

Chemical diversity of groundwater in the Carboniferous–Permian aquifer in the Unisław Śląski – Sokołowsko area (the Sudetes, Poland); a geochemical modelling approach

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ABSTRACT:

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Groundwater in the Carboniferous–Permian sedimentary aquifer in the vicinity of Unisław Śląski – Sokołowsko (Intra-Sudetic Basin, the Sudetes, SW Poland) manifests spatial chemical diversity. The water chemistry varies from fresh calcium-magnesium-bicarbonate groundwater at the recharge area to calcium-sodium-sulphate mineral water downwards the basin. Geochemical mass balance modelling confirms that the main chemistry features of the sulphate mineral water are controlled by dedolomitization and calcium common-ion effects. Congruent dissolution of gypsum promotes incongruent dissolution of dolomite with calcite precipitation. Cation exchange between Ca^{2+} (and Mg^{2+}) solutes and Na^+ (and K^+) also takes place. The sulphate mineral water shows elevated concentrations of numerous trace elements. Iron, zinc and manganese originate from dissolution of carbonates (dolomite and/or siderite) and/or sulphides. The hydrogeological system studied should be considered as a series of individual flow systems. The results of preliminary geochemical modelling corroborate the role of mixing in the formation of the spatial pattern of the aqueous chemistry in the system. The main factor that controls groundwater chemistry is the mixing of two components: modern (tritium-bearing) fresh water and older (pre-bomb Holocene) sulphate mineral water.

Key words: Groundwater chemistry, Sulphate waters, Dedolomitization, Groundwater mixing, Geochemical modelling, the Sudetes, Poland.

INTRODUCTION

The Upper Palaeozoic sedimentary rocks in the Sudetes Mts. (SW Poland) usually form aquifers poor in groundwater. In the course of exploration for drinking-water in the area of Unisław Śląski –

Sokołowsko (south of Wałbrzych, the Sudetes) in the 1960s and 1980s groundwater resources were found in Carboniferous and Permian sedimentary rocks. The Carboniferous–Permian aquifer is exploited in the northern part of the area only, because water in the southern part does not comply

with drinking-water standards in terms of sulphate, iron, manganese, trace elements (e.g. As, B) and hardness levels. Abstraction of fresh groundwater in the area of the village of Unisław Śląski entails the risk of sulphate mineral water intrusion from the south. Hydrogeochemical investigations are provided to recognise the origin of groundwater quality and water-rock interactions. The paper focuses on the application of geochemical modelling to explain the origin of the sulphate mineral water and the chemical diversity in the hydrogeological system. The results of the geochemical modelling are to be regarded as preliminary only. Complementary geochemical and isotopic researches of groundwater and aquifer rocks are in progress.

METHODS

Groundwater was sampled in wells of the intake in Unisław Śląski (Text-fig. 1) and in an unused borehole (no. 5p) in Sokółowosko after a few days pumping. Groundwater was also sampled in selected perennial springs located in the area. At each site a normal sample and a double sample were taken, totalling 16 normal and 16 double groundwater samples. Field measurements include SEC, pH, Eh, T. Redox potential was measured without atmosphere contact in a through-flow chamber or by probe using platinum-Ag/AgCl electrode, and corrected with respect to the H₂ electrode according to the empirical for-

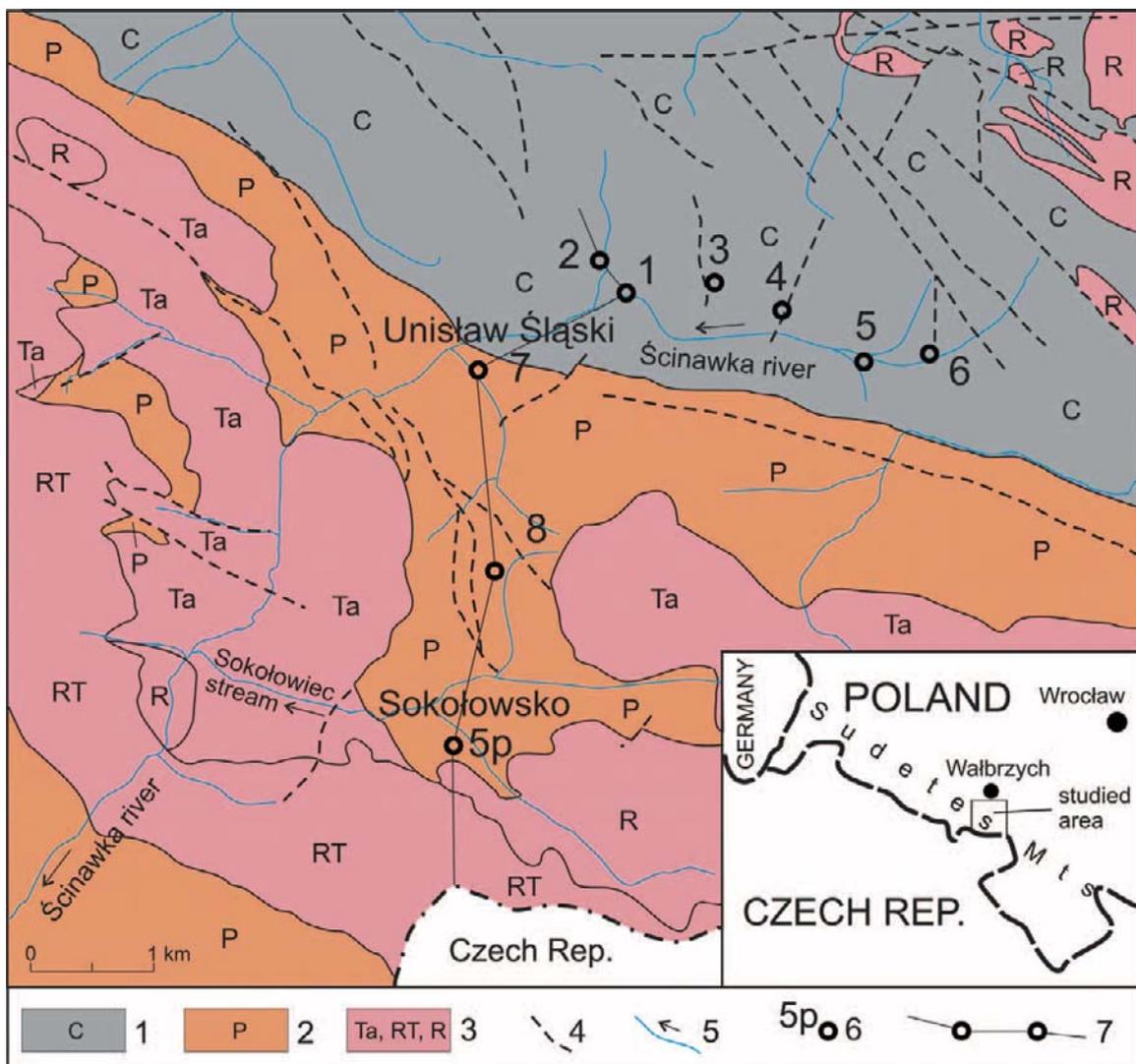


Fig. 1. Geological map of the studied area (after GROCHOLSKI 1971, BOSSOWSKI & *al.* 1994, AWDANKIEWICZ 1999). Explanations: 1 – Carboniferous sedimentary rocks; 2 – Permian sedimentary rocks; 3 – volcanic rocks: trachyandesites, rhyolitic tuffs and rhyolites, respectively; 4 – faults; 5 – waterways; 6 – wells; 7 – geological cross-section line

