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Geochemistry and age of groundwater in a hydrochemically diversified aquifer (Permo-Carboniferous, the Intra-Sudetic Synclinorium, SW Poland) derived from geochemical modelling and isotopic studies

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ABSTRACT:

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Comprehensive investigations of groundwater were performed in a sedimentary aquifer of Permo-Carboniferous, Intra-Sudetic Synclinorium, in SW Poland. The investigation included aqueous chemical and isotopic composition, chemistry of mineral phases, geochemical modelling, and tritium and radiocarbon groundwater dating. Chemical diversity in the groundwater system is created by the mixing of modern fresh water and older sulphate water with higher dissolved solids. The system is treated as a system of flows of two end-member water types. Geochemical modelling is used for: (1) explaining the origin of the chemistry of both water components, (2) quantifying the groundwater mixing, (3) correcting the radiocarbon age of the groundwater for the effects of chemical water-rock interactions, and (4) calculating reaction rates. Study of stable (C, S, O, H) and unstable (^{3}H, ^{14}C) isotopes allowed the inverse mass balance geochemical models to be verified and specified, and the groundwater to be dated.

The chemistry of the modern, tritium-bearing, fresh water is a result of dissolution of limestones, dolomites and gypsum. The mean tritium-age of this water, based on the lumped-parameter approach, varies between 10 and 200 years. The sulphate mineral water owes its chemistry to the process of dedolomitization driven by gypsum dissolution. Its radiocarbon age is about 5.9 ka BP, i.e., during the Mid-Holocene Climatic Optimum. Rates of chemical reactions responsible for the formation of sulphate type water are estimated to be: dissolution of gypsum (2.85 μmol/L/year) and dolomite (0.21 μmol/L/year), calcite precipitation (0.20 μmol/L/year), organic matter decomposition (0.08 μmol/L/year).

Key words: Groundwater geochemistry; Geochemical modelling; Dedolomitization; Groundwater mixing; Groundwater dating; Radiocarbon; Tritium; Stable isotopes; Reaction rates; The Sudetes; Poland.

INTRODUCTION

The Ścinawka River catchment is located in the Middle Sudetes Mts. (Lower Silesia), partly in Poland and partly in the Czech Republic. The study area comprises the uppermost part of the Ścinawka River catchment and is composed of Carboniferous–Permian sedimentary and partly volcanogenic rocks. Fresh groundwater which occurs in the sedimentary rocks is found in the area of the village of Unisław Śląski and supplies water to the town of Wałbrzych and adjacent localities. The chemical composition of the groundwater in the Carboniferous–Permian sedimentary aquifer manifests a distinct spatial diversity. In the southern part of the study area the groundwater does not comply with drinking water standards, e.g., in terms of sulphate, iron, manganese, and hardness levels. In the area of Sokołowsko, south of Unisław Śląski, sulphate mineral water has been found in the 1980s. Sokołowsko (formerly Görbersdorf) has been well-known in Europe since the 1850s as a famous health resort for the treatment of tuberculosis and lung diseases. These diseases are still being treated in Sokołowsko. Documentation of the quality and origin of mineral water might be helpful in the development of medicine at the health resort in Sokołowsko. Unfortunately, the presence of mineral water may also evoke geogenic contamination. Excessive exploitation of fresh groundwater might entail the risk that sulphate mineral water will intrude from the southern part of the aquifer system northwards and result in the deterioration of the quality of the potable fresh water. Geochemical investigations of groundwater in the present study have been carried out for: (1) deciphering the origin of the chemistry and the "age" of both the fresh and mineral groundwaters, and (2) explaining the spatial pattern of the groundwater chemistry.

METHODS

The present study covered: (1) chemical and isotopic analyses of groundwater and mineral phases (carbonates, gypsum), (2) geochemical modelling of interactions in the groundwater-rock system, (3) tritium and radiocarbon dating of groundwater.

Groundwater was sampled in the production wells which belong to the intake located in the vicinity of the village of Unisław Śląski, and in the unused well (no. 5p) in Sokołowsko (Text-fig. 1). Field measurement on the groundwater comprises T, pH, redox (E_H), specific electric conductivity (SEC), and gases (O_2, H_2S) concentration. The redox potential was measured without atmosphere contact in a through-flow chamber or by probe, using a platinum-Ag/AgCl electrode. It was corrected with respect to the standard hydrogen electrode according to the empirical formulae of Nordstrom (1977). Water samples for chemical analysis were filtered in the field by cellulose-nitrate 0.45 μm membrane filters and stored in LDPE bottles. Chemical analysis of solutes include main anion and cation solutes (bicarbonates, sulphates, chlorides, phosphates, fluorides, nitrates, calcium, magnesium, sodium, potassium), and trace elements. Analyses of cation and trace elements were carried out in the ACME Analytical Laboratories (Vancouver, Canada) by the inductively coupled plasma mass spectrometry (ICP-MS) method. Other chemical determinations were made in laboratories at the Faculty of Geology, University of Warsaw.

Isotopic research covered stable ($\delta^{34}S$-SO_4, $\delta^{13}C$-DIC, $\delta^{18}O$, $\delta^{2}H$) and unstable (^{3}H, ^{14}C) isotopes in groundwater, $\delta^{13}C$ and $\delta^{18}O$ in carbonate minerals, and $\delta^{34}S$ and $\delta^{18}O$ in gypsum. Isotopic determinations in groundwater were repeated on samples taken at different seasons. The sulphates and DIC were sampled for $\delta^{34}S$ and $\delta^{13}C$ determination by precipitation from solution in the field as $BaSO_4$ and $BaCO_3$ respectively. In the field, slurries were filtered by a 0.45μm nylone membrane, rinsed by deionised water to flush out chlorides (from $BaCl_2$), and transferred into shipping vessels.

The $\delta^{13}C$ of the DIC and carbonate solids was determined in the Institute of Geological Sciences (Polish Academy of Sciences, Warsaw). The $\delta^{34}S$ of the sulphate solutes was determined in the Institute of Geological Sciences (Polish Academy of Sciences, Warsaw), and in the Department of Mass Spectrometry, Faculty of Mathematics, Physics and Computer Science (Maria Curie-Skłodowska University, Lublin), where the $\delta^{34}S$ and $\delta^{18}O$ of a gypsum sample were also analyzed. The $\delta^{18}O$ and $\delta^{2}H$ of water samples were analyzed partly in the Department of Environmental Physics, Faculty of Physics and Applied Computer Science (AGH – University of Science and Technology, Cracow) and partly in the Institute of Geological Sciences (Polish Academy of Sciences, Warsaw). Stable isotope composition ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, $\delta^{34}S$) was measured by isotope ratio mass spectrometry. Stable isotope composition ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$) was expressed versus VSMOW and VPDB standards respectively (Coplen 1996). The $\delta^{34}S$ was expressed versus the VCDT standard. Standard analytical uncertainties of the $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$ and $\delta^{34}S$ analyses were 0.1‰, 1‰, 0.1‰, and 0.1‰ respectively.

Determination of radiocarbon activity was performed in the Poznań Radiocarbon Laboratory by the accelerator mass spectrometry (AMS) method in $BaCO_3$ solid precipitated in the field. Tritium activity was determined in the Institute of Nuclear Chemistry and Technology (Warsaw) by liquid scintillation spectrometry. Uncertainties of tritium and radiocarbon determinations are reported in Table 4.

The carbonates (limestones, dolomites, calcites) were also analyzed for metal (Ca, Mg, Fe, Mn, Sr, Ba, Zn) content in the labotatories of the Faculty of Geology, University of Warsaw.

The PHREEQC code (Parkhurst and Appelo 1999) has been applied for the geochemical modelling of groundwater. Speciation, reaction path, inverse mass balance, and mixing modelling were performed.

Tritium data acquired during the present study were interpreted for individual wells by the lumped-parameter approach using the FLOWPC code (ver. 3.2) (Małoszewski and Zuber 1996) to obtain the mean tracer ages of the sampled water and the age distribution functions. Tritium input function was prepared using monthly precipitation records from the station in Mieroszów, which is located 4–5 km south of the study area. Tritium records in precipitation were obtained from the Global Network of Isotopes in Precipitation (GNIP) database (http://isohis.iaea.org). Tritium content in precipitation data from the station in Cracow was extrapolated to data from Vienna and Ottawa stations using correlation parameters given by Duliński *et al*. (2001) and IAEA (2002). The tritium input function was estimated with the ratio of summer-to-winter infiltration coefficients equal to 0.70 (Grabczak *et al*. 1984; Małoszewski and Zuber 1996). As the summer months were taken from April to September, and winter months from October to March.

GEOLOGICAL SETTING AND HYDROGEOLOGY

The Ścinawka River catchment is situated in the central part of the Sudetes Mts. (SW Poland). From a geological viewpoint the study area is located in the Intra-Sudetic Synclinorium, which is a syn- to post-orogenic basin initiated during the Visean (Turnau *et al*. 2002). The basin is filled by a thick complex (up to 10 km) of Carboniferous-Permian terrestrial clastic sediments (Nemec *et al*. 1982; Dziedzic and Teisseyre 1990) with volcanogenic rocks (Awdankiewicz 1999a,b, 2004). The Carboniferous–Permian succession is locally overlain by a thin cover of terrestrial Lower Triassic sandstones and Upper Cretaceous marine deposits.

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 (Text-fig. 1) comprising the Ludwikowice Member (Upper Stefanian), and the Krajanów and Zagórzyn members (Lower Autunian) (Text-fig. 2). The sedimentary rocks were deposited in intermittent alluvial and lacustrine environments under arid conditions (Wojewoda and Mastalerz 1989; Bossowski and Ihnatowicz 1994). In the southern part of the area, Permian volcanogenic rocks (trachyandesites, rhyolites and rhyolitic tuffs) occur (Awdankiewicz 1999a,b).

The Ludwikowice Member is composed of polymictic conglomerates and sandstones, rarely with mudstones and shales. The main features of the mineral composition of these rocks consist of the presence of numerous fragments of volcanic rocks (rhyolites, trachytes) and feldspars, with chloritised biotite, carbonates (mainly calcite, dolomite), gypsum, sericitised and kaolinitised feldspars, argillaceous-siliceous cement with neogenic calcite, gypsum and limonite (Bossowski 1996, 1997; Mastalerz and Nehyba 1997).

The Krajanów Member is composed of sandstones and mudstones with claystones, limestones, calcareous mudstones, bituminous limestones and mudstones at the top of the profile. In the clastic rocks, 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 occur.

The Zagórzyn Member is composed mainly of mudstones and claystones, with sandstones. Fragments of volcanic rocks and feldspars are rare. Argillaceous-siliceous and ferrous cements are dominant in the bedrock. Xenomorphic calcite, dolomite, illite, kaolinite can also be found. Dispersed pyrite and organic matter occur rarely.

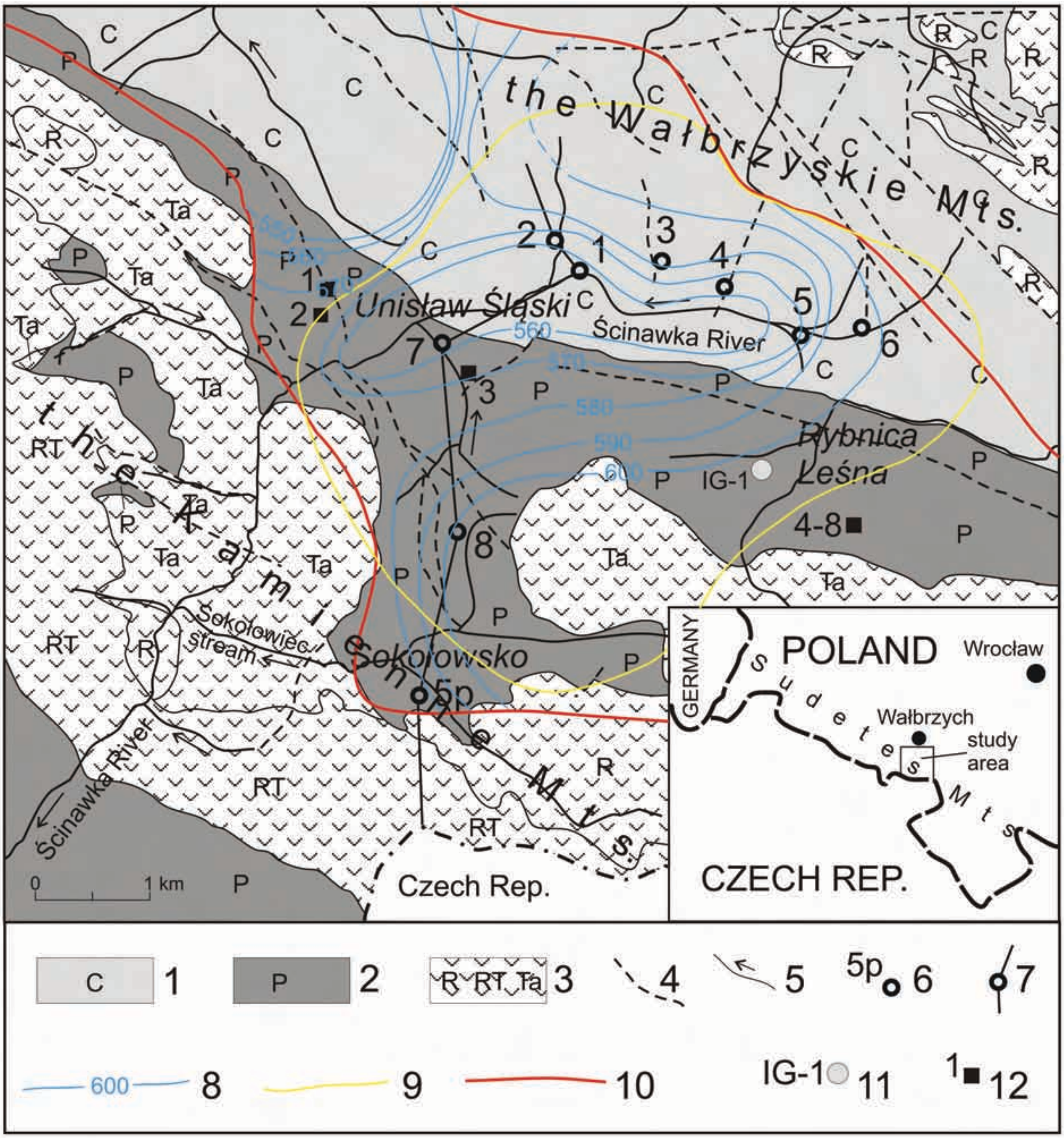
The most reactive phases in the aquifer rocks are gypsum, carbonates (dolomite, calcite, siderite), sulphides (mainly pyrite) and dispersed organic matter. The presence of these phases in the bedrock plays a crucial role in the groundwater chemistry.

The groundwater investigated occurs in sedimentary lithostratigraphic units of the Ludwikowice, Krajanów and Zagórzyn members. The source of recharge to the hydrogeological system studied is effective infiltration of precipitation on the outcrops. Unconfined conditions occur in the northern part of the area, and are noted only in well no. 2, which is located on the slope of the Wałbrzyskie Mts., north of the village of Unisław Śląski (Text-fig. 1). Groundwater flow within both the unconfined and confined parts of the system is predominantly through fissures. Water-bearing rocks are mainly fractured conglomerates and sandstones in the northern part of the study area, and mudstones in the southern part.

The hydrogeological conditions in the upper part of the Ścinawka River catchment were investigated mainly during the water prospecting works in the 1960s and the first half of the 1980's (Wójcicka and Tarkowski 1968; Dąbrowski and Szafranek 1982; Szafranek *et al*. 1986). The groundwater chemistry of shallow water-bearing horizons in the Kamienne Mts. and in the Ścinawka River catchment was documented mainly by Dobrzyński (1997) and Wiśniewska (2003).

Generally, the Carboniferous and Permian sedimentary rocks in the Intra-Sudetic Synclinorium have poor hydraulic properties (Malinowski 1991; Paczyński and Sadurski 2007). One of the places where good hydrogeologic conditions were noted is the area of Sokołowsko and Unisław Śląski, with the yield reaching up to 110 m^3/h (in well 5p at Sokołowsko).

