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## Hydrogeochemical investigation in the region of Horní Jiřetín and Jezeří forests in North Bohemia

### Hydrogeochemický výzkum v oblasti Horního Jiřetína a Jezeřských lesů v severních Čechách

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**Abstract:** The subject of the hydrogeochemical study in the Horní Jiřetín and Jezeří forests region in North Bohemia was groundwater from Quaternary deposits, volcanic breccia, Tertiary sediments of the North Bohemian Basin and from gneisses forming the basement of the Tertiary basin and the adjacent massif of the Krušné hory Mts. The investigation results are a contribution of geological sciences to recognition of the environmental state in this anthropogenically loaded part of our Earth.

The investigation verified specific chemical and physico-chemical properties of groundwater from shallow collector of Quaternary deposits (dominant ions  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , pH = 5.8–6.4,  $\delta^{34}\text{S} = +3.1\text{‰}$  and from deeper situated collectors of Tertiary sandstones and gneisses (prevailing ions  $\text{Na}^+$ ,  $\text{HCO}_3^-$ , pH = 7.2–7.9,  $\delta^{34}\text{S} = -0.5\text{‰}$  and  $-1.4\text{‰}$  – gneisses) and volcanic breccia ( $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , pH = 7.1). The ascertained vertical hydrochemical zoning (shallow collector – sandstones, gneisses) and local occurrence of groundwater of Mg- $\text{HCO}_3$  type are connected with long lasting input of anthropogenic sulfur in form of acidic atmospheric deposition into the hydrogeological system of the studied part of the Krušné hory region, with different petrochemical character and hydraulic properties of the collector studied and with the occurrence of Tertiary claystones and argillized volcanites, separating hydrochemically different shallow and deep collectors functioning as a hydrogeological insulator.

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In the years 1982–1985, the region of Horní Jiřetín and Jezeří forests in the Krušné hory Mts. underwent a hydrogeochemical exploration which was part of a complex geological exploration of the foreland of the open pit brown-coal Československé armády Mine.

The research was carried out on a morphologically prominent territory (264–924 m a.s.l.) covering part of the

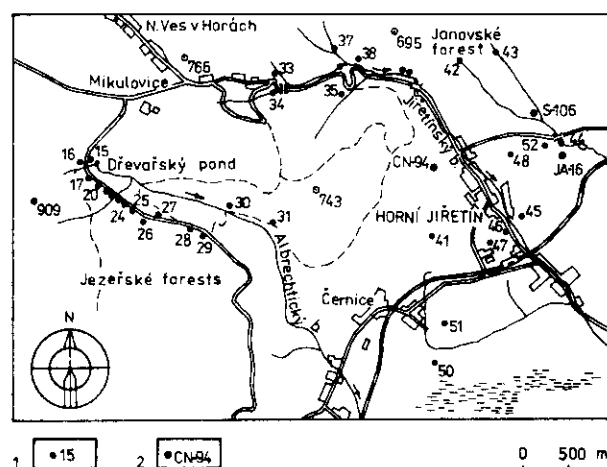
North Bohemian Basin between the villages of Janov and Černice and the adjacent Krušné hory massif as far as Mikulovice village.

Owing to a complicated geological structure, on the comparatively small area (ca. 30 km<sup>2</sup>) we could study chemical and physical properties of groundwater from several collectors, differing in their stratigraphic position, hydraulic parameters and petrochemical character (Quaternary deposits, volcanic breccia, Tertiary basin sediments, crystalline complex of the basement of the basin and the Krušné hory mountain slopes).

The hydrogeochemical investigation of the water-saturated zone was, with respect to the searched origin of selected compounds in groundwater, supplemented by an orientational study of qualitative properties of wet atmospheric deposition in the given area.

#### Methods

The samples of groundwaters were taken from debris spring, which in the mountainous part of the studied area in many places naturally drain the collector of Quaternary deposits, from hydrogeological wells by the end of pumping tests, and from artesian wells with positive delivery level directly from the overflow at the head of the well.



1. The region of the hydrogeochemical investigation 1 – taking places of naturally issuing groundwater; 2 – wells with overflow.

Hydrogeological boreholes constructed in such a way that in one point it was possible to study separately groundwater from several collectors enabled us to study vertical hydrochemical zoning.

The groundwater was sampled into polyethylene bottles of 0.1 and 2 litre volume, washed with hydrochloric acid and distilled water and rinsed with the groundwater assigned for the analysis.

In the laboratories of Aquatest the water samples were subjected to a standard set of analyses involving pH, electroconductivity, chemical oxygen demand, total hardness ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ), acid and alkali neutralization capacity, alkali metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ),  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{H}_4\text{SiO}_4$ . Average contents of selected compounds are given in table 1.

In the following text as well as in the equilibrium calculations only laboratory values of pH are presented. Because it is known that these values can prominently differ from the pH values obtained directly in the field (PAČES, 1972), a linear model  $Y = a + b.X$  was additionally tested by means of regression analysis, and samples from 17 taking places of the studied area the relation between laboratory pH (PHL) and field pH (PHT) was verified and expressed by the equation

$$\text{PHL} = 0.52 + 0.93 \cdot \text{PHT} \quad (1)$$

The close relationship between PHL and PHT is indicated also by a high positive value of the correlation coefficient (0.9). So it is obvious that in this case the laboratory values of pH will not substantially influence the results of the equilibrium calculations, and at the same time they can be used as one of the characteristic qualitative parameters of the studied collectors.