mulae of NORDSTROM (1977). Water samples were filtered by cellulose nitrate 0.45 μm membrane filters and stored in LDPE bottles. Anions (bicarbonates, sulphates, chlorides, fluorides, phosphates, nitrates) were determined by spectrophotometric, HPLC or volumetric methods, and the main cations and trace elements were determined by ICP-AES and/or FAAS methods. Duplicated analytical measurements of the main solutes (SO_4 , Ca, Mg, Na) were taken on all samples (normal and double samples) to estimate field and analytical errors by the variance analysis (ANOVA). Tritium and sulphur isotopes ($\delta^{34}\text{S-SO}_4$) were also analysed in groundwater. Samples for $\delta^{34}\text{S}$ determination were prepared by precipitation of BaSO_4 in the field. Tritium was analysed in the Institute of Nuclear Chemistry and Technology (Warsaw), and sulphur stable isotopes in the Institute of Geological Sciences (Polish Academy of Sciences, Warsaw). Computer code PHREEQCI v.2.11 (PARKHURST & APPELO 1999) was used for speciation/solubility, inverse mass balance geochemical modelling and for modelling of water mixing process.

SITE GEOLOGY AND HYDROGEOLOGY

The area studied is situated in the central part of the Sudetes Mts. (SW Poland). From a geological viewpoint the area is located in the Intra-Sudetic Basin, which is filled by a thick complex of Lower Carboniferous–Lower Permian terrestrial molasse with volcanogenic rocks, locally overlain by

a thin cover of terrestrial Lower Triassic sandstones and Upper Cretaceous marine deposits (DZIEDZIC & TEISSEYRE 1990). In the vicinity of Unisław Śląski and Sokołowsko the bedrocks are clastic rocks (conglomerates, sandstones, mudstones) with clays and limestones of Late Carboniferous–Early Permian ages. In the southern part of the area Permian volcanic rocks (trachyandesites, rhyolites and rhyolitic tuffs) occur (Text-fig. 1). The groundwater investigated in this study occurs in Upper Stefanian (Ludwikowice Member) and Lower Autunian (Krajanów and Zagórzyn members) sedimentary lithostratigraphic units. The sedimentary rocks were deposited in intermittent alluvial and lacustrine environments in a hot arid/semi-arid climate (BOSSOWSKI & IHNATOWICZ 1994). They include assemblages of reactive solid phases, such as carbonates (dolomite, calcite, siderite), gypsum, pyrite, organic matter (Table 1).

The exploited groundwater occurs in fissured aquifers. The water intake in Unisław Śląski consists of eight wells (nos. 1–8; Text-fig. 1). Well no. 1 has been in operation since 1909 (renewed in 1967). Well no. 2 has been exploited since 1961, and wells nos. 3–6 since 1968 (WÓJCICKA & TARKOWSKI 1968). Wells nos. 7 and 8 were drilled in 1985 (SZAFRANEK & *al.* 1986), and exploited since November 1991. The total discharge of the intake in the years 1992–2004 varied between 123.4 and 154.5 thousand m^3/month . Four wells (nos. 1, 2, 7, and 8) provide about 85% of the total discharge of the intake. Well no. 5p in Sokołowsko was drilled in 1980. The volume of abstracted groundwater initially was 110 m^3/h , at the draw-

Lithostratigraphic units	Lithology	Main features of mineral composition
Zagórzyn Member (Autunian)	Mudstones and claystones with sandstones	Rarely fragments of volcanic rocks and feldspars, argillaceous-siliceous and ferrous cement, xenomorphic calcite, dolomite, illite, kaolinite, rarely dispersed pyrite and organic matter
Krajanów Member (Autunian)	Sandstones and mudstones with claystones, limestones, calcareous mudstones, bituminous limestones and mudstones at top	Fragments of volcanics and feldspars, chloritised clay schists, gypsum cement and covers, argillaceous-siliceous cement, ferrous pigment, siderite, bituminous mass, illite, calcite veins, dispersed pyrite and organic matter
Ludwikowice Member (Stefanian)	Polymictic conglomerates and sandstones, rarely mudstones and shales	Numerous fragments of volcanic rocks (rhyolites, trachytes) and feldspars, chloritised biotite, carbonates (mainly calcite), gypsum, sericitised and kaolinitised feldspars, argillaceous-siliceous cement with neogenic calcite, gypsum, and limonite

Table 1. Mineralogical characteristics of sedimentary rocks in the Unisław Śląski – Sokołowsko area (after BOSSOWSKI 1996, 1997)

Well	Altitude, m a.s.l.	Well depth, m	Screened intervals (below the surface level, m)
2	582.1	96.5	32.5 - 86.7
1	582.5	88.8	43.5 - 47.5
			60.7 - 67.7
			75.7 - 77.7
			81.0 - 86.0
7	569.8	100.0	60.0 - 85.0
8	620.0	220.0	71.9 - 102.5 160.5 - 197.7
5p	570.0	350.0	49.4 - 60.6 (fresh water)
			72.3 - 92.2 (fresh water)
			176.15 - 266.6 (sulphate mineral water)
			305.6 - 314.3 (sulphate mineral water)

Table 2. General characteristics of wells

down of 25 metres (DĄBROWSKI & SZAFRANEK 1982). The well has never been exploited due to poor water quality. At present its specific discharge is less than 40% of the initial value (DOBRZYŃSKI & MITRĘGA 2002). In the well four water-bearing horizons are screened (Table 2). The hydrodynamic conditions in the well are typical of a discharge

area – there is a higher hydraulic head in deeper horizons. The two upper horizons yield fresh waters, whereas the two deeper ones yield sulphate mineral waters. Field parameters were determined in the well and water samples were taken at particular depths during the research pumping.

The Ścinawka River is the main base level of groundwater drainage in the upper part of the catchment in the vicinity of Unisław Śląski (Text-fig. 1) whereas in the Sokołowsko valley the Sokołowiec stream, a tributary of the Ścinawka River, is the local drainage base level. Water abstraction in wells nos. 7 and 8 changed the flow pattern, and activated flow of sulphate mineral water northwards. This is indicated by trends of groundwater chemistry noted in wells 7 and 1 (WIŚNIEWSKA 2003).

