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## **APPLICATION OF GEOCHEMICAL MODELING FOR ANALYSIS OF CHANGES IN GROUNDWATER CHEMISTRY IN KARST AREA (CASE STUDY FROM GYPSUM KARST IN THE CZARNY POTOK VALLEY, SW UKRAINE)**

*key words:* karst processes, geochemical model, Ukraine

### **AIM**

The aim of the geochemical modeling was to describe (quantitatively and qualitatively) modifications of water chemical composition on flow path through gypsum matrix and forming of flow caves (jaskinie przepływowe). Distribution of molar concentration of each determined element in a sample among its main speciations has been analysed and ability of water to dissolve rock matrix in a vadial zone has been estimated. Saturation index has been used to evaluate water capability to dissolve mineral phases. Also a load of dissolved minerals has been calculated.

### **INVESTIGATION SITE**

The investigation site was located in the valley of Czarny Potok (fig. 1). Czarny Potok is a right inflow of Dniestr. It is situated in the Bukovinian part of inter-river (międzyrzecze) of Prut – Dniestr in its watershed zone (strefa wododziałowa). Czarny Potok has length of 14km and its watershed is about 48km<sup>2</sup> with average inclination of 8,2%. Average altitude of the watershed is 260m and the maximal over-land flow module is 3l/s km<sup>2</sup>/year.

Karst forms, especially caves in area of Jurkowce and Pogorilowce, have been well known since XIX century. Detailed research on karst in this area has been carried out since 1980's (Andrzejczuk, 1986; Ridusz, Kupricz, 2003). The area of research is representative as active karst processes take place in there. Karst processes are intensified by surface water infiltrating the massif through karst fissures, ponors and other karst forms. Another advantage of the site is that the old flow zones are still active. The factor that presently influence natural processes is anthropopression that vary in the region.

Czarny Potok successively cuts the quaternary deposits, neogenian (badenian) gypsum and cretaceous carbonates. Gypsum has a cryptocrystalline structure and patchy gray and white color. In the roof part of the complex big and well formed crystals of gypsum dominate while in the bottom part, cryptocrystalline forms are common.

Czarny Potok valley is situated over the post-neogenian fault which western part lies about 10 to 15m below its eastern part. The eastern part of the fault is a trunk (zrąb) with vertical walls. In the western part of the area a weakly permeable layer of gruss exists. No advanced forms of karst have been found in there.

An active karst in the Czarny Potok catchment is present in the river valley. The amount of karst forms decreases from the bottom of the valley towards the watershed area (from 4,5 to 1,2/km<sup>2</sup>). This variability is caused by existence of thick layer of the gruss in the watershed zone that can reach up to 10m.

In the area of the eastern wing of the fault, parallel to the river valley, a number of ponors exist. All of them are in hydraulic contact with caves. The longest cave, Czarnopotocka, is more than 1km long. Caves present in this area are generally of one channel structure type and all of them are permanently or temporarily flooded. Width of each cave varies from 1 – 2m to 3-5m while the height is about 0,5 to 1m. A complete fulfillment of caves is possible when water flow in hydrogeological system is high.

Presently, as a consequence of human made changes in terrain morphology, change in structure of alimentation zone take place. At the site where the stream enters the karst system, its valley has been almost completely blocked (fig. 2) and surface water can enter the system only temporarily through the water gate. A constant minimal flow (lower than 0,05L/s) is an effect of surface water infiltration from ponds to karst system through old river-bed fulfilled by alluvial material. The karst channel is buried at the depth of 20-25m below ground level. It lies parallel to the river valley and the underground flow is stable. There are sites where the stream appears at surface and is alimented by some other concentrated inflows. The second component of karst system alimentation are surface and atmospheric waters entering

it through ponors. Presently, the river-bed, as it has been deepened, leads on almost 100% of water. Only when the flow is extremely high, a significant amount of water gets into the old river-bed and enters the karst system.

No regular chemical research has been conducted in the area of Czarny Potok before 2006. Since October 2006 regular observations has been carried out (Solovey, 2007; Solovey, Jóźwiak, 2007).