In perennial springs and artesian wells the chemical and physico-chemical properties of the groundwater were observed in dependence upon time, for a period of at least one year, in about one-month intervals.

With respect to the presumed influence of the groundwater by a long-lasting admission of anthropogenic sulfur into hydrogeological system of the studied Krušné hory region, and in order to verify the relationship between the precipitation water and groundwater, the standard chemical analyses were supplemented by an isotopic study of sulfur in dissolved sulfates ( $^{34}\text{S}/^{32}\text{S}$ ) and water molecules ( $^3\text{H}$ ). These analyses were performed in the Research Institute of Brown Coal in Most ( $^3\text{H}$ ) and in the Czech Geological Survey in Prague (sulfur isotopes).

Atmospheric water (melted snow) underwent the same set of analyses as the groundwater.

### Compound contents in groundwater

Average contents of selected ions and  $\text{H}_4\text{SiO}_4$  in groundwater of the studied collectors are given in table 1.

From the given outline it is evident that of the groundwater from shallow collector of the Quaternary deposits are characteristic molar ratios of alkaline earths to alkali metals and hydrogencarbonates to sulfates [(Ca + Mg) :

(Na + K) = 2.0,  $\text{HCO}_3 : \text{SO}_4 = 0.6$ ], acid reaction of the solution (average pH = 6.1) and low average of Li ( $0.002 \text{ mmol.l}^{-1}$ ) and  $\text{F}^-$  ( $0.01 \text{ mmol.l}^{-1}$ ). Mean  $\delta^{34}\text{S}$  values of sulfates of naturally issuing groundwater make  $+3.1 \pm 0.9 \text{ ‰}$  (6 streams in the mountainous part of the studied area,  $n = 44$ ).

Different chemical properties were verified in groundwater from deeper collectors, composed of volcanic breccia, Tertiary sandstones and gneisses.

Of the given collectors, ratios of hydrogencarbonates to sulfates (6.7), nearly neutral reaction of water (pH = 7.3) and higher average contents of Li ( $0.02 \text{ mmol.l}^{-1}$ ) and  $\text{F}^-$  ( $0.021 \text{ mmol.l}^{-1}$ ) are characteristic. In groundwater from gneisses and sandstones the main cations are represented by alkali metals [(Ca + Mg) : (Na + K) = 0.43]. In the case of the volcanic breccia the prevailing contents of alkaline earths with dominant role of Mg was ascertained [(Ca + Mg) : (Na + K) = 2.4, Ca : Mg = 0.7].

Isotopic composition of sulfate sulfur of deeper circulating groundwater was studied from an overflow well JA-16, collecting water from gneisses with argillized basalt in the overlie (depth of the well 150 m, open section 42–81 m, constant overflow  $0.8 \text{ l.s}^{-1}$ , constant temperature of water  $13.2 \text{ °C}$ ,  $n = 17$ ) and further from the well CN-94, drilled in gneisses passing directly into Quaternary deposits (well depth 82 m, open section 20–82 m, seasonal water overflow from March to October with the yield of ca.  $0.01 \text{ l.s}^{-1}$ , temperature of groundwater  $8 \text{ °C}$ , one measurement of sulfur isotopic ratio performed in August 1985).

Groundwater from both the boreholes had slightly negative  $\delta^{34}\text{S}$  (JA-16,  $-1.4 \pm 0.1 \text{ ‰}$ , CN-94,  $-0.5 \text{ ‰}$  – V. Šmejkal, pers. comm.).

Tritium activity of three samples taken from the overflow well JA-16 was lower than 3 T.U. (P. Trýzna, pers. comm.).

MOSER and RAUERT (1980) give the value  $5 \pm 5 \text{ T.U.}$  as the average tritium activity of precipitation water in Europe before 1952.

Groundwater of phreatic water body as well as of the deeper situated collectors with exception of artesian wells exhibited roughly the same average  $\text{Cl}^-$  contents ( $0.4\text{--}0.5 \text{ mmol.l}^{-1}$ ).

Contents of all dissolved substances fluctuated from  $3.5 \text{ mmol.l}^{-1}$  (Quaternary deposits of the mountainous part of the area) to  $12.3 \text{ mmol.l}^{-1}$  (basement gneisses).

In all the groundwater samples the  $\text{Na}^+$  ion contents were by an order of magnitude higher than those of  $\text{K}^+$  ions in spite of the fact that the average contents of these elements in the upper continental crust are almost equal (Na – 2.89 %, K – 2.80 % – TAYLOR and MCLENAN, 1985). This relationship between the contents of dissolved alkali metals is of general validity for groundwater uninfluenced by anthropogenic agents (agricultural activity) and is being explained by an easy bond of  $\text{K}^+$  ion with small ionic radius in structures of clay minerals and a high resistivity of K feldspar compared with Na-Ca feldspars during weathering processes (HEM, 1970).