The mean rainfall rate in the study area slightly exceeds 800 mm/a, and the evaporation index is about 550 mm/a (Kowalski 1992). Effective infiltration ranges between 140 and 190 mm/a; only the eastern



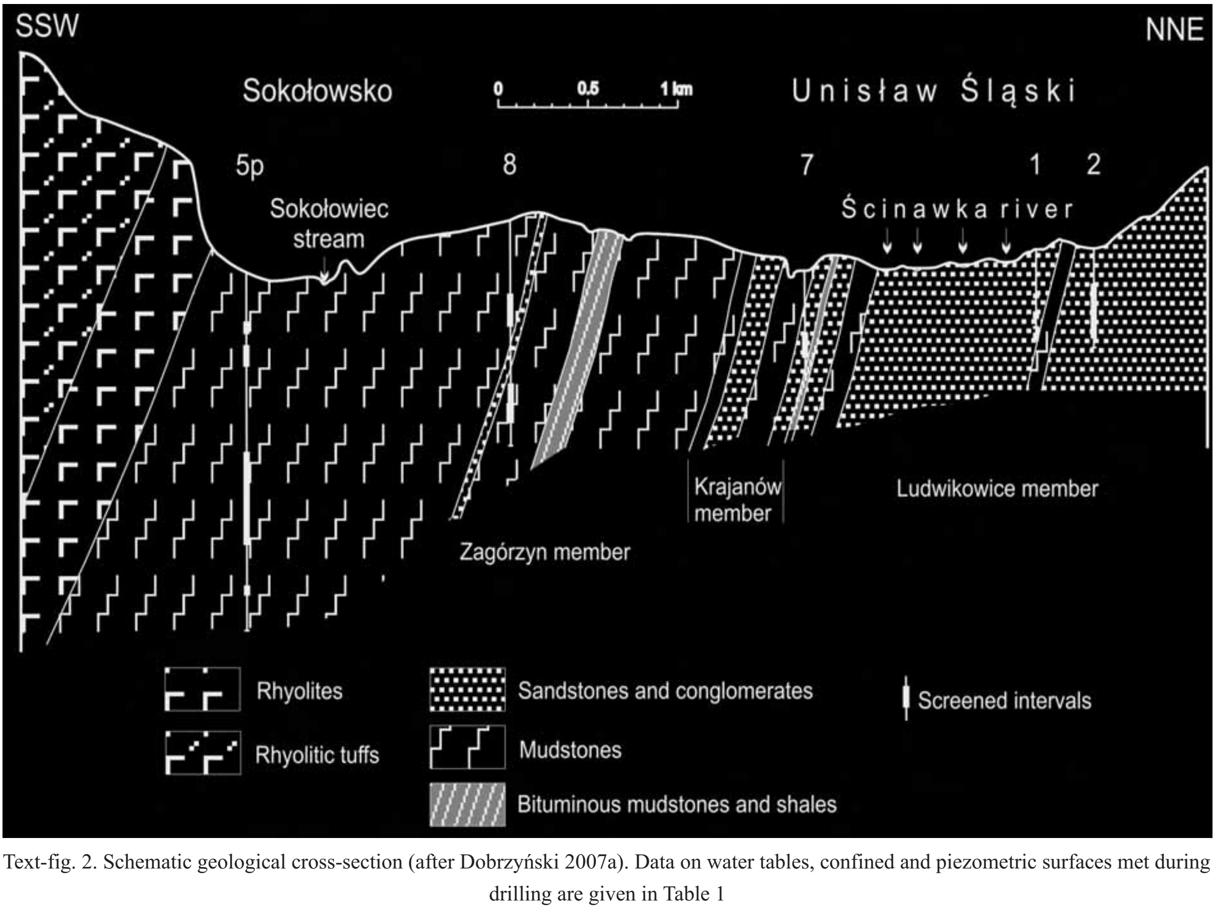
Text-fig. 1. Hydrogeological sketch map of the area studied (after Grocholski 1971; Bossowski *et al*. 1994; Awdankiewicz 1999a; Wojtkowiak 2000a, 2002a). Explanations: 1 – Carboniferous sedimentary rocks; 2 – Permian sedimentary rocks; 3 – volcanic rocks: rhyolites (R), rhyolitic tuffs (RT) and trachyandesites (Ta), respectively; 4 – faults; 5 – water-courses; 6 – wells; 7 – geological cross-section line; 8 – hydroizohypses; 9 – limit of depression cone; 10 – boundary of the hydrogeological unit; 11 – Unisław Śląski IG-1 deep borehole; 12 – sites of carbonate rock sampling (samples nos. 1 to 3 from outcrops, samples nos. 4 to 8 from the abandoned mine tunnel by the village of Rybnica Leśna). Hydroizohypses, limit of depression cone, and boundary of the hydrogeological unit after Wojtkowiak (2000a, 2002a) part of the Sokołowiec stream catchment exceeds 190 mm/a (Poprawski *et al*. 1996). The hydraulic conductivity of subsurface water-bearing horizon ranges from $2.5\cdot10^{-6}$ m/s to $4.0\cdot10^{-5}$ m/s (Poprawski *et al*. 1996). The hydraulic conductivity values found from pumping tests range between $0.7\cdot10^{-5}$ m/s and $3.5\cdot10^{-4}$ m/s (Table 1). Higher values are noted in Carboniferous conglomerates and sandstones (N of Unisław Śląski), close to the recharge zone (wells nos. 1, 2, 3), and in mudstones with sandstones of the Zagórzyn Member (well 5p in Sokołowsko). Disposable resources of groundwater in the upper part of the Ścinawka River catchment are estimated at 5.64 L/s/km^2, whereas present-day groundwater withdrawal is about 5.05 L/s/km^2. Specific underground runoff is about 2.51 L/s/km^2 (Poprawski *et al*. 1996).

The study area is located within the hydrogeological unit numbered 5abP$_1$II (on the Wałbrzych sheet of the hydrogeological map; Wojtkowiak 2000a). This unit continues on the adjoining hydrogeological map – sheet Kamienna Góra (Wojtkowiak 2002a) as the unit no. 9abP$_1$I. Both of these hydrogeological maps incorrectly indicate the stratigraphy of the water-bearing rocks as a Permian aquifer. Apart from Lower Permian rocks, mainly Upper Carboniferous rocks form the aquifer in this area.

The Ścinawka River is the main base level of groundwater drainage in the upper part of the catchment in the vicinity of Unisław Śląski whereas in the area of the village of Sokołowsko the Sokołowiec stream, a tributary of the Ścinawka River, is the local drainage base level.

Water abstraction induced the local depression cone around Unisław Śląski, along the Ścinawka River (Text-fig. 1). The water intake in Unisław Śląski consists of eight production wells (nos. 1–8; Text-fig. 1), but actually only five of them are operating. Well 1 of the intake in Unisław Śląski has operated since 1909 (renewed in 1967). Wells 2–6 have operated since the 1960s. Abstraction of water from wells 7 and 8 started in 1991. Well 6 has been out of operation since 1999 due to the high level of manganese and iron. Well 8 has been unused since 2005 because of the arsenic content exceeding the drinking-water standard. Well. 4 is operating only periodically due to technical problems.

Hydrogeochemical investigations of the present study were carried out mainly in wells 2, 1, 7 and 8. Sampling and measurement of water in well 8 were



Text-fig. 2. Schematic geological cross-section (after Dobrzyński 2007a). Data on water tables, confined and piezometric surfaces met during drilling are given in Table 1

Well	Altitude, m a.s.l. (Well depth, m)	Stratigraphy of water-bearing horizon(s) ---------- Start of operation	Water tables, confined surfaces and piezometric surfaces met during drilling (below ground level, m)	Screened intervals (below ground level, m)	Hydraulic conductivity[1], m/s
1	582.10 (88.8)	C_2 1909/1967[2]	4.0 – 4.0 20.6 – 2.8 29.0 – 2.8 41.5 – 2.8 60.2 – 2.8 74.0 – 2.8 81.0 – 2.8	43.5 – 47.5 60.25 – 67.25 75.25 – 77.25 81.0 – 86.0	$1.37 \cdot 10^{-4}$
2	592.50 (96.5)	C_2 1961	6.0 – 6.0	32.49 – 86.72	$1.53 \cdot 10^{-5}$
3	614.61 (75.0)	C_2 1968	1.0 – 1.0 28.0 – +12.0 43.0 – +12.0 68.0 – +12.0	52.0 – 65.0 68.5 – 71.5	$1.9 \cdot 10^{-5}$
4	612.20 (91.0)	C_2 1968	3.0 – 3.0 65.2 – +5.0 78.0 – +5.0	65.53 – 73.63 78.40 – 88.00	$0.69 \cdot 10^{-5}$
5	613.05 (217.5)	C_2 1968	3.0 – 3.0 187.5 – +2.0 198.0 – +2.0	188.3 – 194.5 198.8 – 214.3	$0.9 \cdot 10^{-5}$
6	629.11 (187.0)	C_2 1968	1.5 – 1.5 14.0 – +1.0	136.89 – 143.66 150.58 – 163.90 178.80 – 182.19	$1.0 \cdot 10^{-5}$
7	569.8 (100.0)	P_1 1991	60.0 – +1.5	60.0 – 85.0	$1.05 \cdot 10^{-5}$
8	620.0 (220.0)	P_1 1991	11.5 – 11.5 160.5 – +0.3	71.9 – 102.5 160.5 – 197.7	$1.0 \cdot 10^{-5}$
5p	570.0 (350.0)	P_1 1980[3]	80.0 – 9.50 195.0 – 8.0 308.0 – 5.85	49.4 – 60.6 (fresh water) 72.3 – 92.2 (fresh water) 176.2 – 266.6 (mineral water) 305.6 – 314.3 (mineral water)	$3.5 \cdot 10^{-4}$

1 – values from pumping tests. For wells 1 to 6 after Wójcicka and Tarkowski (1968); for well 7 after Szafranek *et al.* (1986); for well 8 estimated after data from Szafranek *et al.* (1986); for well 5p after Dąbrowski and Szafranek (1982). 2 – the second date indicates year of the renew of a well. 3 – year of the drilling works, the well is unused

Table 1. General characteristics of water wells in the area of Unisław Śląski – Sokołowsko

possible after closing because of artesian flow which re-established shortly after disconnection of the pump. Groundwater chemistry was also investigated in unused well 5p located in Sokołowsko (Text-fig. 1). Well 5p, drilled in 1980, has never been exploited due to poor water quality, which decreased the well efficiency significantly. Originally, in well 5p a discharge of 110 m^3/h was recorded at a drawdown of 25 m, which gave a specific discharge of well of 4.4 $m^3/h/1m$ (Dąbrowski and Szafranek 1982). During the research pumping test in 2000, there was a discharge of 37.4 m^3/h at the drawdown of 15.3 m, which yielded the specific discharge of well of 2.44 $m^3/h/1m$.

In well 5p four water-bearing horizons were 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 water, whereas the two deeper ones yield sulphate mineral water. Field physicochemical parameters were determined in well

Well no.	pH[1]	TDS	Hardness	HCO_3	SO_4	Cl	NO_3	Ca	Mg	Size
		mg/L	$mgCaCO_3/L$	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
1	6.85	368.2	206.7	115.9	137.8	16.2	10.6	59.1	17.1	50
2	7.01	205.2	116.7	88.0	52.7	11.6	9.2	38.0	7.1	47
3	7.20	307.8	192.0	180.7	78.9	14.9	1.1	70.9	7.3	47
4	7.62	397.9	235.9	169.5	132.4	13.9	2.7	84.7	8.6	46
5	7.41	328.4	180.6	151.9	101.0	15.0	10.5	61.8	8.6	37
6	7.75	322.2	199.5	196.6	80.3	14.6	1.1	73.2	7.8	41
7	7.33	532.8	296.3	121.3	268.7	8.3	5.9	111.0	10.9	40
8	7.36	1050.9	527.4	111.9	568.7	6.2	3.0	182.7	24.1	33

1 – values calculated upon the mean H^+ molal concentration

Table 2. Mean value of selected physicochemical parameters of groundwater exploited at the intake in Unisław Śląski (after data upon the present study and archival data)

5p and water samples were taken by a submersed sampler at particular depths during the research pumping. Due to a higher hydraulic head in deeper, sulphate horizons and an upward flow in the well column, sampling of sulphate mineral water in well 5p is also possible using a sampler lowered above a screened interval of sulphate-water horizons.

The sulphate mineral water from well 5p represents the most chemically evolved groundwater found in the area, and is the primary subject of research carried out in this study.

The sulphate mineral water found in Sokołowsko shows the unique chemistry in the Intra-Sudetic Synclinorium as well as in the whole of the Sudetes Mts. In Poland, similar mineral water occurs in two spas, i.e., sulphate-bicarbonate-calcium-magnesium waters in Swoszowice and sulphate-chloride-calcium-sodium waters in Wieniec. It should be pointed out that the above-mentioned water also contains sulphides, boron, and radon (Swoszowice) or sulphides, fluorides, bromides and iodines (Wieniec). Sulphate mineral water in Sokołowsko contains some concentration of boron and sulphides, but its applicability for balneological purposes or mineral water bottling needs further hydrogeochemical examination.

It must be emphasized that the excessive abstraction of fresh water in Unisław Śląski entails the risk that sulphate groundwater in the area of Sokołowsko valley might flow northwards and intrude into the exploited fresh water horizons. The threat has become more probable since 1991, when the abstraction of water from wells nos 8 and 7 was started. Activation of a sulphate mineral water inflow process was suggested by Wiśniewska (2003).

Groundwater from well 5p was sampled and analysed a few times during drilling (in 1980) and pumping tests in the 1980s. Unfortunately, these archival chemical analyses illustrate composition of mixed water from the well because of the intercurrent inflows from the four screened horizons. The chemical composition of the sulphate mineral water was documented initially by the author in 2000, as part of the the KBN research project (no. 9 T12B 044 18). Investigations of sulphate water, particularly trace elements and isotopic composition, were continued by the author in the following years.

GROUNDWATER CHEMISTRY

The chemistry of the groundwater in the Permian–Carboniferous sedimentary aquifer can be characterized by data acquired in the present study, and by archival data. Archival data on water chemistry includes general analysis made after drilling and analysis by sanitary survey and waterworks. In the present study complex chemical analysis of groundwater from selected wells was accomplished. These analyses covered chemical and isotopic examinations.

The chemistry of the groundwater from wells that belong to the water intake in Unisław Śląski shows an appreciable spatial pattern. Water from wells in Carboniferous siliciclastic rocks located in the upper course of the Ścinawka River (wells 1, 3 to 6; Text-fig. 1) shows unequivocal affinities. They have low salinity (mean TDS value ranges from 300 to 400 mg/L), and its chemical composition is dominated by bicarbonate and calcium ions (Table 2).

Water from wells (2, 1, 7, 8, 5p) located along the dip of sedimentary beds (Text-figs 1, 2) reveal a completely different pattern. The groundwater chemistry is varies successively from fresh water in well 2 (in an unconfined part of the aquifer) to mineral water in well 5p, in Sokołowsko. The salinity of the groundwater and

Parameter	Well no. 2	Well no. 1	Well no. 7	Well no. 8	Well no. 5p[1]
T [ºC]	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
DOX[3]	4.47	2.32	2.87	<0.01	0.60
H_2S	<0.01	<0.01	0.03	0.01	0.44
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	0.2	0.2
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	0.004	0.010	0.006	0.006	0.045
As[4]	0.0062	0.0036	0.0092	0.0887	0.1023
B[4]	0.022	0.048	0.144	0.304	1.114
Ba	0.127	0.044	0.038	0.017	0.011
Fe	0.005	0.010	0.010	0.060	0.66
Li[4]	0.005	0.011	0.031	0.035	0.121
Mn	0.0005	0.001	0.011	0.086	0.126
Mo[4]	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
PCC[5]	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 mineral water horizons in well no. 5p; 2 – specific electric conductivity compensated for 25°C; 3 – dissolved oxygen; 4 – element not included in the geochemical models; 5 – prevalent chemical character (hydrochemical type) according to ion concentration exceeding 20% meq/L.

Table 3. Chemical composition of groundwater from wells 2, 1, 7, 8 and 5p (after Dobrzyński 2007a; updated). Concentrations in mg/L

the concentration of most solutes increase southwards, towards the centre of the sedimentary Intra-Sudetic Synclinorium. Actually, only the content of chloride, fluoride, nitrate, and barium decreases. The prevalent chemical character of the water gradually changes from the Ca-HCO_3-SO_4 type (in well 2) to the Ca-Na-SO_4 type (mineral water horizons in well 5p) (Table 3). The present subject of study is the geochemistry of groundwater illustrating this hydrochemical pattern.