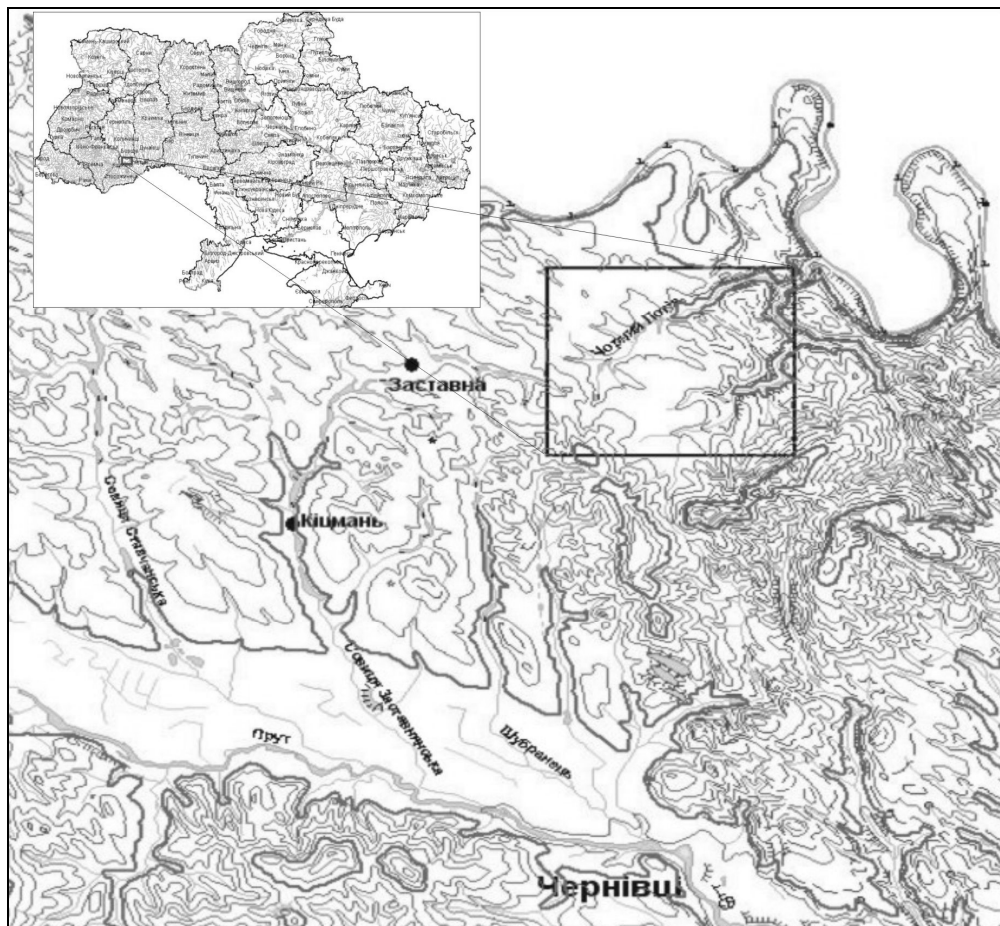


Fig. 1. Location of the research area. *Source: compiled by the authors.*

### CONCEPTUAL MODEL

Water in Czarny Potok catchment circulate in a shallow and mediate system where gypsum minerals are common. Rainfall infiltration declines in top parts of the

catchment through karst funnels and ponors. Infiltrating water condenses by transpiration and evapotranspiration. In the soil level further condensation happens while ion exchange processes are strongly limited due to low amount of mineral phases. Water infiltrating through the soil level is undersaturated with respect to almost all minerals existing in the matrix. Dynamic processes, like flow rate decrease, connected with water infiltration inside the massif take place in a vadic zone. It is possible to omit the lateral influx in spetiation calculations. The dynamics of gypsum solubility depends on many factors e.g. pH-Eh conditions, infiltrating water chemistry, ion exchange, solubility and precipitation of mineral phases, oxygen and carbon dioxide presence and many others. As water residence time in the system is longer, its capability to dissolve minerals decreases. Elongation of residence time is an effect of considerable changes in flow rate connected witch anthropopression. In geochemical calculations this process is expressed by increase of saturation index.

