HCO_3-Cl$
Nesvady	GN-1	2008	1,505	1,283-1,494	Pontian	sands, sandstones	2.7	$1.36.10^{-4}$	60	0.5	2.9	$Na-HCO_3$
Šurany	GŠM-1	1989	1,500	892-1,400	Pontian	sands	3.5	$2.2.10^{-4}$	49	0.5	3	$Na-Cl-HCO_3$
Komárno	M-2	1971	1,060	771-1,025	Pontian-Pannonian	sands	4.5^{+}		42	0.51	3.9	$Na-HCO_3-Cl$
Komárno	FGK-1	1976	1,970	904-1,082	Pontian-Pannonian	sands	4	$9.2.10^{-5}$	45	0.5	2	$Na-HCO_3-Cl$
Sereď	SEG-1	2011	1,800	1,505-1,779	Pannonian	sandstones	9^{+}	$2.11.10^{-4}$	66	1.94	5.1	$Na-HCO_3-Cl$
Komárno high block												
Patince	SB-1	1959	226	130-160	Triassic	limestones	29.1		26	-	0.7	$Ca-Mg-HCO_3$
Patince	SB-2	1972	160	129-146	Lias-Triassic	limestones	45		27	2.26	0.7	$Ca-Mg-HCO_3$
Patince	SB-3	1982	170	132-167	Triassic	limestones	29.4		26	1.35	0.7	$Ca-Mg-HCO_3$
Virt	JRD	1973	260		Triassic	limestones, dolomites	6.6		26	0.3	0.7	$Ca-Mg-HCO_3$
Virt	HVB-1	1973	241	139-233	Triassic	limestones, dolomites	10^{+}	$2.76.10^{-3}$	26	0.46	0.7	$Ca-Mg-HCO_3$
Virt	vrt VŠE	1976	280	155-263	Triassic	limestones, dolomites	18.3^{+}	$2.07.10^{-4}$	24	0.69	0.7	$Ca-Mg-HCO_3$
Štúrovo	FGŠ-1	1975	210	77-128	Triassic	dolomitic limestones	70	$2.56.10^{-2}$	40	7.33	0.8	$Ca-Mg-HCO_3-SO_4$
Štúrovo	VŠ-1	1988	125	65-113	Triassic	dolomites, limestones	49	$1.36.10^{-2}$	39	4.86	0.7	$Ca-Mg-HCO_3-SO_4$
Obid	FGO-1	1979	1,000	736-1,000	Triassic	dolomites, limestones	2.1	$5.0.10^{-3}$	20	0.05	0.8	$Ca-Mg-HCO_3$
Kravany	FGKr-1	1979	1,021	723-920	Triassic	dolomites, limestones	5.5	$2.04.10^{-4}$	20	0.12	0.8	$Ca-Mg-HCO_3$
Komárno marginal block												
Komárno	M-1	1967	1,221	1,140-1,221	Mesozoic	limestones, dolomites	1.6		42	0.18	2.2	$Na-Ca-Mg-SO_4-HCO_3-Cl$

Locality	Borehole	Year of realization	Deep of borehole [m]	Open interval of borehole [m]	Age of aquifer	Lithology of aquifer	Yield [l . s^{-1}]	T [m^2. s^{-1}]	Temperature at well head [°C]	Heat power [MWt]	TDS [g . l^{-1}]	Chemical water type
Komárno	M-3	1976	1,184	1,139-1,184	Jurassic, Triassic	dolomitic limestones	5	1.4.10^{-4}	51	0.75	3.1	Ca-Na-Mg-SO_4-Cl-HCO_3
Komárno	FGK-1	1976	1,970	1,696-1,964	Triassic	limestones, dolomites	3.3	1.5.10^{-4}	64	0.67	2.9	Ca-Na-Mg-SO_4-Cl
Marcelová	GTM-1	1987	1,763	1,037-1,761	Neogene, Triassic	conglomerates, limestones	6	1.7.10^{-4}	56	1.02	90	Na-Cl
Levice block												
Podhájska	Po-1	1973	1,900	1,155-1,740	Badenian, Triassic	conglomerates, limestones	53		80	14.42	19.6	Na-Cl
Podhájska	GRP-1*	1986	1,470	995-1,365	Badenian, Triassic	conglomerates, dolomites, limestones	28	1.97.10^{-3}	69	6.32	19.2	Na-Cl
Dubník Depression												
Bruty	VTB-1	1990	1,927	1,599-1,905	Badenian	sandstones, conglomerates	15^{+}		75	2.4	30	Na-Cl
Svätý Peter	PTG-11	1990	1,856	972-1,321	Neogene	sand	6		50	0.88	5.3	Na-Cl
Želiezovce	HGŽ-1	1972	350	100-234	Neogene	sands, sandstones	13.5 $^{+}$	3.05.10^{-3}	18	0.17	1.6	Na-Ca-HCO_3
Želiezovce	HGŽ-3	1990	916	342-900	Badenian	clastics	1.5 $^{+}$		52	0.25	10	Na-SO_4-Cl
Komjatice Depression												
Komjatice	G-1	1989	1,830	1,509-1,700	Pannonian	sands, sandstones	12		78	2.5	20.1	Na-Ca-Cl-HCO_3
Topoľčany embayment and Bánovce Basin												
Malé Bielice	MB-3	1974	160	80-100	Palaeogene	carbonatic breccias	8.5	2.81.10^{-3}	40	0.89	1.1	Ca-Mg-HCO_3
Veľké Bielice	VB-3	1983	102	27-90	Palaeogene	carbonatic breccias	8.3 $^{+}$	3.11.10^{-3}	39	0.83	0.8	Ca-Mg-HCO_3
Brodzany	HGT-9	1982	160	133-139	Triassic	carbonates	1.7 $^{+}$	1.16.10^{-4}	32	0.12	1.5	Ca-Mg-HCO_3-SO_4
Topoľčany	FGTz-1	1985	2,106	1,512-1,917	Triassic	carbonates	2.0 $^{+}$	6.70.10^{-6}	55	0.33	5.9	Na-HCO_3-SO_4
Partizánske	FGTz-2	2004	998	401-970	Triassic	dolomites, limestones	12.5 $^{+}$	3.55.10^{-3}	33	0.94	0.7	Ca-Mg-HCO_3
Partizánske	HGTP-1	2000	500	265-474	Triassic	carbonates	18.8 $^{+}$	7.83.10^{-3}	20	0.37	0.7	Ca-Mg-HCO_3
Bánovce nad Bebravou	BnB-1	1984	2,025	2,000-2,025	Triassic	dolomites	17 $^{+}$	6.37.10^{-5}	40	1.78	0.7	Ca-Mg-HCO_3-Cl
Trnava embayment												
Koplotovce	KB-1	1976	118	78-108	Triassic	dolomites	14.5	6.87.10^{-3}	24	0.55	2.52	Ca-Mg-HCO_3-SO_4
Piešťany embayment												
Nové Mesto nad Váhom-Zelená Voda	GZV-1	2008	1,206	985-1,155	Mesozoic	carbonates	10	1.82.10^{-4}	19.4	0.18	1.41	Mg-Ca-SO_4
Vienna Basin												
Šaštín-Stráže	RGL-2	1983	2,605	2,005-2,570	Eggenburgian, Triassic	conglomerates, limestones	12	2.61.10^{-4}	73	2.91	10.9	Na-Cl

Locality	Borehole	Year of realization	Deep of borehole [m]	Open interval of borehole [m]	Age of aquifer	Lithology of aquifer	Yield [l . s^{-1}]	T [m^2 . s^{-1}]	Temperature at well head [°C]	Heat power [MWt]	TDS [g . l^{-1}]	Chemical water type
Lakšárska Nová Ves	RGL-1	1984	2,100	1,242-2,065	Eggenburgian, Triassic	conglomerates, limestones	25	2.58.10^{-3}	78	6.59	6.8	Na-Ca-Cl-SO_4
Ilava Basin												
Belušské Slatiny	BHS-3	1990	1,761	-	-	-	-		-	-	-	-
Žilina Basin												
Rajec	RK-22	1974	1,308	1,064-1,308	Triassic	carbonates	22		26	0.6	0.5	Ca-Mg-HCO_3
Stráňavy	HŽK-2	1990	600	335-500; 500-559	Palaeogene--Triassic	sandstones, dolomites	22	3.03.10^{-2}	24	0.84	0.4	Ca-Mg-HCO_3-SO_4
Kamenná Poruba	RTŠ-1	1991	1,831	1,370-1,830	Triassic	carbonates	13.4	7.3.10^{-4}	42	1.51	0.5	Ca-Mg-HCO_3
Žilina	HŽK-10	1993	2,258	-	-	-	-		-	-	-	-
Horná Nitra Basin												
Laskár	Š-1-NB II	1980	1,851	1,677-1,851	Triassic	carbonates	22	2.78.10^{-3}	59	4.08	0.8	Ca-Na-Mg-HCO_3-SO_4
Chalmová	BCH-3	1983	150	30-120	Triassic	carbonates	5.0 $^{+}$		39	0.5	1.9	Ca-Mg-SO_4-HCO_3
Chalmová	HCH-1	1992	200	50-194	Triassic	carbonates	13.4^{+}	9.25.10^{-2}	33	1.01	1.3	Ca-Mg-SO_4-HCO_3
Handlová	FGHn-1	2002	475	370-430	Palaeogene-Triassic	breccias, dolomites	2.5 $^{+}$		19	0.05	0.4	Ca-Mg-HCO_3
Handlová	RH-1	2010	1,201	862-1,179	Permian-Mesozoic	sandstones, carbonates	15 $^{+}$	2.02.10^{-4}	37.5	1.41	1.06	Ca-Mg-SO_4-HCO_3
Turiec Basin												
Turčianske Teplice	TTK-1	1977	56	46-56	Mesozoic	carbonates	3.5		27	0.18	1.5	Ca-Mg-HCO_3-SO_4
Diviacky Háj	HM-2	1989	403	90-140	Mesozoic	carbonates	4 $^{+}$	5.68.10^{-3}	42	0.45	1.6	Ca-Mg-HCO_3-SO_4
Diviacky Háj	TTŠ-1	1988	1,503	810-1,124	Triassic	carbonates	12.4		54	2.02	2.5	Ca-Mg-HCO_3-SO_4
Martin	ZGT-3	1990	2,461	-	-	-	-		-	-	-	-
Skorušina Basin												
Oravice	OZ-1	1979	600	342-561	Triassic	dolomites	35	3.21.10^{-3}	28	1.09	0.8	Ca-HCO_3
Oravice	OZ-2	1991	1,601	950-1,565	Triassic	dolomites	100	3.08.10^{-3}	56	17.2	1.3	Ca-Mg-HCO_3
Liptov Basin												
Pavčina Lehota	FGL-1	1977	2,129	1,315-1,570	Triassic	carbonates	6 $^{+}$	3.19.10^{-5}	32	0.43	0.5	Mg-Ca-HCO_3-SO_4
Bešeňová	ZGL-1	1987	1,987	1,540-1,987	Triassic	dolomites	27	1.16.10^{-4}	62	5.3	3	Ca-Mg-SO_4-HCO_3
Bešeňová	FBe-1	2006	400				5.4		25	0.23	3.6	Ca-Mg-HCO_3-SO_4
Bešeňová	FGTB-1	2011	1,833	1,623-1,814	Mesozoic	carbonates	32		66	6.83	3	Ca-Mg-SO_4-HCO_3
Liptovská Kokava	ZGL-3	1990	2,373	1,475-2,365	Triassic	carbonates	20 $^{+}$	1.82.10^{-3}	43	2.39	4.4	Ca-Mg-HCO_3-SO_4
Liptovský Trnovec	ZGL-2/A	1992	2,500	1,624-2,486	Triassic	carbonates	31	1.02.10^{-3}	60	5.18	4.7	Ca-Na-Mg-HCO_3-SO_4

Locality	Borehole	Year of realization	Deep of borehole [m]	Open interval of borehole [m]	Age of aquifer	Lithology of aquifer	Yield [l . s^{-1}]	T [m^2 . s^{-1}]	Temperature at well head [°C]	Heat power [MWt]	TDS [g . l^{-1}]	Chemical water type
Levoča Basin W and S part												
Vrbov	Vr-1	1982	1,742	1,493-1,734	Triassic	dolomites	28.3	$2.40.10^{-3}$	56	4.86	4	Ca-Mg-HCO$_3$-SO$_4$
Vrbov	Vr-2	1989	2,502	1,539-1,983	Triassic	carbonates	33	$6.38.10^{-4}$	59	6.08	4	Ca-Mg-HCO$_3$-SO$_4$
Letanovce	HKJ-4	1989	607	408-589	Triassic	carbonates	8	$8.80.10^{-4}$	25	0.33	0.6	Ca-Mg-HCO$_3$
Arnutovce	HKJ-3	1990	1,133	489-1,133	Triassic	carbonates	11.8	$1.40.10^{-3}$	31	0.79	1.4	Ca-Mg-HCO$_3$
Poprad	PP-1	1994	1,205	634-1,128	Triassic	dolomites	61.2	$6.54.10^{-3}$	48	6.6	2.8	Ca-Mg-SO$_4$-HCO$_3$
Stará Lesná	FGP-1	1995	3,616	1,431-2,092	Triassic	dolomites	22	$5.41.10^{-4}$	58	3.95	3.2	Ca-Mg-HCO$_3$
Veľký Slavkov	VSČ-1	2007	2,400	1,877-2,353	Mesozoic	dolomites, limestones	27	$3.10.10^{-4}$	57	4.75	3.5	Ca-Mg-HCO$_3$
Danišovce	DH-1	1997	1,000	800-1000	Permian, Mesozoic	breccias, sandstones, shales	-		-	-	-	-
Veľká Lomnica	GVL-1	2006	2,100		Triassic	carbonates	35		62	6.88		
Levoča Basin NE part												
Plavnica	Pl-1	1988	3,500	2,306-3,360	Palaeogene, Triassic	sandstones, carbonates	5		65	12	10	Na-Cl
Plavnica	Pl-2	1989	3,500	2,500-3,010	Palaeogene, Triassic	sandstones, carbonates	4		53	0.57	12.3	Na-Cl
Lipany	L-1*****	1978	4,000	3,184-3,390	Triassic	dolomites	10	$1.87.10^{-4}$	85	2.93	9.4	Na-HCO$_3$-Cl-SO4
Lipany	L-2	1981	3,500	3,176-3,245	Triassic	dolomites	4.5		51	0.68	8.7	Na-Cl
Košice Basin												
Valaliky	KAH-3	1976	190	158-171	Neogene	sandy clay	7.2^{+}	$7.27.10^{-4}$	21	0.18	2.2	Na-Cl
Valaliky	KAH-5	1976	160	124-148	Neogene	gravels, sands	14.3^{+}	$1.19.10^{-3}$	21	0.36	0.7	Na-HCO$_3$
Šebastovce	KAH-6	1976	164	45-149	Neogene	gravels, sands	10^{+}	$2.44.10^{-3}$	18	0.12	3.6	Na-Ca-Cl-HCO$_3$
Košice	G-4	1982	310	72-273	Triassic-Permian	dolomites, palaeoandesites	4.9^{+}	$1.91.10^{-3}$	26	0.22	4.5	Na-Ca-Mg-HCO$_3$-Cl
Ďurkov	GTD-1	1998	3,210	2,109-3,155	Triassic	dolomites	56	$2.09.10^{-4}$	125	25	30	Na-Cl
Ďurkov	GTD-2***	1998	3,151	2,600-3,104	Triassic	dolomites	50	$1.34.10^{-4}$	129	24	30	Na-Cl
Ďurkov	GTD-3***	1999	2,252	2,223-2,246	Triassic	dolomites	65		123	29	31	Na-Cl
Humenne ridge												
Sobrance	TMS-1	1975	823	487-625	Neogene	sands. sandstones	4	$3.80.10^{-4}$	29	0.25	11.9	Ca-Na-Cl-SO$_4$
Kaluža	GTH-1	2005/2013	600/940.1	454-594; 600-836; 847-938	Mesozoic	dolomites, limestones	4^{+}	$4.15.10^{-5}$	39.4	0.41	13.9	Na-Cl
Central Slovakian Neogene volcanics NW part												
Kremnica	KŠ-1****	1976	531	476-531	Mesozoic	carbonates	23.2	$7.71.10^{-4}$	47	3.1	1.5	Ca-Mg-SO$_4$-HCO$_3$
Vyhne	H-1	1967	92	19-78	Triassic	limestones, dolomites	5	$5.73.10^{-3}$	36	0.44	1.1	Ca-Mg-HCO$_3$-SO$_4$

Locality	Borehole	Year of realization	Deep of borehole [m]	Open interval of borehole [m]	Age of aquifer	Lithology of aquifer	Yield [l . s^{-1}]	T [m^2 . s^{-1}]	Temperature at well head [°C]	Heat power [MWt]	TDS [g . l^{-1}]	Chemical water type
Vyhne	HGV-3	2009	64	46-54	Mesozoic	limestones	5.5 $^{+}$	2.05.10^{-2}	29	0.32	0.9	Ca-HCO_3
Zlatno	R-3	1975	710	660-710	Neogene, Triassic	palaeoandesites, dolomites	10		35	0.84	5	Ca-Mg-SO_4-HCO_3
Lukavica	LKC-4	1980	876	792-851	Triassic	carbonates	10	1.68.10^{-5}	35	0.8	0.4	Ca-Mg-HCO_3
Sklené Teplice	ST-4	1981	1,820	1,453-1,695	Triassic	carbonates	16	2.51.10^{-4}	57	3	2.6	Ca-SO_4-HCO_3
Sklené Teplice	ST-5	1987	1,001	800-1,001	Triassic	dolomites	4.4 $^{+}$	2.15.10^{-4}	46	0.57	2.7	Ca-Mg-SO_4-HCO_3
Sielnica	KMV-1	2004	417	353-407	Mesozoic	limestones	3	7.74.10^{-3}	33	0.23	2.2	Ca-SO_4
Topoľčianky	KD-1	1984	500	404-500	Triassic	dolomites	3.5		27	0.17	4.5	Ca-Mg-SO_4-HCO_3
Žiar nad Hronom	RGŽ-2	2000	2,500	-	-	-	-		-	-	-	-
Central Slovakian Neogene volcanics SE part												
Kalinčiakovo	HBV-1	1968	80	15-70	Triassic	limestones	25 $^{+}$		25	1.05	1	Ca-Mg-HCO_3-SO_4
Kalinčiakovo	HBV-2a	1968	65	11 to 49	Triassic	limestones	11.1 $^{+}$		25	0.46	1	Ca-Mg-HCO_3-SO_4
Santovka	B-3A	1998	73	45-64	Badenian	sandstones, lithothamnium limestones	15.5		26	0.71	5.7	Ca-Mg-HCO_3
Banská Štiavnica	HR-1	2005	910	748-829	Neogene	andesites, altered veins filling	12.5 $^{+}$	5.13.10^{-4}	46	1.62	2.4	Na-Ca-SO_4-HCO_3
Horné Strháre − Trenč Graben												
Dolná Strehová	M-4	1956	520	520	Neogene	sand	2.5		35.4	0.21	0.4	Na-HCO_3
Dolná Strehová	HGDŠ-1	1985	625	593-615	Neogene	sand	0.15/4.0 $^{+}$	8.85.10^{-4}	35.2	0.09/0.34	0.4	Na-HCO_3
Slovenské Kľačany	TSK-1	1991	600	500-560; 581-587	Neogene	sand	2	1.70.10^{-3}	38	0.2	0.7	Na-HCO_3
Vinica	HG-18		320		Neogene	sand	10		21	0.25	3.1	Na-HCO_3
Lučenec Basin – Rapovce structure												
Rapovce	GTL-2	2007	1,501	957-1,439	Triassic	carbonates	11.2	5.24.10^{-4}	38	1.04	12.6	Na-HCO_3
Rimava Basin												
Bátka	RKZ-1	1989	658	435-658	Triassic	carbonates	-		-	-	-	-
Tornaľa	HM-5	1973	158	155-157.5	Triassic	limestones	45	5.86.10^{-2}	18	0.56	1.8	Ca-HCO_3
Cakov	BČ-3	1984	876	489-874	Triassic	carbonates	3.3	1.74.10^{-4}	29	0.19	5.9	Ca-Mg-HCO_3
Rimavské Janovce	GRS-1	2003	2,020	767-1,008	Triassic	carbonates	10.5 $^{+}$	2.41.10^{-4}	33	1.01	1.7	Ca-Mg-HCO_3
Ivanice	FGRk-1	2007	1,050	618-1,050	-	-	-		-	-	-	-
Lučenec Basin – Rapovce structure												
Rapovce	GTL-2	2007	1,501	957-1,439	Triassic	carbonates	11.2	5.24.10^{-4}	38	1.04	12.6	Na-HCO_3

*Note: * – re-injection borehole, ** – geothermal observation borehole, *** – oblique well (perforated section corresponds to the length, not the depth), **** borehole developed from adit. ***** – structural-geological borehole, adapted in 2006 – 2008 as geothermal borehole, now 3,400 m deep, $^{+}$ – yield at pumping, ^{X} – collapsed borehole.*

of the coefficient of transmissivity contained greater share of sandy component, which deposited on the slope of the subsiding basin and finer particles of the pelitic component were deposited to larger distance from the basin edge. In evaluating the aquifers of each prospective geothermal area of Slovakia based on the T value (condition over 3 wells in the area) the Košická kotlina Basin seems to be the most favourable, followed by the Central Depression of the Danube Basin (Tab. 1.7). The drillings carried out in the Košická kotlina Basin were mainly located in the area of predominance of sand deposits transported by the then Hornád palaeoflow. The drillings in the Central Depression of the Danube Basin are distributed across the whole area with different proportion of sandy component. The depth of the wells in the Košická kotlina Basin ranges from 160 m to 190 m, while in the Central Depression the borehole depths are ranging from 290 m to 3,303 m and Md of the wells depth is 1,800 m.

The lowest value of the transmissivity coefficient T for Neogene sediments in the wells has been documented in the Central Depression of the Danube Basin – W and SE edge (Chorvátsky Grob – FGB-1) Strháre-Trenč Graben (Slovenské Kľačany – TSK-1) and Humenné Ridge (Sobrance – TNS-1).

The Neogene sediments (sands, sandstones, conglomerates) of the Western Carpathians have got an important position in the process of the mineral waters formation and their accumulation. First, they are aquifers of significant thicknesses in the basins and depressions, and secondly they were often deposited directly upon the Mesozoic basement of the Central and Inner Carpathians. This way, the basal clastics of Neogene together contribute to the genesis of the mineral waters of the Vienna Basin and Levice block. This fact is the best documented by sources of mineral water along the Levice-Turovce thermal Springs Line that stretches with the length of about 20 km. On this line surge out the mineral waters of varied chemical composition with very different content of CO_2, at many places this phenomenon is accompanied by deposition of travertine. The function of horst in all its length changes due to its gradual subsidence, but also due to a change in the nature of Mesozoic sediments. The Neogene sediments that overlay the western part of the Horst, are Sarmatian in age (tuffaceous siltstones and claystones) and in the

Tab. 1.6 The transmissivity coefficient for Mesozoic aquifers in Slovakia verified by deep boreholes

Age of aquifer	**Lithology of aquifer**		**Yield [l . s^{-1}]**	**T [m^2 . s^{-1}]**	**Temperature at well head [°C]**	**Heat power [MWt]**	**TDS [g . l^{-1}]**
Mesozoic	carbonates	n	77	56	77	76	76
		Min	1.6	$6.70 . 10^{-6}$	18.0	0.1	0.4
		Max	100.0	$9.25 . 10^{-2}$	129.0	29.0	90.0
		Md	12.4	$8.26 . 10^{-4}$	39.0	0.9	1.8
		Mn	19.4	$5.87 . 10^{-3}$	44.7	3.3	5.5
		G	12.3	$9.08 . 10^{-4}$	40.1	1.2	2.2
		σ / σ log T	19.0	0.90	23.1	5.7	11.9

*Note: **t** – transmissivity coefficient, **n** – count of boreholes, **Min** – minimum value, **Max** – maximum value, **Md** – median, **Mn** – arithmetic mean, **G** – geometrical mean,* σ *– standard deviation,* σ log T *– standard deviation of the transmissivity coefficient logarithm values, **TDS** – total dissolved solids*

Tab. 1.7 Values of geometric means of coefficient of transmissivity and standard deviation of the transmissivity coefficient logarithm values, calculated for different aquifer types of perspective geothermal areas in Slovakia

Perspective geothermal area	**Type of aquifer**	**n**	**G(T)**	**σ log T**
Komárno marginal block	C	3	$1.53 . 10^{-4}$	0.04
Liptovská kotlina Basin	C	4	$2.88 . 10^{-4}$	0.82
Central Depression of the Danube Basin	N	43	$5.27 . 10^{-4}$	0.57
Topoľčany embayment and Bánovská kotlina Basin	C	7	$5.32 . 10^{-4}$	1.16
Košická kotlina Basin – carbonates	C	3	$3.77 . 10^{-4}$	0.62
Košická kotlina Basin – Neogene sediments	N	3	$1.28 . 10^{-3}$	0.26
Central Slovakian Neogene volcanics NW part	C	7	$9.37 . 10^{-4}$	1.08
Levočská kotlina Basin W and S part	C	7	$1.11 . 10^{-3}$	0.44
Rimavská kotlina Basin	C	3	$1.35 . 10^{-3}$	1.42
Komárno high block	C	6	$2.42 . 10^{-3}$	0.9
Upper Nitra Basin	C	3	$3.73 . 10^{-3}$	1.33

*Note: **C** – Mesozoic carbonates with karst-fissure permeability, **N** – Neogene sediments with intergranular permeability, **n** – count of boreholes, **G(T)** – geometrical mean of the transmissivity coefficient **T** [m^2 . s^{-1}]; **σ log T**– standard deviation of the transmissivity coefficient logarithm values;*

Tab. 1.8 Values of standard specific capacities and geometric means of derived values of transmissivity and hydraulic conductivity coefficients, calculated for aquifers of the Inner Carpathian Palaeogene & Buda Palaeogene sediments in Slovakia (Malík et al., 2007)

No.	Description	Origin and classification	Group	n	M[1q]	Md[1q]	G[T]	σ log T	G[K]
58	Calcareous siltstones and claystones, occasionally with coal intercalations	Shallow sea sediments of the Buda Palaeogene	PG	116	0.054	0.068	$1.15 . 10^{-4}$	0.92	$4.66 . 10^{-6}$
59	Sands, marly and calcareous sands, decomposed sandstones and siltstones	Shallow sea sediments of the Buda Palaeogene	PG	16	0.126	0.141	$3.44 . 10^{-4}$	0.56	$1.29 . 10^{-5}$
60	Gravels, decomposed conglomerates	Shallow sea sediments of the Buda Palaeogene	PG	3	0.151	0.120	$1.40 . 10^{-4}$	0.25	$1.34 . 10^{-5}$
61	Claystones, calcareous claystones and marls and layers with overwhelming claystones/ marlstones over sandstones, including menilite layers	Marine sediments of Inner Carpathian Palaeogene	PG	127	0.107	0.117	$1.73 . 10^{-4}$	0.81	$1.39 . 10^{-5}$
62	Claystone flysch – flysch with prevailing claystones or marlstones	Flysch sediments of Inner Carpathian Palaeogene and Late Cretaceous	PG	7	0.010	0.012	$9.60 . 10^{-6}$	0.57	$4.70 . 10^{-7}$
63	Normal flysch – claystones/marls, siltstones	Flysch sediments of Inner Carpathian Palaeogene and Late Cretaceous	PG	220	0.102	0.102	$1.49 . 10^{-4}$	0.77	$1.11 . 10^{-5}$
64	Sandstone flysch – flysch with prevailing sandstones	Flysch sediments of Inner Carpathian Palaeogene and Late Cretaceous	PG	13	0.120	0.100	$1.21 . 10^{-4}$	0.65	$5.51 . 10^{-6}$
65	Conglomerate flysch – flysch with prevailing conglomerates	Flysch sediments of Inner Carpathian Palaeogene and Late Cretaceous	PG	4	0.158	0.178	$3.94 . 10^{-4}$	0.62	$2.06 . 10^{-5}$
66	Sandstones with thin intercalations of claystones	Flysch sediments of Inner Carpathian Palaeogene and Late Cretaceous	PG	120	0.123	0.145	$2.02 . 10^{-4}$	0.74	$7.92 . 10^{-6}$
67	Multicomponent conglomerates and breccias, variably with beds of sandstones	Sea sediments and subaqueous slides of Inner Carpathian Palaeogene	PG	17	0.068	0.078	$7.70 . 10^{-5}$	0.80	$3.68 . 10^{-6}$
68	Calcareous breccias and conglomerates, sandy limestones, and limestones, variably with beds of sandstones, occasionally also marlstones	Sea sediments of Inner Carpathian Palaeogene and Late Cretaceous	PG	60	0.251	0.209	$3.58 . 10^{-4}$	0.99	$1.58 . 10^{-5}$

Explanation of abbreviations: ***n*** *– number of interpreted hydraulic tests on hydrogeological boreholes and wells;* ***M(¹q)*** *– arithmetic mean of the standard specific capacity* ***¹q*** *[l . s⁻¹ . m⁻¹];* ***Md(¹q)*** *– median value of the standard specific capacity* ***¹q****;* ***G(T)*** *– geometrical mean of the transmissivity coefficient* ***T*** *[m² . s⁻¹]; σ log* **T** *– standard deviation of the transmissivity coefficient logarithm values;* ***G(K)*** *– geometrical mean of the hydraulic conductivity coefficient* ***K*** *[m . s⁻¹];* ***PG*** *– group of Palaeogene sediments.*

Tab. 1.9 Characteristics of the Neogene sedimentary aquifers verified through deep boreholes

Age of aquifer	Lithology of aquifer		Yield [l . s⁻¹]	T [m² . s⁻¹]	Temperature at well head [°C]	Heat power [MWt]	TDS [g . l⁻¹]
Neogene	sediments	n	58	49	58	57	58
		Min	0.3	$4.17 . 10^{-5}$	18.0	0.01	0.4
		Max	25.0	$6.93 . 10^{-3}$	91.0	6.8	30.0
		Md	10.0	$5.14 . 10^{-4}$	52.0	1.6	2.6
		Mn	10.5	$1.02 . 10^{-3}$	52.1	1.9	4.2
		G	7.7	**$5.35 . 10^{-4}$**	47.4	1.0	2.6
		σ / σ log T	6.9	0.51	20.3	1.8	5.3

Note: ***n*** *– count of boreholes,* ***Min*** *– minimum value,* ***Max*** *– maximum value,* ***Md*** *– median,* ***Mn*** *– arithmetic mean,* ***G*** *– geometrical mean, σ – standard deviation, σ log T – standard deviation of the transmissivity coefficient logarithm values* eastern part Badenian in age (epiclastic sandstones). The complexity of geological and tectonic structure of the area is a reflection of orogenic processes, where one part of the territory subsided (Danube Basin), other on was lifted up (*Štiavnica* Stratovolcano). The presence of multiple aquifers with varied nature of the water in terms of the chemical and isotopic composition portrays well the complexity of forming of different chemical types of the mineral waters of the Western Carpathians.

1.4.5 Aquifers of mineral waters in neovolcanites

The complex is characterized by neovolcanite rocks of fissure-intergranular permeability. The regional tectonic lines are essential elements in the accumulation and distribution of mineral waters either due to complex neovolcanic rocks as well as the basement, which is built of Mesozoic sediments and rocks of Crystalline. Therefore sources of mineral waters are often present in the rock environment of neovolcanites which have their origin in the bedrock formed by Mesozoic rocks as in the case of sources Kremnica – KŠ-1, Vyhne – H-1, Vyhne – HGV-3, Lukavica – LKC-4, Sklené Teplice – ST-4 and Sklené Teplice – ST-5.

The greatest potential for accumulation of mineral water in rock complexes of the Central Slovakian neovolcanites, which contributed to the formation of mineral waters in Santovka – Dudince area, have Badenian volcanic epiclastics. These sediments fill the depression at the contact of neovolcanites with their basement. Tuffaceous sandstones were documented by 80 m deep borehole Dvorníky – HG-3 northeast of Dudince. Pumping tests lasting 16 days documented yield $Q = 10.5\ l\ .\ s^{-1}/s = 7.5$ m. The value of the coefficient of hydraulic conductivity for these aquifers was $k = 8.10^{-5}\ m\ .\ s^{-1}$ and of the transmissivity coefficient $T = 3.24\ .\ 10^{-3}\ m^2\ s^{-1}$. The water was of chemical type Ca-HCO_3 and TDS amounted to 0.32 g . l^{-1} (Hlavatý & Fecek, 1973). The wells HT-1 and HIP-13 in Hontianske Trsťany were 150 m and 173 m deep; they documented the tuffaceous sand to sandstone of thicknesses of 40 m and 120 m. For the well-HT 1 it was documented yield $Q = 12\ l\ .\ s^{-1}/s = 1.43$ m by hydrodynamic test lasting 36 days. The water was of chemical type Ca-Na-HCO_3 with TDS 0.54 g . l^{-1}. The evaluation of the pumping test gave the value of coefficient of hydraulic conductivity $k = 6.25\ .\ 10^{-5}\ m\ .\ s^{-1}$ and transmissivity coefficient $T = 2.07\ .\ 10^{-2}\ m^2\ .\ s^{-1}$ (Lauko & Novomestská, 1989). 30 days-long hydrodynamic test in the borehole HIP-13 documented yield $Q = 5.7\ l\ .\ s^{-1}/s = 6.5$ m (s = drawdown). The water was of chemical type Ca-HCO_3 with TDS 0.56 g . l^{-1} and temperature 17 °C. Hydraulic parameters determined from the evaluation of the pumping tests gave coefficient of hydraulic conductivity $k = 3.33\ .\ 10^{-5}\ m\ .\ s^{-1}$ and transmissivity coefficient $T = 2.47.10^{-3}\ m^2\ .\ s^{-1}$ (Fecek et al., 1981).

The aquifers of mineral waters in neovolcanites (Badenian andesites) documented by deep borehole Rusovce – HGB-1 in the Danube Basin reached a value of the transmissivity coefficient $T = 1.14\ .\ 10^{-5}\ m^2\ .\ s^{-1}$ (Bondarenková et al., 1977). Tectonic affected neovolcanites rock complexes in Banská Štiavnica were explored by borehole HR-1. Hydrodynamic tests documented favourable conditions for the accumulation of mineral water in altered andesite vein filling and the coefficient of transmissivity $T = 5.13\ .\ 10^{-4}\ m^2\ .\ s^{-1}$ (Remšík et al., 2007).

1.5 Conclusions

The richness of any country in the incidence of sources of mineral waters is either a manifestation of specific natural conditions or technical maturity. In the Slovak conditions the number of natural sources clearly outweighs the artificial ones; however, the physical state of some of them is not very good. By the inventory of the sources of mineral water in 1997-2000, 1,687 sources were documented in Slovakia; 111 were not found, 297 expired and 30 have been destroyed. Among the 111 not found sources 80 accounted for springs and 27 for wells; 4 of them were dug wells. In some places there occurs a destruction of natural sources due to various factors, but still there is a need to implement new sources to ensure supplies for the purposes of filling the mineral waters into the consumer packaging, for medical care, recreation and use of their thermal-energy potential.

The largest representation of mineral waters in Slovakia is recognized in the zones of the Central Western Carpathians (43 %), of which account for most of the sources Inner Carpathian Palaeogene (24.1 %) and Mesozoic sediments (15.2 %). The smallest number of sources accounted for metamorphic rocks (3.2 %) and magmatic rocks (1.5 %). The second most numerous sources of mineral water fall within Neogene sediments (31.7 %). This structural-geological facies manifests the largest representation of the mineral water sources that have been acquired through technical works (the number of wells far outweighs the number of springs). The third and fourth most numerous sources of mineral water fall within the Flysch Zone (13.3 %) and Neovolcanites (6.8 %). The lowest representation of mineral water is within the Klippen Belt (4.2 %).

The mineral water sources in Slovakia are characterized by quite a varied representation of chemical water types with a wide range of TDS, temperature and yield. Colourful presence of chemical types of mineral water depends on the nature of the aquifers of mineral water, the tectonic disturbances and storage conditions at depth.

Individual structural-tectonic zones of the Western Carpathians in Slovakia are characterized by representation of mineral waters of different chemical types. In the Flysch Zone in the near-surface zone chemical type Ca-HCO_3 is dominant, while with the increasing depth the share of the component A_1 increases according Palmer-Gazda classification of groundwater. Some sources with shallow water circulation exhibit H_2S presence. On major fault lines emerge waters of chemical type Na-HCO_3 and Na-HCO_3-Cl, eventually Na-Cl-HCO_3. An interesting feature is the presence of mineral water of chemical type Mg-SO_4-HCO_3 (Zbudský Rokytov) or the presence of thermal water of chemical type Na-Cl in the well FPJ-1 in Oravská Polhora with TDS up to 50 g . l^{-1} and a water temperature of 31.3 °C, which was documented in the sediment of the Obidowa-Słopnice-Zboj unit.

Mineral waters of the Klippen Belt with shallow ground water circulation are of dominant chemical types Ca-Mg-HCO_3 and Ca-Na-HCO_3. Waters with deeper circulation, surging along the tectonic lines are of chemical-type Na-HCO_3 (Nimnica) and Ca-Mg-HCO_3-SO_4 (Mojtín). Water from Belušské Slatiny descends into greater depth and at the surface it reaches a temperature of 21.5 °C.

In the zone of the Central Western Carpathians thanks to its variegated rock representation there are present the most chemical types of mineral waters. The mineral waters of Crystalline with shallow circulation are of chemical types Ca-Mg-HCO_3 and Na-HCO_3. At greater depth, and within the tectonic zones the water of chemical type Na-HCO_3 is present with water temperature up to 25 °C. In the Vlachovo and Čučma a province of nitrogen acratotherms has been earmarked. The Mesozoic sediments of the Krížna Nappe are characterized by mineral waters of chemical type Ca-Mg-HCO_3-SO_4, which in the case of deep circulation reach a temperature of 33 – 53 °C. Carbonated mineral waters of this nappe are of the same chemical type, but achieve a lower temperature of 20 – 45 °C. In the Plavnica – Lipany area, near the Klippen Belt the Mesozoic sediments Krížna Nappe were verified by wells of depth of 3,500 m to 4,000 m in the bedrock of the Inner Carpathian Palaeogene sediments. These Mesozoic sediments are water-saturated and the water is of chemical types Na-HCO_3-Cl-SO_4 and Na-Cl. Mesozoic sediments of the Choč Nappe are characterized by the presence of acratotherms of chemical type Ca-Mg-HCO_3. At some places (e.g. Kalinčiakovo, Vyhne) from the Mesozoic sediments of the Choč Nappe surge mineral waters of chemical type Ca-Mg-HCO_3-SO_4. Carbonic and weakly mineralized mineral waters of the Mesozoic sediments of the Choč Nappe are of chemical types Ca-Mg-HCO_3, Ca-Mg-HCO_3 and Ca-Mg-HCO_3-SO_4. The carbonates of the Hungarian Central Highlands in the area of Patince – Komárno bind thermal waters (20 – 40 °C).

Mineral waters Inner Carpathian Palaeogene are characterized by the presence of mineral water of chemical types Ca-Mg-HCO_3 and Na-HCO_3; sometimes even with the presence of H_2S. Cold carbonated waters are of che- mical types Ca-Mg-HCO_3, Ca-Mg-Na-HCO_3 and in contact with the Hornádska kotlina Basin and Branisko Mts. surge mineral waters of chemical type Ca-Mg-Na-HCO_3-Cl (Slatvina, Vojkovce). Neogene sediments have a wide representation of chemical types of mineral water with a wide range of TDS. Mineral waters with shallow circulation are the chemical type Ca-Mg-HCO_3 and with increasing depth they are enriched in component A_1 according to Palmer-Gazda classification of groundwater. In the Záhorská nížina Lowland the mineral waters from greater depths are of chemical types Ca-SO_4, Na-SO_4. At great depths of the Neogene basin we encounter the highly mineralized waters of chemical type Na-Cl. While in the case of the Central Depression of the Danube Basin and Záhorská nížina Lowland the waters are with thalassogenic mineralization, in the case of the Eastern Slovakia Basin dominate the water with halitogenic mineralization.

Nature of water from neovolcanites is greatly influenced by their deep position. Mineral waters of shallow circulation are of chemical types Ca-Mg-HCO_3, Ca-Mg-Na-HCO_3 Na-Ca-Mg-HCO_3. The mineral waters of deeper circulation reach higher temperatures and are of chemical type Na-Ca-SO_4-HCO_3. Provided the neovolcanites complex is a part of the sedimentary basin fills then the waters are of chemical type Na-Cl or with thalassogenic or halitogenic mineralization.

The most important aquifers from the genetic viewpoint of mineral waters in Slovakia are the Mesozoic sediments of the Central Western Carpathian and the Neogene sediments of the basins filling.

For the Crystalline aquifers (metasomatic limestone in phyllites of the Gelnica Series), the borehole GVL-1 in Vlachovo gave the transmissivity coefficient $T = 1.15 \cdot 10^{-3}\ m^2 \cdot s^{-1}$. Favourable characteristics for accumulation of mineral water were also found from at the contact of greisens with the phyllites of the Gelnica Series (RS-1 borehole Čučma).

The Mesozoic aquifers (limestones and dolomites) of the mineral waters have been verified by 79 hydrogeological boreholes (56 pumping tests) and the value of the geometric mean of the transmissivity coefficient $G(T) = 9.08 \cdot 10^{-4}\ m^2 \cdot s^{-1}$. Drillings carried out in the environment of Mesozoic carbonates are also reported to have relatively large yields (Md Q = 12.4 l . s^{-1}/Mn Q = 19.4 l . s^{-1}), whereas the most productive is the borehole OZ-2 in *Oravic*e (Q = 100 l . s^{-1}).

For the Inner Carpathian Palaeogene aquifers (sandstones, conglomerates, breccias), the transmissivity coefficient T value was obtained for the elevation part of the bedrock within the discharge area of Malé and Veľké Bielice. The value of this indicator ranges from $2.81 \cdot 10^{-3}\ m^2 \cdot s^{-1}$ to $3.11 \cdot 10^{-3}\ m^2 \cdot s^{-1}$. Specified range of values for faulted breccia exceeds the value of $G(T) = 3.58 \cdot 10^{-4}\ m^2 \cdot s^{-1}$ obtained for a set of wells to which data were available from 60 pumping tests across Slovakia.

The Neogene sedimentary aquifers (sands, sandstones, conglomerates) of the mineral waters have been verified by 58 hydrogeological boreholes (49 pumping tests) and the value of the geometric mean of the transmissivity coefficient $G(T) = 5.35 \cdot 10^{-4}\ m^2 \cdot s^{-1}$. The drillings carried out in the Neogene sediments environment achieved balanced yield (Md Q = 10.0 l . s^{-1}/Mn Q = 10.5 l . s^{-1}), whereas the most productive wells FGG-2 and FGG-3 are in Galanta (Q = 25 l . s^{-1}).

The neovolcanites aquifers (volcanic epiclastics) of mineral waters, which are involved in the formation of the mineral water in Santovka – Dudince have been verified by 3 hydrogeological boreholes 80-173 meters deep. The values of the transmissivity coefficient $T = 2.47 \cdot 10^{-2}\ m^2 \cdot s^{-1}$ to $T = 2.07 \cdot 10^{-2}\ m^2 \cdot s^{-1}$. These aquifers (Badenian andesites) were encountered by deep borehole HGB-1 in Rusovce in the Danube Basin; the value of the transmi- ssivity coefficient $T = 1.14 \cdot 10^{-5}\ m^2 \cdot s^{-1}$. In the area of Banská Štiavnica in the tectonically affected neovolcanite rock complexes the transmissivity coefficient $T = 5.13 \cdot 10^{-4}\ m^2 \cdot s^{-1}$.

1.6 References

Andrusov, D., 1958: Geológia československých Karpát I. SAV Bratislava. 304 p.

Biely, A. (editor), Bezák, V., Elecko, M., Kaliciak, M., Konecný, V., Lexa, J., Mello, J., Nemcok, J., Potfaj, M., Rakús, M., Vass, D., Vozár, J., Vozárová, A., 1996: Geological Map of Slovakia 1:500 000, Ministry of Environment of Slovak Republic, State Geological Institute of Dionýz Štúr, Bratislava, (explanations in Slovak and English).

Bondarenková, Z.,Franko, O., Hramec, J., Zbořil, Ľ, Motlíková, H., 1977: Bratislava – Rusovce – geotermálny vrt HGB-1. Vyhľadávací hydrogeologický prieskum. Účel: Možnosti získať termálnu vodu v tejto oblasti. Slovenský geologický úrad; Bratislava. IGHP; Žilina:. VIKUV Budapešť. Geofond Archive (ID 48993). 39 p.

Brodňan, M. & Nemsilová, M., 1960: Štúrovo – Podunajská nížina – hnedé uhlie. Záverečná správa. Geofond, Bratislava.

Fecek, P., Ďungelová, H., Droppa, V., 1981: Neogén Ipeľskej pahorkatiny. Vyhľadávací hydrogeologický prieskum – pitná voda. Cieľ: Zhromaždenie a spracovanie prvotných a druhotných informácií k následnému zhodnoteniu klimatických, hydrologických, geologicko-litologických, hydrogeologických a hydrochemických pomerov územia, s vyčíslením prírodných zdrojov a využiteľného množstva ako i rámcového stanovenia ochrany podzemných vôd pre kategóriu C2. IGHP, Žilina. SGO, Bratislava. Geofond Archive (ID 58410). 165 p.

Franko, O. & Bodiš, D., 1989: Paleohydrogeology of Mineral Waters of the Inner West Carpathians. Západ. Karpaty. Séria Hydrogeológia a inžinierska geológia 8. p. 145 – 163.

Franko, O. & Melioris, L., 2000: Minerálne a termálne vody Slovenska – vznik a rozšírenie. Podzemná voda VI./2000 Č. 1. Slovenská asociácia hydrogeológov. p. 5 – 28.

Franko, O. & Snopko, S., 1979: Dusíkové akratotermy v Spišsko-gemerskom rudohorí (Nová hydrogeochemická provincia minerálnych vôd kryštalinika Západných Karpát). Geologické práce, Správy 72. Geologický ústav Dionýza Štúra. p. 149 – 168.

Franko, O., Gazda, S ., Michalíček, M., 1975: Tvorba a klasifikácia minerálnych vôd Západných Karpát. Geol. ústav D. Štúra Bratislava. 230 p .

Hlavatý, Z. & Fecek, P., 1973: Dvorníky – doplňujúci hydrogeologický prieskum. Cieľ: Zabezpečenie náhradného vodného zdroja pre vodovod Dudince. IGHP, Bratislava. Geofond Archive (ID 29605), 9 p.

Jetel, J., 1999: Hydrogeologická a hydrogeochemická mapa Ľubovnianskej vrchoviny a Pienin 1 : 50 000 – textové vysvetlivky. Geofond, Bratislava.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1977: Minerálne vody I., Osveta Martin.436 p.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1978: Minerálne vody II., Osveta Martin.1040 p.

Krásný, J., 1993: Classification of transmissivity magnitude and variation. Ground Water, 31, 2, p. 230 – 236.

Lauko, V., & Novomestská, D., 1989: Hontianske Trsťany – vyhodnotenie hydrogeologického prieskumného vrtu HT-1. Hydrogeologický prieskum. Ciel: Overiť možnosti získania zdroja pitnej a úžitkovej vody. Vodné zdroje, Bratislava. Geofond Archive (ID 70951). 16 p.

Maheľ, M., 1952: Minerálne pramene Slovenska so zreteľom na geologickú stavbu. Práce ŠGÚ. 62 p.

Malík, P., Bačová, N., Hronček, S., Ivanič, B., Kočický, D., Maglay, J., Malík, P., Ondrášik, M., Šefčík, P., Černák, R., Švasta, J. & Lexa, J., 2007: Zostavovanie geologických máp v mierke 1 : 50 000 pre potreby integrovaného manažmentu krajiny [Composition of geological maps at a scale of 1 : 50,000 for the landscape management needs, in Slovak]. Manuscript, Geofond Archive of the SGIDŠ, No. 88158, 554 p.

Marcin, D., Cicmanová, S., Olekšák, S., Bajtoš, P., Teťák, F., 2005: Základná hydrogeologická a hydrogeochemická mapa pohoria Čergov v mierke 1 : 50 000. Čiastková záverečná správa. Geofond Archive, Bratislava. 132 p.

Nemčok, J., Zakovič, M., Gašpariková, V., Ďurkovič, T., Snopková P., Vrana, K., Hanzel, V., 1990: Vysvetlivky ku geologickej mape Pienin, Čergova, Ľubovnianskej a Ondavskej vrchoviny. V mierke 1 : 50 000. Geologický ústav Dionýza Štúra, Bratislava. 131 p.

Rebro, A., Matejčeková, E., Bergerová, A., Frnčo, M., 1989: Nimnica – prieskumno-exploatačný vrt B-10 na minerálnu vodu v kúpeľoch. Podrobný inžinierskogeologický prieskum. IGHP, Žilina. Geofond Archive (ID 70913). 28 p.

Rebro, A., Matejčeková, E., Jurdík, M., Židek, L., 1978: Nimnica – vrt B-7 a B-8, balneologický prieskum, účel: vybudovanie nových zdrojov minerálnych vôd. Predbežný hydrogeologický prieskum. IGHP, Žilina. Geofond Archive (ID 40560). 34 p.

Remšík, A., Malík, P., Bajtoš, P., Rapant, S., Bottlik, F., Bačová, N., Michalko, J., Benková, K., Krčmová, K., Fendek, M., Marcin, D., Černák, R., Helma, J., Šimon, L., Mrosko, J., Moravská, A., Maďar, D., Weis, K., Grand, T., Ujpál, Z., Šivo, A., Richtáriková, M., Jánošík, E., Kováčik, J., Daříček, A., 2007: Neovulkanity severných svahov Štiavnických vrchov. Vyhľadávací hydrogeologický prieskum. Zodpovedný riešiteľ: A. Remšík. MŽP SR Bratislava; SGIDŠ, Bratislava. Geofond Archive (ID 88800), 224 p.

Urban, K., Malý, J., Pavúr, K., 1962: Nosice – správa o hydrogeologickom prieskume minerálnych prameňov 1958 – 1961. Geologický prieskum, Žilina. Geofond Archive (ID 8730). 65 p.

Teťák, F., Kováčik, M., Pešková, I., Nagy, A., Buček, S., Maglay, J., Vlačiky, M., Laurinc, D., Žecová, K., Zlinská, A., Liščák, P., Marcin, D., Žilka, A., Kucharič, Ľ., Gluch, A., Baláž, P., 2016: Vysvetlivky ku geologickej mape regiónu Biela Orava. MŽP SR a ŠGÚDŠ, Bratislava, 217 s. (Explanations to the Geological Map of the Biela Orava region), p. 144-148. ISBN 978-80-8174-016-9.

Zakovič, M., Bodiš, D., Fendek, M., Potfaj, M., Gabauer, G. & Bálint, J., 1988: Geologický výskum jódo-brómových vôd vo vybraných oblastiach SSR. Manuskript – archív SGIDŠ Bratislava, 68 p.

Zakovič, M., Halečka, J., Marcin, D., 2006: Podklady pre návrh ochranných pásiem zdroja prírodnej minerálnej vody Veronika (LZ-6) v Ľubovnianskych kúpeľoch. Podzemná voda XII./2006 Č. 2. Slovenská asociácia hydrogeológov. p. 156 – 167.

Zakovič, M., Hanzel, V., Gazda, S., 1993: Vysvetlivky k hydrogeologickej mape v mierke 1:50 000 – Levočské vrchy. Geofond, Bratislava.

Zakovič, M., Potfaj, M., Fendek, M., Bodiš, D., 2009: Jódo-brómové podzemné vody v oblasti Oravskej Polhory. Podzemná voda XV 2/2009. Slovenská asociácia hydrogeológov. p. 230 – 239.

Zeman, M., Machková, N., Trulíková ml, B., Švaralová, M. & Weissensteiner, J., 2000: Minerálne pramene Slovenskej republiky. SAŽP, Banská Bystrica. /http://www.sazp.sk/slovak/struktura/ceev/DPZ/pramene/pramene.html/.

Slovak Geol. Mag., 16, 2 (2016), 27 – 40

Beginnings of the Isotope Research of Mineral and Thermal Groundwaters of Slovakia

Juraj Michalko

State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Mlynská dolina 1, 817 04 Bratislava, Slovakia; juraj.michalko@geology.sk

Abstract: The period from late 60s to mid-eighties of the 20th century in Slovak conditions can be regarded in terms of knowledge of the isotopic composition of mineral water as pioneer years. The first data from the turn of the 60/70's come from foreign authors, although the department dealing with the isotope geology at that-time GIDŠ existed since the mid-50s. It was, however, designed to date the K/Ar method and research deposits (isotopes of Pb, S). Oriented research, including mineral waters, has developed after investment into the instrumentation and sample preparation facilities in mid-80's. The results were published just in reports and later only partly quoted by other authors. The article summarizes the state of knowledge of the isotopic composition of mineral water and dissolved substances in them in the mid-eighties of the last century.

Key words: mineral waters, O and H isotopes, sulphate, hydrogen sulphide, Slovakia

2.1 Introduction

Mineral and thermal waters in Slovakia are an important phenomenon. The complex geological structure of the Western Carpathians with typical tectonic evolution and favourable climatic conditions in the past and now have created conditions for the emergence of a diverse range of hydrogeological structures, and consequently the groundwater sources of different genetic types. The diverse rock environment, often coupled with pervasive CO_2 and higher temperatures creates favourable conditions for the development of mineral and thermal waters with varied chemical composition, often with beneficial effects on the human health. Knowledge of the distribution of stable and radioactive isotopes in the water and the rock environment along with hydrogeology and hydrogeochemistry provide one of the important tools in understanding the characteristics, origin, genesis, time delays and pathways for circulation of mineral water, and thus contribute to improving the protection and use of this natural wealth.

Isotopic research in Slovakia began in the mid-50s of the last century. Workplace built in the predecessors of the SGIDŠ was focused on geochronology (K-Ar method) and research of deposits (isotopes of S and Pb). The first analyses of mineral waters came mainly from foreign authors. Upon the upgrade of the facility and methodological upgrade of the department at the turn of the 70/80's of 20th century a considerable attention was paid to the study of stable isotopes (O, H, C, S) in the waters, of course, including the mineral, thermal and geothermal ones. The results are usually published only in reports, which were from time-to-time quoted cited. The article summarizes and illustrates the state of isotope research in the field of mineral and thermal waters in Slovakia in the mid-80s of the 20th century.

2.2 Isotope research of waters in Slovakia

Knowledge of the distribution of isotopes in nature and their patterns are closely linked to the development of chemistry, and particularly physics from the late 19th century. Since the beginning these lessons were used (directly or indirectly) to solve the problems of geological character. A significant shift in the use of radioactive and stable isotopes in geological practice occurred at the beginning of the second half of the last century when practically usable mass spectrometer was constructed, the necessary theoretical background was compiled and preparation procedures and relevant international standards were prepared.

This trend has also caught SGIDŠ, where since the mid-50s Dr. Ing. Kantor developed Department of Isotope Geology, focusing on the dating of rocks (K-Ar, Pb-Pb) and research in ore deposits (isotopes Pb and S). At the turn of 70/80s, the analytical base was expanded on new mass spectrometer to measure stable isotopes of light elements (Finnigan MAT 250) and methods for measuring the isotopic composition of H, O, S, C (lately N) in different geological materials have been developed including water and substances dissolved therein. Despite repeated attempts measurement of δ^2H using reduction method did not provide results with sufficient reproducibility, and thus data on hydrogen isotopic composition of water are rare. Their measurement was resumed in the second half of the 90s and later, especially after getting analysers LWIA and IR (isotope ratio) of the spectrometer DELTA Advantage. It is now possible to measure the isotopic composition of H, O, C, N, S in water and components dissolved in it, and in other geological materials (sulphides, sulphates, carbonates, shells, gases).

Waters dating based on the activity of tritium was addressed by NRL WRI, ^{14}C dating by the Department of Nuclear Physics FMFI of Comenius University, Bratislava .

Accurate measurement of isotopes (isotope ratio) in natural substances requires extensive analytical tools, either from the viewpoint of samples adjusting to the measuring environment, or in terms of the measurements of the isotopic composition itself. Also for these reasons, knowledge of isotopic composition in hydrogeological practice in Slovakia was enhanced gradually. Currently, rapid development of technology simplifies and facilitates the acquisition of isotopic data, which consists in the application of isotopes of other elements (e.g. He, B, Li, Cl, Ar, noble gases), both in accessibility (decreasing price of analyses) of data from the "classic" sphere. Isotope geology becomes more and more adopted discipline and in many countries collecting data on the isotopic composition of precipitation, surface water, selected sources of mineral, thermal and ordinary groundwaters has become standard part of state monitoring. Since 1961 the International Atomic Energy Agency at UNESCO organizes observation networks for monitoring the isotopic composition of water in the different phases of the hydrological cycle: precipitation (GNIP), rivers and creating further GNIR (air humidity, plants..).

In Slovakia (Department of Isotope Geology at SGIDŠ) the relevant analytical and interpretative base for monitoring the isotopic composition of waters was developed in early 80s, since then the amount of data on the isotopic composition of various genetic types of water, including mineral and thermal water has gradually expanded, and correspondingly increase the amount of respective knowledge. Data on the isotopic composition of water from the previous period is patchy and usually came from foreign authors.

2.3 Regional selective characteristics of the isotopic composition of mineral and thermal waters in Slovakia

First knowledge of the isotope composition of mineral and thermal waters in Slovakia are dated back to the turn of 60s of the last century. This includes nationwide selective characteristics of selected sources – to analyse the isotopic composition by the then-available methodology the authors chose important or most interesting sources of mineral and thermal waters from the entire territory of Czechoslovakia. In that period Slovakia accounted for about one third of the national territory. From geological point of view the whole territory of Slovakia belongs to the Western Carpathians within which the easternmost parts of the Czech Republic fall, as well. In this category of activities in the field of isotope characteristics of mineral and thermal waters in Slovakia notable were works by Barnes & O'Neil in Čadek & Pačes, (1976), Šmejkal et al. (1971 and 1981), Kantor (1985).

The isotopic composition of hydrogen, oxygen and dissolved inorganic carbon (DIC) in selected sources of mineral and thermal waters (32) in California, the Czech Republic and Slovakia was deal with Barnes & O'Neil in Čadek & Pačes, (1976). From Slovakia 14 sources were sampled from major spas and also geothermal well in Patince (Tab. 2.1). Among the Slovak sources the authors (Barnes & O'Neil in Čadek & Pačes, 1976) included four sources, which are located on the Moravian side of the Carpathians (depicted in Tab. 2.1 by * and in the Fig. 2.1 by squares). Based on the proximity to a Global Meteoric Water Line (GMWL) almost all investigated waters are derived from local precipitation. The exception are waters from Luhačovice, Napajedla and Bardejov Spa (in Fig. 2.1 they deviate from GMWL), in which they assumed the formation of the final composition as a result of mixing of local groundwater of meteoric origin with metamorphic waters (arrows in Fig. 2.1) with similar composition as a water source Soda Spring in Fort Bragg, California (Fig. 2.1). Currently, the endmember considers water with

Tab. 2.1 Stable isotope data from Slovak mineral and thermal groundwaters. * sources from part of the Western Carpathians belonging to the territory of the Czech Republic (from Barnes & O'Neil in Čadek & Pačes, 1976)

Locality	$\delta^{13}C_{DIC}$ PDB [‰]	$\delta^{2}H_{H2O}$ SMOW [‰]	$\delta^{18}O_{H2O}$ SMOW [‰]	t [°C]	HCO_3^- [$mg \cdot l^{-1}$]	Cl^- [$mg \cdot l^{-1}$]	Rock environment
Bardejov Spa	-0.5	-61.1	-6.1	11	300	460	Flysch
Korytnica	-3.6	-68.3	-10.3	7	1,200	4	Dolomite
Nosice	-3.8	-69.7	-10.3	11	2,244	81	Flysch
Trenčianske Teplice	-6.9	-71.0	-10.4	40	420	100	Flysch
Vyšné Ružbachy	0.2	-73.5	-10.7	20	1,150	18	Limestone, dolomite
Martin	-2.6	-76.2	-11.0				Lacustrine, underlain by flysch
Liptovský Ján	-1.3	-73.9	-10.9	29	2,060	24	Dolomite
Piešťany	-7.3	-78.3	-11.3	65	260	110	Limestone, dolomite
Kováčová	-9.5	-78.3	-11.3	46	732	4	Dolomite
Sliač	-2.6	-80.4	-11.8	33	1,195	51	Tuff, sandstone
Dudince	-2.5	-80.5	-11.4		3,000	320	Quartzite, limestone
Sivá Brada	-0.2	-82.9	-11.5	12	3,900	290	Flysch
Komárno	-4.2	-88.0	-12.0	48	561	490	Limestone, dolomite
Patince	-9.0	-75.5	-10.8		460	24	Alluvium
Darkov *	-11.3	-42.0	-6.2	12	230	12,200	Flysch
Luhačovice *	1.1	-51.2	-1.9	11	5,100	2,281	Flysch
Napajedla *	3.6	-54.2	-5.4	15	2,700	1,450	Flysch
Teplice nad Bečvou*	-3.8	-71.5	-10.4	22	1,900	39	Greywacke

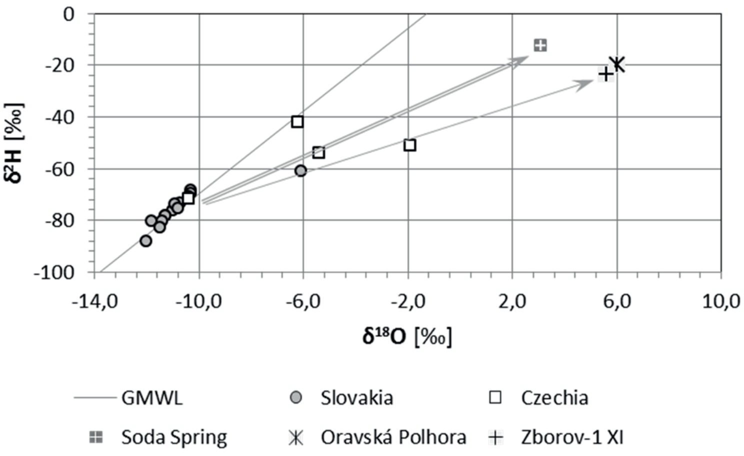


Fig. 2.1 Isotope composition of mineral waters of Slovakia. Data by Barnes & O'Neil in Čadek & Pačes, 1976. The arrows represent mixing line between two endmembers: 1. local groundwater of meteoric origin with δ^2H ~ -70 ‰ and $\delta^{18}O$ ~ -10 ‰ and 2. metamorphic water; a) Soda Spring, California; b) boreholes in Zborov and Oravská Polhora

an isotopic composition similar to the water from the well Zborov-1, (XI[th] horizon) with $\delta^{18}O$ = +5.61 ‰ and δ^2H = -23.4 ‰ or water of the FPJ-1 borehole in Oravská Polhora with $\delta^{18}O$ = +6 ,08 ‰, δ^2H = -19.7 ‰ (Michalko et al., 1991, Michalko, 1998, Zakovič et al., 2009). The increase in the heavy isotope oxygen in water due to water-rock interaction (oxygen shift) seems to be non-realistic. The apparent increase in the proportion of light isotopes of both elements in mineral waters in the direction from North to South is explained by the impact of rain shadow of high mountains of Carpathian mountain range. Later research has shown that it is more a function of the Mean Residence Time (MRT) and the climate conditions at the time of infiltration.

The total inorganic carbon (DIC) present in water sources investigated was in the range of about $\delta^{13}C$ ca -4 ‰ to +4 ‰; the authors (Barnes & O'Neil in Čadek & Pačes, 1976) interpreted the origin from marine carbonates. For samples with isotopically lighter carbon they assume the impact of incomplete dissolution of carbonates accompanied by carbon isotope fractionation.

Relatively much attention was paid in this period to the distribution of sulphur isotopes present in the mineral and thermal waters in different forms. The research resided in the fact that the sources of sulphur present in the rock environment have characteristic isotopic composition, allowing to identify the origin of sulphur present in the water, thus circulation of groundwater and water-rock interaction. Provided, the isotopic composition of sulphur was changed by processes occurring in the groundwater during circulation (redox processes, mixing ..), it is necessary to reconstruct the original initial conditions. By the beginning of the 80s there was completed a perception of the development of the isotopic composition of sulphate (sulphur and oxygen) in the World Ocean (Nielsen & Ricke, 1964, Nielsen, 1979, Claypool et al., 1980). The isotopic composition of sulphur present in the form of sulphide and in sulphatic form in sedimentary rocks in the Western Carpathians was dealt by Kantor & Sládková 1979, Kantor et al. 1982.

Šmejkal et al., 1971 and 1981 dealt with the isotopic composition of sulphur present in the water from selected sources of mineral water in Czechoslovakia. Based on the findings of concentration and isotopic composition of SO_4^{2-} and H_2S in water there were reconstructed the relevant characteristics of the initial sulphate – its concentration and isotopic composition of sulphur from the sulphate present in the water prior to bacterial reduction. In the period of 1969 – 1978 there were conducted 41 analyses of this type from 25 mineral water sources across Slovakia (Tab. 2.2, Fig. 2.2). To them should be added 10 analyses from seven sources of thermal water with the circulation bound to the aquifers of the Flysch Zone of the Western Carpathians in Bohemia. The sources originate either from the environment of Mesozoic carbonates of the Central Western Carpathians, or from the Flysch Zone of the Western Carpathians. In the first phase (sampling in 1969) the authors (Šmejkal et al., 1971) used the know-ledge and analytical potential of the University of Alberta, Edmonton (postdoctoral fellowship) while primarily focused on the Czech part of the Flysch Zone. Thereafter (1970 – 1978) facilities of the ÚÚG were used, either in Prague or in Brno (Šmejkal et al., 1981).

The water of sources studied (Šmejkal et al., 1971, 1981) contains $\delta^{34}S$ of the present sulphate ranging from -25.7 ‰ to + 34.1 ‰, $\delta^{34}S$ of coexisting H_2S from -71.1 ‰ to +17.1 ‰ at sulphate concentrations of 11 mg . l^{-1} to 1,431 mg . l^{-1}, sulphane from 0.8 mg . l^{-1} to 600 mg . l^{-1}. The exemption constitutes a source of Šaratica, wherein the hydrogen sulphide is not present (reduction does not take place), and sulphate concentration is 13,000 mg . l^{-1}. The degree of reduction reaction – the conversion of the initial sulphate to sulphide – is moving in a range from 0.1 % to 97 %, while the successive samplings for each source are not always the same. This fact depends on the activity of the bacteria, i.e. slightly changing living environment, especially on food sufficiency, which constitutes carbon present in water in organic form. This fact Šmejkal et al. (l.c.) attributed also to differences in the degree of conversion of the sulphur in the sources related to the Flysch Zone – in units (Rača and Magura) rich in organic matter it is high, the external units where the organic carbon content in water is low, the conversion occurs on a small scale. In the isotopic composition of sulphur in immediate sulphate groups for both basic sources, there are systematic differences; depleted sulphur is typical for sulphate in water bound to flysch (mean = $\delta^{34}S$ 2.5 ‰), while sulphate present in Mesozoic water sources is characterized by average value $\delta^{34}S$ = 25.5 ‰. This difference is even more pronounced for upgraded initial isotopic composition of sulphate, i.e. the original composition of sulphate present in the water prior to bacterial reduction. The average value for water flysch is $\delta^{34}S$ = -10.9 ‰; $\delta^{34}S$ of the initial sulphate in water sources bound to Mesozoic is 22.9 ‰. The sulphate is present in the rock environment of an aquifer. Šmejkal et al. (1981) assumes the origin of enriched sulphur corresponding to the development of the World Ocean (Claypool et al. 1980) in the evaporites of the Mesozoic Ocean, particularly of Middle Triassic age (Röt, Oberer Bundsandstein, Werfenian). Source of very light sulphur present in the flysch rocks ($\delta^{34}S$ to -25 ‰) they assume in sulphides which (most likely) originated from (bacterial?) reduction of marine sulphate of an of ocean respective age.

Kantor (1985) interprets the results of the analysis (by Rybár, 1971) of the isotopic composition of sulphur in the sulphate present in the water of 35 sources of mineral water (Tab. 2.3, Fig. 2.2). Precipitation of hydrogen sulphide present in the water of some sources was not successful at sampling, so it was not possible to reconstruct the original composition of sulphur – as a direct result of water-rock interaction. However, in most sources the sulphate reduction does not take place (and if any, so at a very low level), and thus it is possible to characterize the original source of sulphur directly. Relevant data on the chemical composition Kantor (1985) takes from Franko (1975) and Krahulec et al. (1977, 1978; Tab. 2.3). The examined sources were selected to characterize the significant structures. The bulk of the sources are located in the central zone of the Western Carpathians and is bound to Mesozoic carbonate complexes of Tatricum, Fatricum and Hronicum with a characteristic alternation of collector rocks and aquicludes and with complex tectonic structure. In the selected set, there are also several mineral water sources sampled by Šmejkal et al. (1981); the values $\delta^{34}S_{SO4}$ are similar, mostly within the analytical error range.

Differences in reported values are rather attributable to the dynamics, or to the temporal time changing of the course of bacterial reduction. Studied mineral waters were of variable composition either in terms of sulphate content (from 98 mg . l^{-1} to 4,366 mg . l^{-1}) as well as the isotopic composition – determined $\delta^{34}S_{SO4}$ ranged from -11.18 ‰ to 33.23 ‰.

The acquired data yielded knowledge on the origin of sulphur, and also the genesis and mutual relations of the mineral waters. Based on the isotopic composition of sulphur in the water of dissolved sulphate Kantor (1985) distinguished three basic sources of springs with several sub-groups. In the first group there are sources of mineral water with sulphur derived from the dissolution of evaporites of marine origin characterized by a higher representation of the heavy isotope of sulphur. The original isotopic composition of evaporites has been preserved or was only minimally altered as a result of reduction. The second group consists of mineral water sources, which sulphur cannot be derived from evaporites of marine origin. High share of light isotope of sulphur, $\delta^{34}S$ values are around 0 ‰ and are often (highly) negative. They originated from the oxidation of pyrite present in the sediment. The third main group is mineral water, in which in the formation of sulphate sulphur both sources are involved. As an examples Kantor (l.c.) points to the water from Solivar with $\delta^{34}S$ = 10.97 ‰. He assumes a presence of the sulphate of Neogene Sea ($\delta^{34}S$ ~ 23 ‰) and the sulphate formed by oxidation of sulphide sulphur present in the sediment in the form of pyrite. This process is likely to be applied already at sedimentation, because Kantor & Sládková (1979) demonstrated the increased amount of light isotopes of sulphur in the sulphate sulphur of Karpatian sediments from this area.

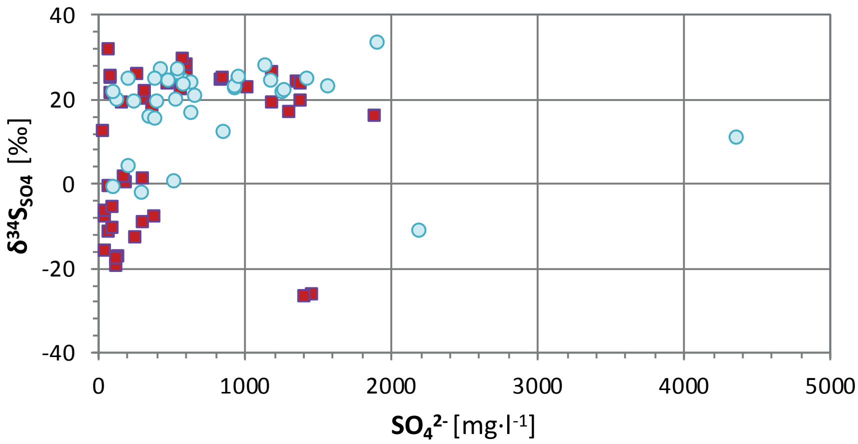


Fig. 2.2 Dependence of isotope composition of sulphur of dissolved sulphate on sulphate concentration. In groundwater with co-existing hydrogen sulphide reconstructed values are used (tab.2.2) for original initial sulphate. There are two main groups of sulphur sources in groundwater – Triassic Ocean evaporites with characteristic heavy sulphur ($\delta^{34}S$ ~ 20 ‰) and pyrite present in sediments (in one case sulphide of hydrothermal origin) with depleted sulphur ($\delta^{34}S$ from ca -20 ‰ up to ca 0 ‰). Sulphate with extremely heavy sulphur ($\delta^{34}S$ > 30 ‰) represents residual sulphate after reduction. Data by Šmejkal et al (1971, 1981) and Kantor (1985), Tabs.2.2, 2.3.

The sources with marine sulphate he subdivided in line with the evolution of the isotopic composition of marine sulphate (Claypool et al., 1980, Balderer in Pearson ed., 1991) according the age to springs with sulphur derived from evaporites of Late Triassic age (Keuper), Permian-Early Triassic age and evaporites with high presence of heavy isotopes of sulphur of the upper part of the Early Triassic (+ equivalents of Röt, Werfenian). Representatives of the first group are two springs from Valča with a sulphur $\delta^{34}S$ = 16.63 ‰ and 15.24 ‰. Light sulphur ($\delta^{34}S$ = 12.40 ‰) of the spring in Rovné derived from evaporites (Permian) – Early Triassic complexes (Kantor & Sládková, 1979 Kantor, 1982). The largest representation have springs with sulphur derived from the higher parts of evaporites of the Early Triassic (+ equivalents of Röt, Werfenian) which are characterized by $\delta^{34}S$ values> 20 ‰ to 28 ‰. In some sources (e.g. Sivá Brada) the enrich-

Tab. 2.2 Data of isotope composition of dissolved sulphate in mineral water and co-existing hydrogen sulphide. Reconstruction of original characteristics of primary sulphate. Data from Šmejkal et al. (1971, 1981), original characteristics recalculated by author. * Springs in Western Carpathians territory belonging to the Czech Republic.

N°	Locality	Source		Date	Instantaneous sulphate				Con-version [%]	Original sulphate	
					SO_4 [mg·l^{-1}]	H_2S [mg·l^{-1}]	$\delta^{34}S_{SO4}$ [‰] CDT	$\delta^{34}S_{H2S}$ [‰]		$\delta^{34}S_{SO4}$ [‰] CDT	SO_4 [mg·l^{-1}]
Mesozoic carbonates											
1.	Banská Bystrica		BB-10	1970	1,011.0	2.8	23.1	n	0.8	ca 23	1,018.9
				1971	941.0	0.8	24.2	n	0.1	ca 24	943.3
2.	Belušské Slatiny	kúpeľný	PB-3	1971	301.0	4.6	22.1	-24.0	4.1	20.2	314.0
		kúpeľný	PB-3	1975	308.0	2.4	23.2	-28.1	2.1	22.1	314.8
3.	Dudince	S-3	ZV-70	1970	557.0	7.0	26.4	-16.2	3.4	24.9	576.7
		S-3	ZV-70	1975	598.0	5.2	28.4	n	2.4	n	612.7
3.	Lipovce	S-2	PV-100	1971	77.0	4.8	25.1	n	15.0	n	90.5
		S-2	PV-100	1972	n	4.8	26.7	-26.6	n	n	
		S-2	PV-100	1975	147.0	4.5	23.9	-29.7	8.0	19.6	159.7
4.	Liptovské Sliače	Čertovica	LM-67	1970	469.0	2.8	23.8	n	1.7	ca 23.5	476.9
5.	Liptovský Ján	B-2	LM-46	1971	836.0	1.2	24.7	n	0.4	n	839.4
		B-2	LM-46	1972	840.0	1.2	25.6	-28.3	0.5	25.4	843.4
6.	Malinovec Santovka	B-3	LE-15	1970	571.0	8.2	27.5	-12.8	4.0	25.9	594.1
		B-3	LE-15	1975	600.0	7.5	27.7	n	3.4	n	621.1
7.	Mýto pod Ďumbierom		BB-58	1972	67.0	1.1	34.1	-12.4	4.4	32.0	70.1
8.	Patince	SB-1	KO-4	1975	71.0	3.5	25.6	-4.5	12.2	21.9	80.9
9.	Piešťany	Trajan	TR-4	1969	525.0	11.0	24.4	-6.3	3.0	23.5	556.0
		Trajan	TR-4	1971	528.0	11.0	25.1	-15.6	5.0	22.8	559.0
		Trajan	TR-4	1975	n	6.5	26.4	-16.8	n	n	
10.	Plavecký Peter	SE-18	SE-18	1975	184.0	28.0	33.6	8.8	30.0	26.1	262.9
11.	Sivá Brada		SNV-5	1970	1,178.0	1.2	26.6	-1.5	0.3	26.5	1,181.4
12.	Sliač	Spring A	ZV-8	1970	1,350.0	1.7	24.3	n	0.3	ca 24.1	1,354.8
13.	Slovany, Smrdutá voda		TM-15	1975	353.0	2.6	19.7	-36.0	2.0	18.6	360.3
14.	Smrdáky	Jozef I	SE-20	1969	35.0	450.0	21.8	17.1	97.0	17.2	1,303.5
		Jozef I	SE-20	1975	192.0	600.0	21.2	15.8	90.0	16.3	1,883.3
15.	Sobranecké kúpele	kúpeľný	ML-8	1971	556.0	220.0	32.9	7.3	53.0	19.3	1,176.2
		kúpeľný	ML-8	1975	505.0	24.0	32.8	8.6	12.0	30.0	572.7
16.	Stankovany	medokýš	LM-124	1971	1,373.0	2.5	24.2	-33.5	0.5	23.8	1,380.0
		medokýš	LM-124	1972	n	3.3	24.2	n	n	n	
17.	Trenčianske Teplice	V-3	TE-54	1971	1,362.0	4.5	20.3	-33.5	0.9	19.7	1,374.7
		V-3	TE-54	1975	n	4.0	20.0	-28.4	n	n	
Flysch rock environment											
18.	Hruštín		DK-5	1971	37	1.5	-3.3	-44.1	10.3	-7.5	41.2
19.	Keľča		HN-7	1971	130	60.0	27.6	-36.6	56.5	-8.7	299.1
			HN-7	1975	178	70.0	25.8	-38.0	52.6	-7.7	375.3
20.	Malá Poľana		HN-8	1971	93	32.0	24.8	-24.8	49.2	0.4	183.2
			HN-8	1975	100	24.0	19.3	-24.4	40.4	1.7	167.7
21.	Oravská Polhora			1975	25	6.0	-2.4	-11.6	40.4	-6.1	41.9
22.	Osadné		HN-11	1971	11	1.1	-0.6	n	22.0	n	14.1
23.	Šarišský Štiavnik			1972	36	9.0	-0.6	-25.8	41.3	-11.0	61.4
24.	Vrchpredmier Klokočov			1971	28	2.6	-9.7	-37.5	20.7	-15.5	35.3
25.	Vyšný Orlík		BV-80	1971	41	28.0	20.9	-39.8	65.8	-19.0	119.9
			BV-80	1975	114	48.0	19.9	-40.1	54.3	-12.7	249.3
27.	* Čejč			1969	250	18.0	6.9	-24.3	16.9	1.6	300.7
28.	* Kladeruby			1970	110	1.0	0.6	n	2.5	n	112.8
29.	* Napajedla	Slanica		1969	57	12.8	-1.7	-23.9	38.8	-10.3	93.1
		Slanica		1975	37	7.5	8.5	-15.4	36.4	-0.2	58.1
30	* Šaratice			1978	13,000	0.0	-19.6	n	0.0	-19.6	13,000.0
31.	* Šitbořice			1970	1,431	7.1	-25.3	-68.1	1.4	-25.9	1,451.0
				1975	1,384	6.0	-25.7	-71.1	1.2	-26.2	1,400.9
32.	* Vizovice	Dudík		1969	82	15.3	-6.3	-37.7	34.5	-17.1	125.1
		Švajda		1975	59	13.0	6.5	-24.3	38.3	-5.3	95.6
33.	* Želechovice			1969	91	7.7	-13.2	-35.6	19.3	-17.5	112.7

Tab. 2.3 $\delta^{34}S$ data of sulphate dissolved in mineral water. Data by Kantor (1985), analyses of $\delta^{34}S$ carried out by Rybár (1971)

N°	Locality	Source	Groundwater type	t [°C]	TDS [g·l⁻¹]	SO_4 [mg·l⁻¹]	H_2S [mg·l⁻¹]	$\delta^{34}S_{SO4}$ CDT [‰]
1.	Baldovce	Deák	HCO_3-SO_4-Ca-Mg	10.0	5.67	421.8	0.0	27.04
2.	Banská Bystrica	Altánka	HCO_3-SO_4-Ca-Mg	17.4	3.48	937.8	0.0	22.54
3.	Budiš	B-1				660.1		20.95
4.	Buzica	crossing	HCO_3-Cl-Na	17.2	10.62	630.8	0.0	24.11
5.	Dudince	S-3	HCO_3-Na-Ca	28.0	5.34	549.8	9.0	26.05
6.	Jánovce	Spa spring	HCO_3-SO_4-Ca-Mg	23.2	3.66	960.4	0.0	25.47
7.	South-Slovakian coal basin	borehole PS				98.4		-0.63
8.	Kalinčiakovo	Ilona	HCO_3-SO_4-Ca-Mg	25.5	0.96	241.6	0.0	19.30
9.	Kalinka					202.1		4.20
10.	Korytnica	Jozef	SO_4-HCO_3-Ca-Mg	6.5	3.47	1,421.7	0.0	24.70
11.	Kováčová	Borehole at a house	SO_4-HCO_3-Ca-Mg	46.2	2.78	1,262.5	0.6	21.51
12.	Lipovec	Solivar	HCO_3-Na-Ca	6.0	2.99	102.3	0.0	21.73
13.	Lúčky	Helena	SO_4-HCO_3-Ca-Mg	25.5	2.84	1,174.8	0.0	24.58
14.	Ľupčianska dolina Valley					1,277.3		22.35
15.	Michaľany	Borehole at railway station	HCO_3-Cl-Na	10.0	21.30	1,907.7	0.1	33.23
16.	Pôtor					300.4		-2.30
17.	Rovná					855.9		12.20
18.	Santovka	B-6	HCO_3-Ca-Na	16.2	3.46	349.8		15.71
19.	Santovka Malinovec	B-3	HCO_3-Na-Ca	27.5	5.60	577.8	0.6	24.56
20.	Sivá Brada		HCO_3-SO_4-Ca-Mg	12.3	7.19	1,146.9	0.8	28.09
21.	Slatina					396.3	9.5	19.63
22.	Slatina	Prameň pri MNV	HCO_3-Na-Ca	14.0	3.13	123.0	0.0	19.93
23.	Sliač	Spa spring	SO_4-HCO_3-Ca-Mg	33.0	3.89	1,574.4	0.0	23.05
24.	Sobrance	Spa spring	Cl-Na	13.9	9.86	548.1	23.9	27.24
25.	Solivar	brines				4,366.4		10.97
26.	Šindliar		HCO_3-Ca	9.0	2.62	213.6	0.0	24.70
27.	Šošár (Želovce)	spring Slaná voda				517.3		0.70
28.	Švermovo	Šťavica	HCO_3-SO_4-Ca-Mg	13.0	2.99	382.7	0.3	24.93
29.	Tisovec		HCO_3-SO_4-Ca-Mg	10.0	2,332.20	583.9	0.0	23.53
30.	Turčianske Teplice	Červený bazén	SO_4-HCO_3-Ca-Mg	37.5	1.34	530.0	0.0	19.83
31.	Valča	Smrdutá voda (Sloviansky p.)				638.2		16.68
32.	Valča	Creek below Smrdutá voda				384.8		15.24
33.	Vyšný Sliač	spring Čertovica	HCO_3-SO_4-Ca-Mg	20.2	3.05	476.9	2.0	24.56
34.	Zbudský Rokytov					2,192.9		-11.18
35.	Železnô					936.7		23.19

ment can be attributed to low bacterial reduction intensity. The importance of isotopically light sulphur ($\delta^{34}S \sim 5$ ‰), so-called background sulphur present in springs with low sulphate concentration when mixing pointed out Malík & Michalko (2002). The result of mixing of large quantities of groundwater with this sulphur and the groundwater with sulphur derived from marine evaporites of Werfenian age ($\delta^{34}S \sim 25$ ‰) is the sulphate with values of $\delta^{34}S$ characteristic for the Late Triassic Ocean sulphate derivatives, which can lead to misinterpretation.