Table 1  
Average chemical composition of the studied groundwater

source	streams		S-106				wells	
rock	Quaternary deposits		volcanic breccia	sandstones	basement gneisses	gneisses of the Krušné hory mountain slope		
number of assessment	688	39	1	11	12	32	17	
Na <sup>2+</sup>	0.41	0.63	0.62	1.6	4.6	1.6	0.8	
K <sup>+</sup>	0.056	0.095	0.08	0.15	0.3	0.15	0.05	
Li	0.001	0.003	0.004	0.014	0.05	0.006	0.009	
Ca <sup>2+</sup>	0.58	0.99	0.72	0.61	0.42	0.52	0.69	
Mg <sup>2+</sup>	0.29	0.50	0.97	0.54	0.39	0.27	0.52	
NH <sub>4</sub> <sup>+</sup>	0.006	0.017	0.009	0.09	0.26	0.06	0.01	
Mn	0.001	0.011	0.001	0.005	0.01	0.009	0.0005	
Fe	0.004	0.07	0.007	0.09	0.054	0.24	0.029	
Cl <sup>-</sup>	0.32	0.41	0.14	0.52	0.50	0.44	0.16	
NO <sub>3</sub> <sup>-</sup>	0.21	0.22	0	0.11	0.1	0.04	0.013	
HCO <sub>3</sub> <sup>-</sup>	0.28	0.82	3.25	2.05	4.6	2.2	2.6	
SO <sub>4</sub> <sup>2-</sup>	0.71	1.2	0.37	0.58	0.52	0.44	0.29	
F <sup>-</sup>	0.01	0.01	0.011	0.026	0.028	0.026	0.014	
H <sub>4</sub> SiO <sub>4</sub>	0.61	0.59	1.8	0.42	0.45	0.62	1.1	
H <sup>+</sup> .1000	1.58	0.4	0.079	0.063	0.012	0.05	0.063	

Contents of the substances in mmol.l<sup>-1</sup>

The concentration of both Na<sup>+</sup> and K<sup>+</sup> ions in the groundwater of all the collectors studied overtops several times the contents of another alkali metal, lithium. This ratio is conditioned by low average Li contents in the upper continental crust (20 ppm – TAYLOR - MCLENNAN, 1985).

Higher average Fe contents in the Earth's crust compared with the average crustal abundance of manganese explains the prevailing concentration of Fe over Mn in groundwater of all the collectors studied.

Nitrate contents were raised both in the Quaternary collector and locally even in deeper circulating groundwater. This fact is associated with anthropogenic effects in the studied area – either with the agricultural activity, nitrogen atmospheric deposition (MATTHESS, 1988) or large-area deforestation of the Krušné hory Mts. resulting from negative impact of industrial exhalation linked up with nitrogen washing off of the soil into groundwater collectors (BORMAN - LIKENS, 1970).

### Formation of groundwater chemical composition

#### Effects of acid atmospheric deposition

The studied region of the Krušné hory Mts. is upon an intensive load of acid atmospheric deposition (PAČES, 1984). This is acid wet fall-out with pH averaging 4.19, prevailing SO<sub>4</sub><sup>2-</sup> ions and comparatively high NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> contents, moreover dry atmospheric fall-out in form of acid SO<sub>2</sub> and NO<sub>x</sub> gases and deposition of fly ash bearing acidifying particles.

Natural pH of precipitation water is 5.66 and it is a result of chemical balance between atmospheric water and carbon dioxide, in the atmosphere represented by 0.03 % (STUMM - MORGAN, 1981).

The acidity of the precipitation water in the Krušné hory region is conditioned by industrial exhalations. During winter time, with inversion temperatures of the air, in the lower part of the atmosphere the sulfur dioxide concentration can reach for short time as much as about 6000 µg.m<sup>-3</sup> (information from the Czech hydrometeorological survey in Ústí nad Labem from the year 1993).

According to MOLDAN (1980) the average pH of cumulative precipitation from the Most region was in 1977–1979 3.82 and other ions contents were as follows (mmol.l<sup>-1</sup>): SO<sub>4</sub><sup>2-</sup> 0.19, NH<sub>4</sub><sup>+</sup> 0.14, NO<sub>3</sub><sup>-</sup> 0.061, Ca<sup>2+</sup> 0.0435. In 1986–1987 the same author (B. Moldan, 1988 – personal communication) mentions the average pH of precipitation from Vysoká Pec – 4.26, and adds the contents of other ions (mmol.l<sup>-1</sup>): SO<sub>4</sub><sup>2-</sup> 0.1, NH<sub>4</sub><sup>+</sup> 0.1, NO<sub>3</sub><sup>-</sup> 0.06, F<sup>-</sup> 0.017, Ca<sup>2+</sup> 0.03. From the isotopic analysis of sulfur in sulfates of melted snow taken by the present author in the March of 1987 in the region of the Jezeří forests we obtained the value of δ<sup>34</sup>S = +4.4 ‰. The sulfate contents in the snow water was 0.13 mmol.l<sup>-1</sup> and its pH made 3.98.