Among the mineral phases in the research site carbonates and sulfates dominate. Common minerals are: gypsum (with modified chemical composition), calcite, aragonite. Also oxides and hydroxides of Fe, Mn, Al, amorphous and cryptocrystalline silica forms and clay minerals are present. Elevated concentration of magnesium can locally cause existence of carboniferous minerals enriched in Mg. That means that dolomitization and dedolomitization can occur in the environment.

## METHODOLOGY

Ground- and surface water have been sampled seven times in period from October 2006 to September 2007 to create geochemical models and verify the conceptual model. In each sample concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, SiO<sub>2</sub> and 20 other elements have been measured. Temperature, volume and rate of flow, pH, Eh, conductivity, dissolved oxygen and dissolved carbon dioxide were measured in the field.

Geochemical calculations were conducted with use of PHREEQCI ver. 2.139 computer code (Parkhurst, Appelo, 1999) with **phreeqc.dat** database. Saturation indexes (SI) of were calculated to evaluate the equilibrium state for each mineral and gaseous phase.

$$SI = \frac{IAP}{KT}$$

IAP – ion activity product

KT – equilibrium constant in temperature T.

In a solution where equilibrium exists and dissolution is equal to precipitation saturation index is zero. In solutions undersaturated in respect to a mineral phase SI has a negative value and water has a tendency to dissolve minerals. When SI has

a positive value solution is oversaturated in respect to mineral phase. As thermodynamic data are not homogenous it is assumed that equilibrium state is defined by equation (Józwiak, 2004):