GROUNDWATER CHEMISTRY

Groundwater in Carboniferous–Permian rocks shows variable geochemistry. Waters from wells (nos. 1, 3–6) located in the upper part of the Ścinawka River catchment (Text-fig. 1), along the outcrops of Carboniferous siliciclastic rocks, present similar compositions. They have low mineralization. Total dissolved solids in these waters usu-

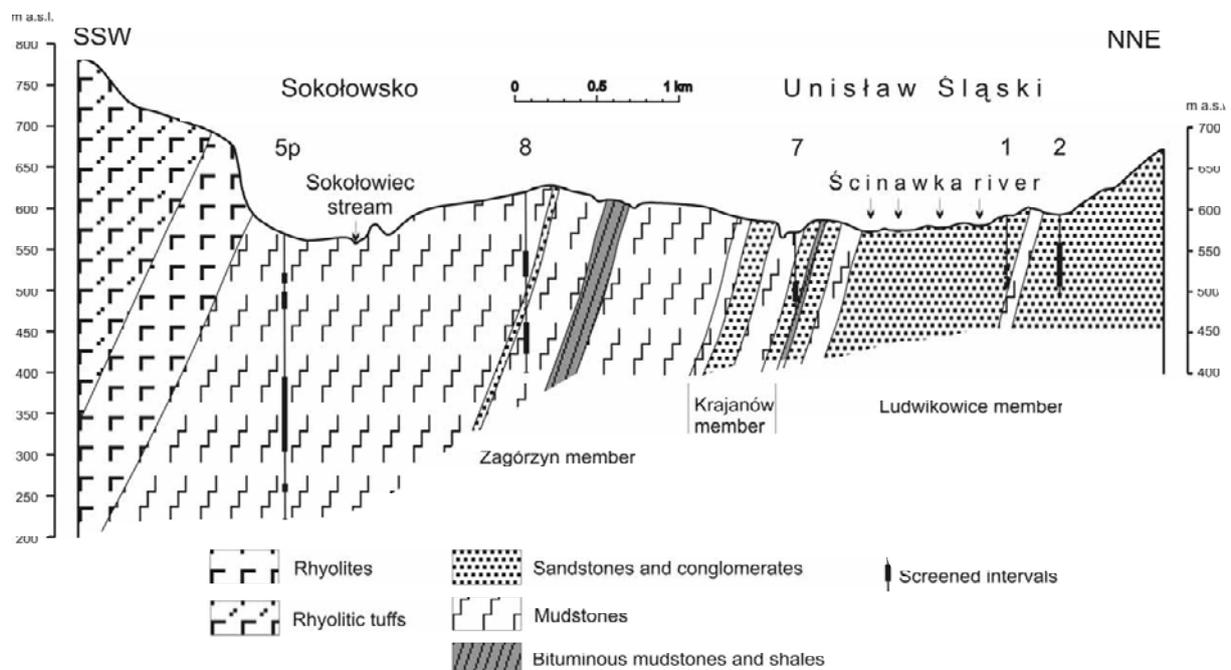


Fig. 2. Schematic geological cross-section

ally do not exceed 400 mg/L. The calcium-magnesium-bicarbonate and calcium-magnesium-bicarbonate-sulphate hydrochemical types prevail in these waters.

Groundwater abstracted from wells situated along the dip of beds (Text-fig. 2) – i.e. from well no. 2, by wells nos. 1, 7, 8, to well no. 5p – manifests different hydrochemical features. The chemical composition of the water varies from fresh water in the unconfined part of the aquifer at the recharge area (in well no. 2) to mineral water southward, in the deepest well 5p in Sokołowsko (Table 3). Over the short distance of about 4 km distinct changes in water quality are noted. The concentrations of most solutes, i.e. sulphates, calcium, magnesium, sodium, iron, manganese, strontium, boron, arsenic, ammonium, zinc, lithium, molybdenum increase southwards. Therefore, the hydrochemical type changes gradually from the Ca-HCO₃ type in well no. 2 to the Ca-Na-SO₄ type in the well no. 5p (Table 3). Only the content of chloride, fluoride, nitrate, and barium decreases.

A similar pattern of trace element concentrations is also known from other sedimentary aquifers. For instance, a net strontium and arsenic increase, and barium decrease was found in the Triassic sandstone aquifer in England (EDMUNDS & *al.* 1982). However, in this aquifer smaller differences of concentration of the above mentioned solutes are noted on a longer – about 30 km – flow path distance.

The diversity of chloride and fluoride concentration in the aquifer studied is probably due to variation in the composition of the recharge water. The estimated water residence time in the area of groundwater flow to the wells (nos. 2 and 1) that are located closest to the recharge area is probably between 6 and 13 years (see further text). In the part of the Sudetes Mts studied, the average concentration of chloride and fluoride in wet atmospheric deposition in the first half of the 1990s was 5.1 and 0.05 mg/L respectively (DOBRYŃSKI 1997). Evapotranspiration of rainfall at a factor of about 2 (DOBRYŃSKI 1997) leads to Cl and F concentrations which are broadly consistent with the composition of groundwater from well no. 2. This suggests that the role of local chloride and fluoride contamination sources might be negligible.

The average sulphate concentration in wet atmospheric deposition was 14.7 mg/L (DOBRYŃSKI 1997). Sulphate concentration in groundwater

from well no. 2 (38.8 mg/L SO₄; Table 3) is higher than the value inferred after evapotranspiration (at a factor of 2) and indicates that part of the sulphates can originate from soil, probably due to the process of biomass decomposition.

Chemical analyses given in Table 3 were made of waters sampled during the period of low groundwater flows in the Ścinawka valley to minimise the effect of intensive infiltration on the groundwater chemistry. This refers especially to wells nos. 2 and 1, situated near the recharge area and the Ścinawka River.

The general features of the aquifer chemistry have been characterised using compiled archival data and data acquired in this study. The groundwater chemistry is dominated by the dissolution of gypsum (Text-fig. 3). A constant Ca/SO₄ molar ratio of about 1 (especially in water from wells nos. 1 and 7) indicates that dissolution of gypsum controls the concentration of calcium and sulphate. Deviation from the regular dissolution pattern is noted both at the lowest and at the highest Ca and SO₄ concentrations. Bicarbonate and calcium concentrations increase initially, probably due to dissolution of carbonate minerals. However, in the deeper part of the aquifer some process removes dissolved inorganic carbon (Text-fig. 4). Bicarbonate concentration varies most in the water from wells nos. 2 and 1 which are located by the recharge area and by the Ścinawka River. This variation is due to seasonal changes of alkalinity caused by the hydrologic regime. The effects of snow melt and heavy rains on the quantity and quality of water abstracted from wells located by the Ścinawka River have been observed (WIŚNIEWSKA 2003). Magnesium concentration also shows a regular pattern, and increases as the calcium content increases (Text-fig. 5). Two sub-populations of waters might be distinguished: waters from wells nos. 1 and 2; and waters from wells nos. 7, 8, and 5p.

An interesting geochemical feature is the elevated concentration of strontium, arsenic, boron, and zinc in the sulphate groundwater (Table 3). Unfortunately, at present there is a lack of detailed geochemical data on trace elements in the sedimentary rocks of the aquifer. Strontium in the groundwater certainly originates from dissolution of gypsum. Zinc probably originates from the dissolution of carbonate (dolomite, siderite) and/or pyrite. Arsenic might occur in organic mat-

ter and in iron sulphide (pyrite). Both solids were deposited in a deep lacustrine reducing environment (BOSSOWSKI 1996, 1997). Arsenic might also

be adsorbed onto iron (oxy)hydroxide phases. Boron probably occurs as an adsorbed phase onto clay minerals.