High proportion of heavy isotopes of sulphur in mineral waters from the Neogene sediments of the Eastern Slovakia Lowland (Sobrance, Michaľany) Kantor (1985) attributed to the effect of recent (bacterial reduction) and syngenetic processes. Kantor & Sládková (1979) and Kantor et al. (1982) demonstrated the sulphur enrichment in Badenian evaporites of subincumbent and basal parts of salt deposits. In both cases (sulphur enrichment of Badenian Sea and vice versa, the depletion of sulphur in sulphate of Karpatian Sea) the processes were probably of supra-regional character.

Group of mineral waters with sulphate originating from the oxidation of sulphide sulphur present in the collector rock environment Kantor (1985) divided by the origin of sulphate into three groups. Sources with depleted sulphur derived from pyrites from rocks of the Flysch

Zone represents the spring in Zbudský Rokytov with 2,193 mg . l^{-1} SO_4^{2-} with $\delta^{34}S$ = -11.18 ‰. The sulphate of the sources from the Neogene sediments of the South-Slovakian coal basin (Pôtor, Slaný prameň in Želovce and well PS) with sulphate concentration of 93 mg . l^{-1} to 517 mg . l^{-1} as $\delta^{34}S$ = -2.30 ‰ to 0.70 ‰; it also comes from the oxidation of sulphide, probably synsedimentary sulphur. In contrast, water from a gallery for noble sulphur in Kalinka (sulphate concentration 202 mg . l^{-1} and $\delta^{34}S$ = 4.20 ‰) represents a group of mineral waters in which sulphate comes from the oxidation of sulphides of hydrothermal origin.

2.4 Regional and local targeted research

In the early period, in addition to work aimed at general reviews of isotope pattern of mineral water sources nationwide the acquisition of knowledge of the isotopic composition of water and/or dissolved compounds was a relevant part of the work aimed at solving specific problems of origin, protection and utilization of mineral water in local or regional scales. This group of works carried out in the mid-80s can includes studies of the isotopic composition of geothermal waters of the Central Depression of the Danube Basin, research in mineral waters of the crystalline of the Nízke Tatry Mts. and the solution of the genesis of geothermal waters of the Vienna Basin.

The first indication of the isotopic composition of water from a geothermal well from Slovakia brought Barnes & O'Neil in Čadek & Pačes, (1976), who on the basis of the values $\delta^{18}O$ = -10.8 ‰ and δ^2H = -75.5 ‰ of the water in the well in Patince defined its origin from precipitation (Tab. 2.1). They assumed for inorganic carbon ($\delta^{13}C$ = 9.0 ‰) the impact of incomplete dissolution of carbonates.

The first data on the isotopic composition of geothermal water from the Central Depression of the Danube Basin in terms of isotopes of hydrogen and oxygen are the result of activities of the organization VIKÚV. Analysis of seven water wells in 1976 provided Franko & Bodiš (1989), after their rearrangement Michalko (in Franko et al., 2000; Tab. 2.4). Based on isotopic data (δ^2H ranges from -68.2 ‰ to -96.0 ‰ and $\delta^{18}O$ from -9.8 ‰ to -13.8 ‰) meteoric origin of waters can be assumed.

An acknowledged fact that the mineralization and temperature of geothermal water of the Neogene sediments of the Central Depression of the Danube Basin increase with depth has been confirmed and supplemented by data on oxygen isotopic composition of these waters. Kantor (1985), in collaboration with Bodiš indicates $\delta^{18}O$ of geothermal water from 16 wells, of which one was from the edge of Levice marginal block (Po-1 in Podhájska) and Komárno elevated block (M-3 in Komárno), the other fourteen from the Central Depression of the Danube Basin (Tab. 2.5, Fig. 2.3). Wide range of $\delta^{18}O$ values (from -1.98 ‰ to -13.18 ‰) of geothermal waters demonstrates the varied and complex conditions of their origin and formation. For depleted water Kantor (l.c.) assumed a meteoric origin, whereas he excludes recent precipitations as their source by comparing the average rainfall in Vienna (annual average of -9.4 ‰ $\delta^{18}O$ to -10.3 ‰). As a source of depleted meteoric water he doesn't exclude meteoric water from glaciation periods; he considers a source of water brought by the Danube River into the Danube Plain from the Alps. The data provided observations of the isotopic composition of the Danube, Morava and Váh, and also knowledge of the isotopic composition of groundwater from overlying Quaternary sediments in piezometer PZ-I in Šamorín. Kantor (l.c.) determined the presence of isotopically depleted water from the Danube River bank infiltration to a depth of 154 m, $\delta^{18}O$ ranging from -10.59 ‰ to -11.82 ‰ what corresponds to the average composition of the Danube water. In support of this interpretation is also increase in the light isotope of oxygen from peripheral to central part of the basin in profile Chorvátsky Grob, Kráľová pri Senci, Diakovce, $\delta^{18}O$ from -11.25 ‰ through -11.93 ‰ to -13.18 ‰. In the marginal parts of the Basin he assumed meteoric origin of water infiltrated from the Malé Karpaty Mts.

Geothermal water of borehole Kol-3 in Nesvady with high presence of heavy oxygen isotope ($\delta^{18}O$ = -1.98 ‰) captured in the Pannonian sediments is considered to be a fossil marine water. Gradual changes in favour of the light isotope with decreasing depth of wells of tapped Pontian aquifers manifest changes in the isotopic composition – from Sarmatian to Quaternary – gradual turning from sea through brackish and finally lacustrine water. The second option is mixing among seawaters and depleted waters of meteoric origin (according to Kantor l.c. of Danube origin) present either in sandy Dacian sediments in the well Di-1 ($\delta^{18}O$ = -13.18 ‰), or Pontian – drilling FGGa-1 in Gabčíkovo ($\delta^{18}O$ = – 12.51 ‰) and FGT-1 Topoľníky ($\delta^{18}O$ = -12.09 ‰), or in the Quaternary gravels. In favour of idea about alpine origin of depleted constituent, is the presence of large volumes of these waters in the overlying Quaternary gravels and gravels/sands. This assumption was preferred by Franko (2001) and the followers, despite the already known data on the MRT of the majority of geothermal water wells (the first tens of thousands of years; Franko et al., 1995). Therefore the isotopically light water dates back to the cold climate. In water derived from precipitation in the area of the Alps and brought by the then Danube it can be assumed increased presence of the light isotope of oxygen (and hydrogen) compared to today. The Danube water effect (of unknown age) on the formation of geothermal waters is conceded the central part of the Basin.

Tab. 2.4 First isotope data from geothermal wells of Central Depression of the Danube Basin. Unpublished data from 1976 (VIKÚV) in Franko & Bodiš (1989), rearranged after Franko et al. (2000)

Locality	**Source**	$\delta^{18}O_{H2O}$ SMOW [‰]	δ^2H_{H2O} SMOW [‰]
Diakovce	Di-1	-13.8	-96.0
Topoľníky	FGT-1	-12.8	-90.8
Kráľová pri Senci	FGS-1/A	-11.1	-77.2
Chorvátsky Grob	FGB-1/A	-11.5	-82.0
Galanta	FGG-1	-11.1	-78.0
Čalovo	Č-1	-9.8	-68.2
Dunajská Streda	DS-1	-10.9	-77.0

Tab. 2.5 Basic and isotope composition data of geothermal wells in Podunajská panva (Danube) Basin water (Data byKantor, 1985)

Locality	Source	Hydrogeological structure	Well depth [m]	Watered section [m]		Age	Lithology	Sampling date	t [°C]	Q [$l \cdot s^{-1}$]	$d^{18}O_{H2O}$ [‰] SMOW	TDS [$g \cdot l^{-1}$]	Cl^- [$mg \cdot l^{-1}$]
				from	to								
Diakovce	Di-1	Central Depression of Danube Basin	3,303	720	810	Dacian	sands	30.03.1983	38.0	4.0	-13.18		3.5
Diakovce	Di-2		1,551	1,416.5	1,535.5	Pontian	sands	30.03.1983	68.0	12.0	-11.40	2.10	290.0
Dunajská Streda	DS-1		2,500	2,183	2,432	Pontian	sands	30.03.1983	91.5	15.2	-7.31	6.90	2,440.0
Dvory nad Žitavou	FGDŽ-1		2,500	1,024	1,616	Pontian	sands	30.03.1983	62.0	7.2	-9.10	3.40	1,515.0
Gabčíkovo	FGGa-1		2,582	1,122	1,926	Pontian	sands	30.03.1983	52.0	1.0	-12.51	1.10	
Horná Potôň	FGHP-1		2,500	1,364	1,963	Pontian	sands	30.03.1983	68.0	20.0	-10.03	4.70	1,443.0
Chorvátsky Grob	FGB-1/A		500	276.21	299.67	Pontian	sands	30.03.1983	24.0	3.5	-11.25	0.49	33.0
(Nesvady)	Kol-3							30.03.1983			-1.98		5,184.0
Komárno	M-2		1,060	771	1,025	Pontian – Pannonian	sands	30.03.1983	42.0	4.5	-10.95	0.51	915.0
Kráľová pri Senci	FGS-1/A		1,500	910	1,235	Pontian	sands	30.03.1983	52.0	13.0	-11.93	7.70	1,379.0
Topoľníky	FGT-1		2,501	1,394.4	2,043	Pontian	sands	30.03.1983	74.0	23.0	-12.09	2.20	250.0
Tvrdošovce	FGTv-1		2,406	587	1,362	Pontian	sands	30.03.1983	70.0	20.0	-11.34	15.00	123.0
Veľký Meder	Č-1		2,502	2,289	2,380	Pontian	sands	30.03.1983	92.0	7.6	-8.77	5.10	2,090.0
Vincov les	FGG-1		1,990	1,212.5	1,470	Pontian	sands	30.03.1983	62.0	15.0	-10.97	3.20	316.0
Vlčany	FGV-1		2,500	1,244	1,852	Pontian	sands	30.03.1983	62.6	10.0	-11.83	2.10	
Komárno	M-3	Komárno high block	1,184	1,139	1,184	Triassic + Jurassic	dolomites. limestones	30.03.1983	51.0	5.0	-12.58	3.10	
Podhájska	Po-1	Levice marginal block	1,900	1,155	1,740	Badenian Triassic	clastic dolomites, quartzites	30.03.1983	80.0	53.0	-6.63	19.60	9,536.0

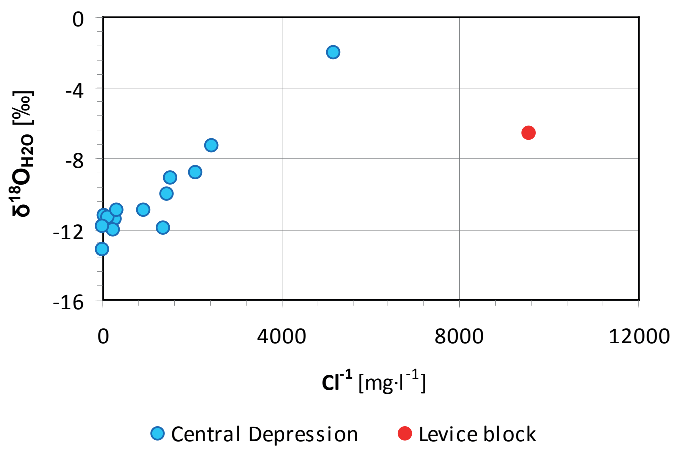


Fig. 2.3 Geothermal water of Central Depression of the Podunajská panva Basin; relationship between $\delta^{18}O_{H2O}$ / Cl^- concentration

According Kantor (1985) the conduits for depleted water present in carbonates of the Komárno elevated block in borehole M-3 at depth of 1,139 – 1,184 meters ($\delta^{18}O$ = -12.58 ‰) creates the system of Komárno faults; however he did not exclude its origin in local precipitation waters during glaciations. For its source are now considered karst waters infiltrating from the South. Problematic seems to be isotopically heavier water ($\delta^{18}O$ = -10.95 ‰) tapped in the borehole M-2 in overlying Pontian sands.

In water ($\delta^{18}O$ = -6.63 ‰) tapped in the borehole Ro-1 in Badenian clastic rocks and Triassic dolomites the author (l.c.) assumes a significant proportion of marine water. At this site the author (l.c.) upgraded the research on study of the isotopic composition of incrust (Tab. 6). The incrust is composed of calcite and aragonite lamina. There were sampled four lamina; brown-coloured aragonite and calcite near the base were likely affected by turbulent conditions at the time of their origin.

On the basis of the relevant data obtained from the two white aragonite lamina (Tab.2.6) and the assumed steady state Kantor (l.c.) determined precipitation temperature of 65 °C and 68 °C. In fact, the well water at the collar reaches 80 °C, which is justified by non-reaching of steady state. Carbonates are also isotopically markedly different from carbonates of marine origin.

The idea of the origin of water in local rainfall, in transport by rivers of the higher altitudes of the Western Carpathians, but also about its penetration to the Basin from the marginal mountains is evidenced by higher residence time (and hydraulic properties of aquifer rocks), and also by the fact that in shallow Neogene horizons they were documented in more than 20 wells with confined groundwater level meteoric water (Bottlik et al. 2013; Michalko et al. 2015). Their $\delta^{18}O$ isotopic composition ranged from -11.16 ‰ to -13.90 ‰, with mean value -12.75 ‰, apparently of glaciation age. In formation of geothermal waters in the Danube basin area there are involved different constituents. Evident is share of the water of marine origin; (Fig. 2.3) however, a sea is progressively substituted by brackish environment, so chemical and isotopic composition change over time. The other constituent is isotopically light water coming from precipitation of the cold period – it gets in the Basin area from surrounding mountains or by palaeoflows. Large amounts of isotopically light meteoric water mainly from the Alpine delivers – and delivered – the Danube River. In cases where the final composition of geothermal water was affected by water of marine origin, the determined ^{14}C ages have to be perceived as the mixed ones. This fact was not taken into account by Franko (2001) and subsequently Franko et al. (2008), Povinec et al. (2010a, 2010b). The need to determine the criteria to distinguish different kinds of waters and estimate their share in the final composition of the geothermal waters was pointed out by Kantor (1985).

Tab. 2.6 Isotope composition of the incrust from the borehole Po-1 in Podhájska

Layer N°	Mineral	$\delta^{13}C$ [‰] PDB	$\delta^{18}O$ [‰] PDB	$\delta^{18}O$ [‰] SMOW
1	Aragonite – brown coloured from Fe component	1.60	-11.28	19.23
2	Calcite – brown coloured from Fe component	1.08	-13.49	16.95
3	Aragonite – first white non-coloured layer	1.34	-14.90	15.50
4	Aragonite – white colour	1.15	-15.08	15.23

As part of a detailed hydrogeochemical research of mineral waters of crystalline of the Nízke Tatry Mts. (Rapant 1991, 1994, Rapant et al., 1986) there were applied findings of the isotopic composition of oxygen (and hydrogen) of water (Tab. 2.7). Two pieces of information about the isotopic composition of sulphur are coming from nationwide surveys by Šmejkal et al. (1981) and Kantor (1985) (Fig. 2.1, Tab. 2.2). Based on the findings of $\delta^{18}O_{H2O}$ Kantor (1985) attributed the waters of all monitored sources meteoric origin; the isotopic composition of hydrogen he didn't specified (Tab.2.7). The data come from the archives of the former Department of Isotope Geology SGIDŠ (Michalko, 1998). Large differences in the distribution of oxygen isotopes Kantor (l.c.) attributes to differences in altitudes of catchments, or the effect of precipitation of cold and warm periods. Based on the identity of the values $\delta^{18}O$ he supposes homogenization for springs in Malužiná (LM-96, LM-97), and thus a longer residence time, or deeper circulation. The share of fossil water of Neogene Sea in the composition of the water of these springs and spring Boženy Němcovej in Bacúch characterized by a high chloride content, he referred to only as a theoretical possibility. He considered these waters to be of clearly meteoric origin (Fig. 2.4). Thus, the presence of rich spectra sporomorphs of Neogene age in water of several springs (Planderová, Rapant reportedly in oral Kantor, 1985, Rapant et al., 1986, Rapant, 1991, 1994) he explains by the interaction of mineral water with the sediments of the Neogene age.

In evaluating the chemical composition and genesis of geothermal waters of the Slovak part of the Vienna Ba-

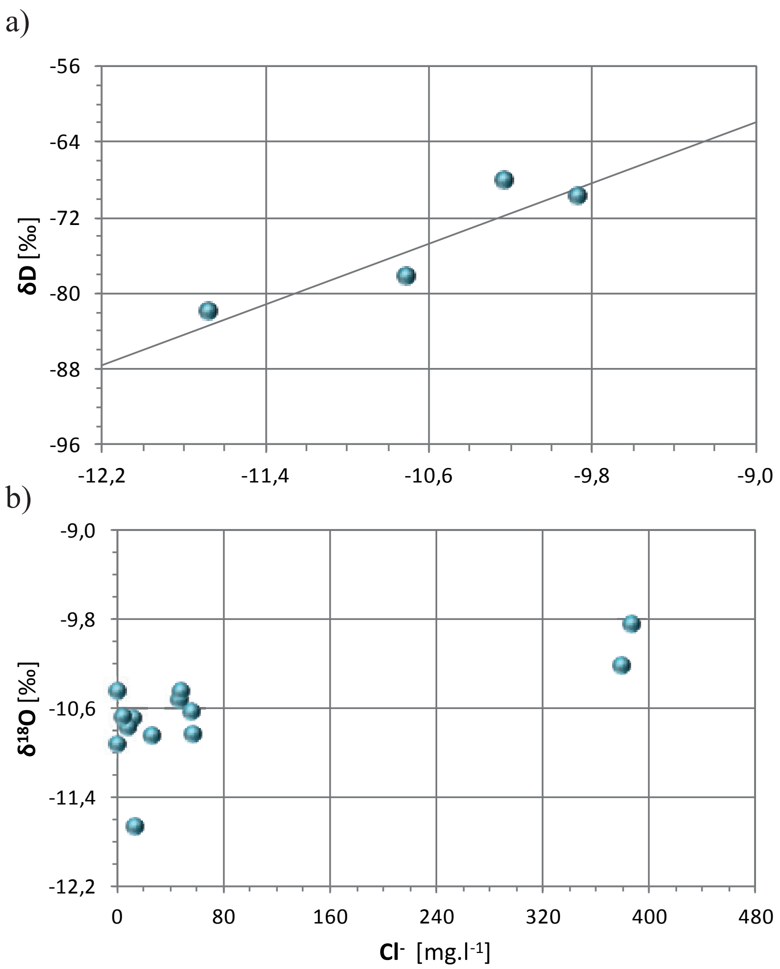


Fig. 2.4 Mineral waters from crystalline environment of the Nízke Tatry Mts.; a) isotope composition of O and H, b) relationships between $\delta^{18}O_{H2O}$ and Cl^- concentration

sin (Bodiš in Remšík et al., 1985) the hydrogeochemical data provided the basis, along with the knowledge of the geological setting of pre-Neogene bedrock and Neogene itself, the characteristics of evaporites and isotopic analyses. Based on the factor analysis of hydrogeochemical data there were allocated three factors, namely the so-called "marine", in which positive factor scores achieved Na^+, K^+, Cl^-, Br^-, I^-; SO_4^{2-} was significantly negative. The second factor ("metamorphosis II") with significant correlation between bicarbonates and sulphates represents infiltration degradation, or interaction water-anhydrite. The third factor "metamorphosis I" represents the water-rock interaction and is characterized by a positive saturation of magnesium, calcium, chloride, sodium, and the TDS. Results of the analysis were interpreted in real environs of hydrogeological structures.

In the hydrogeological structure of the Láb-Malacky elevation with adjacent sunken blocks there are present in the Mesozoic basement strong brines of distinct sodium-chloride type with TDS 90 – 128 g . l^{-1}. Low sulphate concentrations, although in the rock environment anhydrite presence is evidenced, result from inhibitory action of $CaCl_2$, which blocks the dissolution of anhydrite. Ion-exchange processes increase the total dissolved solids and $CaCl_2$ content. After reaching a steady state in a closed system the reaction does not take place at present. Probably in the Early Karpathian penetrated in the emerged area of elevation the sea lagoons; their brines infiltrated into Triassic carbonates. However, evaporation due to the contribution of meteoric water into the lagoon had not taken place up to a degree of precipitation of salts, as it is evidenced by isotopic composition ($\delta^{18}O$ = -2.5 ‰, Buzek in Remšík et al., 1985) of brine from the horizon from 2,873 to 2,877 m of drilling Láb-120.

In Závod-Studienka sunken zone marinogenic waters have been found, degraded to some degree, of distinct sodium-chloride type with TDS in the range of 15 – 25 g . l^{-1}. The degree of degradation decreases with depth.

In the hydrogeological structure of Šaštín elevation (Bodiš in Remšík et al., 1985) and adjacent sunken zones waters of indistinct sodium chloride character are present with TDS 7 – 15 g . l^{-1}. The waters are bound to aquifer constituted by Eggenburgian clastics and Triassic dolomites of the Choč Nappe. The structure is characterized by the differentiation of water in the depth and lateral direction (SW-NE). In the Šaštín area significant interaction with anhydrite is involved in the formation of the water. In the well Šaštín-12 Kantor et al. (1982) provided Late Triassic characteristic values $\delta^{34}S$ from 14.4 ‰ to 17.0 ‰ for the anhydrite present in the Haupt Dolomite (overlaying Lunz Mb., 10 samples from a depth of 4,193-4,953 m). The anhydrites from the base of the Lunz Mb. (two samples from a depth of 5,700 – 5,830 meters) referred to as the upper part Oponice Limestone (Němec & Kocák, 1982, in Kantor, 1982) are significantly enriched in the heavy isotopes of sulphur – $\delta^{34}S$ = 22.5 ‰ and 22.8 ‰. The waters are rich in sulphates and hydrogen sulphide, although at present its formation does not take place. Bodiš (in Remšík et al., 1985) assumes start-up of the biological processes responsible for the formation of H_2S by mixing of waters of marine and meteoric origin, their termination at the subsidence of Inner-Carpathian units and subsequent increase in temperature to nearly 100 °C.

In Lakšárska Nová Ves elevation there are two basic types of water. At greater depths (well LNV-7) marinogenic waters are present with TDS from 34.7 to 43.8 g . l^{-1}. Bodiš (in Remšík et al., 1985) considers them represent infiltrated marine waters affected by reaction with the surrounding geological environment, especially anhydrites. They have preserved thanks to the presence of impermeable Lunz Mb. Anhydrites from a depth of 6,043 – 6,400 m (4 samples) showed the isotopic composition of sulphur ($\delta^{34}S$ from 15.6 to 17.2 ‰) characteristic for evaporites of the Late Triassic (Kantor, 1982). In the basal Eggenburgian clastics and upper parts of Inner-Carpathian units

Tab. 2.7 Isotope composition of O and H in mineral waters of the Nízke Tatry Mts. (data by Kantor, 1985)

Locality	Source	Source labeling	Type	$\delta^{18}O_{H2O}$ SMOW [‰]		$\delta^{2}H_{H2O}$ SMOW [‰]	Cl^- [$mg \cdot l^{-1}$]	$\delta^{34}S_{SO4}$ [‰] CDT
				08.12.84	05.06.85			
Bacúch	spring B. Němcovej	BB-1	HCO_3-Cl-Na	-10.22		-68.3	380.7	
Jarabá		BB-45	HCO_3-SO_4-Ca-Mg	-10.59				
Jarabá	Bachláč	BB-46	HCO_3-SO_4-Ca-Mg		-10.70	-78.4	13.2	
Jarabá	Kumštová	BB-48	HCO_3-Ca-Mg-Na		-10.64		57.2	
Jarabá	Predjasienok	BB-47	HCO_3-Ca-Mg		-10.46		2.0	
Jarabá	Husárka, vrt H-1	BB-50	HCO_3-Ca-Na-Mg		-11.67	-82.1	13.8	
Jarabá	Kyslá	BB-49	HCO_3-Ca-Mg		-10.78		9.2	
Liptovská Lúžna	Banské	LM-61	HCO_3-Ca-Mg		-10.69		5.4	
Malužiná	Main spring	LM-96	SO_4-HCO_3-Ca-Mg	-10.53	-10.44		48.0	
Malužiná	Kadlub	LM-97		-10.45	-10.44		48.9	
Mýto pod Ďumbierom		BB-57	HCO_3-Cl-Na		-9.86	-69.9	387.5	
Mýto pod Ďumbierom		BB-58	HCO_3-Cl-Na	-9.81				32.0
Pohronský Bukovec		BB-61	HCO_3-Na	-10.84			58.0	
Vyšná Boca		LM-146			-10.86			
Vyšná Boca	Behind Church	LM-136	HCO_3-Ca-Mg	-10.86			27.3	
Železnô	Ž-1	LM-101			-10.93		1.2	23.2

Tab. 2.8 Isotope data from sources of mineral water in Slovak part of Vienna Basin. Data by Kantor in Remšík et al. 1985. All numbers for original sulphate recalculated by author. [1]Data by Šmejkal et al., 1981 (Tab.2.2) used by Bodiš in Remšík et al., 1985, [2]Data by Bodiš in Remšík et al., 1985, [3](Mean data Kantor in Remšík et al., 1985)

Locality	Source	Watered section [m]	Sampling date	$\delta^{18}O_{H2O}$ SMOW [‰]	$\delta^{2}H_{H2O}$ SMOW [‰]	Instantaneous sulphate				Original sulphate	
						SO_4 [$mg \cdot l^{-1}$]	H_2S [$mg \cdot l^{-1}$]	$\delta^{34}S_{SO4}$ [‰] CDT	$\delta^{34}S_{H2S}$ [‰] CDT	SO_4 [$mg \cdot l^{-1}$]	$\delta^{34}S_{SO4}$ [‰] CDT
[1]Plavecký Peter			1975			184.0	28.0	33.6	8.6	262.9	26.1
[1]Smrdáky	Jozef I		1969			35.0	450.0	21.8	17.1	1,303.5	17.2
			1975			192.0	600.0	21.2	15.8	1,883.3	16.4
	RGL-1	1,242 – 1,322	03.02.84	-10.90		[2]1,372.6	[2]234.2	43.09	2.33	2,032.8	29.9
		1,242 – 1,322	08.02.84	-10.76	-74.2						
		1,242 – 1,562	29.03.84	-10.91	-81.0	[3]1,371.4	[3]222.6	44.15	2.17	1,998.9	31.0
		1,100 – 2,100	02.04.84	-10.95	-77.1						
		1,100 – 2,100	18.04.84			[3]1,371.4	[3]222.6	43.69	2.89	1,998.9	30.9
Kuklov	Kuklov-3	2,900	02.02.84								23.39

sodium-chloride waters are present with TDS = 5 – 7 g . l^{-1}. In view of the isotopic composition of H and O the meteoric origin of waters is probable (Kantor in Remšík et al., 1985), and their composition is the result of the water-rock interaction. The Na-Cl component originates from reaction with overlying Neogene sediments; sulphates emerged thanks to anhydrite dissolution. On the basis of the water from well RGL-1 (Tab. 2.8) reconstructed sulphate features high enrichment in heavy isotope of sulphur, which is characteristic of Röt and its equivalents. Sulphuric acid with trivalent Fe oxides is the result of (bacterial) oxidation of pyrite. Kantor (in Remšík et al., 1985) reports that for achieving the isotopic steady state, fractionation in the system of dissolved sulphate – gaseous hydrogen sulphide should correspond temperatures of 140 °C – 150 °C, in the system bisulphate – hydrogen sulphide the temperature of 110 °C.

Springs of mineral waters with hydrogen sulphide are located along the NW edge of the Malé Karpaty Mts. are considered to represent natural seepages of groundwater from the Lakšárska Nová Ves elevation (Bodiš in Remšík et al., 1985). In favour of this idea is the isotopic composition of sulphur in their water solutes (Tab. 2.8), which can hardly come from Neogene of the Vienna Basin. For gypsum present in these sediments in Devín, Devínska Nová Ves, Stupava Kantor (1982) found $\delta^{34}S$ in the range of -13.0 ‰ to -31.5 ‰ and thus it can not be considered synsedimentary mineral. Similarly differing are the values characteristic for the marine evaporites of Neogene Sea in terms of the isotopic composition of oxygen $\delta^{18}O_{SO4}$ which ranges from -3.48 ‰ to +6.15 ‰. The crystallization water in gypsum is not of marine origin, as well. Based on data on the isotopic composition ($\delta^{18}O$ from -6.1 ‰ to -7.0 ‰ of 3 samples) the water from which the gypsum precipitated had isotopic composition $\delta^{18}O$ = -9.6 ‰ to -10.5 ‰, which corresponds to the composition of the current precipitations (Kantor et al., 1982). Knowledge of the isotopic composition of pyrite present in the sediment ($\delta^{34}S$ = -6.6 ‰ to -46.1 ‰) confirms the idea of Květ (Bodiš in Remšík et al., 1985) that the formation of gypsum in the Neogene of the Vienna Basin is due to the reaction of sulphuric acid with carbonates. The acid along with trivalent Fe-oxides is the result of (bacterial) oxidation of pyrite.

2.5 Conclusions

Knowledge of the isotopic composition of mineral water in Slovakia achieved in mid-eighties of the last century consisted of two nationwide thematic publications of foreign authors and a number of specialized SGIDŠ studies to address specific problems of the genesis of mineral water in selected regions. The research focused on the knowledge about isotopic composition of hydrogen and oxygen in the water and also in the isotopic composition of water-dissolved constituents, especially sulphur present in sulphate and also sulphide forms.

Based on knowledge of isotopes representation in the basic components of the water molecule the meteoric water origin was confirmed without a doubt in substantial part of the investigated sources of mineral water. The isotopic composition of oxygen and hydrogen in most mineral waters followed the global line of meteoric water and corresponded to precipitations. Water with increased representation of unusually light isotopes H and O in the sedimentary infill of the Central Depression of the Danube Basin of Neogene age were considered either meteoric waters brought by the Danube River from the Alps, or for meteoric waters coming from colder periods. They could be brought into the Basin by local palaeo-streams or due to transfer from the surrounding mountains. In the deep levels of the sedimentation space, some geothermal wells uncovered waters whose isotopic composition is close to the isotope composition of ocean water. Transitional composition was considered to represent either direct composition of brackish water gradually depleted Neogene Sea, or the result of the mixing of fossil seawater with groundwater of meteoric origin. It was raised and discussed the question of the appropriate criteria to address these problems. Mineral waters enriched in the heavy isotopes of H and O in some mineral waters from the Palaeogene Flysch Zone sediments were considered a result of mixing between the (then hypothetical) water source of metamorphic origin with groundwater coming from local precipitation. Mineral waters of the Nízke Tatry Crystalline have meteoric origin and their chemical composition and the presence of Neogene sporomorphs has to be explained by contact with rocks of appropriate age. Large differences in the distribution of oxygen are considered to be a result of different altitudes of infiltration areas, or the result of circulation. For sodium-chloride waters present in the shallower aquifers of the Lakšárska Nová Ves elevation of the Slovak part of the Vienna Basin meteoric origin has been demonstrated.

Inorganic carbon present in the water sources investigated in the range of from about $\delta^{13}C$ ‰ -4 to +4 ‰ comes from the dissolution of marine carbonates. The increased presence of light carbon isotope in some mineral waters is explained by incomplete dissolution of carbonates with isotopic fractionation of carbon.

Thanks to the available analytical and sizing techniques the research in constituents dissolved in water components was aimed at the study of sulphur present in the water in various forms. The mineral waters, in which due to the ongoing bacterial reduction coexist SO_4^{2-} and H_2S there was characterized level of the ongoing reaction and the conditions were also reconstructed (concentration and isotopic composition of sulphur) of sulphate present in the water prior to the start of activity of the bacteria. Based on knowledge of the isotopic composition of sulphur in sulphate (and possibly hydrogen sulphide) there were determined two main sources of sulphur. Isotopically heavy sulphur comes from the dissolution of evaporites of marine origin. In the case its isotopic composition was not affected by other processes (mixing, oxidation-reduction processes, sorption, adsorption ....), based on the ratio of isotopes of sulphur (and oxygen) in sulphate we can estimate the age of marine sediments with which the water was in contact. In our conditions this involves distinction among the Permian-Early Triassic, Early-Middle Triassic, or Late Triassic and Neogene sediments. Sulphate extra-enriched in sulphur ($\delta^{34}S$ > 30 ‰) is regarded as the residual sulphate after reduction. Highly depleted sulphur present in some waters bound to rock complexes of Flysch Zone is the result of (at least) two-stage reduction of the original sulphate of Palaeogene Sea. During the first stage the enriched residual sulphate was degraded; resulting isotopically light sulphide has been preserved in the sediment in the form of pyrite. This light sulphur in the sulphide form becomes part of the groundwater due to the water-rock interaction in which as a result of bacterial reduction particularly isotopically depleted hydrogen sulphide is formed. Analogously isotopically enriched (heavy) sulphate in the mineral waters that surge out in the Neogene filling of the Vienna Basin – rich in pyrite and gypsum with a very light sulphur – is considered a consequence of transfer of mineral water with heavy sulphur from the deeper layers of the Basin deposits.

For the interpretation of findings of great importance was ongoing and in parallel research into isotopic composition of rivers, ordinary groundwater, later on precipitations, isotopic composition of carbonate rocks and shells, as well as sulphides and sulphates present in the rock environment.

The results obtained in the initial stages of isotope research in the field of mineral water have contributed to the knowledge on the formation of the mineral waters in the Slovak Republic and created conditions for a wider application of isotope geology in this area.

Acknowledgements: "This publication is the result of the project implementation: Ekotechnológia vyhľadania a hodnotenia náhradných zdrojov pitných podzemných vôd, pilotné územie BSK (Ecotechnology of Identifying and Assessment of Alternative Drinking Groundwater Sources), ITMS: 26240220003 supported by the Operational Programme Research and Development funded by the ERDF"

2.6 References

Barnes, I. & O'Neil, J. R.: Metamorphic reactions in flysch rocks. In Čadek, J. & Pačes, T. eds. 1976: Proceedings of international symposium on water-rock interaction, Czechoslovakia, ÚÚG, p. 309 – 316, 509-21-827.

Bottlik, F., Bodiš, D., Fordinál, K., Maglay, J., Michalko, J., Remšík, A., Lenhardtová, E. & Slaninka, I., 2013: Základná hydrogeologická a hydrogeochemická mapa severnej časti Podunajskej roviny v mierke 1 : 50 000. Čiastková záverečná správa, ŠGÚDŠ Bratislava, 214 p.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980: The age of sulphur and oxygen isotopes in marine sulphates and their mutual interpretation, Chem. Geol, 28, p. 199 – 260.

Franko O., 1975: Správa o nových zdrojoch termálnych vôd a možnostiach získania ďalších zdrojov v Podunajskej nížine Bratislava: GÚDŠ, Archív Geofond ID 34796, 37 p.

Franko, O. & Bodiš, D., 1989: Paleohydrogeology of mineral waters of the Inner West Carpathians. Západné Karpaty, séria hydrogeológia a inžinierska geológia, 8, Bratislava, p. 145 – 163.

Franko, O., Bodiš, D., Michalko, J., Remšík, A., Šivo, A., Bálint, J., 1995: Geotermálna energia Slovenska, Final report of 1991 – 1994, Manuscript, Geofond, Bratislava.

Franko, O., Michalko, J., Šivo, A., 2000: Isotopes of oxygen and ^{14}C in the geothermal waters of the Pliocene sediments of Danube basin. Sympozja i Konferencje nr. 45, IGSMiE PAN, Krakow , p. 229 – 239.

Franko, O., 2001: Pôvod a vývoj minerálnych a termálnych vôd Slovenska v priestore a čase z pohľadu veku travertínov a izotopov O, H a ^{14}C.- Podzemná voda ISSN 1335-1052, VII, 2/2001, p. 26 – 45.

Franko, O., Šivo, A., Richtáriková, M., Povinec, P., 2008: Radiocarbon Ages of Mineral and Thermal Waters of Slovakia. Acta Physica Universitatis Comenianae Vol. XLVIII-XLIX, Number 1&2, p. 111 – 124.

Kantor, J., 1985: Izotopová charakteristika vôd rôznych genetických typov, Manuscript, Geofond Archive SGIDŠ, Bratislava.

Kantor J., Ďurkovičová J., Eliáš K., Rybár M., Garaj M., Ferenčíková E., Hašková A., 1982: Genetická charakteristika evaporitov Západných Karpát podľa izotopov síry, Interim final report; Bratislava, GÚDŠ, Geofond Archive (ID 55064), 345 p.

Kantor, J., & Sládková, M., 1979: Izotopy síry v evaporitoch Západných Karpát I. – Interim final report of 1979. Bratislava, GÚDŠ, Geofond Archive (ID 45341), 125 p.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1977: Minerálne vody Slovenska. Balneografia a krenografia. 1., Martin, Osveta, 456 p.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1978: Minerálne vody Slovenska. Krenografia. 2., Martin, Osveta, 1,040 p.

Malík, P., & Michalko, J., 2002: Pôvod sulfátu rozpusteného vo vode vybraných krasovo-puklinových prameňov revúckeho zlomového pásma. (The origin of the sulphate dissolved in the groundwater of the selected karst-fissure springs in the Revúca fault zone). Podzemná voda č. 2 / 2002, Slovenská asociácia hydrogeológov, Bratislava, 67 – 78, ISSN, p. 1,325 – 1,052.

Michalko, J., 1998: Izotopová charakteristika podzemných vôd Slovenska. Kandidátska dizertačná práca, SAV, Bratislava, 94 p.

Michalko J., Bodiš D., Fendek M., 1991: Izotopové hydrogeochemické a hydrogeologické zhodnotenie vrtu Zborov-1, Bratislava: Interim report, GÚDŠ, Geofond Archive ID 76601/18, 41 p.

Michalko, J., Bodiš, D., Ženišová, Z., Malík, P., Kordík, J., Čech, P., Grolmusová, Z., Luptáková, A., Bottlik, F., Švasta, J., Káša, Š., 2015: Groundwater and surface water interactions in the Podunajská nížina lowland and Trnavská pahorkatina hills. Podzemná voda. ISSN 1335-1052. Roč.21, č.1 (2015), p. 24 – 39.

Nielsen, H., 1979: Sulphur isotopes, in Jäger, E. & Hunziker, J. eds.: Lectures in Isotope Geology, Berlin, Springer, p. 283 – 312.

Nielsen, H. & Ricke, W., 1964: Schwefel-Isotopenverhältnisse von Evaporiten aus Deutschland. Ein Beitrag zur Kenntnis von $\delta^{34}S$ im Meerwasser-Sulphat. Geochim. Cosmochim. Acta, 28, p. 577 – 591.

Pearson, F. J. jr., Balderer, W., Loosli, H.H., Lehmann, B.E., Matter, A., Peters, Tj., Schmassmann, H., Gautschi, A. 1991: Applied Isotope Hydrogeology. A Case Study in Northern Switzerland, Elsevier, Netherlands, ISBN 0-444-88983-3, p. 439.

Povinec, P., Franko, O., Šivo, A., Richtáriková, M., Breier, R., Aggarwal, P.K., Araguás-Araguás, L., 2010a: Spatial radiocarbon and stable carbon isotope variability of mineral and thermal waters in Slovakia. Radiocarbon, Vol. 52, Nr. 2–3, 2010, p. 1,056 – 1,067.

Povinec, P., Šivo, A., Richtáriková, M., Breier, R., Lúčan, Ľ., Aggarwal, P.K., Araguás-Araguás, L.J.,2010b: Spatial distribution of isotopes in grounwater of Slovakia Acta Physica Universitatis Comenianae-New Series, Vol. 50-51, No. 1&2 (2009-2010). – Bratislava: Comenius University Press, 2010. – p. 143 – 153. – ISBN 978-80-223-2750-3.

Rapant, S., 1991: Hydrogeologické pomery kryštalinika Nízkych Tatier, Thesis, Faculty of Natural Sciences of Comenius University, Bratislava, 179 p.

Rapant, S., 1994: Geochémia prírodných vôd kryštalinika Nízkych Tatier, Západné Karpaty, sér. Hydrogeológia a inžinierska geológia 12, p. 177 – 219, ISBN 80-85314-28-2

Rapant, S., Planderová, E., Bodiš, D., 1986: Aplikácia palinológie v hydrochémii. Mineralia Slovaca. Roč. 1986, roč. 18, č. 1, p. 79 – 88.

Remšík A., Fendek, M., Bodiš D., Král, M., .Zbořil. L., Kantor, J., Puchnerová M. 1985: Geotermálna energia Viedenskej panvy - prognózne zásoby, čiastková záverečná správa; Bratislava, ŠGÚDŠ, Manuscript, Geofond Archive SGIDŠ, 121 p.

Šmejkal, V., Michalíček, M., Krouse, H.R., 1971: Sulphur isotope fractionation in some springs of the Carpathian mountain systém in Czechoslovakia. Čas. Miner. Geol., 16, 3, Prague, p. 275 – 283.

Šmejkal, V., Hladíková, J., Michalíček, M., Procházková, V., 1981: Schwefelisotopenuntersuchungen an Sulphaten der Mineralwässer im Westkarpaten – System der ČSSR und in Westbohmen, Freib. Forsch. – II C 360, p. 57 – 74.

Zakovič, M., Potfaj, M., Fendek, M., Bodiš, D., 2009: Jódo-brómové podzemné vody v oblasti Oravskej Polhory. Podzemná voda. – Roč. 15, č. 2, 2009, p. 230 – 239, ISSN p. 1335 – 1052.

Slovak Geol. Mag., 16, 2 (2016), 41 – 56

Mineral Waters of the Slovak Spas – Chemical Analysis, History and Present

Dušan Bodiš[1], Jarmila Božíková[2], Daniela Mackových[3]

[1]State Geological Institute of Dionýz Štúr, Dept. of Environmental Geochemistry, Mlynská dolina 1, 817 04 Bratislava, Slovakia; dusan.bodis@geology.sk
[2]ISS MoH SR, Limbová 2, 837 52 Bratislava, FCE SUT, Radlinského 11, 810 05 Bratislava, Slovakia
[3]State Geological Institute of Dionýz Štúr, Regional Centre Spišská Nová Ves – Geoanalytical Laboratories, Markušovská cesta 1, 052 40 Spišská Nová Ves, Slovakia

Abstract: The basis for understanding the properties of mineral water as a favourable medium for the body is a chemical analysis. While mankind has long gone to the knowledge, thousands of years took place. History of chemical analysis of water began obviously with alchemy, which had prepared some background for scientific analytical chemistry. A criterion for assessing the chemical analyses is the comparability of historical results with the current ones. This criterion may be dated back to the turn of the 18th and 19th centuries. An example is a comparison of historical and current analyses of mineral waters of the Sliač Spa covering the period 1834 – 2016. Historically, for the documentation of the chemical composition of mineral water in Slovakia the 20th Century is the most important. Evaluation and classification of the chemical composition of mineral water is closely linked with exact results of chemical analyses. The first scientific classification of natural waters was developed in 1847 by an American geochemist Clarke. One of the oldest classifications, which are used even today, compiled Palmer in 1911. Slovakia is currently using assessment of natural waters, as proposed by Gazda in 1971 and it's actually a certain modification of the "Palmer system" with greater sensitivity and distinguishing ability of chemical water characteristics. Hereinafter, the paper evaluates mineral water of 18 spas in Slovakia. Distribution of species is made using thermodynamic model and it characterises the proportion of free ions and complexes in water. Interactions water-mineral-gas are ranked based on likely saturation index of plausible mineral phases. From geochemical analysis, it can be said that the dominant mineralization process of formation of mineral waters of the spa is the dissolution of carbonates. The second process that can significantly affect the resulting chemical composition is the dissolution of gypsum. Silicon is present in the mineral waters in particular in the form of un-dissociated H_4SiO_4. Acceleration of virtually all geochemical processes is alleviated by high levels of carbon dioxide, water temperature in the collector and a long residence time of groundwater in the rock environment. The result is a high TDS value in the range of 1,299 – 29,903 mg . l^{-1} (except for acratotherms). In addition to water-rock-gas interaction in some mineral waters of spas an important role play biological processes (presence of H_2S) and preserving relict marine water.

Key words: alchemy, analytical chemistry, balneology, classification of mineral water, thermodynamic model, distribution of species, mineralization processes

3.1 Introduction

Mineral water differentiates from ordinary groundwater by its chemical composition and physical properties. It can be stated that it represents a natural anomaly that has developed due to specific geological, hydrogeological, geochemical and tectonic conditions and is stored in the hydrogeological structure.

The mineral waters from the viewpoint of chemical composition contain the same substances as the ordinary groundwater, but in larger amounts, and in other quantitative ratios. Simply speaking, the solutes form three groups. The first group are compounds which are present in large quantities. Among the cations Na^+, K^+, Ca^{2+}, Mg^{2+} are present and among the anions HCO_3^-, SO_4^{2-}, Cl^-. The second group represent on the order less abundant cations such as Li^+, NH_4^+, Sr^{2+}, Ba^{2+}, Fe^{2+}, Mn^{2+} etc., among the anions Br^-, I^-, F^-, NO_3^-, AsO_4^{3-} etc., among the non-electrolytes H_2SiO_3 and HBO_2. The third group represent trace elements Zn^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+} and others. Similar conditions are valid for dissolved and free gases. High content may have gases CO_2, CH_4 and N_2. On order lower is the H_2S content. Some of the mineral waters are enriched with radium and radon, others contain smaller quantities of helium and argon. The groundwater turns to the mineral water by exceedance of a certain limit in the content of dissolved substances and gases. To determine the quality of mineral water and its use in balneology it is necessary to quantitatively determine various cations, anions, gas content and its physical properties.

The paper presents the development of knowledge about mineral waters through their properties and composition. It resides in historical documents and current chemical composition of water in 18 spas in Slovakia with recognized natural healing waters.

3.2 History of chemical analysis

Using of natural mineral water for therapeutic purposes dates back far into the beginning of human culture. First it was interest in learning about water and its force as impact on natural processes, but also on the human body. As early as 604 A.D., Lao Tzu, Chinese philosopher and founder of Taoism quoted: "Water is the softest thing, yet it can penetrate mountains and earth". An admirable knowledge at that time, which recognized in nature the action of two materials without the knowledge of geochemical processes. The beneficial effects of water on the human body apparently had roots in the principle of "try and see", for example, effects of thermal water, etc.

The knowledge of the water composition was examined in the past mostly by alchemists. The alchemy was the art, how to separate a part of the universe from existence in time and achieve improvement of this part, which meant gold for metals, longevity for man and his immortality. Improvement of the material was sought by action of various media (philosopher's stone for metals, the elixir of life for the people), while spiritual enlightenment evolved smoothly from an uncovered form.

The alchemy extends its beginnings in ancient times, it runs through the entire Middle Ages and its traces are still observed in the first century of Early Modern Times. Epicentre of the alchemy was probably in China, from where it spread to India, ancient Egypt, and from there to Greece. In Europe, alchemists focused more on metals. For centuries, there was a belief that there are only seven metals, i.e. the same number as then known planets. The pinnacle of European alchemy is considered the period of rule of Emperor Rudolf II; in his courtyard many alchemists like Kelley, De Brahe, Kepler and others, were active.

In the 17^{th} Century iatrochemistry had unfolded that the production of gold, the philosopher's stone and the elixir of life was replaced by the care of people's health and chemotherapy. Its main representative was Paracelsus, who began to use inorganic materials in the treatment, especially those of antimony and mercury. Paracelsus is also considered the founder of toxicology mainly because he defined the poisons in the form of "any substance is a poison, it depends only on its quantity".

From this brief characteristics of alchemy is clear that, in fact, it had not been science, but philosophy. On the other hand, it should be noted that the period of alchemy was beneficial for modern chemistry for example, it brought distillation apparatuses, mortar, banks, the development of basic experimental procedures and techniques, and not least the discovery of full range of elements and compounds.

From chemical discoveries it should be mentioned that after the 11^{th} Century sulphuric acid was known, termed the spiritus vitrioli or oleum vitrioli. The term vitriol for its glassy appearance (from the Latin vitreus – glass) was used to term crystalohydrates of metal sulphates, of which it was produced. Inter alia, it was also acquired by the decomposition – "distillation" of alums. Hydrochloric acid was obtained by the action of sulphuric acid on common salt. It was called spiritus saline. To this day it is called in German Salzgeist, that is the spirit of salt. Similarly, it was known as nitric acid mixture produced by saltpeter (sodium nitrate or potassium) heating with a mixture of copper sulphate and alums. There exist a description of aqua regia from 1270, which was prepared by the action of nitric acid upon ammonium chloride. In terms of the development of chemistry, after the discovery of iron the discovery of strong mineral acids was the biggest achievement. The time difference of the two discoveries is 3,000 years. Random discovered reactions of acid with potash (potassium carbonate) and other bases such as calcium hydroxide, and carbonates, gave impetus for the systematic examination of reactions for the preparation of salts, which we would term now neutralization reaction. Among other inorganic reactions there were disclosed reactions for the preparation of silver nitrate by dissolving silver in nitric acid and the preparation of silver chloride by hydrochloric acid action on nitrate. Copper was prepared by the so-called cementation, which is the effect of non-noble metal, for example, iron on solutions containing soluble copper compounds. Red mercuric sulphide was prepared synthetically, i.e. the mineral cinnabar, namely by direct compounding mercury and sulphur, which was very helpful in understanding the chemistry of mercury. Cinnabar was known already in ancient times as a medicine. Our predecessors already recognized a number of other mercury compounds. They did prepare various forms of iron oxide, in particular as colorants. By stibnite heating (antimony sulphide) with iron pure antimony was prepared and recognized as a new metal.

After completing 30 Years' War (1618 – 1648) and its hardships the alchemy faded away. This period can be called transition with regard chemistry as a science. Great advances of the 18^{th} Century were achieved by the fact, that the issues discussed were focused on the problem of combustion, resulting in the so-called phlogiston theory. This theory was introduced by G. E. Stahl, who had used in support few ideas of his teacher J. J. Becher. Late 18^{th} Century A. L. Lavoisier disproved all the arguments of the phlogiston theory and replaced them with new theory of oxidation.

The 19^{th} Century was in the field of analytical chemistry a period of consolidation. New scientists emerged with their discoveries, as Lomonosov, Lavoisier, Dalton, Avogadro, Mendeleev, Nobel and many others. From a methodological point of view there were used gravimetric and volumetric methods of analysis. Instrumental methods became important for analytical chemistry by the end of the 19^{th} Century. Almost immediately after its discovery a spectroscope was accepted as a means of qualitative analysis. Important role gained a refractometer and a polarimeter not only in purely scientific laboratories, but also in practice in the Food and Drug Administration.

3.3 Chemical analysis of water

Chemical analysis of water enables a detailed view of its composition, properties, applications and ultimately provides a picture of its origin. Very nicely this view can quote convey of important Slovak poet A. Sládkovič: "Alas, who sees in the sea only water, who can't hear a deaf nature, who sees in the stones just stones".

The healing effects of various mineral waters in Europe are described in books and articles about the year 1500. To complement the medical information on the effects of mineral water, some authors attempted to explain the chemical composition of dissolved salts. For example, a Spanish physicist Limon Montero 1697 divided water into two groups – drinking water and mineral water. Drinking water containing negligible amounts of solutes, and mineral waters containing minerals and metals in a significant content. These solid materials enrich the water by circulating through the rock and minerals. Like almost authors before about 1770, Limon Montero did not have neither a clear concept of the chemical composition nor relative amounts of material in the water (Davis & Davis, 1997).

Scientific basis of balneology has been systematically built up since the 18th Century, when there were recorded the first chemical explorations of mineral waters. In the first issue of the scientific journal "Physical and Chemical Essays" (1779), Torben Bergman, Professor of Chemistry and Pharmacy at Uppsala University in Sweden, wrote about chemical analysis of natural waters, including the mineral ones. He noted that if the weighed amount of mineral water is evaporated in the smoke, the weight of the residue is negligible compared to the weight of water; however, the residue may comprise six to eight earth metal salts and ingredients. Bergman said that "accurate water analysis can be considered as one of the most difficult problems in the chemistry" (Bergman, 1779). Although there were problems of identifying small quantities of salts with similar chemical properties, there was no guarantee that the residue will contain the same compounds as mineral water. This means that at the analysis of mineral water, the chemists have encountered many difficulties. The analyst had to be smart and to have a lot of experimental experience. Most of those who wrote on this topic in the Seventeenth to the early Nineteenth centuries were physicians practicing medicine in spas. Among the most famous belonged Robert Boyle and Friedrich Hoffmann. The work by Boyle "Memoirs of a natural history of mineral waters", published in 1685, contained many original solutions with regard to the knowledge of the time. The introduction stated that it was necessary to take into account geological environment, through which a mineral water passes. Then followed the tests – temperature and density of water (using a hydrostatic scales), transparency, colour, smell. To put water drop under the microscope and examine how many moving particles appear in it. To detect and observe sediment and particles formation during storage on the air, during the boiling and freezing process of water. To measure viscosity. After these tests, subsequent chemical examination of water and distillation residue follow. Boyle also used tannin solution to test the presence of iron (black colour) and copper (red precipitate). He stated that the tannin should be carefully added, because the intensity of colour indicates the number of elements in the water. He proposed also other agents – rose extract, pomegranate extract, Brazilian wood, etc. He described the new reagent, which he called "volatile sulpherous spirit" that gave with the lead a black colouration. Boyle studied many reagents to prove the chemical elements. Several authors agree that he was the actual founder of chemistry as a science. Boyle separated chemistry from medicine, and gave it a new direction.

Another important book is by Hoffmann "Methodus examinandi aquas salubres" which was published in 1703 (Coley, 1990). In this book he described the analyses of many types of mineral waters. His work was underpinned by the knowledge described by Boyle. The components that were recognizable in the mineral water were sodium, potassium sulphide; iron was indicated by the presence of red colour in the sediment. The presence of dissolved iron he indicated by the presence of carbon dioxide. If carbon dioxide was expelled by boiling, iron fell out of solution. In the same way, he showed the presence of Fe, which came out of solution as vitriol (iron sulphide). The presence of alkali metals he determined with ammonia. He also discovered the presence of magnesium salts and separated them from calcium salts. Sulphidic waters he determined with silver salt by formation of black silver sulphide precipitate. Hoffmann had the belief that water is a complex of etheric and solid substances. Hoffmann's work is recognized as a significant contribution to the chemical examination of mineral water, but described chemical tests which he introduced, cannot be classified as a systematic method for the analysis of mineral water. This became an important goal of later authors of the Eighteenth Century (Szabadváry, 1966).

The first one who attempted to systematize the analysis of mineral waters in England was Thomas Short, doctor from Sheffield, who wrote about some English mineral waters in 1730 (Coley, 1990). Short criticized all previous analysts of mineral waters, including Boyle and Hoffmann and tried, though without much success, to develop methods of mineral waters testing, using proven agents such as vegetable colours, silver nitrate, mercury salts, sugar, certain acids, ammonia. While he was able to identify some of the basic compounds of mineral waters, he didn't manage to determine volatile components, which had healing properties.

In 1740 William Brownringg, doctor of Whitehaven, conducted experiments with water from spas in Belgium. He came with the recognition that volatile gases from the mineral waters were the same as gas from coal mines. The publication was issued in 1765 (Hamlin, 1990). Later in 1770, Bergman recognized the importance of dissolved air in water; he named it as a "direct acid". He identified the hydrogen sulphide and nitrogen in various mineral waters. To determine the sulphates he used barium chloride, to evidence chloride, he used silver nitrate, concentrated nitric acid for evidence of sulphides, oxalic acid for the detection of calcium, ferrocyanide for iron. Bergman knowledge of the composition and the analysis of mineral waters created scientific basis in the coming years.

One of the drawbacks of investigators of that time was the fact that they expressed the components of mineral waters as solid salts. For example, the ions Ca^{2+} and SO_4^{2-} they expressed as $CaSO_4$. Only in 1900 upon Arrhenius (1859 – 1927) discovery of the theory of dissociation and ionization, the scientists began to take into account the elements in ionic form. Analyses of mineral water were "almost" complete, expressed as the elements in ionic form (Palmer, 1911). In Tab. 3.1 the chemical elements are included with the date of their discovery in waters (Hammond, 1967).

Major innovation of mineral water analyses was the discovery of spectrographic method by Robert Bunsen and Gustav Kirchhoff. In 1857 Bunsen devised a method to identify volatile metals in the flame using a platinum wire. The proof resided in different colours of the flame for each element. Three years later, in cooperation with Kirchhoff,

Tab. 3.1 Date of discovery of some chemical elements, important for water analysis

Element	Discovery date	Scientist credited with the discovery
Boron	1808	Davy, Guy-Lussac, and Thenard
Bromine	1826	Balard
Calcium	1808	Davy, Berzelius, and Pontin
Carbon	Prehistory	-
Chlorine	1810	Davy
Fluorine	1886	Moisson
Iodine	1811	Courtois
Iron	Prehistory	-
Magnesium	1808	Davy
Nitrogen	1772	Rutherford
Oxygen	1775	Lavoisier
Potassium	1807	Davy
Silicon	1824	Berzelius
Sodium	1807	Davy
Sulphur	Prehistory	-

he contributed by important improvement of the method. Coloured light from the flame they left to pass through a prism and to reflect a spectrum at a white wall. Almost immediately they discovered two new elements, caesium and rubidium. Only a very small amount of sample was needed for the detection of elements by spectroscopy. Since 1860, thanks to their sensitivity and comfort the spectroscopic methods belonged among the most important methods for the analysis of groundwater.

Given the nature of related problems, it is easy to see why those who tried to reveal the chemical composition of mineral water in the Eighteenth Century met with many difficulties. Even the simple technique – evaporation of water, which enables to obtain the dissolved solids in the solid form, was a problem for a chemist of that time (Coley, 1990).

Currently, the analysis of mineral waters still means a challenge at solving complex matrix, although the development of methodologies in the Twentieth Century progressed enormously. For the analysis of mineral waters techniques are now routinely used such as gravimetric, volumetric analysis, electrochemical methods, spectrophotometry, ion chromatography, atomic absorption spectrophotometry – flame, hydride generation, electrothermal atomisation, atomic emission spectrometry with inductively coupled plasma and the latest techniques for the determination of elements in ultra-trace concentrations – mass spectrometry with inductively coupled plasma.

3.4 Chemical analyses of mineral water in Slovakia

Obviously, in the amount of historical information on the chemical composition of mineral water in Slovakia, it is impossible to designate any analysis by the term "the oldest chemical analysis of mineral water". This is due to a variety of criteria on this issue. If we choose a criterion – the comparability of historical analyses with the current ones, it can be said that revolution in analytical methods and the expression of the results of chemical analysis occurred at the turn of the 18th and 19th centuries. In the chemical analyses of the early 19th Century, there were already the breakdowns of the contents of the main components expressed in the form of salts. Later, this form of expression changed using the oxides, e.g. CaO, MgO, R_2O_3, etc. The current form of expression of the results of chemical analyses in ionic form was launched at the beginning of the 20th century.

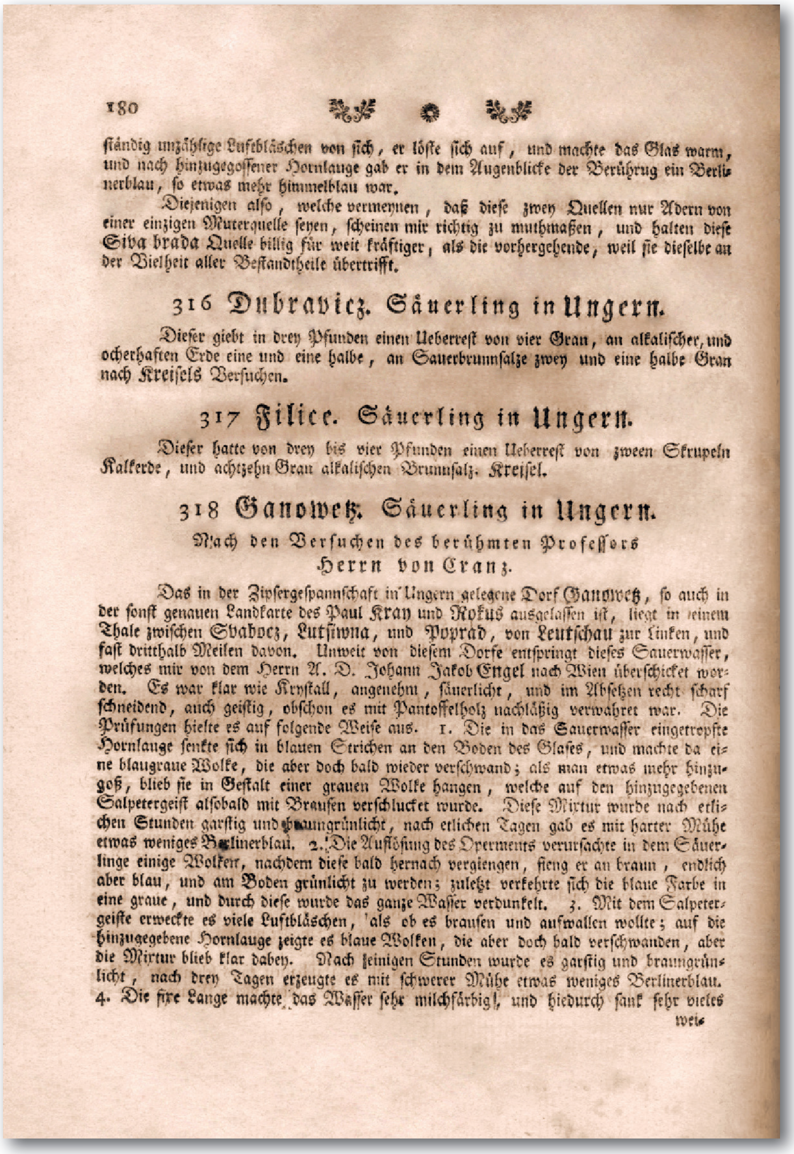
History of learning and discovery of mineral waters in Slovakia is very well described in translations and works of A. Rebro (Rebro, 1983, 1996 and others). Definitely, the father of balneography can be regarded J. Wernher who by his work "De admirandis Hungariae aquis hypomnemation", published in 1556 in Basel, stunned the then world. He systematically described and represented 22 sites of mineral water. He was interested in and examined the properties of waters. In Špania Dolina Valley, where copper was mined, there were reports about the source from which greenish water flows out, in which can be found after settling grains of chrysocolla. At Sliač he described a depression with malignant vapours. When above this depression the stick tied cock or hen were tentatively shoved, leaving them under the influence of vapours, these birds so quickly perished, as though they were strangled (Wernher, 1556). It was probably the depression with expelled carbon dioxide, that at that time people were not yet aware. From a chemical point of view, the most famous is description of copper acquisition from mine waters in Smolník. Practically it was a process (popularly cementation), where less noble metal (using the pieces of pig iron) precipitated copper from water.

Interesting contribution on the composition of mineral water provided Tomas Jordan from Cluj by work "O vodách hojitedlných neb teplicech moravských" (*On healing and thermal waters of Moravia*) in 1581. He described them in Trenčianske Teplice. The work also provided information about collection of undisturbed sample of water, which was carried out in such a manner, that he charged the servants to emplace to the bottom of the pool a pitcher closed with a cork stopper. This was opened by one servant who took the water in the pitcher, closed it and the second servant pulled him by his legs above the water. The pure sample was subjected to distillation. What remained after distillation resembled the pharmacists copper sulphate, which is also called alumen plumeum. If it was put on the fire, whiteness was not lost. Therefore he concluded that hot water of Trenčín contained a lot of very fine sulphur fumes and with them was also a large amount of mixed sulphate (alum).

Significant work was compiled during the Habsburg Empire by Johan Heinrich von Crantz in 1777. The work was created as a summary of the results of the first official registration of mineral resources from the years 1763 – 1769. It was a huge work with 306 pages containing a sources register. From Slovakia he described 158 sites with mineral water, which in many cases appeared in writing for the first time. In terms of chemical analysis, the work is very inconsistent (supplied by many informants) and consists of some experiments with a variety of acids, salts, and dyes to characterize the chemical composition of water. An example of one page of the original of this work, which describes site Gánovce, is on Fig. 3.1.

First older chemical analyses, which could be already compared with the current ones were made in the early 19th Century. In these cases, at the analyses adjustment, there may occur various irregularities, which were summarized by Hyánková (1989):

- Inconsistencies in the marking and naming of mineral water sources and sites of their occurrence;
- Inconsistencies in the use of chemical terminology, in which there were used various combinations of German, Hungarian and Latin names of individual compounds;
- Inconsistencies in the form of expressing bound carbon dioxide, mostly referred to as carbonates;
- Incompleteness of chemical analyses in terms of representation of the main ions;
- Inconsistencies in the quantification of results, which were in the old analyses somewhere expressed in grans for 16 ounces, or 32 ounces, and sometimes also in the pharmaceutical, or civilian pounds.



180

ständig unzählige Luftbläschen von sich, er löste sich auf, und machte das Glas warm, und nach hinzugegossener Hornlauge gab er in dem Augenblicke der Berührug ein Berlinerblau, so etwas mehr himmelblau war.

Diejenigen also, welche vermeynen, daß diese zwey Quellen nur Adern von einer einzigen Muterquelle seyen, scheinen mir richtig zu muthmaßen, und halten diese Siva brada Quelle billig für weit kräftiger, als die vorhergehende, weil sie dieselbe an der Vielheit aller Bestandtheile übertrifft.

316 Dubravicz. Säuerling in Ungern.

Dieser giebt in drey Pfunden einen Ueberrest von vier Gran, an alkalischer, und ocherhaften Erde eine und eine halbe, an Sauerbrunnsalze zwey und eine halbe Gran nach Kreisels Versuchen.

317 Filice. Säuerling in Ungern.

Dieser hatte von drey bis vier Pfunden einen Ueberrest von zween Skrupeln Kalkerde, und achtzehn Gran alkalischen Brunnsalz. Kreisel.

318 Ganowetz. Säuerling in Ungern.

Nach den Versuchen des berühmten Professors Herrn von Cranz.

Das in der Zipsergespannschaft in Ungern gelegene Dorf Ganowetz, so auch in der sonst genauen Landkarte des Paul Kray und Rokus ausgelassen ist, liegt in einem Thale zwischen Svabocz, Lutsiwna, und Poprad, von Leutschau zur Linken, und fast dritthalb Meilen davon. Unweit von diesem Dorfe entspringt dieses Sauerwasser, welches mir von dem Herrn A. D. Johann Jakob Engel nach Wien überschicket worden. Es war klar wie Krystall, angenehm, säuerlicht, und im Absetzen recht scharf schneidend, auch geistig, obschon es mit Pantoffelholz nachläßig verwahret war. Die Prüfungen hielte es auf folgende Weise aus. 1. Die in das Sauerwasser eingetropfte Hornlauge senkte sich in blauen Strichen an den Boden des Glases, und machte da eine blaugraue Wolke, die aber doch bald wieder verschwand; als man etwas mehr hinzugoß, blieb sie in Gestalt einer grauen Wolke hangen, welche auf den hinzugegebenen Salpetergeist alsobald mit Brausen verschlucket wurde. Diese Mixtur wurde nach etlichen Stunden garstig und braungrünlicht, nach etlichen Tagen gab es mit harter Mühe etwas weniges Berlinerblau. 2. Die Auflösung des Operments verursachte in dem Säuerlinge einige Wolken, nachdem diese bald hernach vergiengen, fieng er an braun, endlich aber blau, und am Boden grünlicht zu werden; zuletzt verkehrte sich die blaue Farbe in eine graue, und durch diese wurde das ganze Wasser verdunkelt. 3. Mit dem Salpetergeiste erweckte es viele Luftbläschen, als ob es brausen und aufwallen wollte; auf die hinzugegebene Hornlauge zeigte es blaue Wolken, die aber doch bald verschwanden, aber die Mixtur blieb klar dabey. Nach einigen Stunden wurde es garstig und braungrünlicht, nach drey Tagen erzeugte es mit schwerer Mühe etwas weniges Berlinerblau. 4. Die fixe Lauge machte das Wasser sehr milchfärbig, und hiedurch sank sehr vieles

wei-

Fig. 3.1 Example of the work by von Crantz (1777) – Gánovce

Tab. 3.2 Chemical analyses of the source Sliač Kúpeľný from various periods

Year of analysis	1834	1855	1882	1921	1950	1967	2016
Analyst	Wagner	Hauch	Than	Prokeš	Nemejc	*	**
Na	sum (Na+K)	sum (Na+K)	56.4	65.36	57.9	57	58.49
K	134.9	104.4	36.9	43.25	32.3	34.2	39.36
Li	2.08	3.87	0.05	0.05	1.1	1.37	0.228
Ca	621.8	643	639.9	643.82	699.2	709.42	685.78
Mg	126.7	217.9	184.8	151.84	188.1	184.83	174.36
Fe	2.7	9.58	7.57	9.51	1.83	7.2	2.44
Mn	-	-	0.65	0.72	-	0.8	1.01
Cl	7.2	4	4.42	6.12	4.3	51.93	6.38
SO_4	1,375	1,632	1,534	1,750.55	1,540.4	1,630.77	1,584.7
HCO_3	880.7	1,304	1,158	763.65	1,316	1,195.6	1,162.4
H_2SiO_3	37.7	15.6	30.7	35.3	-	13.19	15.84
CO_2	1,200	1,301	1,269	1,468.8	-	1,415	1,749.88

*Note: results in mg . l^{-1}, * Franko et al., 1975, **ISS MoH SR*

As an example of a comparison of chemical analyses Location Sliač is presented. The recalculated analyses since 1834 to the most recent from 2016 were at disposal (Tab. 3.2). The analyses of the years 1834 and 1855 are incomplete because they express sodium and potassium content as summation and they lack determination of manganese. In other analyses, the contents of Na and K are comparable, indicating both the analytical precision and the stability of the two components. Lithium content varies in the range of 0.05 – 3.87 mg . l^{-1}, which can probably be explained by an analytical technique other than that of the last test (Analytical Method ICP-AES). The content of calcium and magnesium is likely to be comparable, and is highly dependent on the chemical stabilization of the samples taken to the laboratory. It is still possible certain dispersion of values that can be caused by different contents of carbon dioxide over time and depending on the sampling of mineral water. The content of bicarbonate can be assessed similarly.

From the viewpoint of historical documentation of the chemical composition of mineral water in Slovakia the most important is 20th Century. The first one was "Balneography of Slovakia" (Hensel, 1951). The author illustrates the chemical analyses of the 46 spas in Slovakia. In addition, the work also analyses indicated non-spa sources classified according to the then districts. The work also contains analyses of gases and peloids. Another important work is the "Mineral waters of Slovakia, balneography and crenography" (Krahulec et al., 1977, 1978). As the name suggests, it consists of two parts, the first is balneography in which the chemical analyses of 17 spas are presented. The second part consists of practical results of registration of mineral water in Slovakia by districts. In the then re- gistration there were recorded around 1,200 mineral water sources. Very important is the third work "Genesis and classification of mineral waters of the Western Carpathians" (Franko et al., 1975). The work includes 81 chemical analyses of mineral waters. Significant, however, is the hydrogeological and hydrogeochemical assessment. The work provides essential information for understanding the formation and genesis of mineral waters in Slovakia.

3.5 Classification of the chemical composition of mineral water

Classification of the chemical composition of natural waters is practically linked to the very beginning of the examination of the content of total dissolved solids and gaseous substances in water. In connection with the increased use of mineral water for spa and therapeutic purposes and advances in analytical methods there have been accumulated a considerable number of chemical analyses mainly in Germany and Russia. At that time, typing of mineral waters according to chemical composition did La Rua in 1779 and Hofmann in 1815.

The first scientific classification of natural waters drew up in 1847 the famous American geochemist F. Clarke. He divided the waters according to three basic characteristics:

– Dissolved salt content;
– Hardness (summation of salts of alkaline earth elements);
– Alkalinity (summation of salts of constant acids);

whereas the results of chemical analyses he expressed in the form of oxides and anhydrites.

Rather large milestone in the expressing of the chemical composition of waters was drawn up by Viennese chemist C. Than in 1864, who proposed an equivalent form. This was later elaborated with S. Arrhenius, W. Ostwald and others. These authors showed that in aqueous solution the individual components are not in the form of oxides and salts, as was previously believed, but in the form of cations and anions.

Another important factor that influenced the reporting of results of chemical analyses was elaboration of definition of a system of combining acid (or anions) and bases (or cations). In the mid-19th Century Bunsen (1874) and Fresenius (1876) submitted two different ways of such a combination. The Bunsen method consisted of a sequence of loss of salt from a solution at water evaporation. The Fresenius method consisted in the gradual emergence of chemical compounds in relation to their reactive acids and bases in a row $Na^+/+K^+/-Mg^{2+}-Ca^{2+}$, NO_3^- – SO_4^{2-} – $HCO_3^-/+CO_3^{2+}$. It can be said that the principles of Fresenius – combination of cations and anions in the direction of decrease in the solubility of the salts, wherein the content of cations and anions is represented by C. Than in equivalent values, have become virtually permanent scientific basis for the development of hydrochemical classification of natural waters. One of the earliest classifications of this type is the classification of C. Palmer, published in the USA designed by Stabler (1911) and amended by Rogers (1917). It is based on so-called "Palmer Indices".

The classification of medicinal mineral waters, according to Hynie (1963) sets out two basic directions – medical and chemical, or chemical – geological. The medical direction classifies water according to representation of ions in solution in relation to the human organism and the chemical – geological one actually to determine the genesis of mineral water. Hynie (1963) draws attention to one of the most important things: "We cannot alter or combine balneological classification systems and nomenclature with geochemical classification systems and nomenclature, applicable to all natural water".

Jetel (1975) essentially divides the classifications of the chemical composition of natural waters into genetic and descriptive ones. At the genetic classification the abovementioned author provides an interesting remark: "Classification which, based on formal chemical or physical parameters, would allow for unambiguous genetic classification, does not yet exist, and it is uncertain whether it can exist".

Geochemical issues of mineral waters in the Western Carpathians, based on data by Hensel (1951), were dealt with Mahel' (1952), later by Hynie (1963). The formation and classification of mineral waters of the Western Carpathians is in the focus of the work Franko et al. (1975). In this work, for the division of the mineral waters according the chemical composition, the classification by Gazda (1971) is used. This is a modification of Palmer's classification system, where in addition of the principle of ion combinations the principle of the prevailing characteristic is used. This classification eliminates small resolution of the original Palmer's indices by splitting the first and second salinity on the chloride, sulphate ones and nitrate, as appropriate. The other division of the second salinity into magnesium-chloride and calcium-chloride components allows to build on other classifications, such as by Alekin, Sulin, etc. It further distinguishes on the principle of the prevailing characteristics basic, intermediate and mixed types of water. The above classification is still used in Slovakia to evaluate groundwater, in particular, and mineral and geothermal water in its scope.

3.6 Characteristics of the components of mineral water of spas

Geochemical characterization of mineral water of spas is made on the basis of assessment of 18 spas in Slovakia. Because in individual spas there can be mineral water sources of different chemical composition, their choice was made so that the spas having several such sources are represented by several analyses in the selection. Chemical analyses represent the situation of 2016. Some discrepancy in the number of spas is due to the fact that in the Čilistov site the spa is currently not operated (Fig. 3.2).

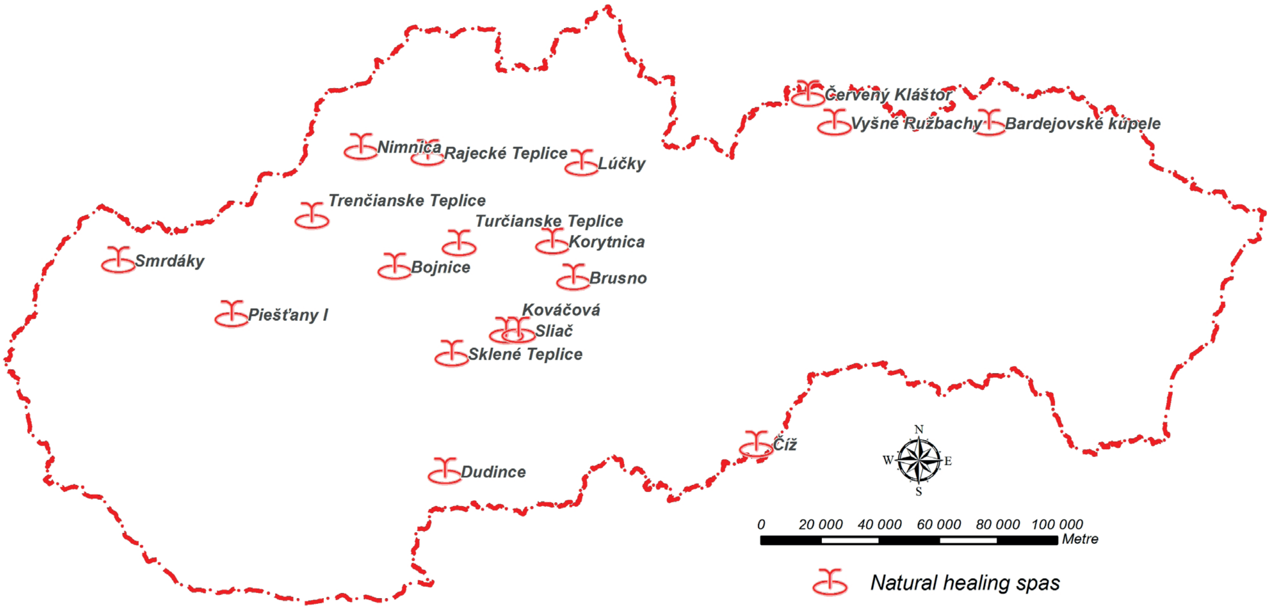


Fig. 3.2 Current spas in Slovakia

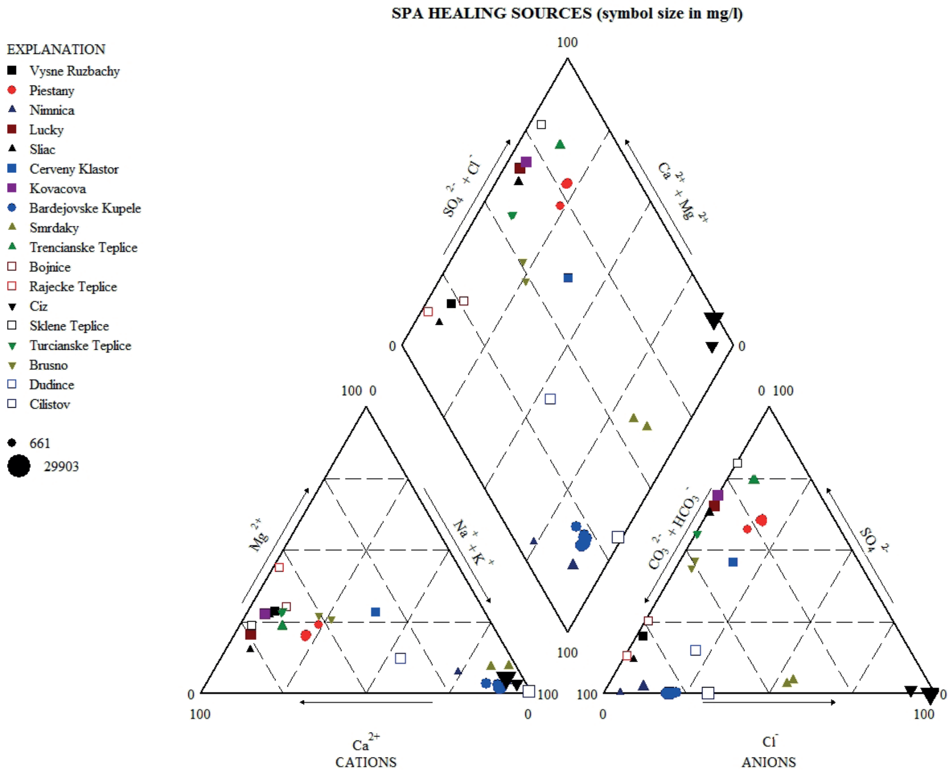


Fig. 3.3 Systemisation of chemical composition of mineral waters of the Slovak spas

The rating is made of a total of 36 chemical analyses. Variety of chemical composition is best documentable by Piper diagram (Fig. 3.3).