Complete chemical analysis of water from wells 2, 1, 7, 8 and 5p (Table 3) acquired during the present study was used as input data for geochemical modelling, and for deciphering the origin of fresh water and sulphate mineral water in the Carboniferous–Permian sedimentary rocks.

Procedures of the QA/QC (quality assurance/quality control) programme applied (Dobrzyński 2007a) indicated that the predominant solutes in the groundwater were investigated with a high degree of precision. The random errors relating to the sampling and analytical errors together constituted less than 0.2% of the total hydrochemical variability. This means that the hydrochemical data reflect very well the natural, geochemical distribution of the main solutes in the aquifer.

A previous study (Dobrzyński 2007a) showed that the chemistry of the groundwater was dominated by the dissolution products of gypsum and carbonates, i.e. by sulphate, bicarbonate and calcium ions. The concentrations of both sulphate and calcium solutes increase down the aquifer system, and the SO_4/Ca molal ratio shows a value of about 1 in most waters. The bicarbonate concentration initially increases going down the aquifer due to the dissolution of car-

Parameter	Well no. 2	Well no. 1	Well no. 7	Well no. 8	Well no. 5p[1]
^{3}H [TU] [2]	n.a.	n.a.	16.2 (±0.5)	4.0 (±0.5)	3.2/5.9 (±0.5)[3]
^{3}H [TU] [4]	10.18 (±0.37)	8.23 (±0.33)	6.5 (±0.73)	2.86 (±0.26)	2.44 (±0.29)
^{3}H [TU] [5]	10.04 (±0.42)	10.62 (±0.13)	6.91 (±0.19)	3.17 (±0.10)	2.98 (±0.28)
^{3}H [TU] [6]	9.59 (±0.38)	7.55 (±0.53)	7.17 (±0.46)	3.00 (±0.15)	2.82 (±0.33)
^{14}C [pmC] [7]	59.39 (±0.23)	46.19 (±0.26)	36.79 (±0.19)	41.68 (±0.27)	26.94 (±0.19)
δ^2H VSMOW (Aug.-2000)	n.a.	n.a.	–71.7	–70.2	–68.3
δ^{18}O VSMOW (Aug.-2000)	n.a.	n.a.	–10.67	–10.58	–10.31
δ^2H VSMOW (Mar.-2005)	–76.17	–78.09	–75.96	–72.94	–71.04
δ^{18}O VSMOW (Mar.-2005)	–10.04	–10.87	–10.66	–10.52	–10.22
δ^2H VSMOW (Oct.-2006)	–72.45	–74.25	–72.80	–69.80	n.a.
δ^{18}O VSMOW (Oct.-2006)	–10.08	–10.20	–10.44	–9.32	n.a.
δ^{13}C-DIC (Jul.-2003)	–14.73	–14.38	–12.11	–9.15	n.a.
δ^{13}C-DIC (Jul.-2004)	n.a.	n.a.	n.a.	–11.90	–16.26
δ^{13}C-DIC (Mar.-2005)	n.a.	–18.56	–13.98	–12.29	–16.51
δ^{13}C-DIC (Aug.-2006)	–16.18	–17.73	–15.11	–13.01	n.a.
δ^{34}S-SO$_4$ (Aug.-2000)	n.a.	n.a.	11.46	11.88	13.87
δ^{34}S-SO$_4$ (Jul.-2003)	8.03	12.31	11.72	12.24	n.a.
δ^{34}S-SO$_4$ (Mar.-2005)	n.a.	8.02	8.83	9.35	10.60
δ^{34}S-SO$_4$ (Oct.-2006)	10.13	12.15	14.21	14.50	n.a.

1 – composition of water from the sulphate horizons in well no. 5p; 2 – samples taken in August 2000; 3 – tritium content before and after pumping test, respectively; 4 – sampled in September 2004; 5 – sampled in March 2005; 6 – sampled in October 2007; 7 – sampled in September 2005; n.a. – not analyzed

Table 4. Isotopic data on groundwater studied

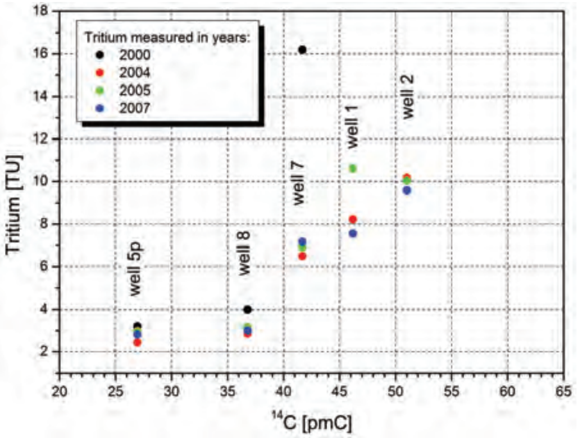
bonate minerals, especially in the recharge zone of the aquifer. However, in the deeper, southern part of the aquifer, the bicarbonates are gradually depleted due to calcite precipitation.

The chemical and isotopic data acquired unequivocally evidence gradual changes of groundwater composition (Table 3). The explanation of this regular pattern was one of the aims of the studies. The sampled wells (2, 1, 7, 8, 5p) are situated along the dip of the beds. However, the hydrogeological conditions indicate that they are not located on the same single flow path, and the groundwater chemistry pattern could not be considered to be a result of chemical evolution.

Isotopic patterns in groundwater

The set of stable and unstable isotopes was examined in the groundwater. The results are given in Table 4. Similarly to the chemical composition, the isotopic composition, of both solvent (water) and solutes, shows regular patterns in the groundwater.

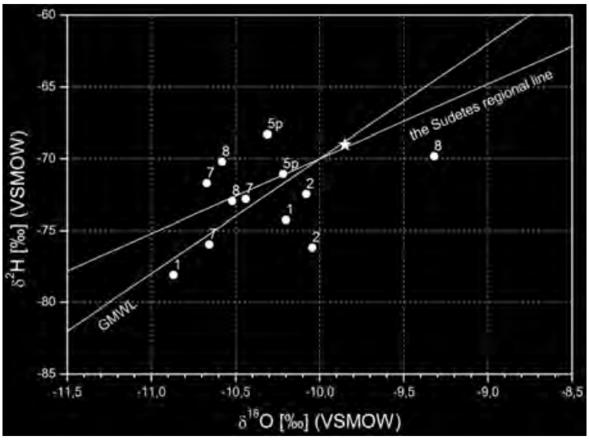
Determination of unstable isotopes reveals the presence of both tritium and radiocarbon in the groundwater. Tritium activity measured in the groundwater in years 2000–2007 varies between 2.4 TU and 16.2 TU, and indicates the effect of modern day recharge. Radiocarbon activity (between 27 pmC and



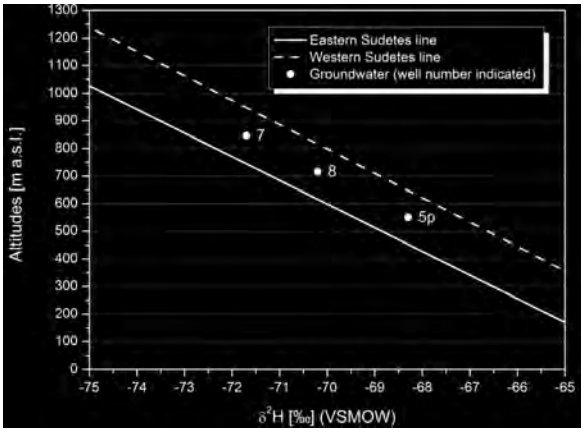
Text-fig. 3. Tritium vs. radiocarbon in groundwater

59 pmC) suggests the role of young and/or modern groundwater. The lower the tritium contents in the groundwater, the lower the radiocarbon activity. Both tritium and radiocarbon activities decrease southwards, from well 2 to well 5p (Table 4, Text-fig. 3).

The oxygen and hydrogen isotope ratios in the groundwater studied vary between –9.2‰ and –10.9‰, and –68.3‰ and –78.1‰, for oxygen and hydrogen respectively, and are similar to variations noted in fresh groundwater of the Sudetes (Ciężkowski and Kryza 1989, 1997). Differences of isotope ratio between summer and winter half-years are visible. They manifest mainly for hydrogen stable isotopes, and are of about 3–4‰ (Table 4, Text-fig. 4). Seasonal isotopic variations in shallow groundwater surely reflect seasonal variations of the isotopic composition of the precipitation in the area. Data on summer half-year oxygen and hydrogen ratios were used for estimating the altitudes of the recharge zone for wells 7, 8 and 5p. Field data were compared with the Sudetic isotopic altitude curves given by Ciężkowski and Kryza (1989) for eastern and western regions of the Sudetes. The study area is located in the central part of the Sudetes. Considering the continental effect in the Sudetes, it was assumed that the altitude relationship for the study area should be intermediate between the altitude curves given by Ciężkowski and Kryza (1989).

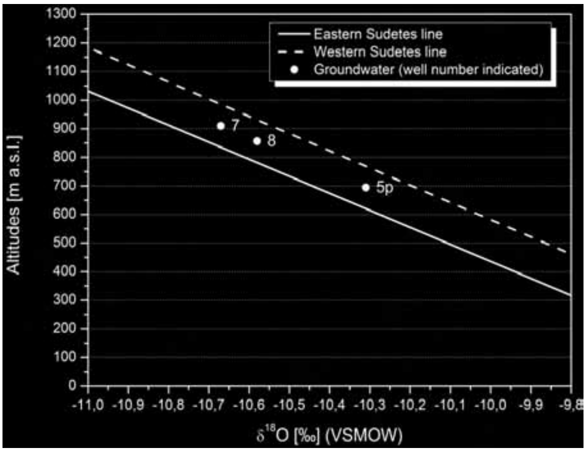


Text-fig. 4. Stable hydrogen versus oxygen isotopic composition in groundwater. The Sudetes regional line ($\delta^2H = 5.2176\ \delta^{18}O - 17.82$) after Ciężkowski and Kryza (1997). GMWL – global meteoritic water line, $\delta^2H = 8\ \delta^{18}O + 10$ (after Craig 1961). Star indicates average composition of Holocene infiltration waters in foreland of the studied part of the Sudetes after d'Obyrn *et al*. (1997)

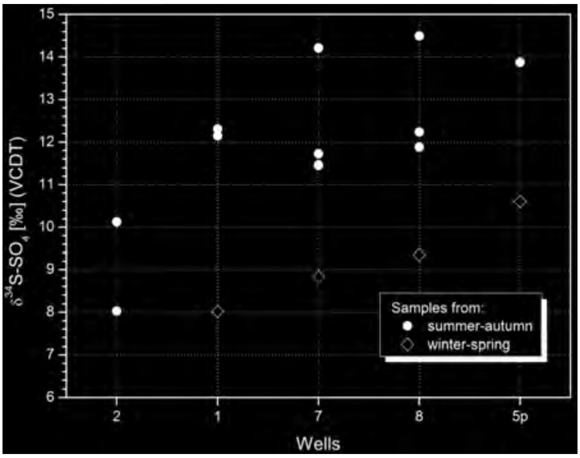


Text-fig. 5. Stable hydrogen composition of groundwater in summer compared with the Sudetic isotopic altitude curves after Ciężkowski and Kryza (1989)

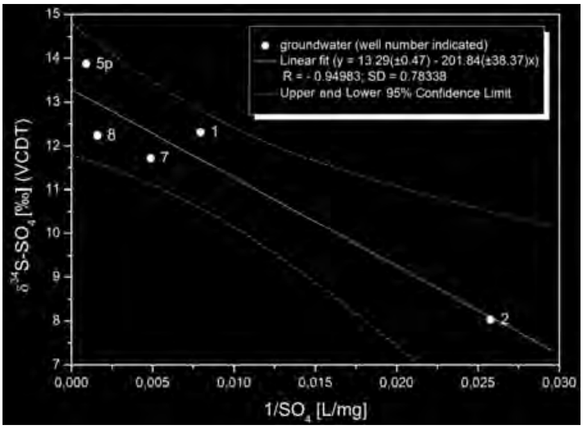
The mean altitudes of the recharge area estimated from altitude curves are: 695 and 550 m a.s.l. (well 5p), 856 and 716 m a.s.l. (well 8), 910 and 846 m a.s.l. (well 7), for the δ^{18}O and δ^2H data respectively. Altitudes estimated from δ^2H are lower than those esti-



Text-fig. 6. Stable oxygen composition of groundwater in summer compared with the Sudetic isotopic altitude curves after Ciężkowski and Kryza (1989)



Text-fig. 7. Sulphur isotopic composition of groundwater in summer-autumn and winter-spring half-years



Text-fig. 8. The δ^{34}S-SO$_4$ as a function of reciprocal of the sulphate concentration in groundwater

mated from δ^{18}O data (Text-figs 5, 6). The difference is greatest in the groundwater from well 5p, and smallest in well 7. The mean altitude of the recharge area for well 5p estimated from δ^2H (550 m a.s.l.) is even lower than the well altitude (570 m a.s.l.). This is probably caused by a sulphate mineral water component, and the occurrence of dissolved hydrogen sulphide in sulphate water. Isotope exchange between hydrogen sulphide and water might cause the hydrogen to become heavier. The sulphate water component is highest in the groundwater from well 5p. Water mixing will be discussed further below.

The heights of the mountain ranges surrounding the study area exceed 800 m a.s.l. The highest elevations in the area are: Lesista Wielka – 853 m m a.s.l., Bukowiec – 886 m a.s.l., Waligóra – 936 m a.s.l. The altitudes of the recharge area estimated from δ^{18}O seem to be more suitable for the studied aquifer, and better fit the altitudes of the adjacent mountains. The altitudes from δ^2H are surely underestimated.

The isotopic composition of S-SO$_4$ presents the same spatial pattern as the sulphate concentration in the groundwater. Generally, the δ^{34}S-SO$_4$ value increases southwards in the study area (Text-fig. 7). The δ^{34}S-SO$_4$ ranges from +8‰ to +14.5‰. The lightest sulphur has been found in the groundwater from wells 2 and 1, which adjoin the recharge zone. The δ^{34}S-SO$_4$ for anthropogenic sulphate in precipitation in industrialized areas of the northern hemisphere ranges usually between –3‰ and +9‰ (Krouse and Mayer 2000). Significant variations of δ^{34}S-SO$_4$ in precipitation since 1993 have been documented in Wrocław, the capital city of the Lower Silesia region (Jędrysek 2000, 2003; Górka *et al.* 2008). In the years 1994–1995, the δ^{34}S-SO$_4$ of precipitation in Wrocław varied from +0.9‰ to +6.0‰ (Jędrysek 2000). The lower values of δ^{34}S-SO$_4$ in the groundwater studied, near +8‰, show the significant effect of modern recharge in wells 2 and 1. The mean tritium age of the water (chapter Tritium age of groundwater) indicates that the groundwater in both wells recharged in the mid-1990s.

The dissolution of gypsum (or anhydrite) occurs without measurable isotope effects, and so the isotope contents in the SO_4^{2-} solute can be used as a tracer for sulphate origin. The increase in sulphate concentrations in the groundwater results from the gypsum dissolution. Assuming that gypsum is the source phase of the heavier sulphur, the relationship between δ^{34}S-SO$_4$ and the reciprocal of the SO$_4$ concentration (Text-fig. 8) indicates that the mineral should have δ^{34}S about +13.3‰ (±0.5‰).

One should note that groundwater samples from the winter-spring period have lighter (of about 3‰–5‰) sulphur composition than water samples from the summer-autumn period. These variations confirm the effect of seasonal fresh water recharge not only in the case of operating wells (2, 1, 7, 8), but also in water recharging deeper (sulphate) horizons in unused well 5p.