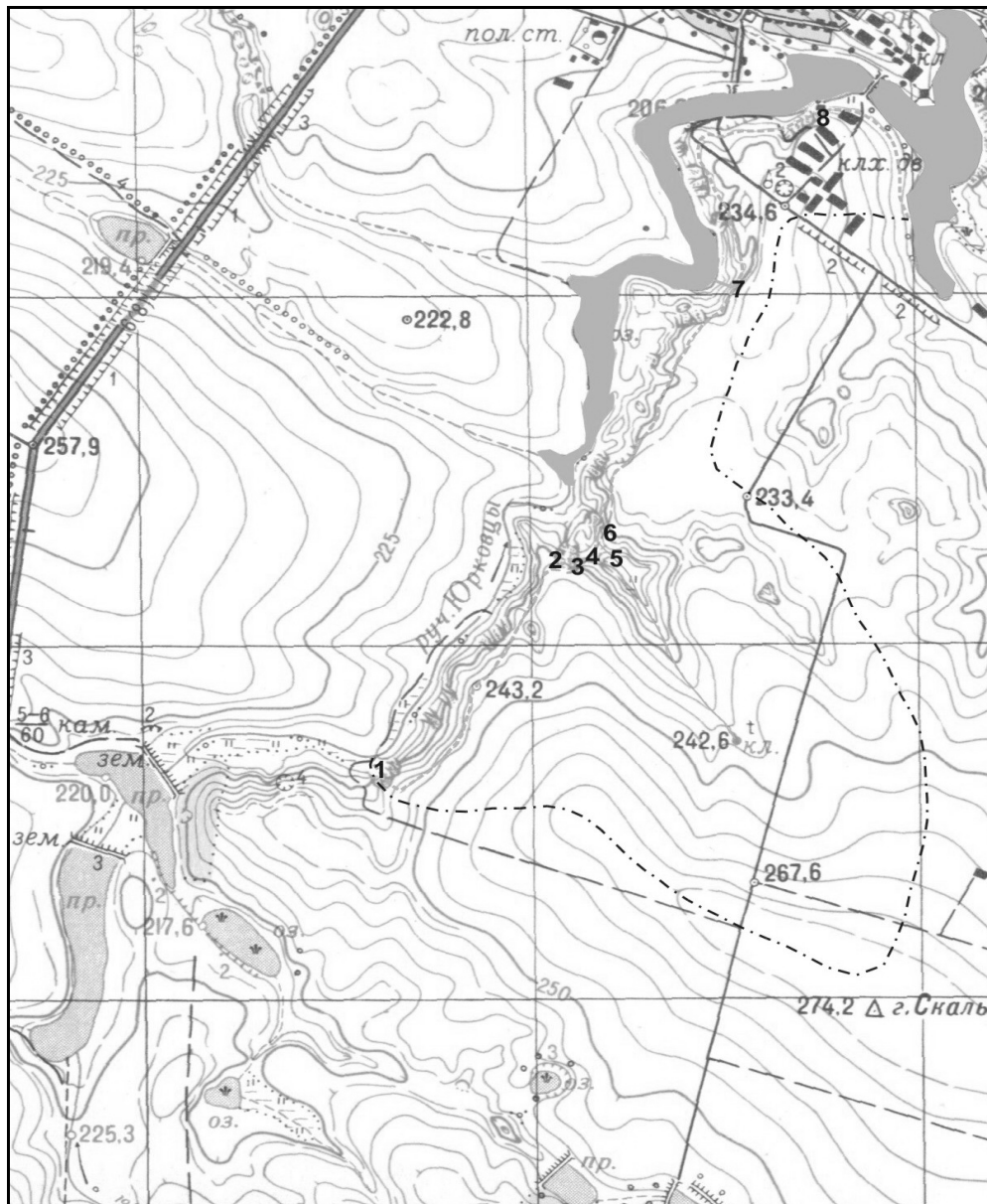


Fig. 2. Location of sampling sites in the valley of Czarny Potok. Source: compiled by the authors.

$$SI = 0 \pm 5\% \times \log K$$

PHREEQC has capabilities to calculate: (1) element concentration in units defined by the user, (2) activities of solutions and individual elements, (3) pH, pe, (4) speciations, (5) saturation index, (6) moles transfer of phase that tends to an equilibrium in reversible and irreversible reactions, (7) ion exchange, (8) surface complexation, (9) gaseous phase equilibrium with settled volume and constant pressure, (10) advection in one dimensional transport, (11) dissolution and precipitation of mineral phases, (12) mixing, (13) oxidation and reduction processes, (14) temperature changes effects, (15) evaporation effect (condensation), (16) dispersion in one dimensional transport and diffusion in stagnant zones, (17) isotopic balance in inverse modeling, (18) share of organic matter in reactions, (19) kinetically controlled reactions, (20) formation or decomposition of ideal, multicomponent or non-ideal binary solid solution.

## RESULTS

Fresh water of mineralization about 656 – 1055mg/L and of HCO<sub>3</sub>-Ca type dominate in point 1. SI value for gypsum is about -1,71. Values of SI for carbonate phases (SI<sub>calcite</sub> = 0,40; SI<sub>dolomite</sub> = 0,38; SI<sub>aragonite</sub> = 0,24 – Tab. 2) indicate that precipitation of these phases is possible at the site where water enters the karst system. It might be caused by low values of dissolved carbon dioxide present in water (CO<sub>2</sub> is consumed in silicates decomposition processes). Concentration of CO<sub>2</sub> in point 1 varied from 8,8 to 14,08mg/L. A similar trend can be observed for silicate minerals – crystalline and cryptocrystalline forms (quartz and chalcedony) are practically insoluble. Only an amorphous silica has capability to dissolve in groundwater what causes constant increase in its concentration on a flow path (from 5 to 20mg/L). Water at the entrance to the system is highly undersaturated in respect to main minerals (gypsum, anhydrite).

Water from point 1 flows through Czarnopotocka cave and appears on the surface after 1700m at point 2. Primarily it was a spring with high efficiency (about 3,4 times greater flow rate (0,075m<sup>3</sup>/s) than at present in point 1). In summer 2008 works on false pond has been conducted to retain water. While works took place, the water refuge from the pond into the massif was observed. In the winter season when the pond is not used for retention, hydrogeologic conditions will become as they used to be before pond had been made. In the summer time groundwater in point 2 have higher mineralization (1662 – 3506 mg/L). Such great value means that water is practically saturated in respect to calcium sulfate – SO<sub>4</sub> concentration varies from 700 to 2911 mg/L.

**Tab. 1** Chosen statistical parameters of water from Czarny Potok chemistry in period from October 2006 to September 2007.