Diversity of content of each major ions in the mineral waters of the spas in Slovakia documents the situation of individual points and their projections in a triangular diagrams. They are located at their peaks with maximum representation of ions. Similarly, it is also seen in the central quadrangle, where the projection points are distributed in an area of the peaks. An exemption among the cations is magnesium, which only in exceptional cases exceeds the calcium content in mineral waters, due to interactions with the rock and the prevalent share of limestone in the hydrogeological structures of the spa sources. Similarly to the chemical composition of mineral water, the TDS is in a wide diapason (Fig. 3.2) from 661 mg . l^{-1} to 29,903 mg . l^{-1}. The lowest values are characteristic for acratotherms (Rajecké Teplice and Bojnice) and the highest ones for somewhat degraded relict marine waters of strong Na-Cl type in Číž.

Basic statistical characteristics of the mineral water of spas is presented in Tab. 3.3. It documents the variability of the components of water and in most cases their uneven distribution. Differences in mean and median, and similarly large differences in minimum and maximum values refer to different natural conditions of the evolution of these waters. In terms of content of gases it can be said that most of the mineral water is oversaturated with gaseous carbon dioxide. The occurrence of hydrogen sulphide is a subject to specific conditions, in which, moreover, biological processes also participate, in this case the desulphurication bacteria. A characteristic example is the Spa Smrdáky. An interesting feature is the presence of both gases in the Dudince mineral water, which can be said world rarity. All components are the products of natural processes, and have evolved in relatively stable conditions mostly in deeper hydrogeological structures for long periods of time. Iron and manganese contents are of natural origin and are typical for most mineral waters of the Western Carpathians. Naturally raised organic matter content, expressed as COD, is characteristic mainly for mineral water of Na-Cl

Tab. 3.3 Main statistical parameters of chemical composition of mineral waters of spas

	Mean	**Median**	**St. dev.**	**Minimum**	**Maximum**	**Lower quartile**	**Upper quartile**
T_w	32.39	29.60	19.89	11.60	67.20	14.00	46.00
pH	6.77	6.72	0.32	6.20	7.69	6.57	6.89
TDS	4,045.7	2,589.0	5,170.4	661.0	29,903.0	1,432.0	5,143.0
CO_2	865.89	597.50	883.40	0.00	2,486.88	90.20	1,565.94
H_2S	29.231	0.036	114.356	0.000	496.000	0.005	5.150
Li	0.758	0.340	0.871	0.009	3.640	0.190	1.250
Na	873.58	95.00	1,874.16	4.20	10,400.00	50.75	1,009.50
K	28.65	21.55	25.10	1.80	131.00	14.00	36.55
NH_4	4.972	0.425	13.418	0.005	71.300	0.149	3.830
Mg	68.00	48.90	61.01	7.20	350.00	28.75	87.44
Ca	239.71	221.50	175.51	15.10	685.78	110.00	277.88
Sr	6.514	5.616	9.086	0.320	53.900	0.838	9.314
Fe	1.720	0.050	4.543	0.003	24.260	0.014	0.535
Mn	0.212	0.036	0.311	0.001	1.071	0.007	0.417
Ba	0.521	0.070	1.037	0.018	5.190	0.032	0.455
Al	0.054	0.013	0.108	0.000	0.530	0.010	0.046
F	1.54	1.59	1.12	0.05	3.72	0.42	2.10
Cl	916.47	122.50	3,116.36	2.84	17,800.00	16.71	538.50
Br	6.165	0.250	22.945	0.000	120.000	0.100	1.935
I	3.273	0.050	13.606	0.002	76.600	0.025	0.541
HCO_3	1,363.37	728.00	1,441.13	262.00	4,972.00	407.05	1,810.00
SO_4	453.22	459.00	483.44	1.80	1,584.70	24.27	582.00
SiO_2	35.72	29.01	22.87	6.70	108.89	19.35	46.20
COD	3.667	1.115	9.624	0.150	44.300	0.150	2.730

Note: all the data, except T_w (water temperature °C) and pH are in mg . l^{-1}

chemical type, linked mainly to the geochemically and hydrogeologically closed structures. An example provides the already mentioned mineral water in Číž.

At present, it is interesting to know the proportion of species distribution of major and trace elements in mineral water. In the following text there are examples of the value of the total content of selected elements compared to different forms of the element in the complexes and free ions. These findings are relevant in balneology at their behaviour in the human body, but also for the overall characteristics of mineral water and its genesis in sense of modelling of plausible mineral phases in the water-rock-gas interactions.

The above mentioned characteristics of mineral waters were analysed using the code PHREEQC (Parkhurst & Appello, 1999) with a database WATEQ. Background information provided chemical analyses of 36 sources of natural medicinal resources. In the following charts the sites are listed in number format as follows: 1- Vyšné Ružbachy, 2, 3, 4, 5, 6, 7, 8- Piešťany, 9, 10- Nimnica, 11- Lúčky, 12, 13- Sliač, 14- Červený Kláštor, 15- Kováčová, 16, 17, 18, 19, 20, 21- Bardejovské kúpele, 22, 23- Smrdáky, 24, 25- Trenčianske Teplice, 26- Bojnice, 27- Rajecké Teplice, 28, 29- Číž, 30- Sklené Teplice, 31, 32- Turčianske Teplice, 33, 34- Brusno, 35- Dudince and 36- Čilistov.

Calcium in the mineral waters of the spas occurs mainly as free ion Ca^{2+} (Fig. 3.4). The highest percentage (98.5 %) it has in the mineral water source BČ-5 in Číž. The chemical composition of the water, despite the Na-Cl type, reaches one of the highest contents of calcium and magnesium, and sulphates are practically complete absent. The share of complexes $CaHCO_3^+$ and $CaSO_4^0$ represents the second major calcium species. Their presence practically depends on the representation of bicarbonates and sulphates in mineral waters. In the sulphatogenic waters the complex of $CaSO_4^0$ is in prevail (sites Trenčianske

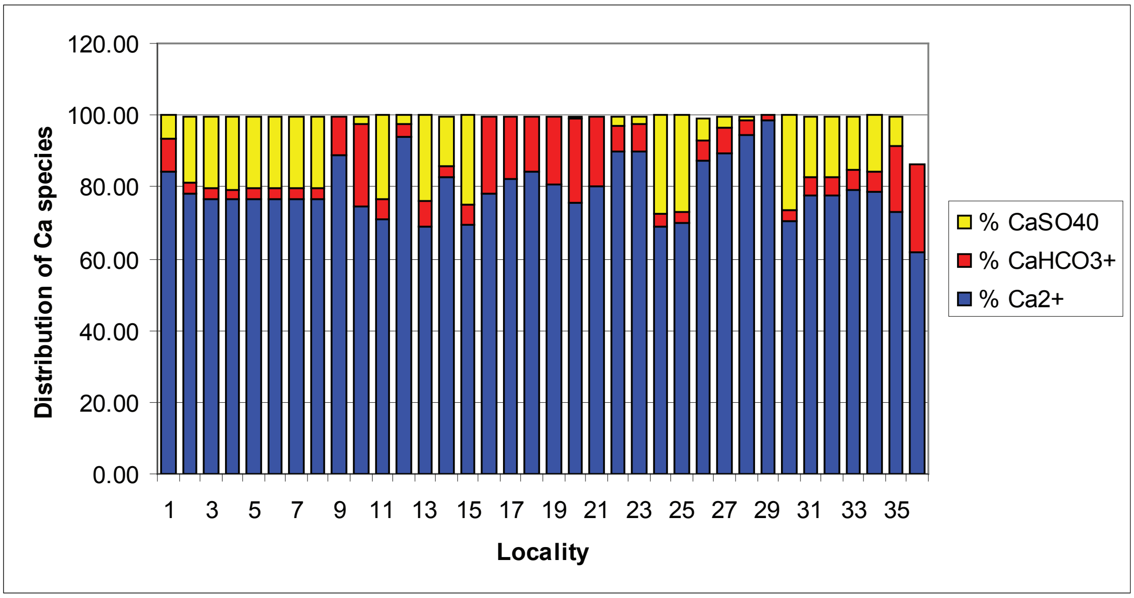


Fig. 3.4 Distribution of calcium species in mineral waters

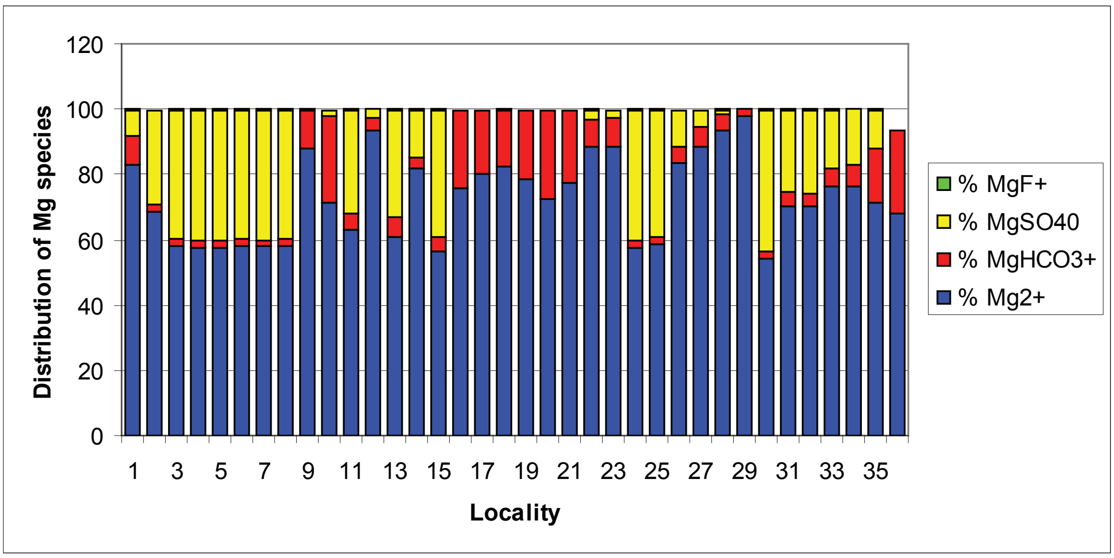


Fig. 3.5 Distribution of magnesium species in mineral waters

Teplice, Sklené Teplice, Kováčová, Sliač and Lúčky) and vice versa $CaHCO_3^+$ in mineral waters of Bardejov Spa, Nimnica and Čilistov with Na-HCO_3 type of waters. Share of the $CaSO_4^0$ complex is only 0.03 % in mineral water in Čilistov, where it is also the lowest content of sulphates. The rest (Fig. 3.4) represent a $CaCO_3^0$ complex.

Species distribution of magnesium is very similar to calcium by free ion representation, as well as by complexes $MgHCO_3^+$ and $MgSO_4^0$ (Fig. 3.5). This is due to the similarity of geochemical properties of these two elements and presence, or absence of gypsum/anhydrite in the circulation path of mineral waters. Distribution of the MgF^+ complex is within the range of 0.01 to 12.52 %, with a maximum in the mineral waters of Piešťany. Similarly to calcium, about 10 % of the magnesium is present in the form of $MgCO_3^0$ complex with the occurrence in the water well FGČ-1, Čilistov.

Distribution of potassium and lithium in all mineral waters is mainly represented by free ions of K^+ and Li^+, and in a much lower percentage in complexes $NaSO_4^-$ and $LiSO_4^-$.

Bromine in all mineral water of the spas occurs only in the form of the free Br^- ion.

Similarly to other waters, the distribution of fluorine species is the subject of their chemical composition and thus their genesis. The highest percentage in the mineral waters of the spas has free ion F^-. In most cases it reaches more than 90 % of the amount of fluorine in the water (Fig. 3.6).

The exception is the spring Štefánik (Sliač), which is a mineral water with a low TDS (661 mg . l^{-1}), carbonated. It is formed below sedimentary volcanic complexes shallow under the surface. Proof of this is high content of SiO_2, up to 108.89 mg . l^{-1}. In addition to the free ion F^-, this mineral water contains also the complexes AlF^{2+}, AlF_2^+ and AlF_3^0. Different species distribution of fluorine is in mineral water of Brusno with complexes AlF_2^+, MgF^+, AlF_3^0 and in Dudince with complexes MgF^+, AlF_2^- and NaF^0 (Fig. 3.6).

In most mineral waters silicon is present as undissociated H_4SiO_4. When expressed as a percentage of total silicon it represents more than 99.5 %. The second silicon species

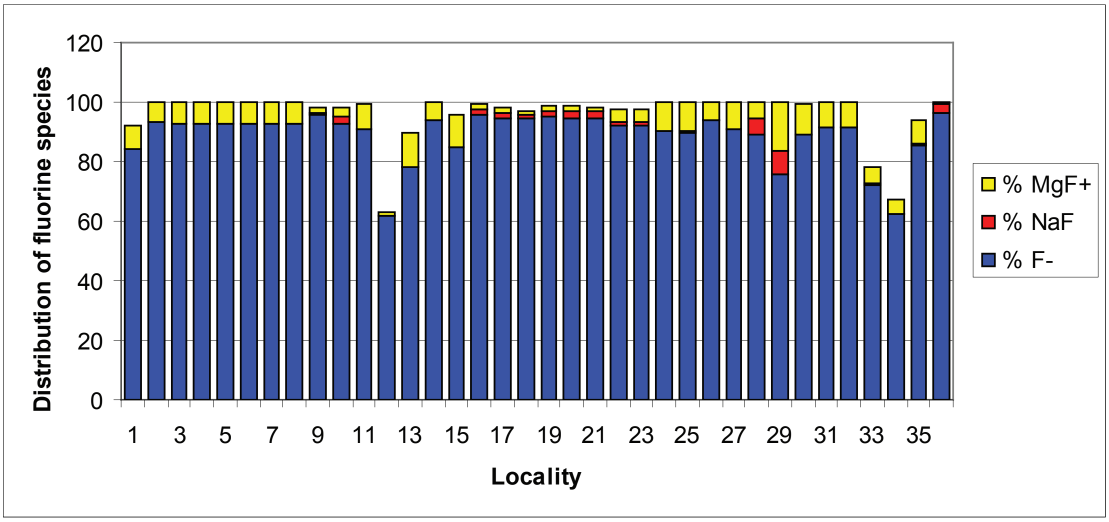


Fig. 3.6 Distribution of fluorine species in mineral waters

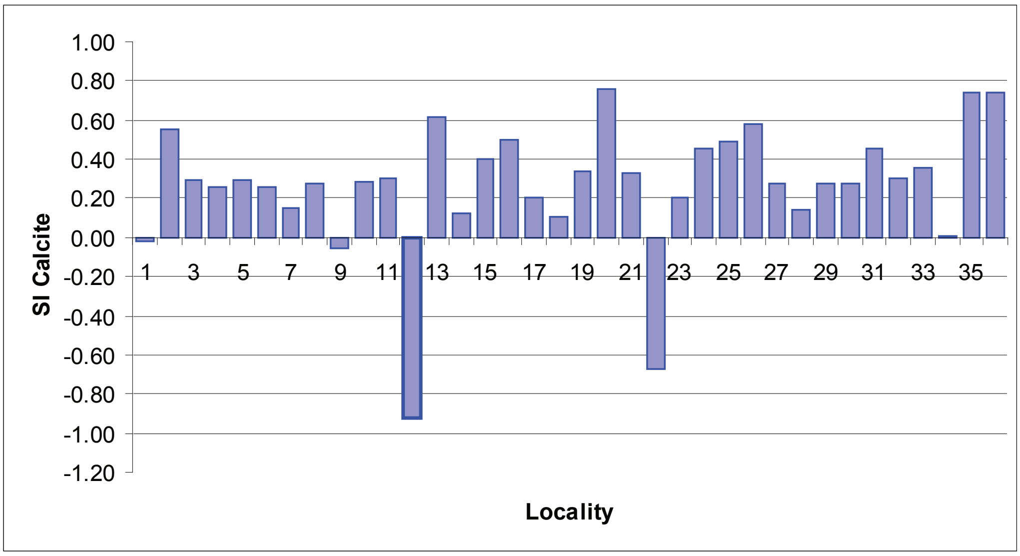


Fig. 3.7 Saturation indices for calcite in mineral waters

in solution is $H_3SiO_4^-$; the content is within the range 0.02 to 0.52 %. Interesting case is the mineral water in Čilistov; the said complex silicon reaches 13.2 %. This is probably mainly due to a higher pH (7.69) resulting from absence of carbon dioxide. In general, the concentration of this complex increases with increasing pH of natural waters.

The main mineralization processes in the formation of the chemical composition of mineral waters of the spas in Slovakia are essentially conditioned by two factors. The first one is the source of the elements in the rock environment of the hydrogeological structure. The second are the conditions for the acceleration of geochemical processes, especially temperature, partial pressure of carbon dioxide and water residence time within the collector. Of course, another factor that determines the variety of chemical types of mineral waters in Slovakia, is for example, preservation of relics of sea water and the presence of gas of chemical and biological origin.

It can be stated that in terms of interaction water-rock-gas the most important mineralization process is dissolution of carbonates. This process is the most abundant, or it affects practically all of the mineral waters. This is also the case where the collectors are not carbonate rocks, e.g. flysch sediments of the Palaeogene and Neogene of the Western Carpathians, which are always to some extent calcareous (calcareous sediments cemented by lime).

The condition of the source of calcium and also magnesium in rock environment of mineral water circulation is met.

The main mineralization processes were evaluated by saturation indices calculated using the code PHREEQC. Steady-states of carbonate minerals dissolution are presented in the examples of calcite, aragonite and dolomite (Figs. 3.7, 3.8, 3.9).

In most of mineral waters calcite is present as supersaturated phase, that means, it will precipitate from the water in the form of carbonate incrusts (Fig. 3.7). In some cases, it has a negative effect in distributors and consumption places (swimming pools and baths) of water. Undersaturated mineral phase is calcite in the cases of Nimnica, Sliač (spring Štefánik) and Smrdáky (Source Josef I). All said mineral waters have the lowest calcium content, which

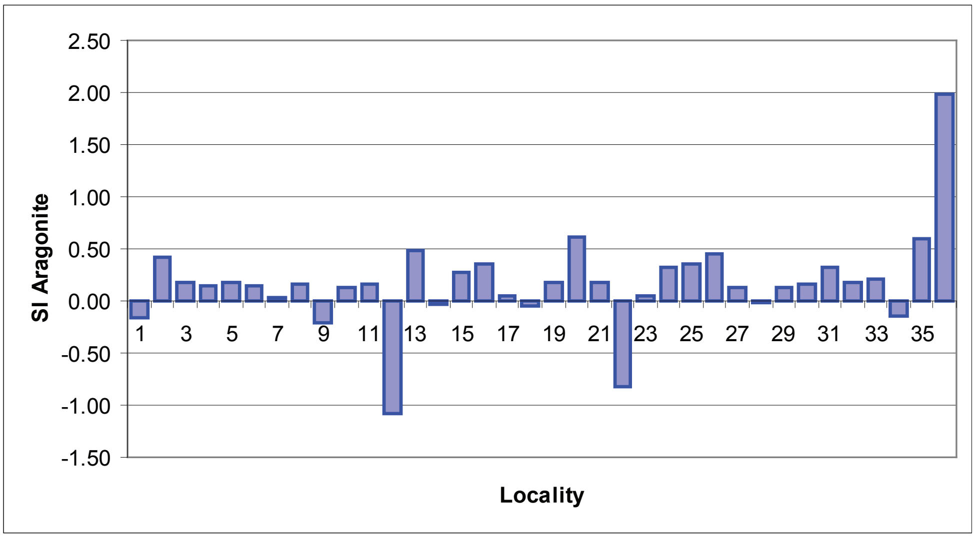


Fig. 3.8 Saturation indices for aragonite in mineral waters

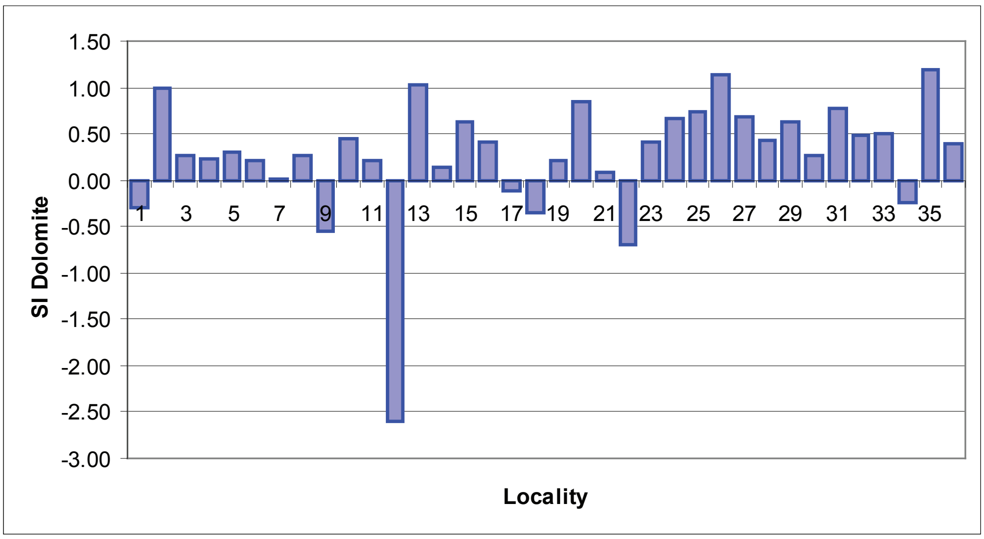


Fig. 3.9 Saturation indices for dolomite in mineral waters

means that within the rock environment of circulation there is no greater source. Mineral phases aragonite and dolomite in the saturation indices exhibit similar behaviour, as well (Figs. 3.8, 3.9).

The second significant mineralization process is the dissolution of gypsum, or anhydrite. From the results of thermodynamic modelling of these mineral phases (Figs. 3.10, 3.11) it follows that all mineral waters are undersaturated against gypsum/anhydrite.

Five sites of mineral water can be assessed to be closer to the equilibrium value of the saturation index, which is -0.07 – -0.15. These are the sites Sliač (Kúpeľný I.a), Trenčianske Teplice (two sources), Sklené Teplice and Lúčky. The sulphate content of these mineral waters is between 1,250 – 1,584 mg . l^{-1}. Their source of gypsum is present in the Triassic sediments of collectors.

In terms of saturation indices and of the formation of the chemical composition of mineral waters, equilibrium of mineral quartz is interesting. In most mineral waters chalcedony is supersaturated (Fig. 3.12). Undersaturated phase of chalcedony is in the water of the site Nimnica; the reason is the low temperature as well as low levels of silica in the rock environment circulation. Other location is Rajecké Teplice, with a sufficiently high temperature (36.4 °C at the well head), but the SiO_2 content in the mineral water is one of the lowest (14 mg . l^{-1}), as its formation takes place almost exclusively in the environment of carbonates with limestone dominance.

Amorphous silica is in all mineral waters a undersaturated mineral phase (Fig. 3.13). The exception is the water source Štefánik (Sliač), which, as described above, has the highest content of SiO_2 of the evaluated mineral waters, thus satisfying the requirements of high silica source in the volcanic rock environment of the chemical composition formation.

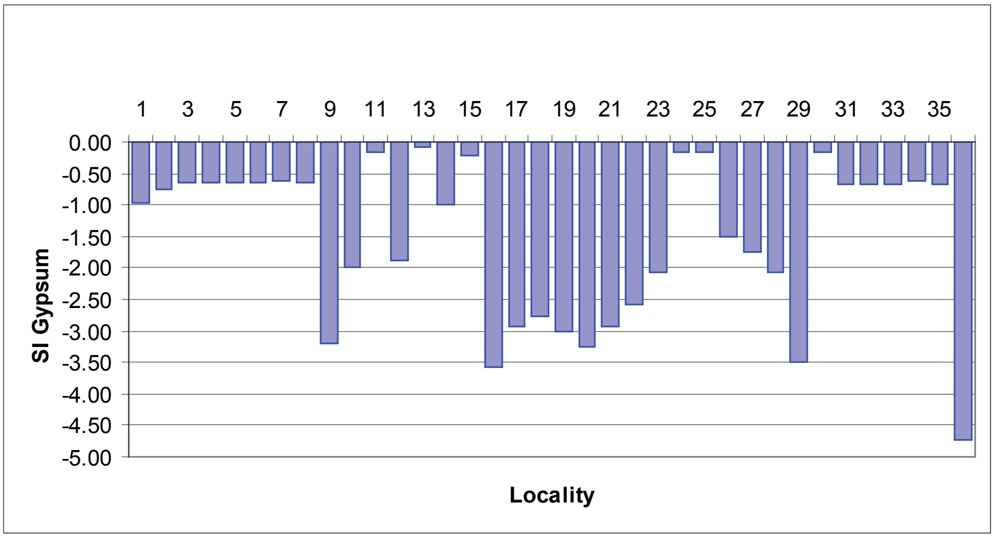


Fig. 3.10 Saturation indices for gypsum in mineral waters

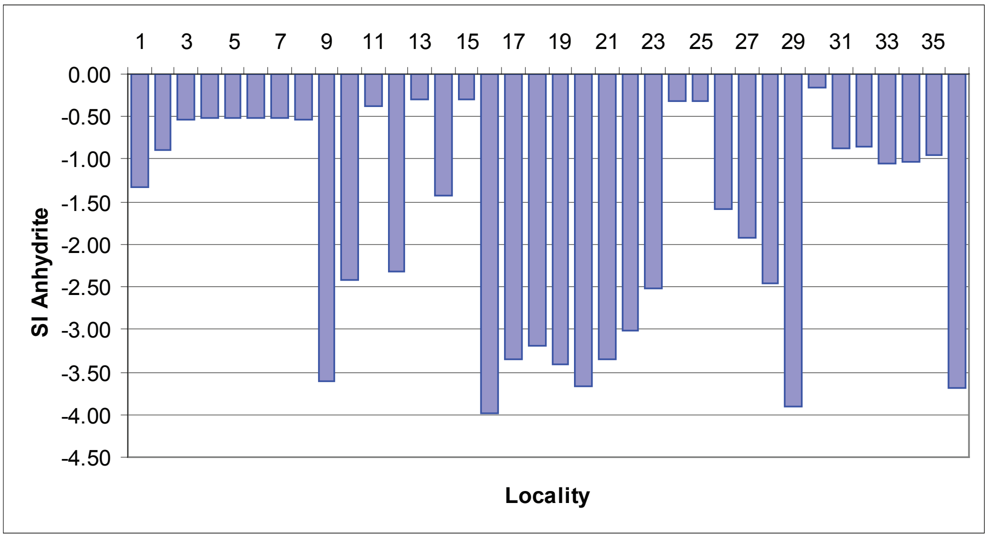


Fig. 3.11 Saturation indices for anhydrite in mineral waters

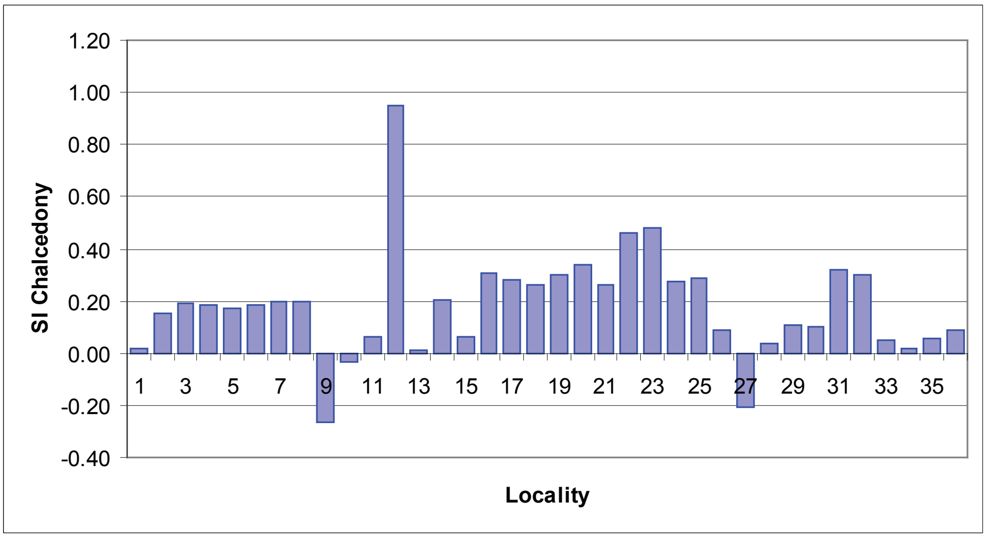


Fig. 3.12 Saturation indices for chalcedony in mineral waters

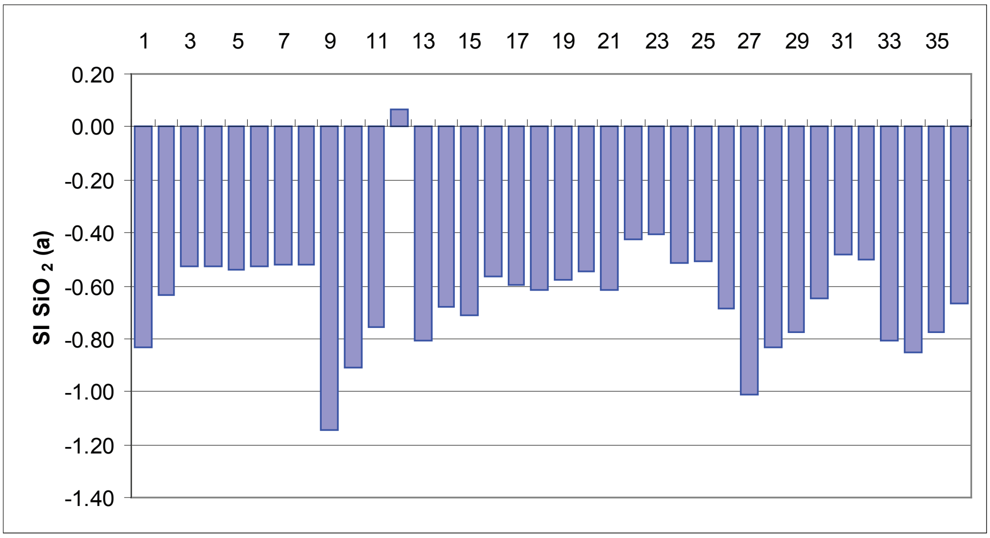


Fig. 3.13 Saturation indices for amorphous SiO_2 in mineral waters

3.7 Conclusions

The path of human society to the knowledge of exact values of the chemical composition of mineral water has been very long and lasted for several millennia. Finding of enjoyable and beneficial effects of mineral waters started probably in the form of "try and see", possibly in hot springs or in its refreshing taste at drinking. During the prevailing alchemy, which extends its beginnings in ancient times and through the entire Middle Ages the composition of mineral water was examined. Epicentre of alchemy was probably China, from where it had spread to India, ancient Egypt, and from there to Greece. In fact, the alchemy did not constitute a science, but philosophy. On the other hand, it should be noted that the period of alchemy was beneficial for modern chemistry for example, by introducing distillation apparatuses, mortar, banks, the development of basic experimental procedures and techniques, and not least the discovery of full range of elements and compounds.

After completing 30 Years' War (1618 – 1648) and its hardships the alchemy experienced decline. This period can be called transition with regard chemistry as a science. Great advance of the 18th Century was the fact, that the issues studied were focused in the problem of combustion, resulting in the so-called phlogiston theory. This theory was introduced by G. E. Stahl, who used also some ideas of his teacher J. J. Becher. In the late 18th Century A. L. Lavoisier disproved all the arguments of the phlogiston theory and replaced them with the new one – the theory of oxidation.

Revolution in analytical methods and in the expression of the results of chemical analyses happened at the turn of the 18th and 19th centuries. The chemical analyses of the early 19th Century already examined the contents of the main components expressed in the form of salts. Later, this form of expression changed using the oxides, e.g. CaO, MgO, R_2O_3, etc. The current form of expression of the results of chemical analysis in ionic form was introduced at the beginning of the 20th Century.

With the development and refinement of chemical analyses of mineral waters it becomes more and more urgent their evaluation in the classification form. Rather large milestone in the expressing of the chemical composition of water was drawn up in 1864 by Viennese chemist C. Than, who proposed an equivalent form. This was later elaborated by S. Arrhenius, W. Ostwald and others. These authors showed that in aqueous solution the components are not in the form of oxides and salts, as previously believed, but in the form of cations and anions.

The next important factor that influenced the reporting of results of chemical analyses was the elaboration of definition of a system of combining acids (or anions) and bases (or cations). One of the oldest classifications, which is used even today, was invented by Palmer (1911).

Of the current chemical analyses there are presented geochemical characteristics of mineral waters on the basis of 18 spas in Slovakia. By way of examples there are displayed the total contents of selected elements compared to various forms of the element in the complexes. These findings are relevant in balneology at the estimation of their behaviour in the human body, but also for the overall characteristics of mineral water and its genesis within the meaning of modelling of plausible mineral phases in the water-rock-gas interactions.

Calcium in the mineral waters of the spas occurs mainly as free ion Ca^{2+}. The highest percentage (98.5 %) it attains in the mineral water source BČ-5 in Číž. The chemical composition of the water, despite the Na-Cl type, is one of the highest contents of calcium and magnesium, in the absence of sulphate. The share of complexes $CaHCO_3^+$ and $CaSO_4^0$ represents the second major calcium species. The distribution of magnesium species is very similar to calcium in representation of a free ion, as well as complexes $MgHCO_3^+$ and $MgSO_4^0$. In all mineral waters distribution of potassium and lithium is mainly represented by free ions K^+ and Li^+ and to a much lower percentage in the form of complexes KSO_4^- and $LiSO_4^-$. Bromine in all mineral water of the spas occurs only in the form of the free Br^- ion. Free F^- ion in mineral waters of the spas has the highest percentage representation; in most cases more than 90 % of the amount of fluorine in the water. In most mineral waters silicon is present in the form of un-dissociated H_4SiO_4. These results can be a good basis for balneological evaluation of mineral waters and their effects on the human body.

The main mineralization processes of the formation of the chemical composition of mineral waters of the Slovak spas are essentially conditioned by two factors. The first is the source of the element in the rock environment of the hydrogeological structure. The second are the conditions for the acceleration of geochemical processes, especially temperature, partial pressure of carbon dioxide and water residence time within the collector. Of course, other factors that determine the variety of chemical types of mineral waters in Slovakia, are for example, preservation of relicts of marine water and the presence of gas of chemical and biological origin.

The results of the thermodynamic analysis indicate that, in terms of interaction water-rock-gas the most important mineralization process in the formation of the chemical composition of mineral waters in the spas is dissolution of carbonates and gypsum sediments of Mesozoic, Palaeogene and Neogene complexes of the Western Carpathians in interaction with carbon dioxide.

3.8. References

Bergman, T., 1779: Opuscula Physica et Chemica. 3 vols. 8vo. Holmlae.

Bodiš, D., Kordík, J., Slaninka, I., Malík, P., Liščák, P., Panák, D., Božíková, J., Marcin, D., 2010: Mineral waters in Slovakia – Evaluation of chemical composition stability using both historical records and the most recent data. Journal of Geochemical Exploration 107, p. 382 – 390.

Bunsen, R., 1874: Anleitung zur Analyse der Aschen und Mineralwasser. Heidelberg, C. Winter

Coley, N., G., 1990: Medical History. Supplement No. 10, p. 56 – 66.

Crantz, H., J., N., 1777: Gesundbrunnen der Oestereichischen Monarchie. Wien, 306 p.

Davis, N., S., Davis, A., G., 1997: Saratoga Springs and Early Hydrogeochemistry in the United States. Groundwater, Volume 35, Issue 2, p. 347 – 356.

Franko, O., Gazda, S., Michalíček, M., 1975: Tvorba a klasifikácia minerálnych vôd Západných Karpát. Geologický ústav Dionýza Štúra, Bratislava, 230 p.

Fresenius, R., 1876: Analyse der warmen Quelle zu Assmannshausen. Kreidel.

Gazda, S., 1971: Modifikácia Palmerovho klasifikačného systému. Hydrogeologická ročenka 1970 – 1971, Bratislava, p. 122 – 126.

Gazda, S., 1974: Chemizmus vôd Západných Karpát a jeho genetická klasifikácia. In: Materiály z III. celoslovenskej geologickej konferencie, II. časť, SGÚ Bratislava, p. 43 – 50.

Hamlin, C., A., 1990: Science of Impurity, Water Analysis in Nineteenth Century Britain. Adam Hilger , Publisher, Bristol, Great Britain, 342 p.

Hammond, C., R., 1967: The Elements. In: Handbook of Chemistry and Physics. 48th edition R.C. Weast, ed. The Chemical Rubber Company, Cleveland, Ohio, p. B-97 to B-147.

Hensel, J., 1951: Balneografia Slovenska. Slovenská akadémia vied a umení, Bratislava, 456 p.

Hyánková, K., 1989: Komparabilita starších a súčasných analýz minerálnych vôd. Zborník prednášok, IV. Balneohistorická konferencia, Bojnice, p. 68 – 88.

Hynie, O., 1963: Hydrogeologie ČSSR II. Nakladatelství ČSAV, Praha, 767 p.

Jetel, J., 1975: Klasifikácia chemizmu podzemných vôd. Geol. práce, Správy 62, GÚDŠ, Bratislava, p. 9 – 18.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1977: Minerálne vody Slovenska – balneografia a krenografia 1. Vydavateľstvo Osveta.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1978: Minerálne vody Slovenska – balneografia a krenografia 2. Vydavateľstvo Osveta.

Maheľ, M., 1952: Minerálne pramene Slovenska so zreteľom na geologickú stavbu. Práce štátneho geologického ústavu, zošit 27, Bratislava 84 p.

Limón Montero, A., 1697: Espejo cristalino de las aguas de España Francisco Garcia Fernandez, Alcalá, Spain. Reprinted by the Instituto Geológico y Minero de España in 1979. 432 p.

Palmer, Ch., 1911: The geochemical interpretation of water analysis. U.S. Geological Survey, Bull. 479, Washington, 31 p.

Parkhurst, D., L. & Appelo, C., A., J., 1999: User s guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99 – 4259, 310 p.

Rebro, A., 1983: S Matejom Belom o kúpeľoch a minerálnych vodách. ALFA, Bratislava, 211 p.

Rebro, A., 1996: Vzácne a obdivované vody Slovenska. Balneologické múzeum Piešťany, Turista Piešťany, PRO SLOVAKIA, 182 p.

Rogers, G., S., 1917: The interpretation of water analysis by the geologist. Econ. Geol. Vol. 12, Lancaster, p. 66 – 88.

Stabler, H., 1911: Some stream waters of the western United States. Geol. Surv. Wat. Supply Pap. 274, Washington, 188 p.

Szabadváry, F., 1966: History of Analytical Chemistry. Pergamon Press, p. 30 – 31.

Wehrner, J., 1556: De admirandis Hungariae aquis hypommemation. Bazilej. Preklad Rebro, A., 1974, Osveta, Martin.

Slovak Geol. Mag., 16, 2 (2016), 57 – 70

Mineral Waters in Slovakia, Legislation and Their Use

Jarmila Božíková[1], Dušan Bodiš[2]

[1]ISS MoH SR, Limbová 2, 837 52 Bratislava, Slovakia
FCE SUT, Radlinského 11, 810 05 Bratislava, Slovakia, jarmila.bozikova@gmail.com
[2]State Geological Institute of Dionýz Štúr, Dept. of Environmental Geochemistry,
Mlynská dolina 1, 817 04 Bratislava, Slovakia

Abstract: Slovak spas legislation in current conditions has great history. Since the establishment of the Slovak Republic until 2006, a separate law is in effect that regulates the conditions for recognized sources. There have been set out the conditions for the recognition of sources, such as natural healing sources and natural mineral sources. Natural healing waters are preferably used for a spa treatment. Natural mineral water is packed in consumer packaging. Since water is mineral wealth of the state, the Act sets out the obligations of the user towards the state. At present, Slovakia there are registered 21 existing statutes for spa locations with 31 licenses issued for the operation of natural health spas.

Key words: mineral water, legislation, monitoring, balneology, history, present

4.1 Introduction

Mineral and thermal springs and sources in Slovakia are a generally known fact. Their diversity is conditioned by the unique geological setting. Of the many recorded mineral resources it is allocated a separate part of the resources that are recognized as natural mineral waters and natural healing waters. The existence of this national wealth has historically conditioned the emergence of spas in areas with healing waters. Mineral waters have been already for two centuries filled into packages and distributed to consumers.

Regulations that provide a legal status to the use of these waters have a historical basis. A separate law regulating the basic conditions for characterizing the properties of water, its recommended use, and the relationship between the beneficiary and the national wealth – the water, has been in practice for 10 years. The Act is comprehensive legislation on the recognition and use of natural healing resources and natural mineral waters, spa areas and announcing their status and issuance of natural health resorts. It is in accordance with the Slovak Constitution and international commitments of the Slovak Republic.

4.2 Legislation

4.2.1 History of provisions

The first regulations on protection of sources of mineral water in our area are from the second half of the 19th Century and they concerned Spas Piešťany, Trenčianske Teplice, Dudince, Bojnice and Sliač. The issue treated was in the territory of Hungary (and thus Slovakia) historically for the first time brought in legislation by the Hungarian Health and Water Act of 1876, section no. 1 XIV – no. 1 XXIII and by Edicts of the Hungarian Ministry of the Interior from 1893 no. 44404 implementing ministerial provisions (e.g. Regulation no. 45689/1885 on the protection of natural springs). Protection zones and expropriation for the purpose of water sources protection was treated by Act section no. XLI/1881. The Act of 1885 determined protection zones, which secured the owners that nobody could dig or drill in them without a particular permission

- in relation to groundwaters, mineral springs and mineral waters under the Act Art. XXIII/1885 on Water Law (as amended by Act Art. XVIII/1913),
- and in relation to the springs of healing, therapeutic bath and medicinal waters under the Act Art. XIV/1876 on the organization of public health and the implementing ministerial regulations (e.g. Regulation no. 44404/1893 on the supervision of spas and medical places; Vandrová et al., 2002).

Of these laws is derived the basic legislation in force until now. They relate to the use of water resources for treatment, spa treatment in spas and operating medical spas, spa environment protection, etc., and for drinking purposes. While the legislation dealing with water was comprehensive and of high quality, the issue of exploitation of natural resources, mineral waters and health spa was not comprehensive. It formed a part of the provisions in particular in general medical regulations. Legislative attempts of the Czechoslovak government on consolidation the law in the Czech Republic and Slovakia by the adoption of single and for the whole Czechoslovakia Uniform Act on spas and sources in 1925 was unsuccessful (Reich Law no. 68/1907 Coll. on health and provincial regulations for Bohemia Act no. No 49/1914 Coll.B., for Moravia Act no. 38/1868 Coll.M., and for Silesia the Act no. 30/1907 Coll.).

The above laws were amended in 1920 and were in force up to 1955. The decisive legal regime relating to the issues treated in the management of groundwater is substantially preserved until now. Austrian and Hungarian legislation on water law were repealed in the Czech Republic and Slovakia by December 31, 1954, and replaced by a single Czechoslovak Act no. 11/1955 Coll. on water management (as amended by Act no. 12/1959 Coll.). This law was repealed by Law no. 138/1973 Coll. on Water (Water Act) and by the Act of the Slovak National Council no. 135/1974 Coll. on state administration in water management (Vandrová et al., 2002).

The issue of healing resources was excluded from the general health rules in the Czech Republic by Government Decree no. 223/1939 Coll. on the protection of natural healing resources. The issue of medical spas was described by Act no. 43/1955 Coll. on the Czechoslovak spas and sources. That above Act abolished government decree and also regulates the issue of protection of medicinal natural resources and natural health spas. Although this law united different legal regimes in the Czech Republic and Slovakia, but provided only stringent framework (26 paragraphs in total) leaving a wide space for the regulations of the Ministry of Health and the Inspectorate for the protection of natural health spas and natural medicinal resources.

At that time, it was issued Decree of the MoH SSR no. 151/1956 on the protection of natural health spas and natural healing resources and their exploitation. Later, in 1965, it was released ČSN 86 8000 Natural healing water and natural mineral table water, which was in force until 2006.

By the Act no. 20/1966 Coll. on the Health Care of the People entering in force by July 1, 1966, the reintegration of the issues treated in general health regulations occurred. The Act was repealed as of January 1, 1995, and its issues were divided into several laws: in the Act no. 272/1994 Coll. on the Protection of Human Health, in the Act no. 273/1994 Coll. on Health Insurance, Health Insurance Financing and in the Act no. 277/1994 Coll. on Health Care.

In the years 1972 to 1994 there were issued and effective the following regulations:

– Decree no. 15/1972 of the Ministry of Health SSR on the protection and development of natural health spas and natural healing resources, and Directive SGO SSR no. 55/1977 for obtaining documents for the determination of the protection zones of natural healing sources and natural sources of mineral table water.
– Decree of Ministry of Health SSR no. 77/1982 Coll., which amended the Decree no. 15/1972 Coll.
– ON 86 8001 Natural healing water and natural mineral water table from 1984.
– Guidelines of SGO and the Ministry of Health in 1989 on the establishment of protection zones of natural healing sources and natural sources of mineral table water.
– Slovak National Council Act no. 52/1988 Coll. on geological works and on the Slovak Geological Office (Geological Act).
– Slovak National Council Act no. 44/1988 Coll. on the protection and use of mineral resources (Mining Act), as amended by Act of the Slovak National Council no. 498/1991 Coll. and certain related provisions.
– Act no. 138/1973 on water (Water Act).
– Ministry Decree no. 116/1996 Coll. on the parameters under which climatic conditions can be declared favourable for the treatment and on the ways of their promulgating.

The aforementioned legislative measures replaced the older, outdated policies and regulations and stressed the importance of Slovak natural spas. The spas are facilities for preventive and curative health care of the people.

In subsequent years, some legal provisions and legislative standards abolished and replaced with new ones – e.g.:

- Act no. 313/1999 on geological works and on state administration (Geological Act).
- Decree of the Ministry of the Environment no 141/2000 implementing Geological Act.
- Act of Parliament SR no. 184/2002 on waters and on amendment of certain laws (Water Act).
- Decree of the Ministry of Agriculture, the Ministry of Health no. 2313/2000 – 100, issuing the chapter of the Foodstuffs Code SR, providing for drinks.

After 2000, there were issued new laws and other binding rules related to the preparation of the first legislative separate adjustment for natural mineral waters and natural healing waters:

– New Water Act no. 364/2004 Coll., Act no. 569/2007 Coll. on geological works (Geological Act) and health laws:
– Act no. 576/2004 Coll. on healthcare, services related to health care and on amendments to certain laws;
– Act no. 577/2004 Coll. on the scope of health care covered by public health insurance and on payments for services related to health care;
– Act no. 578/2004 Coll. on healthcare providers, health workers and professional organizations in the health and on amendments to certain laws.

4.2.2 The current legislation

Act no. 538/2005 Coll. on natural healing waters, natural healing spas, spa sites and natural mineral waters as amended; hereinafter Spa Act is the first separate legislative regulation in force for Slovak Health Spa. It entered into force on January 1, 2006, some parts as of March 1, 2006. The Spa Act comprises six general legislative provisions. Natural healing resources and natural mineral waters as part of the groundwater are state-owned. This follows from the Constitution of the Slovak Republic and these types of water are not part of the plots. The Act lays down the conditions under which natural healing water and natural mineral water are removed from the natural healing resource or natural mineral sources list, and become the property of a natural or legal person.

Work on the new draft of so-called Spa Act began in March 2003, i.e. before May 1, 2004, when the Slovak Republic was accepted as a member of the EU. On that date it was necessary to approximate the EU Directive into our legislation. Government Ordinance no. 263/2004 Coll. on the conditions for the recognition of natural mineral waters transposes the following legislation of the European Communities and the European Union:

1. Council Directive 80/777/EEC of 15 July 1980 on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral waters, as amended by Council Directive 85/7/EEC of 19 December 1984 and of the European Parliament and of the Council 96/70/EC of 28 October 1996.
2. Commission Directive 2003/40/EC of 16 May 2003 establishing the list, concentration limits and labelling requirements for the constituents of natural mineral waters and the conditions for using ozone-enriched air for the treatment of natural mineral waters and spring waters.

By the Act 538/2005 Coll. as of January 1, 2006, Slovak Republic Government Order no. 236/2004 Coll. on the conditions for the recognition of natural mineral waters, was cancelled. The Spa Act partially accepted parts of the Water Framework Directive 2000/60/EC establishing a framework for Community action in the field of water.

Inspectorate of Spas and Springs (ISS) was established in line with the Spa Act at the Ministry of Health (MoH) to ensure the supervision of compliance with the obligations laid down in this Act and provisions designed accordingly. The State Spa Commission (SSC), according to the Spa Act legally was established at the Ministry to carry out its tasks in the field of natural mineral waters, natural medicinal waters, natural health spas and climatic conditions suitable for medical treatment. The SSC is administrative body with ruling right at first instance. Under the provisions of the Spa Act the SSC is composed of seven members who are appointed for a five-year term. As a rule, the SSC Chairman is the Director of ISS MoH. Proposals for other candidates for the post of SSC member are submitted to the Minister of Health, Minister of Environment, civic associations and interest associations of legal persons whose activities are related to the performance of spa treatment or exploitation of natural mineral resources, and the republican association of municipalities. The conditions for the establishment of SSC are specified in the Statute. Commission members are experts in the field of balneology, hydrogeology, balneotechnique, and of course the spa praxis.

First draft of a separate so-called Spa Act, which was adopted in 2005, sets out the substantive and procedural framework legislation. It involves three interrelated but nevertheless autonomous ranges of topics. The common denominator is the protection and use of natural resources of groundwater, gas, favourable climate for the treatment or drinking for medical purposes and as food – natural mineral waters.

Natural healing resources, their recognition, protection and use create the first circuit of the law. These are all natural resources, as defined in Act on Environment, in which there has been proven by scientifically recognized methods, that their media (water, gas) are in original condition, are protected and have a proven healing effects on the human body and can be for used treatment. For their recognition method and form of use for the treatment are not required (e.g. drinking, packs, bath), but the simple fact of therapeutic effects.

Climatic conditions are also a natural source in the spirit defined by the Environment Act. Their medium is the air quality – longevity of sunlight, ozone concentration, purity of air – at a particular site – the village or indoor climatic environment – stable temperature, chemical composition of indoor and cave air humidity. Under climatotherapy we understand treatment by means of staying in a place which has a particularly favourable climate and curative effects. It uses complex climatic parameters affecting reactivity of sick persons and thus helps them to cope with the disease on their own. It helps mobilize their own reserves. Climatic conditions favourable for the treatment have been traditionally used for the treatment in climate spas, nursing homes, etc.

Climatic conditions suitable for treatment are assessed by Decree no. 87/2006 Coll. They must be approved by the SSC of the Ministry of Health. The site must also provide spa environment and place where there are natural spas is declared a spa area. The users of the favourable climatic conditions for the treatment are obliged to ensure that they follow the provisions of health care in natural health resorts. At the same time the results of the measurement are submitted to the Ministry of Health – Inspectorate of Spas and Springs.

Natural spas are medical facilities based on the use of natural healing source or climatic conditions favourable for treatment in terms of spa treatment pursuant to provisions of health care. The issue of health spas consists essentially of two circuits:

- Issues relating to the use of medicines supply, i.e. tapping of medicinal medium, treatment of medicinal medium, protection of the healing source, spa and its status, spa area, spa environment;
- Health issues, i.e. medical care, material and technical equipment, including disposing of health professionals, indications and therapeutic procedures, requirements for medical facilities.

The issue of mineral waters is treated in a separate section of the Act. They are groundwater, which by reason of their physical properties, chemical composition and physiological effects on the human body are different from other natural waters.

The system of state administration bodies in cases stipulated by the law resides in the current legal situation, including specific competencies, namely:

- The Ministry of Health is crucial administrative authority in respect of natural medicinal resources, natural health spas and natural mineral waters continuously since the first legislation in 1876. The Act established the first-instance administrative authority – the State Spa Commission of the Ministry (SSC) and the Appellate Body is the Minister.
- Bodies of food supervision are the authorities in respect of bottling and distribution of natural mineral waters in the scope under the Food Act. These packaged marketed waters are food.

The Inspectorate of Spas and Springs at the Ministry of Health does not change over time. The Inspectorate has worked continuously since 1908; it was changed only level of competence and name. Under the current name ISS is working as a body, which was created under an agreement with the Board of Commissioners for Health in January 1, 1958. Since August 1, 1960 terminated capabilities of several Slovak authorities and Inspectorate of Czechoslovak Spas in Prague gained competence in spas also in Slovakia. In Bratislava there was re-established Inspectorate of Spas and Sources at the Ministry of Health of Czechoslovakia from July 1, 1967, where the continuous competence till today. During its almost 50 years of activity the Inspectorate addressed a number of issues of legislative, organizational, control and other spheres. The Inspectorate was involved in the creation of laws, regulations, decrees and other provisions related to its agenda.

Protection zones, however, are the most important ways to protect resources. The institution of resource protection zones has almost 150 years of tradition. The protection zones are also used by other laws, for example to protect water resources, nature conservation, the protection of railways and roads, etc. It is therefore necessary to include the protection of the resources already in preparation, plans and project activities as well as to the procedure for the authorization of any activity within a protection zone. This applies to land-use activities, documentation of nature and landscape, construction activities and use of buildings, the exploitation of mining minerals and wood, processing of raw materials, goods production, preparation and approval of departmental and municipal policies and development programmes, etc.

In the legislation on water general reporting obligations are transposed. Each person has an obligation to report occurrence of groundwater at his own costs not only to water management body, but also the Ministry of Health. Two levels of protection zones are established and their purpose is monitored. The protection zones are determined by the Ministry of Health which makes proposals for the designation of the land. The safety zone is the area around the source of the seepage with the strictest regime. In the safety zone can access only the employee who is directly responsible for protecting source – balneotechnologist. Act no. 538/2005 Coll. introduced establishing working activities and tasks that are provided by balneotechnologist. The balneotechnologist is a person who has fulfilled the specific conditions for issuance of the certificate by SSC Ministry of Health. The certificate is valid for five years.

Recognition is historically formed procedural legal act by which natural healing source or natural mineral water becomes a natural source, for example, groundwater is recognized as the healing one, or the mineral one. The recognition regime has existed since the first statutory regulation of the last Century; since 1955 it is known as the promulgation. Until 1994 the Recognition (Announcing) had the form of a decision made in administrative proceedings and was associated with the decision on its use (§ 47 of the Act no. 20/1966 Coll.). Since 1994 sources are declared by a decree and subsequently a decision on the administrative proceedings of the use of issued.

The use of natural healing sources and natural mineral water is subject to permission of the Ministry – the SSC decision. It is excluded also by applicable European directives to authorize the use of natural mineral water through the filling into consumer packaging and placing on the market under various trade brands.

The Act collects obligations of a beneficiary from natural healing source and natural mineral water. The beneficiary are granted the obligations in terms of the decision on exploitation, which he must accept at the use of a recognized source. The beneficiary is also obliged to contribute to the costs associated with the use and protection of a source.

Spa area historically meant a municipality or part of the municipality in which there were recognized spas and spa charges levied. The spa area has been taken into account in land-use planning activities as an area protected from the harmful effects of industry, agriculture and transport. It is depicted in the local plan. From 1955 to 2006, it was announced by the government resolution. The spa area is the heart of a spa town. It includes part of spa place immediately around the spa. The spa area is necessary for the operation of a health spa for spa treatment. The Ministry of Health executes the state supervision over its protection in the form of expert opinions to the activities authorization. The Statute of the spa area is determined by government regulation; it states the regime within the spa area and defines the boundaries of the spa area.

A detailed methodology for carrying out analyses and issuing opinions was adjusted by Ministry Decree no. 100/2006 Coll. The Decree was compiled in response to the requirements of Annex to Council Directive 80/777/EEC, as amended by European Parliament and Council Directive 96/70/EC. The same rules apply for the recognition of natural mineral waters across the EU. This involves implementation of the physical, physico-chemical, chemical, microbiological and biological analyses for natural healing source or natural mineral water.

4.3 Monitoring of sources

The monitoring system of natural healing resources and natural mineral resources is enshrined and defined in § 2 sec. 14 of the Spa Act. It is a system through which the monitoring of regime of is carried out hydrogeological, chemical, physical, microbiological and biological indicators of natural medicinal resources, natural mineral resources, observational wells, monitoring stations and meteorological characteristics of the area concerned. It is defined as the regime monitoring of selected parameters on the selected sources and evaluation of the obtained data for the purposes of internal and external resource protection, microbial contamination, protection against the risks of pollution and impact assessment of wastewater. The system is open to the extent that it can be supplemented, for example, on components of protection against the risk and impact assessment of wastewater (Božíková, 2014).

In Slovakia there are currently 1,782 registered natural mineral resources. In total there are now monitored 156 objects, 122 of which is recognized as a natural healing source, natural or mineral source, and other unrecognized sources. Natural healing water, differs from the groundwater by its origin, the content of total dissolved solids or gaseous substances (above 1,000 mg . l^{-1}), content of hydrogen sulphide and other trace elements.

The monitoring system allows continuous evaluation of source parameters subject to regular monitoring and documenting the measured values across the overall hydrogeological structure. This allows to immediately indicate the damage of a source or affecting the circulatory pathways of mineral water independently ISS MoH directly by users of sources. The data are collected and archived in a database system, complemented by tools of their collection and immediate processing and tied to a geographic information system. Each site has its mirrored data, geographic and structured display at the ISS MoH. By processing of summary documentation characterizing individual objects in the database there were inserted at the beginning in the Monitoring system around 4 million individual data. During the solution inventory of resources and monitoring objects was processed at defined sites. Prior to the installation of measuring facilities and eventual adjustments of collars of drillings and tapping lines there was processed inventory of recognized technical resources and monitoring objects.

Range of monitoring of selected regimen components on individual sources and objects is specified in the authorization for the use of sources. The user of a source is legally obliged to establish and operate a monitoring system of natural healing sources and natural mineral sources and observation wells connected to a central monitoring system (CIS) of the Ministry of Health. Conditions of the permit to use a source and continuously provide information for the database of the Ministry and operate a local information system (LIS) are mandatory for approval. Currently the monitoring in the Slovak Republic involves a total of 39 sites, 37 of which use LIS ISS MoH, and this condition ensures data transfer to CIS ISS MoH.

4.4 Use of natural medicinal resources and natural mineral resources

The authorisation of the use of natural curative source (NHS) and natural mineral source (NMS) is possible only in the case of water from a source which has been recognized a natural healing water (NHW) or a natural mineral water (NMW). Upon the publication of the decision of NHW or NMW water it is possible to submit an application for a license to use the resources. Natural healing resources *are to be primarily used for therapeutic purposes* and may be used only to the extent permitted. Requirements for obtaining, treatment, bottling, labelling and marketing of natural mineral waters in consumer packaging is governed by Act no. 152/1995 Coll. on Food, as amended. The Spa Act allows use of the full capacity of many natural healing water of a particular resource. Therefore, the applicant must provide proof of a useful amount of NHW or NMW. This creates prerequisites for the eventual use of the source to other users, provided the available quantity of water in the collector allows it. The law also strictly observes the arrangement of economic issues preceding the application. It commits to substantiate agreement on the disbursement of funds for research of NHW or NMW provided a person didn't finance the research. The applicant must provide a method for disposing of waste and unused waters which must be disposed of in accordance with special regulations. The application for a license to use the resources may also be a request for authorization for water treatment.

The Act provides requirements for the authorization of a resource, responsibilities of a resource beneficiary, conditions for modification and revocation of use of a resource. The Spa Act sets out the conditions of termination of permit to use a resource, conditions under which it is possible to use a source by another user and the professional supervision of use and protection. The use of natural healing resources and natural mineral water is controlled by the monitoring system, according to § 2 sec. 14 of the Act.

Natural healing water is distinguished from ordinary groundwater by its origin, the content of total dissolved solids or content of dissolved gaseous substances (above 1,000 mg . l^{-1}), the content of hydrogen sulphide and other trace elements. The waters are classified according to several criteria, for example the total dissolued solids, the predominant iones, temperature, osmotic pressure, etc. Natural mineral waters in consumer packs contain the description of all the features provided by an accredited laboratory.

4.5 Spa treatment

Balneology can be called a summary of specific activities, infrastructure and human resources in the areas of knowledge and practices focused on the knowledge of natural healing sources and implementation of techniques and procedures for the treatment of various diseases. The overall aim of the balneology is the prevention and treatment of human diseases, forces regeneration and relaxation. It is associated with the harnessing of natural healing resources, beautiful natural environment and cultural environment composition (Kriš, 2011).

Approval of a spa treatment following a request made by the competent doctor to the patient on the basis of public health insurance is possible according to the indication, which is provided for in the Act no. 577/2004 Coll. For each diagnosis categories of residence are defined in indication list. Bases on the current health insurance an insured person can ask for reimbursement for spa treatment stay in category A or B. Staying in category A is fully covered by public health insurance. To stay in category B health care is covered by the public insurance and accommodating at the patient's expenses. It is also possible to pay the whole spa stay by the client himself at full value.

Authorization to operate natural health spas and spa treatment centres (license) shall be issued on the basis of the declared medicinal properties of recognized natural healing source or climatic conditions and the fulfilment of mandatory personnel and material – technical requirements for a spa treatment. Within the administrative procedure the operator has also to submit documentation that defines the Spa Act. In the application he shall, inter alia, declare professions of the staff with a valid license to be engaged in professional activities (Decree no. 100/2006 Coll.). Upon meeting the all conditions the applicant is granted a permit decision. Annex 6 (Act no. 577/25004 Coll.) contains the tabulated list of indications for spa treatment: adults I. – XII. and children (under 18 years) XXI. – XXX.

4.5.1 Natural Health Spa

Geological evolution of the Western Carpathians create conditions for varied and rich representation of natural healing, mineral and thermal waters in the Slovak Republic. These treasures of the Earth were used by the inhabitants of this territory since the initial settlement to treat various health ailments. Documentary evidence of the therapeutic use of medicinal waters in Slovakia date back to the 12th Century. Archaeological excavations, however, push the assumptions of the healing waters utilisation in considerably earlier periods.

Slovakia is rich in climates that pose beneficial effect on human health. Mountain and Alpine climate, based on long-term scientific validation is used in seven locations for climate treatment.

Spa treatment in Slovakia is an integral part of health care. It uses the latest scientific developments in the field of balneology, physical medicine, health food and medical rehabilitation. It is targeted not only to the immediate and subsequent spa treatment but also to the prevention of a wide range of diseases. The spas have built spa environment with plenty of cultivated greenery, quiet zones, sports facilities, cultural facilities, abounding in rich gastronomic offer, high quality air. Just for the high quality environment and infrastructure the spas have become popular centres for holding conferences, congresses, festivals, and places for recreation and relaxation of healthy people. Of the total number of guests in the Slovak spas up to 40 % is from abroad, mainly from EU countries.

4.5.2 The oldest spa sites

The territory of present-day Slovakia was known at the beginning of the 13th Century and later by the occurrence of healing waters. The oldest documents describe the healing springs in Bardejov, Bojnice Piešťany, Sliač, Trenčianske and Turčianske Teplice (Fig. 4.1).

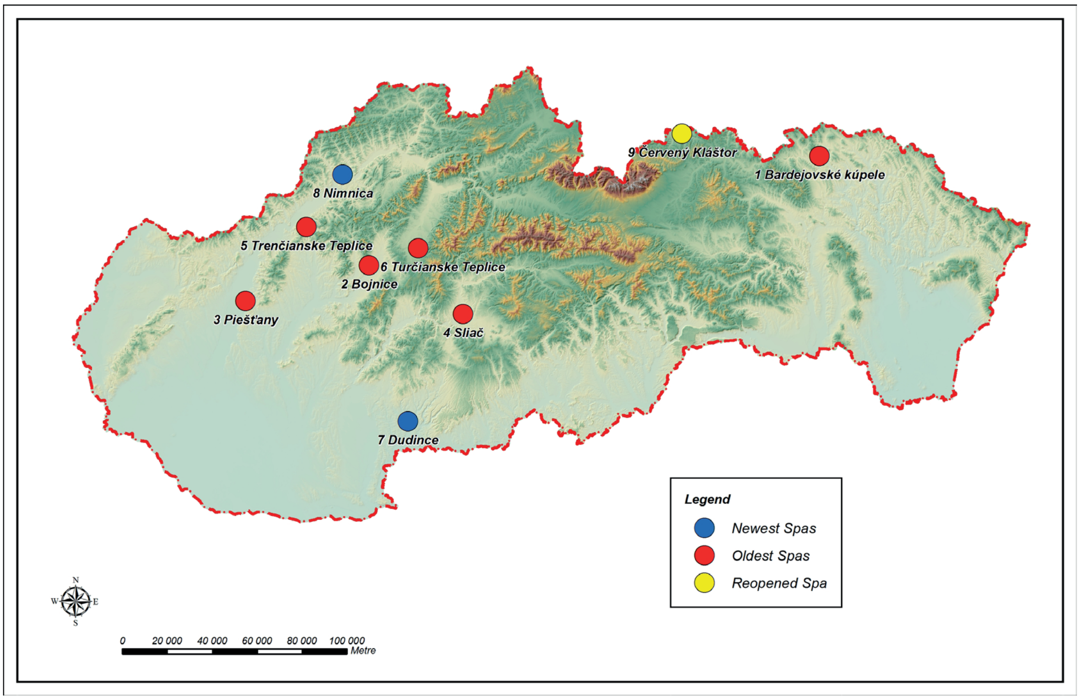


Fig. 4.1 Operating spas in Slovakia.

Bardejov Spa

The first mention of Bardejov (Fig. 4.2) springs of healing water is from 1247. Hungarian King Bela IV. do-

Fig. 4.2 Bardejov Spa – Bath House Alžbeta (Elisabeth)

Tab. 4.1 Indication list for balneological treatment

Indication for adults		Indication for children (< 18 years old)	
I.	Oncological diseases	XXI.	Oncological diseases
II.	Circulatory system diseases	XXII.	Circulatory system diseases
III.	Diseases of the digestive tract	XXIII.	Diseases of the digestive tract
IV.	Metabolic and endocrine diseases	XXIV.	Metabolic and endocrine diseases
V.	Non-tuberculosisrespiratory diseases	XXV.	Non-tuberculosisrespiratory diseases
VI.	Neurological diseases	XXVI.	Neurological diseases
VII.	Diseases of the locomotor system	XXVII.	Diseases of the locomotor system
VIII.	Diseases of the kidneys and urinary tract	XXVIII.	Diseases of the kidneys and urinary tract
IX.	Mental diseases	XXIX.	Gynaecological diseases
X.	Skin diseases	XXX.	Skin diseases
XI.	Gynaecological diseases		
XII.	Occupational diseases		

nated the territory of today's Spa and springs to the city of Bardejov. The healing effects of springs were known to residents for a very long time. Since 1505 they were in service booths for bathing of sick. The inflow of visitors from the ranks of Polish and Hungarian nobility stimulated the construction of brick buildings known from 1777. The most important visitor of royal families in the 19th Century were: Polish Queen Maria Kazimiera Sobieski and in 1895 the Empress Elizabeth, known as Sisi.

The first written scientific report on the results of the analysis of the two most widely used Hlavný and Kúpeľný sources was compiled in the year 1795 by prof. Paul Kitaibel in Pest. According to him, Bardejov waters are suitable against headaches, for the treatment of contractions, epilepsy, hypochondria, gynaecological diseases, gout, kidney stones and stomach diseases. Based on this assessment, the Bardejov mineral water began to be bottled and exported to Budapest, Warsaw, Berlin, Frankfurt. In the first half of the 19th Century there were recorded 13 mineral springs (Archive of ISS MoH).

Currently the Bardejov Spa utilizes the largest number of natural medicinal sources in Slovakia. 10 springs are used for spa treatment – external and internal balneotherapy. Their physical – chemical composition is quite different, which creates conditions for the treatment of a wide range of indications. Mostly they are highly mineralised cold waters, weak acid, hypotonic, bicarbonate, sodium, carbonic, high in boron content and with lithium content increased. The Bardejov Spa is among the few spas in Slovakia providing treatment of children.

Based on the different characteristics of the springs the Bardejov Spa is allowed to treat indications:

- adults – I., II., III., IV., V., VII., VIII., XI., XII.,
- children – XXI., XXII., XXIII. XXIV., XXV., XXVI., XXVIII., XXIX.

Bojnice Spa

Thermal waters in Bojnice (Fig. 4.3) surges to the Earth's surface by natural seeps; they brought the attention of local people. The first written evidence of their existence emerged in the letters of the Zobor Monastery from 1113 A.D. Later, several scholars, e.g. Nicholas Isthvanffi, Juraj Wernher, who in 1549 in his book Deadmirandis Hungarie acquis hypomnemation states that these sources were used in the then Spa facilities, whose amenities outclassed any other spa in Slovakia. The Bojnice Spa were referred to by Matej Bel in his famous work Notitia Hungariae novae historico-geographica. Extensive Spa construction took place under the property by the Thurzo Family and since 1637 by the Pálffy Family. The company was awarded in 1942 the title spas by the State. After the Second World War the Spa was nationalized by the state. By late 90s they were privatized and it still operates in this mode.

Natural healing water in Bojnice is characterized as low-mineralised, slightly alkaline, hypotonic hydrogen-carbon-sulphate and calcium-magnesium thermal water with a temperature of 46 – 47 °C (Piatko, 2006).

Currently, the Spa Bojnice, a.s. uses natural healing sources based on the Decision of the State Spa Commission (+SKK) of 2012, no. 10068/2011-41/2012/+SKK. Of the total amount of usable thermal mineral water of the discharge area

Fig. 4.3 Bojnice – Spa House Lysec

for the hydrogeological structure in Bojnice in category B recognized are natural healing sources (BR-1, BR-2, BR-3 and Z-2) with 22.5 l . s^{-1} and unrecognized thermal natural healing sources 6.7 l . s^{-1} (BR-6 and PA-7).

Natural healing properties of water provide treatment for external balneotherapy: musculoskeletal disorders, neurological diseases, urological and gynaecological problems. According to the classification in the indicator list indications are: VI., VII., VIII., XI. and XII.

Piešťany Spa

The first written mention of Piešťany (Fig. 4.4) (called Pescan) was found in Zobor Deed of Hungarian king Koloman I. of 1113. At the turn of the 13th and 14th centuries Piešťany was part of estate of Matúš Čák of Trenčín, Landlord of Váh and Tatras. After 200 years of various ownerships the city acquired Alexei Thurzo. Administrative activities of the town in the 16th Century are evidenced by the first letter written in Slovak in 1564, written by Piešťany Mayor Valo Kudlas to Trnava Magistracy. The most beautiful memory of Piešťany thermal water, baths and living in them, left behind Adam Trajan of Benešov in his ode "Healing Spa Piešťany" from 1642. In the years 1720 – 1848 the city belonged to the Erdődy Family.

The Spa belonged to the Erdődy Family until 1940. Count Erdődy founded the Spa park.

In the 19th Century, the first expert – balneologist Francis Ernest Scherer worked in the Spa, author of the work "The healing springs and spas in Hungary" (Leipzig 1837), later founder of the Military Spa Institute in Piešťany (1863).

The largest Spa boom began after 1889 after the Spa was rented by Winter Family from Erdődys. In the late 19th Century, in 1894 there emerged symbol of the Spa – Crutch, which is today in the emblem of Piešťany. Through development and modernization of the Spas by Winters international prestige of the Spa raised. Old tradition of the Piešťany Spa treatment and its success is based mainly on the medicinal use of natural healing factors, which include thermal water, sulphuric mud and climatic conditions (Archive of ISS MoH).

Based on the physical – chemical analysis of water the recognized natural healing sources are considered as: moderately mineralised, slightly acidic, sulphate – hydrogen carbonate, calcium – sodium – magnesium, sulphurous, hypotonic with increased content of fluorine and silica. According to balneological assessment it is a hot water having the temperature 65 – 67 ºC at collar. A unique ecosystem is a live appearance of sulphurous mud. After pulling out of the mud from the bypass oxbow of the Váh River the mud is matured for a year in special pools under a constant inflow of Piešťany thermal water. Thanks to the action of thermal water, algae and sulphur bacteria the water is enriched in minerals and becomes the best natural means for the treatment and protection of cartilage, joints and intervertebral discs. The Piešťany Spa, even today of European significance, is focused on degenerative diseases of the musculoskeletal system, spine diseases, conditions after injuries and after surgeries of the musculoskeletal system, central and peripheral nervous system, scoliosis, chronic rheumatism and many others.

The user of the natural medicinal sources Cmunt (borehole V-1), Hynie (borehole V-4A), Trajan (borehole V-5), Torkoš (borehole V-8) and Crato (borehole-10) in Piešťany is the Slovak Health Spa Piešťany a. s., which is permitted to use natural healing source for curative purposes in the provision of spa treatment in the following range of indications: VI., VII., XII., XXVI., XXVII.

Fig. 4.4 Napoleon Spa in Piešťany

Sliač Spa

The oldest written record of Sliač (Fig. 4.5) springs dates back to 1244. Since the mid-15th Century many prominent scholars and writers refer to them. The Sliač Spa operated already in the 16th Century. The carbon dioxide content was the cause of sudden unexplained death of birds and animals at surges (Piatko, 2006).

In the world there are known only 4 spa places at which emanate springs of natural isothermal temperature with a high content of carbon dioxide. The healing waters of such composition are excellent means to treat damage to blood vessels and the heart. According to Decree no. 100/2006 Coll. natural healing water Sliač is characterized

Fig. 4.5 Sliač Spa – Spa House

as moderately mineralised, low thermal (temperature 32 to 32.5 ºC), slightly acidic, hypotonic, sulphate – hydrogen carbonate, calcium – magnesium, carbonated water with increased content of fluorine. The surging gas contains 99.7 % of natural carbon dioxide.

Recognized sources in Sliač can be used for external and internal balneotherapy – drinking cures. In the internal balneotherapy the water is recommended in addition to drink for the treatment of osteoporosis, functional disorders of intestinal motility, gallbladder roads failure, supportive treatment of diabetes.

The Sliač Spa offers ongoing treatment in the following indications: I., II. and VII.

Trenčianske Teplice Spa

It is believed that springs located in the picturesque valley of the river Teplička were probably already know by the Romans. The first written record of stream and spring is from 1242. The earliest mention of the Spa is from 1488. Their fate always related to the ownership of Trenčín estate. The Spa development is linked to the estate of the Family Illesházy during the years 1600 – 1835. Since 1715 it was protected by a special patent. After seven generations of the Family Illesházy ownership the Spa was bought by a Viennese financier Baron G. Sina. He managed to improve and raise the Spa to the European scale. In addition to building new spa facilities he improved overall care of the Spa guests. There were built complexes Sina, Hammam, Zrkadliská. He restored also the park. After World War I, Prof. F. Lenoch published works on the Spa, thereby contributing to its development. (Piatko, 2006). The Spa utilises five curative sources for spa treatment. Their temperature reaches 36 to 40.2 ºC, whereby it is possible to provide balneotherapeutic procedures without modification. The medicinal water is warm, moderately mineralised, sulphate, calcium – magnesium, sulphurous, slightly acidic, hypotonic with increased content of fluorine. Due to increased content of titrated sulphur of about 5 mg . l^{-1}, it is particularly suitable for the treatment of musculoskeletal disorders.

Fig. 4.6 Trenčianske Teplice outdoor pool

Natural healing properties of water in Trenčianske Teplice (Fig. 4.6) allow the treatment of inflammatory rheumatic and degenerative diseases of joints and spine, muscle and non-articular rheumatism, conditions after injuries and fractures, after orthopedic surgery, some diseases of the nervous and skin. For drinking procedures the natural healing water is useful in the treatment of gout, diabetes mellitus, lipid disorders, preventing the formation of stones in the urinary tract and complementary treatment of osteoporosis.

Indicating focus of the procedures: I., II., IV., VI., VII., X., XI., XII.

Turčianske Teplice Spa

Spa Turčianske Teplice (Fig. 4.7) is situated on a plain near the geographic centre of Europe, between Martin and Kremnica. The first historical record of sources was presented in the deed of King Ladislaus IV, who donated the estate to Count Peter. Since 1423 the regenerating and healing properties of water were already known from various sources of information. They were described in the records of prominent visitors, as was King Sigismund and Emperor Maximilian of Habsburg. The first plan of the Spa construction is dated back to 1803. The most famous and most typical building is Modrý kúpeľ (*Blue Bath*; Piatko, 2006). All historic buildings underwent reconstructions based on the tastes of the owners. At present, modern and renovated building of balneo-centre Veľká Fatra forms the central part of the Spa.

The natural healing water has proven healing properties due to its high content of calcium, magnesium and fluorine. It is characterized as mode- rately mineralised sulphate – bicarbonate, calcium – magnesium, with increased content of fluorine, slightly acidic, medium thermal, hypotonic, with total dissolved solids around 1,450 – 1,500 mg . l^{-1}, with a temperature of 38 – 47 ºC and content of CO_2 gas. It is suitable for outdoor and indoor balneotherapy. According to division in accordance with applicable legislation it is suitable for treating indications for both adults as well as children: I., III., VI., VII., VIII., XI., XII., XXI.

Fig. 4.7 Turčianske Teplice – Veľká Fatra Spa House

4.5.3 The newest spas

In the second half of the 20th Century there were recorded new occurrences of mineral water in Slovakia. Consequently, there were established new spa facilities in Dudince and Nimnica, which belong to the category of the newest spas.

Dudince Spa

The Spa Dudince is (Fig. 4.8) located below the eastern flanks of Štiavnická vrchovina Highlands. Presence of mineral water was already mentioned in documents from as early as 1301, the oldest memory about its curative effects is from the year 1549. The text says that in the meadow with mineral springs on the tops of travertine mounds pools were formed. Residents of the neighbourhood were treated here for eye, rheumatism and skin diseases. The water was consumed and exported also abroad (Piatko, 2006).

Despite this rich history the Dudince Spa belongs among the youngest spas in Slovakia. Its modern history began after 1950, when the first bathhouse was built with bathtub departments. Since 1983, the Dudince Spa was granted resort status. The Dudince Spa natural healing water is unique. Its mutual content of carbon dioxide and hydrogen sulphide is unique in Europe. It is suitable for the treatment of musculoskeletal disorders, nervous system and cardiovascular problems.

According to the physico-chemical analysis of natural healing water Dudince, the water is high-mineralised, very low thermal (27.5 ºC), slightly acidic, bicarbonate – chloride, sodium – calcium, sulphurous, carbonic, hypotonic with increased content of calcium, fluorine, lithium and boron.

Indications: II., VI., VII., XII.

Nimnica Spa

The Nimnica Village under name Possessiio Nywnycze was known in chronicles since 1408. The official census of Austria – Hungary reports acidic spring in Nimnica. The Spa (Fig. 4.9) history began with the construction of foundation pit of Priehrada Mládeže (*Dam of Youth*) in the middle of the last Century. In the foundation pit, below the level of the Váh River alkaline spring water appeared. Subsequently, the healing properties of the water source were confirmed to be useful in treating respiratory and digestive system. The Spa was opened in 1959 (Piatko, 2006). At present, the Spa Nimnica treats cardiovascular, gynaecological, neurological, musculoskeletal system diseases. Essential part of therapy are drinking treatments for diseases of the metabolic system, kidney and urinary tract diseases, treatment of goitre.

Recognized natural healing water is characterized as cold, slightly mineralised, slightly acidic, hypotonic, bi-carbonate, sodium, carbonic, iodine, with increased content of lithium and boric acid.

Indicating focus is broad, the Spa provides treatment to children: I., II., III., IV., V., VI., VII., XI., XII., XXV., XXVI., XXVII.

Fig. 4.8 Dudince – Spa houses Smaragd and Rubín (Emerald and Ruby)

Fig. 4.9 Nimnica Spa

In the recent period it emerges a great interest of entrepreneurs to restore the activity of the spas in the places where the operation was discontinued for various reasons. A large number of spas ceased after the World War II. Another part of them terminate their activities during the 70's and 90's of the last Century. From this large number of abandoned spa the Spa in Červený Kláštor again resumes its activities and started operation in 2012.

4.5.4 Recovery of Smerdžonka Spa in ČervenýKláštor

The occurrence of mineral waters in Zamagurie region is modest. Undoubtedly, the most famous mineral spring of Zamaguria region is Smerdžonka, nowadays Červený Kláštor (Fig. 4.10). At the source of Smerdžonka incurred spa in order its healing effects can be enjoyed by the public. As it follows from the record of the last Camaldolese Prior Benčík Gašpar, who came from Svätý Ondrej at Poprad, Camaldolese monks were charmed by the nature around Červený Kláštor. They intended to beautify its surroundings by planting the fruit trees, imported from Poland, and to build a bridge over the Lipník River. The most prominent admirer of the Pieniny Mts. Among the monks was Friar Cyprian, known pharmacist and author of monastery herbarium in 1764.

Smerdžonka as a place of mineral water occurrence is for the first time mentioned in the work "Gesundbrunnen der Österreichischen Monarchie (*Healing wells of the Austrian Monarchy*)" by J.H. Crantz, Vienna 1777. The spa buildings were built later when Smerdžonka was belonging to the religious fund, but after the Camaldolese monks departure from Červený Kláštor in 1782; the first spa buildings were constructed between 1805 – 1820.

Chemical analysis of mineral water in Smerdžonka was published by pharmacist from Poprad-Veľká Aurel W. Scherfel in the study "Ana- lysis of Schwefelwassers of Bades Smerdzonka (*Analysis of Sulphuric Water in the Spa Smerdzonka*)". According to Dr. Engel the mineral water in Smerdžonka is suitable for the treatment of chronic rheumatoid arthritis, pain in the kidney, chronic catarrh of the airways and everywhere wherein hydrogen sulphide is required (Božíková, 2013).

