GYPSUM KARST IN THE WESTERN UKRAINE: HYDROCHEMISTRY AND SOLUTION RATES

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ABSTRACT: Gypsum karst in the western Ukraine underlies a large territory of more than 20,000 km^2 and is represented by a range of stages (evolutionary types), from deep-seated through subjacent to entrenched. Correspondingly, hydrogeological settings of karst development, circulation patterns, and chemical characteristics of groundwaters differ substantially between the respective areas. Based on 1,800 analyses, the paper summarises hydrochemistry of the gypsum-hosting Miocene aquifer. Most of the sampling has been performed in conjunction with a regime study of gypsum-solution rates by means of standard tablets. This study included 53 tablet stations representing varying conditions of water-rock interaction, where 644 weight-loss measurements have been made during 1984–1992. The highest rates are characteristic of entrenched karst, although active dissolution there is localised along well-defined sinking streams with short underground courses, rare vertical-percolation paths, and the water table. Lower, but still quite substantial, rates are characteristic for subjacent and deep-seated (confined) karst. However, the overall dissolution removal is higher there, due to higher rates of flow through the gypsum and the larger area of rock/solvent contact. The results are generalised in order to derive the approximate solution rates that characterise major situations and that are suitable for modeling purposes.

INTRODUCTION

Because of high solubility of gypsum and fast solution rates, sulphate ions commonly dominate in groundwaters of gypsum-karst areas. Hydrochemical studies of karstified and adjacent aquifers shed light on flow pattern and groundwater behaviour in a system. Such studies are particularly informative where a source of sulphate occurs compactly within the geologic section (i.e., as a single bed), so that sulphate ion can be used as an indicator of hydraulic communication between flow-system components, of flow direction, and of intensity.

Dissolution, and hence creation of voids and conduits, is unevenly distributed within a karst system. Evaluation of solutional capacity of groundwaters, based on representative chemical data, is indispensable for verification of speleogenetic concepts, modeling, and prediction of karst development and subsidence-risk assessment. Even more important is determination of actual gypsum-solution rates.

Solution rates from field studies are usually obtained from mass-balance (solute-load) data derived from chemographs and hydrographs, and are related to the aquifer surface or basin area. However, such an approach gives some kind of integrated values for a reference basin, usually not sufficient for detailed analysis due to great spatial and temporal variability of solution rates in a real karst system (Klimchouk et al. 1988; 1996). Specification of solution rates for flow components or zones is rarely achieved, due to difficulties inherent in chemograph and hydrograph separation and evaluation of respective aquifer-surface areas. In this respect, particularly valuable are the field-experimental-regime data on gypsum-solution rates gained in the western Ukraine through the 1980s and 1990s. These rates represent a number of karst settings, flow components, and different situations of water/rock interaction, and are linked with hydrochemical data. This makes it possible to make a fair generalisation and compare the characteristics of karstification processes in different environments.

GEOLOGIC AND HYDROGEOLOGIC BACKGROUND

The Miocene gypsum sequence is widespread on the southwestern edge of the eastern European platform, along the Carpathian Foredeep, where it occupies over 20,000 km^2. Gypsum extends from northwest to southeast for more than 300 km, as a belt ranging from several kilometres to 40–80 km wide. It is the main component of the Miocene evaporite formation that girdles the Carpathian folded region to the northeast, from Poland across the western Ukraine and Moldova to Romania (Fig. 1).

Most Miocene rocks along the platform margin overlie eroded Cretaceous strata, which include terrigenous and carbonate sediments, mostly marls and sandstones. The Miocene succession comprises deposits of Badenian and Sarmatian age. The Lower Badenian unit, beneath the gypsum, includes mainly carbonaceous, argillaceous, and sandy beds (30–90 m thick) adjacent to the foredeep, and these grade into rocks of calcareous bioherm and sandy facies (10–30 m thick) towards the platform interior.

The gypsum sequence, 1040 m thick, is variable in structure and texture, but almost everywhere occurs as a single bed. A layer of evaporitic and epigenetic limestone commonly overlies the gypsum, ranging from half a meter to more than 25 m thick (locally called "Ratynsky"). The gypsum and the Ratynsky Limestone comprise the Tyrassky Formation.

The Tyrassky Formation is overlain by the Upper Badenian unit, which begins with argillaceous and marly lithothamnion limestones and sandstone beds. Above this is a succession of clays and marls, with its lower part in the Upper Badenian (the Kosovsky Formation), and its upper part in the Lower Sarmatian; the total thickness of clays and marls ranges from 40–50 m in the Podol'sky area to 80–100 m in areas adjacent to the foredeep.

The Miocene succession is overlain by the Late-Pliocene and

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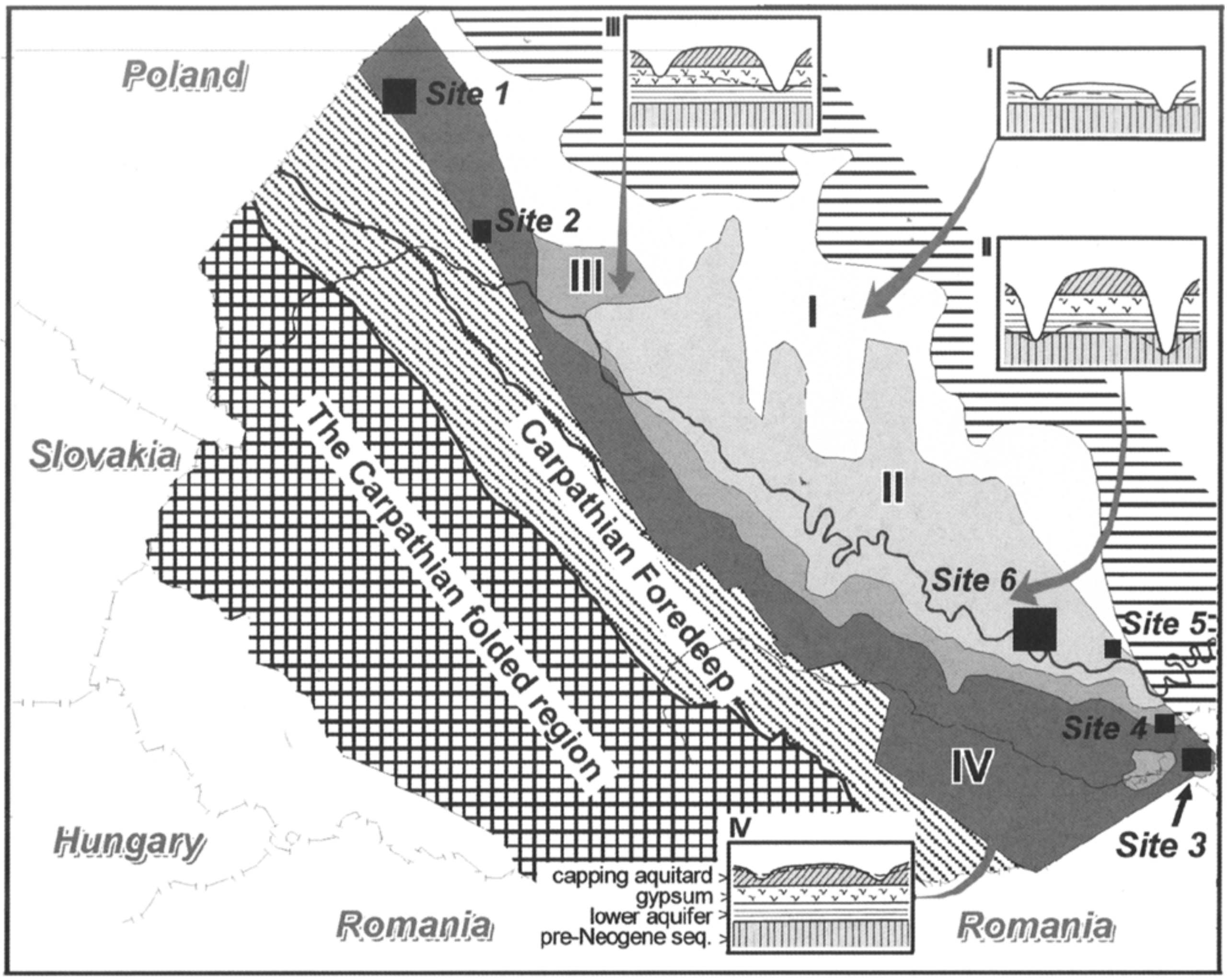