The effects of the acid atmospheric deposition as a whole are in the studied area most expressively manifested in the chemistry of rapidly circulating groundwater from the shallow collector of Quaternary deposits of the mountain region.

In the area of the Jezeří forests, some 900 m a.s.l., with expressive negative effects of acid exhalation on perennial conifers, chemical composition of 16 groundwater issues was monitored within the years 1982–1985. From 251 measurements of pH resulted the average value of 5.4, and, at the same time, the lowest average pH of all the taking places including other springs in the Krušné hory foot was ascertained here – pH 4.4 (JEZERSKÝ, 1987). The same average value of pH (5.4) of groundwater influenced by acid industrial exhalations was determined e.g. in south-east Sweden in shallow wells and small springs (NORDBERG, 1985).

Beside low pH, of naturally issuing groundwater in the studied area are characteristic prevailing contents of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , or  $\text{NO}_3^-$ , and the average  $\text{F}^-$  contents ( $0.01 \text{ mmol.l}^{-1}$ ) identical with the average contents of this ion in the Krušné hory Mts. region precipitation water ( $0.017 \text{ mmol.l}^{-1}$ ). The contents of all dissolved substances is given by the mentioned principal ions  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{H}_4\text{SiO}_4$  and equals to  $3.5 \text{ mmol.l}^{-1}$ .

Comparing the chemical composition of 16 springs discharging about 800 m a.s.l. with that of the lowermost situated sources (ca. 400 m a.s.l.), it is obvious that with the lowering sea-level of the issue and rising distance from watershed the average pH of groundwater increases from 5.4 in the mountain region to 6.5 at the foot of the Krušné hory slope, and at the same time the contents of other components go up ( $\text{mmol.l}^{-1}$ ):  $\text{SO}_4^{2-}$  0.55–0.96,  $\text{HCO}_3^-$  0.17–0.43,  $\text{Ca}^{2+}$  0.47–0.94,  $\text{Na}^+$  0.23–0.83.

Average values of  $\delta^{34}\text{S}$  of sulfates of naturally issuing groundwater (+1.3 to 4.3 ‰) get close to the  $\delta^{34}\text{S}$  value of snow water from the Krušné hory Mts. (+4.4 ‰). The small difference observed between these values result from the influence of the groundwater from the shallow aquifer by precipitation water with anthropogenic sulfates, however, natural origin of the sulfates dissolved in the water of the phreatic collector cannot be excluded.

Chemical properties identical with natural issues of groundwater exhibited also the groundwater detected by hydrogeological wells in Quaternary deposits and sporadically even in gneisses of the Krušné hory slope (acid reaction of the solution, principal ions  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , fluorides contents corresponding to the precipitation water from Krušné hory region). This chemical state of the gneisses is a result of overflowing of the groundwater from phreatic collector influenced by anthropogenic agents into deeper collector without hydrogeological isolator.

In collectors formed of volcanic breccia, Tertiary sandstones and gneisses in the basement of the basin, and in most of the groundwater samples from gneisses of the Krušné hory mountain slope the influences of the acid atmospheric deposition are not traceable. This implies from the chemical composition of the groundwater obtained from the mentioned collectors during unrepeatd takings (dominant ions  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Mg}^{2+}$  in the case of volcanic breccia,  $\text{HCO}_3^-$ , alkaline reaction of the solution)

as well as from long-lasting monitoring of chemical properties of the overflow from the well JA-16, capturing groundwater from gneisses with argillized basalts in the overlie (characteristic ions  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , alkaline reaction of water). Different source of sulfates of the overflowing water compared with the groundwater from Quaternary collector is indicated by negative values of  $\delta^{34}\text{S}$  (–1.4 ‰ on the average). The isolation of the groundwater circulation in the mentioned borehole is shown by the tritium activity of water being lower than 3 T.U., stationary chemical composition of the groundwater, constant yield, as well as the temperature of the overflow.

Complicated hydrogeological conditions in gneisses of the Krušné hory mountain slope are indicated by the well CN-94 with seasonal overflow of the groundwater. According to the overflow in the period from March to October and the groundwater level below the surface in the remaining months we may guess that water in the gneiss is supplied from snow melting.

The measurement of the tritium activity of the overflow (less than 3 T.U.) showing that the water is over 30 years old, the  $\delta^{34}\text{S}$  value (–0.5 ‰) differing from that of the shallow groundwater, and inexpressive changes in the groundwater chemical composition with time do not, however, support this idea.

#### Influences of the rock environment

The minerals of the rock through which the studied water flows, are the quartz, aluminosilicates, and accessory phases. These may be a source of most ions and  $\text{H}_4\text{SiO}_4$  contained in the studied water.