The composition of stable carbon isotopes (^{12}C, ^{13}C) in carbon species dissolved in groundwater depends on the δ^{13}C of carbon source and sink phases, and on fractionation between carbon species. The composition of carbon isotopes in groundwater depends mainly on the composition of soil carbon dioxide and on carbonate minerals. Vegetation in the study area follows the Calvin (C$_3$) photosynthetic cycle and, therefore, biomass is assumed to have $\delta^{13}C \approx -25$‰, and $^{14}C \approx 100$ pmC. Due to the small fractionation effect soil $CO_{2(g)}$ has $\delta^{13}C \approx -23$‰ and $^{14}C \approx 100.5$ pmC (Clark and Fritz 1997). The effects of fractionation, at isotopic equilibrium and at 25°C, between $CO_{2(g)}$ and dissolved carbonate species i ($CO_{2(aq)}$, HCO_3^-, CO_3^{2-}) can be described by isotopic enrichment, $\varepsilon^{13}C_{i/CO_{2(g)}}$: ≈ –1.1‰, ≈ +7.9‰, and ≈ +5.9‰, for the above-mentioned species respectively (Mook *et al.* 1974; Zhang *et al.* 1995; Szaran 1997, 1998; Leśniak and Zawidzki 2006). In the groundwater studied, the HCO_3^- ion is the main form of dissolved inorganic carbon. Enrichment during precipitating of pure calcite and magnesium calcite with respect to HCO_3^- is rated at about +0.8‰ to +1.1‰ (Romanek *et al.* 1992; Clark and Fritz 1997; Jimenez-Lopez *et al.* 2001, 2006).

Dissolved inorganic carbon (DIC) derives from soil CO_2 and carbonate minerals. The concentration of DIC in recharging groundwater depends, e.g., on CO_2 pressure, opening of the system with respect to the CO_2 source, temperature and the equilibrium state with carbonate minerals. The mean pressure of soil CO_2 (P_{CO_2}) in the study area was estimated from the evapotranspiration accordingly to the relationship given by Brook *et al.* (1983):

$$\log P_{CO_2} = -3.47 + 2.09\,(1 - e^{(-0.00172MET)}) \qquad (1)$$

where, MET – mean annual evapotranspiration, in mm.

Taking evaporation of 550 mm/a in the study area (after Kowalski 1992) as the value of MET, $\log P_{CO_2}$ is ≈ –2.19.

The overall $\delta^{13}C$ of DIC in groundwater depends on the proportions of dissolved carbonate species. Estimation of $\delta^{13}C$-DIC in groundwater can be made by using geochemical codes, such as PHREEQC. The final value of $\delta^{13}C$-DIC for different CO_2 systems might be estimated as follows.

In a system open to soil carbon dioxide, when the bedrock is free of carbonates and other C-sources, the $\delta^{13}C$ of CO_2 determines the $\delta^{13}C$ of groundwater because of the quick exchange between CO_2 and water. Under these conditions, water of pH = 7.0 and T = 10°C equilibrated with $\log P_{CO_2} = -2.19$ contains 0.347 mmol of H_2CO_3 and 11 μmol of HCO_3^- (concentrations calculated by using the PHREEQC code). The content of CO_3^{2-} is negligible. Taking $\delta^{13}C$ of the H_2CO_3 and HCO_3^- species as –24.3‰ and –13.3‰ (isotopic enrichments estimated for T = 10°C) respectively, the $\delta^{13}C$ of water is –23.96 ‰.

In an open system with soil CO_2 at equilibrium with calcite, water of pH = 7.0 and T = 10°C equilibrated both with $\log P_{CO_2} = -2.19$ and calcite, contains 0.347 mmol H_2CO_3, 3.557 mmol HCO_3^-, and 4 μmol CO_3^{2-}. Taking $\delta^{13}C$ for the H_2CO_3 and HCO_3^- species as –24.3‰, –13.3‰, and –15.5‰ respectively, the $\delta^{13}C$ of water is –14.3‰.

In the case of calcite dissolution in a closed system with CO_2, dissolved inorganic carbon (DIC) originated in equal amounts from both CO_2(g) and $CaCO_3$(s). At initial $\log P_{CO_2} = -2.19$, the concentrations of DIC species in equilibrium with calcite are: 3.6 μmol H_2CO_3, 709 μmol HCO_3^- and 14 μmol CO_3^{2-}. Therefore, for instance, dissolution of marine carbonates ($\delta^{13}C$ ≈ 0‰) results in $\delta^{13}C$-DIC ≈ –6.7‰.

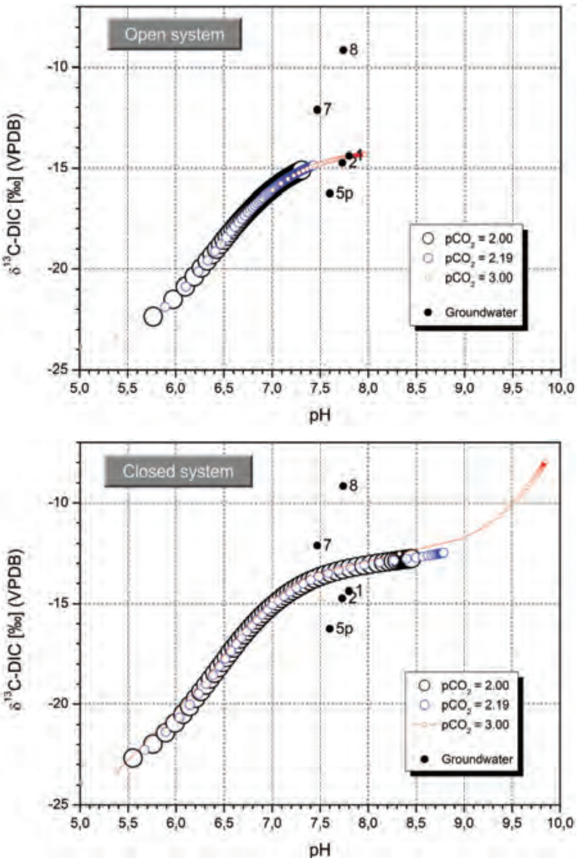
The $\delta^{13}C$-DIC values given above for open and closed systems with calcite dissolution should be regarded as rough ones only because they take into account the final species activities at equilibrium with calcite, and not the effects of fractionation during dissolution kinetics of calcite.

At isotopic equilibrium, the isotopic compositions of the C-species are interrelated by temperature-dependent fractionation factors. The isotopic composition of the DIC is the weighted mean of isotopic composition of the C-solutes.

The evolution of $\delta^{13}C$-DIC during kinetic dissolution of calcite in open and closed systems with different pCO_2 values was calculated as reaction path models by using the PHREEQC code. Calculation was performed for 15°C (temperature close to the temperature of sulphate waters in well 5p), by using the following functions of fractionation factors between gaseous CO_2 and C-solutes: $\varepsilon^{13}C_{CO_{2(aq)}/CO_{2(g)}} = -1.31 + 0.0049\,t$ (Zhang *et al.* 1995); $\varepsilon^{13}C_{HCO_3^-/CO_{2(g)}} = -0.0954\,t + 10.41$ (Szaran 1997); $\varepsilon^{13}C_{CO_3^{2-}/CO_{2(g)}} = 9802/T - 27.121$ (Leśniak and Zawidzki 2006); where t and T is temperature in degrees Celsius and Kelvin respectively. In the calculation, the following values were assumed: $\delta^{13}C$ = –23‰ for soil CO_2, and $\delta^{13}C$ = –1.8‰ for dissolving carbonate ($CaCO_3$). $\delta^{13}C$ = –1.8‰ was taken as a mean $\delta^{13}C$ value of the carbonate rocks in the study area (see Table 7; chapter Model for sulphate mineral groundwater). The evolution of $\delta^{13}C$-DIC during the dissolution of calcite, at different CO_2 contents, in both open and closed systems is shown in Text-figs 9A,B.

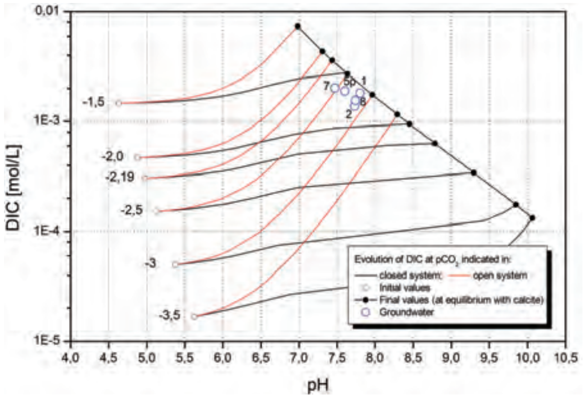
Groundwater from wells 1 and 2 fits well with the simulated evolution path for an open system (Text-fig. 9A). The strongest effects of open system conditions are the most probable in these wells. Well 2 has a free water table, and well 1 shows the effects of water inflow from the Ścinawka River. The $\delta^{13}C$-DIC in both wells suggests that the initial CO_2 pressure in the real system might be lower than the pCO_2=2.19 assumed, but higher than pCO_2=3.0.

The stable carbon isotopes in the remaining wells (7, 8, 5p) do not satisfy the open system conditions. In groundwater from these wells, there is inflow of the deeper component of sulphate mineral water (see chapter Origin of groundwater chemistry). The shifting of groundwater from wells 7 and



Text-fig. 9. Evolution of δ^{13}C-DIC in groundwater during equilibration with calcite, under conditions of open (Text-fig. 9A) and closed (Text-fig. 9B) systems, at different CO_2 contents. Well number indicated

8 towards heavier isotopic composition is probably caused by the effects of a closed system and the dissolution of carbonates isotopically heavier than $\delta^{13}C = -1.8$‰ assumed for the calculation. The δ^{13}C-DIC in the sulphate water from well 5p is surprisingly low compared to that in other groundwater. Since the proportion of the modern, fresh water component in the groundwater from well 5p is the lowest (only about 35%; chapter Modelling of the effects of groundwater mixing), the shift towards a lighter isotopic composition can probably be related to the chemistry of a deeper, sulphate water component. In sulphate mineral water the lowest redox potential and the presence of hydrogen sulphide have been found (Table 3). According to the results of inverse geochemical modelling (see chapter Sulphate mineral water) sulphate mineral water occurs in the conditions of a closed system with respect to CO_2, and the source of the hydrogen sulphide is a reduction of sulphate ions with the participation of organic matter dispersed in bedrocks. Release of

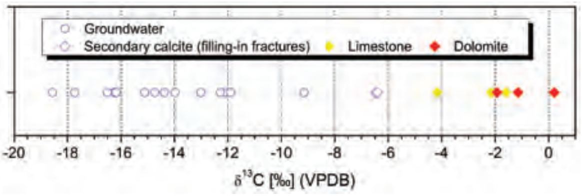


Text-fig. 10. Evolution of DIC concentration in groundwater during equilibration with calcite, under conditions of open and closed systems, and different CO_2 concentrations. Well number indicated

isotopically light carbon into solution due to organic matter oxidation might be responsible for lightening the isotopic composition of the carbon isotopes in the sulphate mineral water.

Comparison of DIC concentration in groundwater with PHREEQC-simulated evolution paths at different CO_2 pressures does not yield an unequivocal pattern (Text-fig. 10). This surely results from the mixing of present-day fresh water with deeper mineral water. Assuming the conditions of an open system in the active zone of wells 1 and 2, the initial CO_2 amount should be about $pCO_2 = -2.8$, which is consistent with the δ^{13}C-DIC pattern (Text-fig. 9A). The pattern of DIC in other wells (7, 8, 5p) pinpoints the initial pCO_2 at about –1.75. This value is much higher than that assumed from the empirical formula of equation (1).

In the groundwater studied, δ^{13}C ranges from –18.6‰ to –9.2‰ (Table 4, Text-fig. 11), usually between –16.5‰ and –12‰. These values in the exploited groundwater correspond to conditions that are intermediate between open and closed systems with respect to CO_2. The heaviest carbon isotopic composition, near to the closed system conditions, is found in the groundwater of well 8. The lightest composition of δ^{13}C, in the groundwater sample from well



Text-fig. 11. Stable carbon isotopic composition of DIC in groundwater and carbonate mineral phases. Isotopic composition of the carbonates is given in Table 7

1 (March 2005; Table 4), is undoubtedly caused by seasonal inflow of infiltrating water. This sample was taken soon after the snowmelt event.

The wells sampled (2, 1, 7, 8, 5p) are not located on the same flow path. Chemical and isotopic patterns found in the groundwater are interpreted in this study as the effect of the mixing of two groundwater components. The first component is assumed to be fresh water of composition affected by present-day recharge. It contains, e.g., tritium, a high radiocarbon concentration and modern atmospheric sulphates. The second component is an older sulphate-rich mineral water. It has lower radiocarbon activity, gypsum-originated sulphate, and is probably tritium-free. This thesis will be discussed in detail further below.

SPECIATION/SOLUBILITY GEOCHEMICAL MODELLING

The chemical composition of the water from wells 2, 1, 7, 8 and 5p (Table 3) was used in the geochemical modelling. The speciation/solubility calculation is an integral part of geochemical modelling. Speciation modelling provides information on species activity and the distribution of chemical elements amongst aqueous species (solutes). The saturation state of water with respect to solid and gaseous phases is calculated based upon species activity.

An increase in groundwater salinity southwards, from well 2 to well 5p, leads to changes of saturation indexes, SI (Table 5). Positive SI values indicate a tendency to-

	Wells				
Phase	2	1	7	8	5p
K-feldspar	-0.424	0.323	0.068	–0.471	0.534
Albite	–2.202	–1.293	–1.533	–0.664	0.014
Anorthite	–3.911	–2.859	–3.184	–2.694	–1.205
Muscovite	6.436	8.017	7.866	6.232	9.254
Biotite (phlogopite)	–7.597	–5.397	–8.410	–5.947	–6.366
Kaolinite	3.377	4.324	4.370	3.588	5.244
Chlorite	–6.712	–3.655	–8.081	–2.677	–3.605
Gypsum	–2.169	–1.549	–1.168	–0.611	–0.288
Celestite	–3.059	–2.132	–1.438	–0.252	–0.198
Barite	0.477	0.406	0.443	0.187	0.075
Calcite	–0.452	–0.138	–0.229	0.189	0.243
Dolomite	–1.522	–0.695	–1.349	–0.286	–0.500
Rhodochrosite	–2.831	–2.454	–1.710	–0.693	–0.671
Smithsonite	–2.734	–2.647	–2.730	–3.035	–1.371
Witherite	–3.229	–3.620	–4.050	–4.402	–4.784
Strontianite	–2.511	–1.879	–1.661	–0.647	–0.861
Siderite	–4.781	–4.142	–3.439	–3.193	–0.212
Pyrite	n.c.	n.c.	22.809	22.373	16.634
Ferrihydrite	1.382	1.815	1.660	2.190	0.558
Goethite	6.758	7.116	6.993	7.730	6.092
Fluoride	–2.973	–2.897	–2.709	–4.659	–4.551
Halite	–8.887	–8.456	–8.961	–9.558	–9.213

n.c. – not calculated by PHREEQC due to the lack of sulphide solute in groundwater.

Table. 5. Saturation index (SI) of groundwater with respect to selected mineral phases. Calculation executed by using the PHREEQC code with *wateq4f.dat* database, upon updated hydrochemical data given in Table 3 wards dissolution of the phases and negative values signify theoretical conditions for precipitation of the phases, or ingassing and outgassing in the case of gases.

The saturation state of water with respect to sulphate-bearing minerals (gypsum, celestite, and barite) approaches equilibrium, while the concentration of sulphate ion increases. The saturation state with respect to Mg, Fe, Mn, Zn-bearing carbonates increases but the groundwater is still undersaturated with them. Releasing significant amounts of calcium and carbonate into solution brings about supersaturation of the groundwater with calcite. Plagioclases, biotites and chlorites which occur in sedimentary bedrock present an undersaturation state.

Saturation indexes for the most reactive mineral phases which occur in the bedrock were used in the construction of the conceptual geochemical models.

CONCEPTUAL MODELS OF INVERSE MASS BALANCE FOR FRESH AND MINERAL GROUNDWATER

The origin of the groundwater chemistry has been deciphered by means of geochemical modelling and isotopic investigations. For both groundwater components (fresh water and mineral water) separate conceptual inverse mass balance models were constructed (Table 6). The fundamentals of mass balance modelling have been described, e.g., by Plummer *et al.* (1983); Plummer (1985); Parkhurst and Plummer (1993). Inverse mass balance modelling deduces the mass transfer reactions that take place between two genetically-connected water samples that might have been responsible for the differences of chemical (and isotopic) composition between them. The chemistry of input and output water is required in inverse mass balance modelling. Usually samples originate from observation points along a flow path and illustrate the evolution of the groundwater chemistry. The correct model balances changes of water composition noted between input water and output water.