Figure 1. Zonality of evolutionary types of the gypsum karst in the western Ukraine. Zones of different karst types are indicated by Roman numbers: I = the gypsum is entirely denuded, II = entrenched karst, III = subjacent karst, IV = deep-seated (confined) karst.

Pleistocene glacio-fluvial sands and loams in the northwest section of the gypsum belt (Sites 1 and 2 on Fig. 1), and by sand and gravel alluvial-terrace deposits left by the Dniester and Prut Rivers through the Late Pliocene–Pleistocene in the Podol'sky and Bukovinsky areas (Sites 3 through 6). Many buried valleys, of Early to Middle Pleistocene age, are entrenched 30 to 50 m into the Kosovsky and Sarmatian clays, and locally into the upper part of the Tyrassky Formation.

The present distribution of the Miocene formations and the levels of their denudation vary in a regular way from the platform interior towards the foredeep (Andrejchouk 1988; Klimchouk & Andrejchouk 1988). The Tyrassky Formation dips 1° to 3° towards the foredeep, and is disrupted by block faults in the transition zone. To the south and southwest of the Dniester Valley, large tectonic blocks drop down as a series of steps, the thickness of clay overburden increases, and the depth of erosional entrenchment decreases. Along the tectonic boundary with the foredeep, the Tyrassky Formation drops down to a depth of 1,000 m and more. This variation, the result of differential neotectonic movement, played an important role in the hydrogeological evolution of the Miocene aquifer system. It resulted in the differentiation of the platform edge into the four zones (Fig. 1), three of which represent the distinct types of gypsum karst: entrenched, subjacent, and deep-seated. The gypsum bed is largely drained in the entrenched karst zone, is partly inundated in the subjacent karst zone, and remains under artesian confinement in the deep-seated karst zone.

In hydrogeologic terms, the region represents the southwestern portion of the Volyno–Podolsky artesian basin (Shestopalov 1989). Sarmatian and Kosovsky clays and marls are an upper, confining unit. The lower part of the Kosovsky Formation and the limestone bed of the Tyrassky Formation form the original *upper aquifer* (above the gypsum); the Lower Badenian sandy carbonate beds, in places together with the Carboniferous sediments, form the *lower aquifer* (below the gypsum), the latter being the major regional one. The role of the gypsum unit has changed with time, from initially being an aquiclude, intervening between two aquifers, to a karstified aquifer with well-developed conduit permeability (Klimchouk 1997a, 2000b).

Regional flow is from the platform interior, where confining clays and the gypsum are denuded, toward the large and deep Dniester Valley and the Carpathian foredeep. In the narrow northwest part of the gypsum belt (Sites 1 and 2), the artesian monoclinal slope is most clearly developed (Fig. 2): infiltration recharge occurs on Rostochje and Opolje Hills, where both the Upper Badenian and Lower Badenian sediments are exposed. Flow becomes confined towards the foredeep, being "separated" by the gypsum into the upper and lower aquifers. On the opposite flank of the confined flow area, along the very platform margin, regional faulting has brought the Miocene aquifers into lateral contact with the thick Kosovsky clay sequence. Further flow in this direction is prevented and upward discharge occurs locally, focused upon areas where the confining properties of the capping sediments are weakened by stratigraphic or tectonic discontinuities, or by incised erosional valleys.

However, in the wide southeast section of the gypsum belt, the incised river valleys separate the Miocene sequence into a number of isolated, deeply drained interfluves. This is the entrenched karst zone (Podol'sky area, Sites 5 and 6) where most of the explored, presently relict, maze caves are located. South-southeast of Dniester (Bukovinsky area, Sites 3 and 4), the gypsum remains largely intact and is partly inundated (subjacent karst). Farther in this direction, with an increase of the gypsum occurrence and decrease of the erosional entrenchment, the Miocene aquifer system becomes confined.

In the confined-flow area, the groundwater-flow pattern includes a lateral component in the lower aquifer (and in the upper aquifer, to a lesser extent), and an upward component through the gypsum in areas of potentiometric lows where extensive gypsum-cave systems are developed.

METHODS OF STUDY

Water Chemistry and Saturation Index

Water chemistry in the gypsum karst of the western Ukraine is characterised from 1,800 samples analysed for major cations and anions. Water temperature and pH were measured in the field. In the resultant database, ion content is expressed in mg/dm^3, mg-eq/dm^3, and in %-eq. TDS content was calculated in mg/dm^3.

Water-chemistry data were used to calculate, for each sample, the *Saturation Index* (*SIg*), characterising a degree of deviation of a natural solute from equilibrium with respect to gypsum. *SIg* is zero if water is in equilibrium with gypsum, it has negative values for undersaturated solutions, and positive values for supersaturated ones.

Sampling Strategy and Datasets

The original sampling was performed in conjunction with various karst-research projects conducted from 1982 to 1992. It was aimed at individual characterisation of different karst hydrogeologic settings (confined, unconfined) and of each distinct components of the respective circulation systems; i.e., various recharge sources, flow within, and discharge from, individual aquifers, etc. In many localities, continuous sampling was performed to reveal chemical variability through different flow regimes. Besides our original analyses, available historic data from literature and technical reports were incorporated into the resultant database to amplify characterisation of some system components, or periods, poorly covered by our own sampling. Chemical data from other sources were incorporated if proper identification of samples were possible, with regard to time and circulation pattern. The overall database totals 1,800 analyses. Table 1 gives mean TDS and SO_4 contents, as well as averaged *SIg* and gypsum-solution rates for principal situations studied.