From the viewpoint of rock chemical composition we can speak about groundwater circulation in two different environments – acid rocks (gneisses, Tertiary sandstones, Quaternary deposits) and a mafic rock (volcanic breccia). The differences in the chemical composition are given, among other, also by a general higher MgO content in the mafic rock than in the acid ones (BOUŠKA et al., 1980). Higher MgO content in the volcanic breccia in form of easily decomposable mafic aluminosilicates conditions the dominant role of the  $\text{Mg}^{2+}$  ion in the groundwater from the mafic rock (molar ratios  $\text{Ca/Mg} = 0.7$ ,  $\text{Na/Mg} = 0.6$ ) in contrast to the groundwater from Quaternary deposits ( $\text{Ca/Mg} = 2$ ,  $\text{Na/Mg} = 1.3$ ) and sandstones and gneisses ( $\text{Ca/Mg} = 1.3$ ,  $\text{Na/Mg} = 6.5$ ).

The mineral phases forming acid aluminosilicate rocks have strong weathering resistance. This fact is being reflected especially in low pH of debris streams draining the collector of mountain Quaternary deposits, influenced by the support of anthropogenic ions of  $\text{H}^+$ .

Table 2 summarizes the results of calculations of average deviations of the studied groundwater from individual collectors, from the equilibrium with chosen mineral couples and individual minerals, particularly with orthoclase, albite, anortite, and clay minerals illite and montmorillonite with respect to kaolinite in the environment

Table 2

Deviations of the groundwater from collectors of the studied region from equilibria (influence of ion couples on chemical equilibrium is neglected)

source	streams	S-106	wells			JA-16	
rock	Quaternary deposits		volcanic breccia	sandstones	basement gneisses	gneisses of the Krušné hory mountain slope	
partial pressure CO <sub>2</sub> 1000	2.2	1.62	1.29	0.65	0.28	0.55	0.81
Albite-kaolinite	-4.08	-3.31	-1.7	-2.1	-1.16	-2.18	-1.95
Orthoclase-kaolinite	-2.11	-1.29	0.24	-0.65	0.51	1.64	-0.3
Anortite-kaolinite	-9.87	-8.47	-7.2	-7.08	-5.86	-6.94	-7.01
Illite-kaolinite	-2.51	-1.68	-1.44	-0.88	0.12	0.47	-0.67
Ca-montmorillonite-kaolinite	-0.14	0.09	0.91	0.085	0.395	0.35	0.64
Gypsum	-2.15	-1.75	-2.4	-2.28	-2.52	-2.44	-2.49
Calcite	-3.1	-1.9	-0.7	-0.9	0.004	-0.8	-0.7
Forsterite	-18.47	-15.75	-12.55	-12.65	-10.09	-12.65	-12.26
Pyrite	-112.5	-120.5	-	-	-	-	-1.6
Limonite	0.097	3.1	-	-	-	-	-4.1

Deviations of the groundwater from the Quaternary deposits from the chemical equilibrium with pyrite and limonite were calculated for presumed Eh = 0.4 V, in the case of well JA-16 measured Eh = -0.14 V

of the given solution. The calculations were based on the average chemical composition of groundwater from individual collectors, relationships for calculation of ionic strength of the solution and activity coefficients mentioned by PITZER (1980) and equations for calculation of nonequilibrium indexes proper (PAČES, 1983, CHROBOK, 1975, ZVEREV, 1967).

From the outline in Table 2 it is obvious that kaolinite is in the environment of studied solutions a thermodynamically stable phase when compared with orthoclase and the final members of the row of Ca-Na feldspars. An exception is the groundwater from the Krušné hory mountain slope gneisses, where kaolinite with regard to orthoclase is unstable.

In the groundwater of all collectors rising negative values of deviations of feldspars from the equilibrium with kaolinite in the direction orthoclase-albite-anortite have been ascertained. This fact is associated with a generally valid lowering resistivity of feldspars during exogenic processes in the row orthoclase-albite-anortite (OLLIER, 1984).

In the environment of groundwater from the Quaternary collector and from volcanic breccia, kaolinite is a stable phase with respect to illite. In collectors built of gneisses and Tertiary sandstones both the minerals are roughly equilibrated. In the groundwater of all collectors equilibrium between kaolinite and Ca-montmorillonite has been verified. Kaolinite stability with respect to feldspars and clay minerals, and/or equilibrium between kaolinite and clay minerals, was verified by PAČES (1983) on a larger set of groundwater samples from acid aluminosilicate rocks.

Groundwater of all collectors was unsaturated with respect to gypsum and forsterite and also as regards calcite

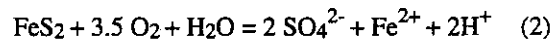
(with exception of basement gneisses, where calcite is in equilibrium with water).

From the comparison of deviation values of groundwaters of all collectors from equilibrium with forsterite and values of feldspars deviations from the equilibrium with kaolinite it is obvious that in the Quaternary collector, contrary to deeper takings in volcanic breccia, sandstones, and gneisses, the highest negative values have been recorded. This fact is probably conditioned by a short period during which the rapidly circulating groundwater could dissolve the minerals.

The raising relative saturation of the groundwater as regards calcite in the sequence Quaternary collector – sandstones, volcanic breccia, gneisses of the Krušné hory mountain slope – basement gneisses is due to a drop of balanced partial pressure of carbon dioxide in the same direction.

Supposing that Eh of the groundwater from freatic collector is +0.4 V (HEM, 1970), and further values on the contents of substances determined by chemical analyses (Fe, H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>), by means of balanced calculations it has been found out that shallow groundwater can dissolve pyrite and that it is equilibrated to oversaturated with respect to ferric hydroxide.