Data on bedrock mineralogy (Mastalerz and Nehyba 1997; Bossowski 1996, 1997), saturation indexes (Table 5) and isotopic data (Table 4) were the basis for the assumptions used to construct the conceptual models. Details of both mass balance models are described below.

Model for fresh groundwater

The groundwater from well 2 has the lowest mineralization of all the wells studied, and only in this well is the water table free. The groundwater from well 2 was assumed to be representative of fresh water in the recharge zone. Modelling between precipitation (input water) and groundwater in well 2 (output water) was performed to elucidate the origin of the fresh groundwater chemistry. The inverse mass balance model for fresh water, given previously by Dobrzyński (2008), is extended in the present study.

The weighted mean chemical composition of wet deposition in the study area was taken from Dobrzyński (1997). As a first step, the chemistry of wet deposition was equilibrated with present atmospheric CO_2. Gaseous (CO_2, O_2, N_2) and a wide set of solid phases are included in the conceptual model. Dissolution of calcite, dolomite and gypsum has been taken into account. Dissolution of carbonates was assumed to be the main source of trace elements (Fe, Mn, Zn, Ba, Sr) in the groundwater, and these elements were considered in the model as pure end-member solid phases (siderite, rhodochrosite, smithsonite, witherite, strontianite). Siderite was assumed as an iron source phase, because the groundwater in well 2 is undersaturated with respect to the mineral (SI = –4.78, Table 5) and at the same time supersaturated with respect to iron (oxy)hydroxides, like goethite, FeOOH or ferrihydrite, $Fe(OH)_3$, SI = 6.76 and 1.38 respectively. In the inverse model for fresh water (Dobrzyński, 2008), dissolution of strontium-bearing gypsum was considered as a Sr source, and included in the model as a strontium sulphate, celestite. Well no. 2 abstracts water from conglomerates and sandstones of the Lud-

Inverse mass balance model	Relation
Model for fresh groundwater	Weighted mean chemical composition of precipitation (equilibrated with atmospheric CO_2) $\Downarrow$ Chemical composition of fresh groundwater (from well 2)
Model for sulphate mineral groundwater	Chemical composition of fresh groundwater (from well 2) $\Downarrow$ Chemical composition of groundwater from sulphate horizons (in well 5p) equilibrated with gypsum

Table 6. Scheme of inverse mass balance models

wikowice Member. The recent chemical study of gypsum sample from these rocks (from cores of the deep borehole Unisław Śląski IG-1 located in Rybnica Leśna; see Text-fig. 1) showed that the gypsum analyzed is actually strontium-free. It contains only about 0.03% mol. of Sr (Przychodzka, personal communication). In the present geochemical modelling, a carbonate phase (strontianite) is included as a potential Sr-source phase. In the real geochemical system, some amounts of Sr and Ba might also originate from dissolution of alkali feldspars, but carbonates were recognised as more reactive phases than feldspars.

The assemblage of plausible solid phases included in the model comprises carbonate (calcite, dolomite, siderite, smithsonite, rhodochrosite, witherite, strontianite), sulphate (gypsum), silicate (albite, chlorite, illite, kaolinite) and halogen (halite, fluorite) minerals. Halite and fluorite play the role of hypothetical phases only, and were used for balancing chlorides and fluorides originated from the atmospheric deposition. The role of Cl and F from source mineral phases in the soil and the bedrock, and from local chloride and fluoride contamination sources, seems to be negligible in the study area (Dobrzyński 2008).

Model for sulphate mineral groundwater

The groundwater from the sulphate horizons in well 5p is the most evolved in the area. The main characteristic of this water is a high sulphate content caused by gypsum dissolution (Dobrzyński 2007a,b). However, the sulphate groundwater is still slightly undersaturated with gypsum (SI= –0.29; Table 5). At the same time, the groundwater contains measureable tritium (Table 4). Tritium activity in the sulphate horizons increased during the pumping test (Table 4), which confirmed the influence of fresh water recharge in the active zone of well 5p. It was assumed that the sulphate groundwater from the horizons screened was a mixture of sulphate mineral groundwater with fresh groundwater components. The presence of both hydrogen sulphide and oxygen dissolved in the sulphate groundwater (Table 3) also confirms the concept of mixing in the active zone of well 5p.

Studies by Liu and Nancollas (1971) showed that gypsum dissolution proceeds quickly. In saturated conditions, dissolution of gypsum and reaching saturation state is mainly determined by the flow velocity (Kuechler *et al*. 2004). Mazor (1992) stated that groundwater might reach equilibrium with gypsum in as short a time as a month. Reaching the chemical equilibrium at a time-scale of tens or hundreds of years certainly seems to be possible, and the sulphate water component occurring in the hydrogeological system studied is considered to be at equilibrium with respect to gypsum.

Inverse geochemical modelling for the sulphate mineral water was performed between recharge fresh groundwater (input water) and sulphate groundwater (output water). The chemical composition of the groundwater from well 2 was taken as representative of fresh groundwater recharging the system. The chemistry of the groundwater from the sulphate horizons (in well 5p) was equilibrated with gypsum, and in this way modified composition assumed as composition of output water in the inverse geochemical modelling.

Solid, gas and exchange phases are included in the mass balance model. Similarly to the model for fresh groundwater, dissolution of gypsum and Mg, Fe, Mn, Zn-bearing carbonates was included. The sulphate mineral groundwater is supersaturated with respect to calcite (Table 5), and the mineral is assumed to be precipitating. Barite is supersaturated and its precipitation can cause a small decrease in barium concentration in groundwater. Both sulphate and carbonate minerals were considered as source phases for strontium, and the roles of both celestite and strontianite were taken into account in the geochemical model. Alkali feldspars are supersaturated and are not included in the model. Of silicate phases, biotite (phlogopite), chlorite and kaolinite were included in the model. Dispersed organic matter occurs at low amounts in the bedrock and is incorporated into the model as CH_2O. The sulphate mineral water contains hydrogen sulphide (Table 3) and is supersaturated with pyrite (Table 5). The mineral is considered as a possible sink phase for iron released from siderite. Ion exchange between sodium (adsorbed onto clay minerals) and calcium solute is assumed to be a sodium source, as in the preliminary inverse model for sulphate water (Dobrzyński 2007a). Precipitation of halite and fluorite is not thermodynamically possible (Table 5), but both minerals are incorporated as sink phases for explaining the decrease in chloride and fluoride respectively.

Isotopic data on aqueous and solid phases have also been included in the model of the sulphate mineral water for balancing the chemical reactions. Inclusion of isotopic data provides an additional criterion for testing and validating the mass balance model.

The isotopic compositions of C- and S-bearing phases included in the model were taken from the author's own data and from cited data. From data acquired during the present study (Table 4), the isotopic

Sample number	Description	Lithostratigraphic Member	δ^{13}C VPDB [‰]	δ^{18}O VPDB [‰]
1	Limestone	Krajanów	–4.17	–11.69
2	Dolomite	Krajanów	–1.14	3.83
3	Limestone	Krajanów	–2.14	–5.09
4	Dolomite (with calcite)	Zagórzyn	–1.93	–0.28
5	Dolomite	Zagórzyn	0.21	1.81
6	Limestone (with traces of dolomite)	Zagórzyn	–1.58	–8.89
7	Calcite (fracture fillings)	Zagórzyn	–6.48	–9.49
8	Calcite (fracture fillings)	Zagórzyn	–6.40	–8.37

Samples nos. 1 and 2 were taken from outcrops by railway tunnel in Unisław Śląski; sample no. 3 from outcrop south of the well no. 7; and samples nos. from 4 to 8 from abandoned mine tunnel, located south of Rybnica Leśna village. For location see Text-fig. 1.

Table 7. Stable isotope data (δ^{13}C, δ^{18}O) on carbonate solids

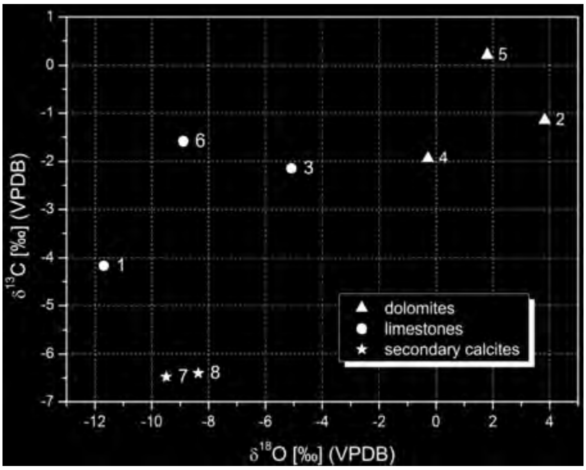
composition for δ^{34}S-SO$_4$ and for δ^{13}C-DIC in fresh water (well 2) and sulphate water equilibrated with gypsum (well 5p) were taken +8‰ and +13.9‰, and –14.7‰ and –9‰ respectively.

The carbon stable isotope ratio was determined in carbonates (dolomites, limestones, calcites) sampled at outcrops of different lithostratigraphic members in the study area (Table 7). The X-ray diffraction analysis of the carbonates revealed that two samples (nos. 7 and 8) represent almost pure calcite, whereas others samples correspond to limestones and dolomites with variable contribution of calcite and dolomite. The chemical composition of the carbonates is discussed below in chapter "Results of inverse modelling for sulphate mineral water against chemical composition of carbonates". The dolomites and limestones studied have δ^{13}C values of about 0‰ to –2‰, and –1.6‰ to –4.2‰ respectively. Neoformed calcite fill-in fractures is isotopically lighter (δ^{13}C ≈ –6.4‰) than carbonate rocks (dolomites, limestones). Small fractionation (≈ +1‰) between HCO$_3^-$ and CaCO$_3$(s) occurs during calcite precipitation (e.g., Clark and Fritz 1997). Assuming that the prevalent carbon solutes were bicarbonates, the groundwater from which neoformed calcite had been precipitated probably had δ^{13}C-DIC ≈ –7.5‰. This value is slightly heavier than the heaviest δ^{13}C-DIC found in the groundwater (Table 4).

The δ^{13}C of the lacustrine limestones and dolomites studied is slightly negative (usually between –1‰ and –2‰; Table 7, Text-fig. 12) and lighter than typical for marine carbonates. Due to dolomite-calcite fractionation control, calcites are typically more impoverished in ^{13}C than dolomites (Clark and Fritz 1997). Substitution of an atom of lower mass (like Mg^{2+}) by Ca^{2+} in the structure of a carbonate mineral favours the enrichment of the carbon isotope of greater mass in the solid phase (e.g. ^{13}C versus ^{12}C in the carbonate anion). The difference in δ^{13}C between the dolomites and limestones studied (≈2‰) is similar to published data, e.g., Sheppard and Schwarcz (1970) calculated that in a dolomite-calcite system, dolomite is enriched in ^{13}C by about 2.4‰, at 20°C.

Dolomites and limestones in the study area were deposited in a lacustrine environment under an arid climate. Carbon and oxygen isotope compositions of carbonates precipitated in lakes, which represent a closed system, usually show strong correlations (Hoefs 1997). Lightening the carbon isotope composition is accompanied by, usually stronger, lightening of the oxygen isotope composition. An analogous pattern is seen in dolomites and limestones from the study area (Table 7, Text-fig. 12).

In the conceptual model, the δ^{13}C values for dissolving carbonates (mainly dolomite) and for precipitating calcite were taken –0.5‰ and –6.4‰,



Text-fig. 12. Carbon vs. oxygen isotopic composition of carbonate mineral phases. Sample numbers as in Table 7. For location of samples see Text-fig. 1

respectively. The $\delta^{13}C$ for organic matter (CH_2O) was assumed of –25‰.

The presence of gypsum has been noted in Carboniferous–Permian sedimentary rocks from the study of cores from deep boreholes in the Intra-Sudetic Synclinorium (Bossowski 1996, 1997; Mastalerz and Nehyba 1997). Gypsum has been also observed in cores from water wells in Unisław Śląski and Sokołowsko. In well no. 5p (in Sokołowsko), gypsum mineralization was commonly found in screened water-bearing horizons of fractured mudstones of the Zagórzyn Member (Dąbrowski and Szafranek 1982). Unfortunately, core samples from the water wells studied are unavailable, because all cores have been lost and/or destroyed. From the author's observation in the study area, gypsum is absent from field outcrops as well as in the abandoned mine tunnel (in the village of Rybnica Leśna; Text-fig. 1).

At present, the only available sample of gypsum from the study area comes from cores of conglomerates and sandstones of the Ludwikowice Member in the Unisław Śląski IG-1 borehole. Isotopic analysis of this gypsum sample revealed $\delta^{34}S$ of +11.30(±0.05)‰ (vs. VCDT), and $\delta^{18}O$ of +12.56(±0.08)‰ (vs. VSMOW). There are no data on the isotope composition of other terrestrial gypsum samples from Permian-Carboniferous strata in the Sudetes for comparison. The gypsum studied formed under terrestrial conditions. It has an isotopic composition lighter than that of marine evaporites of the same age. The Stefanian–Autunian marine evaporites usually have $\delta^{34}S$ values from about +14.5‰ to +12.5‰ (Claypool *et al.* 1980; Strauss 1997). The $\delta^{18}O$ value of the gypsum studied is similar to the range of $\delta^{18}O$ values for Permian marine gypsum (e.g., Claypool *et al.* 1980; Cortecci *et al.* 1981).

The $\delta^{34}S$ value obtained from the gypsum is not consistent with the isotopic composition of gypsum (≈+13.3‰) inferred from the aqueous chemistry. The divergence might be caused by the fact that the gypsum originates from different strata (Ludwikowice Member, Stefanian) from those in which the sulphate mineral water occurs (Zagórzyn Member, Autunian).

In the inverse mass balance model, $\delta^{34}S = +14‰$ was taken for gypsum, and for celestite, both minerals dissolving, as similar to the heaviest $\delta^{34}S\text{-}SO_4$ values found in the groundwater (Table 4, Text-fig. 7). Crystallization of sulphate minerals gives a small sulphur fractionation, of +1‰ to +2‰, at an average +1.65‰ (±0.12‰) (Claypool *et al.* 1980). For precipitating barite, $\delta^{34}S = +15.5‰$ was assumed in the model.

Saturation state (Table 5) indicates that conditions favourable to pyrite precipitation occur in environment of the sulphate mineral water. The isotopic composition of dissolved sulphide hydrogen has not been determined, due to the low H_2S concentration. The $\delta^{34}S$ value of pyrite has been estimated from the inferred isotopic composition of sulphide hydrogen.

Sulphide hydrogen in the groundwater studied probably results from biologically mediated sulphate reduction in the presence of organic matter, according to the reaction:

$$SO_4^{2-} + 2CH_2O = 2HCO_3^- + H_2S \qquad (2)$$

Sulphur isotopes are strongly fractionated by biological processes, particularly during the dissimilatory bacterial reduction of sulphate to sulphide. The difference in $\delta^{34}S$ values between dissolved sulphate and dissolved sulphide depends on the isotopic composition of the sulphate source (most often gypsum in bedrock), the fractionation factor and the Rayleigh distillation process. Bacterial sulphate reduction in the groundwater studied occurs under closed system conditions (one can assume that sulphide remains with the sulphate mineral groundwater), however, due to the excess of the sulphate source phase (gypsum occurs in the bedrock), the Rayleigh distillation model cannot be applied. Bacterial sulphate reduction ($SO_4 \Rightarrow H_2S$) dominates in most groundwater systems, and the enrichment ($\varepsilon^{34}S_{SO_4\text{-}H_2S}$) usually varies between –20‰ and –40‰ (Clark and Fritz 1997).

The presumable effect of kinetic fractionation during sulphate reduction in the groundwater studied was estimated using the separation parameter $^{34}\Delta$ after Pearson and Rightmire (1980):

$$^{34}\Delta = \delta^{34}S_{SO_4} - \delta^{34}S_{H_2S} \qquad (3)$$

The empirical formula after Plummer *et al.* (1990) was applied for calculation of isotope separation:

$$^{34}\Delta = 54 - 0.40\,t \qquad (4)$$

where, t is temperature in Celsius degrees.