Point no.	pH	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	N-NO <sub>3</sub> <sup>-</sup>	N-NO <sub>2</sub> <sup>-</sup>	N-NH <sub>3</sub>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	
		[mg/l]										
1	min	7.60	366.18	80.00	45.23	0.20	0.01	0.00	15.30	8.40	68.50	22.66
	max	7.80	638.37	175.00	92.56	3.10	0.03	0.04	25.00	27.30	166.77	28.04
	mean	7.74	493.55	119.50	59.43	1.62	0.02	0.02	19.28	14.19	110.56	24.97
2	min	7.19	349.58	700.00	37.86	1.30	0.00	0.15	14.00	5.79	440.90	22.53
	max	7.40	549.27	2911.00	43.82	5.80	0.06	0.76	22.50	11.00	564.00	25.60
	Mean	7.33	436.85	1503.00	41.83	2.88	0.03	0.46	18.05	7.97	491.93	24.27
4	Min	7.17	327.73	775.00	32.76	0.40	0.01	0.13	15.94	5.90	453.00	24.60
	Max	7.52	436.49	2856.00	43.67	3.50	0.03	0.86	19.90	9.10	646.74	27.39
	Mean	7.38	400.72	1415.17	36.90	1.77	0.02	0.38	17.88	7.39	536.25	25.98
5	Min	7.66	305.15	37.00	24.11	0.20	0.00	0.00	8.01	0.74	37.20	16.75
	Max	8.18	406.46	74.00	63.17	3.70	0.03	0.03	11.00	9.60	107.20	21.43
	Mean	8.06	358.75	50.50	34.03	1.77	0.01	0.01	9.42	2.34	78.47	18.83
6	Min	7.30	324.68	300.00	30.42	0.50	0.00	0.10	11.07	4.50	385.30	20.15
	Max	7.84	440.03	2296.00	41.12	7.00	0.20	0.48	15.92	8.19	635.71	27.15
	Mean	7.53	386.08	1114.33	34.87	2.70	0.07	0.25	13.70	6.02	453.83	23.96
7	Min	6.36	298.19	825.00	38.22	2.00	0.01	0.00	14.90	7.20	433.20	23.60
	Max	7.57	438.68	3239.00	45.87	7.30	0.05	0.44	22.80	10.90	537.40	26.30
	Mean	7.22	380.43	1634.25	42.20	3.88	0.03	0.22	17.67	8.53	474.37	25.13
8	Min	7.75	238.02	550.00	37.29	1.30	0.00	0.00	14.40	6.40	443.80	23.50
	Max	8.00	432.81	1625.00	44.31	4.50	0.03	0.24	25.20	11.60	590.76	31.63
	Mean	7.86	349.27	1017.00	41.19	2.76	0.01	0.15	19.03	9.25	498.93	26.51

Source: compiled by the authors.

Water saturation indexes in respect to sulfate minerals increase and for gypsum it is equal -0,07. The main type of water is SO<sub>4</sub> – Ca. Considerable increase of mineralization (up to 3,2 times) is an effect of “aggressive” interaction of water with mineral phases on the flow path. It is probable that after tens of meters flow, water from point 1 changes its character from HCO<sub>3</sub> – Ca into SO<sub>4</sub> – Ca that is typical for point 2. The observed process is possible as dissolution of gypsum is dynamic. This hypothesis has also been confirmed by geochemical models.

Point no 4 is the outflow site where groundwater leaves Św. Trójcy cave. As the entrance to the cave collapsed groundwater flowing out in the winter season have chemical composition typical for water circulating in gypsum massif while in the summer season its origin partly depends on infiltration from the retention pond.