In confined setting.-- represented by Sites 1 (Jazovsky area) and 2 (Nikolaevsky area), samples were taken from boreholes gauged separately for the lower, the gypsum ("Gypsum aquifer - mid" in the Table 1 and on diagrams), and the upper aquifers by a sampler that enables sampling from specific depths. Samples were taken at the gauge level. In the Jazovsky area, samples were also taken from a sump in the large sulphur quarry, the bottom of which cuts to the top of the gypsum bed ("Gypsum aquifer - top"). Samples from the sump represent upward discharge from the gypsum-karst systems.

In unconfined setting.-- represented by Sites 3 (Zoloushka Cave), 4 (Dankovtsy Collapse), 5 (Seret-Nichlava interfluve, Ozernaya and Optimisticheskaya caves), and 6 (Atlantida cave and Mylevtsy area), the following system components were characterised by sampling (Table 1 and Fig. 4A): 1) precipitation, 2) spring discharge from the Pliocene–Quaternary aquifer, 3) focused surface flow (streams) above the gypsum level, 4) focused percolation through the caprocks sampled in vertical dissolution pipes in caves, 5) flowing cave pools (aquifer "windows"), 6) cave pools perched on clay fill, 7) "downward" spring discharge from the sub-gypsum aquifer, 8) spring discharge from the Cretaceous aquifer, and 9) spring discharge from the Devonian aquifer.

Some of these situations were further categorised according certain criteria significant for chemical evolution of waters. For instance, dripping localities in caves (focused percolation) were classified into three categories, according to a degree of contact between dripping water and the gypsum surface. Sampling in cave pools was performed at fixed levels (depths), and the data grouped into three categories (0–5, 5–15, and >20 cm) to characterise chemical stratification of water.

Gypsum-Solution Rate

The method of field measurements of solution rates (SR), based on weight loss of standard samples (usually tablets), was initially suggested and realised to study the processes in limestone karst (Gams 1981). It appears to be more effective for gypsum than for limestone because of the much higher characteristic dissolution rates and higher spatial unevenness of dissolution in gypsum. This makes errors inherent in measurements relatively insignificant and allows dissolution dynamics to be monitored even over comparatively short timescales (Klimchouk et al. 1988).

Gypsum-solution-rate study by means of standard tablets was

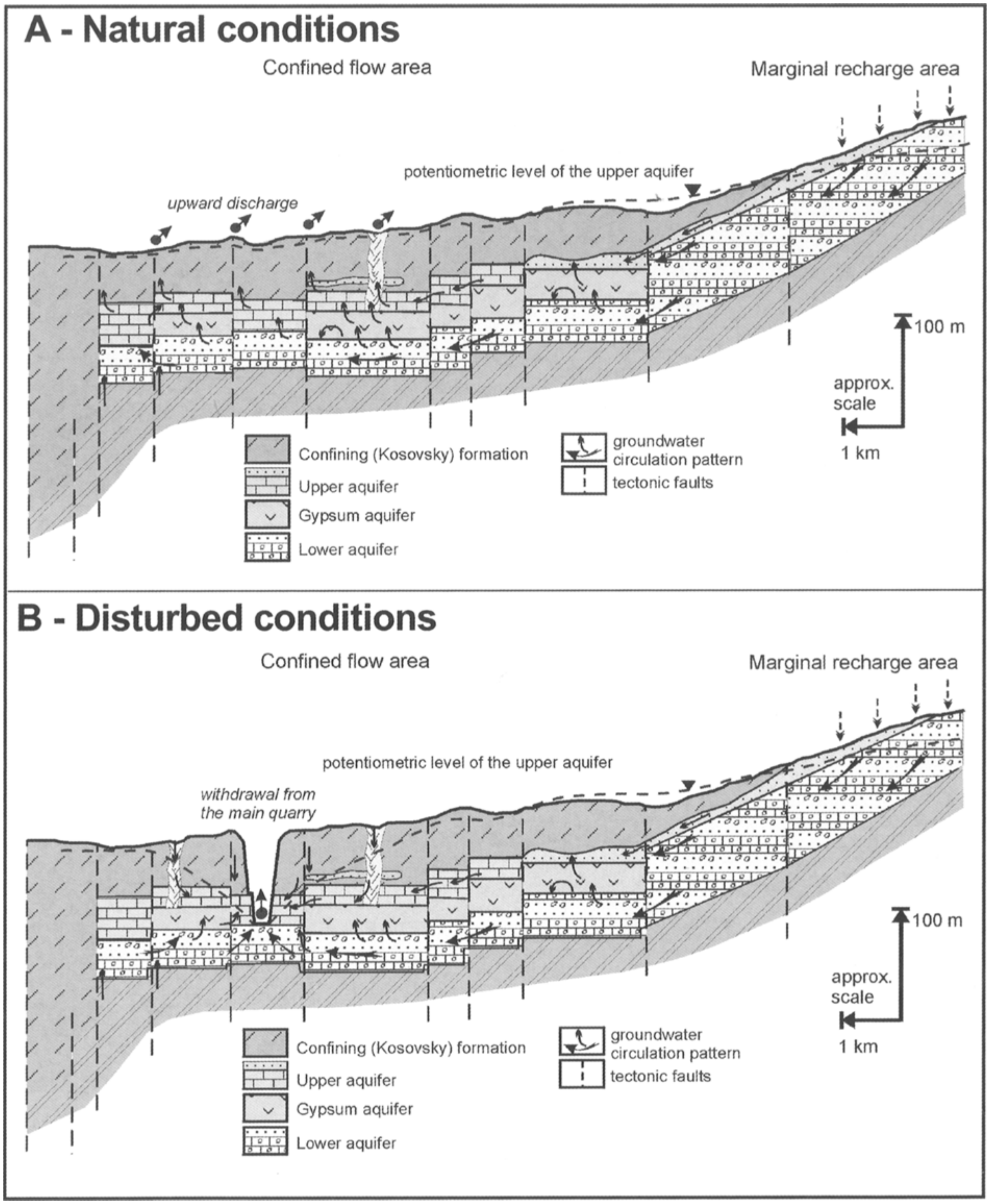

Figure 2. Circulation patterns in the confined Miocene aquifer system (Zone IV) under natural (A) and disturbed (B) conditions.

Table 1. Mean TDS, SO_4, *SIg*, and solution rates in different aquifers and situations of the Miocene aquifer system in the western Ukraine.