One litre of the groundwater from the collector of the Quaternary deposits contains 0.7 to 1.2 mmol SO<sub>4</sub><sup>2-</sup> on the average. This amount is, with respect to the groundwater circulation in the environment with continuous supply of atmospheric oxygen, much higher than would correspond to the pyrite oxidation according to the equation



at maximum solubility of oxygen in water with a 10 °C

temperature ( $0.36 \text{ mmol.l}^{-1}$  – REMY, 1971). In this case the sulfate contents would make just  $0.21 \text{ mmol.l}^{-1}$ .

The relatively low  $\text{SO}_4^{2-}$  contents in groundwater from deeper collectors, especially from gneisses (borehole JA-16) and volcanic breccia ( $0.29\text{--}0.39 \text{ mmol.l}^{-1}$ ) roughly correspond to the mentioned equation of pyrite oxidation (2) at limited oxygen solubility.

The balanced calculations with the used value of  $E_h = -0.14 \text{ V}$  measured in the field indicated a slight undersaturation of the groundwater from well JA-16 as concerns pyrite ( $-1.6$ ) as well as limonite ( $-4.1$ ).

A different source of sulfate sulfur in groundwater from this pilot well if compared with the phreatic collector results from a slightly negative average value of  $\delta^{34}\text{S}$  ( $-1.4 \text{ ‰}$ ).

Besides the chemical properties of the rock environment, the chemical composition of the groundwater is being influenced also by physical properties of the rocks, namely their permeability expressed by the filtration coefficient  $k$  ( $\text{m.s}^{-1}$ ). The evaluation of pumping tests on wells from the individual collectors studied yielded the following average values of  $\log k$  ( $\text{m.s}^{-1}$ ): Quaternary deposits ( $-5.5$ ), Tertiary sandstones ( $-6.2$ ), gneisses of the Krušné hory mountain slope ( $-7.3$ ), basement gneisses ( $-8.5$ ) – SYSEL et al. (1988). The comparison of these values with the averages of a selective molar coefficient  $(\text{Ca} + \text{Mg})/(\text{Na} + \text{K})$  for groundwater from Quaternary deposits (2), Tertiary sandstones (0.66), gneisses of Krušné hory mountain slope (0.45) and the basement gneisses (0.17) reveals that with the increasing permeability of the rock environment the values of the ratio between the mentioned cations change in favour of alkali earths.

This fact can be explained by an easier release of the alkalis in comparison with the alkali earths from aluminosilicates into the solution, by a rapid water exchange in the shallow collector which causes a rapid removal of alkalis from the shallow water-body in comparison with the deeper collectors.

At present, especially the anortite component of Ca-Na feldspars is probably being dissolved in phreatic collector, because alkali metals have been already been leached out from this solid solution prior to.

### Influences of carbon dioxide

By a balanced calculation using the activity of hydrogen-carbonates and groundwater pH of studied collectors it has been ascertained that the solution got mineralized under a balanced partial pressure of carbon dioxide ( $p\text{CO}_2$ ) between  $2.8 \cdot 10^{-4} \text{ MPa}$  and  $2.2 \cdot 10^{-3} \text{ MPa}$ . These pressures accord with the balanced partial pressure of  $\text{CO}_2$  in the soil air ( $5 \cdot 10^{-4}$  to  $1 \cdot 10^{-2} \text{ MPa}$ ) in Central European climatic conditions (GAZDA - PAČES, 1975). The studied groundwater is at the same time oversaturated with respect to  $p\text{CO}_2$  in the atmosphere ( $3 \cdot 10^{-5} \text{ MPa}$ ).

Table 2 indicates that the highest partial pressures of  $\text{CO}_2$  are in the Quaternary collector, which is being con-

nected with an intense decomposition of the organic substance in the surficial layer of weathered rocks. Higher partial pressures of  $\text{CO}_2$  in the shallow collector in comparison with deeper circulations cause a higher reaction ability of phreatic water. The interaction period of water with the rock is, however, very short and this is connected with higher negative values of nonequilibrated indexes for couples water-mafic mineral, feldspars-kaolinite, illite-kaolinite, and at the same time the expressive undersaturation of water in the shallow collector with respect to calcite.

Relatively low partial pressure of carbon dioxide in deeper collectors together with a comparatively low groundwater mineralization and high pH indicate that the circulation paths are isolated from the supplying channels of  $\text{CO}_2$  from the depth.