**Tab. 2.** Variability range of SI in February 2007.

Chosen mineral phases		Direction of groundwater flow and hydrogeochemical interpretation – number of sampling site: from the place where water enters the system up to the drainage zone						5%log KT
Mineral	Formula	1	2	4	5	7	8	
Anhydrite	CaSO <sub>4</sub>	-1.96	-0.33	-0.36	-2.39	-0.37	-0.39	0,218
Gypsum	CaSO <sub>4</sub> : 2H <sub>2</sub> O	-1.71	-0.07	-0.11	-2.13	-0.12	-0.13	0,229
Quartz	SiO <sub>2</sub>	0.13	0.66	0.77	0.51	0.63	0.69	0,199
SiO <sub>2</sub> (a)	SiO <sub>2</sub>	-1.28	-0.71	-0.60	-0.90	-0.75	-0.69	0,136
Aragonite	CaCO <sub>3</sub>	0.24	0.44	0.41	0.35	-0.87	0.91	0,417
Calcite	CaCO <sub>3</sub>	0.40	0.60	0.57	0.51	-0.71	1.07	0,424
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	0.38	0.08	0.03	0.72	-2.54	1.00	0,827
Halite	NaCl	-7.43	-7.10	-7.86	-8.20	-7.78	-7.74	0,079
O <sub>2</sub> (g)	O <sub>2</sub>	-0.70	-0.79	-0.77	-0.74	-0.68	-0.76	0,073
CO <sub>2</sub> (g)	CO <sub>2</sub>	-2.28	-1.93	-1.92	-2.75	-1.18	-2.39	0,073

*Source: compiled by the authors.*

Chemical composition of water in winter season is almost the same as in point 1. Water of SO<sub>4</sub> – Ca type has mineralization of 1778 to 3398 mg/L. Results of geochemical modeling suggest that forming of minerals like calcite is possible.

Basing on geochemical model that includes mixing effect it might be said that share of surface water in shaping groundwater chemistry reached up to 43%.

Further on the flow path, after mixing stream water with water from the lateral tributary, a substantial change in water chemical composition occurs. Shallow groundwater from point no 5 of HCO<sub>3</sub> – Ca type has SI = -1,79 in respect to gypsum. It also has lower values for carbonate minerals what means that water has ability to dissolve these minerals. Water from point no 5 is of atmospheric origin, its mineralization is low (about 651 mg/L) and Na:K ratio is 11,3:1,07 mg/L. pH of water is higher than in other sampling sites and is equal 8,1 what may suggest that processes of dissolving alkaline salts in the soil level are intensive. In October 2006 the stream was flowing only in the gruss layer while presently in many sites water cuts the layer and starts to denudate top part of gypsum level.

Basing on results of geochemical modeling it can be stated that volumetric share of water from lateral tributary in shaping water chemistry in May 2007 was about 15%. After mixing both components water from Czarny Potok changes its type into SO<sub>4</sub> – HCO<sub>3</sub> – Ca.

About 5m further the stream enters the cave Niezapominajka and flows in the underground channel in the eastern part of the fault (its more than probable that in the past stream water user the fault zone as the river-bed). The flow system is not



homogenous as in the following part, towards south-eastern, a number of springs with the same hydrochemical type of water occur. It is probably the advanced hydrogeological karst system where water uses tectonic discontinuities to migrate.

In point no 7 some water from the pond enters the karst system through the ponor. Surface water is of  $\text{SO}_4 - \text{Ca}$  type with mineralization of 1791 – 3695 mg/L and  $\text{SO}_4$  concentration about 825 – 3239 mg/L. As hydrotechnical works has been carried out in this area and the vegetation is abundant there is a lot of organic matter in water and its decomposition causes that Eh is about 50mV. Transition redox conditions can cause sulfide reduction and increase in sulfide concentration. Alimentionation of water in karst system by water from the surface does not significantly influence its ability to denudate rock matrix. Nevertheless, on the flow path from point no 6 to 7 (about 500m) hydrochemical type of water changes from  $\text{SO}_4 - \text{HCO}_3 - \text{Ca}$  to  $\text{SO}_4 - \text{Ca}$ . Water from point no 7 can still interact aggressively with sulfide minerals while its SI suggests oversaturation in respect to calcite, dolomite and aragonite.

Point no 8 is situated in the zone where Czarny Potok exits the karst system and enters downland where the lake is situated (drenaige zone of the karst system). The effluence is multipoint along the lake escapement. SI values in respect to carbonate phases indicate that these minerals can precipitate. SI for gypsum is close to 0 (SI = -0,13) what means equilibrium conditions (tab. 2). Water from point no 8 are of  $\text{SO}_4 - \text{Ca}$  type with mineralization of 1525- 2585 mg/L.