Fig. 4.10 ČervenýKláštor – Dom Zdravia (House of Health)

The Prešov Landlord was also the first architect of Smerdžonka. As a result, Smerdžonka received more and more public perception. Therefore, at the General Assembly of Spiš (Szepes) County, dated December 31, 1887, it was declared that Smerdžonka /Kronenberg in German, Koronahegy in Hungarian/ had to be incorporated among spas. It was supported by the decree of the Ministry of the Interior in 1887. In 1907, the Spa passed into state ownership, which contributed to the further construction. During the First World War, the Spa buildings were partly destroyed, partly heavily damaged. Their operation was renewed in 1928. War events of the WW2 again left their mark; the reactivation occurred in 1949. Subsequently in 1959, the operations were limited and the Spa operations ceased.

Picturesque landscape of Červený Kláštor and interesting history of the Spa was a prerequisite of new owner's thoughts on the Spa revitalisation.

Chronology of the reconstruction of the Spa was as follows:

2004 – Revitalisation of the Spa began.

2006 – First hydrogeological tests. Original ČKB-2 well was impossible to use because of bad technical condition. The new hydrogeological borehole ČKB-2A was situated in the immediate vicinity.

2010 – Recognition of the local source for natural healing source.

09/2010 – First construction work for the building of therapeutic treatments (Dom Zdravia – Health House) began.

11/2011 – Construction of Dom Zdravia – Health House completed.

State Spa Commission of the Ministry of Health issued a Decision on April 26, 2012 on the operation of natural health spa. The Červený Kláštor Spa was inaugurated on July 1, 2012.

Natural healing water is characterized as moderately mineralised, sulphate-bicarbonate, sodium, magnesium, calcium, sulphane, weakly alkaline, cold, hypotonic, with TDS of 1,031 mg . l^{-1}, with a temperature of 8.0 ºC and containing H_2S gas 7.83 mg . l^{-1}.

Appropriate indications for the treatment using natural mineral water, according balneological assessment are as follows: external balneotherapy – musculoskeletal disorders, skin diseases and nervous disorders. For internal balneotherapy – drinking cures: digestive diseases, especially liver diseases (Božíková, 2013).

At present, the ongoing legislative process of approving the Statute of the Spa site, to be published in Government Ordinance.

4.5.5 Spa or wellness

Slovak and European spa facilities provide extensive options of stays from which the client can certainly choose. All products served are based on high-quality medical facilities in the use of recognized natural medicinal sources and recognized climates. The aim of traditional spa stays – based on voucher announced by doctors is to improve the functional potential of a sick, compensate and alleviate symptoms of diseases.

Slovak spa companies after the split of Czechoslovakia were better equipped to provide the so-called acute spa rehabilitation, which can be directly applied after the end of hospital treatment, for example after operations of the locomotion system, cardiovascular disorders, etc. Natural curative spas utilise material – technical, personnel and particularly natural conditions to enrich the products not only of spa treatment. Health tourism products are in high demand. They are mainly stays focused on prevention, healthy lifestyles and are financed from private sources. These stays are suitable for the healthy clients, and often are characterized as the wellbeing stays.

For the last 20 years, natural spas recorded changes in the needs of clients (Figs. 4.11, 4.12) Changes in the structure of Slovak spas clients reflects the average length of stay. In 1990 an average spa stay lasted from 20 to 23 days. Today it is only 11 to 18 days. Foreign clients who prefer a classic spa stay in spa, spend 15 to 18 days.

Provision of services "Wellness" – feel good – is expected in natural health resorts. Spa companies provide these services to complete the treatment programme, in time after for the procedures programme and as a complementary product to other visitors or self-funded clients. Wellness programmes for healthy clients are focused on the beauty of the body and a pleasant experience of the

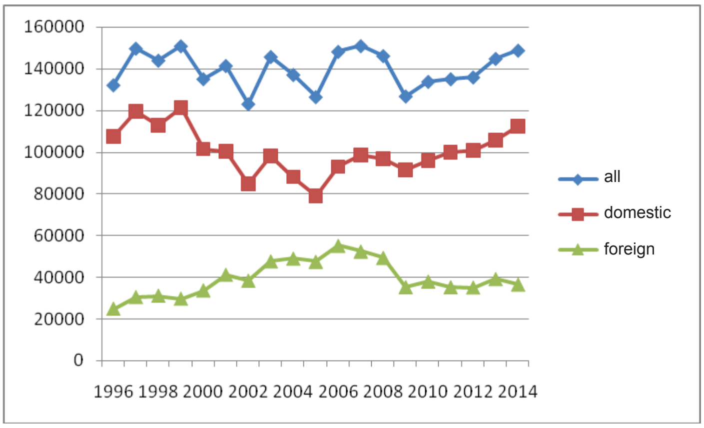


Fig. 4.11 Number of treated clients in natural health resorts – adults (NHICdata)

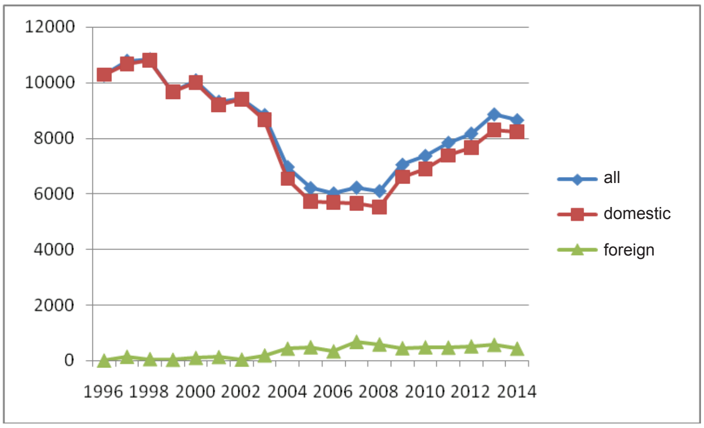


Fig. 4.12 Number of treated clients in natural health resorts – children (NHIC data)

attractive treatments in spas, or hotel complex, and are related to their standard of living.

The names "Wellness" SPA and are often found in the offers of various hotel facilities that have the status of natural health spas. The essence of wellness services is the presence and use of a natural healing source. It's a provision of procedures according to the philosophy of healthy living. The offered services are of various kinds. It may be a device that operates the bath department with drinking water and flavouring agents. Alternatively, it is a beauty treatment, hair salon, nail salon often in connection with courses of meditation and massage services. For a visitor it is sometimes difficult to navigate in such a diverse menu. This problem occurs on an European scale (Smith & Puczkó, 2014).

The main difference for orientation in the menus is a criterion of the occurrence of a natural healing source, which is used in treatments in natural health resorts. Existence of healing source is not a prerequisite for wellness facilities.

After a period of sharp reduction of clients traffic at spas there is currently observed an increase. This reflects the quality of services to clients in combination with the growing concern of the people about health. Short stays are mainly focused on prevention.

4.6 Conclusions

The modern spa treatment is provided in addition to elements of classical balneotherapy, treatment by many means of physical medicine mainly physiotherapy, climatotherapy and diet therapy. The success of the spa treatment significantly contributes to the use of modern functional and diagnostic methods and the introduction of new therapeutic programmess according to the latest scientific knowledge.

The Spa Act fully respects the current results of science and technology in chemistry and earth sciences. It also includes experiences from practice, medical rehabilitation, balneology and physiotherapy. The purpose of the Act is to establish the conditions for the recognition and use of natural healing waters, natural mineral waters, climatic conditions suitable for treatment, ensuring the development of natural health spas and spa resorts.

The first act on spas adopted in the Slovak Republic has brought important contribution to Slovak balneology. There were precisely defined rights and duties of the state administration, as well as owners and operators of spa treatment facilities. New system for authorizing the operation of these medical devices was established. At the same time a progress was achieved in making such operation a mandatory "minimum material-technical and personnel resources of natural health spas and spa treatment centres" provided for in the Regulation.

The level of administration of therapeutic treatments and spa stays in Slovak enterprises has achieved excellence. Medical personnel along with the technical background combined with high quality natural healing sources guarantee the increasing popularity of spa stays for Slovak and foreign clients.

4.7. References

Božíková, J. (2009): Natural curative waters of Slovakia in SPA. In. Medzinárodné geotermálne dni Slovensko 2009: Zborník príspevkov z konferencie. Častá – Papiernička, 26.-28.5.2009. Bratislava : Výskumný ústav vodného hospodárstva, 2009, p. 353 – 359. ISBN 978-80-89062-62-1.

Božíková, J. & Hronček, M. (2013): Balneotechnické riešenie využitia vrtu ČKB-2 v kúpeľoch Červený Kláštor, Zborník-konferencie Balneotechnické dni ´13, Vyd. KZEI, SvF STU Bratislava 2013, ISBN 978-80-227-3935-1, p. 91 – 97.

Kriš, J., Božíková, J. (2011): Spas and balneology in Slovakia. In Instalacje basenowe: Sympozjum Zakopane, Polska, 2011. Gliwice: Politechnika Slaska, 2011, ISBN 978-83-925064-7-8, p. 25 – 37.

Piatko, B. (2006): Liečivé vody a kúpele na Slovensku, vyd. MEDIA SVATAVA, ISBN 80-969210-2-9, 159 p.

Smith, M. & Puczkó, L. (2014): Health, Tourism and Hospitality, Spas, wellness and medical travel. First published 2014 by Routledge, 711 Third Avenue, New York, NY 10017, ISBN 978-0203-08377-2, 52 p.

Vandrová, G., Fendek, M., Štefanovičová, D., Friedlová, S. (2002): Ochrana prírodných liečivých zdrojov a prírodných zdrojov minerálnej stolovej vody na Slo- vensku, Mineralica Slovaca, 34, č. 5-6/2002, Vyd. ŠGÚDŠ Bratislava, ISSN 0369-2086, p. 263 – 274.

Legislative regulations

Act no. 577/2004 Coll. on the scope of health care covered by public health insurance and on payments for services related to health care, as amended by Act no. 720/2004 Coll.

Act no. 538/2005 Coll. on the natural healing waters, natural spas, spa sites and natural mineral waters and on amendment of certain laws.

Decree no. 87/2006 Coll. - Ministry Decree on the requirements for climatic conditions suitable for the treatment and the scope and terms of their monitoring.

Decree no. 100/2006 Coll. - Ministry Decree laying down requirements for the natural healing water and natural mineral water, details of the balneology assessment, distribution, coverage and content of analyses of natural healing waters and natural mineral waters and their products, and requirements for the registration of an accredited laboratory in the list maintained by the SSC.

Decree no. 101/2006 Coll. - Ministry Decree establishing a minimum of material, technical facilities and staffing of natural health spas and spa treatment centres and providing indicationsaccording natural healing waters and climatic conditions suitable for treatment.

Notification no. 175/2006 Coll. - Notification of the Ministry of Health of the details and the method of marking boundaries of spa territory, territory with climatic conditions suitable for treatment and protection zones of natural medicinal resources, natural mineral resources and climatic conditions suitable for treatment.

Rapid Impact Assessment Matrix: Case Study for the Sliač Spa

Branislav Fričovský[1], Ľudmila Jagerčíková[2], Dušan Bodiš[3]

[1]State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Mlynská dolina 1, 817 04 Bratislava, Slovakia, branislav.fricovsky@geology.sk
[2]Kúpele Sliač, 962 31 Sliač, Slovakia, ljagercikova@spa-sliac.sk
[3]State Geological Institute of Dionýz Štúr, Dept. of Environmental Geochemistry, Mlynská dolina 1, 817 04 Bratislava, Slovakia; dusan.bodis@geology.sk

Abstract: Sustainability science repeatedly accents a need to account on an interaction between environment and humans while reporting to use of natural resources and recalling on sustainable production. Praxis around a world has shown that whatever positive an impact on environment a particular project is supposed to pose, it may, in fact, come true. It is because a benefit may come with negative effects on environment during a project construction, or a project may limit or increase human needs by reducing a general wealth of publics. This paper presents construction of Rapid Impact Assessment Matrix (RIAM) and analysis of sustainable development model for the Sliač Spa, an object of remarkable (inter)national reputation, somewhat operated since Late Medieval. Results show that the project contributes on sustainable development of the region, playing major positive impact on regional to national scale, compared to those negative ones related to a local area surrounding the areal mostly. However, a fact that $S_{EB} > S_E$ and, thus $S_{EB} = 0.33$ and $S_E = 0.21$ means the environment around is more sensitive to a pressure on physical-chemical factors than to biota, even the physical-chemical components (PC) has the highest capacity for "consumption" to satisfy human needs during site operation, maintenance or development. Indeed, ran scenarios on optimistic and pessimistic assumptions show that while groundwater depletion and consequent change in chemistry would have had devastating effect onto nature and wealth, improvement in status of houses may contribute to drop in human needs only.

Key words: sustainability, groundwater, Rapid Impact Assessment Matrix, Sliač Spa

5.1 Foreword

It has become a habitual praxis referring to the term of sustainable development only when discussing an issue of energy resources depletion or concerning a climate change. In point of its definition, the sustainable development basically means meeting "*needs of present without compromising the ability of future generations to meet their own needs*" (e.g. Nel & Cooper, 2009). To approach a sustainable society, it is a must to pay sensitivity to the future not dictating welfare criterion at now, meanwhile paying sensitivity to the present avoiding a dictate on a welfare by the future (Chichilnisky, 1997). Indeed, the crux in approaching the goal is to understand fundamental relationship between the environment and humankind, requiring acceptation of complexity of the environment itself (Schellnhuber, 2001). The environment, however, composes not only of (natural) planetary subspheres, but of a human component as well, including its actions and products (Schellnhuber, 1998). If the human interaction with the environment means on how this is treated, then it comes to analogy with, e.g. sustainability of geothermal resources, which is a problem of how these are operated (Rybach, 2007). Thus, amongst energy resources, the sustainable development shall apply to developing, utilization or "conservation" of welfare activities and actions, such as spas, natural and cultural heritage, mineral and drinking water resources etc.

Numerous methods and models have been introduced to quantify a level of sustainability since a concern on sustainable development intensified, divert in approach, clarity of evaluation and an impact of subjectivity (Thompsen, 1990). Strategic Environmental Assessment (SEA) approach evaluates environmental consequences of a planned initiative or a project on par with economic and social considerations to address them for the earliest possible decision making stage, identifying and anticipating possible impacts (Dalal-Clayton & Sadler, 1996). The Sustainability Appraisal approach (SA) develops a framework consisting of objects or targets to achieve social, economical and environmental sustainability for a given action or a project, measurable through a set of quantitative indicators (Shortall, 2010). Application of EIA became a most frequent tool in Slovakia, aimed at minimizing impacts of an activity or a project on environment. Yet this is a most subjective assessment tool, based on a holistic approach only (Pastakia & Madsen, 1995). To minimize a risk of subjectivity, a Rapid Impact Assessment Matrix (RIAM) was proposed, identifying criteria to play role in overall sustainability of a project, evaluated through collating independent semi-quantitative values per each of these (Pastakia, 1998). Praxis has shown that the RIAM contributed to a site-environment analysis with assessment of a level of sustainability, updated with introduction of classification on a nature of sustainability (Phillips, 2010a, b).

Mineral and thermal springs in Sliač area are amongst first described within the territory of the Slovak Republic (Franko, 1998). Earliest quote on their existence comes from 1243 – 1244 when Hungarian King Bela IV granted town privileges to a city of Zvolen, pointing out existence of several thermal springs named *Thermae Ribariensis*, according to a cadastre of Rybár to which they belonged to. An official Sliač Spa settlement dates to a beginning of 19th Century. At this time, three thermal springs: the Dominorum for nobility, the Civium for burgesses, and Rusticorum for publics; and five cold springs: Dorota, Jozef, Lenkey, Adam and Medokýš, serving to all; donated natural pools directly. In 1860 a Count Russeger planted a base for nowadays known spa park. For comparison, a capacity of the resort increased from 300 patients in 1833 to 7,000 patients in 1959. Remediation activities and monitoring in Vlkanová have pointed out a risk of some contamination of mineral and thermal groundwater with benzene and toluene, resultant to dislocation of the Soviet Army in 1968 – 1992 (Gálisová et al., 2012). Nowadays the Sliač Spa is still active, providing service in tourism and balneotherapy. Utilizing isothermal springs as one of a few in the world only, the location has an enormous potential to gain its previous reputation.

This contribution aims to develop a RIAM for Sliač Spa, to classify a level of sustainability of its existence in a first. Then, a nature of the sustainability is identified through describing environmental, biological / ecological, social and economical aspects. This shall help to identify goals necessary to achieve a harmony with a global idea of sustainable development. Authors believe a conduction of RIAM can be beneficial to balneological community as well as a it may represent a background for onward detailed studies, e.g. in defining RIAM criteria values and components strictly related to a sustainability of spa resorts.

5.2 Approach

Early studies on environmental assessment of projects in 80's and 90's repeatedly recorded suffering from inconsistent judgement as lacking a transparent framework, impact significance determination standardization (Wood et al., 2006) and multicriteria assessment tools (Hajkowicz, 2007). Evaluation of a level of heuristic or holistic reasoning in unguided frameworks of individual involved panelists became impossible (Ijäs et al., 2008).

5.2.1 Rapid Impact Assessment Matrix

The RIAM is the matrix-based method developed to balance a risk of subjectivity in holistic and heuristic EIA evaluations (Pastakia, 1998). To achieve the goal, five (Pastakia & Jensen, 1998) or six (Ijäs et al., 2008) criteria have been identified, crucial for sustainable development analysis. A guided approach is secured through setting means by which semi-quantitative criteria are assigned. This yields an individual score per each condition selected for four basic components (Pastakia & Jensen, 1998). Indeed, development of guided evaluation scheme allows use of various conditions or factors grouped according to a component they belong to. The RIAM has been already applied to environmental loads (Al Malek & Mohamed, 2005; El-Naqa, 2005), public water supply (e.g. Kuitunen et al., 2008; Kankam et al., 2005), geothermal energy supply (Arevalo, 2003; Yousefi et al., 2009; González et al., 2015), tourism, transportation or urban planning (e.g. Wei et al., 2014) etc.

5.2.1.1 RIAM criteria

According to (Pastakia & Madsen, 1995), representative criteria for guided evaluation shall meet two principal conditions:

- universality to allow its use in different EIAs;
- must be assigned a value determining its affiliation with a criteria group A or B.

Subsequently (Pastakia & Jensen, 1998) presented clustered groups of criteria (Tab. 5.1). Complexity of the RIAM was, however, improved by implementing a criterion of environments susceptibility (Ijäs et al., 2008) to a condition (Tab. 5.1). As such, the framework shall represent a fundamental tool, meeting claims on objectivity and universality (Phillips, 2010a).

5.2.1.2 RIAM components

A component means a part of biota, abiotic system or service, expected to get under an impact of a project or to be subjected to a change by project activity (Pastakia, 1998): environmental, socio-cultural (SC) and economical (EC). Yet environmental component consists of physical-chemical (PC) and biological-ecological (BE) subcomponents (Tab. 5.2). Each component is then a group of variable aspects describing detailed situation and performance of evaluated project (Pastakia & Jensen, 1998), apparently individual for different cases due to obvious selection of different conditions.

5.2.1.3 RIAM environmental score

Once criteria are given, a semi-quantitative value is assigned to its description (Tab. 5.1). Then, each of individually found active aspect included in a respective group is subjected to an evaluation (Fig. 5.1) based on simple formulae (Pastakia & Jensen, 1998). First, an importance of the aspect to human needs or spatial boundaries is calculated (Eq. 5.1):

$$\boldsymbol{a}\mathbf{T} = (\boldsymbol{a}\mathbf{1}).(\boldsymbol{b}\mathbf{1}) \quad \text{(Eq. 5.1)}$$

where: $\boldsymbol{a}\mathbf{T}$ – total importance or a score per group A, (a1) – spatial or interest condition value, (a2) – magnitude of impact (or change) of a condition.

Use of multiplier to calculate a total importance ensures that the weight of each score is representatively expressed, whereas summation could yield identical results for different conditions. Then, performance and impact on a situation of a condition is calculated (Eq. 5.2):

$$\boldsymbol{b}\mathbf{T} = (\boldsymbol{b}\mathbf{1}) + (\boldsymbol{b}\mathbf{2}) + (\boldsymbol{b}\mathbf{3}) + (\boldsymbol{b}\mathbf{4}) \quad \text{(Eq. 5.2)}$$

where: $\boldsymbol{b}\mathbf{T}$ – total performance or a score per group B, (b1) – value for a condition permanence, (b2) – value of reversibility, (b3) – value of cumulativity, , (b4) – value of susceptibility.

Here, the bT is a sum of all B-conditions. This ensures that the individual value scores cannot influence the overall score, but that the collective importance of all values are completely accounted. Then, a relative environmental score per each condition/aspect is a product of condi-

Tab. 5.1 Review on RIA criteria and semi-quantitative evaluation matrix. Modified after: Pastakia (1998), Pastakia & Jensen (1998), Philips (2010b), Ijäs et al. (2010)

RIAM criteria	Scale	Semi-quantitative value	Description or note
Group A – importance			
(a1) – importance of the impact/aspect	+4	important to national interests/extreme societal importance	extended to the country and international boundaries or a subject of extreme rarity or special protection in the country
	+3	important regionally/significant societal importance	impacts single region or several neighbouring regions, subject of rarity in the region or a subject of some protection
	+2	important to areas outside the local context/ some societal importance	extended to an instant area around a project or a few municipalities, a subject potentially endangered with occasional protection and importance to the society
	+1	important locally/minor societal importance	typically a point-formed area or immediate areal of the evaluated project, or subject of no protection or rareness
	0	no geographical or other recognized significance	an impact or an aspect does not play a significance or is not present currently in the region, country
(a2) – magnitude of impact or change in status-quo	+3	major positive benefit or complete preservation/ conservation	e.g.: preservation of undisturbed groundwater deliverability, forest restoration
	+2	significant improvement in status-quo	e.g.: contribution on significant increase of a soil productivity potential
	+1	improvement or positive benefit	e.g.: decelerates a rate of resource depletion (use of more efficient technologies)
	0	no change in status-quo, no impact on performance	e.g.: no contamination in the surface stream
	-1	negative change to status-quo or some negative impact	e.g.: weakly excesses allowance to groundwater exploitation
	-2	significant negative disbenefit to status-quo	e.g.: build of landfill in environmentally unstable land
	-3	major negative disbenefit or complete destruction	e.g.: destructs special protection area
Group B – performance			
(b1) – permanence	+4	permanent and long-term impact	exposure to the impact is for more than 15 years
	+3	temporary and medium-term impact	exposure to the impact is usually 1-15 years
	+2	temporary and short-term impact	exposure to the impact is usually less than 1 year
	+1	no impact, not applicable, no change to status-quo	an impact or an aspect does not play a significance or is not present currently in the region, country
(b2) – reversibility	+4	irreversible impact on status-quo	permanent change to environment, which restoration is impossible or will take more than 15 years, or no plans to change the actual impact on environment
	+3	slowly reversible impact on status-quo	long-term change to environment, restoration of 1-10 years, or long-term plans to change a project performance
	+2	reversible impact on status-quo	initial status can be restored quickly up to 1 year or there is a plan to modify current site performance
	+1	no impact, not applicable, no change to status-quo	an impact or an aspect does not play a significance or is not present currently in the region, country
(b3) – cumulativity	+4	explicitly synergic impact	aspect or condition has an intrinsic impact on other aspects
	+3	synergic impact	aspect or condition has known impact on other aspects, but it has not been quantified yet
	+2	individual impact	aspect is of individual impact, not interacting with other impacts
	+1	no impact, not applicable, no change to status-quo	an impact or an aspect does not play a significance or is not present currently in the region, country
(b4) – susceptibility	+4	environment extremely sensitive to change	areas of international and national protection, special protection, endangered species etc., risk to human
	+3	environment sensitive to change	areas of local interest, minor protection, less endangered species, no risk to human
	+2	environment stable / unsusceptible to change	areas not protected, not significant or relevant to the society
	+1	no impact, not applicable, no change to status-quo	an impact or an aspect does not play a significance or is not present currently in the region, country

Tab. 5.2 Review on RIAM components, aspects and example on conditions. Modified after: Pastakia & Jensen (1998), Ijäs et al. (2008), Philips (2010b)

Sustainability component cloud	Component/ subcomponent group	Acronym	Example on aspects	Description
Environment	Physical and chemical components	PC	resource quality resource quantity landscape issues site installation	all physical and chemical aspects related to finite and infinite resource or land, including impacts of potential hazards and pollution
	Biological and ecological components	BE	biology ecology land management	all aspects with impact on biota and initial land, species preservation or conservation and interaction with ecological systems or subsystems
Human needs	Social and cultural components	SC	public performance public activities society culture	social and cultural issues affecting individuals and groups, human development and conservation or preservation of heritage
	Economical components	EC	microeconomics macroeconomics site maintenance operation	includes project activities and management, economical impact on environment or society in both, micro and macro scales

tions` importance and performance (Eq. 5.3) in a range of ES = <-192;+192> (Philips, 2010b). Then, each individual score is classified (Tab. 5.3):

$$ES = aT \,.\, bT \qquad \text{(Eq. 5.3)}$$

where: *ES* – relative environmental score.

At the end, the RIAM is presented in a form of matrix leaving reasoned and permanent record about a judgment conducted (Ijäs et al., 2008), available to get broken down into smaller problems according to given components or aspects.

5.2.2 Sustainable development model

Apparently, the environmental score yields negative values for any disbenefitial impact indicated. To avoid issues in interpreting negative scores, the initial count must be upscaled by +192 to each aspect, transforming preliminary rangeband $-192 \leq ES \leq +192$ (Pastakia, 1998) to more applicable positive range $0 \leq ES \leq 384$ (Ijäs et al., 2008).

5.2.2.1 Level of sustainability

According to a concept of sustainable development (e.g. Nel & Cooper, 2009), human actions and needs (H_{NI}) should not compromise an environment (E), so that $E > H_{NI}$, thus an action or a project is sustainably developing if its sustainable score (Eq. 5.4) is $S > 0$. While an environment is described by its actual interaction over total capacity (Eq. 5.5), human needs are defined along social, cultural and economic aspects (Eq. 5.6). Consequently, for a case where human needs exceed a capacity of the environment, an evaluated project cannot be considered sustainable, so that $H_{NI} > E$ and $S < 0$ (Philips, 2010a,b). Evaluation of a level of sustainability then proceeds towards semi-quantitative description (Fig. 5.1) based on E versus H_{NI} relations (Philips, 2010a):

Tab. 5.3 Environmental score evaluation. Modified after: Pastakia & Jensen (1998), Ijäs et al. (2008)

Environmental score range-band	Sustainability classification	Sustainability performance description
+192 to + 108	D (or +4)	major positive impact
+107 to +54	C (or +3)	significant positive impact
+53 to +31	B (or +2)	moderate positive impact
+30 to +1	A (or +1)	slight positive impact
0	N (or 0)	no impact on status-quo
-1 to -30	-A (or -1)	slight negative impact
-31 to -53	-B (or -2)	moderate negative impact
-54 to -107	-C (or -3)	significant negative impact
-108 to -192	-D (or -4)	major negative impact

$$S = E - H_{NI} \qquad \text{(Eq. 5.4);}$$

$$E = \frac{\sum PC + \sum BE}{PC_{max} + BE_{max}} \qquad \text{(Eq. 5.5);}$$

$$H_{NI} = \frac{(SC_{max} - \sum SC) + (EO_{max} - \sum EO)}{SC_{max} + EO_{max}} \qquad \text{(Eq. 5.6)}$$

where: E – environment, H_{NI} – human needs, PC_{max} – capacity of PC component, BE_{max} – capacity of BE component, SC_{max} – capacity of SC component, EO_{max} – capacity of environmental component, S – level of sustainability, thus:

- $S \leq 0$ → not sustainable
- $S = 0.001$ to 0.250 → very weak sustainability
- $S = 0.251$ to 0.5 → weak sustainability
- $S = 0.501$ to 0.75 → strong sustainability

- S = 0.751 to 1 → very strong sustainability

According to (Eq. 5.4), with increasing H_{NI}, there must be a determined value of E, otherwise E > H_{NI} will not occur, meaning that for uncompromised increase in H_{NI}, there shall be an infinite source of E to maintain S > 0, that is, of course, impossible (Phillips, 2010a).

where: S_X – sustainability score for subcomponent or aspect X, X_{act} – actual performance of subcomponent X and X_{max} – capacity of the component X.

In general, a capacity (Phillips, 2010a) of various component X (Eq. 5.8) which systematically enters equations Eq. 5.5 to Eq. 5.9 is given by maximum possible environ-

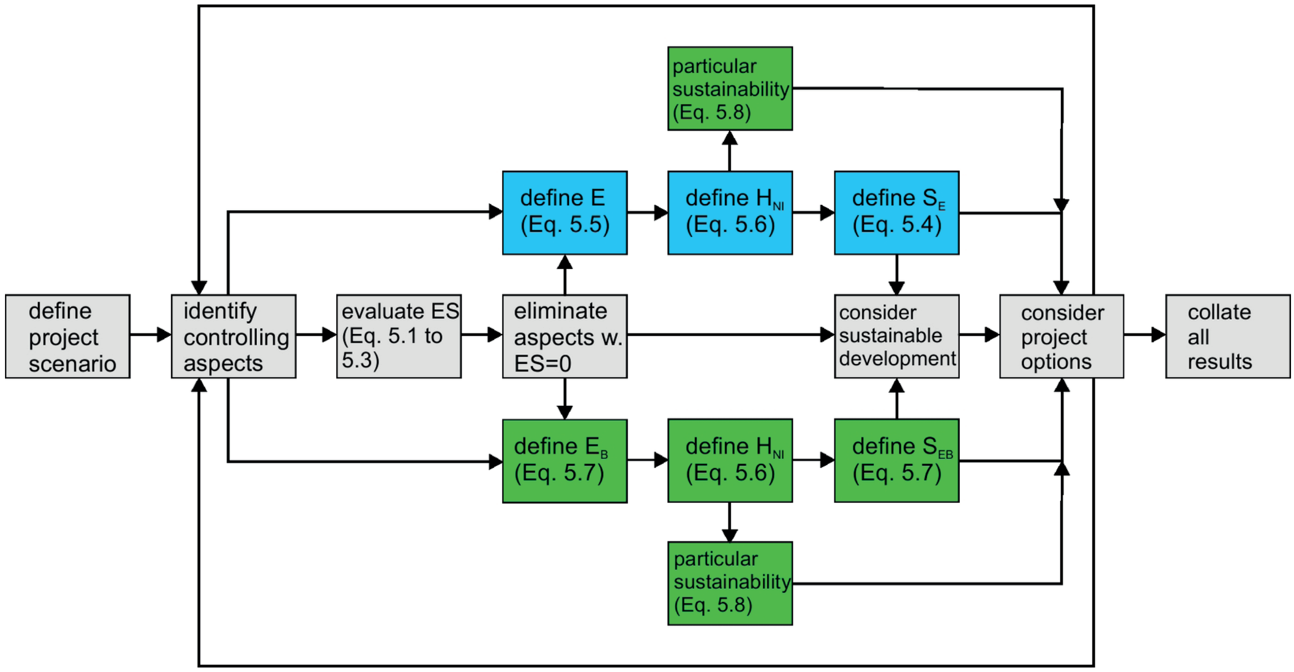


Fig. 5.1 Rapid Impact Assessment Matrix and sustainable development model workflow. Modified after: Pastakia&Jensen (1998), Phillips (2010a), Ijäs et al. (2008)

5.2.2.2 Nature of sustainability

A problem of environmental sustainability model by Pastakia (1998) is that summing up both components (PC + BE) may lap over their lows compared to H_{NI} (Eq. 5.5), yielding apparent sustainability if E > H_{NI} or (PC+BE) > H_{NI} and, thus, S = S_E > 0. A model of ecological sustainability (Eq. 5.7) sums all subcomponents (atmosphere – A, biosphere – B, lithosphere – L and hydrosphere- H) and turns them against a capacity of the system, which is calculated as maximum possible score per each (Phillips, 2010a):

$$S_{EB} = \frac{\sum(B + A + H + L)}{B + \sum A_{\max} + H_{\max} + L_{\max}} \quad \text{(Eq. 5.7).}$$

Analogously, a procedure in (Eq. 5.7) may be applied to each sphere if its actual state, given by an impact of humans posed, is confronted with its capacity, that is a maximum score possible. Schellnhuber (1998, 2001) accents that sustainability requires understanding a dynamic relationship between E and H_{NI}. It means, that the higher is the sustainability performance for E, the less is the performance of H_{NI}. If H_{NI} = ∑SC+∑EO, a general concept of sustainability (Eq. 5.8) allows proportion of each subcomponent and aspect to an intensity of human needs, providing additional options to approach a picture of sustainability at a site:

$$S_{EB} = \frac{X_{act}}{X_{max}} - H_{NI} \quad \text{(Eq. 5.8)}$$

mental score (ES_{max}) score of number of subcomponents (n_X) comprising a set X, thus:

$$X_{\max} = n_X \,.\, ES_{\max} = n_X \,.\, 384 \quad \text{(Eq. 5.9).}$$

5.2.3 Problem definition

Historical documents say the Sliač Spa were founded at the very beginning of 19th Century. Thus, depending on a timescale, their existence may appear sustainable – either with some reference to a necessary scale for, in an example, sustainable operation of geothermal resources, requiring at least 100 – 300 years long production (Axelsson et al., 2001) without decline in production or deliverability over 10 % to the initial (Williams, 2010). However, considering a real on-line project, there is more with it than just a production of waters. Thus, besides the history of site foundation, the problem is to determine and analyze:

- level of sustainable performance of the Sliač Spa at an overall scale;
- identify nature of sustainability;
- analyze capacity the environment provides to the project available for sustainable use.

5.3 Site description

5.3.1 Geology

Geological structure in the Sliač Spa region reflects its geodynamic evolution and geological position, covering a vertical profile from Palaeozoic to Quaternary. The Ľubietová Group of the Veporic Superunit is represented by the Brusno Formation in its typical rhyolite and dacite volcanoclastics, to the SE from the areal (Fig. 5.2). Existence, extension and thickness of Mesozoic nappes is, in major, assumed only, based on deep boreholes data. Mesozoic surface exposure terminates along a Čerín-Vlkanová line to the N, than sinks beneath Neogene volcanosedimentary complexes (Konečný et al., 1983). The Krížna Nappe is the bottom system, exposing with Early Triassic quartzites and arkose sandstones of the Lúžna Formation to the SE. The Choč Nappe system composes of Mid Triassic Ramsau and Main Dolomites, usually dissected into multiple tectonic outliers. The Drienok Nappe represents a superpositioned Mesozoic system, with rare records of Reifling Limestone (organogeneous, cherty) and Wetterstein Limestone (reef, organogeneous limestones) documented to the N, near towns of Vlkanová and Čerín (Bondarenková, et al., 1986).

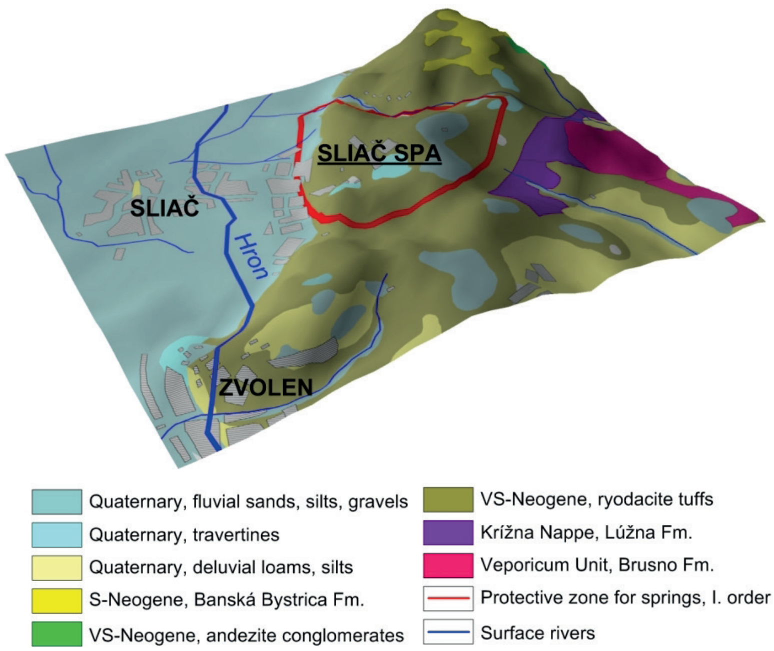


Fig. 5.2 Generalized geological map of the Sliač Spa area

Neogene – Early Sarmatian pumice and rhyodacite tuffs of the Strelnica Formation form a most extended lithotype exposing on the surface in the area (Fig. 5.2), representing external zone of the Poľana Stratovolcano. External zone of the Javorie Stratovolcano exposes to the NW by Mid to Late Sarmatian epiclastic andesite sandstones with conglomerates. The Pliocene aged Banská Bystrica Formation is the only member of the sedimentary Neogene, forming spatially limited surface positions of gravels and silty sands NE from the Spa.

Quaternary fluvial accumulations represent a dominant sedimentary cover in the entire region. Early Pleistocene high terraces show up in form of residual gravels. Mid Pleistocene is developed to the W from the Sliač Town, recording increased proportion of sands and sandy loams. Holocene levee plains compose of loams, sands and gravels. Deluvial formations form slope talus and occasional landslides of sandy loams facies. Pleistocene to Holocene foam sinters and travertines are rare in the region, however, are a clear record on mineral water presence and open type of local hydrogeological structures.

5.3.2 Hydrogeology

Complexity in local hydrogeology reflects variation in geological structure of the entire area. By classification of groundwater regime (Franko et al., 1975) the structure is best described as open with semi-covered discharge area.

Bondarenková et al. (1986) assume the infiltration zone extends to the NWN at slopes of the Kremnické vrchy Mts., as given by piezometry, after gaslift and thermolift effect neglecting. Although there are multiple mineral-thermal water transition pathways distinct in filtration depth and residential longevity within the system. Effective transition realizes in environment of different proportion between intergranular and fissured permeability, according to a host rock. Limestones are, however, typical with kart-fissured permeability (Ryšavá et al., 2008). Vertical extension is then controlled along open longitudinal SW-NE and transverse NW-SE regional and local fault systems (Dzúrik, 2012).

Accumulation zone hosts groundwater in shallow and deep circulation. While the first consists of Neogene volcanosedimentary complexes, the latter forms within Mid Triassic carbonates, drained at a contact with heavily incompact Early Triassic quartzites (Böhm et al., 1993).

Two different discharge zones are documented in the Sliač area, at different elevations. A top one drains deep circulation regime by the Kúpeľný prameň spring, but discharges at the bottom one by Bystrica, Lenkey, Adam springs as well. This has been already expected by Bondarenková et al. (1986). The Štefánik spring represents a natural discharge of shallow circulation (Dzúrik, 2012).

5.3.3 Hydrogeochemistry

Groundwater at the Sliač area is vadose in origin, infiltrated into volcanosedimentary or carbonate environment straight by rainfall, or seeped deeper by hydraulic connection between different aquifers and, apparently, along open fault systems. The free CO_2 is, however, juvenile, originated in buried crystalline, evading shallow aquifers at fault intersections mostly (Dzúrik, 2012).

A difference is evident by groundwater chemistry (Fig. 5.3). Deep drained groundwater is of Ca-SO_4 to SO_4-Ca type, gaining a sulphate compound by dissolution of evaporates (Bondarenková et al., 1986), preferentially gypsum of the Lúžna Formation. A deep circulation and longevity of the group is seen along offset from the rainfall precipitation region on a Gibbs plot (Fig. 5.4), implying tendency to vary the chemistry through deposition of solid phases at (hence the Na/Ca + Ca low region) atmospheric pressure (Gibbs, 1970). This is what exactly happens by sintering and travertine formation nearby the spa areal.

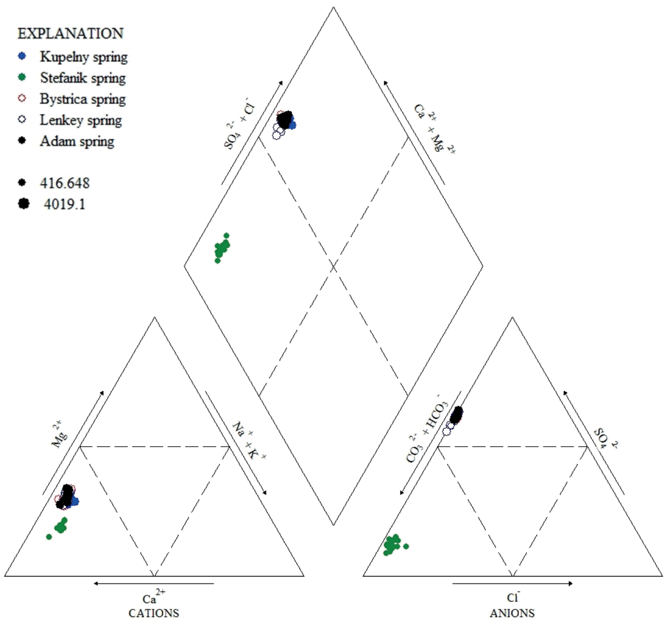


Fig. 5.3 Piper plot of documented Sliač Spa springs in a period 1994-2016

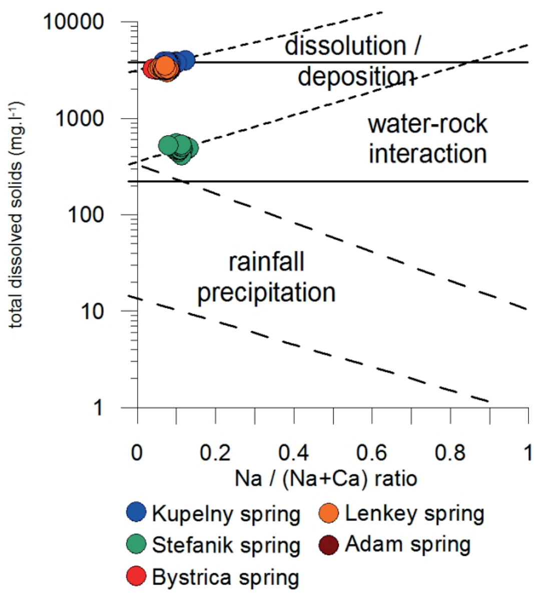


Fig. 5.4 Gibbs plot of documented Sliač Spa springs in a period 1994 – 2016

A good evidence is also given on a maturity plot (Giggenbach, 1991), where region of immature, acid type waters (Fig. 5.5) implies longer circulation and less sensitivity to rainfall variation (at least in terms of groundwater chemistry).

Shallow groundwater distinctly varies in bicarbonate compound and low sulphate content (Fig. 5.3) as lacking a contact with the SO_4 source zone (Early Triassic horizon), preserving Ca-HCO_3 type of chemistry. Apparently, rainfall and rock dissolution control its chemistry (Fig. 5.4), and (after Gibbs, 1970) groundwater shall be in some partial equilibrium with a host rock. An evidence the groundwater chemistry is a product of shallow and fast filtration is given by position of samples of the Štefánik spring in the peripheral region (Ármansson, 2007), given by high bicarbonate proportion.

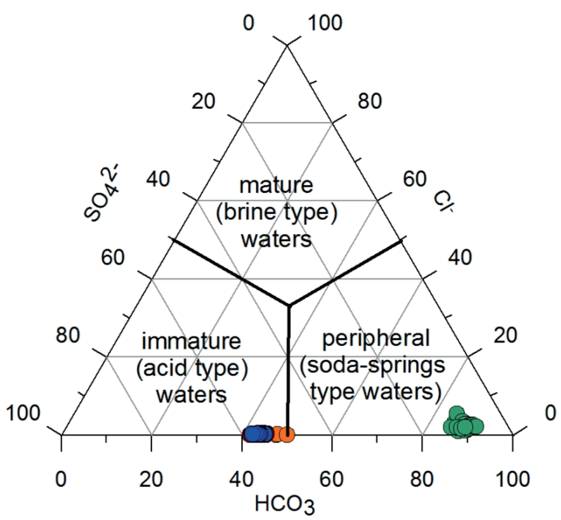


Fig. 5.5 Giggenbach's maturity plot for Sliač Spa springs in a period 1994 – 2016. See previous plot for colour symbols

5.4 Site performance

5.4.1 Physical and chemical components

5.4.1.1 Site installation subcomponents

The site has been founded in woodlands, by the eastern limit of the Sliač Town. An areal consists of 10 buildings and park (Kolonáda) with no outer fence. A situation of the Spa in primary nature promotes use of initial land (PC1) by existence of protective zone. Yet the same areal increases a natural light intensity in the woods (PC9) and cultural or human activities through a year, which produce a level of noise (PC3) above 120 dB, which is critical (Tester et al., 2006), thus negative impact onto biota must be accounted. Similarly, the need for infrastructure operation and maintenance contribute on noise level, however, with negative score limited at its longevity (PC2). Odour production (PC8) has been eliminated, finding no source for so (Tab. 5.4).

5.4.1.2 Resource quantity subcomponents

Since foundation, Sliač Spa use mineral-thermal groundwater at Kúpeľný prameň (T = 33 °C), Štefánik (T = 12 °C), Bystrica (T = 23 °C), Lenkey (T = 22,5 °C) and Adam (T = 23 °C) springs, along with free carbon dioxide yield of 10 l . s^{-1}.

A resource production is given by allowances (Dzúrik, 2012), at Q = 4.8 l . s^{-1} for groundwater and Q = 10 l . s^{-1} for CO_2. Actually, a production (PC17) does not exceed 25 – 75 % of allowed yield, marking a strong positive effect on deliverability (PC15), not recording any decline in discharge or temperature (Fig. 5.6). Accessibility to groundwater resources is, however, restrained by extension of protective zones, contravening principles of sustainable development (Tab. 5.4). Although this is a situation typical for all mineral-thermal and healing springs sensitive to external components (PC18).

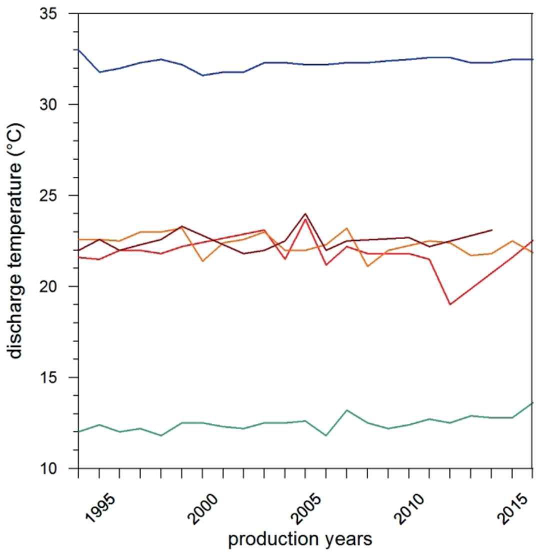


Fig. 5.6 Mean annual discharge temperature record of Sliač springs

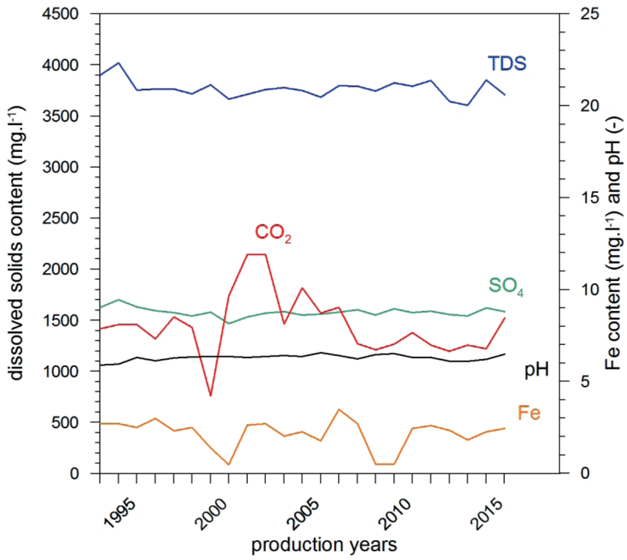


Fig. 5.7 Variation in specific components of the Kúpeľný prameň spring

5.4.1.3 Resource quality subcomponents

Operation of spa is determined on groundwater healing effect preservation. At a site, mineral-thermal water applies in gynecological and cardiovascular diseases, movement and gastroenteritis disorders, and carcinoma treatment. Resource quality is, thus, a crucial performance not only to physical-chemical, but economic and social aspects as well.

Stable production under a critical yield restrains change in groundwater filtration longevity and depth. Periodical measurements at springs record no damage on groundwater quality (PC5), keeping stable chemistry (Fig. 5.7) of exploited water (PC16) in its main components. Finding of Gálisová et al. (2012) on presence of organogeneous pollution originated at the Vlkanová shall not be accounted to activity of the Spa. Areal coverage of protective zone and zone of specific provision contribute positively on a final air quality (PC6).

Currently, water from the Kúpeľný prameň spring is disposed into local drainage channel (PC4) at TDS = 3.5-4.1 $g.l^{-1}$, increasing dissolved solids in a water above its dilution capacity, posing a damage on a surface stream quality and risk on local microbiota. Unfit condition of buildings poses a risk on a soil quality (PC7) amongst (Tab. 5.4).

5.4.1.4 Landscape issues and dynamics subcomponents

Aspects are controlled along possible geodynamics and hazards, caused or limited by human intervention, as well as on surface manifestations of groundwater presence.

No decline in natural springs discharge preserves their manifestation (PC10) at a positive level (Tab. 5.4). An effect is strengthened as these are most important landscape features and propagation of resource existence. Although of high land use efficiency, early construction of hotels at the break of Medieval along with "recent" installation

Tab. 5.4 Rapid impact assessment matrix for physical-chemical (PC) components

Code	Description	a1	a2	b1	b2	b3	b4	aT	bT	ES	ES
PC1	Land use efficiency	3	2	4	1	2	2	6	9	54	C
PC2	Infrastructure impact	2	-1	4	1	2	2	-2	9	-18	-A
PC3	Noise	2	-1	4	2	2	2	-2	10	-20	-A
PC4	Surface water quality	2	-1	4	4	3	3	-2	14	-28	-A
PC5	Groundwater quality	4	3	4	4	3	4	12	15	180	D
PC6	Air quality	3	3	4	3	4	3	9	14	126	D
PC7	Soil quality	1	-1	3	3	3	2	-1	11	-11	-A
PC8	Odour	0	0	1	1	1	1	0	4	0	N
PC9	Light pollution	2	-1	4	2	2	2	-2	10	-20	-A
PC10	Springs manifestations	4	3	4	2	4	4	12	14	168	D
PC11	Erosion	0	0	1	1	1	1	0	4	0	N
PC12	Landslides	4	0	1	1	1	1	0	4	0	N
PC13	Subsidence	0	0	1	1	1	1	0	4	0	N
PC14	Landscape modification	2	-1	4	4	2	4	-2	14	-48	-B
PC15	Deliverability	4	3	4	4	4	4	12	16	192	D
PC16	Geochemical stability	4	3	4	4	4	4	12	16	192	D
PC17	Production stability	4	2	4	4	4	4	8	16	128	D
PC18	Accessibility	1	-3	4	4	4	2	-3	14	-42	-B

of infrastructure have consumed initial relief negatively (PC14).

Geodynamics (PC11 to PC13) have been eliminated as there is no interaction between the Spa and occurrence of landslides, erosion or subsidence, neither of these was observed.

5.4.2 Biological and ecological components

Identification of project impact on biotic systems in surroundings of the spa set a target to search for species of local to national importance in terrestrial or aquatic environment. Evaluation includes possible limits to biota for migration, breeding or wintering rests.

5.4.2.1 Biology subcomponents

Terrestrial ecosystem (BE1 to BE2) plays regional role in importance through fauna (Black stork, Lynx, Brown bear, deers, boars etc.) or flora species. Presence of Spotted eagle (protected) or *Gentiana*, *Agrostemnia*, *Iris*, *Lilium*, *Vinca* or *Cornus* increases performance of the Spa to the biota by extended protection (Tab. 5.5).

While aquatic flora is limited to banks (BE4), mineral water disposal plays negative impact on aquatic microfauna (BE3).

5.4.2.2 Ecology subcomponents

Ecology aims at analysis of pressure posed on living forms and environmental interaction of the Spa with ecosystems of variable capacity and importance.

Specific provisions zone covers entire woods around areal, restraining negative activity within (BE5). An effect rises up because of inhaling therapy realized in woods. Legal protection promotes ecological stability of the entire area (Tab. 5.5), accented through good performance towards biodiversity by extension of pastures and forests of specific provision (BE9).

Natural habitat (BE7), endemism (BE8), relicts (BE9), geodiversity (BE10) and special protection area (BE11) were eliminated. No presence has been recorded until now.

5.4.2.3 Land / country management subcomponents

In sustainability science, land and country management identifies capacity of a surface to provide products supplying a demand, thus the human needs resulted from their interaction with primary and secondary environment.

By Atlas of Landscape SR (2002), the entire region is of low soil productivity (BE13) and low agricultural potential (BE14) sensitive to occasional trashes pollution yielding a negative score (Tab. 5.5).

Primary land (BE6) and land aesthetics (BE16) are, by a contrast, in positive response to existence of the Spa. This is because pastures are situated within protective zone of Ist order for mineral water and the entire areal is seated in primary woods, with, if any, low modification.

5.4.3 Social and cultural components

Social and cultural components aim on human aspects in the environment (Mihaiescu et al., 2015) defining a rate of human wealth, leading towards its conservation, damage, restoration or preservation, including natural and cultural/historical heritage. Then, human needs are inverse to the social and cultural condition of publics (Pastakia & Jensen, 1998).

5.4.3.1 Public performance subcomponents

The subcomponent of public performance evaluates a level of societal development and acceptance of the project status with its impact to the environment and initial country.

Stability in therapeutic and recreation effect of the Spa promotes local public services (SC1), safety (SC4) and health (SC5) with importance extended not only towards local but foreign visitors as well (Tab. 5.6).

Tab. 5.5 Rapid impact assessment matrix for biological-ecological (BE) components

Code	Description	a1	a2	b1	b2	b3	b4	aT	bT	ES	ES
BE1	Terrestrial fauna	3	1	4	2	4	3	3	13	39	B
BE2	Terrestrial flora	3	2	4	2	4	3	6	13	78	C
BE3	Aquatic fauna	1	-1	4	2	3	2	-1	11	11	-A
BE4	Aquatic flora	1	1	4	2	3	2	1	11	11	A
BE5	Forests	4	1	4	4	3	2	4	13	52	B
BE6	Primary agricultural land	1	1	4	4	3	2	1	13	13	A
BE7	Habitat	0	0	1	1	1	1	0	4	0	N
BE8	Endemism	0	0	1	1	1	1	0	4	0	N
BE9	Relicts	0	0	1	1	1	1	0	4	0	N
BE10	Biodiversity	3	3	4	4	3	2	9	13	117	D
BE11	Geodiversity	0	0	1	1	1	1	0	4	0	N
BE12	Special protection area	0	0	1	1	1	1	0	4	0	N
BE13	Soil productivity	2	-1	4	2	2	3	-2	11	-22	-A
BE14	Agricultural potential	2	-1	4	2	2	3	-2	11	-22	-A
BE15	Ecological stability	3	3	4	3	4	3	9	14	126	D
BE16	Land aesthetics	3	1	4	2	3	3	3	12	36	B

Besides, abandonment of 7 out of 9 housing objects calls on negative reactions of publics and its acceptability (SC2) and adaptability (SC3) of the Spa under actual conditions, substantially decreasing a general wealth and increasing human needs.

5.4.3.2 Public activities subcomponents

The group identifies possibilities of environment – human interaction at a scale of capacity it can provide to satisfy general needs of public wealth and conditions.

International importance of the Spa supports a region promotion (SC6) through therapeutics (SC9) improving life quality status, which is of synergic interaction with local socioeconomics. Legal protection of the region, however, reduces opportunities on recreation (SC8) as given by specific provisions in use of the country, yet they do not limit possibilities on tourism (SC10) hence a direct contact of the open Spa areal with a wildlife (Tab. 5.6), creating high confidence in climatic adaptability (SC11) by yield allowances and resource stability.

5.4.3.3 Culture subcomponents

A level of society and its intervention with history and environment is defined along with impact of its activities on heritage. Hence sustainable development shall at least conserve a natural status and makings of a past for the future, an accent is given to its preservation.

There are four declared objects of cultural heritage in the areal: Bratislava (ex Buda), Slovensko (ex Hungaria), Detva (ex Pešť) and the Palace (Fig. 5.8 – 5.9), with the latter active only. The rest is currently abandoned with no special protection or conservation campaigns, technical and historical status drops, contravening principles of sustainability (Tab. 5.6).

By a contrast, there is high cultural habitats (SC15) expected, as the Spa is still performing online, including bathing habitats and cultural events since Medieval. There is no presence of natural (SC13), neither historical (SC14) heritage in a meantime.

5.4.3.4 Society subcomponents

A wealth and development of society shall be given along existing opportunities on education and research, in terms of understanding the environment (nature) and past (history, culture) with empirical consequences for the future (Chichilniski, 1997). The higher is a societal performance, the less are the human needs.

Fig. 5.8 Cultural heritage: hotel Palace at its current condition

Based on historical tradition, education (SC16) opportunities are interdisciplinary, increasing their positive impact onto social wealth, whether it is geology, hydrogeology, archaeology, balneology or life-sciences.

Actually, according to its legal form, the Spa is not a research training centre (SC17). Increasing consensus on potential toluene and benzene groundwater resources contamination as originated in Vlkanová (Gálisová et al., 2012) provides opportunities on external activities.

5.4.4 Economical and technical components

Performance of a project must be identified through its economical performance and level of operation conditions. After Pastakia & Jensen (1998), the higher is the performance, the less environment is needed to reach a

Tab. 5.6 Rapid impact assessment matrix for social-cultural (SC) components

Code	Description	a1	a2	b1	b2	b3	b4	aT	bT	ES	ES
SC1	Public services	4	2	4	1	4	3	8	12	96	C
SC2	Public acceptability	3	-2	3	3	2	3	-6	11	-66	-C
SC3	Public adaptability	3	-1	3	3	2	3	-3	11	-33	-B
SC4	Public safety	3	3	4	4	3	3	9	14	126	D
SC5	Public health	4	2	4	3	3	3	8	13	104	C
SC6	Region promotion	4	1	4	3	3	4	4	14	56	C
SC7	Local migration	1	3	3	4	3	2	3	12	36	B
SC8	Recreation	1	2	3	3	3	2	2	11	22	A
SC9	Therapeutics	4	3	4	4	4	4	12	16	192	D
SC10	Tourism	3	3	4	4	4	2	9	14	126	D
SC11	Climatic adaptability	3	2	3	4	2	2	6	11	66	C
SC12	Cultural heritage	4	-2	3	3	4	3	-8	13	-104	-C
SC13	Natural heritage	0	0	1	1	1	1	0	4	0	N
SC14	Historical heritage	0	0	1	1	1	1	0	4	0	N
SC15	Cultural habitats	2	3	4	4	4	2	6	14	84	C
SC16	Education	1	3	4	4	3	2	3	13	39	B
SC17	Research and science	0	0	1	1	1	1	0	4	0	N
SC18	Archaeology	0	0	1	1	1	1	0	4	0	N

sustainable (well-shaped) level. At such situation, good project economics and technical condition decreases human needs, reducing pressure on the natural resources by consumption. In other words, similar to previous components, economic and technical wealth is inverse to the human needs.

5.4.4.1 Site maintenance subcomponents

Here an accent is put towards external interaction with environment, giving a prioritz to a level of resource (energy, environment) consumption and efficiency of its operation (i.e. primary energy efficiency) compared to initial or expected capital and level.

With a backnote on actual condition of bathhouses, there is no thermal insulation applied to buildings causing intense energy losses during a winter season (EO3), decreasing efficiencies in primary energy supply and consumption, and eliminates an effect of project lifetime by not preserving a technical condition of these (EO2). It is a site paradox that operation of 2 buildings only drops costs (EO4) down by less energy emissions. Yet the project is restrictive to third parties by setting protective and specific provision zones on natural resources (groundwater, woods, initial country land), causing negative (Tab. 5.7) conflicts of interests (EO1).

5.4.4.2 Site operation subcomponents

A current level of a site is most pronounced as a site operation performance, for which a focus is paid for comparison between ideal or primary technical status of objects and effectivity in use and occupation of environment to the current or actual situation.

In fact, current technical condition of bathhouses (EO7) is an essential problem of the Spa, serving in accommodation at only two out of nine buildings: the Palace and the Kúpeľný dom. The houses shut down suffer some level of degradation (Fig. 5.9), with substantial damage on status of equipment (EO8). Abandonment of the Hron, Starý Partizán, Poľana and Amália houses significantly reduces the built-up area efficiency (EO9).

Negative intervention of a problem objects is, however, fairly reduced by low traffic and transport in the area (EO5) and generally sufficient conditions of infrastructure (EO6), limiting a need for onward intervention into primary land and nature (Tab. 5.7).

5.4.4.3 Macroeconomics subcomponents

According to a sustainable development, each environment consumption shall provide a relative wealth to the publics. A way in use of resources shall not then reach a level of break, at which a nature could not balance needs resulted from a poor public status, consequent to ineffective resource management.

Fig. 5.9 Current state of the Slovensko hotel/bathhouse

Tab 5.7 Rapid impact assessment matrix for economical-operation (EO) components

Code	Description	a1	a2	b1	b2	b3	b4	aT	bT	ES	ES
EO1	Conflicts of interests	1	-1	4	3	3	2	-1	12	-22	-A
EO2	Project lifetime	2	-1	3	3	2	2	-2	10	-20	-A
EO3	Energy losses	1	-1	3	3	3	4	-1	13	-13	-A
EO4	Operation costs	4	1	4	3	4	3	5	14	56	C
EO5	Traffic and transport	3	3	4	4	3	4	9	15	135	D
EO6	Infrastructure built-up	2	3	3	4	3	3	6	13	78	C
EO7	Tech. condition-buildings	3	-3	3	3	4	3	-9	13	-117	-D
EO8	Tech. condition-equipment	3	-2	3	3	4	3	-6	13	-78	-C
EO9	Built-up area efficiency	3	-2	4	4	3	3	-6	14	-84	-C
EO10	Health costs	4	2	4	4	4	2	8	14	112	D
EO11	Employment	3	2	3	3	4	3	6	13	78	C
EO12	State donation	0	0	1	1	1	1	0	4	0	N
EO13	International donation	0	0	1	1	1	1	0	4	0	N
EO14	Economic self-sufficiency	4	-1	2	3	4	3	-4	12	-48	-B
EO15	Local pricing	1	-1	3	3	3	3	-1	12	-12	-A
EO16	Housing quality	0	0	1	1	1	1	0	4	0	N
EO17	Property value impact	2	2	4	3	4	3	4	14	56	C

Therapeutic activities and promotion of a public health (Tab. 5.6) systematically reduce primary health costs (EO10), including contribution of good environmental (Tab. 5.4) and ecological (Tab. 5.5) project performance (Tab. 5.7). As far as the Spa exists, there is a potential for work opportunities creation (EO11) increasing social and economic wealth of local publics.

Hence the Spa is actually privately owned, there is no option to apply for neither international (EO13) nor domestic (EO12) financial support, thus those aspects are not applicable, therefore they are eliminated for the RIAM (Tab. 5.7).

5.4.4.3 Microeconomics

Microeconomics considers local region and economic interaction of a project with publics and environment, defining local wealth status.

Because of a worsening driven reduction in visitors and accommodation capacity of the Spa economic self-sufficiency (EO14) declines continuously, turning local pricing (EO15) higher over possible level, as spas attempt to balance a drop in income. Existence of the Spa itself in combination with fairly well status of local environment keeps profitable value of estates (EO17). A potential is to increase a property value with revitalizing the abandoned bathhouses. We could not identify any impact on a housing quality around (EO16).

5.5 Sustainability model

Together 69 aspects clustered into four groups were identified according to their potential to pose an impact on human – environment interaction and human needs (Tab. 5.4 to 5.7; Fig. 5.10). To account only those performing a least, 16 aspects had must been eliminated as irrelevant or inapplicable.

5.5.1 Level of sustainability

Given by (Eq. 5.4) a project may be considered sustainable if score of environment (E) is higher than a score of human needs (H_{NI}) thus $E > H_{NI}$ yielding $S = S_E > 0$ (Phillips, 2010b). The concept in its essence displays positive or negative interaction of humans with environment and its environmental efficiency of resource consumption. Thus, any development (increase of human needs) shall conserve at least a half of resources available (environment) not recording a limitation to the recent wealth ($\sum X_{act} / X_{max} > 0.5$).

5.5.1.1 The Environment (E)

According to a sustainable science, the environment is defined as a sum of PC and BE components. Its size is than actual performance of its aspects over its total capacity (Eq. 5.5).

The size of the environment is $E_{act} = \sum PC_{act} + \sum BE_{act}$. The actual PC is a sum of partial scores (Tab. 5.4) after eliminating those of ES = 0, modified to $ES = ES_{act} + 194$ (Phillips, 2010a). This gives an actual size of PC at $\sum PC$ = 3,561. The same procedure has been applied to define a size of biological-ecological components, yielding a score of $\sum BE$ = 2,529. If total capacity is given by (Eq. 5.9), the maximum capacity of the physical-chemical component counts PC_{max} = 5376 and BE_{max} = 4,224 respectively, including 14 PC and 11 BE aspects. The size (Eq. 5.5) of the environment is then a dimensionless value of E = 0.63.

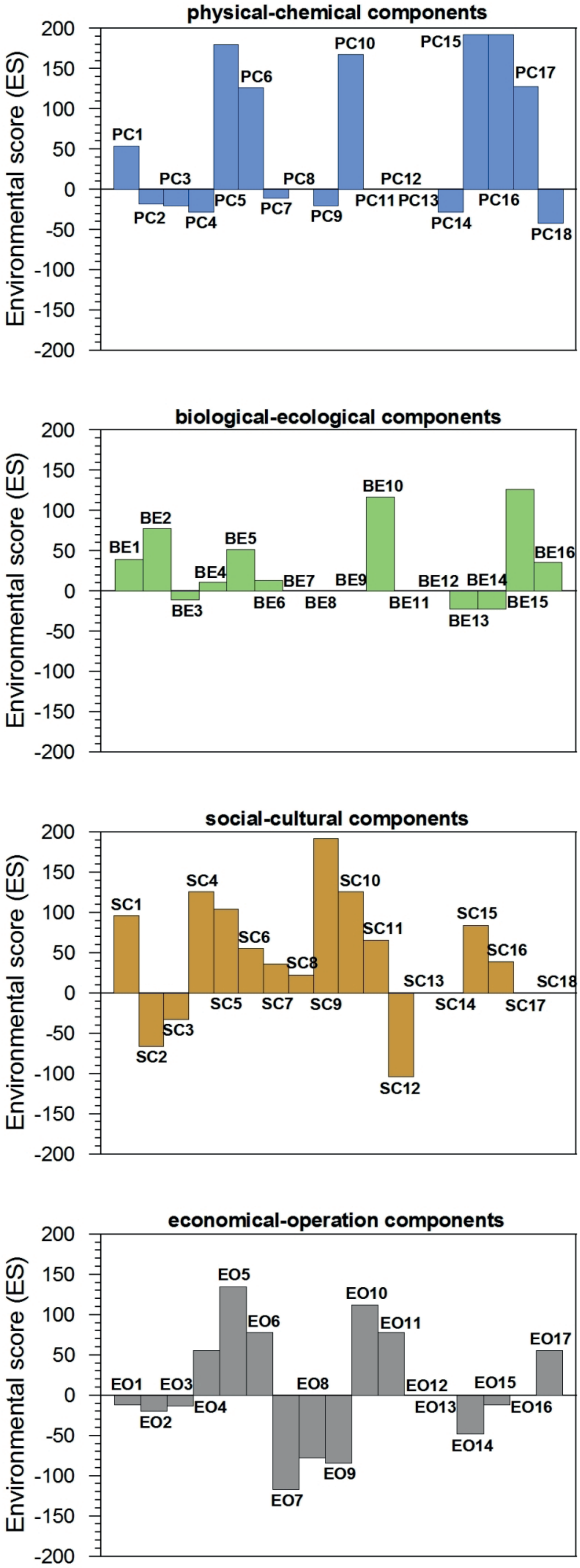


Fig. 5.10 Summary on environmental scores of selected aspects per clustered components

5.5.1.2 The Human needs (H_{NI})

The Human needs represent all actions and interventions of a society towards environment in attempt to provide or sustain a high level of wealth. The higher is the status of actual human performance, the more efficient is the consumption of resources, and, thus, the less environment is limited for the future hence the needs recalled minimize.

Human needs (Eq. 5.6) represent then a pressure on the environment, resultant from insufficient wealth of the publics.

Analogous substitution of relative environmental scores (Tabs. 5.6 to 5.7) after elimination of those of irrelevancy, the actual societal-cultural status accounts $\sum SC = 3{,}432$ and economical status $\sum EO = 2{,}819$, compared to a similar capacity, $EO_{max} = SC_{max} = 5{,}376$. Then, by (Eq. 5.6), the final human needs account $H_{NI} = 0.42$.

5.5.1.3 Environmental sustainability level

Two quantities describe actual performance of the project towards human needs and environment. The E = 0.63 and the $H_{NI} = 0.42$. According to a model of sustainable development (Eq. 5.4), the $E > H_{NI}$ and, thus $S_E = E - H_{NI} = 0.63 - 0.42 = 0.21$.

Following a scheme of (Phillips, 2010a), the recent interaction of the Spa with the environment, and, thus, human needs reflected by existence and impact of the Spa, may be considered as sustainable, even at very weak sustainability level.

When Tabs. 5.4 and 5.5 are grouped with Fig. 5.10, there is only 12 % probability of high environmental score, i.e. ES > 299 that would imply a „major positive impact“ by (Phillips, 2010b). Meanwhile, by the probability distribution constructed from modified ES scores per PC and BE components, there is only 56 % chance of positive impact only. The low score is given by combination of several aspects:

- moderate performance of PC components, as $\sum PC/PC_{max} = 0.66$, given by half of aspects yielding a negative impact onto environment (Tab. 5.4);
- weak performance of BE components, as $\sum BE / BE_{max} = 0.59$, where the most of a performance is held by low areal importance and weak positive impact (Tab. 5.5);
- combination of limited areal importance in social-economic components, where $\sum SC / SC_{max} = 0.64$;
- weak economical performance of the project, hence $\sum EO / EO_{max} = 0.52$. The higher would the $\sum EO$ be, the less H_{NI} will yield better sustainability results.

Disproportions between calculated score and general expectations settle a need to apply for study of a nature of development, providing more detailed hint onto.

5.5.1.4 Ecological sustainability level

A model of ecological sustainability of the site (project) applies when at least three components of the ecological sphere are present (Phillips, 2010a). The environment is a function of physical-chemical and biological-ecological components, thus $E = \sum PC + \sum BE$. Yet both clusters have their own capacity in terms of hydrosphere, atmosphere, lithosphere and biosphere, with their maxima, determining a particular capacity per each (Eq. 5.7).

Reading Tab. 5.4 and Tab. 5.5, the overall size of ecological system is $EB = \sum H + \sum B + \sum A + \sum L = 6{,}090$ at a performance of $E_{EB} = 0.75$. Then, $E_{EB} > E$. After substitution into (Eq. 5.7) and conserving a same level of human needs at $H_{NI} = 0.42$, it is clear that $E_{EB} > H_{NI}$ and thus $S_{EB} = E_{EB} - H_{NI} = 0.33$. Hence $S_{EB} > 0$, the project of the Sliač Spa is ecologically sustainable, however, at a weak level according to a classification by (Phillips, 2010a).

5.5.2 Nature of sustainability

Whether it is an ecological (S_{EB}) or environmental (S_E) sustainability, it is always a function of positive capacity of the environment or component, compared to negative impact of human needs, as a difference between a capacity and actual SC or EO status. It is, especially for a case where $S_{EB} \approx S_E$ is not valid, useful to map partial sustainability performance of key components or aspects.

To help imaging what the environmental performance or consumption of environment is, we plotted polar charts (Fig. 5.11) for each of component group. At each, a radius determines environmental performance (ES/384) for every aspect ranging 0 – 100 %. The red line is a boundary between positive and negative impact regions. For PC and BE components, the more is the circle filled, the higher is the environmental performance of a project to the environment, and, thus, the higher capacity is still available in the environment. At charts for SC and EO, the more is the fill, the less is the human needs count, as the better societal wealth status is already reached, limiting needs in essence. Thus, the deeper below a red line region the SC and EO are, the higher are human needs.

Aspects per each of components are clustered into groups (Tab. 5.2) representing net parts of the natural and human environment. If the $\sum X/X_{max}$ is the performance of PC and BE aspects or wealth status of humans (SC, EO), then a net performance of physical-chemical components of environment (0.66) is the highest amongst, followed by a social-cultural wealth related to existence and activity of the Spa (0.64). The lowest is the economical performance 0.52 (Fig. 5.12), approaching almost negative score (Tab. 5.8).

According to (Eq. 5.8), particular sustainability may be considered per each of component or a group. Similarly to previous, PC component is of highest environmental sustainability level; $S_{E\text{-}PC} = 0.24$ (Tab. 5.8). It means, that there is a most of capacity in the PC components available to vary with some development of the Spa, preserving sustainable behaviour. Indeed, highest scores are calculated for quality and quantity of the resource ($S_{E\text{-}PC} = 0.32$), and ecology ($S_{E\text{-}BEC} = 0.34$). In a contrast, cultural and operational subcomponents yield lowest scores ($S_{E\text{-}X} \leq 0.05$).

A microanalysis on a nature of sustainability executed on ecological subsystems shows that the hydrosphere performs as of highest ecological sustainability $S_{EB\text{-}H} = 0.38$. Biota and lithosphere, both at a level of 0.14 suffer from groundwater disposal and land management.

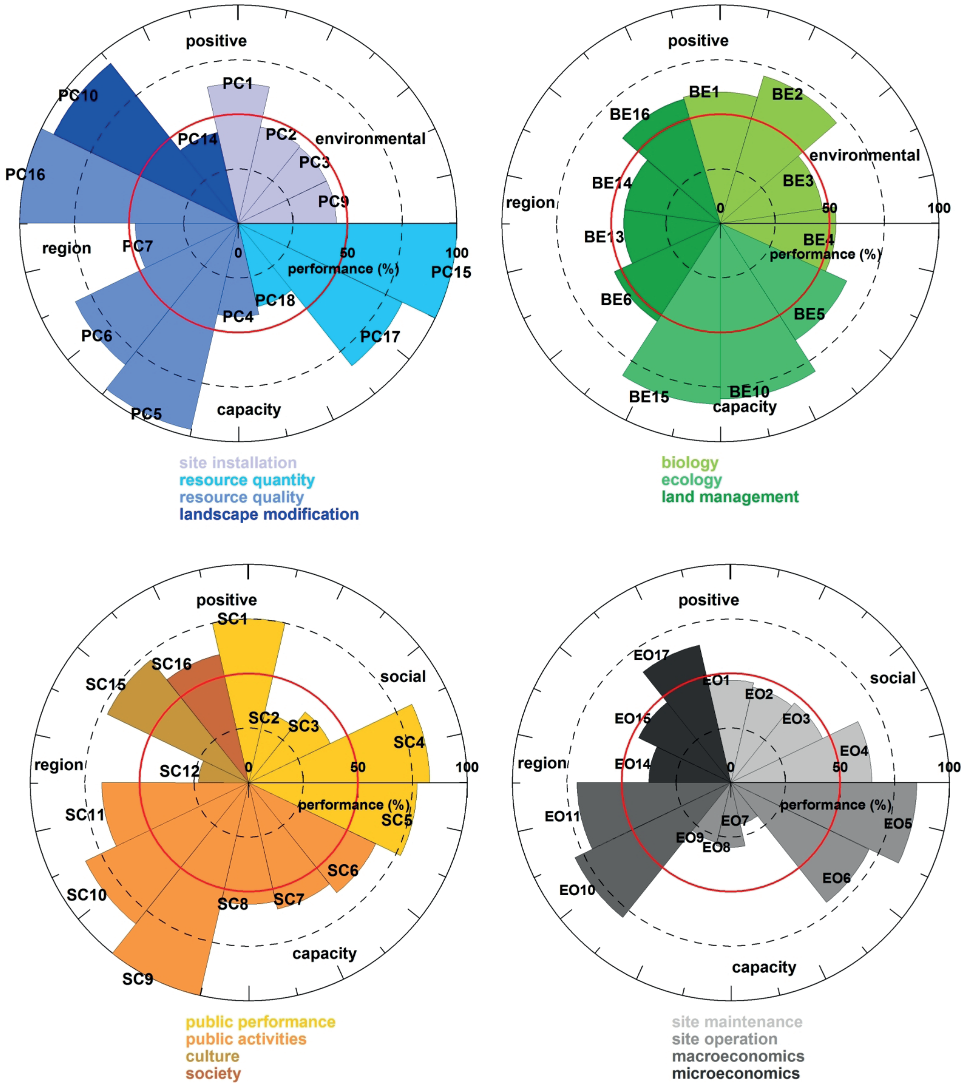


Fig. 5.11 Environmental and social capacity comparison for sustainable development components at the Sliač Spa. See Tabs. 5.4 – 5.7 for acronyms

Tab. 5.8 Environmental and social capacity comparison for sustainable development components at the Sliač Spa

Subcomponent	Code	S_E	S_E level
PC total	PC	0.24	very weak
Site installation	PCA	0.08	very weak
Resource quantity	PCB	0.32	weak
Resource quality	PCC	0.32	weak
Landscape issues	PCD	0.26	weak
BE total	BE	0.18	very weak
Biology	BEA	0.16	very weak
Ecology	BEB	0.34	weak
Land management	BEC	0.08	very weak
SC total	SC	0.22	very weak
Public performance	SCA	0.2	very weak
Public activities	SCB	0.3	weak
Society	SCC	0.05	very weak
Culture	SCD	0.18	very weak
EO total	EO	0.1	very weak
Site maintenance	EOA	0.09	very weak
Site operation	EOB	0.04	very weak
Macroeconomics	EOC	0.33	weak
Microeconomics	EOD	0.08	very weak

5.6 Discussion

The Rapid Impact Assessment Matrix (RIAM) and sustainable development model, either on environmental S_E or ecological scale S_{EB}, are executed at a site of the Sliač Spa.

According to results, the $S_{EB} > S_E$, hence the $S_{EB} = 0.33$ and $S_E = 0.21$, define weak and very weak level of sustainability respectively. A level of sustainability and performance of the Spa (as a complex) with the environment is, in fact, unusual, hence the Spa and its close region come under specific provision on land use, management or public activities; and fall within a protective zone for mineral, medical or thermal springs (groundwater resources).

Reading Tabs. 5.4 to 5.7, there is relatively close score on areal impact of evaluated aspects, with sum of 31 for positive and 22 for negative performance. Negative impact controls an areal and its close vicinity, whilst there is a general positive performance to the regional and national interests of the Spa (Fig. 5.13).

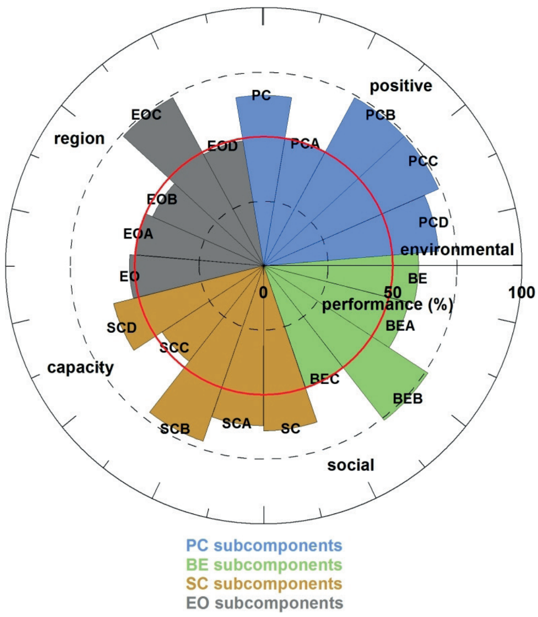


Fig. 5.12 Environmental performance for environmental and human needs subcomponents. See Tab. 5.8 for acronyms

Hence generally sustainable development yielded, the rate of impact is definitely higher for positive aspects (+75) compared to those evaluated as negative (-29). Even importance controls the environmental score in major (Fig. 5.13), there is definitely some impact of performance variations in commutativity and susceptibility of the environment to the impact.

5.6.1 Impact analysis

Two principal components control the overall performance of the Sliač Spa: resource quality/resource quantity and current technical condition of bathhouses. These are, however, not performing separately. To analyze real impact on total performance, we constructed alternative hierarchy chart to identify commutativity of the aspect with other components, keeping original aspects according to Tabs 5.4 – 5.7.

5.6.1.1 Resource sensitivity (negative scenario)

Yield allowances control production of mineral waters. Recently, the amount of groundwater abstraction approaches towards 75 % of the given capacity (see 5.4.1.2). Let us consider a situation the amount of produced groundwater exceeds allowance level over 25 %. Even if the mineral water structure is open, overexploitation may turn springs to cease. If deliverability drops, a project lifetime may not be prolonged too much. Investments into pumping drive then health costs high.

The resource is sensitive to changes in chemistry, controlled by effective filtration velocity, groundwater-rock interaction duration, temperature, etc. Given a fact that the structure is operated in depletive manner (pessimistic assumption) the quality may drop on a recordable scale. At such, chemistry may vary, restraining positive medical effects on a public, affecting acceptability, services and therapeutics on secondary. Hence the resource is disposed into a near channel; increased yields come with destructive effect on aquatic biota.