Study sites Sampled aquifers/situations	Number of samples entire/tablet datasets	TDS, *mg/dm³*		SO_4, *mg/dm³*		*SIg*		SR from gypsum tablets, *mm/yr*
		entire dataset	tablet dataset	entire dataset	tablet dataset	entire dataset	tablet dataset	
Confined conditions								
Site 1: Jazov, pre-quarrying stage								
Upper aquifer	60/-	2751,2	-	1197,6	-	-0,46	-	-
Gypsum aquifer	-	-	-	-	-	-	-	-
Lower aquifer	22/-	1145,2	-	581,3	-	-1,62	-	-
Site 1: Jazov, quarrying stage								
Upper aquifer	35/-	1321,0	-	301,3	-	-1,42	-	-
Gypsum aquifer (top)	42/23	2488,0	2452,3	1381,5	1379,3	0,05	0,06	0,05
Gypsum aquifer ("mid")	36/15	2008,0	2015,3	1214,7	1218,4	-0,03	-0,03	1,36
Lower aquifer	83/24	723,2	1059,5	162,7	415,3	-1,80	-1,16	9,93
Site 2: Nikolaev, quarrying stage								
Upper aquifer	2/-	1020,4	-	592,7	-	-0,44	-	-
Gypsum aquifer	12/-	1812,4	-	1172,2	-	-0,08	-	-
Lower aquifer	2/-	417,3	-	81,4	-	-1,85	-	-
Site 2: Nikolaev, post-quarrying stage								
Upper aquifer	46/24	920,9	1461,4	567,4	899,2	-0,56	-0,21	0,34
Gypsum aquifer	199/47	1756,0	1600,3	1146,2	1030,9	-0,09	-0,13	0,22
Lower aquifer	25	326,6	-	61,7	-	-2,39	-	-
Unconfined conditions								
Precipitation	4	115,9	-	27,6	-	-2,59	-	-
Discharge from the Q aquifer	65	870,0	-	216,1	-	-1,28	-	-
Surface streams	27	899,6	-	246,6	-	-1,26	-	-
Vertical percolation, all samples including:	44/50	1765,3	1974,8	1035,4	1142,2	-0,23	-0,15	0,52
A - poor rock contact	5/1	783,9	607,0	199,8	192,1	-1,29	-1,32	-
B - medium rock contact	25/30	1703,0	1863,8	1038,6	1153,0	-0,14	-	0,06
C - close rock contact	18/19	2163,6	2109,2	1288,3	1227,6	-0,02	-0,04	0,33
Flowing cave pools, all samples including:	131/99	1884,0	1940,9	1083,1	1139,8	-0,11	-0,09	5,29
depth <5cm	41/24	1529,3	1530,6	810,1	830,4	-0,27	-0,26	10,80
depth 5-15cm	41/30	1808,8	1808,3	1040,6	1056,5	-0,12	-0,11	6,59
depth >20cm	50/45	2228,6	2278,1	1336,9	1381,9	0,02	0,03	1,32
Perched cave pools, all samples including:	102/67	2203,8	2197,0	1201,0	1177,9	-0,02	-0,03	0,02
depth <5	22/14	1860,8	2089,8	917,2	1116,9	-0,15	-0,011	0,03
depth 5-15)	13/8	2221,0	2258,8	1253,6	1234,2	-0,002	-0,007	0,01
depth >20	67/45	2313,1	2211,7	1284,0	1180,9	0,02	-0,019	0,01
Discharge from the sub-gypsum aquifer, all samples including:	296/86	1983,6	1923,6	1077,1	1068,7	-0,15	-0,080	16,71
basin 1 (Glybochek)	7/-	1447,1	-	646,7	-	-0,42	-	-
basin 2 (Ozernaya Cave)	172/61	2202,7	2113,8	1252,0	1201,6	-0,02	-0,04	11,55
basin 3 (Optimistichna Cave.)	75/25	1693,9	1723,8	857,8	894,6	-0,24	-0,192	29,32
Discharge from K2 aquifer	124/28	1314,4	1600,2	613,0	849,1	-0,62	-0,203	66,7
Discharge from D aquifer	34/-	912,9	-	311,8	-	-1,11	-	-

performed in the western Ukraine during 1984–1992, with additional measurements in more recent years. In total, 53 stations were organised to characterise different situations of water/rock interaction in the three major intrastratal karst settings: entrenched, subjacent, and deep-seated (confined). Standard tablets 40–45 mm in diameter, 7–8 mm thick and weighing 18–25 g, were produced from a single variety of 97%-pure massive microcrystalline gypsum from the Kudrintzy quarry (Site 6). Before control weighing, the tablets were dried overnight at 40°C, prior to and after exposure. On stations, the tablets were so placed as to avoid any mechanical damage and direct impact of strong water currents. In cave lakes, the tablets were suspended on nylon fishing line at different fixed depths. In springs and boreholes, the tablets were suspended inside widely perforated plastic capsules. In boreholes, such capsules were lowered down and suspended at a gauge level.

Control weighings were generally made every 3 months, but sometimes at other intervals ranging from 1 to 6 months, depending upon actual dissolution dynamics and accessibility of a sample location. Tablets on stations were substituted with new ones each time that their original weight and dimensions changed more than 20% from original parameters. Totally, 644 measurements were made in the coarse of the study. As a rule, they were accompanied by water sampling for chemical analysis and subsequent determination of *SIg* values; respective mean TDS, SO_4, and *SIg* values are given in the Table 1, and these values are derived from the entire dataset.

Solution rate (SR) values are expressed in units of mg/cm^2/day and mm/yr. The latter notation is used through this work, as it is compatible with commonly used units of karst denudation.

All water-chemistry and solution-rate data are geographically related and incorporated into the GIS "Gypsum Karst of the Western Ukraine." The GIS also contains also much other geocoded information about regional geology, tectonics, hydrogeology, and karst features that enables various scientific and practical applications.

HYDROCHEMISTRY OF THE MIOCENE AQUIFER SYSTEM AND GYPSUM-SOLUTION RATES IN DIFFERENT ENVIRONMENTS

Confined Settings

The confined conditions of the Miocene aquifer system were the primary throughout the whole region prior to the Late Pleistocene. Later on, uplifts in the interior parts of the platform and accompanying denudation and deep linear erosion have caused the formation and expansion of subjacent and entrenched karst zones. The neotectonic uplifts were less intense on the very platform edge, along the foredeep boundary, where the confined conditions remained until now and represent the original circulation pattern of the layered artesian system responsible for the specific type of speleogenesis (Klimchouk 1996, 2000a). Because of the positive feedback existing between flow pattern and speleogenesis, the latter in turn has played a fundamental role in establishing the resultant structure of the groundwater exchange in the Miocene aquifer system.

The zone of confined karst is shown in dark tint on Fig. 1. The upper profile on Fig. 2A illustrates the original situation of the artesian monoclinal slope complicated by block faulting, representative for the northwest section of the gypsum belt. On the Rostochje and Opolje uplands, where infiltration recharge occurs, the unconfined aquifer contains HCO_3–Ca waters with TDS of about 0.5 g/dm^3. The system becomes confined towards the gypsum belt and the foredeep, being then "separated" by the gypsum into the upper and lower aquifers. Under natural conditions, the heads in the confined-flow area are well above the bottom of the Kosovsky clays, even above the ground surface in places.

Flow and hydrochemical pattern in the confined-karst zone has been heavily impacted by the opencast mining and associated groundwater withdrawal, so natural and disturbed situations should be distinguished. The disturbed situation has developed in many areas due to massive abstraction of sulphur and clay since the early 1970s. Our datasets of the confined zone represent two sites. Site 1 is the area of the large Jazovsky sulphur quarry, where groundwater withdrawal continued (until recently) through the entire period of our own studies. The pre-quarrying conditions here are characterised only by historic data. Site 2 is the area of the Nikolaevsky quarry, where abstraction of the Kosovsky clays stopped in 1982. For this site our own sampling characterise only the post-quarrying situation, but the situation of the quarrying period can be inferred from historic data.