Parameter	Well no. 2	Well no. 1	Well no. 7	Well no. 8	Well no. 5p ¹
T	11.2	9.3	10.1	15.46	15.3
pH	7.73	7.80	7.47	7.74	7.60
pe	6.373	6.151	5.969	5.556	1.278
SEC ₂₅ ² [μS/cm]	249	460	598	1230	2070
SiO ₂	17.0	18.0	17.3	30.4	19.8
SO ₄	38.8	126	205	625	1113
HCO ₃	84	111	123	95	116
Cl	7.12	9.5	2.4	<0.5	<0.5
F	0.11	0.10	0.10	0.01	0.01
NO ₃	8.11	8.9	4.46	1.94	0.00
Ca	33.5	56.5	98.4	197.7	322.9
Mg	5.8	16.6	9.4	25.9	20.2
Na	6.0	12.6	16.1	54.9	129.5
K	1.1	1.5	1.9	0.3	1.5
Al	<0.01	<0.01	0.02	<0.01	0.001
As	<0.01	<0.01	0.01	0.11	0.14
B ³	0.02	0.05	0.17	0.45	1.41
Ba	0.127	0.044	0.038	0.017	0.011
Fe	<0.01	<0.01	<0.01	0.06	0.66
Li ³	0.005	0.011	0.031	0.035	0.121
Mn	0.001	0.001	0.011	0.086	0.126
Mo ³	0.001	0.001	0.005	0.016	0.022
NH ₄	<0.05	<0.05	<0.05	<0.05	0.13
Sr	0.086	0.291	1.045	8.942	7.836
Zn	0.016	0.018	0.054	0.017	1.052
³ H [TU] ⁴	-	-	16.2(±0.5)	4.0(±0.5)	3.2/5.9 (±0.5) ⁵
³ H [TU] ⁶	10.18(±0.37)	8.23 (±0.33)	6.5 (±0.73)	2.86 (±0.26)	2.44 (±0.29)
δ ³⁴ S-SO ₄	8.03 (±0.2‰)	12.31 (±0.2‰)	11.72 (±0.2‰)	12.24 (±0.2‰)	13.87 (±0.2‰)
Hydrochemical type ⁷	Ca-HCO ₃ -SO ₄	Ca-Mg-SO ₄ -HCO ₃	Ca-SO ₄ -HCO ₃	Ca-SO ₄	Ca-Na-SO ₄

1 – composition of water from the sulphate horizons in well 5p; 2 – specific electric conductivity compensated for 25°C; 3 – element not included in geochemical models; 4 – samples from August 2000; 5 – tritium content before and after pumping test, respectively; 6 – samples from September 2004; 7 – according to ion concentration exceeded 20% meq/L.

Table 3. Chemical composition of groundwater. Concentrations in mg/L

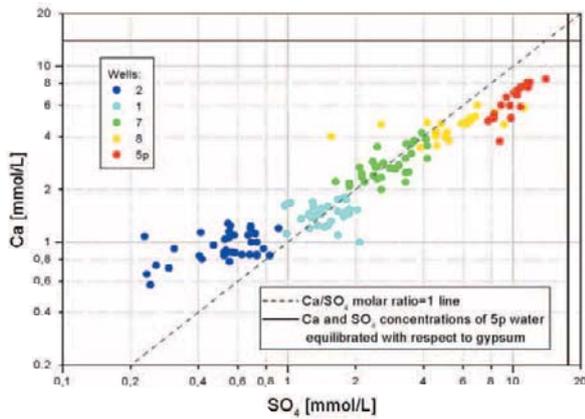


Fig. 3. Calcium vs. sulphate concentration in groundwater

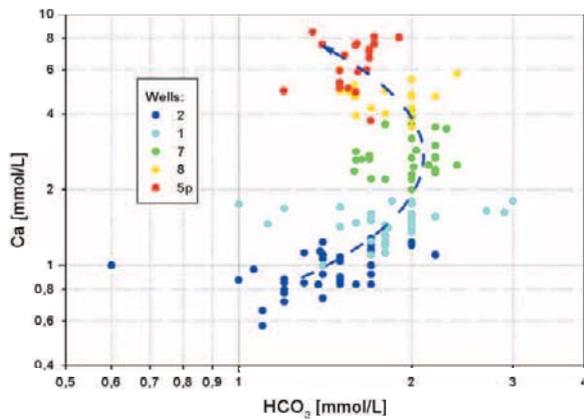


Fig. 4. Calcium vs. bicarbonate concentration in groundwater

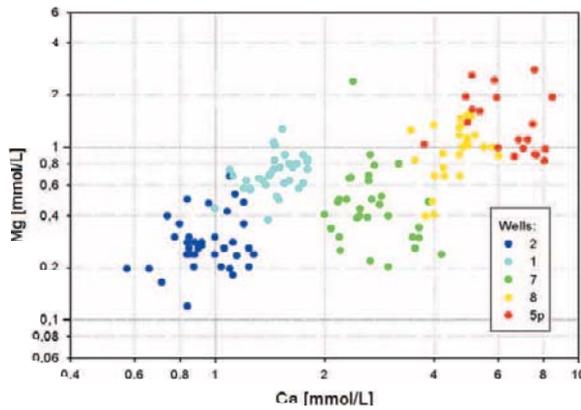


Fig. 5. Magnesium vs. calcium concentration in groundwater

The significant change of groundwater quality between wells nos. 7 and 8 (Table 3) is caused by both hydraulic and lithological factors. Bituminous mudstones and shales (Text-fig. 2) that occur between wells nos. 7 and 8 form a hydraulic barrier. Pumping tests confirmed an impediment to hydraulic connections. Interaction between wells

	% of total variance (S_{total}^2)		
	S_{geoch}^2	S_{samp}^2	S_{anal}^2
Sulphate	99.942	0.043	0.015
Calcium	99.971	0.011	0.018
Magnesium	99.804	0.167	0.029
Sodium	99.956	0.016	0.028

Table 4. Percentage share of geochemical (S_{geoch}^2), sampling (S_{samp}^2) and analytical (S_{anal}^2) variance in total variance (S_{total}^2) for main solutes in studied groundwaters

nos. 7 and 8 has not been noted during pumping tests (SZAFRANEK & al. 1986). Well no. 8 is situated on the pass, about 40–50 metres higher than other wells (Table 2). In this well, despite 15 years of water abstraction, artesian flow is re-established in one day after disconnection of the pump (J. JANISZEWSKI – personal communication).

Duplicated determination of main solutes (SO_4 , Ca, Mg, Na) in all normal and double samples was provided to separate three variance components using classical analysis of variance (ANOVA), according to the scheme: $S_{total}^2 = S_{geoch}^2 + S_{samp}^2 + S_{anal}^2$. The components of total variance (S_{total}^2) are geochemical variance (S_{geoch}^2), sampling variance (S_{samp}^2), and analytical variance (S_{anal}^2). It allows estimation of the precision of the hydrochemical results and the scale of random errors related to sampling (field) procedure and chemical analysis. The results indicate that the main solutes in the water samples were determined with a very high degree of precision. Sampling and analytical errors together constituted less than 0.2% of the total variance (Table 4), at the 95% significance level. The hydrochemical data used in the geochemical modelling therefore reflect the natural geochemical distribution of the main solutes in the groundwater.