Depletion scenario, as simulated by changing performance evaluation (Tab. 5.9) would had have devastating impact on PC components at performance ($\sum PC/PC_{max}$ = 0.37) and sustainability decline ($S_{E\text{-}PC}$ = -0.17). Limitation of groundwater use results in multiple drawns in social ($\sum SC/SC_{max}$ = 0.46;

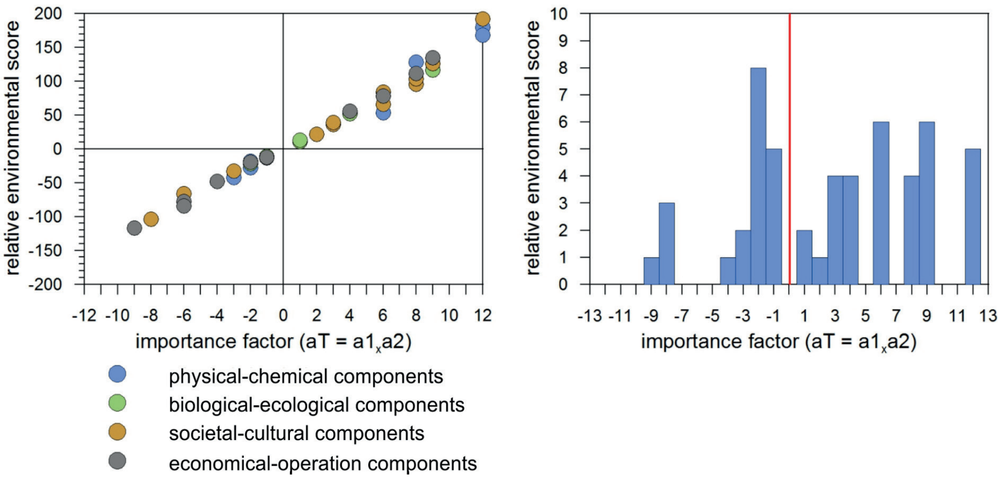


Fig. 5.13 Environmental score (left) and importance factor (right) analysis

Tab. 5.9 Component performance variation setup: resource sensitivity

Code	Description	a1	a2	b1	b2	b3	b4	aT	bT	ES	ES
PC5	groundwater quality	4	-2	4	3	4	4	-8	15	-120	-D
PC4	surface water quality	2	-3	4	2	3	3	-6	12	-72	-C
PC10	springs manifestations	4	-2	4	3	4	4	-8	15	-120	-D
PC15	deliverability	4	-3	4	3	4	4	-12	15	-180	-D
PC16	geochemical stability	4	-2	4	4	4	4	-8	16	-128	-D
PC17	production stability	4	-2	4	3	4	4	-8	15	-120	-D
BE3	aquatic fauna	1	-2	4	2	3	2	-2	11	-22	A
SC1	public services	4	-2	4	2	4	4	-8	14	-112	-D
SC2	public acceptability	3	-2	4	3	3	3	-6	13	-78	-C
SC5	public health	4	1	4	2	4	3	4	13	52	B
SC6	region promotion	4	-2	4	3	4	4	-8	15	-120	-D
SC8	recreation	1	-1	3	3	4	2	-1	12	-12	-A
SC9	therapeutics	4	-2	4	4	4	4	-8	16	-128	-D
SC11	climatic adaptability	3	-1	4	3	4	2	-3	13	-39	-B
EO2	project lifetime	2	-2	4	4	4	2	-4	14	-56	-C
EO10	health costs	4	1	4	2	4	2	4	12	48	B
EO11	employment	3	-2	4	3	4	3	-6	14	-84	-C
EO14	economic self-sufficiency	4	-1	2	3	4	3	-4	12	-48	-B
EO15	local pricing	1	-3	3	3	3	3	-3	12	-36	-B

$S_{E\text{-}SC}$ = -0.08) and EO aspects ($\sum EO/EO_{max}$ = 0.47; $S_{E\text{-}EO}$ = -0.06), as decline in public wealth causes human needs to increase, H_{NI} = 0.47.

At current situation, only biological-ecological components preserve environmental performance ($\sum BE/BE_{max}$ = 0.6) with drop in chemistry of groundwater by depletive reservoir management. This is because the only interaction occurs along groundwater disposal, negative in impact either now. Drop in environmental sustainability of BE components ($S_{E\text{-}PC}$ = 0.06) compared to actual situation responses to an increase in human needs.

Potential combination of decline in environmental performance predicted for almost each of components and sustainable interaction of the Spa with them may result in $S_E < H_{NI}$ thus $S_E < 0$, or $S_E = E – H_{NI}$ = -0.07, describing unsustainable project operation and development.

5.6.1.2 Publics and societal sensitivity (positive scenario)

In above, we set a notion on high H_{NI} (5.5.1-5.5.2). A reason is (Tabs. 5.4 to 5.7) in, say, alarming condition of 7 abandoned bathhouses (3 of which are declared cultural heritage) posing a substantial risk on soil quality, limiting public acceptability or services and adaptability, increasing energy losses and negatively affecting built-up area efficiency. In study on sensitivity of such a project, let us consider a case where investments are put to reconstruct resort objects. Besides positive effects on social needs and regional promotion, creation of tourist opportunities or benefits on preservation of cultural heritage, the action may reduce energy losses, and drive up the efficiency of occupied area usage. However, increasing the number of visitors and active objects comes with increase in noise and light pollution, temporary traffic and transport, and will, as expected, increase not only a property value, but local pricings as well as a consequence of reaching a payback soon (Tab. 5.10).

Managing artificial objects has a straight (positive) impact on public and social wealth. Consequently, initial human needs H_{NI} = 0.42 decrease to 0.36. It is a paradox that reconstruction of buildings plays a negative effect on PC components of the environment, somewhat compensated by reducing negative impact on soil quality and landscape issues. BE performance remains, perhaps, at an initial level, however, sustainability in use of BE part of environment increases $S_{E\text{-}BE}$ = 0.24 as H_{NI} declines. Preservation of PC and increase in $S_{E\text{-}BE}$ may then be understood as a consumption of environment necessary to satisfy wealth creation. Meanwhile, reconstruction plays positive impact not only on reduction of human needs, but increases a social and economic performance of the Spa in general (Tab. 5.10).

Combination of all, performance and H_{NI} reduction effects of increase in condition of residential objects results in increase in environmental, ES = 0.28, and ecological sustainability E_{EB} = 0.44. Thus, after reconstruction, the sustainability level shall increase to weak, creating more confidence into the development in case of uncertainties accounting.

5.6.2 Limitations

Together 69 aspects related to current situation and interaction between the Sliač Spa, environment and public were identified and evaluated subjectively. Still, the environment is a dynamic system. It is a must then to take obtained scores as an actual fingerprint, variable at various intensities, as mostly SC and EO components are the most instable. Even under a best endeavour to create an evaluation background as objective as possible, construction of a finite matrix criteria for spas shall become mandatory in

Tab. 5.10 Component performance variation setup: publics and societal sensitivity

Code	Description	a1	a2	b1	b2	b3	b4	aT	bT	ES	ES
PC3	noise	2	-2	4	4	3	2	-4	13	-52	-B
PC7	soil quality	1	1	3	2	3	2	1	10	10	A
PC9	light pollution	2	-1	4	4	3	2	-2	13	-26	-A
PC14	landscape modification	2	1	4	2	2	4	2	12	24	A
SC1	public services	4	2	4	2	4	3	8	13	104	D
SC2	public acceptability	3	1	3	2	2	3	3	10	30	A
SC3	public adaptability	3	2	3	2	2	3	6	10	60	C
SC6	region promotion	4	2	4	2	4	4	8	14	112	D
SC12	cultural heritage	4	2	4	2	4	3	8	13	104	D
EO2	project lifetime	2	1	3	2	3	2	2	10	20	A
EO3	energy losses	1	2	3	3	4	4	2	14	28	A
EO5	traffic and transport	3	-1	2	2	4	4	-3	12	-36	-B
EO6	infrastructure buildup	2	2	3	3	3	3	4	12	48	B
EO7	tech.condition-buildings	3	2	3	3	4	3	6	13	78	C
EO8	tech.condition-equipment	3	1	3	3	4	3	3	13	39	A
EO14	economic self-sufficiency	4	1	3	2	4	3	4	12	48	B
EO15	local pricing	1	-2	4	3	4	3	-2	14	-28	-A
EO17	property value impact	2	-2	4	3	4	3	-4	14	-56	-B

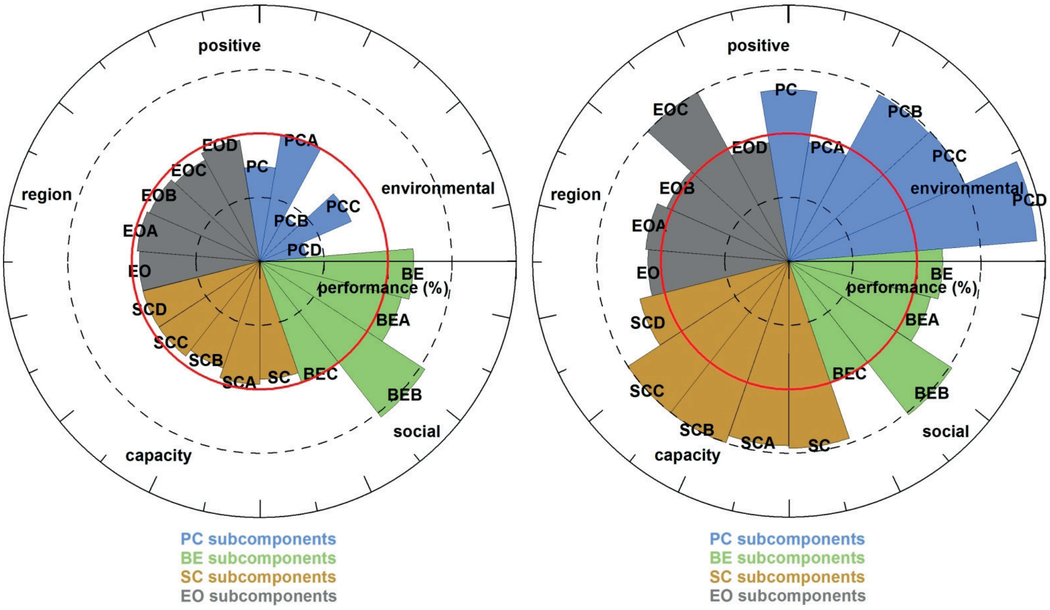


Fig. 5.14 Sensitivity analysis for positive and negative scenarios

Fig. 5.15 Kúpeľný prameň spring – production installation.

such a case, providing comparative background between case studies on not only a national but international scale.

5.7 Conclusions

The Directive of the Ministry of Health of the Slovak Republic No. 89/2000 Coll. On Healing springs and natural resources of mineral table waters declared mineral waters of the Sliač Spa as healing springs. Later, an Action No. 10389-44/2009 by Inspectorate of Spas and Springs set allowances on a use of the Kúpeľný prameň spring to 5 l . s^{-1}. Delineation of protective zones of the I[st] and II[nd] order (Bondarenková et al., 1986) for mineral waters was modified to reflect a current need for protection of the environment (Masiar, 2004). Allowances on production of the Kúpeľný prameň spring are limited to 4.85 l . s^{-1}. Total allowances for mineral groundwater at the Sliač area reach 5.011 l . s^{-1} (Dzúrik, 2012).

The Rapid Impact Assessment Matrix (Pastakia, 1998; Ijäs et al., 2008) and sustainable development model (Phillips, 2010a) have been constructed for the Sliač Spa. At selection phase of the procedure, 69 aspects of environmental and social interaction of the project with a nature and society were identified, playing a positive to negative impact on environment. The environment E (Eq. 5.5) represents a capacity of a nature to provide resources for development (PC + BE), with a critical limit of E = 0.5, meaning that "consumption" of resources in a present conserves the same amount for a future.

At current situation, the E = 0.65. For social-economic aspects (SC, EO), the higher is the wealth status, the less are the human needs (Eq. 5.6), actually yielding a score of 0.42. Then, an environmental sustainability equals $S_E = E - H_{NI} = 0.65\text{-}0.42 = 0.23$, defining actually a project sustainable at a very weak level. To compare, ecological sustainability S_{EB} (Eq. 5.7) scores $S_{EB} = 0.33$. A fact that $S_{EB} > S_E$ means that biotic components of the nature are less sensitive to the potential nature "consumption" (project activity) than the rest in the environment, however the PC components record a highest capacity amongst. Current lows in sustainable development score are, most probably, a consequence of frequently weak importance of positive impacts and variable timeline performance to the environment in combination with high level of human needs given by an objection to reconstruct residential objects, synergistically affecting other social, economic and operation aspects of the Spa.

Executed sensitivity analysis for pessimistic scenario (groundwater depletion) and optimistic scenario (residential objects reconstruction) gives a strong evidence on dependency of the project rather on environment than a rate of human wealth. While groundwater depletion affects BE, SC and EO components, the reconstruction plays a minor role on PC, modifying SC and EO in major only. Indeed, depletion of groundwater (use of resources at 25 % above actual allowances (thus above ≈ 7.5 l . s^{-1}) may result, after some time, in devastation of healing character and initial chemistry of groundwater on which SC and EO components are clearly dependent. Drop in environment capacity (performance) to E = 0.53 with increasing human needs (consequent to reduction of public services and local economics) to H_{NI} = 0.47 gives E < H_{NI}, so that E_S = -0.07, contravening a sustainable development. This is a drop by a magnitude of almost 1.5.

By a contrast, reconstruction of residential objects in spas may increase a general wealth, represented by decline in human needs to H_{NI} = 0.36. Meanwhile, there is a need to account on, at least temporary, negative impact on environment from increased traffic, light pollution and noise (not only during a reconstruction works but from increased number of residents and online residential objects), somewhat balanced by reduction of potential degradation of soil quality and negative land use efficiency. Thus, the performance of the environment may approach E = 0.64. Consequently, E > H_{NI} , yielding S_E = 0.28 (increase by 33 %) and S_{EB} = 0.43 (30 % increase).

Interaction of the Spa with environment is, at least to some extension, limited along specific provisions (restricted land use, public activities, resource mining, etc.) and delineation of protective zones (yield allowances, groundwater chemistry preservation etc.). Conflicts of interests and reduction of third-parties' access to groundwater resources in the area is definitely balanced by positive impact of the Spa on environment and society.

There is a growing pressure on implementation of principles of sustainable development into all spheres of human interaction with the environment. By definition of the sustainable development (e.g. Chichilniski, 1997; Schellnhuber, 1998; Nel-Cooper, 2009; Phillips, 2010a), defining sustainability in use of natural resources cannot avoid analysis of human actions and impacts on environment. An example for the Sliač Spa shows that limitation of sustainability studies on resource deliverability (in this case a groundwater production), which is a well-established praxis, is simply not enough, and there must be a complex picture, accounting on all aspects of repeatedly accented human – nature interaction.

With no doubt left, existence of the Sliač Spa contributes to sustainability and sustainable development on, at least local to regional scale. Restrictions in resource accessibility are evidently balanced by positive impact on a nature and wealth. Good environmental and ecological performance ensures that the risk to the nature is locally low. Continuous studies on groundwater production allowances and periodical groundwater monitoring shall, thus, be mandatory to predict unexpected changes in status-quo, forming a base for societal wealth conservation or increase. At such conditions, strengthening of the sustainable performance is a case of investments to preservation of local residential objects and cultural heritages, and shall be an objective for the close future.

5.8 References

Al Malek, S.A, & Mohamed, A.M.O., 2005: Environmental impact assessment of off shore oil spill on desalination plant. *Desalination*, 185, p. 9 – 30.

Arevalo, A.S., 2003: Rapid environmental assessment tool for extended Berlin geothermal field project. In: *Proceedings International Geothermal Conference*, Reykjavik, Iceland, p. 1 – 7.

Ármansson, H., 2007: Application of geochemical methods in geothermal exploration. In: *Proceedings UNU-GTP Short Course on Surface Exploration for Geothermal Resources*, Lake Naivasha, Kenya, p. 1 – 9.

Axelsson, G., Gudmundsson, A., Steingrímsson, B., Palmason, G., Armannsson, H., Tulinius, H., Flovenz, O.G., Bjornsson, S., Stéfansson, V., 2001: Sustainable production of geothermal energy: suggested definition. *International Geothermal Association News Quaterly*, 43, 1, p. 1 – 2.

Bondarenková, Z., Dzúrik, J., Klaučo, S., Pospiechová, O., Motlíková, H., Kadnár, R., 1986: *Sliač-Kováčová, vyhľadávací HGP. Cieľ: riešenie ochranného pásma kúpeľov Sliač a ochranného pásma kúpeľov Kováčová*. Manuscript – Final Report, Archive, Geofond Bratislava.

Böhm, V., Škvarka, L., Melioris, L., Hyánková, K., Fendeková, M., Ženišová, Z., Malík, P., 1993: Hydrogeologická mapa Zvolenskej kotliny v mierke 1 : 50 000. Manuscript – technical report, Archive, Geofond, Bratislava, 109 p.

Chichilniski, G., 1997: What is sustainable development? *Land Economics*, 73 (4), p. 467 – 491.

Dalal-Clayton, B., & Sadler, B., 1996: Strategic environmental assessment: a rapidly evolving approach. *Environmental Planning Issues*, 19, p. 1 – 13.

Dzúrik, J., 2012: *Sliač- výpočet využiteľných množstiev prírodných liečivých zdrojov*. Manuscript – Final Report, Archive, Geofond Bratislava.

El-Naqa, A., 2005: Environmental impact assessment using rapid impact assessment matrix (RIAM) for Russeifa landfill, Jordan. *Environmental Geology*, 47, p. 632 – 639.

Franko, O., 1998: História hydrogeológie minerálnych vôd na Sliači. *Podzemná voda*, IV, 2, p. 12 – 22.

Franko, O., Gazda, S., Michalíček, M., 1975: Tvorba a klasifikácia minerálnych vôd Západných Karpát. Geological Institute of Dionýz Štúr, Bratislava.

Gálisová, M., Oslík, J., Drahoš, M., 2012: Dosiahnuté výsledky sanačných prác na lokalite znečistenej sovietskou armádou, Sliač-Vlkanová. *Podzemná voda*, XVIII, 2, p. 137 – 147.

Gibbs, R.J., 1970: Mechanisms controlling world water chemistry. *Science*, 170, 1, p. 1088 – 1090.

Giggenbach, W.F. 1991: Chemical techniques in geothermal exploration. In D'Amore, F. (Ed): *Applications of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, p. 119 – 142.

González, Z., González, D., Kretzchmar, T., 2015: First approach of Environmental Impact Assessment of Cerro Prieto geothermal power plant, BC, Mexico. In: *Proceedings World Geothermal Congress 2015*, Melbourne, Australia, p. 1 – 9.

Hajkowicz, S.A., 2007: A comparison of multiple criteria analysis and unaided approaches to environmental decision making. *Environmental Science Policy*, 10, p. 177 – 84.

Ijäs, A., Kuitunen, M.T., Jalava, K., 2008: Developing the RIAM method (rapid impact assessment matrix) in the context of impact significance assessment. *Environmental Impact Assessment Review*, 30, p. 82 – 89.

Kankam, Y.B., Asare, E.B., Gyau-Boakye, P., Nishigaki, M., 2005: Rapid Impact Assessment Matrix- an analytical tool in the prioritization of water resource management problems in Ghana. *Journal of the Faculty of Environmental Science and Technology*, 10, 1, p. 75 – 81.

Konečný, V., Lexa, J., Miháliková, A., Halouzka, R., Miko, O., Dovina, V., Šucha, P., Planderová, E., 1983: Geologická mapa a Vysvetlivky ku geologickej mape 1:25 000, list 36-323 Zvolen. Manuscript – Technical report, Archive, Geofond, Bratislava.

Kuitunen, M., Jalava, K., Hirvonen, K., 2008: Testing the usability of the rapid impact assessment matrix (RIAM) method for comparison of EIA and SEA results. *Environment Impact Assessment Review*, 28, p. 312 – 320.

Masiar, R., 2004: *Revízia ochranných pásiem prírodných liečivých zdrojov na Sliači a v Kováčovej*. Manuscript – Final Report, Archive, Geofond Bratislava.

Mihaiescu, R., Pop, A.I., Muntean, O.L., Mihaiescu, T., Malos, C., Oprea, M.G., Dezsi, S., Ozunu, A., Arghius, V., Baciu, N., Rosian, G., Macicasan, V., 2015: The use of Rapid Impact Assessment Matrix (RIAM) in assessing environmental impacts in protected areas. Case Study: Mountain Glacial Lakes in Romania. *ProEnvironment*, 8, p. 629 – 636.

Nel, W.P., & Cooper, C.J., 2009: Implications of fossil fuel constraints on economic growth and global warming. *Energy Policy*, 37, 1, p. 166 – 180.

Pastakia, C.M.R., 1998: The rapid impact assessment matrix (RIAM) – A new tool for environmental impact assessment. In: Jensen, K. (Ed.): *Environmental Impact Assessment Using the Rapid Impact Assessment Matrix (RIAM)*, Olsen & Olsen, Fredensborg, Denmark, 200 p.

Pastakia, C.M.S., & Madsen, K.N., 1995: A Rapid Assessment Matrix for use in water related projects. In: *Proceedings the Stockholm Water Conference*, Stockholm, Sweden, p. 1 – 10.

Pastakia, C.M.R., & Jensen, A., 1998: The Rapid Impact Assessment Matrix (RIAM) for EIA. *Environmental Impact Assessment Reviews*, 18, p. 461 – 482.

Phillips, J., 2010a: The advancement of a mathematical model of sustainable development. *Sustainable Science*, 5, p. 127 – 142.

Phillips, J., 2010b: Evaluating the level and nature of sustainable development for a geothermal power plant. *Renewable and Sustainable Energy Reviews*, 14, p. 2414 – 2425.

Rybach, L., 2007: Geothermal sustainability. *GeoHeat Centre Bulletin*, 28, 3, p. 2 – 7.

Ryšavá, Z., Fendeková, M., Pekárová, P., 2008: Režim hladiny podzemnej vody v časti Zvolenskej kotliny medzi Banskou Bystricou a Zvolenom. *Podzemná voda*, XIV, 2, p. 161 – 173.

Schellnhuber, H.J., 1998: Part 1: earth system analysis—the concept. In: Schellnhuber H.J. & Wenzel, V. (Eds): *Earth system analysis: integrating science for sustainable development*. Springer, Berlin, p. 3 – 195.

Schellnhuber, H., J., 2001: Earth system analysis and management. In: Ehlers, E. & Kraft T (Eds.) *Understanding the Earth system: compartments, processes and interactions*. Springer, Berlin, p. 17 – 5.

Shortall, R., 2010: *A sustainability assessment protocol for geothermal utilization*. Manuscript, Master's Thesis, University of Iceland, Reykjavik, 310 p.

Tester, J.,W., Anderson, B.,J., Batchelor, A.,S., Blackwell, D.,D., DiPippo, R., Drake, E.,M.., Garnish, J., Livesay, B., Moore, M.,C., Nichols, K., Petty, S., Toksöz, M.,N., Veatch, R.,W., 2006: *The future of geothermal energy. Impact of Enhanced Geothermal Systems (EGS) on the United States in the 21st Century*. Idaho National Laboratory, Renewable energy and power department, Idaho Falls, IH, 372 p.

Thompsen, M.A., 1990: Determining impact significance in EIA: a review of 24 methodologies. *Journal of Environmental Management*, 30, p. 235 – 250.

Wei, L., Yuanbo, X., Fanghua, H., 2014: Applying an improved rapid impact assessment matrix method to strategic environmental assessment of urban planning in China. *Environmental Impact Assessment Review*, 46, p. 13 – 24.

Williams, C.F., 2010: Thermal energy recovery from enhanced geothermal systems- evaluating the potential from deep, high-temperature resources. In: *Proceedings 35th Workshop on Geothermal Reservoir Engineering*, Stanford University, CA, p. 1 – 7.

Wood, G.T., Glasson, J., Becker, J., 2006: EIA scoping in England and Wales: practitioner approaches, perspectives and constraints. *Environmental Impact Assessment Reviews*, 26, p. 221 – 241.

Yousefi, H., Ehara, S., Yousefi, A., Seiedi, F., 2009: Environmental impact assessment of Salaban geothermal power plant, NW Iran. In: *Proceedings 34th Workshop on Geothermal Reservoir Engineering*, Stanford University, CA, p. 1 – 9.

Slovak Geol. Mag., 16, 2 (2016), 91 – 104

New Source of the Geothermal Water in Handlová

Anton Remšík[1], Radovan Černák[1], Jozef Kordík[2], Juraj Michalko[1]

State Geological Institute of Dionýz Štúr, [1]Dept. of Hydrogeology and Geothermal Energy;
[2] Dept. of Environmental Geochemistry,
Mlynská dolina 1, 817 04 Bratislava, Slovakia; radovan.cernak@geology.sk

Abstract: The outcomes of the hydrogeological and hydrogeochemical research of groundwater in a new hydrogeological well RH-1 in Handlová town are presented in the paper. Drilling and research connected to this well were performed within the project „Basic hydrogeological research of Handlovská kotlina Basin" project no. 15 07 that was solved by the State Geological Institute of Dionýz Štúr in years 2007 – 2012. Some results were obtained from the project "Basic hydrogeological and hydrogeochemical maps of Žiar Mts.".

The hydrogeological well RH-1 in town of Handlová (1,201.3 m deep) proved the geothermal water with temperature 37.5 °C at the surface and usable amount of geothermal water 15.0 l . s^{-1}. Inflows of geothermal water into the well (based on the results of geophysical measurements) were in the horizon from 862.0 to 1,201.3 meters. The geothermal water is classified as calcium-magnesium-sulphate-bicarbonate chemical type with a Total Dissolved Solids (TDS) 1,066 mg . l^{-1} with CO_2, H_2S content and is not susceptible to scaling. Thermal water tapped by the well RH-1 is very convenient for bathing and wellness complex. The geothermal water in Handlová town is a renewable resource which is in contrast to lignite mining in the area and opens the possibilities for recreation and sustainable development of the area.

Key words: Handlová, Hornonitrianska kotlina Basin, geothermal energy, resources, well RH-1

6.1 Introduction

State Geological Institute of Dionýz Štúr (SGIDŠ) in Bratislava carried out hydrogeological research in the Handlovská kotlina Basin in years 2007 – 2012. The geological project no. 15 07 "Basic hydrogeological research of the Handlovská kotlina Basin" (Černák et al., 2012) was financed from the budget of the Ministry of Environment SR and was carried out in accordance with the approved concept of geological research and exploration in Slovakia.

The region of the Handlovská kotlina Basin belongs to the deficit areas of Slovakia where systematic hydrogeological survey with identification and acquisition (recovery) of new groundwater resources has not been carried out so far. The results of this project formed the background for planning the sustainable use of groundwater (water supply and other uses), its protection and assessment of environmental impacts in the region.

The aim of the hydrogeological research was focused on the identification of the hydrogeological conditions in the Handlovská kotlina Basin, including the assessment of the relationship between the groundwater with shallow circulation and mineral (geothermal) water. Part of the project was dedicated to calculation of available groundwater and geothermal water amounts in hydrogeologic region PG 063 along with description of geological supporting information for their protection.

Hydrogeological research mainly consisted of hydrogeological mapping, discharge measurements, drilling of hydrogeological wells (shallow and deep), measuring the flow regime and hydrogeological objects and complex hydrogeological assessment of the area with the calculation of the quantity of groundwater.

The paper is focused on new findings that were obtained from the hydrogeological well RH-1 (Remšík and Černák, 2011) in the Handlová town drilled within this project. The aim of the hydrogeological well RH-1 was to verify the amount of groundwater and its chemical properties, description of geological development in the basin and relationship between shallow and geothermal water in the area. The hydrogeological well RH-1 was 1,201.3 meters deep, and so far is the first deep well in the Handlovská kotlina Basin that brought new geological, hydrogeological and hydrogeochemical results.

Earlier works concerning the geological and hydrogeological research consisted of regional and local studies. Geological structure of the area was assessed in regional geological map of the Vtáčnik Mts. and Hornonitrianska kotlina Basin region at scale 1 : 50,000 (Šimon et al., 1997a, b); region Kremnické vrchy Mts. at scale 1: 50,000 (Lexa et al., 1998a, b). The three-dimensional geological model of the Hornonitrianska kotlina Basin was published by Kotulová et al. (2010).

Hydrogeological conditions are outlined on hydrogeological maps published by Kullman et al., (1978, scale 1 : 200,000, sheet 36 – Banská Bystrica), Franko et al. (1993, scale 1 : 50,000, Hydrogeological map of Upper Nitra Basin), Černák et al. (2004, scale 1 : 50,000, Basic hydrogeological and hydrogeochemical maps of the Žiar Mts.). The hydrogeological conditions were described by Marcin (1997 in Šimon et al., 1997b) within the text explanatory notes to geological map of the Vtáčnik Mts. and Hornonitrianska kotlina Basin and 1 : 50,000.

Hydrogeological research including drilling works is based on findings from wells FGHn-1 (depth of 470 m, Fendek et al., 2004). The evaluated area is marginally covered on the western rim of the Handlovská kotlina Basin (hydrogeological survey of the Prievidzská kotlina Basin, borehole HNP-6, depth of 20 m, Bubeník et al., 1976), on the eastern part with research performed by Auxt et al. (1997, "Neovolcanites of the Kremnické vrchy Mts." with well KV-24 of depth 137 m) and hydrogeological research in the northern adjacent Žiar Mts. (Polák, 1997).

Separate hydrogeochemical survey of regional character in this area was not realized, but part of the territory was covered by hydrogeochemical research within works of Auxt et al. (1997), Kováčik et al. (1993), Bátory et al.

(1973), Franko et al. (1993), Bubeník et al. (1976) and Dovina et al. (1985). Overview research performed till 1974 is described in explanatory notes to Basic hydrogeological and hydrogeochemical maps 1: 200,000 (Kullman et al., 1975; Kullman et al. , 1978). An important contribution to the hydrogeochemistry of the area from a regional perspective is given in Geochemical Atlas of the Slovak Republic – Part Groundwater (Rapant et al., 1996). Geological environmental factors and their impact on quality of life for the pilot area of Hornonitrianska kotlina Basin is described in final report of Bodiš et al. (2006).

6.2 Natural conditions

Geomorphological set up

Handlovská kotlina Basin represents the southeast part of Upper Nitra Basin. It has a semi-open nature of the basin (Fig. 6.1).

Altitude ranges from 300 m a.s.l. in Prievidza, to about 500 m a.s.l. in Handlová and the highest point in the area is the hill Grič (971 m) to the southwest of the Handlová town.

The basin is on the N and NE bordered by the Žiar Mts., on the E and SE by the Kremnické vrchy Mts. and on the S and SW by the Vtáčnik Mts. Length of the basin is approximately 14 km, the average width is about 5 km.

Hydrogeological conditions of the Handlovská kotlina Basin and adjacent area

According to the geological structure of the area hydrogeological units with different hydro-geological characteristics, regimes and groundwater chemistry were defined:

- hydrogeological unit crystalline rocks of the Žiar Mts. with fissure permeability;
- hydrogeological unit of Palaeozoic and Mesozoic rocks with fissure and karst-fissure permeability;
- hydrogeological unit of Inner-Carpathian Palaeogene rocks with fissure permeability; hydrogeological unit of Neogene sediments of the Handlovská kotlina Basin with fissure and intergranular permeability;
- hydrogeological unit of Neovolcanic rocks and sediments with fissure and intergranular permeability;
- hydrogeological unit of Quaternary sediments with intergranular permeability.

Generally in granitoids the circulation of groundwater is shallow and is associated with a near-surface zone of disintegration and faulted zones of the massif. Groundwater is of low mineralization, typically silicate or- silicate sulphide type (Ca-HCO_3, Ca-HCO_3-SO_4 and Ca-SO_4) with TDS 90 – 160 mg . l^{-1} (Černák et al., 2004).

On the crystalline massive Mesozoic envelope is developed in three tectonic units (nappes).

Tatricum tectonic unit (Ráztočno Succession) is characterized by strong tectonic reduction. Middle Triassic carbonates and Jurassic limestones, clays, shales, sandstones and conglomerates of the Tatricum are overlain by carbonates of Fatricum tectonic unit. On the south side of the Žiar Mts. Hronicum tectonic unit (Sklené Mesozoic) is developed. Palaeogene clay sediments create barrier for groundwater circulation on the contact with Mesozoic sequences. Based on a detailed hydrogeological mapping of springs and streams it is clear that there is significant deficit in groundwater discharge (at surface) in relation to the infiltration of precipitation (Černák et al., 2012). The highest values of transmissivity are typically assigned to limestones and dolomites which are the main and most important aquifers in the area. The calculated coefficient of transmissivity in the area T = 2.48 . 10^{-5} m^2 . s^1 was obtained from well KV-21 (Auxt, et al., 1997). Groundwater of Mesozoic carbonate is of Ca-Mg-HCO_3 to Ca-HCO_3 chemical type with TDS typically in range 250 – 450 mg . l^{-1}.

On the surface Inner-Carpathian Palaeogene rocks are present in large extent. They are represented

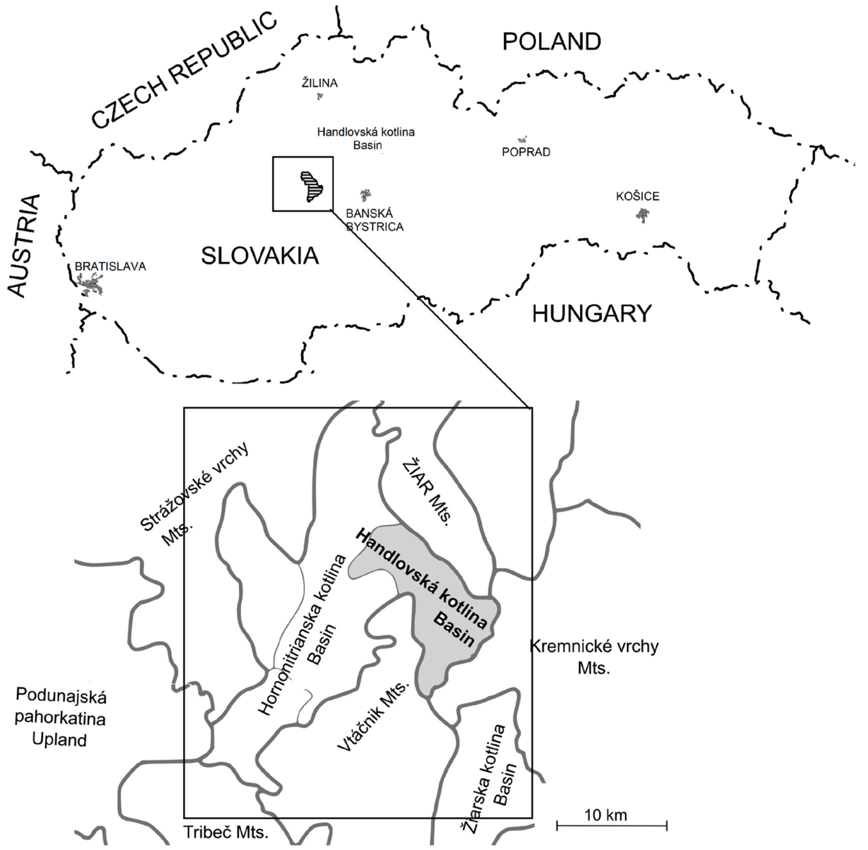


Fig. 6.1 Geomorphological set up of the Handlovská kotlina Basin (Mazúr & Lukniš, 1980)

by Borové Formation (breccia, conglomerates, limestones), marginal (Terchová) formation (clays, positions of conglomerates), Huty and Zuberec formations (clays, flysch) and sandstone of Biely potok Formation (mainly sandstones of Chrenovec Mb.). Groundwater is bound to breccias, conglomerates and sandstones (mainly Borové Fm. and Biely potok Fm.) with fissure permeability. TDS of groundwater with origin in the Borové Fm. in the Handlovská kotlina Basin was in range 176 – 422 mg . l^{-1} with Ca-Mg-HCO_3 chemical type. Palaeogene rocks are in superposition to Palaeozoic-Mesozoic rocks.

Hydrogeological unit of Neogene sediments in the Handlovská kotlina Basin include schliers, clays, tuffites, coal deposits, conglomerates, gravels and sands. Groundwater is bound (linked) to conglomerates, gravels, sands (Kľačany, Lehota and Lelovce Fms.) with fissure and intergranular aquifers. Thus, major hydrogeological aquifers are located mainly in the upper part of the Neogene basin fill. Formation of schliers, clays and clay-tuffite layers (Čausa, Handlová, Nováky, Koš Fms.) represent aquicludes and aquitards. Groundwater from Neogene sediments represent Ca-Mg (K)-(Na)-HCO_3 chemical type with TDS 487 mg . l^{-1} or 658 mg . l^{-1} (based on 2 samples in the Handlovská kotlina Basin).

Hydrogeological unit of Neovolcanic rocks consists of various volcanic rock formations (different types of andesite, volcanic clastic rocks, rhyolites). Fissure permeability prevails especially in andesite, volcanic breccias, conglomerates, volcanic sandstones, siltstones and tuffaceous claystone. Intergranular permeability is prevalent in tuffs and some volcanic breccias. Andesite lava sheets have a drainage function to overlaying volcaniclastic strata with springs yielding up to 10 l . s^{-1}. Groundwater with origin in Neovolcanic effusive rocks is of relatively low TDS of 190 mg . l^{-1} (median 174 mg . l^{-1}). Groundwater from Neovolcanic volcaniclastic has a higher TDS of 335 mg . l^{-1} (median 271 mg . l^{-1}) mainly due to the presence of carbonate components in groundwater. Groundwater is characterized by volcaniclastic Ca (Mg)-HCO_3 type of chemical composition.

Hydrogeological unit of Quaternary sediments includes fluvial, proluvial and deluvial sediments. Fluvial sediments represent the bottom sandy gravel accumulation, gravel and clay in flood plains. The alluvium of the Handlovka River consists of clayey gravel characterized by value of transmissivity coefficient 2.2 . 10^{-4} m^2 . s^{-1}. Fluvial sediments are directly fed from river and aquifer is thus dependent on the river regime. Groundwater in deluvial sediments is dependent on precipitation regime. Groundwater with circulation in fluvial sediments of flood plains have variable chemical composition with Ca (Na)-(Mg)-HCO_3 chemical type and TDS around 500 to 900 mg . l^{-1}.

Geothermal water in the Handlovská kotlina Basin has deeper circulation that is bound to hydrogeothermal structures of pre-Tertiary basement that is located between the Tribeč and Žiar mountains. This morphostructure defined by Fusán et al. (1987) as "Handlovský chrbát" Ridge is built by Mesozoic and Palaeozoic rocks of Fatricum and Hronicum tectonic units. Aquifers of geothermal water are made of mainly Triassic limestones and dolomites. Fig. 6.2 shows geological setup of the Handlovská kotlina Basin.

Within the project "Basic hydrogeological research of the Handlovská kotlina Basin" basic hydrogeological map in scale 1 : 50 000 was compiled showing the lithological content and its hydraulic parameters (as defined in Directive of MoE SR as of 26.10.2004 No. 8/2004-7 on compilation of basic hydrogeological maps at scale of 1 : 50 000).

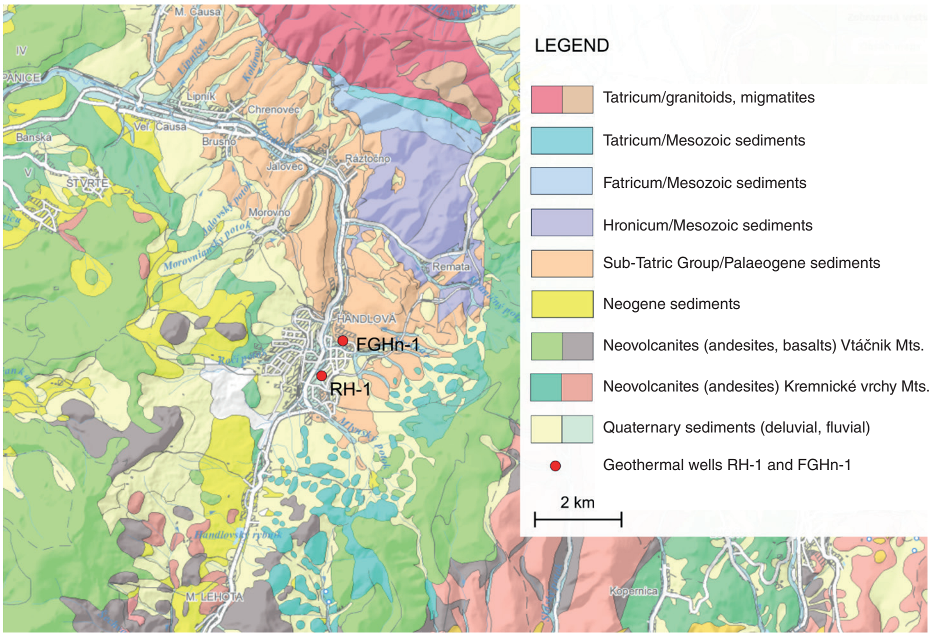


Fig. 6.2 Geological setup of the Handlovská kotlina Basin (http://mapserver.geology.sk)

Mineral and geothermal water in the Handlovská kotlina Basin

Generally, geothermal waters in the Handlovská kotlina are linked to the tectonic units in pre-Tertiary basement, namely Fatricum (Mesozoic limestones) and Hronicum tectonic unit (Triassic carbonates).

There were two reported sources of low temperature geothermal water in the Handlovská kotlina Basin (Krahulec et al., 1978) before the drilling of the well RH-1. They were reported as inflows into the lignite mine in Handlová at a depth of 470 m. The inflow reg. No. PR-12 (l.c.) with yield 10.8 l . s^{-1} and water temperature 32 °C documented in year 1942 was of Ca-Mg-SO_4-HCO_3 chemical type with TDS 2.15 g . l^{-1}. The second inflow (reg. No. PR-11, l.c.) was documented in the year 1945 with yield 2 l . s^{-1}. The temperature and the chemical composition of the water were similar to the previous case though less mineralized (2.05 g . l^{-1}). It was probably the same geothermal water that was reported by Fendek et al. (2004) based on oral information from Ferianc in 2001 (inflow of geothermal water with temperature of 32.5 °C; yield of 5.5 l . s^{-1}; Ca-Mg-SO_4 chemical type and TDS to 2.01 g . l^{-1}). Geothermal water bound to strongly tectonically affected dolomites of Hronicum tectonic unit has been identified on the basis of the Palaeogene rocks in geothermal well FGHn-1 (in Handlová town), 470 m deep (Fendek et al. 2004). Water from well had 19.4 ° C and pumped rate was 2.17 l . s^{-1} with the drawdown of 110.15 meters from the well-head. Chemical type of water was Na-Mg-HCO_3 with TDS 0.39 g . l^{-1}.

Mine water in the Handlovská kotlina Basin

In SW part of investigated area Handlová lignite mine is still in operation. The coal deposit is divided by fault of NNE-SSW direction into eastern high block with mining field Handlová and western block with mining field Cigeľ (Fig. 6.3). Overlaying aquifer system is represented by Lehota Fm. (gravel, sand, clay, sandstone, tuffites, breccias) with intergranular permeability and overlaying Neovolcanites with fissure permeability. The drainage affected mainly overlaying and partly underlying collectors. Pumped amount of mine water from the Handlová mine was rising gradually from 50 l . s^{-1} (in 1960) to 300 l . s^{-1} (in 1980), followed by irregular decline; the average annual yield of water pumped in the dewatering of the mine in 2008 was 117 l . s^{-1} (Beck et al., 2009).

Groundwater with shallow circulation has TDS up to 200 mg . l^{-1}. Groundwater with deeper circulation has higher temperature and total mineralization.

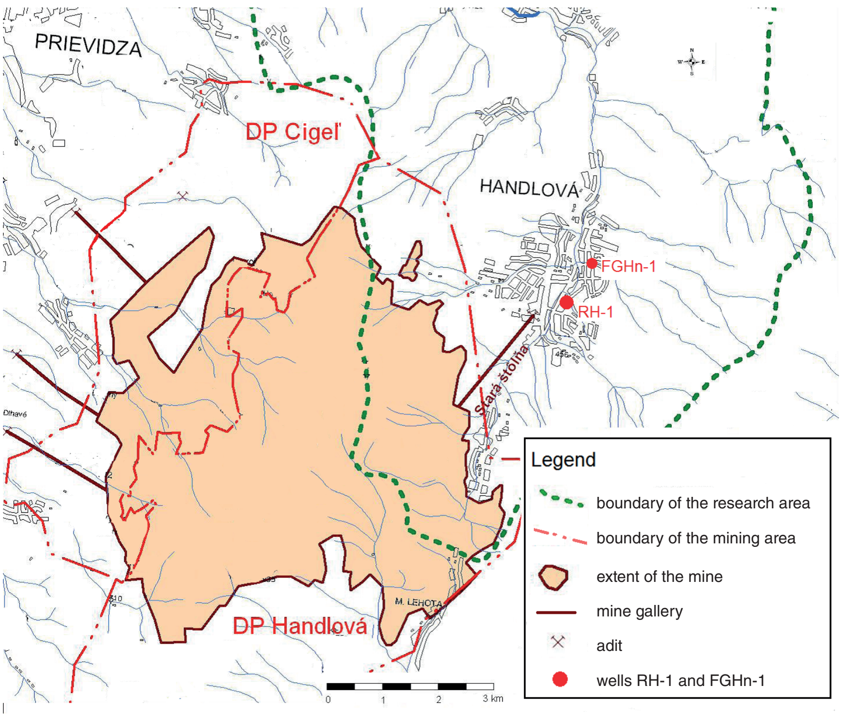


Fig. 6.3 Handlová mine situation in relation to the studied area

6.3 Construction of the hydrogeological well RH-1

Drilling of the hydrogeological well RH-1 in Handlová town

Prior to the drilling, geophysical works (gravimetric and geoelectric measurements) were carried out in 2008 in the larger area of designed well RH-1 (reinterpretation of the measured data performed in 2010). Measured geophysical data provided information for designation of the drilling place.

The well was designed as a hydrogeological well and was drilled and tested in the period between 23. 7. 2008 and 9. 4. 2010. The drilling was performed as the traditional rotary technology with rotation of the whole drill string, from the surface to the bottom with bentonite mix as a drilling fluid.

Prior to the drilling, foundations for the drilling rig were constructed. As a part of that introductory casing (520 mm) in length of 4 m was mounted. Technical works started with drilling diameter Ø 444.5 mm to a depth of 130 m. After external casing cementation was applied with casing diameter 355 mm. The next day (12. 8. 2008) effluence of methane (between casings 520 mm and 355 mm) was recorded with concentration 6%. Measured concentration of methane (in period from 12. 8. to 2. 9. 2008) ranged from 1.5 – 10.0 % with a gradual decrease until it disappeared (24. 9. 2008). Further drilling continued with diameter 311 mm until the depth of 575.2 m and external casing cementation was applied.

After cementing of casing column effluence of methane (from between casings 355 mm and 245 mm) was recorded again. After that sealing with rubber sleeve was applied and methane was driven by pipeline outside the workplace. It should be noted that during drilling to a depth of 575.2 meters there were no signs of gas. Gas leak from the casing annulus (between casings 355 mm and 245 mm) did not cease to the end of drilling. The amount of leaking gas measured (27. 10. 2009) was 0.572 m^3 . hr^{-1}. Based on analysis of the gas sampled at 21. 8. 2009 the me-thane concentration was 96.85 % and nitrogen concentration was 2.61 %.

The drilling continued to a depth of 1,064.40 m with diameter 216 mm without major complications. At a depth of 1,064.40 meters there was complete loss of fluid. Additional drilling was interrupted due to production of drilling fluid. At a depth of about 1,178 m further complete loss of fluid was recorded. Since that time restoration of drilling fluid circulation was unsuccessfull till the final drill depth (1,201.3 m). While drilling at a depth of 1,179 m drilling bit was jammed due to instability of the borehole wall (poor circulation, poor fluid quality due to the losses). Borehole was supported by casing of diameter 178 mm to that depth. After the well logging to a depth of 1,179 m (30. 12. 2009) well screen intervals were selected and well-casing of diameter 178 mm was applied in depth interval from 540.4 to 1,179.0 m. Further drilling was performed by drill bit with diameter 140 mm at a depth between 1,179.0 m and 1,195.0 m. Drilling was interrupted due to loss of drilling fluid. Drilling core (Jurassic limestone) was sampled in the depth interval from 1,195.0 to 1,201.3 m and after this drilling of the well was completed on 10. 1. 2010. Logging at the depth interval 1,179.0 to 1,201.3 m was performed at the same day and sections for well screens were selected. Well casing with a diameter of 114 mm was mounted in depth interval from 1,172.5 to 1,201.30 meters.

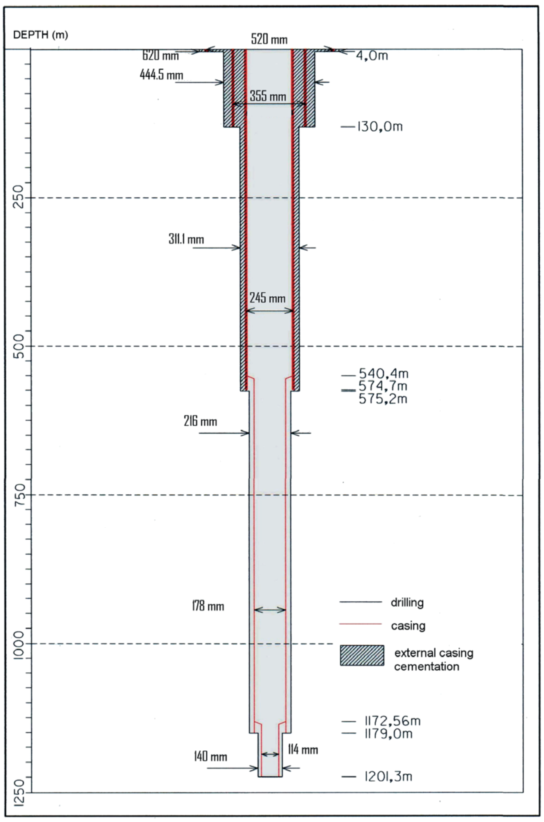
During the drilling drill recoverywas sampled every 5 meters of the borehole depth. Besides that 5 cores were sampled in intervals 0.0 – 8.0 m; 119.0 – 124.5 m; 371.0 – 375.6 m; 567.8 – 574.3 m; 1,195.0 – 1,201.3 m.

The construction of well is outlined in Fig. 6.4a. Perforated casing sections of the column were determined based on the results of geophysical logging measurements and are shown in Fig. 6.4b.

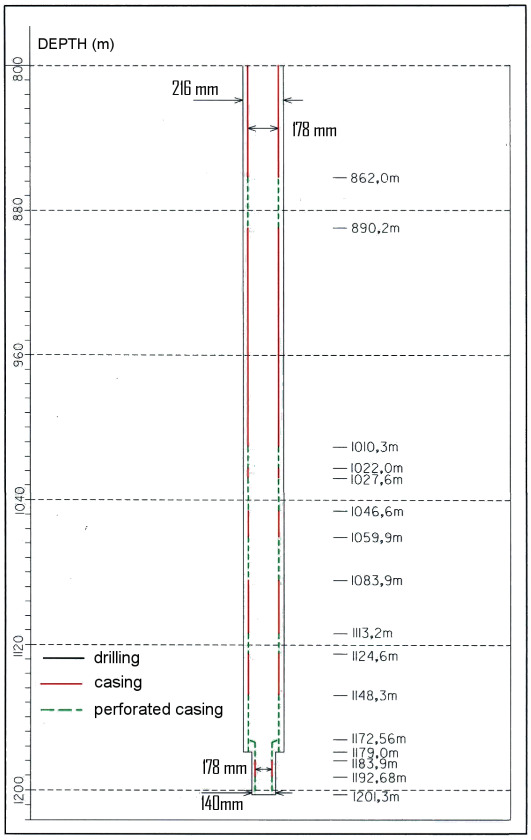
meters, 575.0 to 694.0 meters, 739.5 to 805.5 meters, 868.5 – 968.5 meters. Section from 968.5 to 1,082.7 meters is affected mainly in intervals: from 1,015.0 to 1,018.0 m, from 1,025.0 to 1,041.7 m, from 1,054.6 to 1,055.8 m, from 1,064.3 to 1,082. At the bottom part of the well, from depth of 1,082.7 meters nature of fracturing is changing toward less cavernous, though with more local fractures. Such fractures were documented in depths of 1,116.0 meters, 1,118.5 m, 1,158.5 m, 1,166.5 m, 1,177.5 m, 1,181.8 m and 1,196.9 m.

Water inflow into the wellbore

Inflow of water into the well was documented on the basis of temperature and resistance of the water in the well. Due to high level of cavernosity, drilling was performed using dense clayey drilling fluid that influenced the inflow of water into the well. Fluid resistance across the measuring section was constant and changes in water resistance that would refer to water inflow were not clearly confirmed. However, sections have been reported with changes in temperature gradient, which may be caused by the water inflow into the borehole. Those sections were around 889.8 meters and in intervals 1,032.8 to 1,042.1 m, 1,150.7 to 1,160.1 m, 1,174.0 to 1,179.0 m and 1,194.5 to 1,199.5 m.



a)



b)

Fig. 6.4 a) - The construction of well RH-1; b) - Perforated casing sections of the column

Fracturing of the rock in the well

The whole complex of overlying rock to 968.5 meters is greatly disturbed. Based on drill logging most affected intervals were: 174.1 to 201.9 meters, 434.0 to 507.9

Hydrodynamic tests in the well RH-1

After installation of the casing the recovery of the well was performed on 14. 1. 2010. It consisted of drilling fluid substitution by clean water with focus on washing

Slovak Geol. Mag., 16, 2 (2016), 91 – 104

the screening interval (perforated sections). Afterwards pumping at the rate of 4.16 l . s^{-1} was performed by submersible pump for three days, during which the water temperature reached 31 °C and water level during pumping was at a depth of 43.89 meters below ground. Acid treatment of the well was performed on 28. 1. 2010. After that well was washed again with clean water and pumped by submersible pump for one day. On 2. 2. 2010 – 21. 2. 2010 drilling rig was removed.

Other part of the work was focused on performance of hydrodynamic tests in the well. Hydrodynamic tests were carried out on 23. 2. 2010 – 9. 4. 2010 by company VIKUV (Hungary) (Gyűrüsi, 2010 in Černák et al., 2012).

Step-drawdown test was performed in three steps, each of a duration 1 day with yield Q_1 = 3.0 l . s^{-1}, Q_2 = 6.9 l . s^{-1}, Q_3 = 11.0 l . s^{-1}, which was continuously followed by yield Q = 15 l . s^{-1} for 22.7 days. Afterwards recovery test lasting 15 days was performed.

During hydrodynamic tests hydraulic parameters were investigated. Steady water level in the well before pumping test was on the level 47.94 meters (from the well-head). Level in the well during the hydrodynamic tests (at the pumping rate 15 l . s^{-1}) was at level 47.20 meters (from the well-head) with the temperature of water (at the surface) 37.5 °C.

Temperature measured at the bottom of the well (measuring device was able to reach only to the depth 1,186 m) was 38.5 °C (23. 2. 2010), or 39.9 °C (7. 4. 2010). Based on a set of data temperature from 23. 2. 2010 it can be indicated that in steady state conditions interlayer flow in open interval between 1,070 – 1,186 m is observed (with expected downward direction in the column). Long-term pumping caused heating up of the rock environment around the well. From this data the reciprocal value of temperature gradient G_g amounted 39.67 m/°C.

Vertical profile of the temperature at the end of the pumping phase (22. 3. 2010) and at end of the recovery phase (7. 4. 2010) is shown at the Fig. 6.5. Maximum yield of geothermal water pumped by submersible pump from well RH-1 was 16.7 l . s^{-1}.

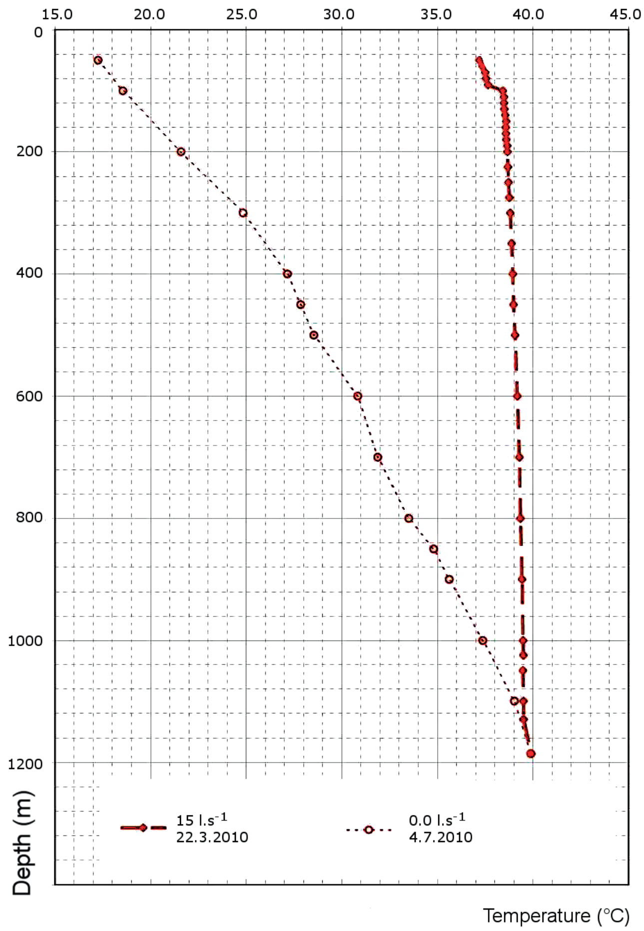


Fig. 6.5 Vertical profile of the temperature at the end of the pumping phase (22. 3. 2010) and at the end of the recovery phase (7. 4. 2010) measured in RH-1 well

Major inflow into the wellbore detected by well logging prior to casing and has a source in sandstones, conglomerates, limestones and dolomites from interval 862.0 to 1,201.3 meters. Measuring of the flow in the well after casing was performed at 22. 3. 2010 (at the end of the pumping phase) with borehole rheometer VIKUV REO-40. Inflow and outflow of water in the well is con-

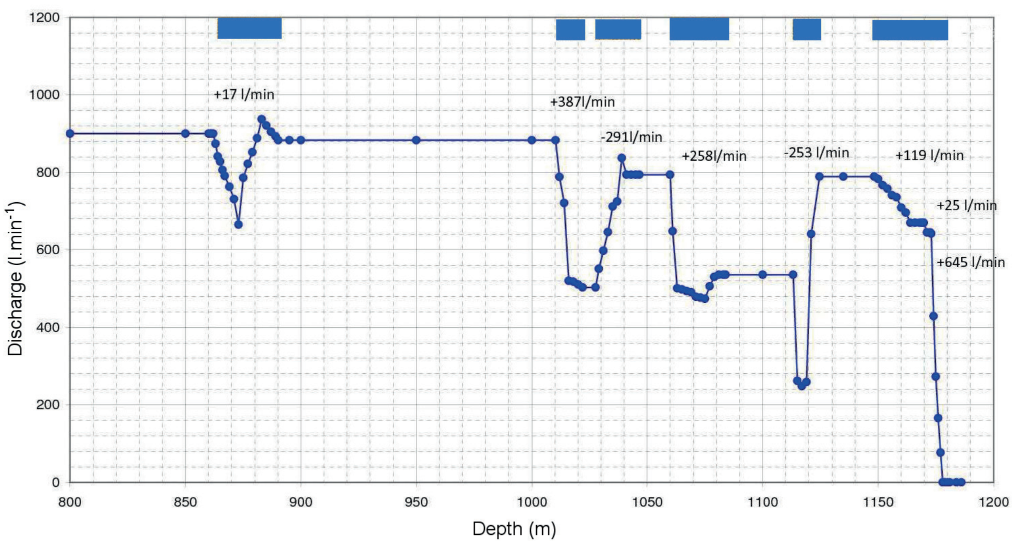


Fig. 6.6 Distribution of inflow and outflow of water in the well RH-1 at pumping rate 15 l . s^{-1} measured on 22.3.2010

nected only to the sections where perforated casing is present. The measured values from measurement in the well are in Fig. 6.6.

Hydraulic parameters of the rock environment were calculated based on pumping and recovery test from data in period February – April 2010 are shown in Tab 6.1.

Tab. 6.1 Calculated hydraulic parameters of aquifer based on measurements from pumping test performed on hydrogeological well RH-1

Tp	$1.423 \cdot 10^{-11}$	m^3	Coefficient of intrinsic (absolute) transmissivity
K_p	$3.557 \cdot 10^{-13}$	m^2	Permeability coefficient
k_f	$5.047 \cdot 10^{-6}$	$m \cdot s^{-1}$	Hydraulic conductivity
T	$2.018 \cdot 10^{-4}$	$m^2 \cdot s^{-1}$	Coefficient of transmissivity

Monitoring of the gases in water from well RH-1 was performed during the constant yield pumping at rate $15\ l \cdot s^{-1}$. Total amount of the gas was $9.48\ l \cdot m^{-3}$ with methane concentration $0.32\ l \cdot m^{-3}$.

By the obtained measurements we assume that groundwater from well RH-1 has origin in fissure environment, aquifer is confined and likely to have a large extent.

6.4 Main results brought by hydrogeological well RH-1

Geological interpretation of the RH-1 well

Known geological profile of the well RH-1 allowed re-interpretation (in 2010) of the measured geophysical data (gravimetric and geoelectric measurements carried out in 2008) and draw attention to geological significance of earlier detected tectonic zone NW-SE, that crosses Handlová fault (NNE-SSW). Based on geophysical results, the NW-SE fault zone most probably separates two different facies of the Tertiary fill – direction NE of the fault without the Neogene sediments and SW with the Neogene sediments. In addition, fault zone of direction NW-SE is likely to separate the two types of pre-Tertiary basement (with interpretations of carbonates to the NE and with different types of bedrock to the SW).

Hydrogeological well RH-1 provided new data into the clarification of the complicated geological structure in the area. Its geological content and lithostratigraphical interpretation are outlined in Tab. 6.2

Chemical composition of geothermal groundwater in the well RH-1 Handlová

Sampling of the groundwater from the well RH-1 for chemical analysis was performed during the pumping test on 5. 3. 2010, 12. 3. 2010 and 17. 3. 2010. The results of chemical analysis of groundwater borehole are summarized in Fig. 6.7.

The temperature of sampled groundwater ranged between 36.6 and 36.9 °C, neutral pH water reaction was in interval 6.9 to 7.04 and total dissolved solids ranged in 1,066 – 1,073 $mg \cdot l^{-1}$ indicate chemical composition. Chemical type of water was classified as $Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$. Dominant cations and anions were Ca^{2+} (165 $mg \cdot l^{-1}$), HCO_3^- (378 – 398 $mg \cdot l^{-1}$) and SO_4^{2-} (368 – 386 $mg \cdot l^{-1}$). The contents of the other basic components were sig-

Tab .6.2 Lithological profile of the well RH-1 in Handlová (based on Buček et al. 2011 in Černák et al., 2012).

Age			Tectonic unit	Lithostratigraphy	Depth (m) FROM	TO	Lithology
QUATERNARY					0.0	4.1	clayey loams, sandy gravel
TERTIARY	PALAEOGENE - NEOGENE	OLIGOCENE - EGGERIAN	SUBTATRIC GROUP	Chrenovec Mb.	4.1	122.7	grey and dark grey micaceous clays and claystones
					122.7	180.0	grey coarse-grained siliceous and micaceous sandstones
		PRIABONIAN - OLIGOCENE		Zuberec Fm.	180.0	310.0	dark grey sandstones and claystones
				Huty Fm.	310.0	371.0	dark grey claystones
		PRIABONIAN		Borové Fm.	371.0	460.0	grey and light grey carbonate conglomerates
PALAEOZOIC	PERMIAN		HRONICUM	Malužiná Fm.	460.0	1,020.0	red shales, siliceous sandstones and conglomerates, arkoses dark shales
	CARBONIFEROUS			Nižná Boca Fm.	1,020.0	1,040.0	light grey shales, sandstones
MESOZOIC	TRIASSIC Late (Rhaetian)			Norovice Fm.	1,040.0	1,070.0	light grey organodetritic limestones, crinoidal limestones, dolomites, shales
	CRETACEOUS Early		FATRICUM	Mráznica Fm.	1,070.0	1,085.0	grey limestones with shale and marly shale layers
				Osnica Fm.	1,085.0	1,090.0	grey and light grey marly limestones with marly shale layers (calpionela limestones, Biancone, maiolica)
	JURASSIC	MALM		Jasenina Fm.	1,090.0	1,097.5	grey, greenish, red, purple limestones with marly shale layers
		DOGGER		Ždiar Fm.	1,097.5	1,105.0	grey and greenish radiolarian limestones
				crinoidal limestones	1,105.0	1,170.0	grey and light grey crinoidal limestones
				?"siliceous fleckenmergel"	1,170.0	1,178.5	dark grey siliceous limestones and crinoidal limestones
		LIAS		?"Allgäu Fm."	1,178.5	1,183.5	grey marly limestones and marly shales (fleckenmergel)
				Hierlatz Limestone	1,183.5	1,201.3	crinoidal limestones of pink and red colours

nificantly lower: Na^+ 20.0 to 30.7 mg . l^{-1}, Mg^{2+} 46.6 to 49.3 mg . l^{-1}, Cl^- 11.0 to 24.1 mg . l^{-1}.

Groundwater chemistry is genetically related to the Middle Triassic carbonates (Hronicum and Fatricum) and Lower Triassic gypsum (Werfenian Mb., as confirmed by isotope research). The rate rMg/rCa (average 0.48) indicates the circulation in the mixed limestone-dolomite environment (however this coefficient can also be affected by the mobilization of calcium in the dissolution of evaporites).

Slightly higher chloride content (11.0 to 24.1 mg . l^{-1}) probably indicates insignificant mixing of water with groundwater from overlying Tertiary sediments containing salt of marine origin.

The increased iron (2.45 to 12.1 mg . l^{-1}) and manganese contents (0.054 to 0.137 mg . l^{-1}) indicate the groundwater movement under reduced conditions. The concentrations of the analysed trace elements are mostly low, below the detection limit of the relevant analytical method. Measured data confirmed the high stability of the chemical composition of the groundwater from the well RH-1 (Kordík in Černák et al., 2012).

On a sample analysed at the end of 16. 3. 2010 the determination of organic and microbiological parameters was made in accordance with Slovak Government Regulation No. 496/2010 (amending and supplementing Slovak Government Regulation No. 354/2006 Coll.) stating requirements on water intended for human consumption and quality control of water intended for human consumption. The water from the well RH-1 was characterized by a slight microbial activity and does not contain any specific organic substances.

In accordance with the Decree of the Ministry of Health of the Slovak Republic no. 100/2006 mineral water from the well RH-1 is described as low temperature, neutral (based on pH), moderately mineralized with prevailing $Ca\text{-}HCO_3\text{-}SO_4$ chemical composition, with increased content iron (of 1 mg . l^{-1}) and sulphate (above 200 mg . l^{-1}).

Chemical composition of geothermal groundwater in adjacent area

Hydrogeothermal structure of Hronicum tectonic unit is characterized by geothermal water of $Ca\text{-}Mg\text{-}HCO_3$ and $Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$ type and TDS around 0.7 – 1.0 g . l^{-1} (Bojnice – well BR-1, Vyhne – well H-1 and well HGV-3, Koš – well Š1-NBII).

Hydrogeothermal structure of Fatricum tectonic unit is characterized by geothermal water of $Ca\text{-}Mg\text{-}HCO_3\text{-}SO_4$ and $Ca\text{-}Mg\text{-}SO_4$ type and TDS around 1.1 to 2.7 g . l^{-1} (inflows in Handlová mine – "Biely prameň", Kremnica – well KŠ-1, Sklené Teplice – wells ST-1 and ST-4, Chalmová – well CH-3, Turčianske Teplice – wells HM-2, TJ-20, TTK-1, TTŠ-1).

It is assumed that the source of geothermal water is rainwater, as indicated by high values of the characterization factor $rHCO_3/rCl$ (20 – 144) suggesting an open hydrogeothermal structure. A characterization factor rMg/rCa (0.36 – 0.49) indicates the circulation of water in the mixed – limestone-dolomitic complex. A considerable proportion of the sulphate component is documented in Sklené Teplice by the high values (above 0.4) of a characterization factor rSO_4/TDS (wells ST-1 and ST-2 with circulation of water in gypsum). Genesis and chemical composition of water from geothermal well FGHn-1 in Handlová is different. Groundwater is of $Na\text{-}Mg\text{-}HCO_3$ type of chemical composition with TDS of about 400 mg . l^{-1} (Tab. 6.3).

Specific features of the chemical composition of above described thermal water sources are evident from Piper diagram in Fig. 6.8.

Significantly different in cationic part is only water borehole FGHn-1.

Other sources of geothermal water are placed in a relatively small cluster with dominant presence of calcium cation. There is an evident increase in the proportion of the sulphate component in the thermal waters of the Fatricum tectonic unit, which is reflected in most cases in the higher levels of total dissolved solids (bottom graph) compared to geothermal waters of the Hronicum tectonic unit. The proportion of the sulphate component in both cases is significantly variable.

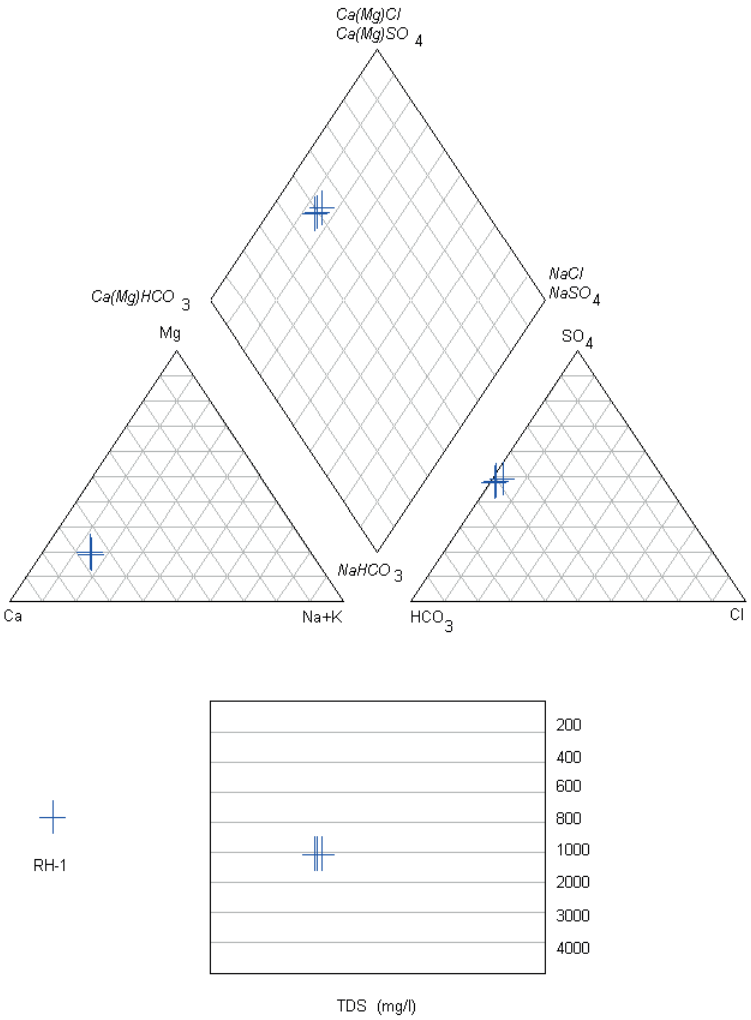


Fig. 6.7 Adapted Piper diagram of the groundwater in the well RH-1

Geothermal water from Hronicum unit in comparison with Fatricum unit water is significantly undersaturated to gypsum and anhydrite. The most significant undersaturation to the anhydrite and gypsum is evident for water from well FGHn-1. In most cases, water from Hronicum and Fatricum units are comparatively supersaturated with aragonite to calcite and dolomite. Significant oversaturation to aragonite, calcite and dolomite was also found in the water supply FGHn-1.

As indicated above, proportion of the sulphate component has significant dispersion in the chemical composition. From this perspective, the share of a characterization factor rSO_4/M with increasing temperature shows notable increase trend (with the exception of Bojnice therma (BR-1) and the source Š1 NBII). This correlation could be related to the length and depth of geothermal waters circulation, where the water with a higher temperature is characterized by a longer residence time in the environment and increase the proportion of sulphates and total dissolved solids in these waters.

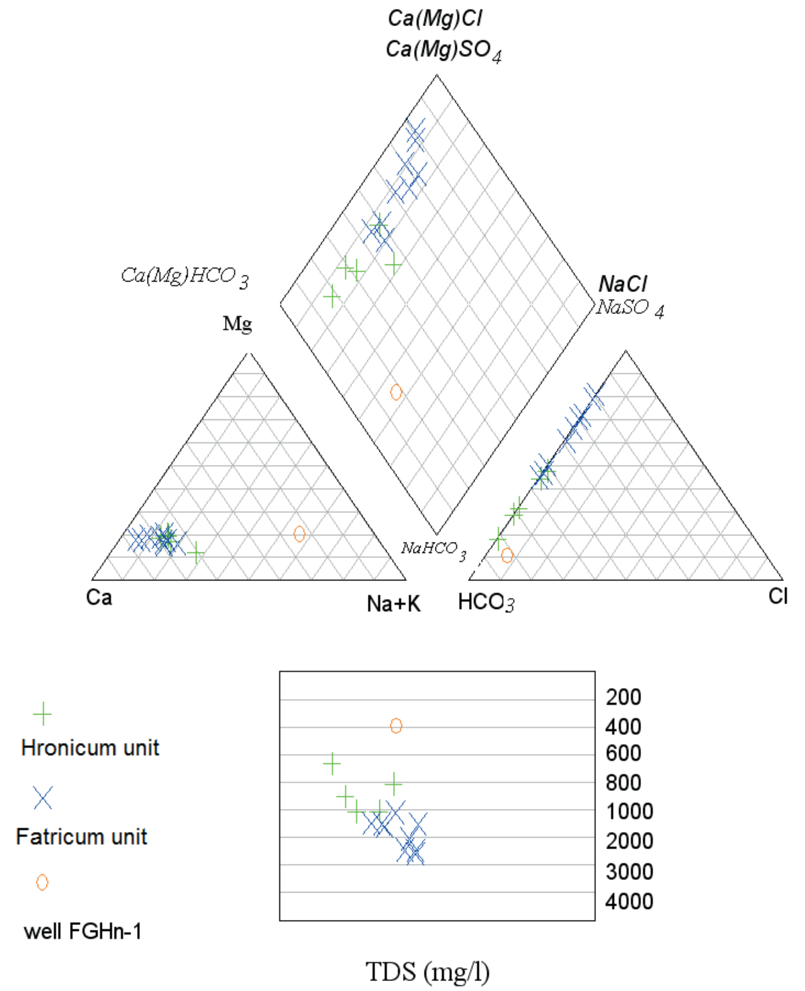


Fig. 6.8 Adapted Piper diagram of geothermal water resources from the Handlovská kotlina Basin and adjacent area (incorporated sources in diagram are from Tab.6.2)

Isotopic composition of geothermal groundwater in well RH-1 and adjacent area

The isotopic composition of oxygen and hydrogen was monitored in precipitation (Prievidza airport) from November 2008 to October 2009. The main factor governing the presence of isotopes in precipitation is the temperature, which is in general function of latitude, altitude, season of the year and age (cold and warm geological period).

The isotopic composition of oxygen and hydrogen in groundwater was monitored in selected resources during the period from December 2008 to February 2010 five times. All monitored groundwater sources, including well RH-1 and a source in Handlová mine (Bajtoš et al., 2011), are of clearly meteoric origin, which is documented by their relationship to the global meteoric line (Fig. 6.9).

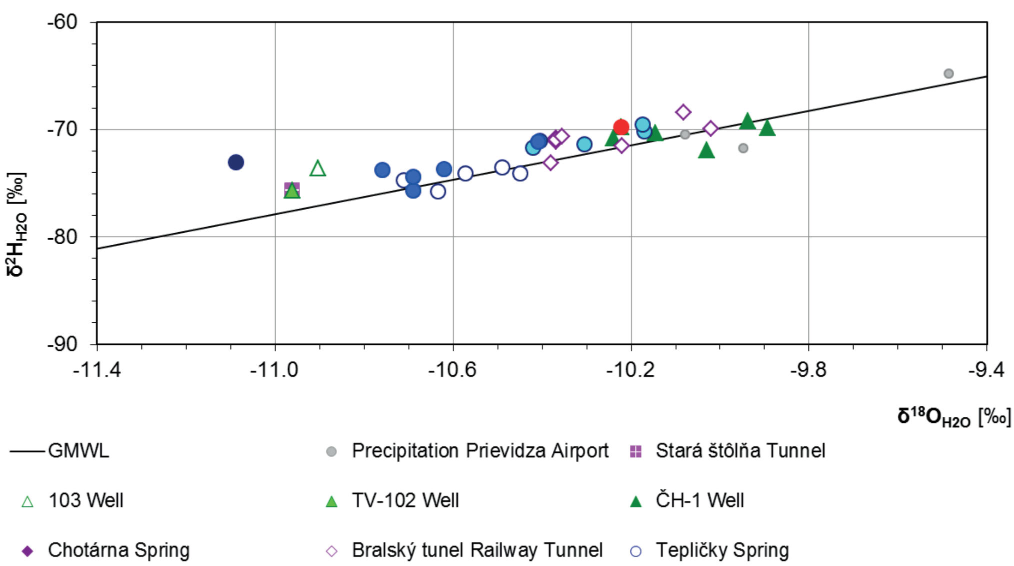


Fig. 6.9 The isotopic composition of oxygen and hydrogen in monitored groundwater resources in the Handlovská kotlina Basin

Tab. 6.3 The chemical composition of selected indicators of geothermal waters of the Hornonitrianska kotlina Basin and adjacent area with anticipated origin in distinguished tectonic units based on chemical composition of the geothermal water

	Source	Site	T water	pH	TDS	SiO_2	free CO_2	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3	$rHCO_3/rCl$	rNa+rK/rMg+rCa	rMg/rCa	rSO_4/M	rSO_4/rCl
Hronicum tectonic unit	RH-1	Handlová	36.9	7.04	1,066	18.4	70.4	28.0	7.7	164.0	49.1	11.0	368.0	398	21.02	0.12	0.49	0.27	24.69
	Š1-NBII	Nováky - Koš	62.0	6.77	816	37.1	88.9	51.2	11.6	140.0	27.4	5.7	288.0	360	36.82	0.27	0.32	0.25	37.43
	BR-1 Jesenius II	Bojnice	46.5	7.35	670	26.8	59.4	19.9	3.0	101.0	29.7	2.4	86.9	394	93.82	0.13	0.48	0.11	26.29
	H-1	Vyhne	35.3	6.50	1,084	31.2	122.3	23.2	22.4	178.0	45.2	2.8	245.3	531	110.16	0.13	0.42	0.18	64.65
	HGV-3	Vyhne	29.1	7.09	909	29.8	70.4	16.6	12.0	152.0	40.1	2.1	187.0	469	127.94	0.09	0.44	0.17	64.80
Fatricum tectonic unit	Baňa Handlová - Biely prameň (inflow in Handlová mine)	Handlová	35.0	6.73	2,074	18.6		67.2	20.4	373.0	93.8	10.1	975.0	498	28.65	0.13	0.41	0.35	71.25
	CH-3	Chalmová	39.5	7.00	1,118	30.5	33.0	26.1	9.8	200.0	53.5	9.1	494.1	317	20.26	0.10	0.44	0.33	40.08
	KŠ-1	Kremnica	44.0		1,542			46.0	19.4	290.6	63.8	7.6	802.0	311	23.94	0.13	0.36	0.38	78.41
	HM-2	Turč. Teplice	42.8	6.85	1,613	49.6	162.8	67.8	10.9	262.9	64.2	6.4	540.4	610	55.57	0.18	0.40	0.26	62.52
	TJ-20	Turč. Teplice	44.7	6.85	1,518	40.4	491.0	45.3	9.9	259.7	62.3	2.5	549.3	549	128.66	0.12	0.40	0.28	163.50
	TTK-1	Turč. Teplice	31.5	7.05	1,505	47.9	436.7	39.6	9.1	245.3	71.0	3.6	485.2	598	97.87	0.11	0.48	0.25	100.87
	TTŠ-1	Turč. Teplice	52.0	7.60	2,477	43.5	70.4	35.0	23.2	462.5	119.2	2.1	1,251.2	531	144.81	0.06	0.42	0.37	433.58
	ST-1	Sklené Teplice	52.1	7.35	2,490	27.0	125.6	21.3	12.1	498.6	113.8	3.2	1,460.7	342	62.04	0.04	0.38	0.42	336.91
	ST-4	Sklené Teplice	46.5	6.75	2,620	22.3	164.0	29.3	21.6	524.3	120.4	3.7	1,494.0	403	63.24	0.05	0.38	0.41	298.03
	FGHn-1	Handlová	20.0	8.76	393	18.0	0.0	51.0	8.3	25.2	20.8	19.1	28.2	217	6.61	0.82	1.36	0.06	1.09

Note: water temperature in °C; TDS, SiO_2, free CO_2, anion, cation content in mg . l^{-1}; information sources: Kordík in Černák et al. (2012): RH-1, Biely prameň, Fendek et al. (2004): FGHn-1, CH-3, Vandrová et al. (1999): HM-2, TJ-20, TTK-1, TTŠ-1, Pirman & Potyš (1990): KŠ-1, Orvan et al. (1967): H-1, Žitňan (2008): HGV-3, Ďurovič (1999 in Černák et al., 2012): ST-4, Struňák et al. (1965): ST-1

Sulphur present in groundwater as sulphate may originate from multiple sources which have characteristic isotopic composition. Gypsum and anhydrite of sedimentary origin from marine water essentially retain the original isotopic composition of marine sulphate. In our conditions the highest representation of the light isotope $\delta^{34}S$ was in water of Permian ocean. For the corresponding evaporites of age (Permian, Lowermost Triassic) $\delta^{34}S$ is around 10 ‰ (4 ‰ – 13 ‰). On the other hand, the highest rate of heavy sulphur isotopes is characteristic for Lower Triassic (Werfenian) sediments, with values $\delta^{34}S$ about 25 ‰ (20 ‰ – 29 ‰). Gypsum and anhydrite are well soluble and the highest concentrations of sulphate have most likely origin in these sediments.