An example of solutions mineralized under higher partial pressures of carbon dioxide are gas-saturated mineral waters. For instance, from newly discovered sources near the studied area we can mention the brine from the well H-8, encountered in the basin gneisses of the Merkur mine dump during the hydrogeological exploration concerned with the prepared driving of a drainage tunnel (JEZERSKÝ, 1986). This brine exhibited the following parameters: total dissolved solids  $63.8 \text{ mmol.l}^{-1}$ , principal ions  $\text{Na}^+$   $22.2 \text{ mmol.l}^{-1}$ ,  $\text{HCO}_3^-$   $33.2 \text{ mmol.l}^{-1}$ , contents of free  $\text{CO}_2$  in the solution (measured in the field)  $15 \text{ mmol.l}^{-1}$ , pH in situ 6.7, Li  $0.16 \text{ mmol.l}^{-1}$ , Rb  $0.0015 \text{ mmol.l}^{-1}$ , temperature  $17^\circ\text{C}$ . A balanced calculation indicated that the studied solution got mineralized at  $p\text{CO}_2$  attaining to  $0.03 \text{ MPa}$ . A higher activity of  $\text{CO}_2$  was in the studied area ascertained also during a gas prospection. In the casing of the mentioned well and in the surrounding cut cracks 70 % contents of  $\text{CO}_2$  was determined.

### Influences of geological conditions

In the hydrology as well as in hydrogeochemistry of geologic structures, especially of a basin character, an important role is being played by spatially extensive occurrences of rock substances with minimum permeability (hydrogeological isolators). They influence pressure conditions in the basement collectors and separate deeper circulations from the phreatic collector with groundwater, whose chemical composition is modified both by natural processes (oxidation of sulfides, dissolution of soil carbon dioxide, intensive hydrolysis of mineral phases) and by not seldom anthropogenic processes (application of fertilizers and pesticides in agriculture and forestry, emissions of acid exhalations during exploitation of fossil energy sources with high sulfur contents, production of gaseous, liquid, and solid wastes in the anthropogenic sphere in general).

The function of hydrogeological isolators in the basin part of the studied area is being fulfilled by up to 150 m thick claystones, in the mountain part of the area by

argillized gneisses, and in the case of local occurrence of volcanic breccia by an argillized mafic rock.

The mentioned low-permeable rocks condition the existence of two hydrogeologically isolated and hydrochemically different zones particularly in the basin part of the studied area – a shallow collector with a fast groundwater circulation, influenced by acid industrial exhalations, and deeper situated, hydraulically interconnected collectors of Tertiary sandstones and basin gneisses with a slow groundwater circulation, without apparent manifestations of anthropogenic influences.

A separate circulation of groundwater qualitatively different from that of the Quaternary collector was observed also in an areally limited occurrence of volcanic breccia and further in most wells in the gneisses of the Krušné hory mountain slope.

## Conclusion

The hydrogeochemical investigation in the environs of Horní Jiřetín and in the region of the Jezeří forests was focused on groundwater from Quaternary deposits, volcanic breccia, Tertiary sandstones, basement gneisses and gneisses forming the mountain part of the studied area.

The investigation revealed prominent differences in chemical properties of groundwater from the Quaternary deposits (principal ions  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , acid reaction of the solution,  $\text{Li } 0.002 \text{ mmol.l}^{-1}$ ) that from gneisses and sandstones which circulates deeper (principal ions  $\text{Na}^+$ ,  $\text{HCO}_3^-$ , alkali reaction of the solution,  $\text{Li } 0.02 \text{ mmol.l}^{-1}$ ) as well as the groundwater from the areally limited body of volcanic breccia ( $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , pH 7.1,  $\text{Li } 0.004 \text{ mmol.l}^{-1}$ ).

The isotopic ratios of sulfur of dissolved sulfates indicated a different source of these ions in the groundwater from phreatic collector ( $\delta^{34}\text{S} = +3.1 \text{ ‰}$ ) and from the gneisses ( $\delta^{34}\text{S} = -0.5$  and  $-1.4 \text{ ‰}$ ) and at the same time a similarity of the shallow groundwater and the atmospheric water ( $\delta^{34}\text{S} = +4.4 \text{ ‰}$ ).

The differences in the chemical composition of groundwaters from the individual collectors (Quaternary deposits, volcanic breccia, gneisses of Krušné hory mountain slope and hydraulically interconnected Tertiary sandstones and basement gneisses) are given by 1. long-lasting action of acid atmospheric deposition, 2. groundwater circulation in chemically different rock environment (acid aluminosilicate rocks – mafic rock), different time of groundwater maintenance in the circulation environment,

and 4. specific geologic conditions of the investigated region (occurrence of hydrogeological isolators on the boundary of the phreatic and deeper-situated collector).

*K tisku doporučil T. Pačes  
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# Hydrogeochemický výzkum v oblasti Horního Jiřetína a Jezeřských lesů v severních Čechách

(Resumé anglického textu)

ZDENĚK JEZEŘSKÝ

Předloženo 31. května 1991

V letech 1982–1985 probíhal v okolí Horního Jiřetína a v oblasti Jezeřských lesů v severních Čechách hydrogeochemický průzkum jako součást regionálního hydrogeologického průzkumu v předpolí povrchového hnědouhelného dolu Česko-slovenské armády (dnes DUK Komořany).