CONCEPTUAL GEOCHEMICAL MODEL

The chemical composition of water from wells nos. 2, 1, 7, 8 and 5p (Table 3) was used in the geochemical modelling. Speciation-solubility calculation affords data on saturation state with respect to mineral phases (Table 5). Calculated saturation indexes were used in construction of the conceptual geochemical model.

The saturation state of water with respect to sulphate minerals (gypsum, celestite, and barite) approaches equilibrium as the sulphate concentration increases (Text-fig. 6). In the conceptual model, it is assumed that celestite dissolution releases Sr into the water, whereas barite precipitation is responsible for Ba depletion. Calcite and dolomite also tend towards equilibrium as the sulphate concentration increases downwards the basin (Text-fig. 7).

The sampled wells are situated along the dip of the beds, but it should be mentioned that the wells are not all located on the same flow path. The Ścinawka River and the Sokółowiec stream were the natural base levels of water drainage before the beginning of groundwater abstraction from new wells (nos. 2–6) in the 1960s (WÓJCICKA & TARKOWSKI 1968). Water abstraction brought about an increase in the size of the depression cone in the area of Uniśław Śląski (DĄBROWSKI & SZAFRANEK 1982). The depression cone probably

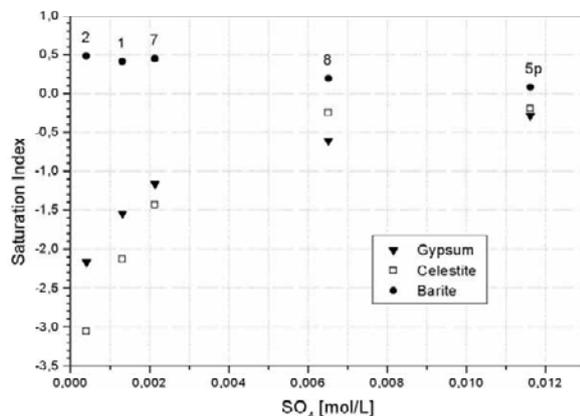


Fig. 6. Saturation index of sulphate minerals vs. sulphate concentration in groundwater

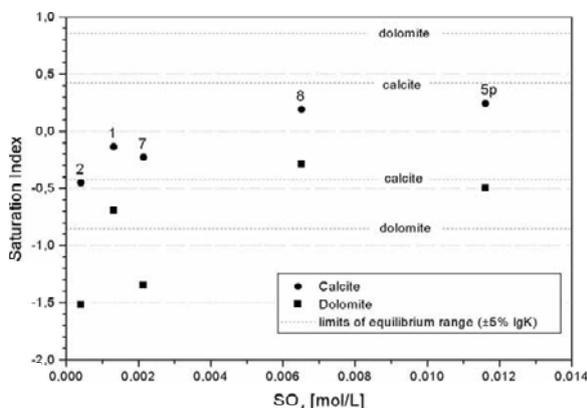


Fig. 7. Saturation index of calcite and dolomite vs. sulphate concentration in groundwater

extended after the start of water exploitation from wells nos. 7 and 8 in 1991. However, there is no groundwater monitoring network in the area.

Two approaches of geochemical modelling were applied: (1) inverse mass balance modelling, and (2) modelling of hypothetical water mixing. In the conceptual inverse mass balance model, waters from the distal wells (nos. 2 and 5p) are considered as “end-member” waters that represent the scale of present-day geochemical diversity in the studied part of the aquifer.

Solid, gas and exchange phases are included in the inverse geochemical modelling. Several scenarios of geochemical model were testified during modelling calculation. Discussion of some factors affecting geochemical modelling is in DOBRZYŃSKI (2005). At present-day hydrochemical data, the conceptual model presented here is chosen.

The assemblage of solid phases (gypsum, celestite, dolomite, siderite, rhodochrosite, smithsonite, pyrite, arsenopyrite, barite, calcite, chlorite, kaolinite, $\text{Fe}(\text{OH})_{3(a)}$), organic matter (represented as CH_2O), gas (CO_2 , O_2 , N_2) and cation exchange phases is included in the inverse model.

Based on the bedrock mineralogy (MASTALERZ & NEHYBA 1997; BOSSOWSKI 1996, 1997) and saturation indexes (Table 5), it is assumed that the main features of the groundwater chemistry are governed by congruent dissolution of gypsum, and incongruent dissolution of dolomite, coupled with calcite precipitation. Barite is probably the sink phase for barium. The lack of geochemical data on the strontium content in gypsum in the bedrock necessitates that strontium sulphate (celestite) is treated as a separate pure phase. Dolomite and siderite dissolution and calcite precipitation are allowed in the modelling. Dissolution of rhodochrosite and smithsonite is a source of Mn and Zn, respectively. Pyrite occurs locally in the aquifer rocks and also may be considered as a hypothetical source phase of iron, additional to siderite. Amongst silicate phases, only chlorite and kaolinite are included in the model. Chlorites are common minerals, and kaolinisation of silicates is often observed in the bedrock (MASTALERZ & NEHYBA 1997, BOSSOWSKI 1996, 1997). Dispersed organic matter commonly occurs at low amounts in the bedrock and is incorporated into the model as CH_2O . Decomposition and oxidation of organic matter might play the role of electron donor in redox reactions with electron

acceptors, such as N(5), Fe(3), Mn(4), As(3) forms. Arsenic that is probably released during organic matter or pyrite dissolution is included into the model as arsenopyrite. Sodium concentration in the groundwater increases distinctly downgradient in the aquifer. Conglomerates and sandstones contain alkali feldspars and fragments of volcanic rocks (rhyolites, trachites). However, alkali feldspar dissolution is not sufficient explanation for such a high sodium increase because of

its low reactivity and high water pH (Table 3). Ion exchange between sodium (adsorbed onto clay minerals) and calcium is assumed as a potential sodium source. A small increase in potassium in the groundwater might also be explained by the ion exchange process. Halite and fluorite respectively are incorporated as hypothetical sink phases in explanation of the decrease in chloride and fluoride. The PHREEQC code can balance small differences in Cl and F concentrations, but precipita-

	Well no.					Equilibrium range $\pm 5\% \lg K_{25}$
	2	1	7	8	5p	
K-feldspar	-1.026	-0.677	0.591	-1.249	-1.119	± 0.029
Albite	-2.804	-2.293	-1.010	-1.442	-1.639	± 0.900
Anorthite	-5.115	-4.859	-2.138	-4.250	-4.512	± 0.986
K-mica	4.630	5.017	9.435	3.898	4.295	± 0.635
Kaolinite	2.173	2.324	5.416	2.032	1.937	± 0.372
Chlorite	-7.917	-5.655	-7.035	-4.234	-6.911	± 0.689
Gypsum	-2.169	-1.549	-1.168	-0.611	-0.288	± 0.229
Celestite	-3.059	-2.132	-1.438	-0.252	-0.198	± 0.332
Barite	0.479	0.409	0.446	0.190	0.078	± 0.499
Calcite	-0.452	-0.138	-0.229	0.189	0.243	± 0.424
Dolomite	-1.522	-0.695	-1.349	-0.286	-0.501	± 0.855
Rhodochrosite	-2.828	-2.449	-1.704	-0.682	-0.658	± 0.555
Smithsonite	-2.733	-2.646	-2.415	-2.779	-1.128	± 0.495
Witherite	-3.228	-3.618	-4.047	-4.398	-4.780	± 0.428
Strontianite	-2.511	-1.879	-1.661	-0.647	-0.861	± 0.464
Siderite	-4.781	-4.142	-3.439	-3.193	-0.199	± 0.545
Pyrite	-139.465	-135.398	-126.505	-126.165	-60.521	± 0.938
Fe(OH) _{3(a)}	1.382	1.815	1.660	2.190	0.558	± 0.245
Goethite	6.758	7.116	6.993	7.730	6.092	± 0.032
Fluorite	-2.973	-2.897	-2.709	-4.659	-4.551	± 0.536
Halite	-8.887	-8.456	-8.961	-9.558	-9.213	± 0.078
Chalcedony	0.169	0.219	0.193	0.370	0.188	± 0.178
SiO _{2(a)}	-0.719	-0.677	-0.700	-0.503	-0.686	± 0.136
Gibbsite	0.061	0.085	1.657	-0.205	-0.071	± 0.406
Al(OH) _{3(a)}	-2.761	-2.756	-1.176	-2.985	-2.853	± 0.540