Another source (depleted sulphur) has origin in scattered sulphides in sediments, in the studied area present mainly in coal deposits. Additional source of sulphur can be considered sulphur which is genetically linked to neovolcanites; in case of a deep source $\delta^{34}S$ with value near zero.

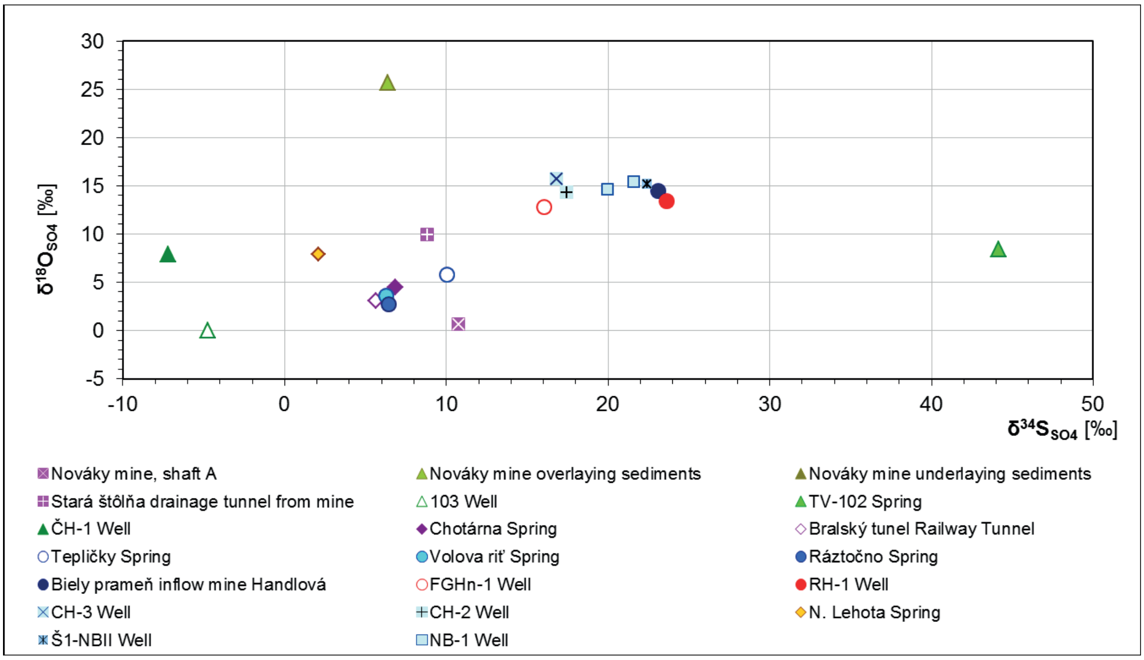


Fig. 6.10 Oxygen isotopic composition of sulphate, depending on the sulphur isotopic composition of sulphate anion in monitored water sources

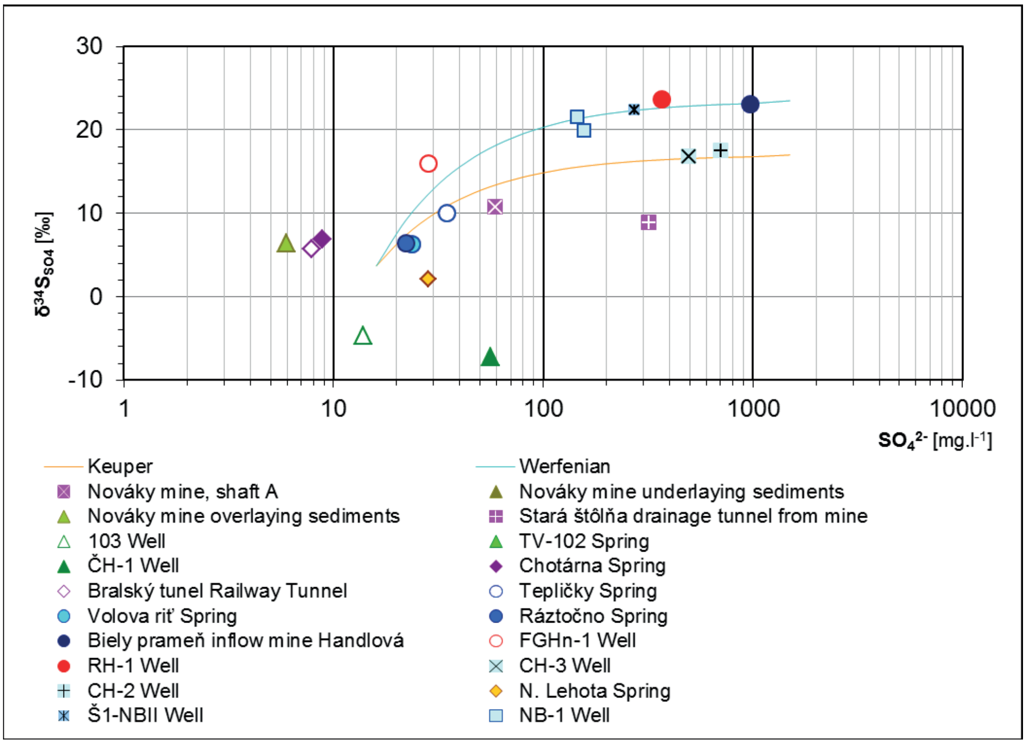


Fig. 6.11 The isotopic composition of the sulphur according to the concentration of the sulphate anion in water

Slovak Geol. Mag., 16, 2 (2016), 91 – 104

Low sulphate concentrations (~ 10 – 30 mg . l^{-1}) in groundwater with relative light sulphur ($\delta^{34}S$ ~ 2 ‰ - 8 ‰) have probably origin in precipitation. As documented by Malík et al. (2000), the isotopic composition of sulphur in the snow from Handlová – Nová Lehota represents value $\delta^{34}S$ = 6.2 ‰ at a concentration of sulphates 4.3 mg . l^{-1}.

The main processes that affect the quality and quantity of sulphate present in the groundwater can be considered dissolution (and precipitation), redox processes and mixing. We do not consider progressive (bacterial) reduction of sulphate based on the findings on the absence of hydrogen sulphide in the water.

In selected groundwater resources isotopic composition of sulphur and oxygen respectively in the water was measured.

Water from Mesozoic bedrock in Handlová mine seepage (source in ”Východná šachta“ (Eastern shaft) 200 m a.s.l., seepage in mine galleries of VIIIth horizon) has isotopically heavy sulphur with $\delta^{34}S$ = 23.1 ‰, which is usually characteristic of sediments of Werfenian Mb. or ocean sediments of Miocene age. The fact that this is the dissolution of the gypsum is demonstrated by high concentration (975 mg . l^{-1}) of the sulphate anion in water. This idea does not contradict either the oxygen isotopic composition of sulphate (Fig. 6.10).

Sulphate present in water in high concentrations detected within three sampled sources – seepage Mesozoic bedrock in Handlová mine seepage (Eastern shaft), geothermal borehole Š1-NBII Laskár and geothermal well RH-1 in Handlová, is from isotopic point of view (sulphur and oxygen) practically identical (Fig. 6.10 and Fig. 6.11). Sulphate probably originates from the same source, wherein the isotopically lighter sulphur suggests the mixing of water with background sulphur (the position of the mixing curve in Fig. 6.11). Thus isotopically enriched sulphur ($\delta^{34}S$ = 23.1 ‰, 22.4 ‰ and 23.6 ‰) is usually characteristic for evaporites (anhydrite) of Werfenian facies (Early Triassic).

6.5 Discussion

The Handlovská kotlina Basin is a part of delineated geothermal groundwater body Hornonitrianska kotlina Basin (“Upper Nitra Basin“ respecting definition and delineation by Franko, Remšík and Fendek, eds., 1995). The Handlovská kotlina Basin is in direct contact with geothermal areas ”Central Slovak Neovolcanites – NW part“. In both defined geothermal groundwater bodies geothermal waters are bound to Triassic carbonates of the Hronicum and Fatricum units, as well as to the basal Palaeogene breccias and conglomerates that are overlying the Triassic carbonates (creating one aquifer).

In the deeper parts tectonic units of Hronicum, Fatricum and Tatricum are present in the Handlovský chrbát Ridge (as defined by Fusán et al., 1987) and its surrounding structures. All three units crop out in Tribeč, Žiar and Veľká Fatra mountain rangess and are possible recharge areas for geothermal waters in the Handlovská kotlina Basin.

At the area of Handlová town, geothermal aquifer linked to Triassic carbonates of Tatricum tectonic unit is less probable due to its considerably reduced form.

Geothermal aquifers in Fatricum and Hronicum tectonic units are segmented by faults into several, more or less partial structures that can be relatively independent in hydraulic and hydrogeochemical regime and temperature.

More extended structures and aquifers are built by carbonate rocks of Fatricum tectonic unit creating transition and accumulation reservoirs of geothermal water. These are situated below the Hronicum tectonic unit represented by carbonate (Triassic dolomites and limestones) or non-carbonate bedrock (Ipoltica Group) (Remšík in Černák et al., 2012). Aquifers of these tectonic units can be interconnected in tectonic zones by geothermal water communication. Triassic carbonates, particularly in the Hronicum unit, can form more or less separate floes in their extension, as well as thickness, due to erosion and tectonic evolution.

Thus Triassic carbonates of Fatricum, Hronicum and the basal Palaeogene clastics can create conditions for the existence of two geothermal aquifers in superposition one above the other, or side by side. The extension of transit-storage and accumulation areas of these structures thus can spread to the mountains of Vtáčnik, Handlovská kotlina Basin, Kremnické vrchy Mts. It can be assumed that geothermal aquifers in given area (geothermal water in the well RH-1) are connected to Handlovský chrbát Ridge built by tectonic Fatricum and Hronicum units and they are ”isolated“ from neighbouring hydrogeothermal structures of Kremnica depression and Žiarska kotlina Basin. However, hydrogeothermal structure spatial definition (surface, thickness, boundary) currently faces a lack of direct data and information.

Geothermal water from Triassic carbonates of Fatricum tectonic unit in the Handlovský chrbát Ridge can be found in two inflows into the mine Handlová at a depth of 470 m (200 m above the see level) in the eastern shaft. Yields were 10.8 l . s^{-1} and 2.0 l . s^{-1} respectively, with water temperature 32 °C. Water is of Ca-Mg-SO_4-HCO_3 type with TDS 2.05 – 2.15 g . l^{-1}, the CO_2 content of 127.6 mg . l^{-1} and H_2S 0.14 mg . l^{-1} (Krahulec et al. , 1978). The same chemical type of water was confirmed by the analysis of water in 2010 (Černák et al., 2012). Similar geothermal water was detected in underground borehole KŠ-1 in Kremnica.

Geothermal water from hydrogeothermal structure of the Hronicum tectonic unit near Handlová is characterized by Ca-Mg-HCO_3 type and TDS around 0.7 – 1.0 g . l^{-1}. The hydrogeological well RH-1 in Handlová (depth 1,201.3 m), tapped geothermal water mainly from Mesozoic limestone and dolomite and from Permian clastic rocks and shales of Hronicum and Fatricum tectonic units in the depth interval of 862 – 1,201 m (441 – 780 m below the see level). The main inflow to the well (87.7 % yield) was from the Jurassic limestones of Fatricum tectonic unit. Yield of the water from well RH-1 was 15.0 l . s^{-1}, water temperature 37.5 °C, chemical type Ca-Mg-HCO_3-SO_4 with TDS 1.07 g . l^{-1}, CO_2 70.4 mg . l^{-1} and H_2S 0.25 mg . l^{-1}. Sulphur had almost the same isotopic composition ($\delta^{34}S_{SO4}$) as the seepage of geothermal water in the mine Handlová (Michalko in Černák et al., 2012). By chemical composition this water shows affinity to aquifer in Fatricum tectonic unit, but with unusually low TDS for this structure. The cause of this can be low CO_2 content, a relatively short circulation time, or can be the result of mixing higher mineralized water form Fatricum tectonic unit with less mineralized water form Hronicum tectonic unit.

In case the geothermal water from the well RH-1 is a result of water mixing with origin in Hronicum and Fatricum units, we cannot attribute recharge to a single area. This idea supports different isotopic composition of oxygen and hydrogen of water in the well RH-1 and seepage of geothermal water in Handlová mine (Michalko in Černák et al., 2012).

Possible mixing of the water can occur at the contact of Hronicum and Fatricum units (in the area of the well RH-1) where at the depth interval 1,040 – 1,201 m (thickness of only 161 m) reduced strata of Jurassic-Cretaceous limestones (Fatricum unit) are overlain by Upper Triassic carbonates (Hronicum unit). Suitable conditions for mixing of the water from different tectonic units are given as well by position of the well at the fault zone of N-S direction (the valley of Handlovka River). Geothermal water remaining in the structure is characterized by its age, which has the value of 9,230 ± 110 years (Šivo & Richtáriková, 2010 in Černák et al., 2012).

6.6 Conclusion

In period 2009 – 2010 the hydrogeological well RH-1 was drilled as a part of regional geological research. Prior to the drilling geophysical measurements were performed and detected tectonic zone of NW-SE direction as a key element in tectonic scheme.

Geothermal water from hydrogeological well RH-1 in Handlová (1,201.3 m deep) is linked to the Mesozoic limestones and dolomites (geothermal aquifer). Inflow of geothermal water into the well (based on the results of geophysical measurements) was in the interval from 862.0 to 1,201.3 meters. Water table in the well before pumping test was at the level of 47.94 meters (from the well-head). Usable amount of geothermal water 15.0 $l . s^{-1}$ was calculated and approved by Ministry of Environment based on 22.7 day pumping test. The water level in the well during the pumping test reached 47.20 meters (from the well-head) and water temperature at the surface was 37.5 °C. Hydraulic parameters of aquifers were calculated. Coefficient of absolute transmissivity valued by $1.423 . 10^{-11} m^3$, permeability coefficient $3.557 . 10^{-13} m^2$, hydraulic conductivity $5.047 . 10^{-6} m . s^{-1}$ and coefficient of transmissivity $2.018 . 10^{-4} m^2 . s^{-1}$. Calculated usable amount of geothermal energy represents 1.41 MW.

Geothermal water is calcium-magnesium-bicarbonate-sulphate chemical type ($Ca-Mg-HCO_3-SO_4$ type) with a TDS of about 1,066 $mg . l^{-1}$ with higher CO_2, H_2S and CH_4 content and is not susceptible to scaling.

The hydrogeological well RH-1 tapped geothermal water linked to Hronicum and Fatricum tectonic with main inflow (87.7 % yield) from the Jurassic limestones of Fatricum tectonic unit as proven by sulphur isotopic composition ($\delta^{34}S_{SO4}$) and chemical composition. Reason for unusually low TDS (for this structure) can be low CO_2 content, a relatively short circulation time, or can be the result of mixing higher mineralized water form Fatricum tectonic unit with less mineralized water form Hronicum tectonic unit. It can be assumed that the geothermal water from the borehole RH-1 has circulation in aquifer with recharge and transit-accumulation zones but has no natural spring area. In this case it is a result of water mixing with origin in Hronicum and Fatricum units and thus we cannot attribute recharge to a single area. Though we assume, that precipitation is main recharge source which means that the source of geothermal water and geothermal energy is renewable. Geothermal water age is estimated to 9,230 ± 110 years based on carbon dating.

Thermal conditions in the Handlová area (well RH-1) were documented at the depth of 500 meters (below surface) with temperature 25 °C, at a depth of 1,000 m with temperature 35 °C and a depth of 1,200 m with the temperature of about 40 °C. The mean value of geothermal gradient for the well RH-1depth section 100 – 1,200 m reached 21.0 $°C . km^{-1}$.

Documented physical and chemical properties of the geothermal water from the well RH-1 have shown that water is very convenient for bathing and wellness complex. The geothermal water in the Handlová town is a renewable resource which opens the opportunities for sustainable use and new activities in the region for example the recreation.

References

Auxt, A., Klúz, M., Šalagová, V., Beracko, I., Galisová, M., Dorčík, G., Szabová, H., Urbaník, J., Berzáková, M., 1997: Neovulkanity Kremnických vrchov – severná časť, vyhľadávací HGP, Žilina, Ingeo, 1997, 133 p.

Bajtoš, P., Cicmanová, S., Baláž, P., Stupák, J., Pramuka, S., Michalko, J., Šesták, P., 2011: Banské vody Slovenska vo vzťahu k horninovému prostrediu a ložiskám nerastných surovín. Final report. Manuscript, Geofond Archive SGIDŠ, Bratislava.

Bátory, V., Takáčová, J., Lopašovský, K., Hauskrecht, J., Palkovičová, M., Makrányiová, Z., 1973: Horná Nitra – HGP, cieľ: overiť zvodnenie štrkopiesčitých terciérnych sedimentov v spomínanej oblasti. Vodné zdroje Bratislava, Manuscript, Geofond Archive SGIDŠ, Bratislava, 30 p.

Beck, J., Šarkan, J., Daubner, P., Sivák, I., Hopková, M., Pipíška, S., Chríbik, J., 2009: Záverečná správa s výpočtom zásob výhradné ložisko Handlová, dobývací priestor Handlová. Surovina: hnedé uhlie. Stav k: 1. 1. 2009. Manuscript, Geofond Archive SGIDŠ, Bratislava, 64 p.

Bodiš, D., Klukanová, A., Švasta, J., Rapant, S., Gajdoš, V., Hók, J., 2006: Vplyv geologických faktorov na kvalitu života, Kvalita života – zdravie, výživa, vzdelávanie, č.2003SP28/OSO 0066/000 00 00, Manuscript, Geofond Archive SGIDŠ, Bratislava.

Bubeník, I., Frličková, M., Beracko, I., Šalaga, I., 1976: Prievidzská kotlina – vyhľadávací hydrogeologický prieskum, HGP, účel: overiť možnosť skrytých priestupov podzemných vôd z okrajových pohorí situovaním vrtov na okraji kotliny, SGÚ Žilina, IGHP, Manuscript, Geofond Archive SGIDŠ, Bratislava, 79 p.

Černák, R., Kordík, J. (eds.), Bottlik, F., Havrila M., Helma J., Kohút M., Šimon L., 2004: Základná hydrogeologická a hydrogeochemická mapa pohoria Žiar v mierke 1: 50 000, Ministerstvo životného prostredia Slovenskej republiky, Štátny geologický ústav Dionýza Štúra, Bratislava, Manuscript, Geofond Archive SGIDŠ, Bratislava.

Černák, R., Remšík, A., Malík, P., Kordík, J., Michalko, J., Bajtoš, P., Baráth, I., Boorová, D., Bottlik, F., Buček, S., Elečko, M., Filo, I., Gregor, M., Jankulár, M., Kohút M., Lenhartová, E., Marcin, D., Olšavský, M., Ondrejka, P., Polák, M., Siráňová, Z., Šimon L., Zlinská, A., Žecová, K., Filo, J., Gretsch, J., Gyürüsi, Cs., Mikuška, J., Olejník, M., Pašteka, R., Šivo, A., 2012: Základný hydrogeologický výskum Handlovskej kotliny, Ministerstvo životného prostredia Slovenskej republiky, Štátny geologický ústav Dionýza Štúra, Bratislava, Manuscript, Geofond Archive SGIDŠ, Bratislava, 181 p.

Directive of the MoE SR as of 26. 10. 2004 No. 8/2004-7 on compilation of basic hydrogeological maps at scale of 1 : 50,000

Dovina, V., Lexa, J., Vrana, K., Konečný, V., Gross, P., Vozár, J., Kullmanová, A., Planderová, E., Sitár, V., 1985: Zhodnotenie hydrogeologických pomerov Vtáčnika, čiastková záverečná správa, 1981 – 1985, Hydrogeologický výskum vybraných oblastí SSR. ŠGÚDŠ Bratislava, Manuscript, Geofond Archive SGIDŠ, Bratislava, 161 p.

Fendek, M., Havrila, M., Šimon, L., Hók, J., Žecová, K., Michalko, J., Bajtoš, P., Obernauer, D., Fendeková, M., Ženišová, Z., Král, M., Grand, T., Džuppa, P., Komoň, J., 2004: Regionálne hydrogeotermálne zhodnotenie Hornonitrianskej kotliny. Manuscript, Geofond Archive SGIDŠ, Bratislava.

Franko, O., Kullman, E., Melioris, L., Vrana, K., 1993: Vysvetlivky ku hydrogeologickej mape 1 : 50 000 regiónu Horná Nitra, Interim final report, Manuscript, Geofond Archive SGIDŠ, Bratislava, 189 p.

Franko, O. (ed.), Remšík, A. (ed.), Fendek, M. (ed.), 1995: Atlas geotermálnej energie Slovenska. Geologický ústav Dionýza Štúra, Bratislava, p. 1 – 267.

Fusán O., Biely A., Ibrmajer J., Plančár J., Rozložník L., 1987: Podložie terciéru vnútorných Západných Karpát. Geol. úst. Dionýza Štúra, Bratislava, p. 7 – 103.

Regulation No. 354/2006 Coll. of 10 May 2006, laying down requirements for water intended for human consumption and quality control of water intended for human consumption.

Kotulová, J., Pauditš, P., Janega, A., Dananaj, I., Halmo, J., Švasta, J., Elečko, M., Šimon, L., Zlocha, M., Šarkan, J., Fazekaš, J., Müller, M., 2010: Hornonitrianska kotlina – trojrozmerné geologické modelovanie exponovaného územia, regionálny geologický výskum, Manuscript, Geofond Archive SGIDŠ.

Kováčik, M., Marsina, K., Vrana, K., Határ, J., Smolárová, H., Čížek, P., Čurlík, J., 1993: Súbor regionálnych máp geofaktorov životného prostredia SR v mierke 1 : 50 000, región Horná Nitra, záverečná správa, projekt: Výskum geologických faktorov životného prostredia, doba riešenia: 1991 – 1993. Manuscript, Geofond Archive SGIDŠ, 30 p.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1978: Minerálne vody Slovenska, 2, vydavateľstvo Osveta, Martin, 1978.

Kullman, E., Gazda, S. et al., 1978: Základná hydrogeologická mapa 1 : 200 000 list 36 – Banská Bystrica, čiastková záverečná správa. Názov úlohy: Základný hydrogeologický výskum spojený s edíciou hydrogeologických máp. Manuscript, Geofond Archive SGIDŠ, 472 p.

Kullman, E., Gazda, S., Jetel, J., Škvarka, L., Franko, O., 1975: Základná hydrogeologická mapa 1: 200 000 list Trnava, čiastková záverečná správa za roky: 1974 – 1975. Názov úlohy v perspektívnom pláne: Edícia hydrogeologických máp. Manuscript, Geofond Archive SGIDŠ, 308 p.

Lexa, J. (ed.), Halouzka, R., Havrila, M., 1998a : Geologická mapa Kremnických vrchov, MŽP SR – GSSR Bratislava.

Lexa, J. (ed.), Halouzka, R., Havrila, M., Hanzel, V., Kubeš, P., Liščák, P., Hojstričová, V., 1998b : Vysvetlivky ku geologickej mape Kremnických vrchov 1 : 50 000. Bratislava, GS SR, Vyd. D. Štúra, 308 p.

Malík, P., Michalko, J., Rapant, S., Scherer, S., 2000: Izotopy síry v zimných zrážkach na území Slovenska, Podzemná voda VI./2000 č. 2, p. 174 – 184

Mazúr, E. & Lukniš, M., 1980: Regionálne geomorfologické členenie SSR 1 : 500 000, Geografický ústav SAV Bratislava.

Orvan, l, 1967: Vyhne – hydrogeologický štruktúrny vrt H- l. Final report, Manuscript, Geofond Archive SGIDŠ, Bratislava, 21 p.

Pirman, L & Potyš, Z., 1990: Turčianske Teplice ochranné pásma, Final report, Manuscript, Geofond Archive SGIDŠ, Bratislava.

Polák, R., 1997: Hydrogeologický rajón M 064 – mezozoikum severnej časti pohoria Žiar, vyhľadávací prieskum, Manuscript, Geofond Archive SGIDŠ, 192 p.

Rapant, S., Vrana, K., Bodiš, D., Doboš, V., Hanzel, V., Kordík, J., Repčoková, Z., Slaninka, I., Zvara, I., 1996: Geochemický atlas Slovenskej republiky – časť podzemné vody. GSSR, Bratislava, 127 p.

Regulation No. 496/2010 Coll., which amends Slovak Republic Government Order No. 354/2006 Coll., laying down requirements on water intended for human consumption and quality control of water intended for human consumption.

Remšík, A. & Černák, R., 2011: Hydrogeologický vrt v Handlovej, Preliminary Report, Manuscript, Geofond Archive SGIDŠ, Bratislava, 14 p.

Struňák, V., 1965: Hydrogeologický prieskum minerálnych vôd v Sklených Tepliciach. Final report, Manuscript, Geofond Archive SGIDŠ, Bratislava.

Šimon, L. (ed.) Elečko, M., Lexa, J., Pristaš, J., Halouzka, R., Konečný, V., Gross, P., Kohút, M., Mello, J., Polák, M., Havrila, M., Vozár, J., 1997a: Geologická mapa Vtáčnika a Hornonitrianskej kotliny.MŽP SR – GSSR Bratislava.

Šimon, L. (ed.) Elečko, M., Lexa, J., Pristaš, J., Halouzka, R., Konečný, V., Gross, P., Kohút, M., Mello, J., Polák, M., Havrila, M., Vozárová, A., Vozár, J., Kohlerová, M., Stolár, M., Jánová, V., Marcin, D. & Szalaiová, V., 1997b: Vysvetlivky ku geologickej mape Vtáčnika a Hornonitrianskej kotliny 1 : 50 000. GSSR, Vyd. D. Štúra, Bratislava, 281 p.

Vandrová, G., Potyš, Z., Urbaník, J., Zuberec, M., Hajčík, J., 1999: Budiš – ochranné pásma minerálnych vôd, vyhľadávací HGP. MŽP SR Bratislava, Ingeo Žilina, Manuscript, 119 p.

Žitňan, M., 2008: Vyhne – vrt HGV-3 – využiteľné množstvá podzemných vôd v kategórii B, doplnkový HGP. Manuscript, AQUA-GEO, Bratislava, 43 p.

Mineral Waters of the Cigeľka Spa

Natália Bačová[1], Jozef Komoň[2], Juraj Michalko[3]

[1] State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Regional Centre, Jesenského 8, 040 01 Košice, Slovakia, natalia.bacova@geology.sk
[2] Koral, s.r.o., Nad Medzou 2, 052 01 Spišská Nová Ves, Slovakia, info@koral.sk
[3] State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Mlynská dolina 1, 817 04 Bratislava, Slovakia, juraj.michalko@geology.sk

Abstract: Cigeľka Village is located in the NE Slovakia, about 20 km NW of Bardejov. Thanks to the mineral waters occurrence with beneficial effects for humans troubled with the digestive system, it has been known since the thirties of the 19th Century. Cigeľka natural mineral water (exploited borehole at CH-1) is a strongly mineralized, carbonic Na-HCO_3-Cl type. The resulting chemical composition is formed by mixing two chemical types of water – Na-HCO_3-(Cl) and Na-Cl – well insulated from the "live" circulation. It gets to the surface along a deep reaching system of faults of NE-SW direction (likely NW continuation of the Muráň tectonic system). The paper is devoted to past achievements (especially the latest) of hydrogeological, hydrogeochemical and geophysical works carried out in the discharge area of the natural mineral water Cigeľka, macrochemical description of the composition of mineral water in Cigeľka, patterns of formation and relationship between this mineral water the and the mineral waters of the Flysch Zone of the Western Carpathians.

Key words: geological and hydrogeological conditions, Flysch Zone, Cigeľka natural mineral water, macrochemical composition, vertical electrical sounding, stable isotopes O and H

7.1 Introduction

On Slovakia-Polish border about 20 km NW of the town of Bardejov is the village Cigeľka. It is known mainly thanks to mineral waters. Their unique properties were reported to Hungary and throughout Europe already in the thirties of the 19th Century by Ludvig Tognio (Rebro, 1996). Already in the fifties of the 19th Century the mineral water was bottled and since 1918 the mineral water from three wells – Slovan, Štefan and Ľudovít – has been used for balneotherapeutic purposes. The natural mineral water Cigeľka (from source CH-1), available on the market today, has beneficial effects on the digestive system, it helps at excessive consumption of food and also in the lack of appetite to eat, at the problems with excess stomach acid.

Geological and hydrogeological conditions of the discharge area of the Cigeľka natural mineral water and its surroundings have been studied since the 50's of the last Century by many prominent hydrogeology and geochemistry experts (Hynie – the first hydro-geological survey drillings in Cigeľka in the years 1953-1957, Jarchovský, Kellner, Haluška, Struňák, Malatinský, Klago, Michalíček and others). For bottling of the mineral water the greatest importance had the results of hydrogeological research of the discharge area in the years 1972 – 1984 (Malatinský et al., 1984), when natural mineral source – borehole CH-1 was developed. In the period 1990 – 1997 in the broader area of Cigeľka a search hydrogeological survey was executed to obtain a basis for drafting the buffer zones of the Cigeľka natural mineral water (Pacindová et al., 1997). Later, the interpreting of original data and the description of these waters and hydrogeological structure were dealt by Marcin (1996, 1999), Bačová & Bačo (1998), Bačová (2006), and Bačová & Michalko (2007).

The paper is focused in selected geological and hydrogeological facts about the discharge area of the Cigeľka natural mineral water. It is dedicated to patterns of forming macrochemical composition of mineral water in the Flysch Zone and Foredeep of the Western Carpathians and in particular to relation between the Cigeľka mineral waters and other mineral waters of the Flysch Zone.

7.2 Methodology

In a summary processing and interpreting the results of hydrogeological research carried out in Cigeľka it is important to consider a number of very relevant knowledge about mineral waters of the Flysch Zone of the Western Carpathians. This results from the fact that, in the case of the Cigeľka natural mineral water the water has high content of dissolved solids, with the likely deep circulation. Therefore it is not possible to describe the formation of the resulting chemical composition without examining the broader context – rules of forming and occurrence of mineral waters within the Flysch Zone. Hydrogeochemical evaluation of the original data always requires selecting the appropriate classifications – those that most contribute to the systematization of knowledge to the clear and vivid interpretations.

For the classification of chemical water types under prevailing ion-chemical type we include in the name the ions with more than 25 meq . l^{-1} % share (classification of Kurlov in Klimentov, 1980); in opposite to commonly used more than 20 meq . l^{-1} %. We point out that in the case of the Cigeľka natural mineral water the chemical symbol is the same in both cases.

To assess the total dissolved solids in mineral waters of the Flysch Zone with wide interval of values (from

230 mg . l^{-1} to 130 g . l^{-1}) the most appropriate is classification by Ivanov (in Franko et al., 1975) with supplementary resolution of weak brines with TDS from 50 to 100 g . l^{-1} and strong brines with TDS greater than 100 g . l^{-1} (in accordance with the classification of groundwater by Švarcev, 1996).

When describing the mineralization processes share in the resulting chemical composition of mineral water we are using genetic classification of the chemical composition of the groundwater of the Western Carpathians (Gazda, 1974), adapted for the purposes of Geological dictionary, part Hydrogeology (Hanzel et al., 1998) by Fľaková et al. (2010).

In terms of origin investigations we term mineral waters in accordance with the genetic classification of groundwater prepared by Kirjuchin et al. (in Švarcev, 1996).

7.3 Geological and hydrogeological conditions of the discharge area

The Cigeľka natural mineral water (CH-1 borehole) is located in the western part of the Nízke Beskydy Mts. (whole Busov) in Rača Partial Nappe of the Magura Nappe (Flysch Zone). Geological and tectonic site conditions and its wider surroundings are described in detail in the work by Bačová and Bačo (1998).

Flysch sediments of the Rača Partial Nappe are represented by Zlín Fm. – Makovica Sandstone (Tvarožec by Nemčok et al., 1990) and Bialowieza Fm. (Figs. 7.1, 7.2). The Makovica Sandstone complex consists of massive sandstone layers over- and under-lain by approximately 1000 m thick fine-rhythmic flysch (Nemčok l. c., 1990). It is a light, coarse-grained sandstone with abundant feldspar, often hued by limonite. Foraminiferal community notes Early Eocene age, but Nummulites facies on the Palaeocene age (Nemčok et al., l. c.). Above the sandstone bodies the Bialowieza Fm. is present. It develops from the sub-base of thick-bedded sandstone. Sandstone and claystone ratio is 1 : 1; thin-bedded fine-grained sandstone is rich in hieroglyphics of organic origin. The claystone at the bottom of the formation is variegated (red, green, grey); in the top of grey and greenish hue. The stratigraphic range is from the Palaeocene to the bottom of the Middle Eocene. It is overlain by the Bystrica Fm. (Luthetian – Latest Eocene). It is a thick- layered alternation of thick-bedded to thin-bedded greywacke sandstone with thick layers of dark grey claystone with shell-like jointing.

Hydrogeological structure of the Cigeľka natural mineral water is considered (in accordance with the classi-

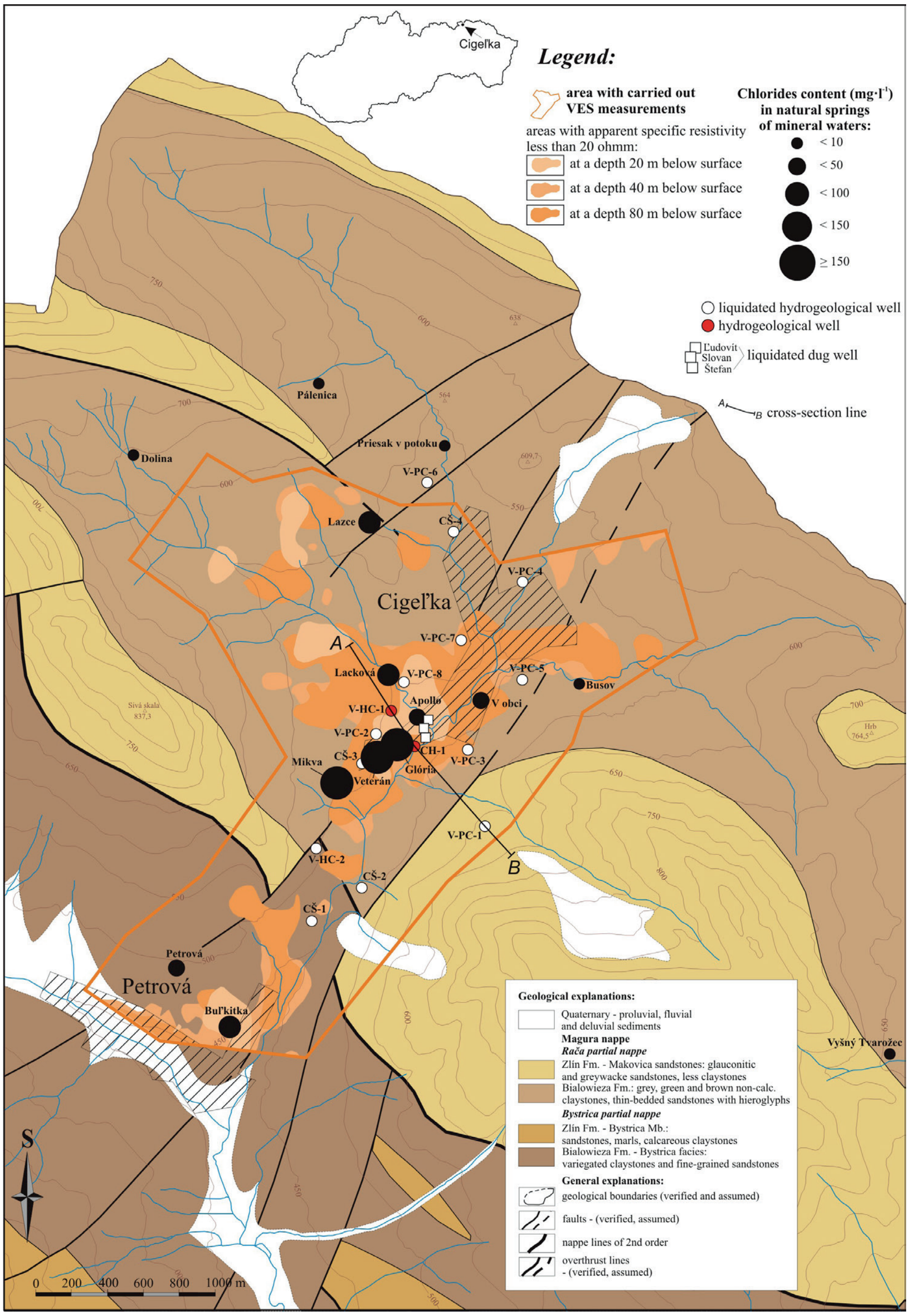


Fig. 7.1 Map of the results interpretation of hydrogeochemical and geophysical work carried out in the years 1990 – 1997 in the field of the Cigeľka natural healing water (based on documents by Straník, 1965; Bačo in Pacindová et al., 1997, modified)

fication of Franko et al., 1975) for semiclosed structure (without catchment) with partially covered discharge area. In more detail it is characterized in work by Bačová and Bačo (1998). In the area studied and its surroundings, there are many natural springs of mineral water. They are depicted in Fig. 7.1. In the same figure there are located former trial wells and hydrogeological boreholes that provided significant knowledge on mineral waters, but later they were destroyed.

Schematic geological section across the Oľchovec Valley (Fig. 7.2) through hydrogeological drillings V-HC-1, CH-1 and V-PC-1.

The Cigeľka natural mineral water is exploited of the hydrogeological borehole CH-1 (202.5 m) excavated in the years 1972 – 1973 (Malatinský et al., 1984). The borehole lithology consists of Bialowieza Fm. (top depth interval – mainly claystone facies, bottom depth interval – mostly sandstone facies, Fig. 7.2). Heavily mineralized carbonated water with a chemical type of Na-HCO_3-Cl is tapped at a depth of 178 – 200 meters. The yield is about 0.15 – 0.40 l . s^{-1}.

In the scope of the search hydrogeological survey in the years 1990 – 1997 (Pacindová et al., 1997) hydrogeological well V-HC-1 was excavated (between 1/1992 – 2/1992). It reached a depth of 212.6 meters (from 75.9 m to the final depth – mostly sandstone Bialowieza Fm. or bottom of the Bialowieza Fm. Late Palaeocene to Early Eocene in age – Samuel, in Pacindová et al., 1997). The progress of technical work in the hole development was quite complicated.

CO_2 present in rocks and mineral water was causing the problem. Since the drilling was performed in the protection zone of mineral water, it was not possible to use a sufficiently heavy drilling mud, which would prevent eruptions emerging. The first eruption of the drilling fluid with mineral water occurred at a drilling laydown to a depth of 79 m. It lasted about 15 minutes, the height of jet of water reached up to 3 m. When casing a borehole interval from 50 to 130 meters there was another eruption of up to 15 m, lasting about an hour. After washing the well it occurred incoherent impulsive overflow of mineral water from the well. The average yield of the overflow calculated from measuring the volume of water spilled from the well over two hours, was 0.021 l . s^{-1}. Heavily mineralized water (20.5 g . l^{-1}) had a chemical type of Na-HCO_3-Cl. In the course of further borehole development the eruption happened through the drill rod (height of about 16 m, the duration of about 30 minutes, the well produced the fragments of the rock with a diameter of 0.5 cm). With increasing depth of the borehole, the duration of the eruption increased. After the final hole casing it was found that eruptions of mixture of gas and water occurred about once a day after water level in the well reached to a about 1 m below the surface. After the eruption the water table dropped to a depth of about 75 – 80 meters.

Due to the high gas-saturation of rocks and mineral water and more or less regular eruptions, overflow tests were carried out by so-called siphoning. The tests preceded the execution of reconstruction works in bottling borehole CH-1 in order to monitor the pressure on its collar and overflow yield. It was necessary to replace the incrusted

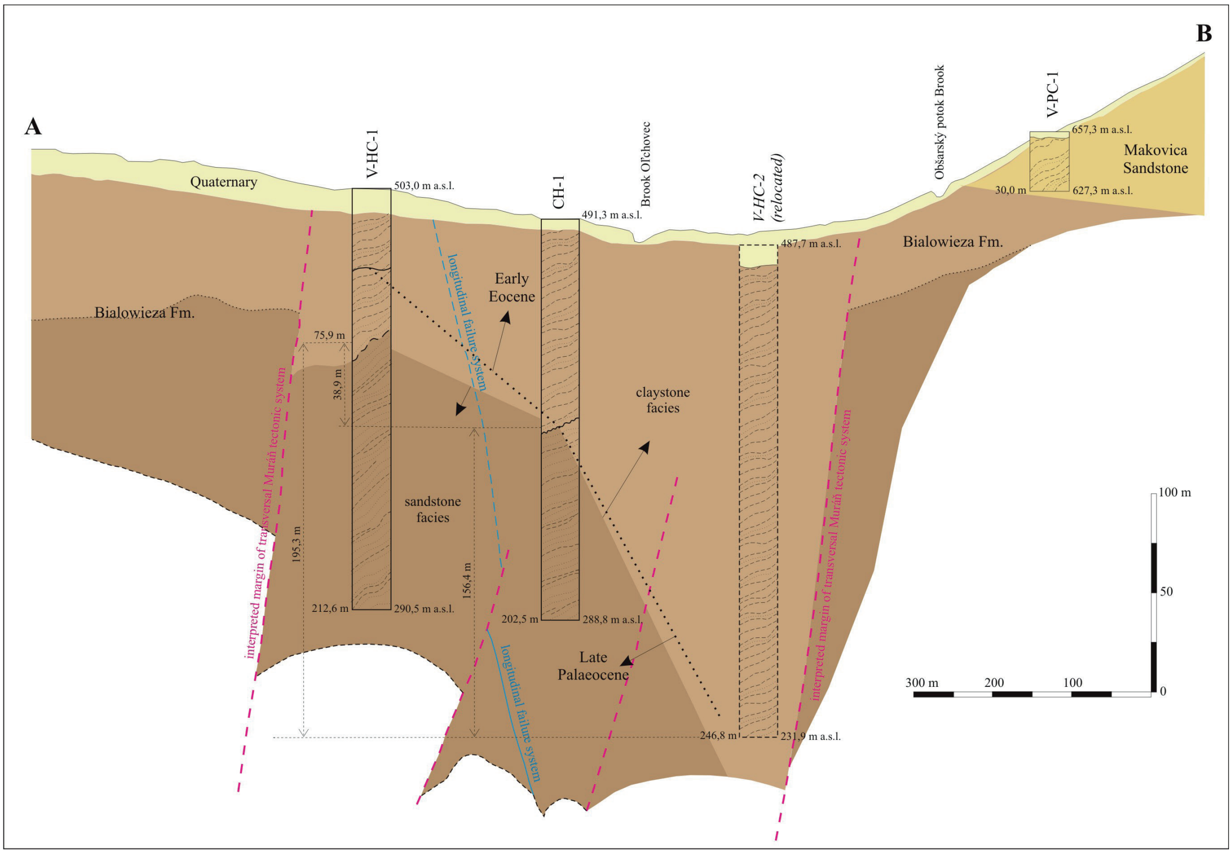


Fig. 7.2 Schematic litho-geological section through discharge area of the natural healing water Cigeľka (compiled by Bačo, 1997; modified)

Slovak Geol. Mag., 16, 2 (2016), 105 – 124

discharge pipe and install functional gauges. The incrust is formed in the pressure pipe from the depth of about 50 m below the surface (Fig. 7. 3). During operation of the Filling Plant in Cigeľka it is necessary to replace the discharge line after about seven to ten years.

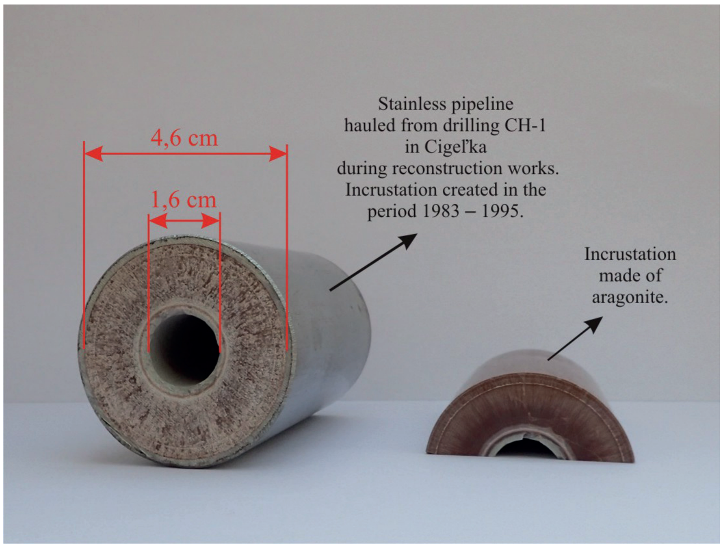


Fig. 7.3 Incrust in the discharge line of the well CH-1 in Cigeľka (photo: Bačová)

The overflow tests in borehole V-HC-1 consisted of three stages – three embedment depths of the discharge pipe (201, 150 and 102 m). During the hydrodynamic tests two-phase fluid – a mixture of gas and water – existed in the borehole V-HC-1. In place of inflow into the borehole the pressure was below the saturation pressure of water with carbon dioxide at the beginning of hydrodynamic tests even when borehole was capped, indicating the existence of the two-phase flow in the collectors immediately surrounding the well. For exploitation of mineral water from the well W-HC-1 based on the results of carried out hydrodynamic tests it was recommended to embed the column to the technically real depth (Jetel, in Pacindová et al., 1997). In the last phase of the first stage of the hydrodynamic test the overflow yield reached 0.076 l . s^{-1}.

Hydrogeological borehole V-HC-2 began to be drilled in August, 1992. The projected depth of 650 m was breached because of considerable technical problems during drilling and casing. The difficulties were caused by different borehole lithology than anticipated, and by the drilling fluid used, which was not sufficiently dense due to the pressure conditions in the borehole (bentonite, lovosa, micro-crushed limestone). Under these circumstances it was not possible to keep the design well structures, therefore the excavation completed at 246.8 meters.

In the scope of the search hydrogeological survey in the years 1990 – 1997 (Pacindová et al., 1997) in the discharge area of the spring the Cigeľka natural mineral water VES field measurements were made (Komoň et al., in Pacindová et al., l. c.). The intention was to distinguish lithological interface between claystone – sandstone. Special conditions in this area – claystone rock environment and underneath environments with a predominance of sandstone with heavily mineralized water (TDS with 30 g . l^{-1}) – did not achieve this goal, but brought another important lesson. Minimum resistance anomalies (below 20 ohmm) substantially correspond to the chemical composition of mineral water from the natural springs known and hydrogeological boreholes. In the most extensive central anomaly (Fig. 7.1) there is documented the presence of mineral water with the highest total dissolved solids content. It can therefore be assumed that space with minimal resistance of the ground follows the presence of strongly mineralized water in a predominantly sandstone Bialowieza Fm.

The following figures (Figs. 7.4, 7.5, 7.6) document CO_2 effervescences in natural mineral springs in the area of deep fault zone of NE-SW direction (likely NW con-

Fig. 7.4 CO_2 effervescence observed in the spring Veterán (photo: Bačová, 24. 8. 2009)

Fig. 7.5 Intense CO_2 effervescence in the spring Mikva (photo: Bačová, 11. 6. 2014)

Fig. 7.6 CO_2 effervescence in the spring Buľkitka (photo: Bačová, 29. 10. 2014)

tinuation of the Muráň tectonic system – Pospíšil et al., 1989). Springs, Pramene Veterán, Mikva and Buľkitka are depicted in Fig. 7.1. Currently they are abandoned, except the first one. Even at the end of the last Century at the margin of the discharge area of the Cigeľka mineral water there were observed effervescences of CO_2 in the artificial pond, used for recreational purposes (Fig. 7.7).

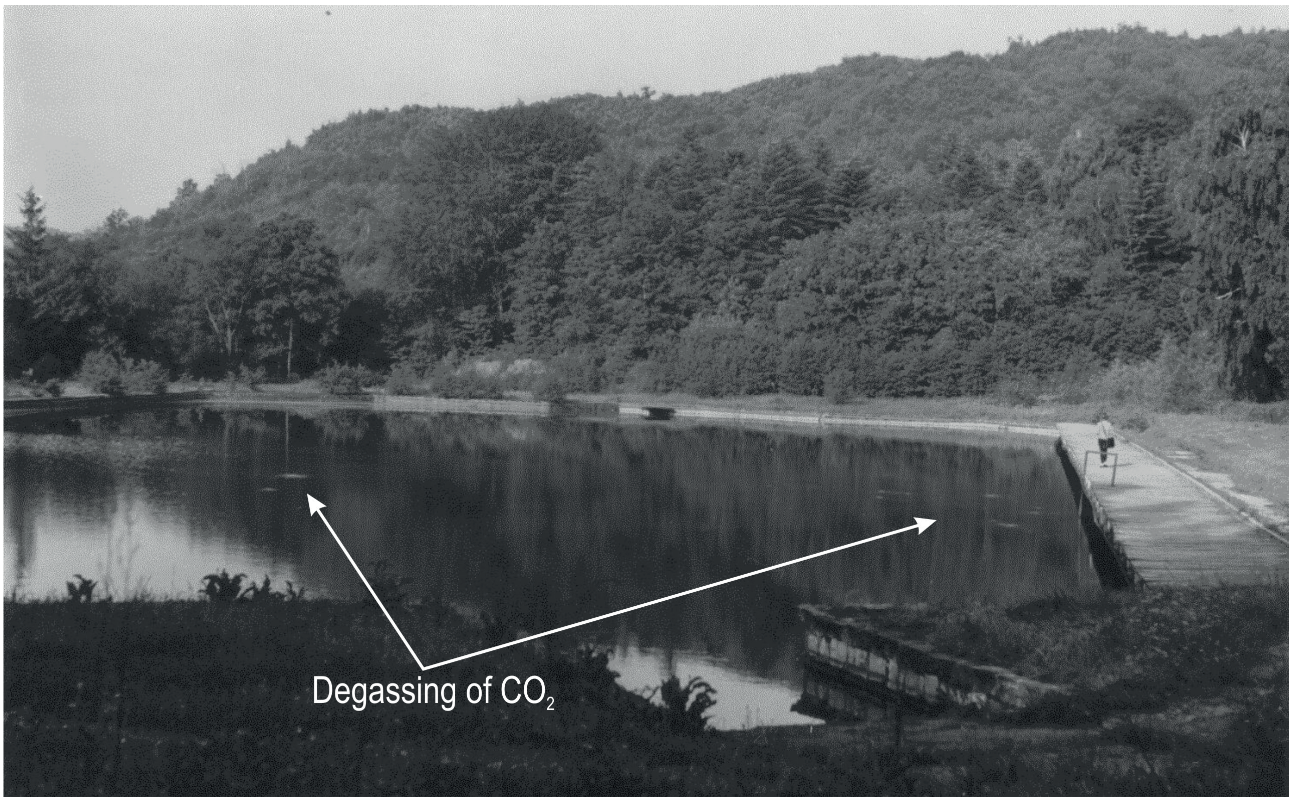


Fig. 7.7 CO_2 effervescence in the pond in Cigeľka (photograph of 1995)

Tab. 7.1 Chemical composition of the Cigeľka natural mineral water from the well CH-1 and V-HC-1

Analysis Date	TDS	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HCO_3^-	CO_2	I^-	B	Br^-	Analysis by
	[g . l^{-1}]	[mg . l^{-1}]											
well CH-1													
1973	28.98		8,295		208.42	78.79	16.46	16,657.9	2,710	2.60	98.77	28.0	IGHP
25.3.1981	30.30	12.70	8,286	285	207.60	91.40	17.20	16,845.7	2,250		139.41		Slovakoterma Piešťany
10.2.1982	29.15		8,217	340	201.10	56.10	19.70	16,138.5	2,253				Slovakoterma Piešťany
16.8.1983	29.48		8,203	850	209.10	80.50	18.30	16,791.5	2,250				Slovakoterma Piešťany
22.8.1984	29.52	12.70	8,001	345	208.45	79.80	17.50	16,461.0	2,803	6.72	143.30	24.1	Slovakoterma Piešťany
24.6.1986	29.76	10.20	8,379	154	163.53	74.42	376.32	16,474.9	1,950				Slovakoterma Piešťany
29.9.1987	29.64		8,145	205	204.70	75.00	18.50	16,783.1	2,670		135.22		Slovakoterma Piešťany
27.8.1992	29.37		8,336	135	184.20	92.00	15.00	16,690.3	1,925				GSSR Bratislava
14.9.1993	29.57		8,401	141	170.80	88.85	22.00	16,894.3	2,177				GSSR Bratislava
21.7.1994	28.91	9.80	7,680	145	200.96	85.31	17.29	16,962.5					GSSR Bratislava
5.10.1994	30.46	7.20	8,453	150	169.00	90.70	15.00	17,125.7	2,012				GSSR Bratislava
27.3.1995	28.07	7.46	7,500	140	267.65	46.37	7.82	16,626.9					GSSR Bratislava
11.4.1995	29.23	10.42	8,410	156	172.06	92.75	18.93	16,657.4		12.69	110.90		GSSR Bratislava
2.5.1995	29.26	10.71	9,067	286	168.24	68.40	9.88	15,868.3		13.55	173.40		GSSR Bratislava
9.12.2005	30.31	10.80	8,385	235	173.00	78.30	17.05	16,653.0	2,187	1.53		19.8	BEL/NOVAMANN International. s.r.o.
well V-HC-1													
2.6.1992	15.99	5.20	4,150	1	250.50	18.23	71.61	9,304.9	2,150				GSSR Bratislava
30.6.1992	20.50	6.85	5,950	208	80.16	72.92	174.09	10,744.9	2,360				GSSR Bratislava
30.9.1992	28.65	8.85	8,050	156	241.15	170.61	15.64	14,918.4	2,620				GSSR Bratislava
10.2.1993	29.21	9.50	8,125	190	26.95	4.84	45.29	16,840.4	2,680				GSSR Bratislava
24.3.1993	29.15	18.10	8,050	16	259.48	66.57	4.12	16,809.9	2,230				GSSR Bratislava
1.6.1993	26.87	9.10	7,500	145	54.17	58.40	16.87	13,210.0	2,750				GSSR Bratislava
24.8.1993	27.59	6.48	6,514	145	230.74	66.92	4.52	14,826.9	1,950				GSSR Bratislava
24.11.1993	30.48	7.20	7,717	148	29.94	296.55	9.88	17,938.7	2,040				GSSR Bratislava
8.4.1995	29.61	9.94	8,620	165	210.30	75.36	23.46	16,748.9	2,640	12.69	102.60		GSSR Bratislava
1.5.1995	29.20	10.75	8,978	173	195.01	2.90	9.88	14,662.1		14.00	160.50		GSSR Bratislava
1.5.1995	29.64	42.60	8,200	200	216.43	77.82	26.13	16,470.0	1,210	13.75	128.00	19.05	Unigeo. a.s. Ostrava

7.4 Chemical composition of mineral water in Cigeľka and its vicinity

The Cigeľka natural mineral water (previously supplied to the commercial network as a "natural healing water Cigeľka", later "natural healing water Cigeľka") is exploited at the well CH-1; the chemical type is Na-HCO_3-Cl. In accordance with the Health Ministry Decree no. 100/2006 Coll. as amended (with effect from 1. 7. 2013) is a bicarbonate-chloride sodium carbonic brine, with increased content of *sodium, chlorides*, *iodine, hydrogen-carbonates* with increased content of nutrient-physiological elements – *lithium, magnesium, calcium and boron*, neutral, cold. It is likely formed by mixing two types of water – Na-HCO_3-(Cl) and Na-Cl – at the conduits to the surface (Bačová & Bačo, 1998), where it penetrates thanks to deep-reaching fault system of NE-SW direction. Its presence (dispersion) in the rock environment of the discharge area is manifested in increased chloride content of weakly mineralized waters of natural springs (Fig. 7.1). Selected characteristics of the chemical composition of mineral water from boreholes CH-1 and V-HC-1 are shown in Tab. 1. Analyses of deep gas samples and samples taken from the separator in the course of hydrodynamic tests in borehole V-HC-1 (in 1995) are presented in the Tab. 7.2.

Tab. 7.2 Gas analyses – well V-HC-1 (Prokop, 1995 in Pacindová et al., 1997)

Gas composition	**CO_2**	**CH_4**	**N_2**	**H_2**
Gas sample	[meq . l^{-1} %]			
From separator	98.646	0.716	0.637	0.001
Deep sampling - 98 m	99.012	0.93	0.006	0.053
Deep sampling - 100 m	99.16	0.833	0.007	0

Macrochemical composition of mineral water in Cigeľka and its wider area is described in Tab. 3. In the case of water from the hydrogeological boreholes and dug wells (including perished or destroyed) situated nearby bottling plant in Cigeľka (Fig. 7.8 right – green circles), the water is of the type Na-HCO_3-Cl with a TDS of greater than 10 g . l^{-1}, except for the well TD-3 (4.8 g . l^{-1}). The content of chloride and bicarbonate indicate a positive linear correlation with high level of significance.

Dark blue triangles in the diagram (Fig. 7.8) represent the mineral water springs:

- In the discharge area of the Cigeľka natural mineral water,
- Buľkitka in Petrová (springing south of Cigeľka, also in the area of deep reaching fault zone of NE-SW direction – likely NW continuation of the Muráň tectonic system),
- in Frička,
- in Nižný and Vyšný Tvarožec.

They are waters of the type Na-HCO_3 with high chloride content (range 9 – 12 meq . l^{-1} %; in the case of mineral water from the spring Buľkitka in Petrová 7 meq . l^{-1} %). Here, too, we observe significant positive linear relationship between the content of bicarbonate and chloride.

Other mineral water springs remote off the discharge area of the Cigeľka natural mineral water and from the surrounding area (Hrabské, Petrová, Gaboltov; Fig.7.8 – blue circles) have indeed increased the TDS with varying proportions hydro-silicatogenic mineralization, but they are not impacted by heavily mineralized water with high chloride content (deeper circulation).

The relationship between sodium and chlorides in the mineral waters of Cigeľka and its surroundings (Fig. 7.8

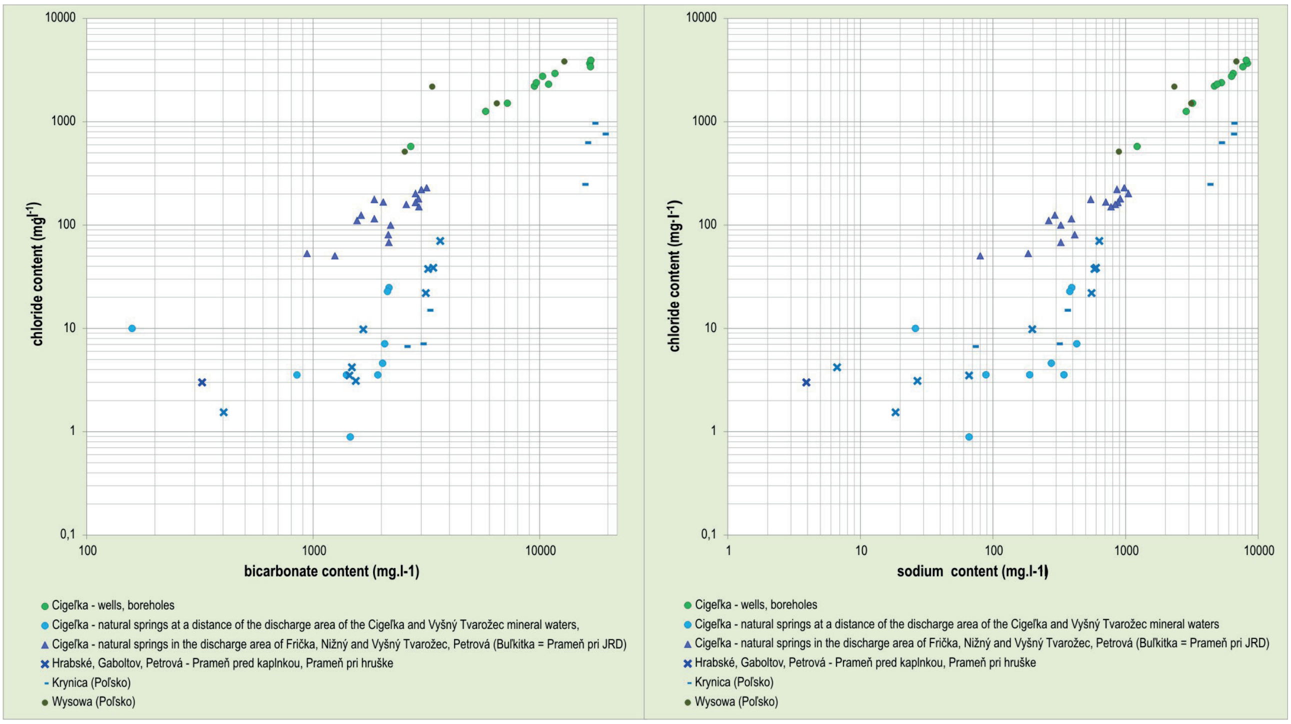


Fig. 7.8 Bicarbonate, chloride and sodium content in the Cigeľka mineral waters source and its surroundings

Tab. 7.3 Selected data on the macrochemical composition of mineral waters in wider surroundings of the discharge area of the Cigeľka natural mineral water

Source of mineral water (depth)	TDS	Na^+	Cl^-	HCO_3^-	Chemical water type [≥ 25 meq . l^{-1} %]	Data source
	[mg . l^{-1}]					
Cigeľka, Štefan (BV-26G), 29 m	19,145	4,670	2,212	9,484	Na-HCO_3-Cl	Krahulec et al., 1978
Cigeľka, VIII (CH-1; BV-99), 200 m	28,976	8,295	3,680	16,658	Na-HCO_3-Cl	Krahulec et al., 1978
Cigeľka, (V-HC-1) 212 m	29,214	8,125	3,936	16,840	Na-HCO_3-Cl	Pacindová et al., 1997
Cigeľka, well P-1 (BV-92)	28,800	7,655	3,408	16,775	Na-HCO_3-Cl	Franko & Kolářová, 1983
Cigeľka, well CŠ-3 (90 m)	4,802	1,220	576	2,697	Na-HCO_3-Cl	Haluška, 1967
Cigeľka, Ľudovít	21,868	6,475	2,936	11,690	Na-HCO_3-Cl	Hensel et al., 1955
Cigeľka, Ľudovít	12,290	3,200	1,511	7,200	Na-HCO_3-Cl	Michalíček & Květ, 1960
Cigeľka, Štefan (BV-26G), 29 m	17,978	5,287	2,389	9,675	Na-HCO_3-Cl	Hensel et al., 1955
Cigeľka, Štefan (BV-26G), 29 m	18,581	4,900	2,312	10,959	Na-HCO_3-Cl	Michalíček & Květ, 1960
Cigeľka, Slovan	10,072	2,860	1,259	5,773	Na-HCO_3-Cl	Michalíček & Květ, 1960
Cigeľka, well V-PC-8	21,946	6,300	2,757	10,312	Na-HCO_3-Cl	Pacindová et al., 1997
Cigeľka, Mikva	4,380	1,050	202	2,831	Na-HCO_3	Pacindová et al., 1997
Cigeľka, Mikva (BV-24)	4,372	911	180	2,917	Na-HCO_3	Krahulec et al., 1978
Cigeľka, Prameň v obci	2,902	393	25	2,163	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Prameň v obci (BV-25)	2,922	380	23	2,130	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Veterán (BV-26)	4,211	874	166	2,831	Na-HCO_3	Krahulec et al., 1978
Cigeľka, Veterán* (BV-26)	3,825	835	159	2,578	Na-HCO_3	Pacindová et al., 1997
Cigeľka, Dolina	1,879	189	4	1,403	Na-Ca-Mg-HCO_3	Pacindová et al., 1997
Cigeľka, Busov	1,150	89	4	848	Ca-Na-HCO_3	Pacindová et al., 1997
Cigeľka, Pálenica	1,949	66	1	1,458	Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Lazce I (BV-21)	2,727	275	5	2,026	Ca-Na-HCO_3	Krahulec et al., 1977
Cigeľka, Lazce II (BV-22)	3,050	414	81	2,148	Na-Ca-HCO_3	Krahulec et al., 1977
Cigeľka, Lazce*	2,824	546	177	1,861	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Glória*	3,117	710	168	2,041	Na-HCO_3	Pacindová et al., 1997
Cigeľka, Lacková*	1,778	80	51	1,248	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Matka (BV-26D)	324	26	10	159	Ca-Na-HCO_3-SO_4	Krahulec et al., 1977
Nižný Tvarožec	1,410	184	53	940	Na-Ca-HCO_3	Pacindová et al., 1997
Nižný Tvarožec, Kvašna voda (BV-53)	2,264	263	111	1,562	Na-Ca-HCO_3	Krahulec et al., 1977
Vyšný Tvarožec 1	2,687	343	4	1,931	Ca-Na-HCO_3	Pacindová et al., 1997
Vyšný Tvarožec 2	2,753	428	7	2,068	Na-Mg-HCO_3	Pacindová et al., 1997
Vyšný Tvarožec (BV-76)	2,374	292	125	1,629	Na-Ca-HCO_3	Krahulec et al., 1977
Frička, Frička 1	4,389	860	222	3,002	Na-HCO_3	Pacindová et al., 1997
Frička, Frička 2	4,145	775	151	2,929	Na-Mg-Ca-HCO_3	Pacindová et al., 1997
Frička, Frička 3 - Plazínska	2,669	390	115	1,861	Na-Ca-HCO_3	Pacindová et al., 1997
Frička, Kyselka (BV-29)	4,688	979	231	3,170	Na-HCO_3	Krahulec et al., 1977
Hrabské, Prameň na hraniciach (BV-40)	516	4	3	323	Ca-HCO_3	Krahulec et al., 1977
Hrabské, Prameň nad potokom (BV-35)	4,355	582	38	3,220	Na-HCO_3	Krahulec et al., 1977
Hrabské, Prameň na hornom konci (BV-36)	4,355	554	22	3,145	Na-Ca-HCO_3	Krahulec et al., 1977
Hrabské, Prameň pri poľnej ceste (BV-38)	2,149	7	4	1,482	Ca-HCO_3	Krahulec et al., 1977
Hrabské, Prameň pri gerlachovskom chotári (BV-39)	4,569	598	39	3,390	Na-Ca-HCO_3	Krahulec et al., 1977
Hrabské, Tri pramene v potoku (BV-41)	4,998	633	70	3,640	Na-Ca-HCO_3	Krahulec et al., 1977
Petrová, Prameň pred kaplnkou (BV-54)	1,949	66	4	1,445	Ca-HCO_3	Krahulec et al., 1977
Petrová, Prameň pri hruške (BV-55)	2,074	27	3	1,544	Ca-HCO_3	Krahulec et al., 1977
Petrová, Prameň pri JRD (BV-56)	3,026	325	68	2,160	Ca-Na-HCO_3	Krahulec et al., 1977
Petrová, Buľkitka	3,085	325	100	2,197	Ca-Na-HCO_3	Pacindová et al., 1997
Gaboltov, Prameň pri kríži (BV-30)	2,217	198	10	1,666	Ca-Na-HCO_3	Krahulec et al., 1977
Gaboltov, Prameň pri ceste (BV-87)	610	18	2	403	Ca-HCO_3	Krahulec et al., 1977
Krynica - Zuber I	22,619	5,074	628	15,921	Na-HCO_3	Rajchel, 2012
Krynica - Zuber II	21,045	4,151	248	15,494	Na-HCO_3	Rajchel, 2012
Krynica - Zuber III	25,372	6,311	968	17,141	Na-HCO_3	Rajchel, 2012
Krynica - Zuber IV	27,218	6,270	762	19,038	Na-HCO_3	Rajchel, 2012
Krynica - Mieczyslaw	4,278	350	15	3,202	Ca-Na-HCO_3	Rajchel, 2012
Krynica - Glówny	3,434	71	7	2,537	Ca-HCO_3	Rajchel, 2012
Krynica - Slotwinka	3,927	304	7	2,988	Mg-Na-HCO_3	Rajchel, 2012
Wysowa - Alexandra	24,714	6,834	3,829	12,850	Na-HCO_3-Cl	Rajchel, 2012
Wysowa - Franciszek	8,936	2,333	2,187	3,356	Na-Cl-HCO_3	Rajchel, 2012
Wysowa - Anna	11,738	3,122	1,507	6,468	Na-HCO_3-Cl	Rajchel, 2012
Wysowa - Władysław	4,376	890	514	2,538	Na-HCO_3-Cl	Rajchel, 2012

right) is also characterized by significant dependence in the above-described two Na-HCO_3-Cl and Na-HCO_3 types.

Both graphs (Fig. 7.8) are supplemented by information on the content macro-components in the mineral waters from the nearby border area in Poland (Tab. 7.3). Weakly to strongly mineralized waters from the sources in the Wysowa Spa (aboutan 4 km of Cigeľka and located on NE continuation of the same deep-reaching fault zone) have nearly identical macrochemical composition (dark green circles in Fig. 7.8). Mineral waters known in Krynica (14 km west of Cigeľka) differ from these waters by significantly lower chloride content.

Carbon dioxide in the rock environment of the Cigeľka discharge area and its wider surroundings is an important phenomenon affecting the transport of mineral water. It is manifested by a large number of natural springs of carbonic mineral waters and the dry spontaneous emissions of CO_2. In Poland they are termed mofettes (e.g. mofettes near Zlockie described in detail by Rajchel & Rajchel (2006), mofettes in the wider area of the spa of Krynica). The origin of this gas (significantly affecting the chemical composition of mineral water) is mainly associated with deep-reaching faults (Muráň tectonic system; Pospíšil et al., 1989) with signs of Neogene magmatism in closer but especially in the wider area. The presence of oxalates (whewellite) found in borehole V-HC-1 in the cracks of sandstone around Cigeľka (Bačo & Pacindová, 1993) may also point to a probable, but not a substantial proportion of carbon (and thus CO_2) of organic origin (Bačo & Pacindová, l.c; Hofmann & Bernasconi, 1998). This is the first description of whewellite (Fig. 7.9a, b) in the Slovak part of the Western Carpathians. On steeply dipping fractures, with a width of up to 1 cm it forms translucent to white--grey crystalline aggregates. In the cavernous parts there are developed crystal planes with a strong glassy luster.

The high presence of CO_2 and the mineral water of Na-HCO_3 type is generally characterized by the formation of dawsonite (Uher & Michalík, 1991). This mineral has been described in the cracks of sandstone from the hydrogeological boreholes V-HC-1 and V-HC-2 (Bačo & Pacindová, 1993) as a relatively abundant filler (Fig. 7.9c, d). In the cracks with a width of a few millimetres to 1.3 centimetres it forms snow-white radiate aggregates with pearl luster.

Results of the determination of stable isotopes of hydrogen and oxygen in the mineral waters of natural springs in the discharge area in Cigeľka and Frička (Michalko, in Pacindová et al., 1997) significantly complement the findings described above. The Cigeľka natural mineral water is not participating in the "live" water cycle, which is confirmed by its isotopic composition [$\delta^{18}O_{H_2O}$ 4,22 ‰ and δD_{H_2O} -37,2 ‰]. These mineral water springs in the discharge area in Cigeľka and the Frička have an increased chloride content, and at the same time increased content of the isotopes ^{18}O and D in comparison with the ordinary groundwater of the territory of interest. This is likely manifestation of strongly mineralized water originating in greater depth.

7.5 The Cigeľka natural mineral water in relation to mineral waters of the Flysch Zone in the Carpathians

Study of the processes of formation and genesis of the Cigeľka mineral water requires to perform the analysis of voluminous information gathered so far – geological, geochemical, hydrogeological and hydrogeochemical. The basis for the subsequent image processing and interpreting the relationship between selected qualitative characteristics of mineral water is a set of data on the chemical composition of mineral waters of the Flysch Zone and the Foredeep of the Western Carpathians (in Moravia, Slovakia, Poland and partly Ukraine), obtained from the available domestic and foreign publications and final reports of various geological tasks.

In Fig. 7.10 there are shown the chemical types of mineral waters of selected sites depicted on the structural scheme of the Flysch Zone and the Foredeep of Carpathians compiled by Lexa et al. (2000). The used classification is based on the principle of the prevailing ions; brackets in the title of the chemical type mean contents of a component in the range 10 – 25 meq . l^{-1} % – in this way only chlorides content is shown in Fig. 7.10. Sources of data used on mineral waters of Moravia, Slovakia and Poland are cited in Fig. 7.11., data on the mineral waters of the territory of Ukraine we received from publications Kolodij & Kojnov (1984).

Macrochemical composition of mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians (Slovakia, Moravia and Poland) is shown in Fig. 7.11. In the chart with a logarithmic scale coefficients $(Na^+ + K^+)/HCO_3^-$ a $(Ca^{2+} + Mg^{2+})/HCO_3^-$ are plotted (Bačová, 2011), calculated from data on ion content expressed in mass concentrations (mg . l^{-1}). The graph provides a comprehensive view of macrochemical composition of mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians. It also allows to assess the likely participation of different mineralization processes in resulting chemical composition of mineral waters at specific sites – including Cigeľka. The set of hydrogeochemical data contains the results of 234 analyzes of mineral waters.

Gradual change in the chemical composition of water from the Na-HCO_3 type through Na-Cl-HCO_3 and Na-Cl-HCO_3 up to Na-Cl type is shown in Fig. 7.11., expressed by signs colour. Bicarbonate waters are represented by the signs of blue colour and chloride waters or waters with a predominance of chloride in anion composition in shades of green. The TDS of water (Fig. 7.12) is in the range 228 – 126,139 mg . l^{-1}.

The highest TDS have chloride waters of the type Na-Cl and Na-Ca-Cl from the space of the Foredeep of the Western Carpathians – present in the Neogene sediments (Lapczyca) and basement of the flysch nappes of Krosno Group (Fig. 7.10., Devonian, borehole U-3A of the Ustroń Spa in Poland, brine exploited at a depth of 1,318 – 1,728 meters – Rajchel et al., 2007). This are highly mineralized waters to strong brines with TDS more

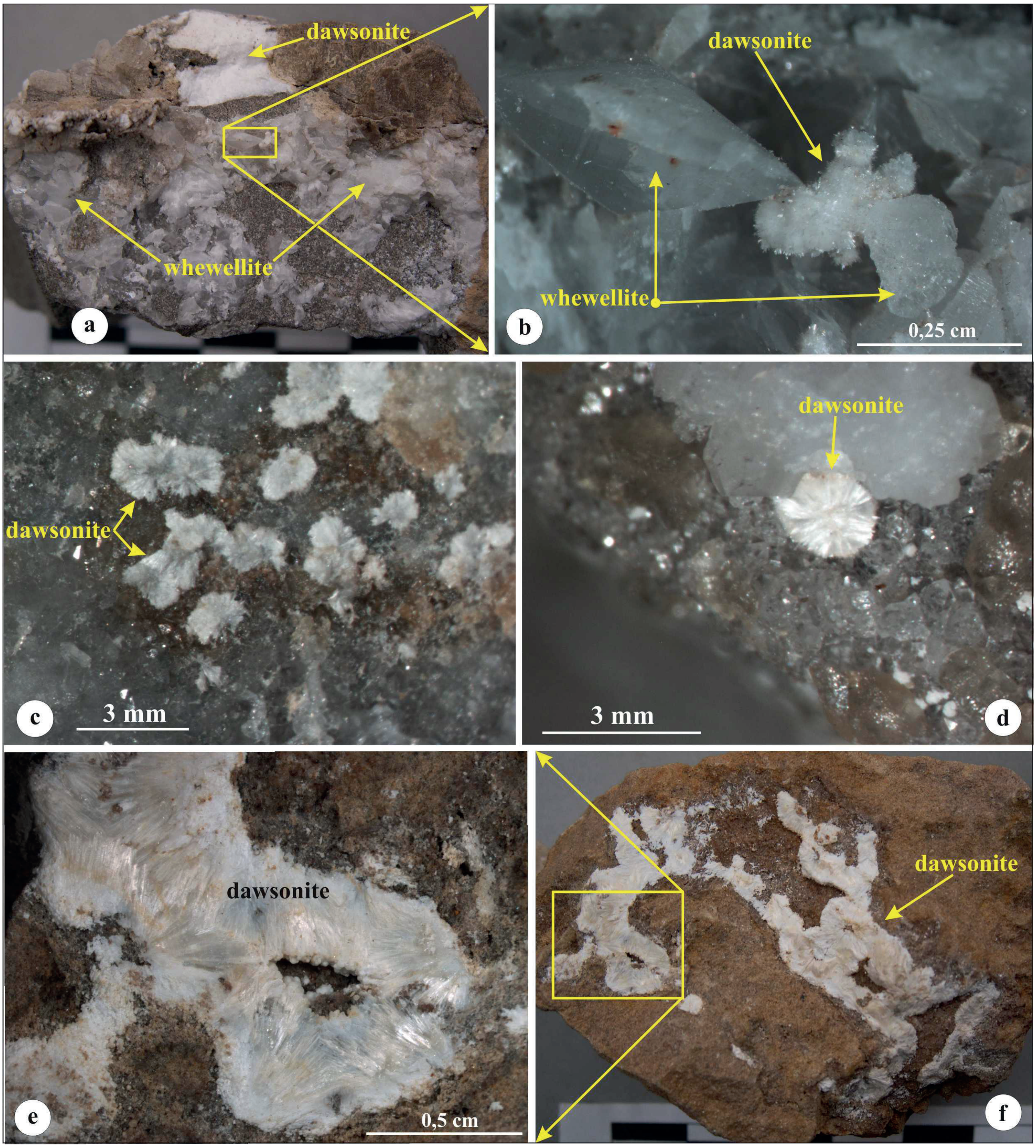


Fig. 7.9 Epigenetic minerals documented in the core recovery of hydrogeological boreholes in Cigeľka. Crystal aggregates of whewellite – Ca (C_2O_4) . H_2O on the wall of crack in sandstone (a), and crystals of whewellite (b) with needle-shaped dawsonite in the borehole V-HC-1/190.6 m. The radial aggregates of dawsonite – NaAl (CO_3) $(OH)_2$ (c, d) in the borehole V-HC-2/42.8 m and radiating thin-needle-shaped aggregates in the sandstone fissure in the valley NW of Cigeľka mineral water plant (e, f). Photo: Bačo.