Zkoumaná oblast o rozloze ca 30 km<sup>2</sup> zahrnuje část severočeské pánve a přilehlý krušnohorský masív. Zde byly sledovány chemické a fyzikální vlastnosti podzemní vody z kvartérních uloženin, vulkanické brekcie, terciérních pískovců, podložních rul a rul, tvořících přilehlý svah Krušných hor. Pro studium chemismu podzemní vody bylo využito četných vývěřů podzemní vody, přirozeně odvodňujících kolektor kvartérních uloženin v horské části zkoumané oblasti, a dále hydrogeologických vrtů, z nichž byla podzemní voda odebírána v závěru čerpacích zkoušek, ověřujících hydraulické vlastnosti jednotlivých kolektorů. Ojedinele byly odběry vody provedeny z přetoku v případě vrtů s kladným piezometrickým nívau hladiny podzemní vody.

Všechny vzorky podzemní vody byly v laboratoři Aquatestu podrobeny kompletním chemickým analýzám (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe, Mn, Li, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>4</sub>SiO<sub>4</sub>, pH), v některých případech bylo provedeno stanovení izotopického poměru sulfátové síry (izotopická laboratoř ČGÚ) a určení tritiové aktivity podzemní vody (laboratoř aplikované jaderné fyziky Výzkumného ústavu pro hnědé uhlí v Mostě).

Z analýz vyplynuly výrazné rozdíly mezi kvartérním kolektorem (hlavní ionty Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, pH 6,1, Li 0,002 mmol.l<sup>-1</sup>, δ<sup>34</sup>S = +3,1 ‰) a hlouběji uloženými zvodněmi v terciérních pískovcích a rulách (hlavní ionty Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, pH 7,5, Li 0,02 mmol.l<sup>-1</sup>, δ<sup>34</sup>S = -0,5 a -1,4 ‰) a plošně omezeným tělesem vulkanické brekcie (hlavní ionty Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, pH 7,1, Li 0,004 mmol.l<sup>-1</sup>).

Na tvorbě chemického složení podzemní vody se ve zkoumané oblasti uplatňují přirozené procesy v systému voda–hornina–půdní atmosféra (rozpuštění půdního oxidu uhličitého, hydrolyza živců, forsteritu a kalcitu, tvorba jílových minerálů, rozpouštění sádrovce, oxidace pyritu) a antropogenní vlivy, související s využíváním hnědého uhlí s vysokým obsahem síry v podkrušnohorských průmyslových komplexech (atmosférická depozice kyselých látek).

Vlivy kyselé atmosférické depozice jako celku se projevují především v mělkém kvartérním kolektoru v horské oblasti v nadmořské výšce okolo 900 m. Zde byly monitorovány prameny s nízkým pH (4,4) a převažujícími obsahy iontů sulfátových a nečistkami i nitrátových. Izotopické poměry síry v sulfátech přirozeně vyvěrající podzemní vody (δ<sup>34</sup>S = +1,3 až 4,3 ‰) byly podobné izotopickému poměru síry v sulfátech atmosférické vody (+4,4 ‰).

Chemismus podzemní vody z hlubších zvodní (vulkanická brekcie, terciérní pískovce, ruly) je výrazně odlišný od mělké zvodně a uvedené antropogenní okyselování zde nebylo ani z dlouhodobého monitorování chemismu (vrt JA-16) pozorováno. Izolovaný oběh podzemní vody zastižená vrtem JA-16 potvrdilo i měření tritiové aktivity vody, jež byla nižší než 3 T.U. Výjimkou mezi hlubšími kolektory jsou některé vrty v rulách, přímo přecházejících do kvartérních uloženin. Jejich podzemní voda má podobné chemické vlastnosti jako podzemní voda z mělkého kolektoru kvartérních uloženin (hlavní ionty Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, kyselá reakce roztoku) a lze předpokládat, že v místech takových vrtů dochází k přetékání vody z freatické zvodně do hlubšího kolektoru.

Specifické chemické složení hlouběji obíhající podzemní vody z vulkanické brekcie, terciérních pískovců, podložních rul a ve většině případů vzorků z rul tvořících horskou část zkoumaného území je dáno existencí terciérních jílovců nebo zjílovatělých vulkanitů a rul s nízkou propustností na rozhraní freatické a hlubší zvodně, pomalým prouděním podzemní vody v hlubších zvodních s koeficientem  $k$  (m.s<sup>-1</sup>) o jeden až tři řády nižším v porovnání s kvartérním kolektorem a cirkulací podzemní vody v chemicky odlišném horninovém prostředí (převaha iontů Ca<sup>2+</sup> nebo Na<sup>+</sup> v podzemní vodě z kyselých alumosilikátových hornin a Mg<sup>2+</sup> v podzemní vodě z mafické horniny).

## Vysvětlivky k tabulkám

1. Průměrné chemické složení zkoumané podzemní vody. Obsahy látek v mmol.l<sup>-1</sup>.
2. Odchyly podzemní vody z kolektorů zkoumané oblasti od chemických rovnováh (vliv iontových párů na chemickou rovnováhu je zanedbán). Odchyly podzemní vody z kvartérních uloženin od chemické rovnováhy s pyritem a limonitem byly počítány za předpokladu Eh = +0,4 V, v případě vrtu JA-16 je změřené Eh = 0,14 V.

## Vysvětlivky k obrázku

1. Oblast hydrogeologického výzkumu. 1 – odběrová místa přirozeně vyvěrající podzemní vody; 2 – přetokové vrty.