Explanations: bolded-italic values indicate over-saturation ($SI > +5\% \lg K$); shadowed cells refer to SI values in the assumed equilibrium range ($\pm 5\% \lg K$).

Table 5. Saturation index of groundwater with respect to selected mineral phases

tion of halite and fluorite is not thermodynamically possible (Table 5).

The conceptual model does not include boron, lithium and molybdenum. Boron probably occurs as an adsorbed form onto clay minerals. Lithium might be released from evaporite minerals, whereas molybdenum from a metal ore, such as pyrite, formed in reducing lacustrine bottom mud.

Dolomite dissolution is taken into account as a magnesium source. Calcite present in the aquifer bedrock can also contain some magnesium, but there are no data on Mg content in calcite. Using Mg-bearing calcite—instead of dolomite—as a source of magnesium, results in a higher mole transfer of dissolved Mg-bearing calcite and of precipitated neoformed calcite (DOBRZYŃSKI

Phase	Model						
	1	2	3	4	5	6	7
CO ₂ (g)	X	X	X	X	4.135E-04	4.384E-04	4.981E-04
O ₂ (g)	1.099E-03	4.384E-04	4.135E-04	X	X	X	X
N ₂ (g)	-6.174E-05						
CH ₂ O	X	5.664E-04	5.763E-04	X	1.628E-04	1.280E-04	X
Gypsum	1.009E-02	1.075E-02	1.077E-02	1.077E-02	1.077E-02	1.075E-02	1.068E-02
Celestite	8.861E-05						
Dolomite	5.162E-04	7.168E-04		5.669E-04	7.168E-04		
Siderite	X	X	9.944E-06	6.612E-04	9.944E-06	X	X
Pyrite	3.372E-04	9.944E-06	X	X	X	9.944E-06	4.408E-05
Rhodochrosite	2.279E-06						
Smithsonite	1.588E-05						
Arsenopyrite	1.805E-06						
Calcite	X	-7.733E-04	-7.932E-04	-7.183E-04	-7.932E-04	-7.733E-04	-7.050E-04
Barite	-8.443E-07						
Kaolinite	-6.397E-05	-4.701E-05	-4.701E-05	-6.199E-05	-4.700E-05		
Chlorite	6.404E-05	4.708E-05		6.206E-05	4.708E-05		
Fe(OH) _{3(a)}	-3.272E-04	X	X	-6.512E-04	X	X	-3.413E-05
„Halite”	-1.951E-04						
„Fluorite”	-1.576E-06						
NaX	5.746E-03	5.715E-03					
KX	1.030E-05						
CaX ₂	-2.878E-03	-2.863E-03					
Sum of transfers	1.444E-02	1.442E-02	1.440E-02	1.334E-02	1.399E-02	1.398E-02	1.391E-02
Redox mole transfers:							
As(3)	9.023E-07						
Fe(3)	-3.272E-04	6.403E-08	6.403E-08	-6.511E-04	6.403E-08	6.403E-08	-3.407E-05
N(-3)	-7.152E-06						
N(0)	-1.235E-04						
O(0)	2.195E-03	8.731E-04	8.234E-04	-3.610E-06			
S(-2)	6.762E-04	2.169E-05	1.805E-06	1.805E-06	1.805E-06	2.169E-05	8.996E-05

Table 6. Mole transfers in found geochemical models with minimum number of phases

2005). The lower the magnesium content in incongruently dissolving Mg-calcite the higher the mole transfers. Magnesium can also take part in the cation exchange and affects the transfer of carbonate minerals. Adsorption of Mg^{2+} leads to an increase in the amount of dissolving dolomite (or Mg-calcite) and precipitated calcite (DOBRZYŃSKI 2005).

Modelling of water mixing was also performed. The water chemistry gradually evolves between recharge area fresh water (well no. 2) and sulphate mineral water (well no. 5p). Waters from these two distal wells are taken as the end-member waters. They illustrate the scale of the present groundwater chemical diversity in the aquifer. Modelling of hypothetical mixing between these two components was carried out at variable fractions, at every 10%. The mixing modelling results were compared with the actual groundwater chemistry. The aim was to test whether the water chemistry in “intermediate” wells (nos. 1, 7, 8) was similar to the result of hypothetical mixing.

MASS BALANCE AND MIXING MODELLING RESULTS

Calculation by the PHREEQC code yields several mass balance models containing a minimal number of phases (Table 6). The modelling calculation was performed at the low uncertainty – of 2.5% and 3.0% for water from well no. 2 and well no. 5p, respectively. The models differ mainly in the mole transfer of: (1) gases (CO_2 , O_2) dissolution, (2) organic matter oxidation, (3) calcite precipitation, (4) the iron source phase (siderite or pyrite), and (5) the presence of an iron sink phase ($Fe(OH)_{3(a)}$). Gypsum and dolomite dissolution transfers differ slightly.

Models nos. 4 and 7 have been selected as those that probably best describe the real system. The models differ from each other in terms of the iron source phase. Model no. 4 includes siderite, and model no. 7 includes pyrite. In the real geochemical system dissolution of both minerals may take place. Released iron is immobilised in iron hydroxides and/or oxyhydroxides such as $Fe(OH)_{3(a)}$ and goethite. Model no. 1 also includes $Fe(OH)_{3(a)}$ as an iron sink phase but was excluded because of unrealistic high oxygen gas transfer and ferrous iron oxidation. Both of the models selected (nos. 4 and 7)

include decrease of Fe(3) and O(0) in redox transfer and simultaneously have the lowest sum of mole transfers.

Modelling of hypothetical water mixing was performed by mixing fresh water (well no. 2) with sulphate water (well no. 5p) at different fractions. Some results are shown in Text-figs 8 and 9. The results are broadly consistent with the groundwater chemistry in terms of gypsum solubility products (Text-fig. 8). There is an evident calcium surplus at low sulphate activity and, inversely, a sulphate surplus at a high calcium content in the groundwater.