The quarries, cut into the caprocks to the top of the Ratynsky limestone (Nikolaevsky quarry) or to the top of the gypsum (Jazovsky quarry), became the focuses of discharge from the Miocene aquifer system. To maintain the operation, groundwaters were pumped out with rates reaching 112,000 m^3/day in the Jazovsky quarry and 288,000 m^3/day in the Nikolaevsky quarry. Such activities, particularly, have resulted in:

1. the fall of the potentiometric surface (up to 90 m in the immediate vicinity of the Jazovsky quarry) and the formation of drawdown cones extending up to 10–12 km away from the quarries;
2. the activation of groundwater circulation and the increase of flow velocities through every horizon (the velocities measured by tracing experiments were up to 2.5 km/day in the Jazovsky area, and up to 10.2 km/day in the Nikolaevsky area);
3. the partial reversal of the circulation pattern; the fall of the head in the upper aquifer gave rise to downward percolation through disturbed zones in the Kosovsky clays and piracy of the surface runoff in the vicinity of the quarries;

4. the respective changes in groundwater chemistry and intensification of karst processes.

The lower aquifer is the major one, due to its laterally "continuous" high transmissivity. Within the areas of potentiometric lows, groundwater from the lower aquifer flows upward into the upper aquifer through conduits in the gypsum (Klimchouk 1997a; 2000b). Lateral flow within the gypsum occurs only locally because of the clustered nature of maze-conduit systems. Analysis of exploration-drilling data suggests the existence of well-developed, multi-storey maze-conduit systems in such areas, similar to the well-known caves documented in the entrenched-karst zone.

Under natural conditions, the lower aquifer in the Jazovsky area contained groundwaters predominantly of HCO_3–Ca composition, or locally of HCO_3–SO_4–Ca or SO_4–Ca composition. TDS contents ranged within 0.15–2.9 g/dm^3 (average 1.14 g/dm^3), and SO_4 contents varied between 0.004 to 2.9 g/dm^3 (average 0.58 g/dm^3). Locally high sulphate contents indicate backward density-driven circulation loops from the conduits in the gypsum; waters high in SO_4 outflow from the gypsum, down to the lower aquifer. Under disturbed conditions, TDS and SO_4 contents in the lower aquifer decreased considerably (average 0.72 and 0.16 g/dm^3, respectively). This can be explained either by an increase of lateral inflow from the adjacent marginal recharge zone, or by breaking of backward circulation loops in the gypsum due to steepened vertical gradients toward the quarry bottom. In places immediately adjacent to the foredeep, Cl–Na methane-bearing waters with TDS up to 7.5 g/dm^3 were identified, incoming along faults from the foredeep, which is an oil- and gas-bearing basin.

Groundwaters entering the gypsum from the lower aquifer are very aggressive with respect to gypsum, being able to dissolve it at rates ranging from 2.48 to 25.57 mm/yr. The average SR in the Jazovsky area is 9.8 mm/yr, and the average *SIg* from the SR-related chemical data is −1.16. These data characterise the disturbed situation; it can be assumed that SR by waters of the lower aquifer at the natural stage would be somewhat lower, as the sulphate content and *SIg* were higher, and circulation intensity was lower before quarrying.

When circulating through the gypsum bed, groundwaters gain SO_4–Ca composition. The contents of SO_4 and dissolution rates vary substantially, depending upon the location of borehole gauges in the cave/fissure system relative to the internal currents structure. Currents rising directly from feeding channels in a conduit system may maintain a rather low SO_4 content and high aggressiveness, even in the middle part of the gypsum, while the bulk water (under sluggish circulation) is more saturated with SO_4 (Klimchouk 1997c). Under disturbed conditions in the Jazovsky area, SO_4 content in the "mid" gypsum (boreholes samples) ranges from 0.98 to 1.54 g/dm^3 (average 1.21 g/dm^3) and *SIg* ranges from -0.2 to 0.05 (average -0.03). Respectively, solution rates in the "mid" gypsum vary in a range of 3.54 to 0.42 mm/yr (1.07 mm/yr in average). When the water comes out of the gypsum (samples from the quarry sump), it contains 1.38 g/dm^3 of SO_4 and eventually is saturated with sulphates (average *SIg* 0.05). Solution rates measured in this situation are quite negligible (0.05 mm/yr).

We do not have water-chemistry and solution-rate data for the gypsum bed in the Jazovsky area during the pre-quarrying period prior to 1970 (natural conditions), although it can be assumed that: 1) the circulation had been more sluggish, 2) the SO_4 content was somewhat higher, and 3) solution rates were lower. With certain reservations, data of the post-quarrying stage in the Nikolaevsky area can be assumed as being representative for natural conditions. The respective average SR (0.22 mm/yr) is about one order of magnitude lower than the "mid" gypsum value in the disturbed Jazovsky area.

In the upper aquifer, waters discharged from the gypsum mix with the lateral-flow component. As a result, SO_4 and TDS contents drop down and *SIg* rises, as compared to the gypsum aquifer, to averages of 0.3 g/dm^3, 1.32 g/dm^3, and −1.4, respectively. Fig. 3A shows that in the Jazovsky area the average SO_4 and TDS contents in the upper aquifer, under disturbed conditions, are substantially lower, when compared to the respective values for the natural stage (SO_4 of 1.2 g/dm^3; TDS of 2.75 g/dm^3). This can be explained by the increase of lateral inflow from the marginal recharge area, and by the involvement of the vertical downward recharge through the capping clays within the drawdown cone of the quarry; both these components dilute the waters rising from the gypsum.

Unconfined Settings

Hydrogeologic conditions and the locations of tablet stations in the entrenched-karst zone (Sites 5 and 6) are generalised in Fig. 4A. In the subjacent karst zone (Sites 3 and 4), the situation is largely similar in the supra-gypsum part of the cross-sections; but it differs in that the gypsum is inundated for most of its thickness, and there are no nearby entrenchments and free drainage out of the aquifers located below the gypsum.

In both zones, the karst systems in gypsum are recharged via two routes: 1) through swallow holes in sinkholes (surface runoff, formed on the capping clays from precipitation and discharge from the perched Pliocene–Quaternary aquifer), and 2) vertical percolation from the Pliocene–Quaternary aquifer along faults or collapse zones that disturb the clay overburden. In both cases, waters have similar HCO_3–Ca composition with a TDS of about 0.87–0.89 g/dm^3. However, they differ much in the flow dynamics. Surface runoff is focused in streams with highly variable discharge, and percolation is represented by drip/trickle localities in caves. The swallowed streams flow for tens of meters inside the caves on the clay fill; they then dissipate, joining the groundwater lens whose surface is located either within the gypsum or in the sub-gypsum aquifer.