### **SPECIATION MODEL**

A form (speciation) in which an element exists in the solution is substantial while its migration in groundwater. For water from Czarny Potok percentage distribution of molar concentrations of chosen elements spetiations has been conducted (tab. 3). In the alimentionation zone and at the entrance to the karst system (point no 1) dominating forms of dissolved elements are simple ionic ones that reaches over 90% of all dissolved species. The only exception is sulfur which simple ionic form is only about 85% (tab. 3). Alkaline elements (Na, K) as well as alkaline metals (Ca, Mg) except simple ionic forms exist also as sulfide and carbonate or bicarbonate complexes.

Along the flow path following trends might be observed:

- decrease in percentage share of simple ionic forms of elements;
- distinct increase (9 – 10 times) in percentage share of undissociated sulfide forms ( $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ) that is connected with increase in alkaline metals concentrations and changes in pH - Eh conditions in the karst system (tab. 3). The increase is proportional to water residence time in the karst system and limitation in contact with atmospheric oxygen.

- domination of acid carbonates (Ca, Mg)HCO<sub>3</sub><sup>+</sup> over bicarbonate forms (CaCO<sub>3</sub>) is limited by low values of pH. Existence of acid carbonates correlates with poor contact of water with atmospheric oxygen – as the contact with atmospheric gases decreases, concentration of acid carbonates increase.
- decrease of HCO<sub>3</sub><sup>-</sup>, and increase in CO<sub>2</sub> concentration that is caused by processes of sulfide reduction and organic matter decomposition. Increase of HCO<sub>3</sub><sup>-</sup> concentration along the flow path might be explained by dissolution of carbon dioxide and dissociation of carbonic acid. The second source of HCO<sub>3</sub><sup>-</sup> is dissolution of carbonate minerals that can temporarily precipitate in the environment (tab. 2).

Alkaline elements (Na, K) due to their geochemical characteristics and migration capabilities are present in the environment mainly in simple ionic forms (Na<sup>+</sup>, K<sup>+</sup>) (tab. 3). At the same time, their percentage share doesn't show any correlation with water residence time in the system. Similarly, Cl and N-NO<sub>3</sub> exist as easily migrating ions – Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, respectively.

Among carbon (C) and sulfur (S) speciations hydrocarbonate and sulfide forms dominate (tab. 3). It is partly connected mainly with matrix lithology (sulfate minerals dominate in the environment) but the dominating factors are pH and Eh conditions. The main form of silica occurrence is orthosilicic acid which dissociate in water of basic character with creation of small amount of H<sub>3</sub>SiO<sub>4</sub><sup>-</sup> forms.

## FINAL REMARKS

The main indicator of karst processes activity is calculated value of chemical denudation. Because water mineralization increases in the drainage zone (point no 8) it can be assumed that Czarny Potok carries in a great amount of dissolved mineral substances, mainly sulfates. Basing on these data, it is possible to evaluate the load of mineral substances that has been taken out of the system. As it was calculated the value is about 571,55m<sup>3</sup>/year.

In the region where research had been conducted, active karst processes take place in the area of river valley. Surface and groundwater present in the river valley are characterized by variable, circulating conditions dependent aggressiveness. Results received while geochemical modeling clearly indicate that water chemical composition in the area of Czarny Potok catchment has been shaped mainly by reactions defined by thermodynamic gypsum (sulfate) equilibrium in shallow and undefined hydrogeological system. In points where water enters the karst system, its capability to dissolve rock matrix is high.

Tab. 3. Percentage share of chosen elements species in water\*.