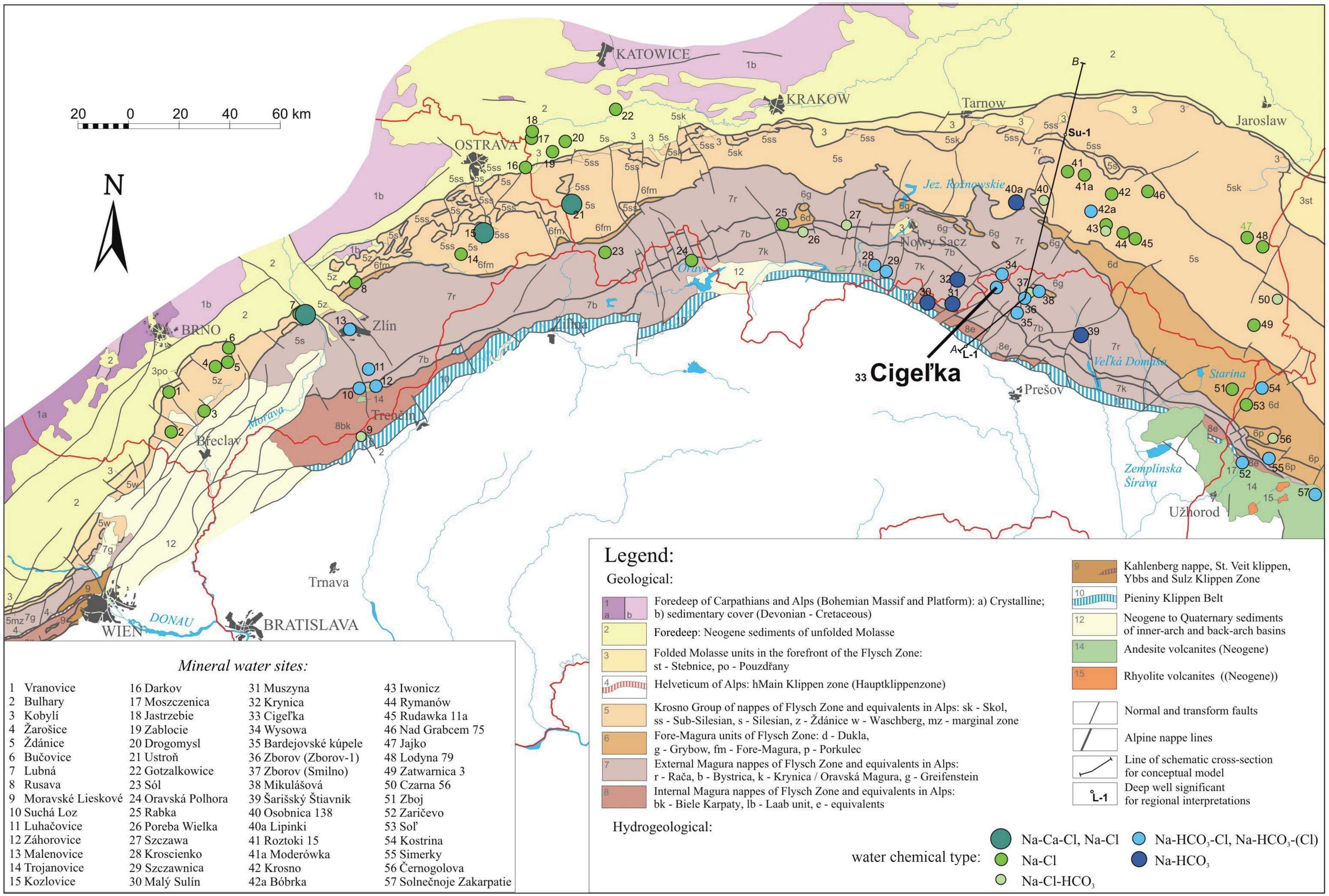


Fig. 7.10 Macrochemical composition of mineral waters of the Flysch Zone and of the Foredeep of Carpathians (Moravia, Slovakia, Poland, partly Ukraine), on the structural scheme (Lexa et al., 2000) – compiled by Bačová, 2013

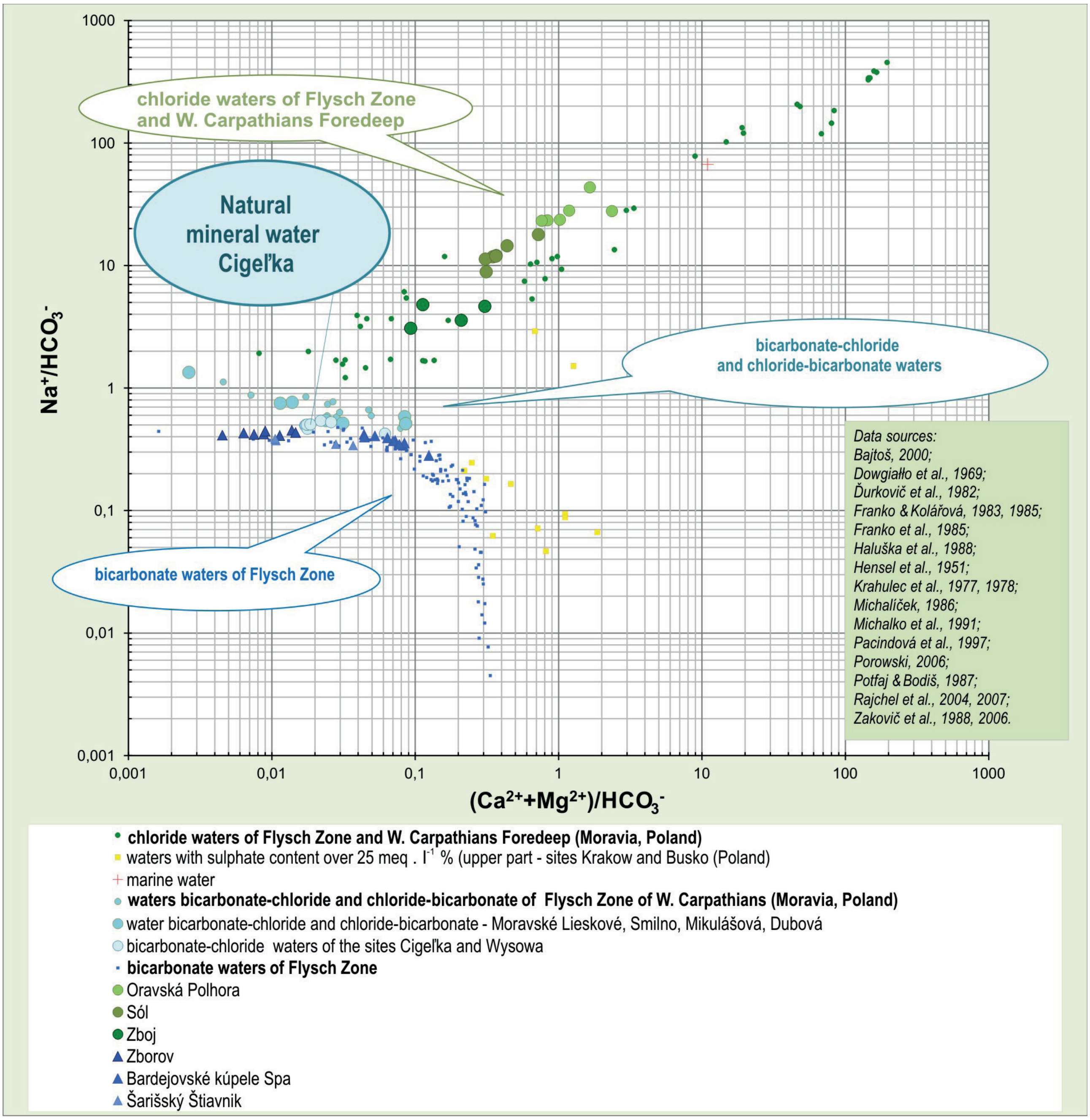


Fig. 7.11 The chemical composition of mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians, with distinguishing of water types and selected sites

than 100 g . l^{-1} (Fig. 7.10 – dark-green ring no. 21). In Fig. 7.11 the strong brine from the Ustroń location is represented by a group of small dark-green rings with the highest content of sodium and chloride – the top right. Within the Flysch Zone in Slovakia the chemical Na-Cl type posses the brines from sites Zboj (Ďurkovič et al., 1982) and Oravská Polhora (Zakovič et al., 2009). From a genetic point of view they are *sedimentation waters – buried* (Kirjuchin et al. in Švarcev 1996, *fossil marine* according to genetic classification of natural waters compiled by Pačes, 1983). Highly mineralized waters to brines, of the type Na-Cl with thalassogenic mineralization always take up a position to the top of the graph (ratio Na^+ / HCO_3^- is greater than 1).

Sodium chloride (Na-Cl) type of groundwater occurs everywhere in the vertical profile as the thickest hydrogeochemical zone – zone of brines. We encounter it at different depths (in the artesian basins it is present only a few hundred meters below the surface, in the hydrogeological massifs it is present in depths of up to several kilometres), but clearly does not depend on the type of rock environment in which it appears. In general, this is the hydrogeochemical stagnation zone (Macioszczyk & Dobrzyński, 2007). The main source of chloride in groundwater is water of seas and lagoons, buried in the course of formation of sedimentary rocks of marine origin.

Bicarbonate water – from the genetic point of view *of meteoric origin* – is shown in Fig. 7.11. at the bottom of the graph – the coefficient of Na^+/HCO_3^- is always less than 1 (predominantly the value is less than 0.5). This includes mineral waters of the type $Na-HCO_3$ from numerous natural springs of the Flysch Zone of Eastern Slovakia – in the chart particularly in the middle of the left lower quadrant (Fig. 7.11). In the same quadrant in the right side of the body representing concentrated mineral waters with a predominance of calcium and magnesium in the cationic composition, whereas these waters are very weakly to weakly mineralized (most natural mineral water springs in the eastern section of the Flysch Zone). Depending on the factors and the processes of formation of bicarbonate water (the residence time in the rock environment, circulation depth, the action of juvenile CO_2, the intensity of the ion exchange processes, etc.), the chemical composition of this water is changing from $Ca(Mg)-HCO_3$ (bottom right quadrant) to $Na-HCO_3$ type (top left quadrant; Fig. 7.11). Mineralization effect of deep CO_2 is manifested by a shift of signs to the top left. The anion composition of mineral waters of the Flysch Zone of the shallowest circulation, forming the upper part of the zone of active water-exchange, with a total dissolved solids generally less than 1 g . l^{-1} is dominated by bicarbonates, which are a normal component of the groundwater. Kirjuchin (2008) notes that the chemical composition of ordinary hydrogen bicarbonate lime waters is formed by biogenic processes and up to half of the carbon gets into the water from biogenic CO_2. The other half comes from carbonate rocks. Even in the mineral waters of the shallow circulation of the eastern section of the Flysch Zone (especially poorly mineralized) bicarbonates are likely of this origin. As a result of the processes of oxidation of sulphides (pyrite) content of sulphates increases in mineral water, resulting in a change in the type of sulphate and bicarbonate-sulphate-hydrogen-carbonate. Reduction processes of sulphates contribute to emergence of sulphane waters. Another important process of formation of the chemical composition of these mineral waters is the hydrolytic degradation of silicate minerals (enriching water in sodium and silicon).

With increasing depth of circulation and residence time of water in the rock environment increase total dissolved solids and other mineralization processes share.

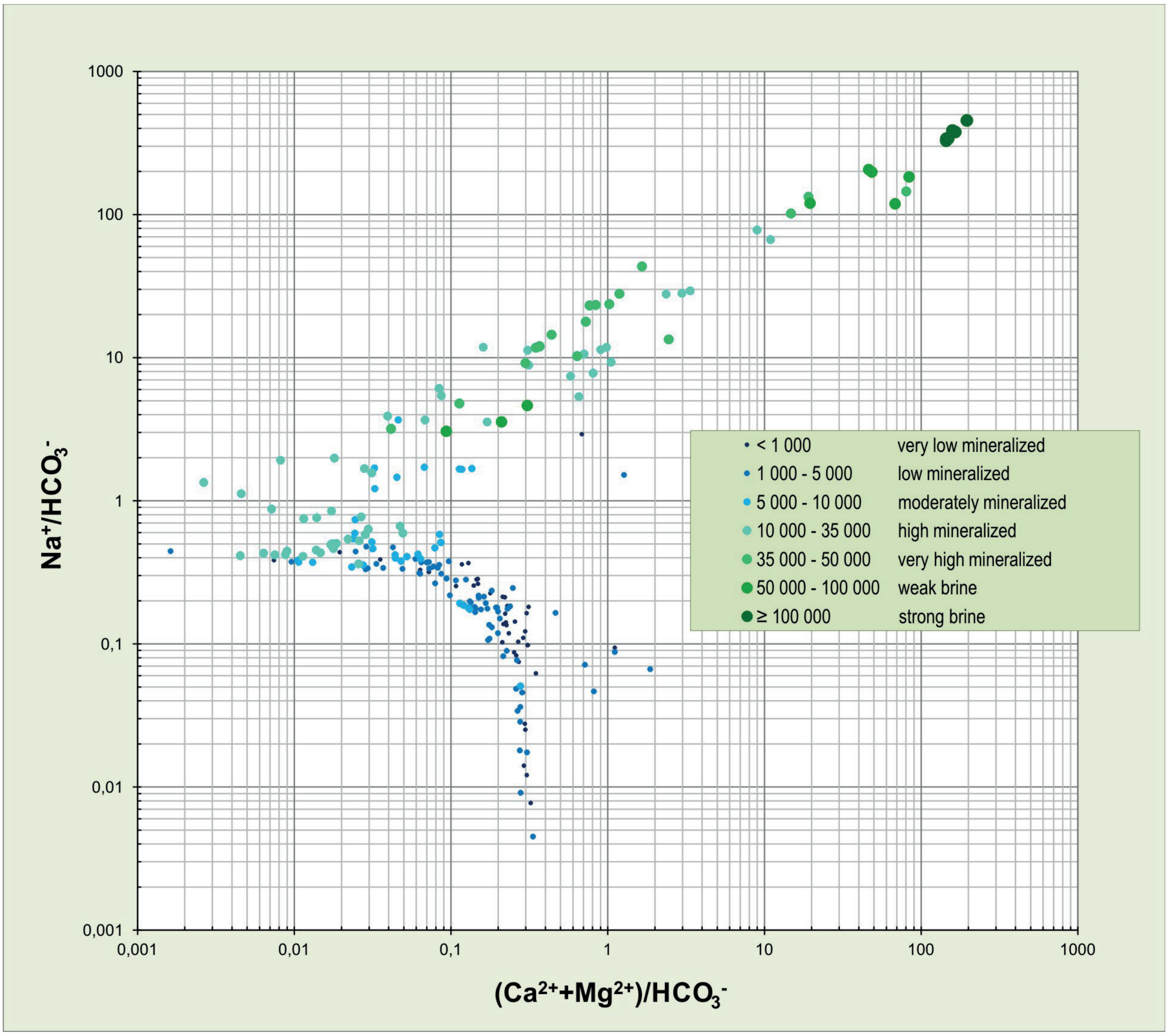


Fig. 7.12 Total dissolved solids (mg . l^{-1}) in mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians

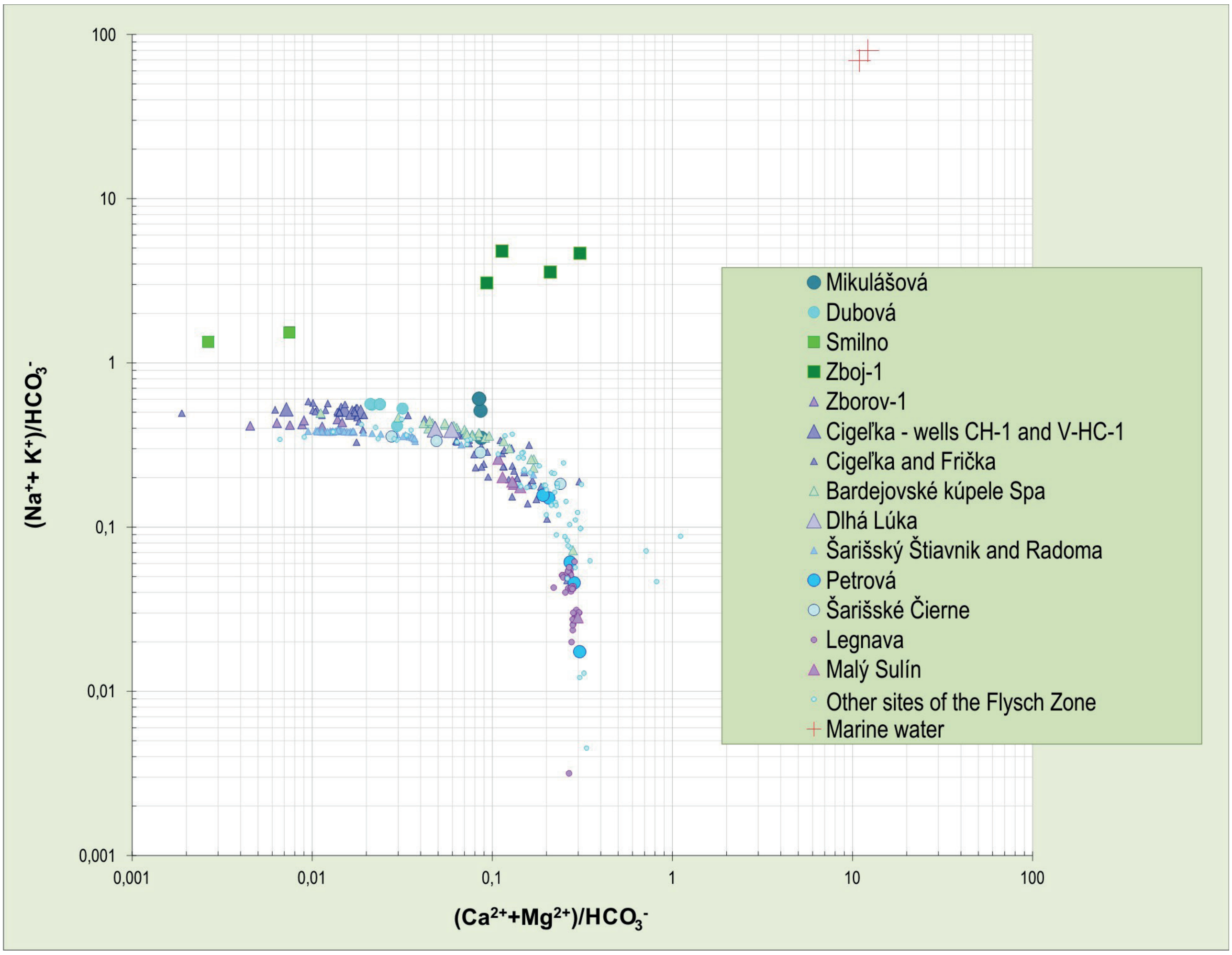


Fig. 7.13 Relationship between coefficients $(Na^+ + K^+)/HCO_3^-$ and $(Ca^{2+} + Mg^{2+})/HCO_3^-$ in the mineral waters of the eastern section of the Flysch Zone

Ion exchange process is becoming important (in claystone complexes), which is manifested by changing the type of water from Ca(Mg)-HCO_3 to Na-HCO_3. The high content of bicarbonates in mineral waters is essentially due to the presence of CO_2 of deep origin.

The values of the coefficient of Na^+/HCO_3^- in the approximate range from 0.5 to 1.5 have mineral waters of the chemical type Na-HCO_3-(Cl) to Na-HCO_3-Cl known from sites in the inner periphery of the Carpathian arc (Fig. 7.10, for example, Luhačovice, Cigeľka, Wysowa, Szczawa). In the graph (Fig. 7.11.) they are represented by water from boreholes CH-1 and V-HC-1 of the source of Cigeľka and the source Alexander in Wysowa (Poland). This includes bicarbonate-chloride and chloride-bicarbonate water (chemical type Na-HCO_3-Cl to Na-Cl-HCO_3) of the area of Moravské Lieskové (well KLK-1), Smilno (borehole Otto-II) and water from Mikulášová and Dubová (natural mineral springs on northern margin of the Smilno tectonic inlier). Their macrochemical composition is the result of mixing of described above meteoric and sedimentation waters in varying proportions.

Detailed insight into the macrochemical composition of mineral waters of the eastern section of the Flysch Zone provides Fig. 7.13. The sample file of processed data includes analyses of 306 water samples taken so far under various stages of registration of mineral waters, hydrogeological research and exploration of springs, wells and boreholes at known locations. Variable share of sedimentation waters of the Na-Cl type in the chemical composition of mineral waters is reflected in the graph by signs with a significant shift upward. The waters of the type Na-HCO_3-Cl and Na-Cl-HCO_3 surge in natural seeps in major tectonically disturbed zones, or they were detected by boreholes (hydrogeological and deep-structural). These are waters of the sites Mikulášová (Krahulec et al., 1977; Franko & Zakovič, 1980), Dubová (Krahulec et al., 1977 and 1978; Franko & Zakovič, 1980), Bardejovské kúpele and Dlhá lúka (Krahulec et al., 1977 and 1978; Haluška & Petrivaldský, 1988), Cigeľka and Wysowa (Krahulec et al., 1977 and 1978; Malatinský et al., 1984; Pacindová et al., 1997; Dowgiałło et al., 1969, Rajchel, 2012), Zborov (borehole Zborov II – Otto /Franko et al., 1985/). The high content of bicarbonates in them reflects the presence of the deep CO_2.

The waters of the type Na-HCO_3 from the sites Šarišský Štiavnik and Radoma, Šarišské Čierne, Pčoliné are examples of the waters, which TDS is increased mainly due to the action of the deep CO_2 and ion exchange processes (water hydrosilicatogenic mineralization).

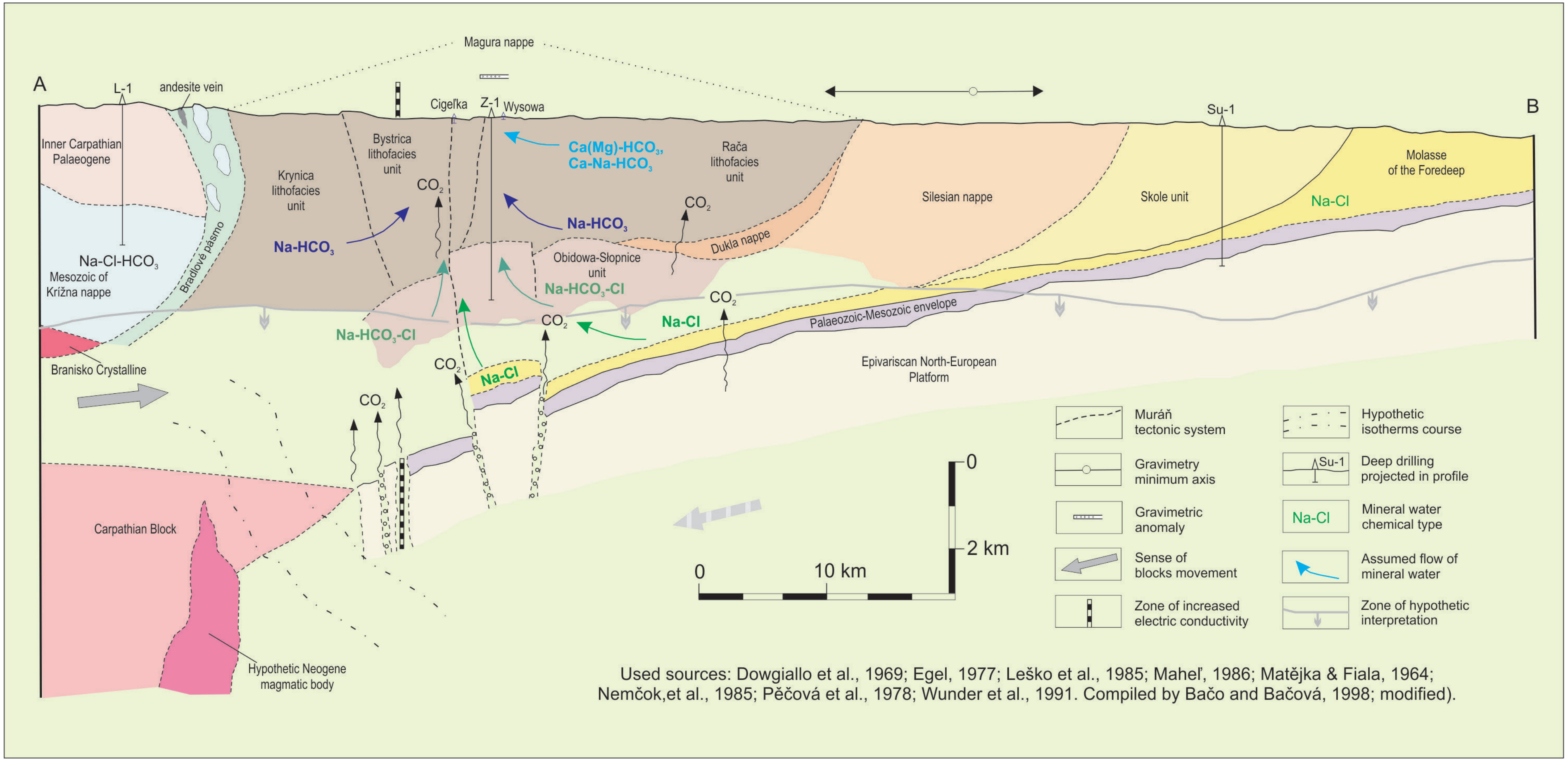


Fig. 7.14 Conceptual model of formation of the chemical composition of the Cigeľka natural mineral water

The Cigeľka natural mineral water (borehole CH-1; 202.5 m), heavily mineralized water from wells Zborov-1 (5,500 m) and Zborov-22 Otto (1,120 m) and weak brine from the well Zboj-1 (5,002 m) have the highest total dissolved solids among previously proven mineral waters of the eastern section of the Flysch Zone. They differ significantly in the content of the dominant macro-components – in chemical type. This stems from differing geological, tectonic and hydrogeological conditions of their formation. The lowest share of the thalassogenic mineralization among them has the well Zborov-1 (hydrogeological and hydrogeochemical results, the content of stable isotopes in the water from a borehole are described in Michalko et al., 1991). In the graph (Fig. 7.13) it is represented by the lowest-lying points on the left, under the signs showing the highly mineralized water from Cigeľka.

The points representing mostly poorly mineralized water with increased content of sulphates and prevailing in anion composition occupy a special position. Bicarbonate-sulphate and sulphate-bicarbonate waters appear at the bottom of the chart to the right (Figs. 7.11 and 7.13). The source of the increased sulphate content in them is the process of oxidation of sulphides (mainly pyrite present in the sandstone-claystone complexes).

According to previously published data on the content of stable isotopes of oxygen ($\delta^{18}O_{H2O}$) and hydrogen (δD_{H2O}) in mineral waters of the Flysch Zone of the Carpathians in Moravia, Slovakia, Poland and Ukraine, it is clear that the isotope heaviest waters are known from sites of the Magura Nappe (Bačová & Michalko, 2007). It allows to express assumption that waters with values $\delta^{18}O_{H2O}$ = 4 ‰ to 6 ‰ (hence Cigeľka, too) are very well sealed from the current meteoric waters by the mighty rock complex of overthrusts of the Magura Flysch.

7.6 The conceptual model formation of chemical composition of the Cigeľka natural mineral water

Knowledge about the discharge area of the Cigeľka natural mineral water, about its chemical composition and its formation, geological and tectonic setting of the area, collected by the geological fieldwork and subsequent processing and interpreting the raw data, resulted in the processing of the conceptual model of formation of this very salty water (Fig. 7.14). The model schematic cross-section is exaggerated in the vertical dimension in order to increase clarity. The intersection plane reflects geological facts that do not occur, de facto.

In the construction of the geological model, we take into account the views of the deep geological structure of this part of the Western Carpathians (especially those that have been graphically expressed) mentioned in the works of the following authors: Leško & Varga (1980), Nemčok et al. (1985), Maheľ (1986), Rudinec (1987) and Wunder et al. (1991).

Surface definition of regional units is adopted and simplified from the maps by Egel (1977) and Nemčok et al. (1985). Position of the Inner-Palaeogene and Mesozoic of the Krížna Nappe (envelope unit in Branisko unit) is interpreted based on the results and interpretation of borehole Lipany-1 (Leško et al., 1982). A method of illustrating the course Klippen Belt primarily took into account the results of the well Hanušovce-1 (Leško et al., 1985). Geological structure in the wider area of Cigeľka is interpreted primarily using the results of the well Smilno-1 (Leško ,1986; Leško et al., 1987) and Zborov-1 (Wunder et al., 1990; 1991) and the deeper subsoil based on the work by Pěčová et al. (1978) and Praus et al. (1984) – Regional geoelectric anomalies, and work by Leško et al. (1979) – Interpretation of the Oligocene-Miocene Molasse. Relationship between the Skola Unit and autochthonous basement – sediments of the Molasse of the Foredeep and northern epi-Variscan platform – we interpreted on the basis of the well Szufnarowa-1 and work by Nemčok et al. (1985).

Views on the formation and origin of mineral water of the Flysch Zone of the Western Carpathians in Poland were published by many authors from the 60's of last Century to the present, with a graphical representation of geological and tectonic conditions in recent years, for example Oszczypko & Zuber (2002) and Zuber & Chowaniec (2009).

The Cigeľka natural mineral water has a chemical composition of the type Na-HCO_3-Cl. In its formation there are involved:

- Meteoric water – formed and accumulated in the environment of the Magura Nappe at greater depth metamorphosed due to ion exchange processes;
- Sedimentation water – probably coming from the basement of the Magura Nappe.

These two components are apparently mixed in the area of conduits to the surface, where they can get from the environment of collector rocks along postorogenic and in this case the transverse only, deep-reaching fault. Penetration of water to the surface in a particular part of this tectonic system is alleviated by local lithological-tectonic conditions.

In the Cigeľka and Wysowa area we assume that they involve:

- Spatial position of the NW border of the longitudinal NW-SE autochthonous elevation of the bedrock – Makovica Ridge – basement of the Smilno tectonic inlier, which in the upper part is probably made up of Oligocene – Miocene Molasse;
- Contrasting arrangement of the basal layers of the Rača lithofacies unit in the Cigeľka area generated by present elevation;
- In the Wysowa area outcrops of Inoceramus layers to the surface;
- The presence of the primary source of mineral water;
- The primary source of gaseous component presence of organic or juvenile origin.

Influence of flysch rock environment upon the chemical composition is manifested not only in a higher sodium content (due to the release of from shales by ion-exchange processes) but also high content of boron, which sources are also Flysch complexes, likely. Chlorine and bromine contents refer to the share of water with thalassogenic mineralization in the chemical composition of the Cigeľka natural mineral water. The high content of bicarbonate is due to the presence of CO_2 of deep origin. The reducing environment in the course of the formation of the chemical composition of the water is reflected in values of Redox potential (Pacindová et al., 1997), and the presence of desulphurisation and ammonisation bacteria. The composition of the gas dissolved in water, does not indicate crude oil or gas bearing capacity of the rock environment. A certain proportion of carbon of organic origin, however, was confirmed by the occurrence of epigenetic mineral of whewellite in Bialowieza sandstone Fm. (in the core recovery of the drill V-HC-1). The high content of stable isotopes ^{18}O and D in water indicates a good sealing of space of water accumulation components from the groundwater of shallower circulation.

In the Magura Nappe of the Flysch Zone of the Carpathians (the area from Moravia to Ukraine) there are three major areas of incidence of moderate to strongly mineralized water of Na-HCO_3 and Na-HCO_3-Cl type (the area of Luhačovice, wider area of Krynica – Cigeľka (Wysowa) – Bardejov Spa, Poľana – Svaľava in Ukraine). These areas are known for the presence of deep-based faults and manifestations of Neogene magmatic activity. Isotopic and chemical composition of the unique Cigeľka natural mineral water points to its deep origin and eventual mixing of water of the Na-Cl type of the Magura Nappe and basement water type Na-HCO_3-(Cl) present at greater depths in the Magura Nappe itself. The high content of bicarbonate is likely mainly due to the presence of presumed deep CO_2 origin [Ukrainian authors (Gucalo et al., 1982) describe an increasing share of depth-based C in bicarbonate mineral waters of the Ukrainian Carpathians in the direction from the Carpathian Foredeep towards the Klippen Belt].

7.7 Conclusions

By summarising the existing knowledge on geological and hydrogeological conditions in the discharge area of the Cigeľka natural mineral water we came to the knowledge of the patterns of occurrence of mineral waters with different types of chemical composition and to create an image of the conduit area of heavily mineralized water to the surface. An important factor, conditioning the output of this precious water to the surface, the presence of CO_2 is likely to be of deep origin, in particular. Figures 7.10 and 7.11 provide a snapshot of the status of mineral waters of Cigeľka in the Flysch Zone of the Carpathians (Moravia, Poland, Slovakia and Ukraine).

When assessing the content of stable isotopes of oxygen and hydrogen the Cigeľka natural mineral water belongs to the heaviest waters of the Carpathian Flysch Zone. From previously published data on the isotopic composition of oxygen ($\delta^{18}O_{H2O}$) and hydrogen (δD_{H2O}) of the mineral waters of the Flysch Zone of the Carpathians in Moravia, Slovakia, Poland and Ukraine, it is clear that isotopically heaviest are the waters from sites representing the area of the Magura Flysch (Bačová & Michalko, 2007). This allows us to express the assumption that waters with the values of $\delta^{18}O_{H2O}$ = 4 ‰ to 6 ‰ (hence Cigeľka, too) are very well insulated from the current meteoric waters by mighty rock complexes of the Magura Flysch Nappes.

7.8 References

Bačo, P. & Pacindová, N., 1993: Whewellit a dawsonit – epigenetické minerály v puklinách pieskovca pri Cigeľke. Mineralia Slov., 25, p. 277 – 281.

Bačová, N. & Bačo, P., 1998: Minerálne vody Cigeľky a ich postavenie vo flyšovom pásme Západných Karpát. Mineralia Slov., 30, p. 453 – 468.

Bačová, N., 2006: Vertikálna hydrogeochemická zonálnosť vo flyšovom pásme Karpát a jej odraz vo výskytoch minerálnych vôd východného Slovenska. In: Rubin, H., Kowalczyk, A., 2006: Zborník príspevkov na X. medzinárodnej vedeckej konferencii HYDROGEOCHEMIA ´06 (Sosnowiec, 23. – 24. jún 2006). Wydzial Nauk o Ziemi, Uniwersytet Ślaski, on CD.

Bačová, N. & Michalko, J., 2007: Vertikálna hydrogeochemická zonálnosť a izotopové zloženie minerálnych vôd flyšového pásma Karpát. In: Szczepański, A., Kmiecik, E., Zurek, A., 2007: XIII Sympozjum Wspólczesne problemy hydrogeologii. Kraków, Wydzial Geologii, Geofizyki i ochrony Środowiska AGH, p. 33 – 41.

Bačová, N., 2011: Makrochemické zloženie minerálnych vôd východoslovenského úseku flyšového pásma Západných Karpát. Mineralia Slov., 43, p. 147 – 156.

Bačová, N., 2013: Minerálne vody flyšového pásma. Dizertačná práca, PriF UK Bratislava, 148 p.

Bajtoš, P., 2000: Šarišský Štiavnik – hydrodynamická skúška prírodného zdroja minerálnej vody Šťavica. Manuscript – – Archive SGIDŠ Bratislava, 22 p.

Dowgiallo, J., Karski, A., Potocki, J., 1969: Geologia surowców balneologicznych. Wydanie I. Warszawa, Wydawnictwa geologiczne, 296 p.

Ďurkovič, T., Koráb, T., Rudinec, R., 1982. Hlboký štruktúrny vrt Zboj-1. Region. Geol. Západ. Karpát, 16, 76 p.

Egel, L., 1977: Map of mineral formations of the Carpathian-Balkan region, 1 : 1 000 000.

Fľaková, R., Ženišová, Z., Seman, M., 2010: Chemická analýza vody v hydrogeológii. Bratislava, Slovenská asociácia hydrogeológov, 166 p.

Franko, O., Gazda, S., Michalíček, M., 1975: Tvorba a klasifikácia minerálnych vôd Západných Karpát. GÚDŠ Bratislava, 232 p.

Franko, O. & Kolářová, M., 1983: Mapa minerálnych vôd ČSSR 1 : 500 000. GÚDŠ Bratislava – ÚÚG Praha.

Franko, O., Kolářová, M., Mateovič, L., 1985: Katalóg dokumentačných bodov k mape minerálnych vôd ČSSR 1 : 500 000. GÚDŠ Bratislava, 103 p.

Franko, O. & Michalíček, M., 1975: Štúdia o jódobrómových vodách. Manuscript – Archive SGIDŠ Bratislava.

Franko, O. & Zakovič, M., 1980: Rekognoskácia minerálnych prameňov SSR – čiastková záverečná správa, úloha: Základný hydrogeologický výskum minerálnych vôd SSR. Manuscript – Archive SGIDŠ Bratislava, 6 p.

Gazda, S., 1974: Chemizmus podzemných vôd Západných Karpát a jeho genetická klasifikácia. In: Materiály z III. celoslovenskej geologickej konferencie, II. časť. Bratislava, Slovenský geologický úrad, p. 45 – 50.

Gucalo, L. K., Krajnov, S. R., Kojnov, I. M., Jarynyč, O. A., 1982: Genezis i formirovanie karbonatnoj sistemy mineraľnych vod Sovetskich Karpat (po izotopnomu sostavu). Geochimija, Moskva, Nauka, 10, p. 1481 – 1497.

Haluška, M., 1967: Cigeľka predbežný hydrogeologický prieskum. Manuscript – Archive SGIDŠ Bratislava.

Haluška, M. & Petrivaldský, P., 1988: Bardejovské kúpele – ochranné pásma. Záverečná správa z vyhľadávacieho hydrogeologického prieskumu. Manuscript – Archive SGIDŠ Bratislava.

Hanzel, V. (ed.), Bodiš, D., Böhm, V., Bujalka, P., Fides, J., Franko, O., Hyánková, K., Jetel, J., 1998: Geologický slovník. Hydrogeológia. Bratislava, Vydavateľstvo Dionýza Štúra. 301 p.

Hensel, J., Igumanová, A., Němejc, J., Novák, J., 1951: Balneografia Slovenska. Slovenská Akadémia Vied a Umení, Bratislava, 456 p.

Hofmann, B. A. & Century, S. M., 1998: Review of occurrences and carbon isotope geochemistry of oxalate minerals: implications for the origin and fate of oxalate in diagenetic and hydrothermal fluids. Chemical Geology, 149, p. 127 – 146.

Kirjuchin, V. A., 2008: Obščaja gidrogeologija. Sankt-Peterburgskij gosudarstvennyj gornyj institut, Sankt-Peterburg, 439 p.

Klimentov, P. P., 1980: Obščaja gidrogeologija. Vysšaja škola, Moskva, 303 p.

Kolodij, V. V., Kojnov, I. M., 1984: Izotopnyj sostav vodoroda i kisleroda podzemnych vod karpatskogo regiona i voprosy ich proischoždenia. Moskva, Geochimija, 5, p. 721 – 733.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1977: Minerálne vody Slovenska. Balneografia a krenografia 1. Martin, Osveta, 456 p.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1978: Minerálne vody Slovenska. Krenografia 2. Martin, Osveta, 1040 p.

Leško, B., Kadlečík, J., Mořkovský, M., Tomek, Č., 1979: Podložie flyšových Karpát na východnom Slovensku interpretované z geofyzikálnych meraní. Mineralia Slov., 11, p. 97 – 114.

Leško, B. & Varga, I., 1980: Alpine elements in the West Carpathian structure and their significance. Mineralia Slov., 12, p. 97 – 130.

Leško, B. et al., 1982: Oporný vrt Lipany-1 (4 000 m). Region. Geol. Západ. Karpát, 18, 205 p.

Leško, B. et al., 1985: Oporný vrt Hanušovce-1 (6 003 m). Region. Geol. Západ. Karpát, 20, 78 p.

Leško, B., 1986: Geologické a naftovoložiskové zhodnotenie vrtu Smilno-1, severovýchodné Slovensko. Mineralia Slov., 18, p. 193 – 212.

Leško, B., Samuel, O., Snopková, P., Ďurkovič, T., Smetana, J., Wunder, D., Širáňová, V., Rudinec, R., Losík, L., Píchová, E., Karkoška, F., Filková, V., Janků, J., Hradil, F., 1987: Oporný vrt Smilno-1 (5,700 m). Region. geol. Západ. Karpát, 22, p. 5 – 133.

Lexa, J., Bezák, V., Elečko, M., Mello, J., Polák, M., Potfaj, M., Vozár, J. (eds.), Schnabel, G. W., Pálenský, P., Császár, G., Rylko, W., Mackiv, B. (Co-eds.), 2000: Geologická mapa Západných Karpát a priľahlých území (1 : 500,000). Bratislava, MŽP SR, SGIDŠ.

Macioszczyk, A. & Dobrzyński, D., 2007: Hydrogeochemia. Strefy aktywnej wymiany wód podziemnych. Warszawa, Wydawnictwo naukowe PWN, 448 p.

Maheľ, M., 1986: Geologická stavba československých Karpát. Bratislava, SAV, 503 p.

Malatinský, K., Matejčeková, E., Frnčo, M., 1984: Hydrogeologický prieskum výverovej štruktúry minerálnej vody Cigeľka – záverečná správa. Manuscript –Archive SGIDŠ Bratislava, 29 p.

Marcin, D., 1996: Hydrogeological structure of mineral waters in Cigeľka. In: Zuurdeeg, B., (ed.), 1996: Internal communications of Commission on mineral and thermal waters. Vianen, IAH – CMTW, Enclosure 11a.

Marcin, D., 1999: Mineral water-bearing hydrogeological structures in the Magura unit of the Flysch Belt, eastern Slovakia. In: Fendeková, M., Fendek, M., (ed.), 1999: Hydrogeology and land use management. Proceedings of XXIX IAH Congress. Bratislava.

Michalíček, M. & Květ, R., 1960: Hydrogeochemický výzkum východoslovenského magurského flyše a dukelsko-užockých vrás. Práce Výzk. Úst. Čs. naft. dolů, 16, publ. 62 – 70, Brno, p. 7 – 68.

Michalíček, M., 1986: Geochemie hlubinných vod a plynů střední Moravy. Sbor. geol. věd, Hydrogeologie, inž. geologie, 18, p. 51 – 147.

Michalko, J., Bodiš, D., Fendek, M., 1991: Izotopové, hydrogeochemical a hydrogeologické zhodnotenie vrtu Zborov-1. Manuscript – Archive SGIDŠ Bratislava.

Nemčok, J., Stráník, Z., Doktor, S. et al., 1985: Štruktúrno-geologický atlas československo-poľských Karpát a ich predpolia. Manuscript – Archive SGIDŠ Bratislava, 51 p.

Nemčok, J., Zakovič, M., Gašparíková, V., Ďurkovič, T., Snopková, P., Vrana, K., Hanzel, V., 1990: Vysvetlivky ku geologickej mape Pienin, Čergova, Ľubovnianskej a Ondavskej vrchoviny, 1 : 50,000. GÚDŠ Bratislava, 131 p.

Oszczypko, N. & Zuber, A., 2002: Geological and isotopic evidence of diagenetic waters in the Polish Flysch Carpathians. Geol. Carpathica, 53, 4, p. 257 – 268.

Pacindová, N., Bačo, P., Jetel, J., Michalko, J., Komoň, J., Krotký, A., Staňa, Š., Samuel, O., Žecová, K., Prokop, M., 1997: Ochranné pásma minerálnej vody Cigeľka. Manuscript – Archive SGIDŠ Bratislava, 150 p.

Pačes, T., 1983: Základy geochemie vod. Academia, Praha, 304 p.

Pěčová, J., Petr, V., Praus, O., 1978: Výsledky magnetovariačních sondáží na prof. P-77 a v oblasti čs. Karpát. In: Výzkum hlubin. geol. stavby v Československu. Sbor. ref. Brno, Geofyzika, p. 43 – 54.

Porowski, A., 2006: Origin of mineralized waters in the Central Carpathian Synclinorium, SE Poland. Studia Geologica Polonica, vol. 125, p. 5 – 67.

Pospíšil, L., Bezák, V., Nemčok, J., Feranec, J., Vass, D., Obernauer, D., 1989: Muránsky tektonický systém významný príklad horizontálnych posunov v Západných Karpatoch. Mineralia Slov., 21, p. 305 – 322.

Potfaj, M. & Bodiš, D., 1987: Nálezová správa o výskyte slanej I-Br vody vo vrte Klanečnica (KLK-1) – (Moravské Lieskové). Manuscript – Archive SGIDŠ Bratislava, 14 p.

Praus, O., Pěčová, J., Červ, V., Pek, J., 1984: Geoelektrické charakteristiky na styku základních geologických bloků v ČSSR. In: Zemská kôra a jej vzťah k nerastným surovinám. Zborník referátov, GÚDŠ Bratislava, p. 137 – 146.

Rajchel, L. & Rajchel, J., 2006: Mofeta ze Zlockiego (Beskid Sadecki) atrakcja geologiczna. Przeglad Geologiczny, vol. 54, 12, p. 1089 – 1092.

Rajchel, L., Śliwa, T., Waligóra, J., 2007: Uwagi o wodach leczniczych Ustronia. In: Szczepański, A., Kmiecik, E., Zurek, A. (red.): XIII Sympozjum Wspólczesne problemy hydrogeologii. Kraków – Krynica 21 – 23 czerwca 2007 (zborník abstraktov z konferencie). Wydzial Geologii, Geofyziki i Ochrony Środowiska AGH, Kraków, p. 969 – 976.

Rajchel, L, 2012: Szczawy i wody kwasowęglowe Karpat polskich. Kraków, Wydawnictwa AGH, 194 p.

Rudinec, R., 1987: Súčasné predstavy o úložných pomeroch vo flyšových súvrstviach, bradlovom pásme a ich podloží na východnom Slovensku z pohľadu ropnej geológie. In: Geologická stavba Západných Karpát vo vzťahu k prognózam nerastných surovín. Zborník referátov, Košice, p. 261 – 272.

Rebro, A., 1996: Vzácne a obdivované vody Slovenska. Balneologické múzeum Piešťany – Turista, Piešťany, 182 p.

Stráník, Z.,1965: Geologie magurského flyše čerchovského pohoří a západní části Ondavské vrchoviny. Sbor. geol. Vied, Rad ZK, 3, p. 125 – 178.

Švarcev, S. L., 1996: Obščaja gidrogeologija. Moskva, Nedra, 423 p.

Uher, P. & Michalík, J., 1991: Dawsonit z vrchnokriedových slieňovcov vo vrte Soblahov. Mineralia Slov., 23, p. 67 – 70.

Wunder, D., Ďurkovič, T., Siráňová, Z., Fejdiová, O., Gašpariková, V., Korábová, K., Píchová, E., Červenka, J., Kozel, J., Snopková, P., Rudinec, R., Smetana, J., 1990: Prognózne overenie zdrojov prírodných uhľovodíkov v zborovskom antiklinóriu. Ropnogeologické zhodnotenie vrtu Zborov-1. Manuscript – Archive SGIDŠ Bratislava, 20 p.

Wunder, D., Koráb, T., Golovackij, J., Višniakov, I., 1991: Ropnogeologický výskum východoslovenského flyšového pásma. Manuscript – Archive SGIDŠ Bratislava, 56 p.

Zakovič, M., Bodiš, D., Fendek, M., Gabauer, G., Bálint, J., 1988: Geologický výskum jódobrómových vôd vo vybraných oblastiach SSR. Manuscript – Archive SGIDŠ Bratislava, 68 p.

Zakovič, M., Halečka, J., Petercová, A., Spišák, Z., Varga, M., 2006: Hydrogeologická štruktúra minerálnej vody Malý Sulín. Podzemná voda, 12, 1, p. 56 – 64.

Zakovič, M., Potfaj, M., Fendek, M., Bodiš, D., 2009: Jódo-brómové vody oblasti Oravskej Polhory. Podzemná voda, XV., 2, p. 230 – 239.

Zuber, A. & Chowaniec, J., 2009: Diagenetic and other highly mineralized waters in the Polish Carpathians. Appl. Geochem., 24, p. 1899 – 1900.

Decree Ministry of Health of the Slovak Republic no. 100/2006 Coll., laying down requirements on natural healing water and natural mineral water, details of the balneology assessment, distribution, coverage and content analysis of natural healing waters and natural mineral waters and their products, and requirements for registration of accredited laboratory to the list maintained by the State Spa Commission (in terms of no. 175/2013 Coll.) with effect from 1. 7. 2013.

Slovak Geol. Mag., 16, 2 (2016), 125 – 147

Mineral Waters of the Dudince Spa

Natália Bačová[1], Zoltán Németh[2], Martin Repčiak[3]

[1]State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Regional Centre, Jesenského 8, 040 01 Košice, Slovakia, natalia.bacova@geology.sk
[2]State Geological Institute of Dionýz Štúr, Dept. of Older Geological Formations, Regional Centre, Jesenského 8, 040 01 Košice, Slovakia
[3]State Geological Institute of Dionýz Štúr, Dept. of Raw Minerals and Geophysics, Regional Centre, Jesenského 8, 040 01 Košice, Slovakia

Abstract: Dudince Spa town is located on the southwestern edge of the district Krupina. Dudince and Santovka area is built of Neogene sediments – Baďany and Sebechleby formations of the Štiavnica Stratovolcano (outer proximal and distal zones). The basement of the Štiavnica Stratovolcano (Mesozoic and Palaeozoic) crops out to the surface only in the area west of Slatina and Santovka. According to the Ministry of Health Decree no. 100/2006 Coll. natural healing water from the source S-3 in Dudince is highly mineralized, carbonic, sulphane, bicarbonate-chloride, sodium-calcium water with increased content of fluoride, lithium, bicarbonate ions, slightly acidic, very low thermal. Mineral waters of "Levice Spring Line" (NW-SE direction – through the line Levice Santovka, Dudince, Slatina to Veľké Turovce) are of very complex origin. In this paper we present an overall view on the chemical composition of mineral waters occurring in this area – evaluation and graphical interpreting of data obtained through the whole period of mineral water sources use is provided (from 60's of the last Century to the present). The set of data contains the results of more than 740 laboratory analyses of samples of mineral water resources in the study area. Macrochemical assessment of the composition of mineral water of the "Levice Spring Line" gives the opportunity to understand regional hydrogeochemical regularities of their formation. It points to the similarities and differences between the mineral waters of the discharge areas of Dudince and Santovka. The mineral waters of Dudince, Santovka and Slatina have mixed chemical composition – formed by multiple processes. Silicatogenic, hydrosilicatogenic and marinogenic mineralizations are in prevail. However, there occur also carbonatogenic and sulphatogenic mineralizations.

Key words: Natural healing water, Dudince Spa, Levice Spring Line, mineral water, macrochemical composition, geophysical work

8.1 Introduction

Dudince Spa (the status of the spa town Dudince was granted in 1983, currently in Government Resolution no. 456/1999, the Ministry of Health Bulletin, item 13) is located on the eastern edge of the Danube Basin, on the southern foot of the Štiavnické Vrchy Mts. and at the western edge of Krupinská vrchovina Upland.

The first written mention of Dudince (Dyud) is already from the year 1284, the first mention of mineral water dates back to 1551. Since 1904, mineral water has been bottled, the first bath (Gutmann) was opened in 1909. The healing waters from the springs have been acknowledged since the Middle Ages (treatment of rheumatism, inflammation of the eyes, skin diseases and digestive problems). The first bath house in Dudince was opened in 1951. The opening ceremony of the Spa House Hont (later renamed Ruby) was held in 1966. The newest is the Spa House Diamant, which was opened in 1986.

Dudince and Santovka area is built of Neogene sediments – Baďany and Sebechleby formations of the Štiavnica Stratovolcano (outer proximal and distal zone, Fig. 8.1). Mesozoic and Palaeozoic fundament of the Štiavnica Stratovolcano crops out only in the area west of Slatina and Santovka.

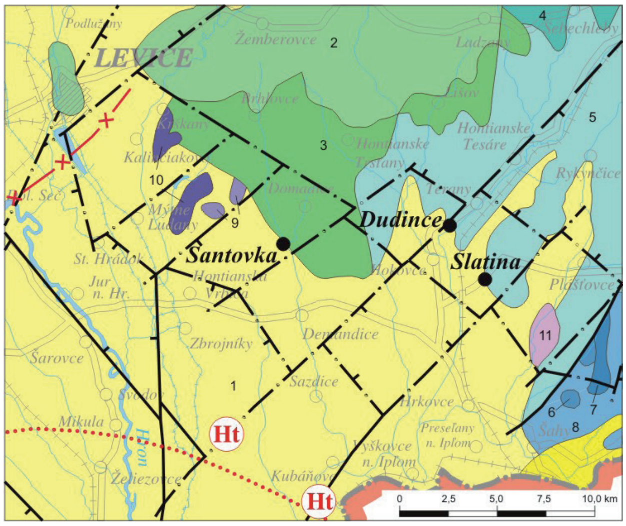


Fig. 8.1 Tectonic conditions in the area of Dudince and Santovka. 1 – Post-rift basinal fill, Neovolcanites: Sarmatian 2 – outer proximal zone, 3 – distal zone; Badenian 4 outer proximal zone, 5 – distal zone, 6 extrusive domes, 7 – breccias, 8 – conglomerates and sandstones; Palaeo-tectonic units: Hronicum 9 – Biely Váh facies, 10 – Čierny Váh facies, 11 – Veporicum – Foederata Series (detail of Tectonic map SR, Bezák et al., 2004, modified)

In this paper we present an overall view on the chemical composition of mineral waters present in this area – evaluation and graphical interpreting of data obtained through the whole period of mineral water sources use is provided (from 60's of the last Century to the present).

8.2 Brief overview of the major work carried out till to date

Hydrogeological surveys and explorations of the mineral waters of the "Levice Spring Line" was addressed by many experts; the most important findings brought works by Hynie (1956; 1957a, b; 1963), Orvan et al. (1965), Holéczyová et al. (1971, 1973, 1975, 1976), Bondarenková & Babíková (1981), Bondarenková (1983), Bondarenková et al. (1984), Melioris & Vass (1982), Melioris et al. (1986), Fendeková & Melioris (1996), Tkáčová (1978, 1980), Vandrová (1988, 1990), Vandrová et al. (1988, 1990, 2008, 2012), Vandrová & Matejčeková (1990), Vandrová & Štefanka (2007). The knowledge gained by these works (especially those last ones) led to calculation of the usable amount of mineral waters from sources in Dudince, Santovka and Slatina and to development of measures for the effective protection of resources (Ministry Decree no. 19/2000 Coll.).

At present, the only used source of natural healing water Dudince Spa – borehole S-3 (60.6 m depth, opened hole section from 52.5 to 60.0 m; Fig. 8.2) was excavated in the 50s of the 20th Century within hydrogeological research carried out by Hynie (1956, 1957a, 1963). During this period, natural springs of mineral water in Dudince had ceased (Hynie stated that there had been 10 of them). Of the nine wells drilled Hynie ordered to equip the boreholes S-3, S-4, S-5, S-6 and V-1. He stated that the initial yield of the object S-3 during the drilling work was 80 l . s^{-1}. It gradually declined and in the nineties it reached merely 10 l . s^{-1} (Rebro, 1996). Later, borehole S-5/A was drilled in the discharge area (Vandrová, 1988) and on the grounds of current swimming pool the hydrogeological drilling HVD-1 (Vandrová & Matejčeková, 1990) and HVD-2 (Vandrová et al., 1990).

Also in Santovka – Malinovec Hynie supervised the first drilling. In 1957, there were excavated three wells (B-1 to B-3), with the result that in the area disappeared many natural mineral water springs. The borehole B-6 – currently used source of natural mineral water in Santovka – was developed in 1964 (Orvan et al., 1965). In 1998 at the grounds of the swimming pool in Santovka a new source of thermal mineral water was drilled – borehole B-3A (Vandrová & Sňahničanová, 1998), which replaced the previously used drill hole B-3. In Slatina operated in the mid-20th Century baths with source Kúpeľný, Viera, Ján and Čulý. Mineral waters had unstable quantitative and qualitative characteristics. The issues of mineral water were also dealt with Hynie in the 60s of the last Century. In this period sources Studňa (*Well*) I, Studňa (*Well*) II and Borehole S-7 were excavated. Until the decommissioning of bottling plant in 2013 there were used in Slatina natural mineral water sources – wells BB-1 and BB-2 (drilled in a detailed hydrogeological . survey in the seventies of the last Century – Holéczyová et al., 1973).

Since 2014 the State Geological Institute of Dionýz Štúr has addressed a project "Search survey of the hydrogeological structure of mineral waters Dudince – Santovka" in the scope of which, inter alia, archival and newly acquired data have been assessed on the chemical composition of mineral water of Dudince, Santovka, Slatina and their vicinity with a goal of the detailed study of their formation processes, likely rock environment of their circulation, accumulation and dissipation.

8.3 Methodology

Natural healing water from the source S-3 in the Dudince Spa has the chemical type Na-Ca-HCO_3-Cl, mineralization 5,682 mg . l^{-1}. Such chemical composition is formed by mixing water from different geological environments as a result of various mineralization processes. Therefore, in summary processing and interpretation of the results of analyses of water samples taken from the sources during the hydrogeological survey made in Dudince it was necessary to get an overview of the chemical composition of groundwater and mineral waters occurring in the wider area. Respecting the specificities of the assembled set of hydrogeochemical data on mineral waters in the territory of interest, the paper introduces hereinafter the classifications and methods of processing.

The assessment of the total dissolved solids in groundwater and mineral waters within the investigated territory (with mineralization range of 286 – 8,676 mg . l^{-1}) is consistent with the classification applicable to natural healing waters (Ministry Decree no. 100/2006 Coll.).

When describing the mineralization processes share on the resulting chemical composition of mineral waters we use genetic classification of the chemical composition of the groundwater of the Western

Fig. 8.2 Natural healing source S-3 Dudince (Photo Bačová, 11. 9. 2013)

Carpathians (Gazda, 1974), adapted in terms of Geological Dictionary, part Hydrogeology Hanzel et al., (1998), Fľaková et al. (2010).

Chemical water types are described in accordance with the classification based on the principle of the prevailing ions – the title includes ions with more than 20 meq . l^{-1} % share. The sample data documenting the chemical composition of mineral water contains the results of more than 740 laboratory analyses of water samples taken from the resources in the study area. Data on the chemical composition of mineral water in the "Levice Spring Line" have been previously evaluated and interpreted as a rule only in relation to the solutions of specific hydrogeological tasks at certain times/areas.

Macrochemical composition of mineral waters is shown in two ways:

- Diagram Langelier-Ludwig (Langelier, Ludwig, 1942), substantially identical to the graph Tolstichin (Tolstichin, 1937). Construction of such a graph requires input data (mass concentrations of the individual macro-compounds – $Na^+ + K^+$, $Ca^{2+} + Mg^{2+}$, $HCO_3^- + CO_3^-$, $Cl^- + SO_4^{2-}$) recalculated to the content in·%, which is then displayed along the axis of the square plot.
- Diagram with a logarithmic scale on both axes, using data from analyses of water samples directly expressed in mass concentrations (Bačová, 2011), while on the axes of the graph coefficients $(Na^+ + K^+)/HCO_3^-$ and $(Ca^{2+} + Mg^{2+})/HCO_3^-$ are plotted.

Such graphic representation and evaluation of the macrocompounds content in mineral waters (supplemented by data on the chemical composition of ordinary groundwaters) gives an overall picture of the chemical composition of mineral waters in the examined area. It enables to assess the likely participation of different mineralization processes in the resulting chemical composition of mineral waters at specific sites; it points to a different portion of a particular process. It contributes significantly to the evaluation of the relationship among the contents of selected macro-compounds of waters.

In the case it would not be possible to define clearly infiltration and transport-accumulation area of mineral water from the results of previous geological research and exploration work, it is very important to process and interpret all the original hydrogeochemical data in detail. Such work could bring us to a knowledge that could substantially contribute to the effective protection of mineral waters, their quantitative and qualitative characteristics.

8.4 Results

8.4.1 The chemical composition of mineral waters in Dudince and its vicinity

Natural healing water from a borehole S-3 Dudince has the chemical type Na-Ca-HCO_3-Cl. In accordance with the Ministry of Health Decree no. 100/2006 Coll. as amended (with effect from July 1, 2013) it is:

By the amount of total dissolved solids *highly mineralized natural healing water*;

According to the content and type of dissolved gaseous substances, *carbonic sulphane*;

According to the content of the prevailing ions *bicarbonate-chloride sodium-calcium*;

According to the content of pharmacologically important ions and compounds of elements of *natural healing water with increased content of fluoride ion, lithium, bicarbonate ion;*

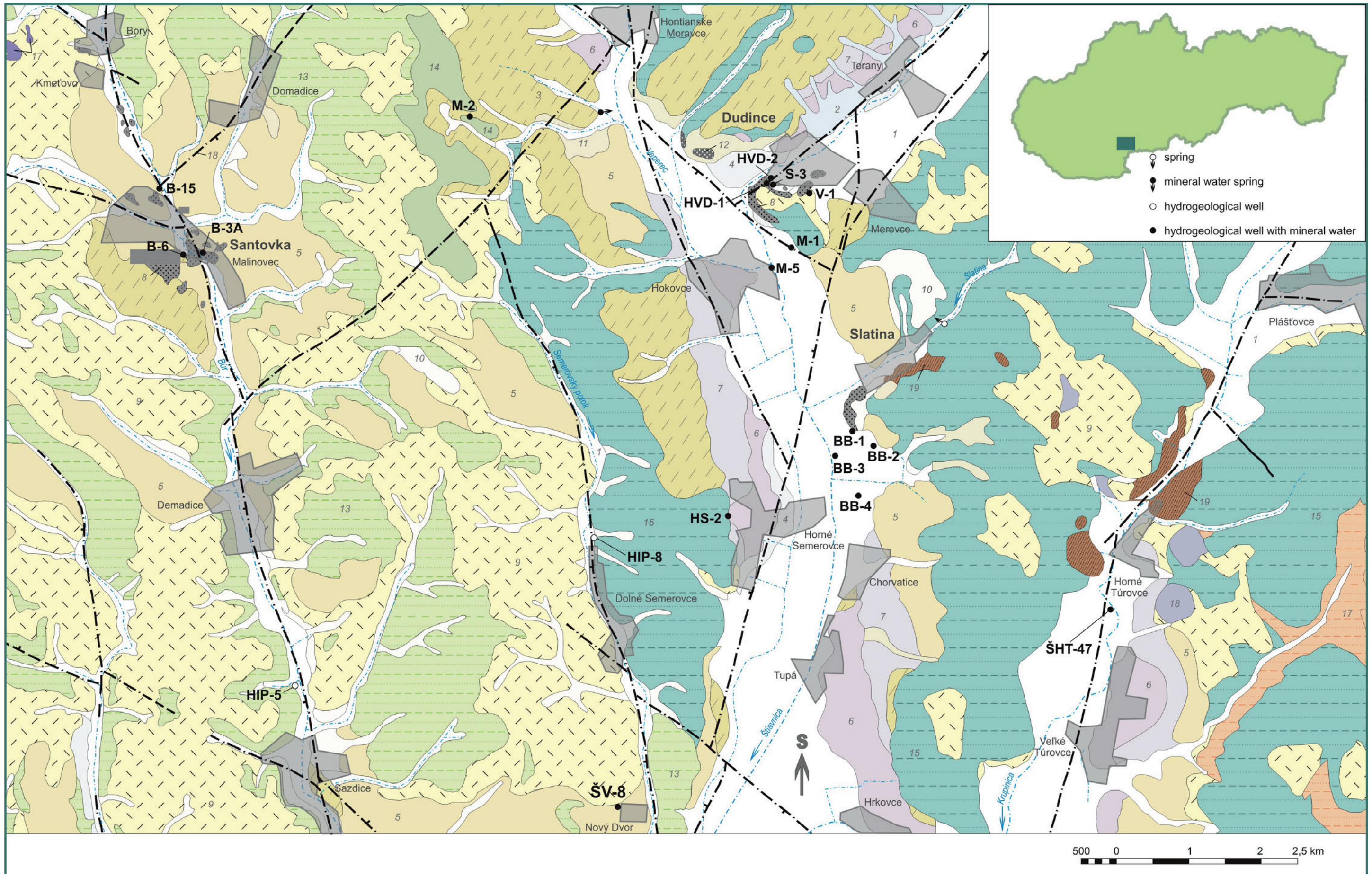
According to pH *slightly acidic*;

According to natural temperature at surge *very low thermal*.

In the section of geological map at scale of 1: 50,000 (compiled from documents Konečný et al., 1998; Nagy et al., 1998) there are displayed the most important hydrogeological objects with mineral water in the area from Santovka to Veľké Turovce (Fig. 8.3). In Tab. 8.1 we present hydrological data on selected wells with mineral water (Dudince, Santovka, Slatina, Hokovce, Mačkáš, Horné and Dolné Semerovce, Veľké Turovce (in the past Stredné and Dolné Turovce) and with ordinary groundwater (wells labelled HIP-1 to HIP-13 – Ipeľská pahorkatina Upland, Fecek, 1981).

Selected qualitative characteristics of mineral waters in Dudince, Santovka, Slatina and vicinity are presented in Tab. 8.2.

Fig. 8.3 Schematic geological map of the area (Konečný et al., 1998; Nagy et al., 1998, modified)



1 – fluvial sediments – prevailingly loamy or loamy-gravelly (Holocene undivided)
2 – proluvial sediments – loams (Pleistocene – Holocene)
3 – deluvial, deluvial-fluvial, eluvial-deluvial and aeolian-deluvial sediments – loams, sandy loams (Pleistocene – Holocene)
4 – fluvial sediments – sandy gravels of bottom accumulation and gravels of low terrace with loess sheet (Late Pleistocene)
5 – aeolian sediments – loess (Late Pleistocene)
6 – fluvial sandy gravels 3rd middle terrace (Middle Pleistocene)
7 – fluvial sandy gravels and gravels 2nd main middle terrace (Middle Pleistocene)
8 – travertines, travertine sinters and foamstones (Quaternary undivided)
9 – eluvial-deluvial loams and deluvial colluvial loams (Quaternary undivided)
10 – deluvial-fluvial loams (Quaternary undivided)
11 – colluvium, landslides (Quaternary)
12 – travertines – solid fresh-water limestones (Neogene: Pontian – Pliocene)
13 – Baďany Fm. – sands, sandstones, tuffaceous clays, tuffites and tuffs, pumice tuffs, conglomerates (Early to Middle Sarmatian)
14 – Ladzany Fm. – epiclastic volcanic sandstones and siltstones with pumice fragments (Early Sarmatian)
15 – Sebechleby Fm. – tuffaceous clays and siltstones (Plášťovce Mb.), tuffaceous sandstones, sandy tuffites (Early to Middle Badenian)
16 – Vinica Fm. – volcaniclastic rocks – breccias, conglomerates, tuffaceous siltstones and claystones (Early Badenian)
17 – Partnach Fm. – clayey shales, clayey limestones (Hronicum – Triassic)
18 – Foederata Group – quartzose sandstones, quartzites, schists – metamorphosed (Veporicum envelope – Triassic)
19 – Foederata Group – Rimava Fm. – sandstones, phyllite schists, conglomerates (Southern Veporicum – Permian)
20 – faults (dash line – assumed, dot-and-dash line – covered by Quaternary)

Tab. 8.1 Selected data on the most important objects with mineral water in the examined area

Site/water source		Well implemented in	Well depth [m]	Open section [m]	Geological data	Yield [l . s^{-1}]	TDS [mg .·l^{-1}]	Chemical type [compounds > 20 meq . l^{-1} %]	Date of analysis	Data source, note
Santovka	B-3	1957	68.7		0.0 − 16.0 Quaternary 16.0 − 68.7 Neogene − Badenian	10 − overflow (exploitable determined – 60s of the last Century)	6,171	**Na-Ca-HCO_3-Cl**	*	Hynie, 1963 (50 overflow originally reported)
	B-3A	1998	73.4	45.3 − 49.3 58.2 − 64.3	0.0 − 16.0 Quaternary 16.0 − 73.4 Neogene − Badenian	Exploitable amount cat. B – 15.5 – overflow (Decision ME SR no. 7601/2008-9.1)	5,941	**Na-Ca-HCO_3-Cl**	*	Vandrová & Štefanka, 2007
	B-4	1963	30	18 − 28	0.0 − 9.0 Quaternary 9.0 − 30.0 Tortonian − Sarmatian	0.03 (s = 3.98)	3,115	**Ca-Na-HCO_3**	*	Orvan et al., 1965
	B-5	1963	29	18 − 26	0.0 − 1.7 Quaternary 1.7 − 29.0 Tortonian − Sarmatian	0.43 (s = 2.75 m)	3,634	**Na-Ca-HCO_3**	*	Orvan et al., 1965
	B-6	1963	42	27.0 − 42.0	0.0 − 7.0 Quaternary 7.0 − 42.0 Tortonian − Sarmatian	Permitted exploitable amount 0.5 – pumping (Decision ME SR no. 01184-46/2013/SSC)	3,698	**Ca-Na-HCO_3**	*	Orvan et al., 1965
	B-7	1964	40		0.0 − 4.0 Quaternary 4.0 − 40.0 Tortonian − Sarmatian		3,553	**Ca-HCO_3-SO_4** **Na-Ca-HCO_3-Cl**	*	Orvan et al., 1965
	B-8	1964	31.8		0.0 − 2.0 Quaternary 2.0 − 31.8 Tortonian − Sarmatian		6,019	**Na-Ca-HCO_3-Cl**	*	Orvan et al., 1965
	Santovka II, B-9	1964	18.2	8.0 − 17.2	0.0 − 8.0 Quaternary 8.0 − 18.2 Tortonian − Sarmatian	0.2 (s = 3.00 m)	3,977	**Na-Ca-HCO_3**	*	Orvan et al., 1965
	B-10	1971 − 1972	57		0.0 − 2.0 Quaternary 2.0 − 57.0 Neogene	0.8 (s = 9.52 m)	5,226	**Na-Ca-HCO_3-Cl**	*	Holéczyová et al., 1975
	Santovka III, B-11	1975	45	10.5 − 19.6	0.0 − 7.5 Quaternary 7.5 − 45.0 Neogene	0.5 (s = 3.68 m)	2,983 6,106	**Ca-Na-HCO_3** **Na-Ca-HCO_3-Cl**	*	Holéczyová et al., 1975
	B-12	1972	30		0.0 − 3.9 Quaternary 3.9 − 30.0 Neogene	0.08 (s = 4.35 m)	4,445	**Na-Ca-HCO_3-SO_4**	7.7.1972	Holéczyová et al., 1975
	B-13	1972	26**	24.0 − 26.0	0.0 − 5.5 Quaternary 5.5 − 26.0 Neogene (tectonic failure line)	1.25 (s = 7.77 m)	6,688	**Na-Ca-HCO_3-Cl-SO_4**	*	Holéczyová et al., 1975; **60 m – Vandrová et al., 1980
	B-14	1973	45	22.0 − 33.0	0.0 − 8.0 Quaternary 8.0 − 45.0 Neogene	0.1 − overflow	5,344	**Na-Ca-HCO_3-Cl**	*	Holéczyová et al., 1975
	B-15	1974 – – 1975	15.7	11.2 − 15.7	0.0 − 5.7 Quaternary 5.7 − 15.7 Neogene	2.0 (s – 6.55 m)	3,428	**Na-Ca-HCO_3**	*	Holéczyová et al., 1975; Vandrová et al., 2008
	Santovka IV, HG-4	1972	19	15.0 − 19.0	0.0 − 9.5 Quaternary 9.5 − 19.0 Neogene	0.4 (s = 12.00 m)	3,257	**Na-Ca-HCO_3**	*	Holéczyová et al., 1975

Continuation of Tab. 8.1

	Site/water source	Well implemented in	Well depth [m]	Open section [m]	Geological data	Yield [l . s^{-1}]	TDS [mg .·l^{-1}]	Chemical type [compounds > 20 meq . l^{-1} %]	Date of analysis	Data source, note
Dudince	Kúpeľný well S-3	1954 1994 – 1995	60.65	52.5 – 60.0	0.0 – 7.5 Quaternary 7.5 – 60.65 Neogene – Badenian	exploitable amount cat. B 6.2 – overflow (Decision ME SR of 25. 9. 2012)	5,682	**Na-Ca-HCO_3-Cl**	*	Hynie, 1963 (70 – 80 overflow in 60s, 9,8 in 90s)
	Gejzír well S-4	1955	70.33	Wooden caisson	0.00 – 7.05 Quaternary 7.05 – 55.2 Neogene – Badenian 55.20 – 70.23 Mesozoic – Early Triassic	2.6	6,191	**Na-Ca-HCO_3-Cl**	*	Hynie, 1963
	Rímsky well V-1	1953	107,5		0.00 – 15.30 Quaternary 15.30 – 103.00 Neogene – Badenian 103.00 – 107.50 Mesozoic – Early Triassic		2,365	**Na-HCO_3-Cl**	*	Hynie, 1963
	well S-5/A	1987	70	39.0 – 65.0	0.0 – 10.2 Quaternary 10.2 – 58.4 Neogene – Badenian 58.4 – 70.0 Mesozoic – Early Triassic (quartzite)	1.2 (s = 9.90 m)	4,839	**Na-Ca-HCO_3**	*	Vandrová, 1988
	well S-6	1956	12		0.0 – 5.0 Quaternary 5.0 – 12.0 Neogene – Badenian		2,440	**Ca-HCO_3 (S-6/A)**	*	Hynie, 1963, Vandrová et al., 1990
	well HVD-1	1989	85	45.0 – 57.0 57.0 – 67.0	0.0 – 9.0 Quaternary 9.0 – 81.0 Neogene – Badenian 81.0 – 85.0 Mesozoic – Early Triassic	exploitable amount cat. B 1.2 – overflow (Decision ME SR of 25. 9. 2012)	5,540	**Na-Ca-HCO_3-Cl**	*	Vandrová & Matejčeková, 1990
	well HVD-2	1990	80	53.0 – 57.0 62.0 – 72.0	0.0 – 10.0 Quaternary 10.0 – 71.0 Neogene – Badenian 71.0 – 80.0 Mesozoic – Early Triassic	0.1 – overflow (0,3 m above surface)	6,425	**Na-Ca-HCO_3-Cl**	*	Vandrová et al., 1990
	Kmeťovce, HIP-3	10.1974	80	54.0 – 76.0	24.0 – Quaternary 80.0 – Late Miocene (from 67 m andesite)	3.0 (s = 17.7 m) 3.4 (s = 31.8 m)	423 – 427	**Ca-Mg-HCO_3**	3. – 4.1975	Fecek, 1981
	Drženice, HIP-4	12.1975	111	29.0 – 107.0 5 sections	3.4 – Quaternary 111.0 – Pannonian	0.1 (s = 45.0 m)	600	**Na-Ca-Mg-HCO_3**	26.3.1975	Fecek, 1981
	Sazdice, HIP-5	12.1972	141	20.0 – 95.0 4 sections	5.0 – Quaternary 141.0 – Badenian, Sarmatian	4.0 (s = 2.1 m)	755 – 791	**Ca-Mg-HCO_3**	4.1973	Fecek, 1981
	Trhyňa (Sikenica) HIP-6	1.1973	165	16.0 – 155.0 5 sections	11.0 – Quaternary 165.0 – Badenian, Sarmatian	< 0.01 (s = 5.2 m)	1,211 – 1,259	**Na-Ca-HCO_3**	1. – 2.1973	Fecek, 1981
	Trhyňa (Lontov) HIP-7	10.1972	250	26.4 – 154.0 7 sections	1.3 – Quaternary 250.0 – Badenian, Sarmatian	4.0 (s = 2.5 m)	749 – 751	**Ca-Na-HCO_3**	6. – 7.1973	Fecek, 1981
	Dolné Semerovce HIP-8	3.1973	203	30.5 – 145.6 3 sections	6.0 – Quaternary 203.0 – Badenian	4.1 (s = 20.2 m)	693 – 698	**Ca-Mg-HCO_3**	5.1973	Fecek, 1981
	Kubáňovo HIP-9	10.1973	202	54.3 – 185.0 5 sections	2.4 – Quaternary 202.0 – Badenian, Sarmatian	2.25 (s = 19.6 m)	955 – 1,123	**Na-Ca-HCO_3**	12.1973	Fecek, 1981
	Hontianske Trsťany HIP-13	1. – 2.1975	205	58.0 – 168.0 4 sections	6.0 – Quaternary 205.0 – Badenian, Sarmatian	5.7 (s = 6.5 m) 5.71 (s = 6.83 m)	558 – 586	**Ca-Mg-HCO_3**	6. – 7.1977	Fecek, 1981
	Mačkáš M-2	1983	490	438 – 469	0.0 – 6.0 Quaternary 6.0 – 300.0 Neogene 300.0 – 490.0 Mesozoic		5,626	**Na-Ca-HCO_3-Cl**	*	Melioris et al., 1986

Continuation of Tab. 8.1

Site/water source		Well implemented in	Well depth [m]	Open section [m]	Geological data	Yield [l . s^{-1}]	TDS [mg .·l^{-1}]	Chemical type [compounds > 20 meq . l^{-1} %]	Date of analysis	Data source, note
Hokovce	M-1	1980	321	150 – 220	0.0 – 3.9 Quaternary 3.9 – 12.0 Neogene 12.0 – 220.0 Palaeozoic (Veporicum envelope)		5,936	**Na-Ca-HCO_3-Cl**	*	Melioris et al., 1986
	M-5	1983	220	150 – 220	0.0 – 5.0 Quaternary 5.0 – 30.0 Neogene 30.0 – 220.0 Palaeozoic (Veporicum envelope)	0.0012 – overflow (0.9 m above surface)	6,442	**Na-Ca-HCO_3-Cl**	*	Melioris et al., 1986
Slatina	well S-7	1957	14.8	9.0 – 12.6	7.5 – 8.3 Early Triassic (quartzites)	1.5	2,758	**Na-Ca-HCO_3-Cl**	26.7.1964	Hynie, 1963
	well S-II (pôv. studňa)	1957	17	12.0 – 15.0		0.8 – 1.4	3,176	**Na-Ca-HCO_3-Cl**	28.3.1964	Hynie, 1963
	well BB-1	1972	34.3	30.0 – 34.3	33.8 – Early Triassic (quartzites)	1.5 (recommended)	4,370	**Na-Ca-HCO_3-Cl**	26.8.1979	Holéczyová et al., 1973; Bondarenková & Bab&ková, 1981
	well BB-2	1972	33.3	31.5 – 33.3	8.0 – Quaternary 33.3 – Neogene	Permitted exploitable amount 1.5 – pumping (Decision no. 00767-026/2011/SSC)	1,840	**Na-HCO_3-Cl**	30.9.1979	Holéczyová et al., 1973; Bondarenková & Babíková, 1981
	well BB-3	1983	150	102 – 130 3 sections	102 – 130 Neogene – Badenian 133 – 150 – Early Triassic (quartzites)	1.5 (s = 4.38 m)	4,735	**Na-Ca-HCO_3-Cl**	3.7.1987	Bondarenková et al., 1984
	well BB-4	1984	233	144 – 178	144 – 178 – Early Triassic (quartzites) 178 – 233 – Permian	1.0 (s = 2.93 m)	5,571	**Na-Ca-HCO_3-Cl**	2.7.1987	Bondarenková et al., 1984
	well BB-5	1987	60		0.0 – 1.8 Quaternary 1.8 – 8.5 Neogene 8.5 – 60.0 Mesozoic – Early Triassic	0.3 (s = 11.53 m)	1,279	**Na-HCO_3-SO_4**	4.11.1987	Vandrová et al., 1988
Semerovce	Dol. Semerovce, ŠV-8	6.1964 – – 9.1966	1,204	550 – 570 853 – 932	0.0 – 17.0 Quaternary 17.0 – 21.0 Sarmatian 21.0 – 542.0 Badenian 542.0 – 688.0 Early Triassic 688.0 – 932.6 Permian 932.6 – 1,203.6 Older Palaeozoic (phyllites)	0.33 (s = 88 m) 0.33 (s = 89 m)	7,028 6,926	**Na-Mg-HCO_3-Cl** **Na-Ca-HCO_3-Cl**	23.3.1967 22.4.1967	Biela, A., 1978; Vass, D. et al., 1981
	Hor. Semerovce, HS-2	1991	150	80 – 145	18.0 – Quaternary 150.0 – Neogene	6.0 (s = 11.83 m)	3,067	**Na-Ca-HCO_3**	1991	Lauko et al., 1991

Continuation of Tab. 8.1

Site/water source		Well implemented in	Well depth [m]	Open section [m]	Geological data	Yield [l . s^{-1}]	TDS [mg .·l^{-1}]	Chemical type [compounds > 20 meq . l^{-1} %]	Date of analysis	Data source, note
Horné Turovce	well ŠHT-47	1975	150	85 − 145	5.8 – 6.1 – Neogene 6.1 – 150.0 – Early Triassic. Permian (phyllites, quartzy sandstones and conglomerates)	0.5 (s = 2.15 m)	3,874	**Na-Ca-HCO_3-Cl**	2.8.1977	Rebro et al., 1978
	well ŠHT-48	1975	160	45 − 50.9 104 – 150	5.4 – 5.9 – Neogene 5.9 – 160.0 – Early Triassic, Permian	0.518 (s = 2.96 m)	5,491	**Na-Ca-HCO_3-Cl**	2.8.1977	Rebro et al., 1978
	well ŠHT-49	1975	150	25 − 95	9.0 – 16.9 – Neogene 16.9 – 150.0 – Early Triassic, Permian	1.45 (s = 6.26 m)	4,932	**Na-Ca-HCO_3-Cl**	2.8.1977	Rebro et al., 1978
Bohunice, HIP-1		10.1974 – – 12.1974	43	27.0 − 43.0	7.0 − Quaternary 43.0 − Late Miocene	0.8 (s = 17.4 m)	304 − 386	**Ca-Mg-HCO_3**	3.1975	Fecek, 1981
Bátovce, HIP-2		12.1974	205	29.0 − 200.0 3 sections	18.0 − Quaternary 205.25 − Miocene (from 195 m andesite)	2.7 (s = 20.0 m)	504	**Ca-Mg-HCO_3**	18.2.1975	Fecek, 1981

Tab. 8.2 Selected data on the macrochemical composition of mineral waters Dudince and the surrounding area

Site	Source	Water t [°C]	pH	TDS	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	F^-	Cl^-	SO_4^{2-}	HCO_3^-	H_2SiO_3	CO_2	H_2S	Chemical type	Source
				[mg.l^{-1}]															
Dudince	ZV-70 S-3	24.0	6.7	5,898	3.24	885	120	502	133	10.2	2.8	553	549	3,087	21.1	1,428	17.00	Na-Ca-HCO_3-Cl	Vandrová et al., 2007
		26.8	6.7	5,548	2.99	776	133	477	123	9.2	2.0	562	563	2,824	21.1	704	6.89	Na-Ca-HCO_3-Cl	Bačová 6.9.2016
	ZV-71 S-4 Gejzír	27.5	5.9	5,341		823	170	380	133			562	532	2,654	52.1	1,312	6.77	Na-Ca-HCO_3-Cl	Krahulec et al., 1977
		16.2	6.8	1,440	0.5	142	34	194	26	2.5	0.8	81	307	635	8.0	381		Na-Ca-HCO_3-Cl	Melioris et al., 1986
	ZV-72 S-5	14.0	7.8	3,091	1.9	746	116	21	27	0.2		346	12	1,776	19.0	40		Na-HCO_3-Cl	Melioris et al., 1986
	ZV-84 S-5/A	16.3	6.5	4,767	2.77	691	110	405	110	7.5	2.8	425	520	2,429	34.2	2,134	2.58	Na-Ca-HCO_3	Vandrová et al., 1990
			5.5	5,400	2.29	705	118	434	126	7.7	2.6	462	482	2,633		905	1.76	Na-Ca-HCO_3	Melioris & Drexler, 2002
	S-6	12.0	6.0	2,350	0.53	76	33	420	47	3.5		24	95	1,599	37.1	1,819	1.50	Ca-HCO_3	Melioris et al., 1986
	S-6/A	11.9	6.5	2,505	0.54	85	38	420	53	4.3	1.9	26	120	1,647	75.8	1,692	0.90	Ca-HCO_3	Vandrová et al., 1990
			6.1	2,388	0.72	86	54	395	45	4.8	2.5	25	122	1,586	47.2	898	0.12	Ca-HCO_3	Bačová 10.11.2015
	ZV-69 V-1 Rímsky	14.7	7.9	2,825	1	630	101	44	73	0.8	0.1	549	8	1,386	5.5	48		Na-HCO_3-Cl	Krahulec et al., 1977
		24.8	7.5	2,363	1.59	455	83	65	61	3.4	1.0	377	6	1,208	18.4	155	0.97	Na-HCO_3-Cl	Vandrová et al., 1990
		14.3		2,897		620	115	48	73			545	15	1,393		44		Na-HCO_3-Cl	Melioris et al., 1986
	ZV-85 HVD-1	30.0	7.4	5,942	3	895	131	502	131		3.2	590	573	3,051	28.7	1,539	6.53	Na-Ca-HCO_3-Cl	Vandrová et al., 1990
	ZV-86 HVD-2	23.5	6.5	6,433	4	998	156	516	142	10.0	2.2	803	479	3,252	26.1	1,379	2.31	Na-Ca-HCO_3-Cl	Vandrová et al., 1990
	ZV-68 well	11.0	6.5	4,864		791		425	107			434	488	2,557	33.8	1,450		Na-Ca-HCO_3	Krahulec et al., 1977
		10.7	6.6	5,086	2.87	792	135	358	137	6.9	1.7	525	504	2,575	18.3	954		Na-Ca-HCO_3-Cl	Melioris et al., 1986
Santovka	LE-15 B-3	26.0	6.5	6,195		939	136	508	162			634	604	3,210	23.4	1,440	5.29	Na-Ca-HCO_3-Cl	Orvan et al., 1965
		26.0	6.4	6,031	18	836	152	501	167			650	578	3,124	27.3	1,325	5.92	Na-Ca-HCO_3-Cl	Holeczyová et al., 1975
	B-3A	25.8	6.6	6,187	3.49	910	133	513	161	9.7	2.6	631	541	3,216		1,306	5.10	Na-Ca-HCO_3-Cl	Vandrová & Sňahničanová, 1998
			6.7	6,067	3.18	851	135	480	146	9.1	1.0	673	612	3,068	22.2	594	3.93	Na-Ca-HCO_3-Cl	Bačová 13.7.2016
	LE-34 B-6	13.6	6.1	4,340		532	100	469	108			372	408	2,343	58.4	2,310	0.46	Ca-Na-HCO_3	Orvan et al., 1965
		14.3	6.3	2,980	0.85	239	40	449	59	3.7		158	331	1,654		1,999		Ca-Na-HCO_3	Vandrová a Sňahničanová, 1998
		11.2	6.2	3,828	1.58	430	70	440	84	5.7	2.4	277	375	2,081		2,426		Na-Ca-HCO_3	Vandrová. 1998
			6.3	3,438	1.36	326	63	428	60	5.1	1.9	234	378	1,779	28.1	691		Ca-Na-HCO_3	Bačová 6.9.2016

Continuation of Tab. 8.2

Site	Source	Water t [°C]	pH	TDS	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	F^-	Cl^-	SO_4^{2-}	HCO_3^-	H_2SiO_3	CO_2	H_2S	Chemical type	Source
				[mg.l^{-1}]															
Slatina	LE-31 B-1	14.0	5.6	3,128	2.18	384	100	276	92	3.5	1.2	259	374	1,629		2,083		Na-Ca-HCO_3	Franko et al., 1975
	LE-39 BB-1	14.8	6.4	4,810	2.62	777	128	360	119	7.3	2.1	652	517	2,203	10.6	2,336		Na-Ca-HCO_3-Cl	Melioris et al., 1986
	LE-40 BB-2	14.5	6.9	3,217	1.96	476	130	241	80	5.3		389	356	1,507	10.8	1,426		Na-Ca-HCO_3-Cl	Bondarenková & Babíková, 1981
			6.5	1,293	0.72	156	42	129	27	2.0	0.3	101	160	635		568		Na-Ca-HCO_3-SO_4	Vandrová et al., 1987
	LE-46 BB-3	19.3	6.7	6,997	3.59	1,147	173	523	174	7.9	2.6	978	757	3,173		1,502		Na-Ca-HCO_3-Cl	Bondarenková et al., 1984
		20.0	6.9	7,037	3.63	1,181	173	518	165	8.3	2.5	993	753	3,185		827		Na-Ca-HCO_3-Cl	Bondarenková et al., 1984
		14.8	6.2	1,351	0.86	181	48	115	35	1.9		113	158	677	12.7	807		Na-Ca-HCO_3	Melioris et al., 1986
			6.4	4,735	2.96	676	125	375	115	6.5		502	327	2,490		1,056		Na-Ca-HCO_3-Cl	Vandrová et al., 1988
	LE-47 BB-4	22.0	6.5	6,739	4.33	1,058	176	516	170	8.2	1.8	865	726	3,142		1,724		Na-Ca-HCO_3-Cl	Bondarenková et al., 1984
		12.1	6.4	5,571	3.6	919	159	361	145	7.9		766	544	2,557		1,899		Na-Ca-HCO_3-Cl	Vandrová et al., 1988
	BB-5	14.0	7.9	1,279	0.94	210	62	61	37	2.4		106	316	452		78		Na-HCO_3-SO_4	Vandrová et al., 1988
	LE-25 S-7		6.9	2,726		420	83	232	63			327	301	1,299				Na-Ca-HCO_3-Cl	VÚFBK. Mariánské Lázně
		10.5	5.9	2,171	2.1	313	64	181	52		2.0	241	248	1,014	33.7	330		Na-Ca-HCO_3-Cl	Krahulec et al., 1977
		12.0	6.5	3,971	2.17	549	118	356	114	5.7	2.0	451	790	1,538	7.0	416		Na-Ca-HCO_3-SO_4-Cl	Melioris et al., 1986
	LE-26 ST-2	9.0	5.9	2,781		416	79	240	73			312	308	1,324	5.2	2,200		Na-Ca-HCO_3-Cl	Krahulec et al., 1977
	borehole on the grounds of service station		7.2	1,538	0.02	21	12	306	39	1.1	0.4	300	235	537	48.1	79		Na-Ca-HCO_3-Cl	Bačová 6.9.2016
Mačkáš	M-2	32.0		5,625		798	120	478	140			493	485	3,033		1,715	8.02	Na-Ca-HCO_3	Melioris et al., 1986
		33.1		5,578		802	113	478	139			525	496	2,965		1,277	11.20	Na-Ca-HCO_3-Cl	Melioris et al., 1986

Continuation of Tab. 8.2

Site	Source	Water t [°C]	pH	TDS	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	F^-	Cl^-	SO_4^{2-}	HCO_3^-	H_2SiO_3	CO_2	H_2S	Chemical type	Source
				[mg.l^{-1}]															
Hokovce	LE-44 M-1	11.4	6.4	6,109		888	160	445	170			644	584	3,124	11.7	1,056		Na-Ca-HCO_3-Cl	Melioris et al., 1986
		16.4	6.6	6,881		1,104	165	481	122			770	637	3,466	12.0	924		Na-Ca-HCO_3-Cl	Melioris et al., 1986
		7.3	6.2	6,358	5.4	701	153	428	162	6.5		627	288	3,624	10.2	2,161		Na-Ca-HCO_3-Cl	Melioris et al., 1986
		13.0	6.0	931	0.22	37	17	121	26	1.5	0.9	39	120	480	63.3	510	0.03	Ca-HCO_3-SO_4	Bačová 28.7.2015
	LE-45 M-5	11.6	6.6	3,704	1.85	567	92	297	93	5.4	1.3	462	375	1,776	14.1	986		Na-Ca-HCO_3-Cl	Melioris et al., 1986
		12.9	6.5	5,350	2.63	865	156	409	123	6.1	1.4	723	560	2,477	5.2	594		Na-Ca-HCO_3-Cl	Melioris et al., 1986
		14.2	6.3	6,832	4.7	1,003	179	537	187	7.6		899	649	3,295	10.4	1,385		Na-Ca-HCO_3-Cl	Melioris et al., 1986
		14.2	6.3	5,054	3.69	702	120	410	119	8.1	1.2	620	633	2,318	56.4	1,220		Na-Ca-HCO_3-Cl	Bačová 28.7.2015
	LE-32 spring at the road	12.9	6.7	1,327	0.61	46	34	160	50	3.2	0.6	25	92	848	33.7	216		Ca-Mg-HCO_3	Bačová 28.7.2015
Hontianske Moravce	ZV-67 spring Kyslá	18.7	6.6	1,625	0.55	156	27	206	36			88	112	1,040	65.8	176	0.01	Ca-Na-HCO_3	Bačová 23.7.2014
Dolné Semerovce	ŠV-8	29.6	6.9	6,934		1,267	82	441	195			1,134	808	2,952		277		Na-Ca-HCO_3-Cl	Franko & Gazda, 1968
		47.3	6.9	6,925		1,231	82	441	207			1,099	791	3,010		295		Na-Ca-HCO_3-Cl	Franko & Gazda, 1968
		19.7	7.0	6,866		1,272	120	341	231			1,134	799	2,913		570		Na-Mg-HCO_3-Cl	Franko & Gazda, 1968
		39.2	7.1	7,027		1,302	120	341	243			1,170	822	2,971		583		Na-Mg-HCO_3-Cl	Franko & Gazda, 1968
Horné Semerovce	HS-2		6.1	3,067	2.04	363	91	284	88	3.4		174	264	1,794				Na-Ca-HCO_3	Lauko et al., 1991
Veľké Turovce	LE-41 ŠHT-47	15.0	6.2	3,874	1.9	575	111	257	130	4.1	1.7	448	240	2,081	5.1	2,128		Na-Ca-Mg-HCO_3-Cl	Rebro et al., 1978
		13.8	6.2	4,040	3.33	627	121	206	109	4.7	2.1	505	267	2,166	15.3	898	0.03	Na-Ca-HCO_3-Cl	Bačová 9.6.2015
	LE-42 ŠHT-48	13.0	6.4	5,491	2.98	932	169	346	136	6.6	2.2	703	523	2,624	8.5	2,638	0.12	Na-Ca-HCO_3-Cl	Rebro et al., 1978
	LE-43 ŠHT-49	14.6	6.3	4,833	2.79	869	147	284	125	6.0	2.1	649	464	2,349	9.3	2,250	0.49	Na-Ca-HCO_3-Cl	Rebro et al., 1978

The chemical composition of the mineral waters of the most important objects in Dudince, Hokovce and Slatina is presented in Fig. 8.4 – map of thickness of Tertiary deposits was compiled on the basis of the results of geophysical works (Tkáčová, 1978). Macrocompounds content is displayed in meq . l^{-1} % using the radar chart.