In the sulphate groundwater, at a temperature of 15.3°C, $^{34}\Delta$ equals 47.9‰, and, at $\delta^{34}S\text{-}SO_4 = 13.9‰$, the $\delta^{34}S$ of H_2S is of –34‰. Pyrite formation produces minimal isotopic fractionation (Krouse and Mayer 2000). Precipitation of pyrite by reaction of H_2S with an iron source results in total fractionations less than 3‰ (Price and Shieh 1979; Bottcher *et al.* 1998). It was assumed that the $\delta^{34}S$ value of pyrite was –31.5‰.

ORIGIN OF GROUNDWATER CHEMISTRY

Fresh groundwater

Inverse geochemical modelling allowed for defining the processes responsible for fresh groundwater chemistry in the recharge zone. Two geochemical models (Table 8) were previously found (Dobrzyński 2008).

	Models after Dobrzyński (2008)		Models after the present study	
Phases	Model 1	Model 2	Model 3	Model 4
	Mole transfers			
CO_2(g)	7.634E-04	5.837E-04	7.634E-04	5.837E-04
O_2(g)	3.031E-04			
N_2(g)	6.534E-05			
Calcite	4.952E-04	2.966E-04	4.933E-04	2.947E-04
Dolomite	–	1.891E-04	–	1.891E-04
Siderite	8.955E-08			
Rhodochrosite	9.103E-09			
Smithsonite	2.448E-07			
Witherite	n.i.		9.249E-07	
Strontianite	n.i.		9.817E-07	
Gypsum	2.760E-04		2.770E-04	
Celestite	9.817E-07		n.i.	
Albite	1.416E-04	1.605E-04	1.416E-04	1.605E-04
Chlorite^1	3.782E-05	–	3.782E-05	–
Illite^1	–3.290E-05			
Kaolinite	–7.198E-05	–4.362E-05	–7.198E-05	–4.362E-05
„Halite”	8.147E-05	7.780E-05	8.147E-05	7.780E-05
„Fluorite”	1.725E-06			

n.i. – phases not included in the model. 1 – Composition of chlorite, $Mg_5Al_2Si_3O_{10}(OH)_8$, and illite, $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_1(OH)_2$ according to *wateq4f.dat* thermodynamic data base.

Table 8. Inverse geochemical models with minimum number of phases found for fresh groundwater in recharge zone after Dobrzyński (2008) and this study

Two other models are proposed in the present study. The differences between the models are: (1) the previous models assumed celestite to be potential strontium source phase, whereas the models in the present study consider strontium carbonate (strontia-nite) as the source of strontium, (2) the new models are extended by the incorporation of barium. According to the convention, a positive value of mole transfer corresponds to source phases (increase of solute(s) concentration), while a negative value corresponds to sink phases.

The main features of all the models are actually the same. The chemical composition of fresh groundwater in the recharge area arises from dissolution of carbonate minerals (mainly calcite and dolomite), gypsum and silicates (feldspars, chlorites). During incongruent dissolution of silicates, secondary, clay phases are formed (like illite, kaolinite). Dissolution of carbonates might also cause a small increase in Fe, Mn, Zn, Ba, and Sr concentration in the water during infiltration throughout the vadose zone. The models differ mainly in the magnesium source phase. In the first and third models, chlorite is the source of magnesium, whereas in the second and fourth models dolomite is the source. Water in the recharge zone might be slightly affected by the atmospheric deposition, and there are no point-sources of contamination in the recharge zone. Therefore, the chemical reactions from the modelling practically illustrate the natural processes in the bedrock.

Higher mass transfer of dissolving calcite than dolomite from the bedrock of the recharge zone is conceivable. The experimental work of Liu *et al*. (2005) proved that dissolution rates of limestone are higher than those of dolomite by a factor of 3–60.

Of the models found (Table 8), model no. 4 seems to be the most probable. Taking into account that the gypsum is strontium-free, the models including carbonate (strontianite) dissolution as a strontium source (models 3 and 4) are adequate. In sedimentary rocks, strontium is predominantly found in carbonate rocks composed of calcite, aragonite and dolomite (Morse and Mackenzie 1990). Considering the magnesium source, dissolution of carbonates (models 2 and 4) is more plausible, due to higher reactivity, than decay of chlorites (models 1 and 3).

The radiocarbon activity in water from well 2 of 59.39 pmC (Table 4) indicates the present-day age of this groundwater. The mole transfer for the carbon-bearing phases (Table 8) after geochemical modelling of the fresh groundwater (models 1 and 2) was used for esti-

	Model no. 1			Model no. 2		
	Mole transfers			Mole transfers		
	Mean	Minimum[1]	Maximum[1]	Mean	Minimum[1]	Maximum[1]
Gypsum	1.677E-02	1.670E-02	1.711E-02	1.666E-02	1.661E-02	1.702E-02
Celestite	–	–	–	8.861E-05	8.612E-05	9.109E-05
Dolomite	5.193E-04	4.850E-04	5.595E-04	5.484E-04	5.159E-04	5.595E-04
Siderite	5.698E-05	2.697E-05	5.932E-05	4.976E-05	2.696E-05	5.932E-05
Rhodochrosite	2.288E-06	2.225E-06	2.352E-06	2.288E-06	2.225E-06	2.352E-06
Smithsonite	1.588E-05	1.543E-05	1.633E-05	1.588E-05	1.543E-05	1.633E-05
Strontianite	8.861E-05	8.612E-05	9.109E-05	–	–	–
Calcite	–1.150E-03	–1.239E-03	–1.065E-03	–1.108E-03	–1.148E-03	–1.017E-03
Barite	–8.443E-07	–8.696E-07	–8.190E-07	–8.443E-07	–8.696E-07	–8.190E-07
Pyrite	–4.524E-05	–4.724E-05	–1.555E-05	–3.801E-05	–4.724E-05	–1.554E-05
Chlorite	8.952E-06	5.382E-06	1.684E-05	6.838E-06	5.381E-06	1.201E-05
Phlogopite	1.030E-05	8.542E-06	1.206E-05	1.136E-05	8.746E-06	1.206E-05
Kaolinite	–1.334E-05	–2.037E-05	–1.063E-05	–1.176E-05	–1.565E-05	–1.063E-05
N2(g)	–6.174E-05	–6.347E-05	–6.001E-05	–6.174E-05	–6.347E-05	–6.001E-05
CH2O	4.754E-04	3.779E-04	4.896E-04	4.501E-04	3.779E-04	4.896E-04
NaX [2]	5.577E-03	5.410E-03	5.744E-03	5.577E-03	5.410E-03	5.744E-03
CaX2 [2]	–2.788E-03	–2.872E-03	–2.705E-03	–2.788E-03	–2.872E-03	–2.705E-03
„Halite” [3]	–1.951E-04	–2.003E-04	–1.900E-04	–1.951E-04	–2.003E-04	–1.900E-04
„Fluorite” [3]	–2.631E-06	–2.710E-06	–2.551E-06	–2.631E-06	–2.710E-06	–2.551E-06

1 – minimum and maximum mole transfers at 2.5% and 2.75% uncertainties assumed in geochemical modelling for input and output waters, respectively; 2 – X indicates the ion exchange phase (sorption complex); 3 – hypothetical phases used for balancing chlorides and fluorides of atmospheric origin

Table 9. Inverse geochemical models with minimum number of phases found for sulphate mineral water

mating the hypothetical radiocarbon activity in the water from well 2 (Dobrzyński 2008). The calculated radiocarbon activity in the groundwater of well 2 is 64.66 pmC (model no. 1, with chlorite) and 59.75 pmC (model no. 2, with dolomite). The second value agrees well with the ^{14}C activity measured in the groundwater. Therefore, the model with dolomite dissolution can be regarded as the more plausible for the real geochemical system. The consistency of calculated ^{14}C activity with measurement in the aquifer is a test of the correctness of the mass balance geochemical model for fresh groundwater in the recharge zone of the system.

Carbonates (calcite, dolomite) occur in the bedrock of the recharge zone. However, water from well 2 still shows slight undersaturation with respect to calcite (SI= –0.452; Table 5). Carbon evolution in groundwater in the recharge zone involves dissolution of soil CO_2 and dissolution of carbonate minerals (mainly calcite):

$$H_2O + C\,O_{2(soil)} + CaCO_{3(s)} = Ca^{2+} + 2HCO_3 \quad (5)$$

Assuming that the dissolving carbonates are ^{14}C-free and soil CO_2 has ^{14}C of ≈100 pmC, under conditions of a system closed to soil CO_2, the ^{14}C activity of DIC should amount to ≈50 pmC. Radiocarbon activity of 59 pmC and slight undersaturation with calcite in the groundwater from well 2 indicates that the groundwater in the active zone of this well represents the conditions of a system not fully closed (semi-closed) to the soil CO_2. It should be emphasized that undoubtedly a degree of the opening of the groundwater system in the recharge zone with respect to CO_2 might be changing seasonally.

Sulphate mineral water

From the inverse mass balance calculation (between fresh water and sulphate mineral water) using updated hydrochemical data and isotopic data two models have been found (Table 9). According to both models, the main chemical features of the sulphate mineral water occurring in the area of Sokołowsko are controlled by gypsum dissolution, dedolomitizaton and calcium common-ion effects.

The congruent dissolution of gypsum releases calcium and sulphates into the water. It drives incongruent dissolution of carbonates (mainly dolomite) with intercurrent calcite precipitation. Calcite precipitation is enhanced by the calcium common-ion effect and dissolution of both gypsum and dolomite. Cation exchange between calcium solute and sodium in the sorption complex seems to be responsible for the increase of sodium in the sulphate water. The quantity of Ca^{2+} cation exchange (2.788E-03 mol), in a confined part of the system, consumes 16.1% of the calcium released from the dissolution of gypsum and dolomite (1.7289E-02 mol). The calculated value of the cation exchange might be slightly overestimated because, in the real geochemical system, part of the sodium might also originate from dissolution of carbonate minerals. Calcites and dolomites of different ages (from Lower Palaeozoic to Recent) usually contain 140–180 ppm of sodium (White 1978).

Sulphate solutes are reduced by bacterial mediation with the decomposition of organic matter, and a small amount of iron sulphide probably forms. Sulphate reduction is a neutral to alkaline reaction, which raises pH and additionally contributes to calcite supersaturation.

The models differ in the source phase for strontium. Model 1, with carbonate dissolution as a source of strontium, probably better fits the sulphate mineral water. Study of the gypsum chemistry revealed that the mineral is very poor in strontium (ca. 0.03% mol.). The author's investigation of carbonate chemical composition shows that carbonates from the study area contain about 0.5% of Sr (Table 10). Dissolution of carbonates is assumed to be a source of Fe, Mn, Zn, and Sr solutes in the sulphate groundwater.

Transformation of dolomite into calcite is commonly observed in bedrocks, and was also interpreted in terms of the low-temperature transformation as the result of the bedrock reaction with calcium sulphate solutions (e.g., Braddock and Bowles 1963). This process requires the presence of a $CaSO_4$ source phase and results in groundwater chemistry dominated by sulphates, calcium and magnesium solutes. The effects of chemical interactions and evolution in the system calcite-gypsum-water were clearly presented by Wigley (1973).

The results of the present geochemical modelling are consistent with the dedolomitization model of Back *et al.* (1983). Dissolution of sulphates (gypsum, anhydrites) brings about an increase in the Ca^{2+}/Mg^{2+} ratio in the solutions. This causes the dolomite to be no longer in equilibrium with water in the pores of the rock matrix, resulting in dissolution of dolomite and an increase in the magnesium concentration of waters. The concentration of both Ca^{2+} and CO_3^{2-} increases and the solution becomes supersaturated with respect to calcite, causing precipitation of the mineral.

Dedolomitization driven by gypsum dissolution is a well recognized process, especially in carbonate aquifer systems containing evaporite sulphates (gypsum, anhydrite) (Hanshaw and Back 1979). This process has been documented in several aquifers on a regional scale, e.g., Yucatan, Mexico (Plummer and Back 1980), Sherwood Sandstones aquifer, England

Sample number[1]	Description	Ca	Mg	Fe	Mn	Sr	Zn	Ba
1	Limestone	107775.10	4884.37	14214.51	3429.03	5099.65	40.24	16.05
2	Dolomite	162386.10	87712.20	33912.70	20106.65	4899.24	73.47	28.79
3	Limestone	278153.63	8765.02	4894.55	5610.82	5019.96	23.90	0.25
4	Dolomite	103470.12	20759.60	1507.04	2676.97	5209.47	10.57	103.32
5	Dolomite	52852.24	6953.21	25773.40	891.23	4961.00	2226.59	19.44
6	Limestone	156161.90	9908.75	25872.60	2819.95	4954.37	2021.38	8.56
7	Calcite	288446.40	6324.16	1794.16	5205.05	5019.80	14.25	0.25
8	Calcite	378380.92	9141.58	5247.64	9748.42	4968.25	111.29	0.94
	Carbonates[2]	302300	47000	3800	1100	610	20	10

1 – location of samples and lithostratigraphic members given in Text-fig. 1 and Table 7. 2 – average concentration of elements in carbonate rocks after Veizer (1983)

Table 10. Chemical composition of carbonates [in ppm]

(Edmunds *et al*. 1982), Madison aquifer (Plummer *et al*. 1990; Busby *et al*. 1991), Floridan aquifers (Wicks and Herman 1994; Sacks and Tihansky 1996), Beuda and Perafita Formations, Spain (Bischoff *et al*. 1994), Baza aquifer, Spain (Hidalgo and Cruz-Sanjulian 2001).

In the study area, similar significant effects of gypsum dissolution and dedolomitization on groundwater quality have been found on a much smaller, local scale.

Results of inverse modelling for sulphate mineral water against chemical composition of carbonates

In the inverse model for sulphate water, the presence of trace elements in dissolving carbonate phases are considered as pure end-member phases (siderite, rhodochrosite, smithsonite, strontianite). Mean mole transfers of dissolving carbonates (after model 1; Table 9) were used for calculating the contribution of trace elements (Fe, Mn, Zn, Sr) in dissolving a hypothetical carbonate phase. Afterwards, the calculated cumulative composition was compared with chemical analyses of carbonates from the study area. The results of calcium, magnesium, iron, manganese, strontium, zinc and barium determination in the carbonates are given in Table 10.

Model 1 (Table 9) provides dissolution of carbonate (dolomite, siderite, rhodochrosite, smithsonite, and strontianite) phases. The cumulative chemical composition of a hypothetical carbonate phase calculated after the mole transfers of the carbonate minerals mentioned above is as follows: $(Ca,Mg)_{0.864}Sr_{0.074}Fe_{0.047}Zn_{0.013}Mn_{0.002}CO_3$. Mole transfers suggest high contributions of strontium and iron in dissolving carbonates. The calculated proportions of all trace elements are probably somewhat overestimated. In the real geochemical system, part of the iron, zinc and manganese might also result from decay of biotites and/or chlorites. Strontium undoubtedly occurs in alkali feldspars but these phases were not included in the model due to the oversaturation of the sulphate water with respect to them (Table 5). A gypsum sample from conglomerates and sandstones of the Ludwikowice Member is actually strontium-free. However, one cannot exclude the possibility that part of the dissolved strontium might originate from gypsum occurring in rocks of other lithostratigraphic members. The sulphate groundwater occurs in the rocks (mudstones and sandstones) of the Zagórzyn Member. Unfortunately, gypsum from these bedrocks cannot to be examined, because the mineral is absent in field outcrops and core material is lacking.

The composition of the hypothetical carbonate ($(Ca,Mg)_{0.864}Sr_{0.074}Fe_{0.047}Zn_{0.013}Mn_{0.002}CO_3$) is the result of dissolution of the end-member carbonates included in the model. Contributions of the trace elements were estimated according to mole transfers, and have an average and a semi-quantitative character. The real mole transfers of dissolving carbonates in a geochemical system mainly depend on magnesium (and trace elements) content in the bedrock carbonates. The lower the content of elements in incongruently dissolving real dolomites (or Mg-bearing calcites), the higher the moles transfer of this phase, and the higher the transfer of precipitating calcite (Dobrzyński 2005).

The compositions of the carbonates sampled in the study area calculated from chemical analyses are presented in Table 11.