DISCUSSION

According to the modelling results, the composition of the sulphate groundwater can be explained by congruent dissolution of gypsum and incongruent dissolution of dolomite with calcite precipitation (classic dedolomitization model). The role of gypsum dissolution is proved using stable sulphur isotopes. The $\delta^{34}S-SO_4$ (VCDT) in the groundwater increases from +8.03 ‰ in water from well no. 2 to +13.87 ‰ in water from well no. 5p (Table 3). The value of $\delta^{34}S-SO_4$ in water from well no. 2 corresponds fairly well to typical values for atmospheric sulphates in the northern hemisphere (CLARK & FRITZ 1997). At present, precise interpretation of “heavier” sulphur in sulphate mineral waters is impossible due to the lack of data on the isotopic composition of Carboniferous/Permian terrestrial gypsum in the Intra-Sudetic Basin. There are no

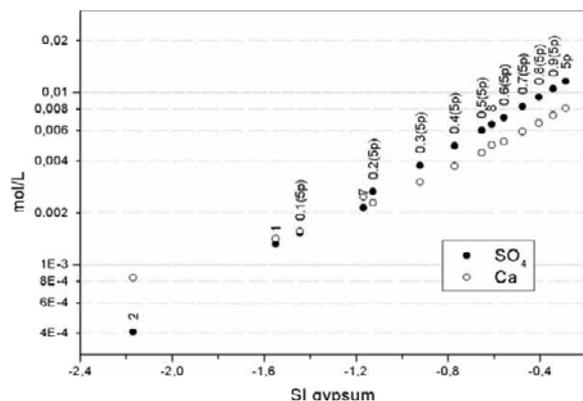


Fig. 8. Sulphate and calcium concentrations in groundwater vs. saturation index (SI) of gypsum compared with results of water mixing modelling. Explanation: 0.1(5p) ÷ 0.9(5p) – fraction of sulphate water component in mixing water

core samples from the water wells investigated, and gypsum is absent at outcrop due to leaching.

Gypsum dissolution favours dolomite dissolution and the formation of MgSO_4^0 complex solute. It promotes further dissolution of both minerals and an increase in the concentration of sulphate and magnesium. Calcite precipitation is enhanced by the common-ion effect with gypsum and dolomite dissolution. Dissolution of both minerals is the source of divalent cations (Ca^{2+} , Mg^{2+}) for the exchange reactions with monovalent cations (Na^+ , K^+), which also favours dissolution of gypsum and dolomite. The process continues until saturation with respect to gypsum is reached.

Dedolomitization driven by gypsum dissolution is well recognized, especially in carbonate systems containing evaporate sulphates (gypsum, anhydrite) (HANSHAW & BACK 1979). This process is documented at a regional scale for numerous aquifers, e.g. Madison aquifer (PLUMMER & *al.* 1990, BUSBY & *al.* 1991), Floridan aquifers (WICKS & HERMAN 1994, SACKS & TIHANSKY 1996), Yucatan, Mexico (PLUMMER & BACK 1980), Beuda and Perafita Formations, Spain (BISCHOFF & *al.* 1994).

Calcium concentration in the sulphate groundwater seems to be controlled by calcite precipitation and Ca^{2+} exchange. Calcite precipitation prevents an increase in inorganic carbon. Bicarbonate concentration remains at a semi-constant level in the groundwater studied, and is controlled by the dedolomitization process. The modelling results suggest that the role of organic matter oxidation is probably negligible. In fact, the aquifer might be regarded as a closed system with respect to CO_2 .

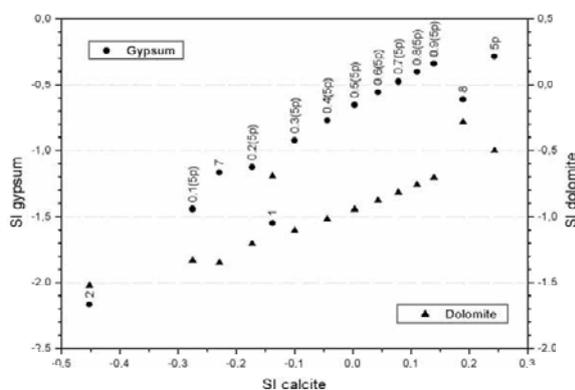


Fig. 9. Saturation index (SI) of gypsum and dolomite vs. SI calcite in groundwater compared with results of water mixing modelling. Explanations as in Text-fig. 8.

In fresh groundwater from the recharge area (well no. 2) sulphate concentration is lower than that controlled by gypsum solubility (Text-fig. 3). At outcrops of sedimentary rocks in the recharge area gypsum is absent and has probably been leached out. Sulphates in fresh recharge groundwater originate from atmospheric deposition and biomass degradation in soil. Calcium in recharge waters comes from the dissolution of carbonate minerals. In the deepest part of the aquifer (wells nos. 8, 5p) calcium concentration decreases slightly below the Ca/SO_4 molar ratio=1 line (Text-fig. 3). Cation exchange between Ca^{2+} and Na^+ can be responsible for this effect. The decrease in magnesium concentration between wells nos. 8 and 5p might also be caused by ion exchange with sodium. The increase in strontium concentration may be explained by the dissolution of hypothetical celestite.

Strontium certainly originates from the dissolution of Sr-bearing gypsum. The mole transfer ratio of celestite to gypsum in the models is 0.0082, which suggests that the hypothetical Sr-bearing gypsum should contain about 0.8% of Sr. This concentration is higher than that of typical primary marine gypsum (ICHIKUNI & MUSHI 1978, HANOR 2000), but can be acceptable for terrestrial gypsum. Weathering of Carboniferous alkali-rich volcanic rocks (trachytes, rhyolites) during the deposition period was probably the main source of strontium. Strontium can also be released into the water from carbonates (dolomite, calcite), but they usually have a lower Sr content than gypsum. Barite precipitation brings about a decrease in barium concentration in groundwater. Equilibrium with respect to barite is the factor commonly controlling barium concentration in natural waters. In the groundwaters studied sulphate concentration seems to be the master variable that controls barium concentration.

Both siderite and pyrite dissolution might be the source of iron. Nowadays, the scale of pyrite dissolution is difficult to determine due to the lack of isotope data for pyrite. At present, the real role of pyrite dissolution is difficult to quantify. The sulphide species and pyrite saturation index were calculated after field redox measurements and speciation modelling. Because all of the redox speciation is out of equilibrium this way provides only a rough estimation of the pyrite saturation state. The hydrogen sulphide content has not been measured in the groundwater.

The hypothetical dissolution of sulphide minerals in the aquifer favours a decrease in gypsum, siderite and calcite transfers (Table 6). The pyrite oxidation does not bring about water acidification because the groundwater is effectively neutralized by carbonate dissolution.

Iron is probably immobilised in precipitated (oxy)hydroxides. The redox potential decreases towards the sulphate waters, from 357 mV (well no. 2) to 73 mV (well no. 5p). The redox potential in the sulphate groundwater probably remains too high to reduce sulphates to sulphides. The hydrogen sulphide content in the groundwater will be measured during the next fieldwork to verify this presumption.