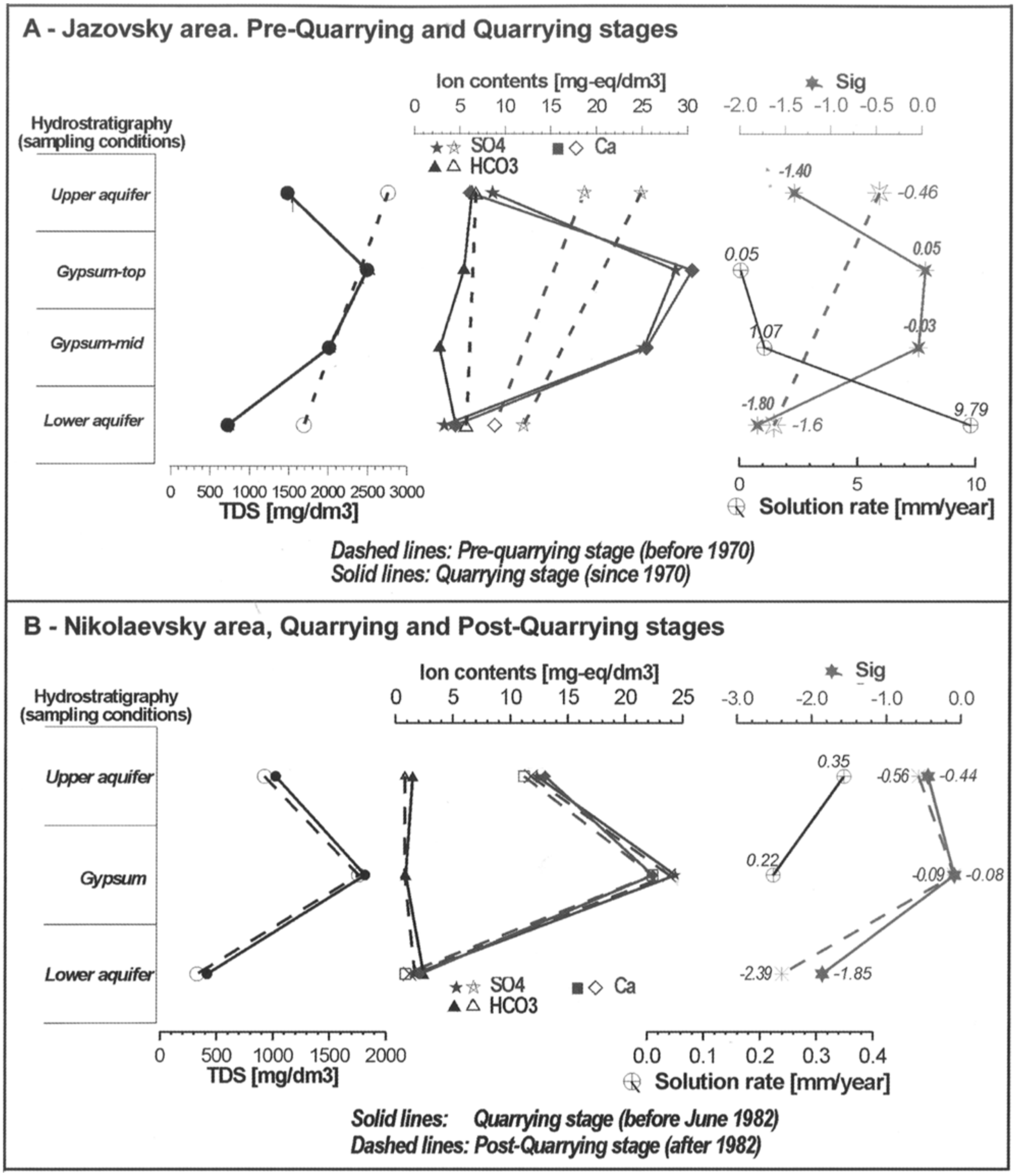

Figure 3. Mean TDS, major ion contents, SIg, and solution rates in waters of the confined Miocene aquifers: A – Jazovsky area, pre-quarrying and quarrying conditions; B – Nikolaevsky area, quarrying and post-quarrying conditions.

Rates of solution by the swallowed streams can be quite high, due to high aggressiveness of water (average *SIg* of –1.26) and high flow velocity. We did not measured SR in streams, because of their highly irregular flow regimes. Such data would be difficult to generalise, due to the influence of flow velocity that is difficult to control. SR values for surface streams in various regions, where the estimates are made by different methods, show variations of a few tens to a few hundreds of mm/yr (Klimchouk et al. 1996). However, streams dissolve the gypsum only in selected short routes in the immediate vicinity to swallow holes, and do not contribute much to the development of the relict maze caves. Only a few short, linear caves attribute their origin solely to such streams.