The dolomites and limestones in the study area were deposited in periodic lakes under arid climatic conditions. Calcites formed in warm, highly mineralized waters usually contain more Mg than those formed in cold and/or low-mineralized waters (Morse and Mackenzie 1990). It was also observed that mole

Sample number[1]	Carbonate phase	Calculated formula
2	Dolomite	$Ca_{0.466}\,Mg_{0.415}\,Fe_{0.07}\,Mn_{0.042}\,Sr_{0.007}\,CO_3$
5	Dolomite	$Ca_{0.607}\,Fe_{0.212}\,Mg_{0.132}\,Sr_{0.026}\,Zn_{0.016}\,Mn_{0.007}\,CO_3$
4	Dolomite (with calcite)	$Ca_{0.723}\,Mg_{0.239}\,Sr_{0.017}\,Mn_{0.014}\,Fe_{0.007}\,CO_3$
6	Limestone (with traces of dolomite)	$Ca_{0.794}\,Fe_{0.094}\,Mg_{0.083}\,Sr_{0.012}\,Mn_{0.011}\,Zn_{0.006}\,CO_3$
1	Limestone	$Ca_{0.823}\,Fe_{0.078}\,Mg_{0.062}\,Mn_{0.019}\,Sr_{0.018}\,CO_3$
3	Limestone	$Ca_{0.919}\,Mg_{0.048}\,Mn_{0.014}\,Fe_{0.012}\,Sr_{0.007}\,CO_3$
8	Calcite	$Ca_{0.930}\,Mg_{0.037}\,Mn_{0.017}\,Fe_{0.009}\,Sr_{0.005}\,Zn_{0.002}\,CO_3$
7	Calcite	$Ca_{0.942}\,Mg_{0.034}\,Mn_{0.012}\,Sr_{0.008}\,Fe_{0.004}\,CO_3$

1 – samples ordered accordingly to the calcium contribution. Location of samples and lithostratigraphic members given in Text-fig. 1 and Table 7

Table 11. Cumulative chemical formula of carbonates

% of $MgCO_3$ strongly influences the co-precipitation of strontium and other co-precipitates.

The chemical composition of the dolomites and limestones ranges widely (Table 10). The rocks are mainly enriched in iron (even up to 21.2% mol. of Fe), manganese, strontium, and zinc. The dolomite and limestone samples actually present an intermediate composition between calcite, dolomite and ankerite. The content of manganese and strontium in the dolomites and limestones ranges from 0.7% mol. to 4.2% mol., and from 0.7 % mol. to 2.6% mol. respectively. The zinc contribution does not exceed 1.6% mol. Veizer (1983) stated that non-marine calcites are usually impoverished in Mg, Sr, Ba and enriched in Zn, Mn, Fe. The results confirm this statement mainly in terms of iron and manganese contents.

The neoformed calcites infilling fractures contain about 3.5% mol of Mg, and overall about 3% mol. of other trace elements. Numerous studies showed that the solubility of Mg-calcite depends on $MgCO_3$ content, and that the most stable are low-Mg calcites of $MgCO_3$ mole fraction between 2% and 3.5% mole $MgCO_3$ (Busenberg and Plummer 1989; Morse and Mackenzie 1990). The composition of the secondary calcites was found to agree well with this statement. The neoformed calcites are poorer in iron, barium and strontium than the other carbonate samples (Tables 10, 11).

Barium and strontium have a larger ionic radius than calcium (Ca^{2+} – 100 pm; Sr^{2+} – 118 pm; Ba^{2+} – 135 pm), and neoformed calcite tends not to incorporate both elements. During the evolution of sulphate water chemistry, concentration of strontium increases because it is not built into secondary phases. Barium probably sinks in precipitating sulphate (barite), and iron in sulphide (pyrite).

Weathering of volcanic material was probably the main source of enrichment of a carbonate rock in Fe, Mn, Sr and Zn. Clasts of sedimentary rocks in the study mainly originated from volcanic material. Fragments of volcanic rocks (rhyodacites, rhyolites, and trachytes), feldspars and chloritized biotite are numerous in sedimentary rocks. Volcanic rocks of the so-called older volcanic suite in the part of the Intra-Sudetic Synclinorium studied contain: Fe (13000–22000 ppm), Mn (80–150 ppm), Sr (75–220 ppm), and Zn (20–40 ppm) (Awdankiewicz 1999b).

The composition of the dissolving hypothetical carbonate (HC) inferred from the geochemical modelling is consistent with the composition of real carbonates (RC), mainly dolomites, in terms of iron and zinc. The Fe content in the HC (4.7% mol.) agrees with the average iron content in the RC, which varies widely (0.7% – 21.2% mol.). The zinc content in the HC (1.3% mol.) agrees with the content in the RC (0% – 1.6% mol.). The calculated content of Sr in the HC (7.4% mol.) is higher than in the RC (0.7% – 2.6% mol.), and indicates that in the real geochemical system part of the strontium might also originate from other phases, like gypsum. The higher contribution of Mn in the RC (0.7% – 4.2% mol.) than in the HC (0.2% mol.) might be explained in various ways. Manganese (with Mn^{2+} ionic radius 89 pm) can be readily immobilized in precipitating calcites. Neoformed calcites contain 1.2 – 1.7% mol of Mn (Table 11). Manganese can also substitute iron in sulphides (pyrites) or be adsorbed onto solids.

Evaluation of changes in bedrock porosity

The processes of dissolution, precipitation and transformations of minerals affect the porosity of aquifer rocks. The dedolomitization process can be schematically described as follows: $Ca_{0.5}Mg_{0.5}CO_3 + 0.5Ca^{2+} = CaCO_3 + 0.5Mg^{2+}$. Because the ionic volume of calcium is higher than that of the magnesium, the forming calcite (limestone) should have smaller porosity. Assuming the density of dolomite and calcite equals 2.85 g/cm^3 and 2.71 g/cm^3 respectively, the replacement of magnesium by calcium results in a 14% decrease in porosity.

However, in the geochemical system studied dedolomitization is accompanied by dissolution of gypsum. The main dissolving-precipitating reactions in the system are dissolution of gypsum and carbonates (mainly dolomite), and precipitation of calcite, and some barite (Table 9). Taking the mean mole transfers as given in Table 9 (for model 1), the formation of 1 litre of sulphate mineral water results in the creation of 1.32 cm^3 of voids. Due to the reactions indicated in model no. 1, the porosity of the aquifer rock is changes negligibly. Assuming an initial total (matrix and fissure) porosity of bedrocks between 5% and 20%, the increase in porosity due to the geochemical reactions responsible for the formation of sulphate mineral water chemistry is only by 0.007% and 0.04% respectively.

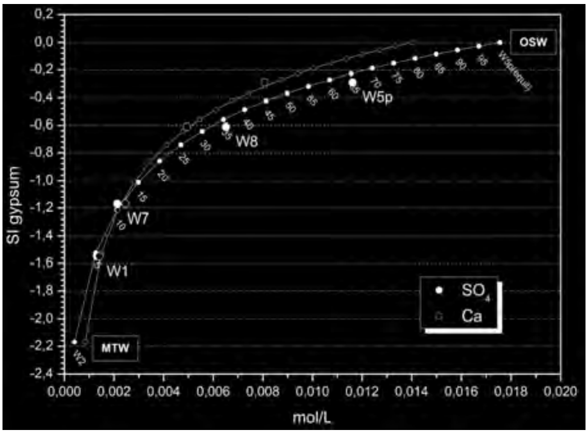
Modelling of the effects of groundwater mixing

Water mixing is a common process in subsurface environments. In Poland, the effect of groundwater mixing is seldom quantified, e.g., it was estimated by Ciężkowski and Szarszewska (1978), Leśniak (1980), Ciężkowski (1990), Kozłowski (1999) in Sudetic and Carpathian curative waters by applying the Ogilvi method.

In the present study, in an attempt to assess and quantify the groundwater mixing process, geochemical modelling was executed by the PHREEQC code. The chemical and isotopic spatial patterns and seasonal variations found in the groundwater studied are regarded as the outcome of the mixing process between two water components. The first component is defined as fresh groundwater of composition affected by modern, post H-bomb recharge. It contains measureable tritium activity. This modern, tritium-bearing water component is henceforth called MTW. The second component is an older sulphate-rich mineral water (hereafter called OSW), which has lower radiocarbon activity than MTW, and is assumed to be tritium-free. In the modelling of the mixing, the chemical composition of fresh groundwater from well 2 has been taken for the chemistry of the MTW component, and the chemistry of sulphate water from well 5p equilibrated with gypsum for the OSW component (Dobrzyński 2007b).

A sulphate ion can be regarded as the most inert solute and the best indicator of water chemistry evolution in the system studied. An increase in sulphate concentration is caused by gypsum dissolution (1.677E-02 mol/kg of water; Table 9). A negligible amount of sulphate fades away in precipitating barite (8.696E-07 mol/kg of water; Table 9), i.e. only 0.005% of releasing sulphates are immobilized due to precipitation.

The result of the modelling agrees well with the real chemistry of the waters. It proves that the water components have been defined correctly, and corroborates the assumption that the water mixing process plays a crucial role in groundwater quality in the study area. The agreement with the real chemistry is apparently best for the solubility products of gypsum, the most reactive phase in the bedrock (Text-fig. 13).



Text-fig. 13. Saturation index (SI) for gypsum vs. Ca and SO_4 concentration compared with the results of water mixing modelling (after Dobrzyński 2007b). Explanations: MTW – modern tritium-bearing water, OSW – old sulphate water; W1, W2, W7, W8, W5p – sampled wells; W5p(equil) – sulphate mineral water from well 5p equilibrated with gypsum (the OSW component); 5 ÷ 95 – percentage of the OSW component

Binary mixing curves (as shown in Text-fig. 13) allowed the water mixing proportions to be estimated (Dobrzyński 2007b). The share of the OSW component in the waters is as follows: in well 1 (about 5%), well 7 (c. 11%), well 8 (c. 36%), well 5p (c. 65%).

These proportions of the OSW component were determined by chemical analyses of water samples from the summer half-year, and are higher than expected. It is conceivable that in the winter half-year and/or snowmelt period the groundwater exploited might contain a higher proportion of the modern, fresh water component than in the summer half-year. The increase in lighter stable isotopes of hydrogen, sulphur and carbon (Table 4) in groundwater in the winter half-year confirms this presumption very well.

GROUNDWATER DATING

The "age" of both groundwater types, fresh and mineral waters, has been quantified using the unstable isotopes, tritium and radiocarbon. The proportion of the mixing water components was also useful in groundwater dating.

Tritium age of groundwater

Tritium records in water wells (Table 4) allowed for an estimation of the mean tritium residence time (so-called tritium age) in the groundwater. Lumped-parameter models (e.g., Małoszewski and Zuber 1982) were applied to find the tritium ages using the FLOWPC code, v.3.2 (Małoszewski and Zuber 1996, 2002).

In the lumped-parameter approach, the relationship between the variable input (C_{in}) and output (C) tracer concentrations was given by Małoszewski and Zuber (1982) as follows:

$$C(t) = \int_0^\infty C_{in}(t-\tau) g(\tau) \exp(-\lambda\tau) d\tau \qquad (6)$$

where: $(t - \tau)$ – the time of entry; τ – the travel time of tracer (age); λ – the decay constant in the case of decaying tracers; and $g(\tau)$ – function called the response function (residence time distribution function). This function describes the output distribution of a tracer instantaneously injected into water entering the hydrogeological system.

Tritium is one of the transient environmental tracers used in hydrogeology. Interpretation of tritium residence time has been accomplished for different

Well	Model	β	τ	P_D	η	Σ
		[-]	[a]	[-]	[-]	[TU]
2	EM	0	10.6	–	–	0.203
2	EPM	0	11.2	–	1.05	0.224
1	DM	0.05	13.0	0.24	–	0.652
1	EM	0.05	8.5	–	–	0.670
1	EPM	0.05	12.8	–	1.46	0.650
1	EPM	0.05	113	–	1.31	0.641
1	DM	0.05	7.2	0.23	–	0.003
1	EPM	0.05	7.3	–	1.45	0.003
1	EPM	0.05	118	–	1.45	0.053
7	DM	0.11	20.5	0.025	–	0.733
7	DM	0.11	21.4	0.005	–	0.540
7	PM	0.11	21.3	–	–	0.494
7	EPM	0.11	18.1	–	2.5	0.920
8	DM	0.36	290	1.00	–	0.117
8	EPM	0.36	207.5	–	1.05	0.111
8	EM	0.36	206.5	–	–	0.109
5p	DM	0.65	98.3	0.20	–	0.125
5p	EPM	0.65	126.4	–	1.38	0.131

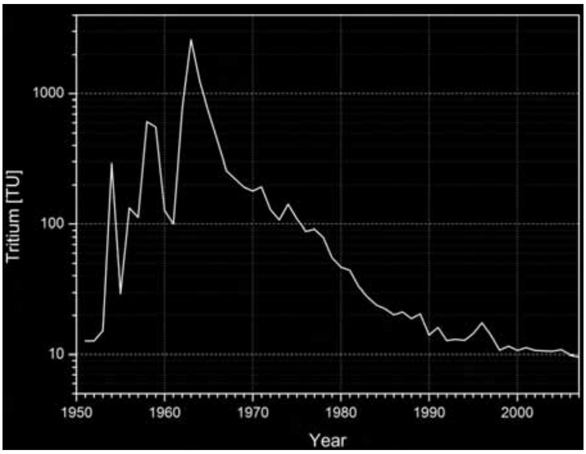
1 – model parameters are: β – extra water component with zero tritium concentration; τ – mean tracer transit time (residence time); P_D – the dispersion parameter ($P_D = 1/Pe = D/vx$, reciprocal of the Peclet number); η – the ratio of the total water volume to the volume with the exponential distribution of transit times, i.e., $\eta = 1$ means the exponential flow model; Σ – goodness of fit in the FLOWPC code defined as (Małoszewski and Zuber 1996): $\Sigma = \left[\sum_{i=1}^{n} (Cm_i - C_i)^2\right]^{1/2} \Big/ n$

where: Cm_i is the i-th measured concentration, C_i is the i-th fitted (calculated) concentration, and n is the number of observations.

Table 12. Best fitted models and their parameters[1] for the tritium data of Table 4

aquifers in Poland (e.g., Ciężkowski and Zuber 1996; Zuber and Ciężkowski 1997, 2002; Zuber *et al*. 2001, 2004, 2005, 2008; Witczak *et al*. 2007).

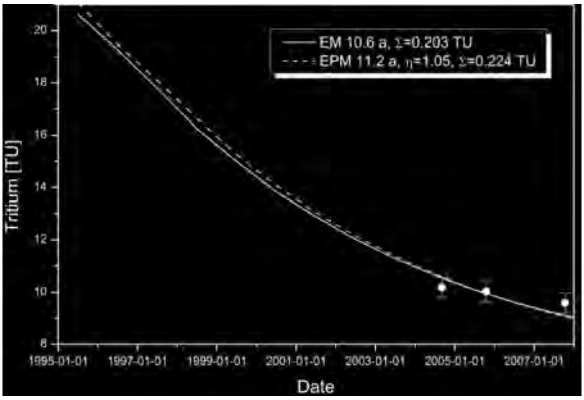
The tritium input function (Text-fig. 14) necessary for tritium age modelling was prepared for the precipitation station nearest the study area using the procedure described by Małoszewski and Zuber (1996). Precipitation records from the station in Mieroszów were used. The tritium input function was calculated using tritium records in precipitation from the station in Cracow where tritium in precipitation has been measured since 1975. For earlier periods, correlated data from the Vienna and Ottawa stations were used (http://isohis.iaea.org; http://kfs.ftj.agh.edu.pl/opady; Duliński *et al*. 2001; IAEA 2002). The ratio of summer to winter infiltration coefficients was taken as equal to 0.70 (Grabczak *et al*. 1984; Małoszewski and Zuber 1996).



Text-fig. 14. Tritium input function used in modelling by FLOWPC code

Roughly estimated tritium ages given earlier (Dobrzyński 2007a) had a preliminary and qualitative character because they were obtained from one or two tritium determinations only, and for an a priori assumed dispersion parameter ($P_D = 0.20$). Subsequent tritium measurements allowed quantification of the tritium residence time much more precisely.