Element	Speciation	Direction of groundwater flow and hydrogeochemical interpretation - no of sampling site: from the place where water enters the system up to the drainage zone					
		1	2	4	5	7	8
C	HCO <sub>3</sub> <sup>-</sup>	93.3	87.8	86.8	96.1	46.7	91.9
	CO <sub>2</sub>	4.8	8.6	9.3	1.9	51.5	3.3
	CaHCO <sub>3</sub> <sup>+</sup>	0.7	2.8	3.1	0.5	1.6	3.1
	MgHCO <sub>3</sub> <sup>+</sup>	0.7			0.5		
	CaCO <sub>3</sub>						0.9
	CO <sub>3</sub> <sup>-2</sup>				0.5		
Ca	Ca <sup>+2</sup>	91.5	64.8	68.0	92	68.9	69.2
	CaHCO <sub>3</sub> <sup>+</sup>	3.2	1.9	1.9	2.9	1.0	2.0
	CaSO <sub>4</sub>	4.6	33.1	29.9	3.2	30.1	28.2
	CaCO <sub>3</sub>	0.8			1.9		0.6
Cl	Cl <sup>-</sup>	100	100	100	100	100	100
K	K <sup>+</sup>	99.8	96.9	97.4	99.9	97.4	97.6
	KSO <sub>4</sub> <sup>-</sup>		3.1	2.6		2.6	2.4
Mg	Mg <sup>+2</sup>	91.2	66.4	69.5	92.1	70.8	71.2
	MgHCO <sub>3</sub> <sup>+</sup>	4.7	2.5	2.5	4.2	1.4	2.7
	MgSO <sub>4</sub>	3.7	30.9	28.0	2.6	27.8	25.8
Na	Na <sup>+</sup>	99.5	97.0	97.5	99.6	97.6	97.6
	NaSO <sub>4</sub> <sup>-</sup>		2.7	2.3		2.2	2.1
S	SO <sub>4</sub> <sup>-2</sup>	85.4	76.1	73.7	89.6	74.0	73.8
	CaSO <sub>4</sub>	9.4	21.6	23.8	6.2	23.6	23.8
	MgSO <sub>4</sub>	4.8	1.9	2.1	4	2.1	2.1
Si	H <sub>4</sub> SiO <sub>4</sub>	99.6	99.8	99.8	99.0	100.0	99.6
	H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>				1.1		0.4

Source: compiled by the authors.

\*Numbers in the table stand for percentage share of each speciation form occurring in the environment in amount greater than 0,5% of total molar concentration of the element.

Along the flow path (especially in the first stage) a violent and drastic changes in water chemical composition take place. Variations in saturation index clearly show that the longer residence time is, the lower water capability to dissolve minerals is. Variations in saturation indexes on the flow path are connected only with inflows from outside the karst area and with loss of water from the individual cave.

The most intense denudation processes take place in the subsoil zone (river valley where no grass layer exist) and in the bank parts of the massif. Observed values of saturation index indicate that precipitation of carbonate phases is possible in this area.

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## SUMMARY

One of the most up to date scientific problems in recognition of karst processes is quantitative evaluation their activity. Basic and distinctive indicators that describe karst processes activity are intensity and magnitude of chemical denudation (Aksiom S.D., 2002). Not only a tool for describing changes taking place in the observed hydrogeological system will be presented in the paper but tools that allow to predict changes that may take place on the spur of the natural and anthropogenic factors.

Only a few methods widely used in hydrogeology are also used in geography. In this paper authors present basis of geochemical modeling that can be widely used.

Geochemical modeling can be divided into two main issues:

- Measurement, assessment and generalization of kinetic and thermodynamic data for solid phases (e.g. minerals), gases and solutions;
- Use of above data in numerical algorithms describing natural and anthropogenically changed systems of interaction between water and matrix (Macioszczyk, Dobrzyński, 2006).

The practical aspects of geochemical modeling concentrate mainly on creating geochemical models of the environment and its changes. Geochemical modeling has been recently widely used for describing chemical composition of groundwater as well as factors and processes shaping it. A geochemical model is a tool that allow for understanding hydrogeochemical processes taking place in the environment. It is a basis for further analysis of system's susceptibility for modifications conducted by human as well as it might be an element of the forecast of the risk of environment contamination. The main advantage of geochemical modeling is simplicity of received data interpretation, possibility of groundwater chemistry origin interpretation, predicting chemistry modifications and also forecasting changes in water quality.

Geochemical models can be divided into three main groups:

- Speciation model – it doesn't include any information about temporal or spatial distribution of processes, it only describe the effect of water – rock – gases interaction in a single point of hydrogeological space;
- Reaction path model – it delivers information about succeeding changes of the hydrogeological system (spatial variability) that take place as an effect of providing a load of mass and/or energy. The time effect can be modeled with use of reaction rate constant;
- Reactive transport model – it include data describing temporal and spatial variability of chemical reactions in the system.