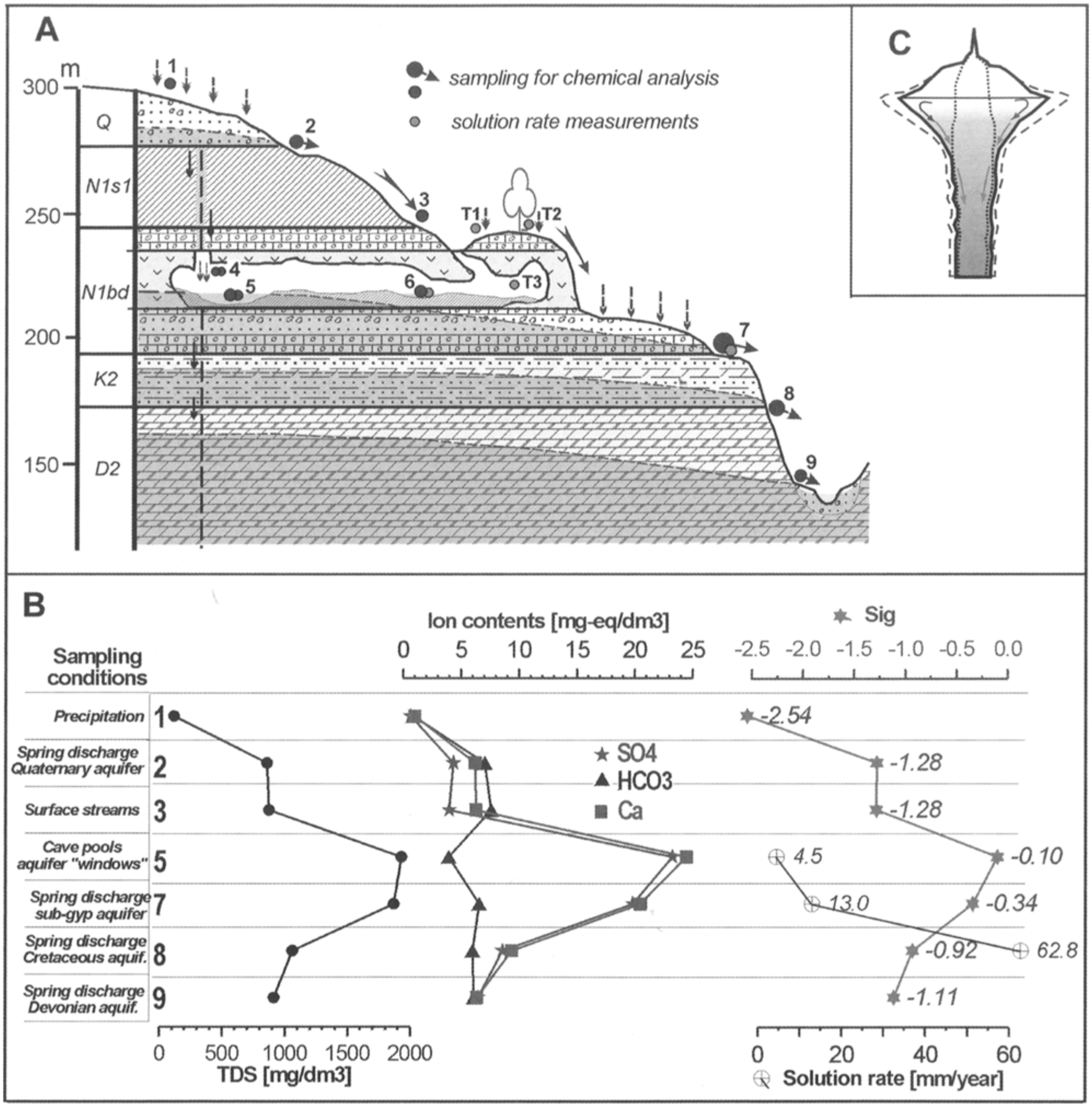

Figure 4. A – The formation of groundwaters and sampling locations in unconfined settings in gypsum-karst areas of the Western Ukraine. B – Mean TDS, major ion contents, SIg, and solution rates in the unconfined groundwater system. C – Scheme illustrating water stratification in cave pools and morphological effects (horizontal notching) of enhanced aggressiveness of the upper water layer.

Focused vertical percolation is responsible for the development of characteristic dissolution pipes ("comins") that are 0.5 to 3 m in diameter and are commonly superimposed on the relict labyrinthic passages. Solution rates generated by such focused vertical percolation (averaged at 0.52 mm/yr) vary greatly between stations and seasons, reflecting the highly irregular percolation regime and local conditions of the water/rock interaction. Hence, these data are difficult to generalise. We roughly classified drip/trickle localities into three categories, according to the degree of contact between water and the rock: A - poor contact (almost free-falling drips or trickles, with brief contact with gypsum); B - medium contact (1 to 2 m length of contact); and C - close contact (at least a few meters of contact). Average *SIg* values vary between C and A from –0.02 to –1.29.

From the viewpoint of contemporary karst development in unconfined settings, the most important situation is the gypsum aquifer. Gypsum strata can be fully drained, or can be inundated to different levels that vary according to different areas, tectonic blocks, seasons, and years. The aquifer in the gypsum is represented by hydraulically connected pools ("flow pools" in the Table 1), whose numbers and sizes depend on the water level relative to the cave-system configuration. Flow is quite sluggish. In Zoloushka cave, where the water table has been progressively lowered during the last 40 years due to pumping from the nearby quarry, there are also pools perched on the clay fill, and they are degrading with time.

Our studies suggest that there is distinct density stratification in the pools due to chemical differences. In flow pools, the average SO_4 contents change from 0.8 g/dm^3 in the uppermost layer (<5 cm), through 1.0 g/dm^3 in the horizon between 5–15 cm, to 1.3 g/dm^3 in the depths below 20 cm. Respectively, the average *SIg* decreases between these levels, from –0.26 through –0.11 to 0.03, and solution rates decrease from 10.8 through 6.59 to 1.32 mm/yr. The fact that solution rates in the uppermost layer are about 10 times higher than in the bulk water at depth is well illustrated by morphological evidence in the caves: horizontal notching in the passage walls (Fig. 4C), mushroom-like shape of the rocks projecting from the water in pools, etc. In the perched pools, SO_4 contents are a little higher, but *SIg* and SR values are lower, when compared with the flow pools: SR averages for the respective datasets are 0.02 and 5.29 mm/yr. Chemical stratification is less distinct.

Considering that most measurements were made under active-circulation conditions in the entrenched-karst zone (Site 5), and that circulation in the gypsum and the subjacent karst zone is probably somewhat more sluggish, the values measured in the flow pools should be regarded as maximums for the unconfined gypsum aquifer. For purposes of speleogenetic modelling, we would generalise solution rates for the bulk aquifer as being on the order of 0.1 mm/yr, and for the upper water layer as being on the order of 1.0 mm/yr. It is remarkable that the former figure roughly corresponds to the above-derived characteristic solution rate for undisturbed, confined circulation in the gypsum; both situations represent quite-sluggish circulation in the gypsum. The latter figure is close to the average SR for the "mid" gypsum in the disturbed, confined conditions; both situations represent somewhat more live circulation. Also, the average SR for the upper water layer, under active unconfined circulation (10.8 mm/yr), is close to SR in waters entering the gypsum from below in the disturbed, confined circulation (9.93 mm/yr). This makes sense, considering natural-convection effects and similar chemistry of recharge sources. Hence, this order of solution rates can be taken as a characteristic in the both confined and unconfined settings for "fresh" waters at the initial contact with gypsum.

The sub-gypsum (lower) aquifer in the unconfined settings receives its recharge in two ways: 1) through the karst systems in the gypsum, where waters gain SO_4–Ca composition and, 2) through direct infiltration in areas where both the capping clays and the gypsum were removed by denudation (see Fig. 4A). In catchments where the gypsum is entirely removed, the springs have a HCO_3–Ca composition and low TDS (0.6 g/dm^3).

In the entrenched karst zone, almost all waters from the gypsum discharges via springs draining the sub-gypsum aquifer on the valley slopes. Their chemistry depends on the proportion between the two recharge sources mentioned above, the saturated thickness in the gypsum, and the general circulation intensity in a particular basin. Table 1 characterises three typical basins (tectonic blocks) studied in the Seret–Nichlava interfluve (Site 5). Basin 1 (Glybochek) contains a little gypsum, and the sub-gypsum aquifer discharges waters of SO_4–HCO_3–Ca composition. In Basin 2 (Ozernaya cave), the gypsum and caprock occupy most of the catchment area, and recharge though the karst system is dominating. In Basin 3 (Optimistychna cave), the sub-gypsum rocks are exposed through a large proportion of the catchment area, so that direct infiltration recharge considerably dilutes the waters that passed through the gypsum. Calculations using mixing equations suggest that in Basin 2 about 87% of discharge consists of water coming through the karst system (the remaining 13% consists of direct infiltration from the non-karstic areas), while in Basin 3 this proportion is 58% versus 42%; this is in agreement with geomorphological characteristics of the basins.

The Upper Cretaceous aquifer in the entrenched-karst zone discharges water through numerous springs on the valley slopes. The major anions are HCO_3 and/or SO_4 and the major cations are Ca and Mg. Variations in the chemical facies and TDS are dictated mainly by the varying SO_4 content that changes through the area from 0.05 to 1.4 g/dm^3. This reflects varying degree of hydraulic communication with the overlying Miocene aquifer, and the varying proportions between the recharge from the overlying aquifer and direct infiltration recharge.