By recent hydrogeological survey works in the years 1983 – 1990 there were obtained new findings, which show that in the past distinguished types of mineral water – Dudince, Santovka and Slatina – cannot be clearly separated accounting for the latest data on the content of determining ions. This is confirmed by Figure 8.4, where in addition to the concentrations of individual macrocompounds data on water mineralization are presented. To show the macrocompounds content in mineral waters from large amounts of archive data there were selected for each

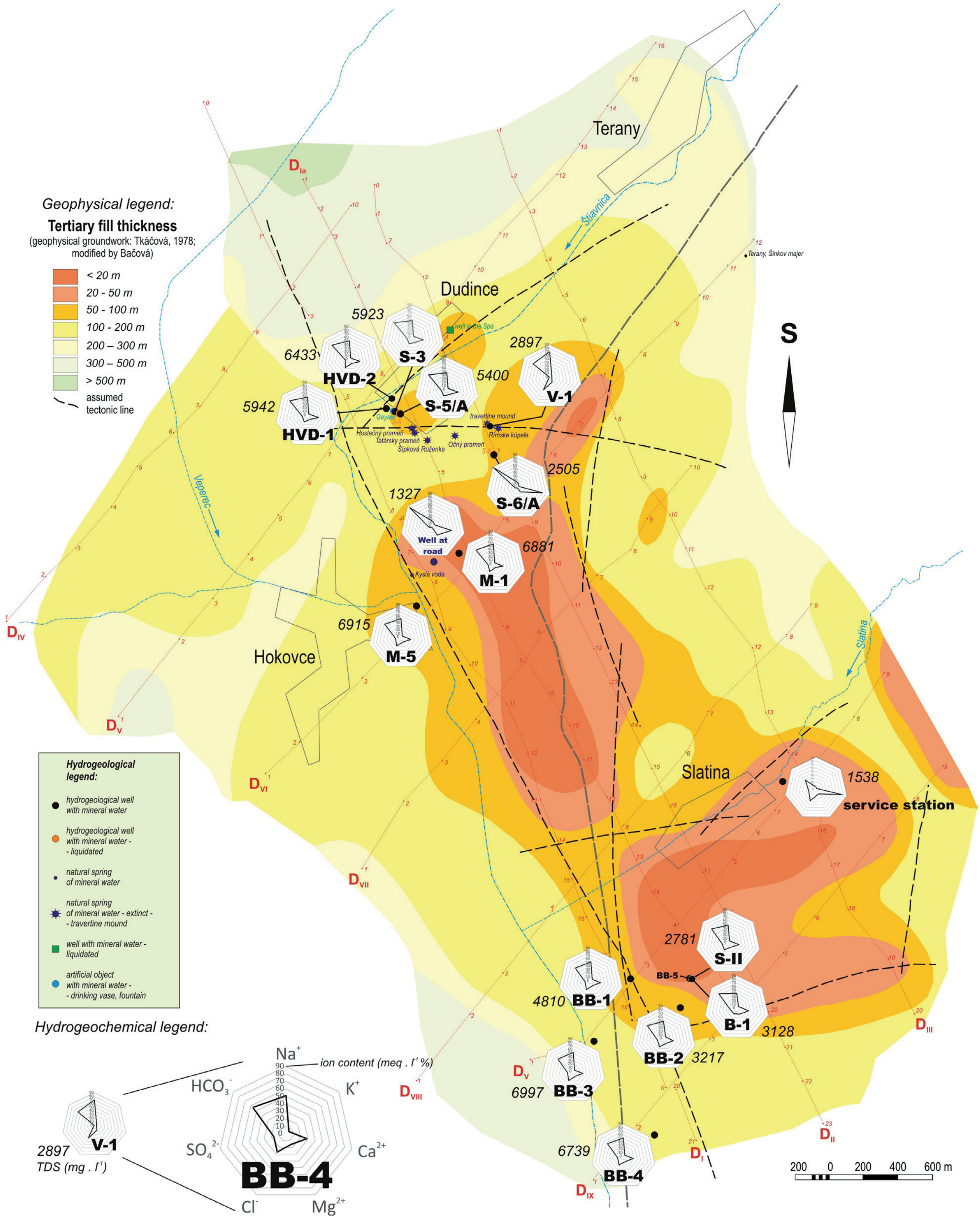


Fig. 8.4 Chemical composition of mineral waters on a base map of the Tertiary sediments thickness in the area of interest

object the analysis of the sample, in which it was detected the highest content of dissolved solids

Up-to-now known data on the thickness of Tertiary filling (represented in the area mostly by tuffs and tuffaceous sediments of Neogene volcanics) the results of drilling works in the area are displayed also on the map of field geophysical measurements – map of the thickness of Tertiary filling (Fig. 8.5., Tkáčová, 1978).

The high accuracy and reliability of geophysical interpretations was confirmed, since the wells drilled in the period after implementation and evaluation of geophysical measurements have determined thickness of Tertiary sediments corresponding to the results provided by geophysics. Tertiary bedrock in the area (determined by the wells HVD-1 and HVD-2 in Dudince and boreholes BB-3, BB-4 and BB-5 in Slatina, Fig. 8.5) are made of southern Ve-

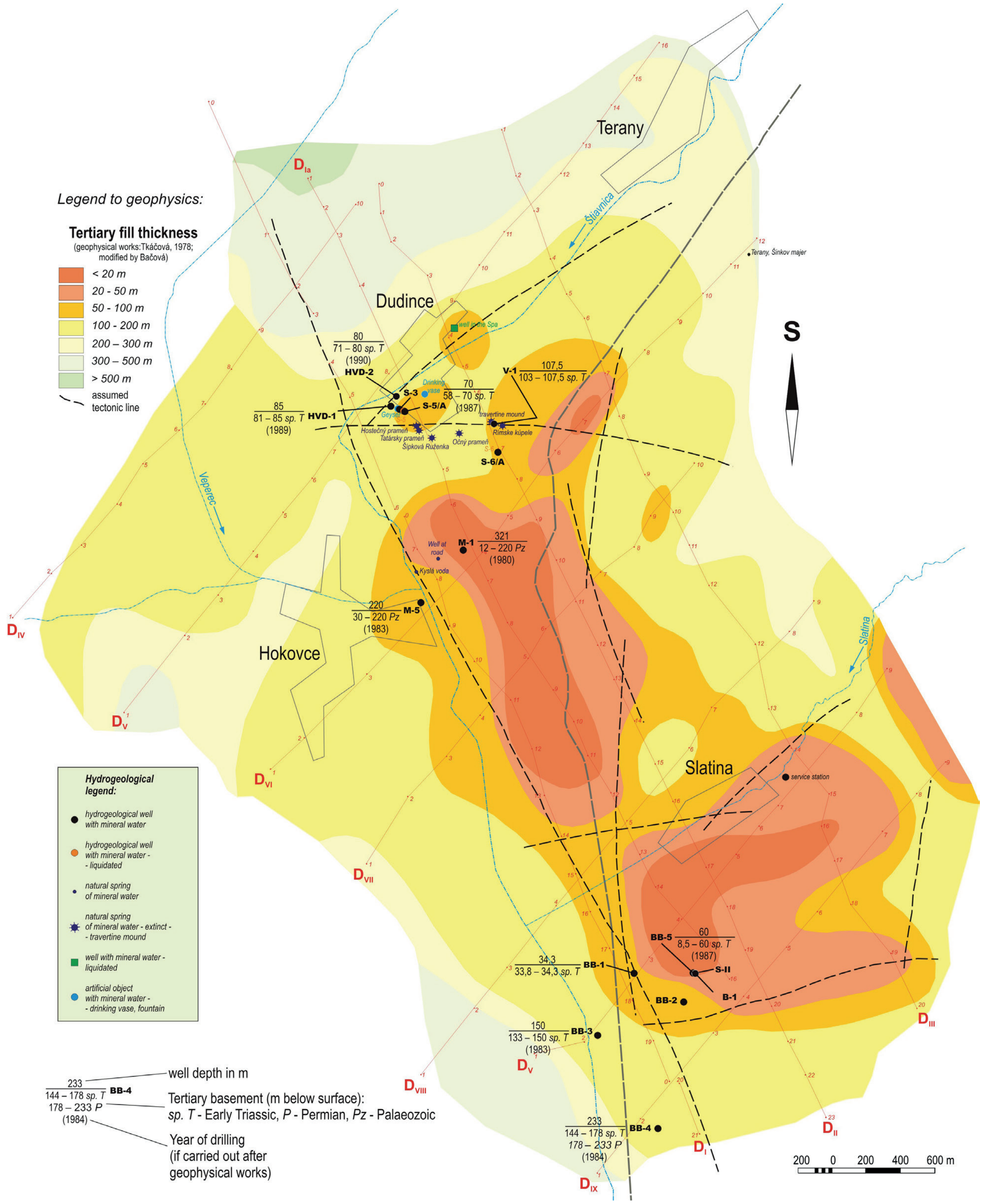


Fig. 8.5 The thickness of Tertiary filling derived from the results of geophysical measurements (Tkáčová, 1978) and the documentation of boreholes

Slovak Geol. Mag., 16, 2 (2016), 125 – 147

poricum rocks – mostly quartzites and quartzose shale of the Early Triassic with underlying quartz conglomerates, phyllite schists of Permian and phyllites, quartzites and metadiabases of Early Palaeozoic (Veporicum crystalline).

8.4.2 Macrochemical composition of mineral waters

Based on the chemical composition the mineral water from Santovka, Dudince and Slatina were assigned to three types (Melioris et al., 1986; Melioris & Trnovec, 1986):

Dudince – characterized by elevated temperature, stable chemical composition, the presence of CO_2 and H_2S (mineral water from a source S-3 in Dudince, B-3A in Santovka and M-2 in Mačkáš – water type Na-Ca-HCO_3-Cl);

Slatina – characterized by lower (with the depth increasing) temperature, higher content of CO_2 and H_2S present only sporadically, wide range of mineralization of water (mineral water from sources in Slatina, M-1 and M-5 in Hokovce – water type Na-Ca-HCO_3-Cl and S-6 Dudince – water type Ca-HCO_3);

Santovka – characterized by wide range of water mineralization, a higher content of CO_2 – like the Slatina type (mineral waters of sources in Santovka: B-6 – chemical type Ca-Na-HCO_3, HG-4 –chemical type Na-Ca-HCO_3 and B-13 – chemical type Na-Ca-HCO_3-Cl-SO_4).

Total dissolved solids in these waters ranges from below 1,000 to 7,670 mg . l^{-1}. CO_2 content varies from several dozens to 3,100 mg . l^{-1}, in some sources high in carbon dioxide (S-3 Dudince, Santovka 3A-B) and at the same time a high content of hydrogen sulphide (found so far in the range of a few milligrams to 20 mg . l^{-1}). In 2014 and 2015 in the waters of the wells S-3 and B3A maximum hydrogen sulphide content was found 5,93 mg . l^{-1}.

Macrochemical composition of mineral water of the "Levice Spring Line" (shown at the Langelier-Ludwig graph in Fig. 8.6) is quite diverse. From typical water with carbonatogenic mineralization (boreholes HBV-1, HBV-2 and HBV-3 in Levice) cez through water of mixed chemical composition (water of deeper circulation, e.g. from sources S-3, HVD-1, HVD-2 in Dudince, B-13, B-3 and B-3A in Santovka, M-2 in Mačkáš, from the wells BB-1, BB-2, BB-3 and BB-4 in Slatina) to the waters with a hydrosilicatogenic mineralization (well HIP-9 in Kubáňovo).

The graph in Fig. 8.6 shows the results of previously conducted analyses of samples of mineral water in the examined area. The data from the work were used: Bondarenková, 1979; Bondarenková & Babíková, 1981; Bondarenková, 1983; Bondarenková et al., 1984; Bondarenková et al., 1988; Čermák & Gaža, 1973; Demian et al., 1991; Dobiš, 1987; Fecek, 1981; Fendek et al., 1989; Franko et al., 1975; Franko & Michalíček, 1975; Franko et al., 1982; Hensel et al., 1955; Holeczyová et al., 1971; Holeczyová et al., 1973; Holeczyová et al., 1975; Holeczyová & Motlíková, 1976; Jalč & Frličková, 1982; Klago et al., 1979;

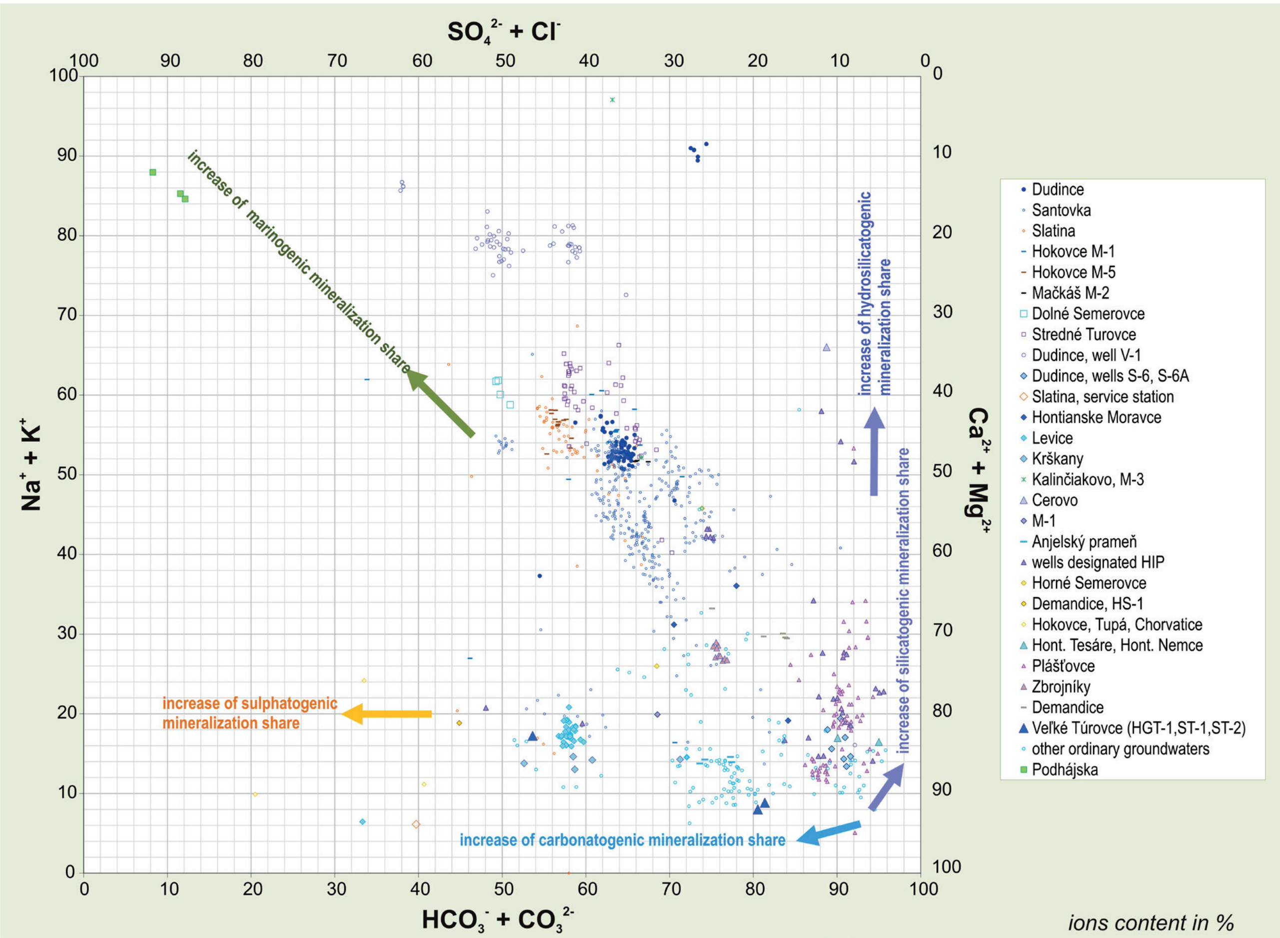


Fig. 8.6 Macrochemical composition of mineral water – Langelier-Ludwig diagram

Krahulec et al., 1977; Lauko et al., 1991; Melioris et al., 1986; Melioris, 1995; Melioris & Drexler, 1997; Melioris & Drexler, 2002; Orvan et al., 1965; Orvan & Hornung, 1968; Ostrolúcky, 1979; Rebro, et al., 1979; Vandrová et al., 1987; Vandrová, 1988; Vandrová 1988a; Vandrová & Potyš, 1988; Vandrová et al., 1988; Vandrová, 1990; Vandrová & Matejčeková, 1990; Vandrová et al., 1990; Vandrová & Sňahničanová, 1998; Vandrová & Štefanka, 2007; Vandrová et al., 2008; Vandrová et al., 2009; Vandrová et al., 2012. In Figs. 8.6 and 8.7 there are maintained the same types of colours and brands for different water sites (or sources).

The chart is supplemented by data on macrocompounds content in common groundwater in the area of the "Levice Spring Line" and its surroundings, obtained from the following works: Čubrík et al., 1985 (Dolné Semerovce); Danielová, 1991 (Veľké Turovce); Demian et al., 1991 (Hontianska Vrbica, Demandice, Tupá, Šahy); Ďuriančík, 1968 (Santovka); Ďuriančík, 1993 (Hokovce); Fecek, 1980; Fecek et al., 1980a, 1980b (vicinity of Plášťovce); Hlavatý & Modlitbová, 1969 (Santovka); Hlavatý et al., 1974 (vicinity of Plášťovce, Medovarce); Izso & Potyš, 1967 (Santovka); Jalč et al., 1981 (Zbrojníky); Jalč, 1982 (Demandice); Jalč & Frličková, 1982 (Dolné Semerovce), 1983 (Hokovce); Jalč, 1983 (Horné Semerovce); Koša et al., 1968 (Rykynčice); Lauko, 1981a, 1981b (Demandice); Lauko et al., 1991 (Horné Semerovce); Laurenčík, 1987a, 1987b (Demandice, Horné Semerovce); Lipovská et al., 1982a, 1982b (Bory, Domadice); Lipovská et al., 1983 (Santovka); Némethyová et al., 1990 (Demandice); Neupauer, 1981 (Hontianske Nemce); Ostrolucký, 1979 (Horné Semerovce); Šimovičová, 1976 (Hontianske Tesáre); Vandrová, 1995 (Santovka).

In Fig. 8.7 the macrochemical composition of the mineral waters of Dudince, Santovka and Slatina is displayed on the chart with a logarithmic scale, where coefficients are plotted calculated from the mass concentrations. To construct such a graph it was necessary to know only the weight concentrations of sodium, potassium, calcium, magnesium, bicarbonates (unlike of the previous graph, where all the data on the content of all the determining ions in waters had to be processed, and calculate the content in meq . l^{-1} %).

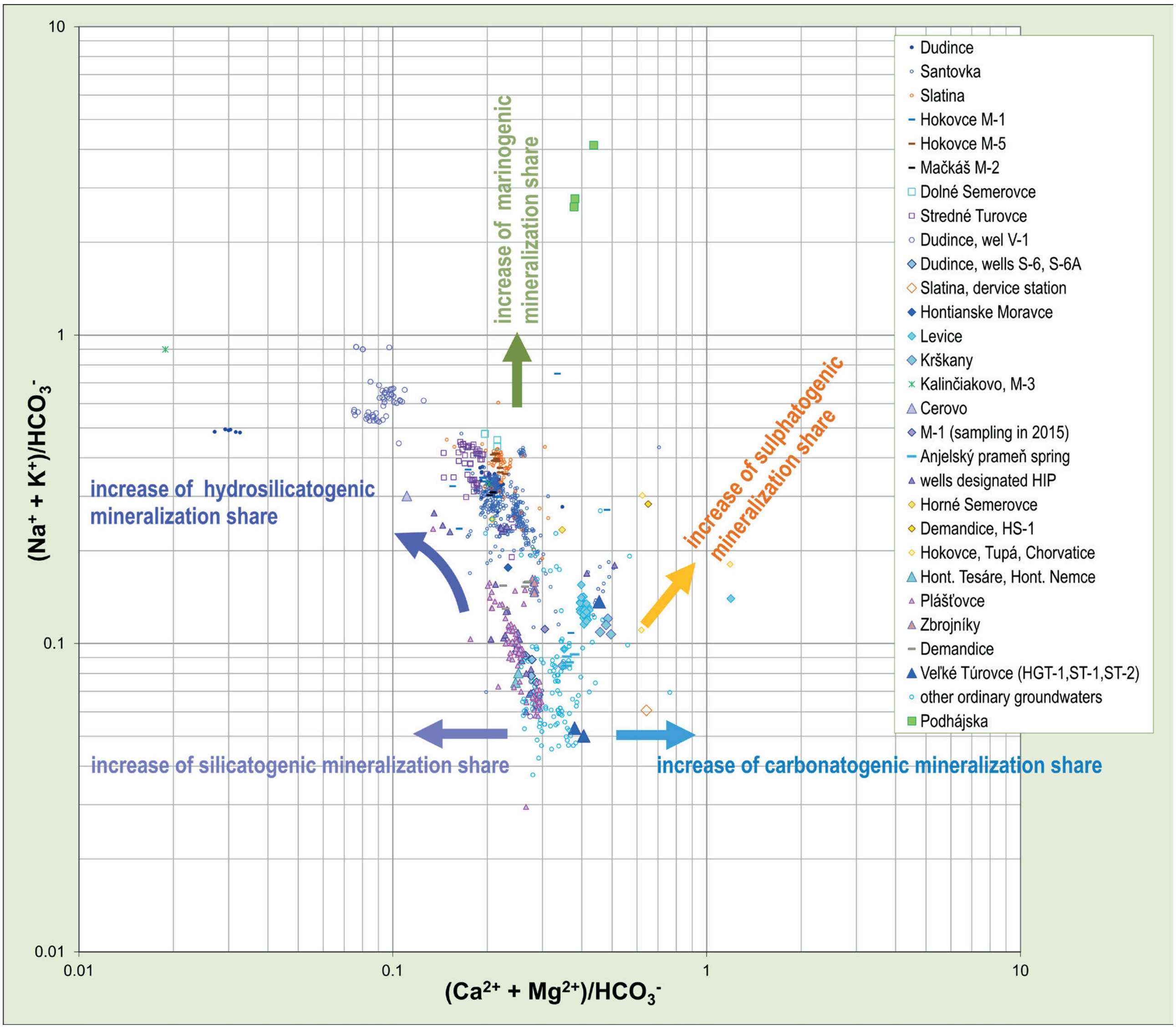


Fig. 8.7 Macrochemical composition of mineral waters – graph by Bačová (2011)

Waters with different macrocompounds content in the chart are defined by their position, which refers to the dominant processes shaping their chemical composition. The lowest points represent water with silicatogenic and carbonatogenic mineralization (with the lowest total dissolved solids content). Upwards and to the left the points are placed showing water with an increasing share of hydrosilicatogenic mineralization, up and to the right with a growing share of sulphatogenic mineralization and straight up rising share of marinogenic mineralization. Around the value of the coefficient $(Na^+ + K^+)/HCO_3^-$ equalling 1 the marinogenic mineralization is prevalent in the waters.

Mineral waters of Dudince, Santovka and Slatina have mixed chemical composition – formed by multiple processes. Silicatogenic, hydrosilicatogenic and marinogenic mineralizations are in prevail. However, carbonatogenic and sulphatogenic mineralizations are also manifested.

Based on current knowledge about mineral waters of the "Levice Spring Line" and also according to graphic display of macrocompounds content the earmarking of the Dudince, Santovka and Slatina types does not seem justified. This is documented by both methods of displaying the chemical composition of mineral waters (Fig. 8.6 and 8.7), and by depiction of the selected data on the qualitative characteristics of these waters in Figs. 8.8, 8.9 and 8.10. In the Dudince and Santovka hydrogeological objects (at different depths) mineral waters were identified satisfying the criteria under which they were earmarked the Dudince and Santovka types, but also the Slatina type. Varied chemical composition and significant differences in mineralization of waters of the objects of the discharge areas (Dudince, Santovka, Slatina) reflect complex geological and tectonic conditions depending upon a variety of factors – such as the position and depth (i.e. the depth of the open section) of each mineral water source, often also a change in the exploited amount of water, CO_2 content. Mineral waters from Slatina are distinctly different from the mineral waters of Dudince and Santovka by a higher share of marinogenic component of the resulting chemical composition.

Content of chlorides and sulphates in mineral waters

Available data on concentrations of chlorides and sulphates in mineral waters of the "Levice Spring Line" are plotted in Fig. 8.8. Investigation of the relationship between these characteristics of the chemical composition of water allows us to distinguish between water with share of carbonatogenic and sulphatogenic mineralizations from the waters in which such mineralization does not exist or its participation in a total dissolved solids content is minimal. From the line along which most points are allocated representing the waters from the investigated territory (with the direction towards the points, showing the content of chloride and sulphate in sea water), towards the upper left corner of the chart the water with increasing presence carbonatogenic and sulphatogenic mineralization are displayed (thermal water from Levice, Krškany). On the other side, there are points representing water with a significant proportion of hydrosilicatogenic and marinogenic mineralizations.

Mineral water from boreholes B-3 and B-3A in Santovka has noticeably higher content of both macrocompounds as natural healing water from a borehole S-3 in Dudince. Slightly lower levels of sulphate and chloride have been found in the water from the well of M-2 in Mačkáš (Fig. 8.8 – bottom graph).

Content of chlorides and bicarbonates in mineral waters

Information on concentration of bicarbonate and chloride in the investigated waters is provided in Fig. 8.9. Mineral waters of different sites (and even specific sources) are distinguished by the same numerals as in the previous figure. In the direction from the lower left corner to the upper right content of each macrocompound rises, reflecting mainly the deep circulation of mineral water (i.e. the depth of the tapping). Upwards right points are placed representing mineral water from the deepest sources (with the greatest depths of open sections in boreholes).

In addition to the above described dependence, the graph manifests another significant linear relationship – the line joining points representing water from wells M-1 Hokovce, M-5 Hokovce, BB-3 and BB-4 Slatina, SV-8 Dolné Semerovce (Fig. 8.9 – the lower graph). This points out to the fact, that the higher is the concentration of bicarbonate in the mineral water; the lower is the concentration of the chloride and the chloride content in the mineral water increases, and content of bicarbonates decreases in the direction from the north to the south.

By comparing the thermal water from a borehole B-3A (Santovka) with natural healing water from a borehole S-3 (Dudince), again we see a difference – the first one has clearly higher content of chlorides and bicarbonates. By comparing with the mineral waters from Slatina and Veľké Turovce these waters have a relatively higher content of bicarbonates, and less chlorides.

The content of sodium and calcium in mineral water

The relationship between sodium and calcium in the mineral waters (Fig. 8.10), similar to the relationship between the content of chloride and sulphate in mineral waters, served to distinguish water having carbonatogenic and sulphatogenic mineralization from the waters without such a mineralization (determining are the hydrosilicatogenic and marinogenic mineralizations). Among the objects in the studied area the highest share marinogenic mineralization have the waters from wells in Slatina, in Stredné Turovce (drillings ŠHT47, SHT-48 and SHT-49) and in Dolné Semerovce (well SV-8). This is confirmed by Fig. 8.10.

8.5 Discussion

From the lessons learned so far by hydrogeological exploration and research work in the area it has been shown that the mineral waters of the "Levice Spring Line" are of a very complex origin. They are formed by the mixing of waters from different geological environments in varying proportions, resulting in a very diverse chemical composition of waters from the existing and destroyed

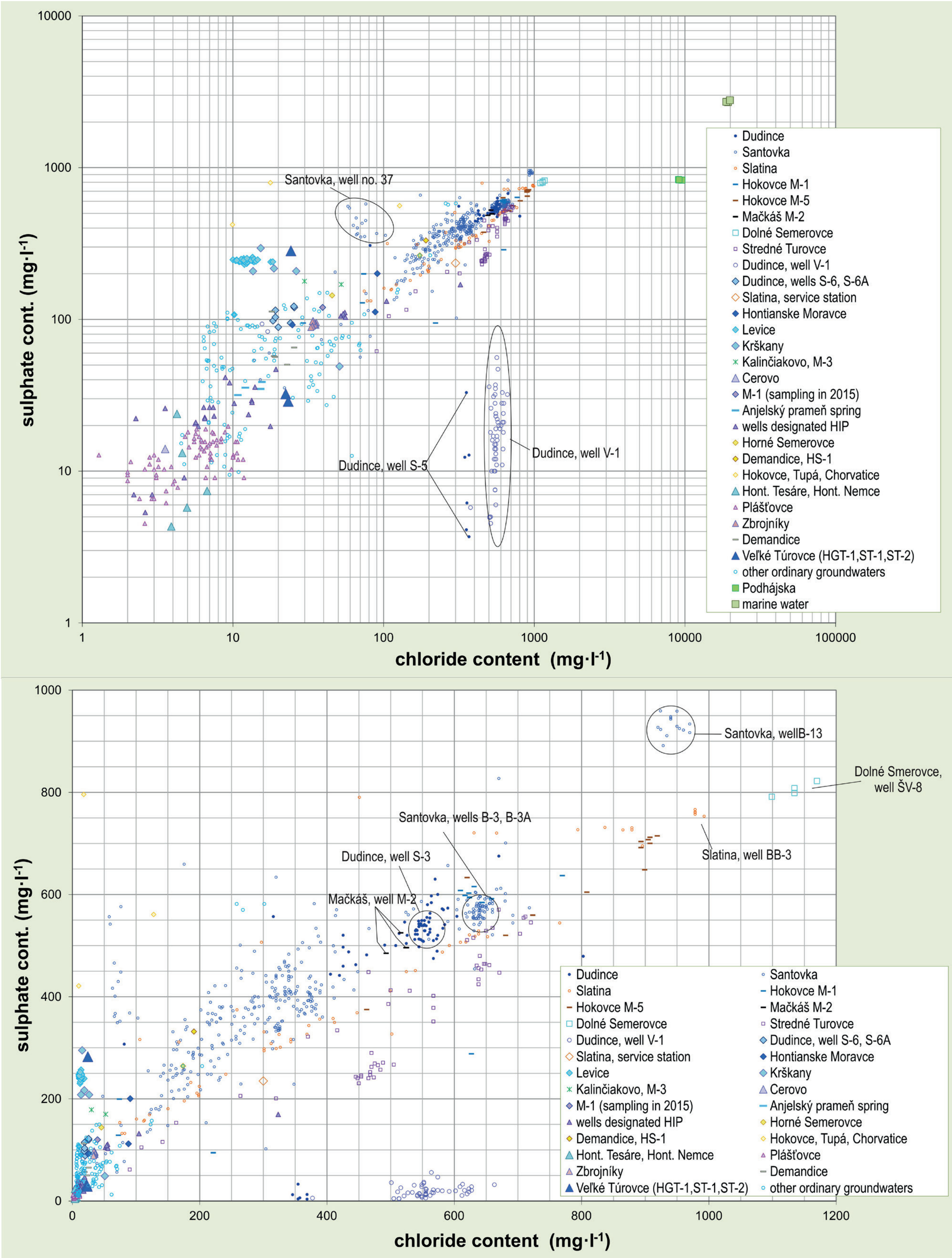


Fig. 8.8 The concentration of chloride and sulphate in mineral waters

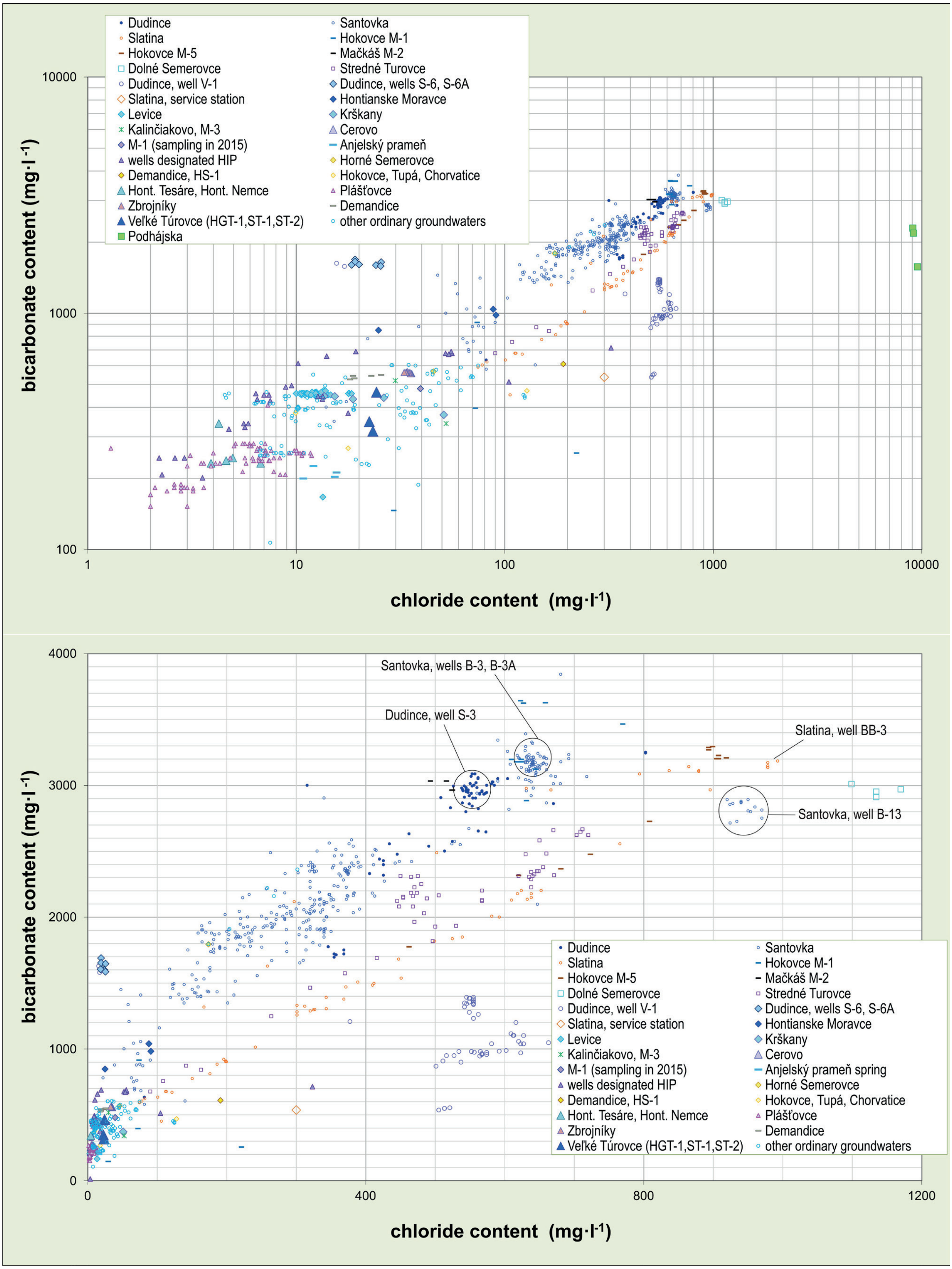


Fig. 8.9 The concentration of bicarbonate and chloride in mineral water

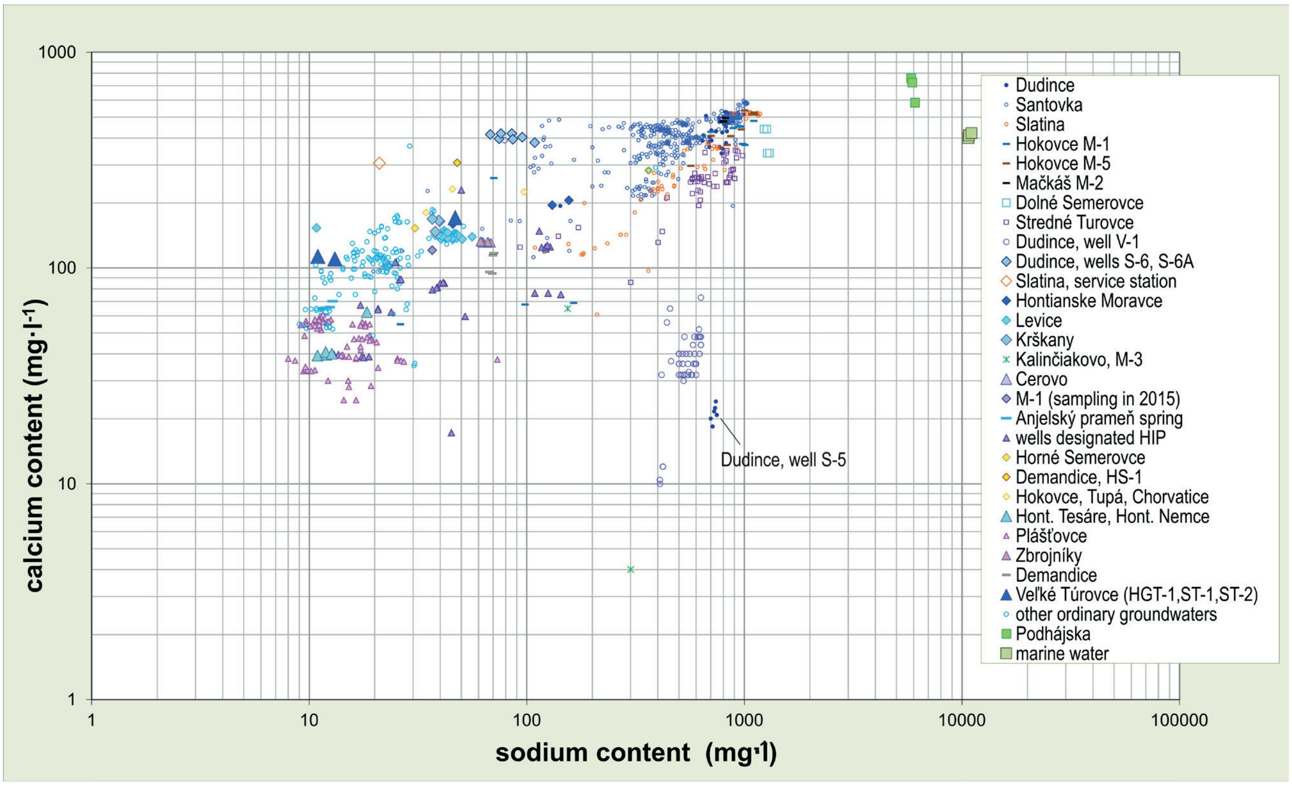


Fig. 8.10 The concentration of sodium and calcium in mineral water

hydrogeological objects. Almost identical chemical composition have the waters from the wells B-3A (Santovka), S-3 (Dudince) and M-2 (Mačkáš). Even here there are some differences – in the water from borehole M-2 has clearly higher share of hydrosilicatogenic mineralization compared to other ones, water from borehole B-3A has the highest share of marinogenic mineralization observed (among all three). The fact that the mineral waters from different sources in the discharge areas Dudince and Santovka are of relatively varied chemical compositions, reflects the complex conditions of their formation (the rock environment intensely tectonically disturbed at the contact volcanic mountain ranges and sedimentary basins with Tertiary bedrock represented by Veporicum rocks, involving deep CO_2).

At the sites Santovka and Dudince natural mineral springs existed in the past. At the time of the first drilling of the wells in the discharge areas at these sites in the 50s and 60s of the last Century all the springs gradually disappeared. At present, at their places only the travertine mounds with conduit remains (channels) in their centres have been preserved (Fig. 8.11). The natural mineral springs occurred in major tectonically disturbed zones (or within the fault crossings).

Drilling works in Dudince and Santovka were carried out in the 70s and 80s of the last Century – primarily with the goal to acquire new sources of mineral waters. In 2015 the last well was excavated (at the site of liquidated borehole S-6) designated as S-6/A. The decline in available mineral waters from existing older objects can be a consequence of their poor technical condition, as well as changing the pressure conditions in the discharge areas. We can conclude on the basis of knowledge of hydrodynamic test results that verified productivity of the most wells gradually declined. As a rule, a verified (or recommended) high yield of wells was stated in the period immediately after the objects construction; later it was often significantly lower. In some cases, the qualitative characteristics of mineral water are directly dependent of the exploited amount – especially in waters of a shallower circulation (borehole B-6 in Santovka, drillings BB-1 and BB-2 in Slatina). These groundwaters quality may also be impacted by climatic factors (such as long-lasting period without rainfall), but also ordinary high groundwater withdrawal near the mineral water source.

Data from long-term observation of the objects of the mineral waters in Dudince and Santovka in the current period are processed and evaluated, but even now we can say that the chemical composition of mineral waters from the source B-3A (and the destroyed borehole B-3) in Santovka and S-3 in Dudince appears to be stable. Our opinion is that given the mixed chemical composition of these waters of the type Na-Ca-HCO_3-Cl (sources B-3A and S-3), in which the waters of different types from different geological environments are involved, we need to consider several catchments, transport routes to the discharge areas and areas of accumulation (this issue was described in detail by Hynie (1957b, 1963), Franko (in Franko et al., 1975), in many works by Melioris (e.g. Melioris et al., 1986; Melioris, 1998 and others – in the references) and byother experts). Currently there are carried out new determinations of stable isotopes of O, H, and S in the mineral water of the objects in this respect until now without any investigation. We assume that the data can significantly contribute to clarifying the existing views.

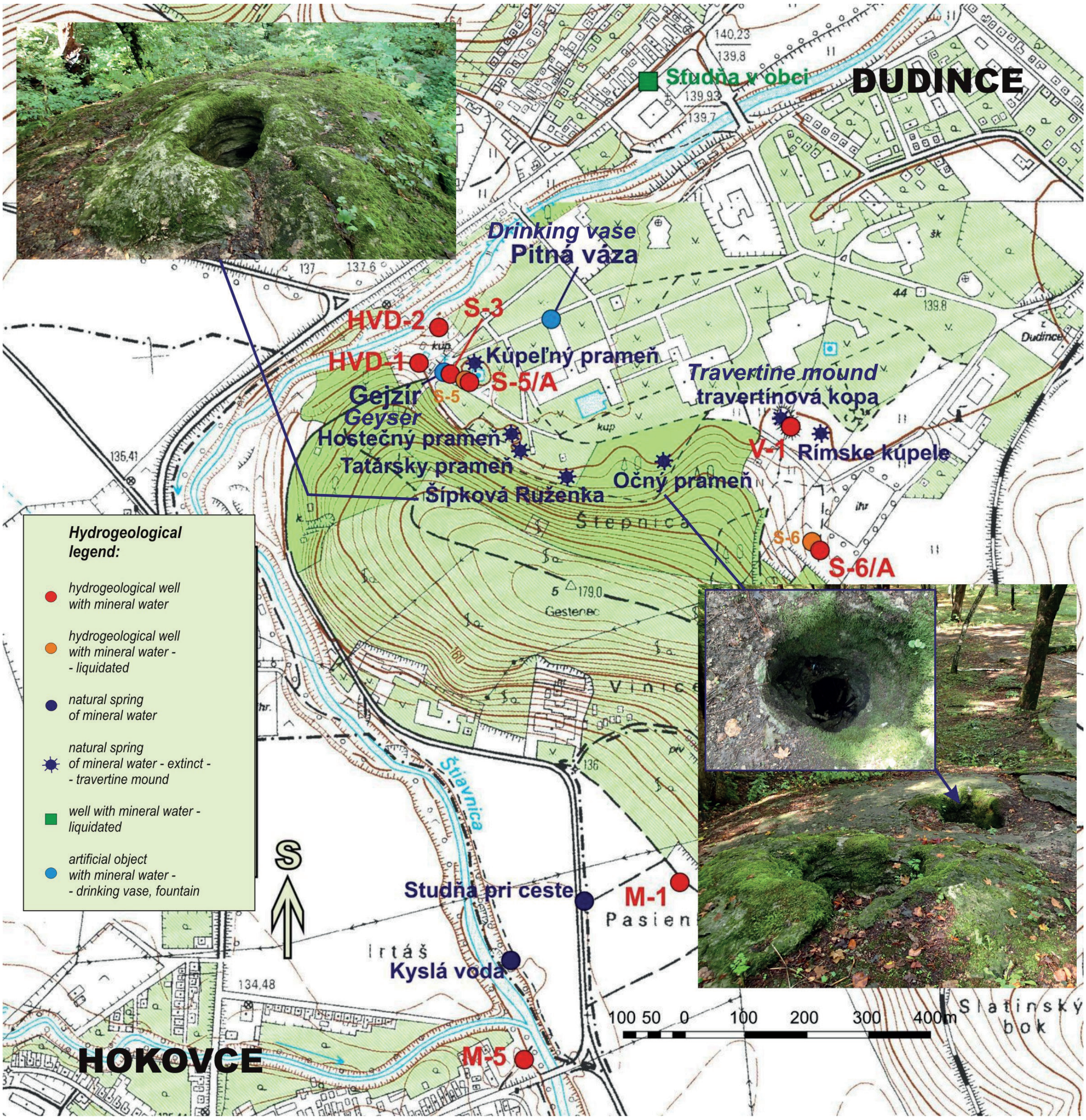


Fig. 8.11 Travertine mounds of extinct springs in Dudince

Hydrogeological structure is defined as a structural geological unit (part of the geological space), which is different from other parts of the geological area by common integrated and continuous circulation of groundwaters from the infiltration area through circulation zone to the drainage area. Its most important characteristic are the geometric shape, size and spatial distribution of hydrogeological collectors (STN 75 0111 Terminology of hydrogeology).

The hydrogeological structure of the mineral waters in the examined area – "Levice Spring Line" (which includes locations Dudince, Santovka, Slatina) – is considered to be complicated, with multiple separate structures and discharge areas. It is classified as the open structure with semi-open and semi-closed discharge areas. Central Slovakian volcanic rocks of the Krupinská vrchovina Mts. or Štiavnické vrchy Mts are considered to be the infiltration areas. It is assumed that the accumulation zone of the natural healing water from the source S-3 in Dudince are volcano-sedimentary rocks between Dudince and Hontianske Tesáre and the special role played the Badenian basal gravel complex in Dudince, which allows for increased accumulation of the mineral water (Melioris et al., 1986, Ministry of Health Decree no. 19/2000 Coll.).

8.6 Conclusion

Macrochemical assessment of the composition of mineral water of the "Levice Spring Line" in this paper makes it possible to realize regional hydrogeochemical regularities in the studied area and its surroundings. It points to the similarities and differences between the mineral waters of the discharge areas of Dudince and Santovka. The silicatogenic and hydrosilicatogenic mineralization contribution can be clearly seen (waters formed in Neogene sediments), marinogenic mineralization (the highest proportion was found in the waters coming from the rock environment Palaeozoic – Permian), and probably also carbonatogenic and sulphatogenic mineralization (water likely originating from Mesozoic carbonate rocks).

In the Dudince Spa the natural healing water is currently used from the source S-3, and it is the natural overflow. Any influence of the pressure conditions (in particular the implementation of new drillings) in the discharge area of Dudince can cause serious operational problems. Equally important is to satisfy the prescribed recoverable amount of the natural mineral water.

8.7 References

Bezák, V., Broska, I., Ivanička, J., Reichwalder, P., Vozár, J., Polák, M., Havrila, M., Mello, J., Biely, A., Plašienka, D., Potfaj, M., Konečný, V., Lexa, J., Kaličiak, M., Janočko, J., Pereszlényi, M., Marko, F., Maglay, J., Pristaš, J., 2004: *Tektonická mapa Slovenskej republiky*. ME SR – SGIDŠ Bratislava.

Bačová, N., 2011: Makrochemické zloženie minerálnych vôd východoslovenského úseku flyšového pásma Západných Karpát. *Mineralia Slovaca*. ISSN 0369-2086, 2011, roč. 43, č. 2, p. 147 – 156.

Biela, A., 1978: Hlboké vrty v zakrytých oblastiach vnútorných Západných Karpát. Regionálna geológia Západných Karpát 11, GIDŠ Bratislava, 224 p.

Bondarenková, Z., 1979: Santovka – likvidácia vrtov a hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava.

Bondarenková, Z. & Babíková, M., 1981: Slatina – vyhľadávací HGP, cieľ: zachytenie minerálnej vody v náhradnom zdroji za vrt BB-2. Manuscript – SGIDŠ Archive Bratislava, 41 p.

Bondarenková, Z., 1983: Hydrogeologické a hydrogeochemické poznatky z prieskumných prác v Santovke. *Mineralia Slovaca*, ISSN 1338-3523, 1983, roč. 15, č. 4, p. 347 – 361.

Bondarenková, Z., Roháčiková, A., Motlíková, H., 1984: Slatina – vyhľadávací HGP, cieľ: zabezpečiť zdroj minerálnej vody. Manuscript – SGIDŠ Archive Bratislava, 47 p.

Bondarenková, Z., Kertész, A., Michalič, J., Pelikán, V., Sokola, K., Vika, K., Král, M., Janči, J., 1988: Zlaté Klasy – Trnávka – výpočet zásob termálnej vody, stav k 31. 12. 1988. Manuscript – SGIDŠ Archive Bratislava, 47 p.

Čermák, D. & Gaža, B., 1973: Podhájska-1, záverečná správa o hlbokej termálnej studni. Manuscript – SGIDŠ Archive Bratislava, 13 p.

Čubrík, M., Motlíková, H., Žákovská, P., 1985: Dolné Semerovce – hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava.

Danielová, K., 1991: Stredné Turovce – vyhodnotenie hydrogeologického prieskumného vrtu ST-1, 2 na lokalite Stredné Turovce pre plánovanú skládku TKO, hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava, 23 p.

Demian, M., Bárdy, J., Vrábľová, M., 1991: Tupá – rieka Hron, pozorovacie sondy, orientačný IG a HG prieskum. Manuscript – SGIDŠ Archive Bratislava.

Dobiš, M., 1987: Vodný zdroj HNZS-1 – Závlahy pozemkov Horné Semerovce, miesto: Hokovce, podrobný HGP. Manuscript – SGIDŠ Archive Bratislava, 4 p.

Ďuriančik, M., 1968: Santovka – vyhodnotenie podrobného hydrogeologického prieskumu – sonda pre bytovku, účel: zabezpečiť požadované množstvo pitnej a užitkovej vody. Manuscript – SGIDŠ Archive Bratislava, 10 p.

Ďuriančik, M., 1993: Vyhodnotenie čerpacej skúšky na vŕtanej studni, rozbory vody a stanovenie PHO pre vodovod Hokovce. Manuscript – SGIDŠ Archive Bratislava.

Fecek, P., Noruláková, H., Ševčíková, J., Obernauer, M., 1980: Plášťovce – hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava.

Fecek, P. et al., 1980: Plášťovce – hydrogeologický prieskum, účel – vyčíslenie využiteľného množstva podzemných vôd. Manuscript – SGIDŠ Archive Bratislava, 40 p.

Fecek, P., 1981: Neogene Ipeľskej pahorkatiny. Manuscript – SGIDŠ Archive Bratislava, 164 p.

Fendek, M., Bodiš, D., Boorová, D., Franko, O., Jančí, J., Kohút, M., Král, M., Papšíková, M., 1989: Reinjektážny vrt GRP-1 Podhájska. *Regionálna geológia Západných Karpát*, GIDŠ Bratislava, č. 24, p. 59 – 100.

Fendeková, M. & Melioris, L., 1996: Hydrodynamická skúška na vrte S-3 v Dudinciach. Manuscript – Katedra hydrogeológie PRIF UK, 43 p.

Fľaková, R., Ženišová, Z., Seman, M., 2010: Chemická analýza vody v hydrogeológii. SAH Bratislava, 166 p.

Franko, O., Gazda, P., Michalíček, M., 1975: Tvorba a klasifikácia minerálnych vôd Západných Karpát. Bratislava, GIDŠ, 232 p.

Franko, O. & Michalíček, M., 1975: Štúdia o jódobrómových vodách. Manuscript – SGIDŠ Archive Bratislava.

Franko, O., Bodiš, D., Brestenská, E., Ondrejíčková, A., Priechodská, Z., Remšík, A., Vass, D., 1982: Správa o výskumnom geotermálnom vrte FGDŽ-1 Dvory nad Žitavou. Čiastková záverečná správa za rok 1982. Manuscript – SGIDŠ Archive Bratislava, 312 p.

Gazda, P., 1974: Chemizmus podzemných vôd Západných Karpát a jeho genetická klasifikácia. In: Leško, B. (ed.): Materiály z III. celoslovenskej geologickej konferencie, II. časť. Bratislava, Slovenský geologický úrad, p. 43 – 50.

Hanzel, V., Franko, O., Jetel, J., Bodiš, D., Böhm, V., Bujalka, P., ‚Fides, J., Hyánková, K., 1998: Geologický slovník. Hydrogeológia. Bratislava, Vydavateľstvo Dionýza Štúra, 301 p.

Hensel, J., Igumanová, A, Němejc, J., Novák, J., 1955: Balneografia Slovenska. Bratislava, SAV, 456 p.

Hlavatý, Z. & Modlitbová, O., 1969: Santovka – vyhodnotenie geologicko-litologického profilu vrtu – kopanej studne HGS-10. Manuscript – SGIDŠ Archive Bratislava, 13 p.

Hlavatý, Z., Fecek, P., Némethy, P., Droppa, V., Kropácsek, A., Machmerová, E., Modlitba, I., Motlíková, H., Janek, J., Cagala, R., Banský, V., Kazmuková, Drobáň, 1975: Stredoslovenské neovulkanity, vyhľadávací hydrogeologický prieskum, III. etapa (Krupinská vrchovina – západná časť). Manuscript – SGIDŠ Archive Bratislava, 141 p.

Holéczyová, Z., Pospíšil, Z., Zvara, J., 1971: Santovka – rozšírenie zdrojov minerálnej vody, podrobný prieskum – I. etapa. Manuscript – SGIDŠ Archive Bratislava, 20 p.

Holéczyová, Z., Gazda, P., Pospíšil, Z., 1973: Slatina – podrobný hydrogeologický – jímací vrtný prieskum. Manuscript – SGIDŠ Archive Bratislava, 40 p.

Holéczyová, Z., Motlíková, H., Mucha, I., Bačová, Z., 1975: Santovka – rozšírenie zdrojov minerálnej vody, podrobný HGP, cieľ: overenie možnosti získať zdroj úžitkovej vody pre prevádzku plniarne. Manuscript – SGIDŠ Archive Bratislava, 138 p.

Holéczyová, Z. & Motlíková, H., 1976: Slatina – plniarenský závod, predbežný HGP, cieľ: získanie doplňujúceho resp. nového zdroja pitnej a úžitkovej vody. Manuscript – SGIDŠ Archive Bratislava, 17 p.

Hynie, O., 1956: Celkové vyhodnocení výsledků vrtních prací v lázních Dudince od jejich začátku do ukončení vrtu S-4 s návrhem plánů dalších vrtů až do konečného využití zřídel. Praha. Archive of MH SR, Bratislava.

Hynie, O., 1957a: Hydrogeologický posudek o výsledku vrtného průzkumu v lázních Dudincích provedeného v r. 1957. Manuscript, Praha.

Hynie, O., 1957b: Hydrogeologie minerálních vod. Státní pedagogické nakladatelství Praha, 224 p.

Hynie, O., 1963: *Hydrogeologie ČSSR II. Minerálne vody.* ČSAV, Praha, 797 p.

Iszo, J. & Potyš, Z., 1967: Santovka – hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava, 21 p.

Jalč, D. & Frličková, M., 1982: Veľké Turovce – hydrogeologický prieskum, účel: overenie možnosti zabezpečiť zdroj podzemnej vody pre svoje vinné hospodárstvo v katastrálnom území Veľkých Turoviec. Manuscript – SGIDŠ Archive Bratislava, 5 p.

Jalč, D., 1982: Demandice – osady – pioniersky tábor, hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava, 7 p.

Jalč, D. & Frličková, M. 1982: Dolné Semerovce – hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava.

Jalč, D., 1983: Horné Semerovce – hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava.

Jalč, D. & Frličková, M., 1983: Hokovce – hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava.

Konečný, V., Lexa, J., Halouzka, R., Dublan, L., Šimon, L., Stolár, M., Nagy, A., Polák, M., Vozár, J., Havrila, M., Pristaš, J., 1998: *Geologická mapa Štiavnických vrchov a Pohronského Inovca (Štiavnický stratovulkán).* GSSR Bratislava.

Koša, J. et al., 1968: Dudince – vodný zdroj, vyhľadávací hydrogeologický prieskum, účel: zaistiť zdroj pitnej a úžitkovej vody. Manuscript – SGIDŠ Archive Bratislava, 19 p.

Krahulec, P., Rebro, A., Uhliarik, J., Zeman, J., 1977: *Minerálne vody Slovenska. Balneografia a krenografia*. 1. Osveta Martin, 456 p.

Klago, M., Matejčeková, E., Jurdík, M., Žídek, L., 1979: Registrácia minerálnych a termálnych vôd – doplnky III. Manuscript – SGIDŠ Archive Bratislava.

Langelier, W. F. & Ludwig, H.F., 1942: Graphical method for indicating the mineral character of natural water. *J. Am. Water Works Assoc.*, 34, p. 335 – 352.

Lauko, V., 1981: Vyhodnotenie hydrogeologického prieskumného vrtu HD-3 na lokalite Demandice. Manuscript – SGIDŠ Archive Bratislava, 11 p.

Lauko, V., Kovácz, T., Kosťov, K., Ševčík, J., 1991: Horné Semerovce – vyhodnotenie vyhľadávacieho HGP, cieľ: získanie zdroja podzemnej vody. Manuscript – SGIDŠ Archive Bratislava.

Laurenčík, J., 1987a: Záverečná správa z čerpacieho pokusu na lokalite Demandice – lekáreň. Manuscript – SGIDŠ Archive Bratislava, 5 p.

Laurenčík, J., 1987b: Záverečná správa hydrogeologického prieskumu na lokalite Horné Semerovce. Manuscript – SGIDŠ Archive Bratislava.

Lipovská, M., Novomestská, D., Palkovičová, M., Tadanaiová, H., 1982a: Vyhodnotenie čerpacej skúšky na jestvujúcej studni LSB-1 v Boroch. Manuscript – SGIDŠ Archive Bratislava.

Lipovská, M., Čepela, J., Palkovičová, M., Markóová, E., 1982b: Vyhodnotenie hydrogeologického prieskumného vrtu HD-2 na lokalite Domadice. Manuscript – SGIDŠ Archive Bratislava.

Lipovská, M., Košč, J., Novomestská, D., Markóová, E., 1983: Santovka – vyhodnotenie hydrogeologického prieskumu, účel: zistenie zdroja pitnej a úžitkovej vody pre hospodárske stredisko JRD Santovka. Manuscript – SGIDŠ Archive Bratislava, 9 p.

Melioris, L. & Vass, D., 1982: Hydrogeologické a geologické pomery levickej žriedelnej línie. GIDŠ Bratislava. *Západné Karpaty, sér. hydrogeológia a inž. geológia*, č. 4, p. 7 – 56.

Melioris, L., Hyánková, K., Pospíšil, P., Böhm, V., Čech, F., Mucha, I., Fendeková, M., Némethy, P., Paulíková, E., Ženišová, Z., 1986: Dudince – Santovka – Slatina, záverečná správa, vyhľadávací HGP, cieľ: zabezpečenie ochrany a racionálneho využívania prírodných liečivých zdrojov minerálnych a termálnych vôd a prírodných zdrojov stolových minerálnych vôd (časť A, B). Manuscript – SGIDŠ Archive Bratislava, 100 p.

Melioris, L. & Trnovec, A., 1986: Levická žriedlová línia – ochranné pásma. Rešeršná správa. Archive of ISS MoH

Melioris, L., 1995: Dudince – hydrogeologický prieskum. Manuscript – ISS Archive Bratislava, 26 p.

Melioris, L. & Drexler, V., 1997: Hydrogeologický prieskum Dudince – dlhodobá HDS na vrte HVD-1. Manuscript – ISS Archive Bratislava, 52 p.

Melioris, L. & Drexler, V., 2002: Sanácia, hydrogeologické zhodnotenie a zabudovanie vrtu S-5/A v Dudinciach. Manuscript – ISS Archive Bratislava, 48 p.

Nagy, A., Halouzka, R., Konečný, V., Dublan, L., Havrila, M., Lexa, J., Pristaš, J., 1998: *Geologická mapa Podunajskej nížiny – východná časť.* GSSR Bratislava.

Némethyová, M., Šarlayová, M., Novomestská, D., 1990: Demandice – hydrogeologický prieskum, účel: zabezpečenie vodného zdroja pre zásobovanie obce Demandice, vyhodnotenie hydrogeologického prieskumného vrtu HVDZ-1. Manuscript – SGIDŠ Archive Bratislava, 16 p.

Neupauer, Ľ., Medveďová, M., Benková, E., Bírošová, M., Slovíček, P., Balunová, J., 1991: Hontianske Nemce – hydrogeologický prieskum, účel: overiť možnosť zásobovania strediskovej obce pitnou vodou z miestnych zdrojov podzemných vôd. Manuscript – SGIDŠ Archive Bratislava, 22 p.

Orvan, J., Dolník, V;., Faltin, M., 1965: Santovka – hydrogeologický prieskum minerálnych vôd, účel: hydrogeologické zhodnotenie postupu hĺbenia jednotlivých vrtov B-4 až B-9 čerpacími pokusmi HGP. Manuscript – SGIDŠ Archive Bratislava, 67 p.

Orvan, J. & Hornung, T., 1968: Santovka II. etapa, podrobný prieskum. Manuscript – SGIDŠ Archive Bratislava, 29 p.

Ostrolúcky, P., 1979: Vyhodnotenie hydrogeologického vrtu HG-2 na lokalite Horné Semerovce – materská škola. Manuscript – SGIDŠ Archive Bratislava.

Rebro, A., Malatinský, K., Matejčeková, E., Jurdík, M., Žídek, L., 1978: Horné Turovce – balneologický prieskum. Manuscript – SGIDŠ Archive Bratislava, 24 p.

Rebro, A., Klago, M., Matejčeková, E., 1979: Registrácia minerálnych a termálnych vôd – doplnky III. Manuscript – SGIDŠ Archive Bratislava.

Šimovičová, Ľ., Motlíková, H., Fecek, P., Hlavatý, Z., 1976: Dudince – HG vrt HGHT-1. Manuscript – SGIDŠ Archive Bratislava, 13 p.

Tkáčová, H., 1978: Dudince – Slatina – geofyzikálny prieskum Levickej žriedelnej línie. Manuscript – SGIDŠ Archive Bratislava, 19 p.

Tkáčová, H., 1980: Geofyzikálny prieskum Levickej žriedelnej línie v oblasti: Santovka – Bory – Kalinčiakovo. Manuscript – SGIDŠ Archive Bratislava, 33 p.

Tolstichin, N. I., 1937: Numeracija prirodnych vod. *Probl. sov. Geol.*, 1937, Tom VII, No. 8.

Vandrová, G., Matejčeková, E., Bujalka, P., 1987: Slatina – vyčistenie zdroja BB-2. Manuscript – SGIDŠ Archive Bratislava, 10 p.
Vandrová, G. & Potyš, Z., 1988: Santovka – zhodnotenie režimu zdrojov prírodných minerálnych vôd. Manuscript – SGIDŠ Archive Bratislava, 58 p.
Vandrová, G., 1988: Dudince – zdroj minerálnej vody S-5A a likvidácia vrtu S-5. Manuscript – SGIDŠ Archive Bratislava.
Vandrová, G., Matejčeková, E., Bujalka, P., 1988: Slatina – náhradný zdroj minerálnej vody, doplnkové hydrogeologické práce. Manuscript – SGIDŠ Archive Bratislava, 16 p.
Vandrová, G., 1990: Santovka – náhradný zdroj minerálnej vody HG-4/A, HGP. Manuscript – SGIDŠ Archive Bratislava.
Vandrová, G. & Matejčeková, E., 1990: Dudince – zdroj minerálnej vody HVD-1, HGP, cieľ: Možnosť získať nový zdroj na zabezpečenie potrebnej kapacity liečivej minerálnej vody pre PLK – Dudince. Manuscript – SGIDŠ Archive Bratislava.
Vandrová, G., Matejčeková, E., Dudáš, J., 1990: Dudince – zdroj minerálnej vody HVD-2, HGP, cieľ: Možnosť získať ďalší nový zdroj minerálnej vody na zabezpečenie potrebnej kapacity liečivej minerálnej vody pre PLK – Dudince. Manuscript – SGIDŠ Archive Bratislava.
Vandrová, G. & Vrábľová, M., 1995: Santovka – zdroj pitnej vody SHG-1, podrobný hydrogeologický prieskum. Manuscript – SGIDŠ Archive Bratislava, 12 p.
Vandrová, G. & Sňahničanová, J., 1998: Santovka – exploatačný zdroj B-3A (kúpalisko). Manuscript – ISS Archive Bratislava, 51 p.
Vandrová, G. & Štefanka, P., 2007: Santovka – revízia exploatačných podmienok zdroja B-3A, doplnkový HGP. Manuscript – SGIDŠ Archive Bratislava, 64 p.
Vandrová, G., Štefanka, P., Červeňan, M., Verešová, M., 2008: Santovka – revízia exploatačných podmienok zdroja B-6 a B-15, doplnkový HGP. Manuscript – SGIDŠ Archive Bratislava, 71 p.
Vandrová, G., Štefanka, P., Chorvatovičová, M., 2012: Kúpele Dudince – revízia exploatačných podmienok prírodných liečivých zdrojov S-3 a HVD-1, podrobný HGP. Manuscript – SGIDŠ Archive Bratislava, 101 p.
Vass, D. et al., 1981: Štruktúrny vrt ŠV-8 (Dolné Semerovce). GIDŠ Bratislava, p. 1 – 106.
Government Resolution no. 456/1999 of 2. 6. 1999, the Ministry of Health Bulletin, amount 13.
Health Ministry Decree no. 19/2000 Coll., which declares protection zones of natural medicinal resources in Dudince natural sources and mineral table water in Santovka and Slatina.
Health Ministry Decree no. 100/2006 Coll., laying down requirements on natural healing water and natural mineral water, details of the balneology assessment, distribution, coverage and content analysis of natural medicinal waters and their products, and requirements for the registration of an accredited laboratory in the list maintained by the State Spa Commission, as amended.
STN 75 0111 Terminology of hydrogeology.

Instructions to authors

General instructions

The Editorial Board of the Slovak Geological Magazine accepts manuscripts in English language.

The Editorial Board accepts or refuses a manuscript with regard to the reviewers` opinions. The authors are informed about a refusal within 14 days after receiving the decision of the Editorial Board. Accepted manuscripts are prepared for a publication in an appropriate issue of the magazine. The author(s) and the publishers enter a contract establishing the rights and duties of both parties during editorial preparation and printing, until the time of a paper publishing. Simultaneously with article the editorial office must receive the corresponding author's proclamation that no part of the manuscript was already published and figures are original as well. Copied figures must be legalized by obtaining the copyright. The proclamation must contain the name of author (authors), title and the address of residence.

Text layout

The text should be arranged as follows: full name of the author(s); title of the paper, number of supplements (in brackets, below the title, e.g. 5 figs., 4 tabs.); key words - maximum 6 key words arranged successively from general to special terms; abstract (max. 300 words presenting principal results, without references); in a footnote of the first page, name of the author(s) as well as her/his/their professional or private address.

The extent of the article is limited to 30 manuscript pages including references, figures and explanations. Publishing of longer articles must be agreed by the Editorial Board.

The text of the paper should be logically divided. Text must be sectionalized by headlines, the position of the main headlines is in the centre of the page, associated headlines start from the left side of the page. The hierarchy of headings can contain maximum three levels (1 - highest level, 2 - lower, 3 - lowermost), being indicated by pencil at the particular heading. Text of the article has to contain the introduction, characterization (state) of investigated problem, used methodology, obtained data, discussion, conclusion and references.

The references in the text should be used preferably in parentheses. Names of cited authors in the text are written without first names or initials (e.g. Matula, 1969); the names of the co-authors are divided (e.g. Mišík & Sýkora, 1981). The name(s) is followed by a comma. If there are more authors, the first one, or the first two only are cited, adding et al. and publication year.

Mathematical and physical symbols of units, such as m, oC should be preceded by a space, e.g. 20 m, 50 oC, etc. In the case of % and ‰, the exemption shall be made: 10%, 2‰. SI units are preferred. Abbreviations of the units such as second, liter, etc. should be written without a period. Compass readings may be substitute by the abbreviations E, W, NW, SSE, etc. Brackets (parentheses) are to be indicated as should be printed, i.e. square brackets, parentheses or compound. Dashes should be typed as double hyphens.

Text of the article must be sent to Editorial office printed in two copies with line spacing 2, as well as on CD. Please for using preferable MS Word editor for PC. Figs. and Tabs. must be delivered in digital form in separate files. Paragraphs are marked with 1 tab space from the left margin, or by a typographic symbol. Greek character in the text must be visualized in the text by its name [e.g. Ʊ (omega)]. Indices and exponents should be properly marked.

Figures and tables

The high quality of illustrations is required. Their aim is the most effective documenting and explaining the text. When drawing them by hand or computer their maximum width 81 mm (width of column) or 170 mm (width of page) must be taken into account. Properly adapted figure (dimensions of letters, thickness of lines) can be reproduced also in the scale 1:1, but there is recommended to prepare figures in larger scale. The pen-drawn figures must be prepared by black ink using the template for figures. The minimum acceptable size of capitals and numbers in camera-ready figure is 2 mm. Maximum dimension of illustration in journal is 170x240 mm. Overlapping of illustrations should be avoided.

Figures compiled using the computer must be printed by high resolution laser printer (min. 300 DPI). For figures drawing the editorial office recommends the Corel Draw software. The very thin lines (hair lines) as well as automatic filling of objects are not allowed. The filling must consist from separately set objects. The raster-type filling of planes is either appropriate.

Each illustration including photographs must contain graphic (metric) scale. Grouped figures, e.g. photographs and diagrams must be compiled as one figure with separate parts designated a, b, c, etc. They are referred to as one picture.

Photographs must be sharp, preferably black & white, contrast, in the form of JPG or TIFF files having resolution of at least 600 DPI.

All figures must contain their number, description and name of author; in the case of maps and sketches an arrow indicating their orientation, and scale.

The explanations used for a series of several maps and profiles should correspond to that in the first figure. Description to figures should be inserted in the text on their proper place.

Each illustration and table must be referred in the text.

The high quality colour illustrations can be published after agreement by editorial office. The costs incurred will be charged to the account of the author (50 EUR for one page).

The Publisher reserves the right to return the graphic supplements back to author after language correction, resp. demand him to replace them by the higher quality ones.

Tables are submitted on separate page. Their layout is accepted in a size of up to A4. More widespread tables are not accepted.

Data are incorporated into table only when there is no possibility to incorporate them into text. The numbering of tables shall be gradual. Short explanation to a table should be included on the same sheet. If the text is longer, it should be typed on a separate sheet.

The author is asked to mark in the text where the figure or the table should be inserted.

References

The list of references should only include the works cited in the text. The references are stated in alphanumeric order, with hanging indent in the second and following lines. The denotation "in press" can be used only in the cases of acceptance of reviewed version of article by editorial board. The denotation "personal information" can be cited only in the text (e.g. Kováčik, pers. information, 2008). When referring the data by other author not being the co-author of referred publication, in the text he is cited in the following form: (Gerda in Kubka, 1975), though in the list of literature is stated only Kubka J., 1975.

Examples of referring:

Book

Gazda L. & Čech M., 1988: Paleozoic of the Medzev nappe. Bratislava, Alfa, 155.

Journal

Vrba P., 1989: Shear zones in the metapelite complexes. Mineralia Slov., 21, 135-142.

Anniversary volume

Návesný D., 1987: High-potassium rhyolites. In: Romanov, V. (ed.): Stratiform deposits of Gemericum. Spec. publ. Slov. Geol. Soc. Košice, 203-215.

Manuscript

Radvanský F., Slivka B., Viktor J. & Srnka T., 1985: Vein deposits of the Jedľovec nappe of Gemericum. Final report from the project SGR-geophysics. Manuscript-archive ŠGÚDŠ Spišská Nová Ves, 28.

Proofs

The authors are obliged to correct the errors, which are due to typing and technical arrangements. The first proof is sent to author(s). The second proof is provided only to the editorial office. It can be sent to authors upon request.

The proofs must be marked clearly and intelligibly, to avoid further errors and doubts. Common typographic symbols are to be used; their list and meaning will be provided by editorial office. Each used symbol must also appear on the margin of the text, if possible on the same line where the error occurred. The deadline and conditions for proof-reading are subject to the contract, which is governed by the Chairman of the Editorial Board.

Final remarks

These instructions are obligatory to all authors. Exceptions can be made by the Editorial Board or the Scientific Editor. Manuscripts not complying with these instructions shall be returned to the authors.

The Editorial Board reserves the right to publish preferentially invited manuscript and to assemble thematic volumes.

The manuscripts should be sent by e-mail to the address:
slovak.geological.magazine[at]geology.sk.

Contents