At present, there are no geochemical data on trace element contents in the aquifer carbonates, but some estimation can be made using the results of geochemical modelling. From the results of model no. 4 (Table 6), the presumable content of zinc and manganese in dolomite and siderite can be evaluated. The stipulated manganese source (rhodochrosite, MnCO_3) and zinc source (smithsonite, ZnCO_3) dissolution mole transfers are $2.279 \cdot 10^{-6}$ and $1.588 \cdot 10^{-5}$, respectively (Table 6). These transfer values were compared with dissolution transfer values for dolomite ($5.669 \cdot 10^{-4}$) and siderite ($6.612 \cdot 10^{-4}$), and it was assumed that both elements (Mn and Zn) are released from only one of those minerals. In order to explain the differences in the concentrations of these elements between the fresh and mineral waters, it can be estimated that the dissolving dolomite and siderite should contain 0.20% Mn and 1.38% Zn, and 0.34% Mn and 2.34% Zn, respectively. The estimated Mn and Zn contents in the carbonates are higher than the average values (0.11% Mn, 0.002% Zn) for marine carbonates, but non-marine carbonates are usually enriched in Zn and Mn (VEIZER 1983) due to the different compositions of surface and shallow groundwater. The estimated content of Mn is only 2–3 times higher than in marine carbonates and seems to be acceptable for terrestrial carbonates. The calculated high content of zinc is too high for carbonates and indicates that in the actual geochemical system zinc might also originate from the dissolution of sulphides.

In the groundwater studied tritium determinations were made. Groundwater tritium-“ages” were estimated using the FLOWPC code

(MAŁOSZEWSKI & ZUBER 1996). The dispersion model with dispersion parameter $D/vx = 0.20$ and input concentration $C_0 = 15.5$ TU initially was assumed. Accordingly to the measurement in the year 2004 (Table 3), tritium varied from 10.18 (± 0.37) TU (well no. 2) to 2.44 (± 0.29) TU (well no. 5p). The mean “tritium” residence times of the groundwater obtained is as follows: wells no. 2 – 8 (± 2) years; well no. 1 – 11 (± 2) y.; well no. 7 – 17 (± 5) y.; well no. 8 – 47 (± 4) y.; well no. 5p – 54 (± 5) y. The groundwater in wells located near the recharge area (wells nos. 2 and 1) originates from modern infiltration from about 10–12 years ago. Assuming different input concentration ($C_0 = 18.0$ and $C_0 = 20.5$), similar residence times of water in well no. 2 are obtained, 10 (± 1) years and 12 (± 3) years, respectively.

Dating of sulphate mineral water will be possible after radiocarbon determination. However, even sulphate groundwater in the deepest well (no. 5p) is also affected by modern recharge. During research pumping in this well the tritium content in water from the sulphate horizon increased from 3.2 TU (before the pumping test) to 5.9 TU (after pumping) (DOBRYŃSKI & MITRĘGA 2002). It indicates that also sulphate mineral water abstracted from well no. 5p is affected by the mixing process. The results confirm that the groundwater abstracted results from the mixing of modern (post H-bomb tests) water and older sulphate mineral water. The latter is probably of pre-bomb Holocene age. The lower the fraction of the sulphate water component the higher the tritium content in the mixed water.

It is assumed that the spatial pattern of groundwater chemistry in the aquifer is the effect of mixing of modern tritium-bearing water with older mineralised water. The results of modelling hypothetical mixing correlate well with the solubility products of gypsum (Text-fig. 8), which is the most reactive phase in the aquifer, and the main source of sulphate and calcium. However, calcium geochemistry in aquifer is complicated by the effect of calcium common-ion among gypsum, dolomite, calcite, and ion exchange.

Inconsistency of saturation indexes for waters from wells nos. 1 and 8 (Text-fig. 9) can arise from the effect of real residence time in flow systems and/or the fact that pH in groundwater is higher than values calculated for mixed waters. Groundwater in the “intermediate” wells (nos. 1,

7, 8) could have an opportunity to evolve further than waters with simulated composition. In the area of groundwater flow to wells nos. 8 and 1 the process of dolomite dissolution might be more intensive in the real geochemical system. Low gypsum dissolution in the recharge area of well no. 1 might be caused by depletion and/or natural differences in the abundance of gypsum in the aquifer rock. Gypsum is usually intimately encased in clay and other lithic material, and thus not continuously in contact with groundwater.

The $\delta^{34}\text{S}$ of sulphate in water from wells nos. 1 and 7 is similar to the value in water from well no. 8 (Text-fig. 10). This indicates that the effects of the initial stage of gypsum dissolution and/or low gypsum content in the bedrock are more important than the mixing effects. Waters were sampled for S isotopes during low groundwater flow in order to reduce the effect of fresh water recharge. The $\delta^{34}\text{S}$ value in groundwater from well no. 2 is the lowest and similar to that of atmospheric sulphates. This also confirms the absence of gypsum in the rocks of the recharge area.

Deviation of actual groundwater chemistry from the results of mixing modelling can also indicate that dissolution/precipitation of the main mineral phases occurs at different rates in particular parts of the hydrogeological system. This might be brought about by several factors, of which the distribution of minerals in the aquifer and the water chemistry are probably the most important. The various lithostratigraphic members differ in mineral composition, e.g. the calcareous and argillaceous rocks of the Krajanów Member contain the most siderite, pyrite and organic matter. The leaching out of reactive phases such as gypsum and pyrite from the bedrock in the recharge area may be also

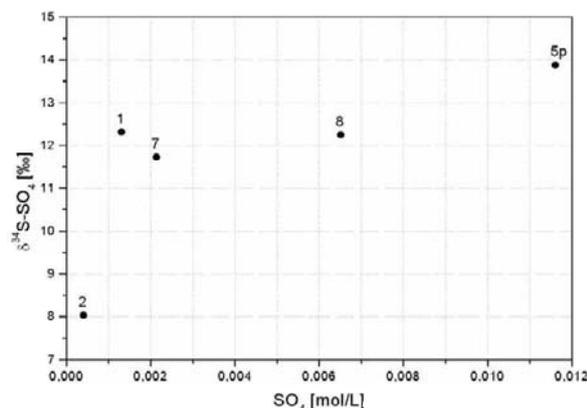


Fig. 10. $\delta^{34}\text{S-SO}_4$ vs. sulphate concentration in groundwater

an important factor. Reaction rate also depends upon solute concentration and saturation state. For instance, the effect of cation exchange appears if the calcium (and magnesium) concentration in groundwater increases sufficiently.

The hydrogeological system studied can be regarded as a series of individual flow systems. Consequently, there are different fractions of both water components in each well. Geochemical modelling strongly supports the assumption that the groundwater chemistry is governed by mixing between modern (post H-bomb) fresh water and older, probably pre-bomb Holocene, sulphate water. The chemistry of water abstracted from particular wells results from the net effects of water components with different transit times and compositions.

Geochemical and isotopic investigations are still being carried out on the Unisław Śląski – Sokółowsko aquifer. Additional investigations of the sulphur ($\delta^{34}\text{S}$) and carbon ($\delta^{13}\text{C}$) isotopes in the solutes and solid phases and of the mineral geochemistry will enable a better description of the system and verify the preliminary geochemical models presented in this paper. Dating of both water components will be possible after further isotope investigations (^{14}C , T). Calculation of water components fraction needs to be verified by geochemical modelling of mixing for each well, using the results of ^{14}C analyses and stable (S, C) isotope determinations.

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