Springs from the Devonian aquifer discharge waters mainly of the HCO_3–Ca or HCO_3–Ca–Mg composition, with a mean TDS of 0.91 g/dm^3. Sulphate content is normally low (0.1–0.2 g/dm^3). In places, waters of HCO_3–SO_4 composition occur with a SO_4 content as high as 0.8–1.0 g/dm^3. This indicates local leakage from the Miocene aquifer via major faults.

CONCLUSIONS

Waters in the Miocene aquifers adjacent to the gypsum bed, as well as the main recharge sources, commonly have a HCO_3–Ca composition and low TDS before they contact with gypsum. Circulating in the gypsum bed, they gain SO_4–Ca composition. Discharged to adjacent aquifers in the downgradient direction of the circulation system (the upper aquifer in confined settings, and the lower aquifer in unconfined settings), sulphate waters mix in different proportions with HCO_3–Ca waters, resulting in composite chemical types.

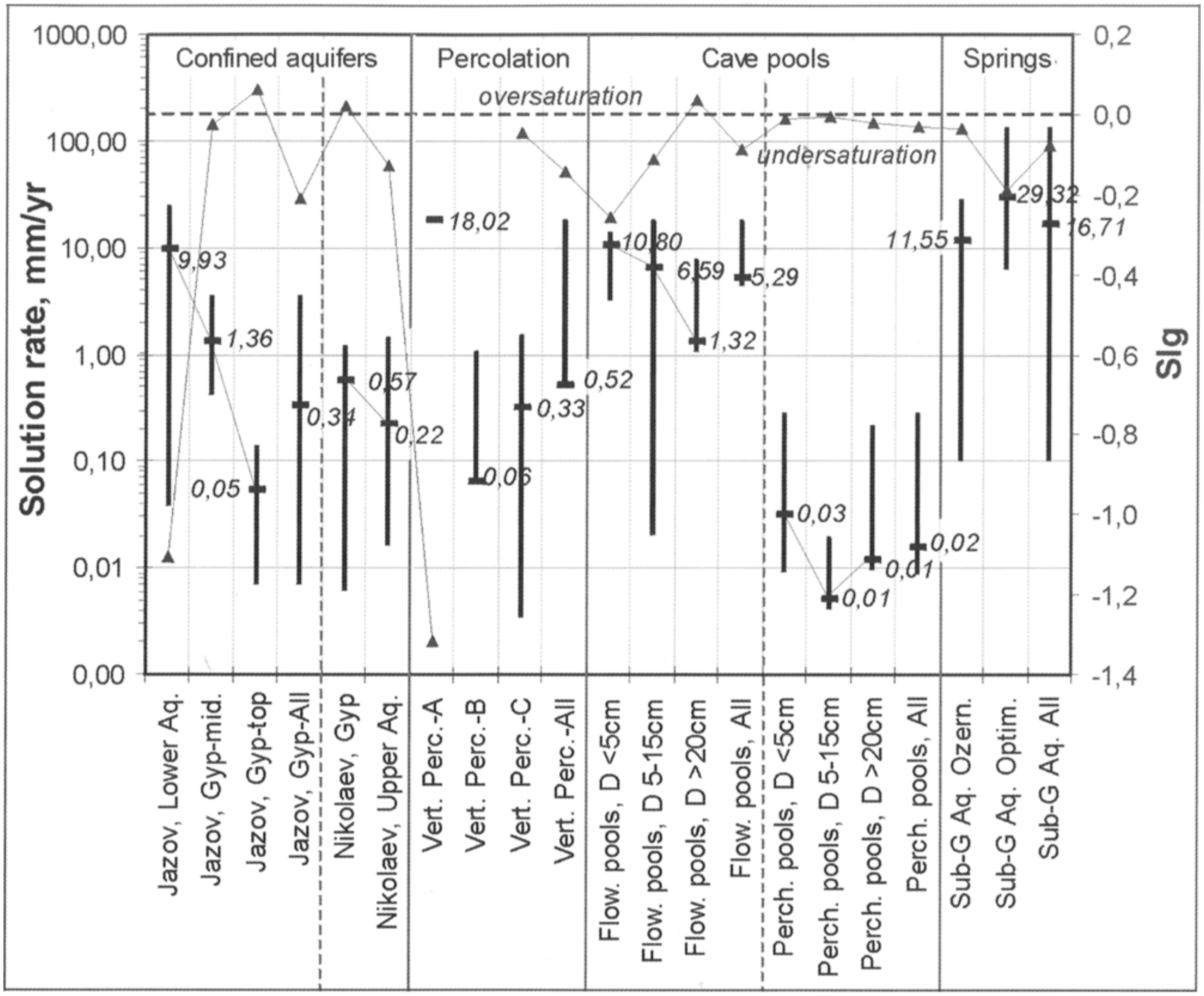

Figure 5. Gypsum-solution rates and SIg in different situations of water-rock interaction.

Table 2. Generalization of gypsum-solution-rate data from the western Ukraine for the purposes of calibration, adjustment, and verification of speleogenetic/karst development models.

Settings and situations of the gypsum aquifer	Relative general circulation intensity	Characteristic range of SO_4 contents, g/dm^3	Approximate SR, mm/yr (order of magnitude)
Unconfined settings, bulk water body	sluggish	1.1 - 1.4	0.1
Confined settings, undisturbed situation	sluggish		
Unconfined settings, the upper layer of water body	moderate	0.8 - 1.2	1.0
Confined settings, disturbed situation	moderate		
Unconfined settings, the upper layer of water body	active	0.4 - 0.8	10.0
Confined settings, the water entering the gypsum from the lower aquifer (buoyant currents within the bulk water body, rising from the feeding channels)	active		

Within the gypsum aquifer, the content of SO_4 and solution rates vary dramatically, depending upon the internal circulation structure within in a cave/fissure system. Under generally sluggish flow conditions, this structure results from a complex interaction of forced and natural convection circulation. In confined settings, currents that rise directly from the feeding channels at the gypsum base may retain a rather low SO_4 content and high aggressiveness, even in the middle part of the bed, while the bulk water in a conduit system is much more saturated with SO_4. In unconfined settings, the effect of density (chemical) stratification is pronounced, with the upper water layer being a lower SO_4 content and higher aggressiveness than the bulk water. Considering such a great variability, any generalisation of the water chemistry and dissolution processes based on limited, occasional sampling can be misleading; comprehensive studies are therefore needed to encompass different flow components, situations, and regimes.

Solution rates depend on water chemistry, but also on the dynamic regime of water (flow rate and velocity). Fig. 5 is a summary graph of gypsum-solution rates measured in different aquifers and situations. For the purposes of conceptual and mathematical modelling of speleogenesis, it is important to derive a valid generalization of solution rates for the most common situations encountered in the gypsum aquifer. Such an attempt, based on the reported data and the above discussion, is presented in Table 2.

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