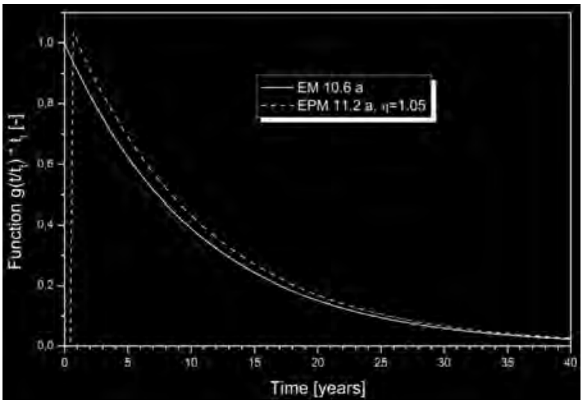
Different lumped-parameter models were checked by using the FLOWPC code. Available geological information was used for selecting the more adequate models. A unique solution is not available due relatively short (eight years) period of tritium observations. The best fitting models for tritium records are given in Table 12. It should be pointed out that the lower the



Text-fig. 15. Tritium data and fitted models, well 2, Unisław Śląski, the Sudetes Mts., Poland

number of parameters sought, the more reliable the model obtained. However, in the study area the one-parameter model (exponential model) is adequate for only one well, which is located in the recharge zone. For the other wells, more-than-one-parameter models have been obtained. The extra water component (β parameter) used in modelling responds to the OSW component and was assumed to be tritium-free. The β value for each well was taken from the results of the geochemical modelling of water mixing.

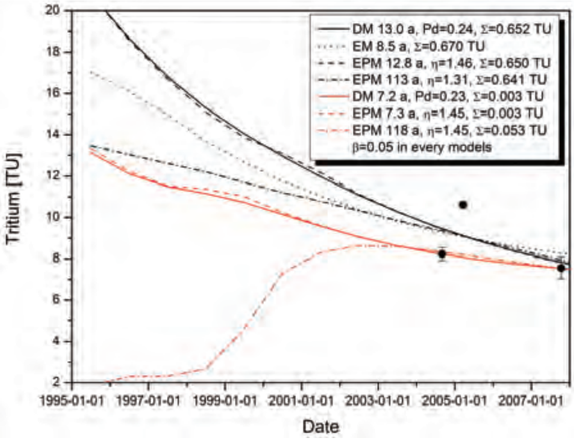
Models fitted to tritium data show possible ranges of mean tritium residence time (tritium ages) in the active zone of each well. Estimation of possible tritium ages is yielded by selected models. Models applied to water wells are characterized in some cases by wide ranges of the tritium residence time. Measurable tritium is transported only along the short flow lines. The cases when mean tritium residence times are larger than the period of the H-bomb era arise from assumed flow model (flow distribution) in the lumped-parameter approach.



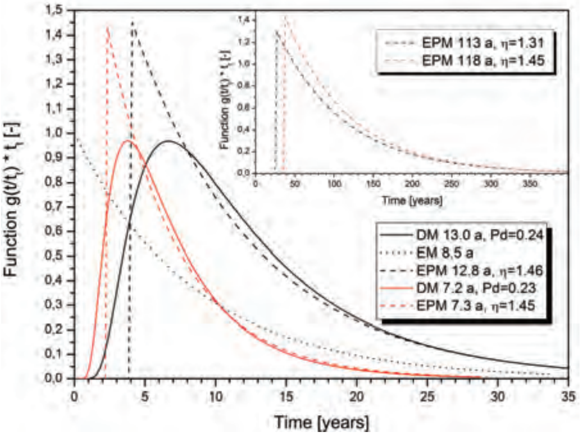
Text-fig. 16. Residence time distribution function for well 2, Unisław Śląski, the Sudetes Mts., Poland (obtained from the FLOWPC code)

For groundwater in the recharge zone (well 2), two models were fitted, the exponential model (EM) and the combined exponential-piston flow model (EPM) (Table 12, Text-figs 15, 16). Both models give similar tritium ages of about 11 years (10.6 y. and 11.2 y. respectively). Groundwater in well 2 has a free water table and exponential flow is applicable to the hydrogeological conditions. However, the model with a small contribution of piston flow (EPM with η = 1.05) is also acceptable.

Four confined water-bearing zones are screened in well 1. The well is located in a drainage zone, very close to the Ścinawka River. Seasonal variations of groundwater chemistry in well 1 were suggested earlier (Wiśniewska 2003) and can also be seen in a tritium increase during snowmelt period (Table 4). Assuming that the tritium increase is brought about by the seasonal event, the fitting of the model was executed in two modes: for all tritium determinations, and for summer half-year data. For two tritium measurements from summer half-year periods, three models fit best (Table 12, Text-figs 17, 18). The dispersion model, with Pd = 0.23, gave a mean residence time of 7.2 years. Two exponential-piston flow models with considerably differing mean residence times (7.3 years and 118 years) were fitted with about a 30% share of piston flow (η = 1.45). For all tritium data (including measurement at snowmelt), several models (dispersion, exponential, exponential-piston flow) at similar goodness of fit (about 0.65 TU) were found. The dispersion model (at Pd = 0.24) yielded a mean residence time of 13.0 years. The exponential model shows a mean time of 8.5 years. The EPM models for all tritium data differ in mean residence time similarly to



Text-fig. 17. Tritium data and fitted models, well 1, Unisław Śląski, the Sudetes Mts., Poland. Models fitted to all measurements in groundwater are marked in black, whereas models for two, lower values noted during the summer half-years marked in red



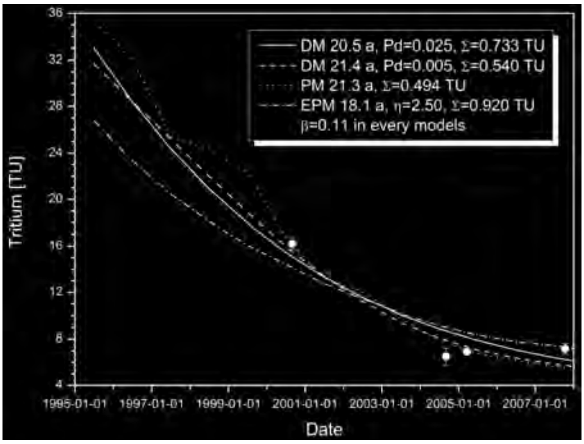
Text-fig. 18. Residence time distribution function for well 1, Unisław Śląski, the Sudetes Mts., Poland (obtained from the FLOWPC code). Models fitted to all measurements in groundwater are marked in black, whereas models for two, lower values noted during the summer half-years marked in red

both EPM models for summer half-year data. One model gave a tritium age 12.8 years at η = 1.46, and the second model – 113 years at η = 1.31.

For the hydrogeological conditions in well 1, the exponential model seems to be inadequate. The very short lines with the theoretical tracer transit time close to zero are not acceptable in the confined flow system of this well; however, the rapid tritium increase after snowmelt indicates inflow of the present-day recharge, perhaps along the well column. The combined exponential-piston flow models are more suitable than the exponential model. Two different EPM models both similarly fitted to the data of well 1 illustrate the lack of unique solutions. In the case of well 1, the lower value of the mean tritium age seems to be more realistic. The eight-year period of tritium records in well 1 does not allow for more precise determinations of the mean tritium age at present.

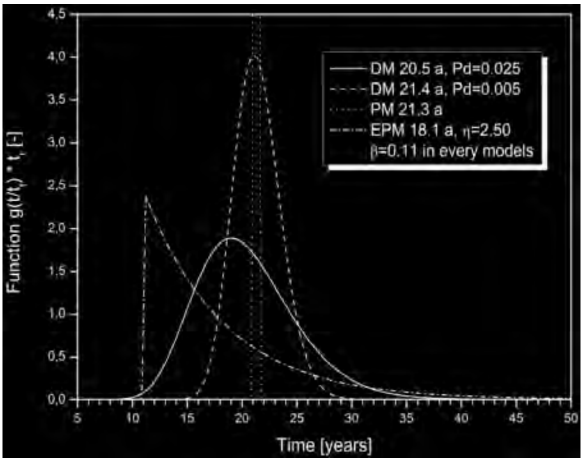
At present, the EPM model with a shorter residence time (τ = 7.3 years, η = 1.45) and the DM model (τ = 7.2 years, Pd = 0.23) for data from summer half-years are chosen as the most reliable for the groundwater flow system of well 1. Both models show the tail of flow lines with tracer residence time of 20–30 years, which is explicable in the drainage zone of Ścinawka River, where well 1 is located.

All models fitted to the tritium data from well 7 yielded very similar values of mean residence time of about 20 years (Text-figs. 19, 20). Two dispersion models with low Pd value (0.025 and 0.005) gave tritium ages of 20.5 and 21.4 years respectively. The lower the dispersion parameter, the slightly longer is the mean residence time, and the better the fit. Fitting results suggest the important role of piston flow and/or low dispersion effect. The piston flow model is shown for comparison. It actually gave the same age (τ = 21.3 y.) as dispersion models and indicated the insignificant role of dispersion in the flow system of well 7. The exponential-piston flow model with a high contribution of piston flow (η = 2.50) shows a slightly worse fit than the DM and PM models. However, mean residence time for the EPM model (τ = 18.1 y.) is similar to that for the latter models. The models fitted support the conclusion that the mean tritium residence time probably varies between 18 and 21 years.

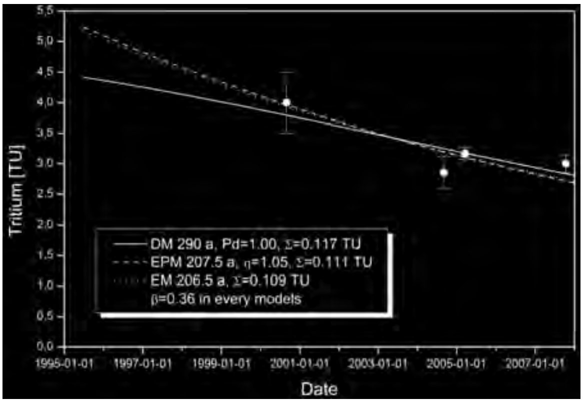


Text-fig. 19. Tritium data and fitted models, well 7, Unisław Śląski, the Sudetes Mts., Poland

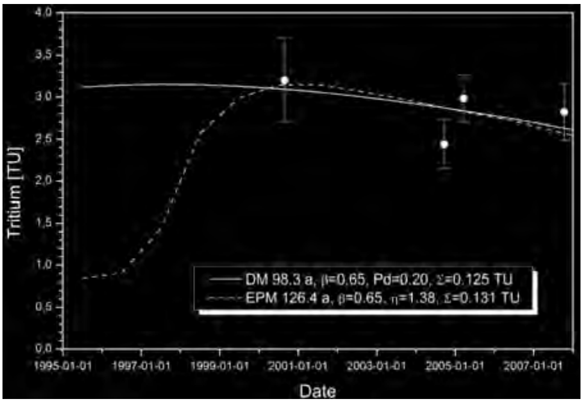
The low values of the dispersion parameter and the narrow age distribution of the modern (tritium-bearing) component might suggest both a relatively local origin of the modern water component and its recharge over a small area.



Text-fig. 20. Residence time distribution function for well 7, Unisław Śląski, the Sudetes Mts., Poland (obtained from the FLOWPC code)



Text-fig. 21. Tritium data and fitted models, well 8, Sokołowsko, the Sudetes Mts., Poland



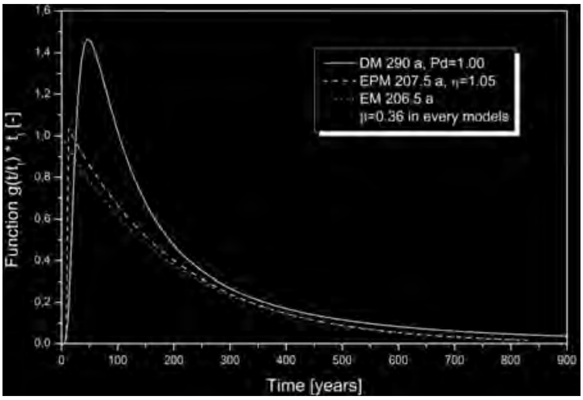
Text-fig. 23. Tritium data and fitted models, sulphate mineral water horizon in well 5p, Sokołowsko, the Sudetes Mts., Poland

Well 7 was originally drilled to a depth of 180 metres. Before screening, the well was shortened by up to 100 m, and the lower part of the well was backfilled using local mineral material. It is conceivable that the small proportion of inflow of the OSW component (a. 11%) might also be caused by vertical flow from the lower, uncased part of the well.

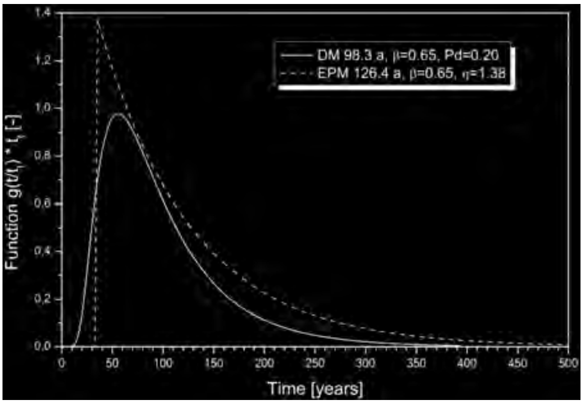
Tritium data from well 8 fit the different models well (Text-figs 21, 22). The exponential-piston flow model and the exponential model both give a long mean residence time of nearly 207 years, with similar goodness of fit (Σ about 0.11 TU). However, the EM model is decidedly inadequate for the flow system of well 8. The dispersion model with a high dispersion parameter (Pd = 1.00) fits to data similarly as the exponential-piston flow model (Σ = 0.12 TU) but gives a longer mean residence time (τ = 290 y.). All the models applied show a long mean residence time and indicate that in the local flow system flow lines with an older fresh groundwater component of an "age" of hundreds of years might occur (Text-fig. 21). The EPM model (with τ = 207.5 years) is recognized as more appropriate for hydrogeological conditions in the active zone of well 8.

Tritium data from the sulphate mineral water horizons in well 5p fit best the dispersion model and the exponential-piston flow model (Text-figs 23, 24). The dispersion model, with Pd = 0.20, gives a mean residence time of 98.3 years; and the EPM model, with η = 1.38, gives a time of 126.4 years. The mean tritium residence time probably varies between 100 and 125 years. Similarly to well 8, time distribution functions for well 5p (Text-fig. 24) indicate the presence of flow lines with groundwater of residence time of hundreds of years. Distribution functions with a "long tail" seem to be realistic and might result from retarded draining of small fissures and matrix micropores.

The mean tritium residence time for the sulphate horizons in well 5p is half as long as that in well 8. This might be caused by the location of well 5p in the local drainage zone (of the Sokołowiec stream), and the appearance of shorter flow lines. It was corrobo-



Text-fig. 22. Residence time distribution function for well 8, Sokołowsko, the Sudetes Mts., Poland (obtained from the FLOWPC code)



Text-fig. 24. Residence time distribution function for sulphate mineral water horizon in well 5p, Sokołowsko, the Sudetes Mts., Poland (obtained from the FLOWPC code) rated by the results of a pumping test, which revealed activation of fresh water inflow and an increase in tritium in the water from the sulphate horizons during pumping (Table 4).

When interpreting ages obtained from tracer data, like tritium, it is necessary to keep in mind that, in fissured rocks, the tracer age usually represents the total water content in the massif, both mobile water in fissures and stagnant water in micropores of the rock matrix. This is the case in the systems when the tracer is entirely molecularly exchanged between mobile water in the fissures and stagnant (or quasi-stagnant) water in the rock matrix. Therefore, the tracer age differs from, and is larger than, the age of mobile water (hydraulic age) derived from Darcy's Law. The factor of proportionality between both ages is the so-called retardation factor (*Rp*). Studies, e.g., by Małoszewski and Zuber (1985), Zuber and Motyka (1994) proved that the *Rp* factor might be very well approximated by the ratio of total massif porosity to fissure porosity.

In the study area, two zones can be distinguished in term of the mean tritium residence time: (1) the northern zone (with wells 2, 1, 7) where mean tritium ages range between 10 and 20 years, and (2) the southern zone (with wells 8 and 5p) where mean tritium ages are one order of magnitude longer – about 100 – 200 years. In the latter zone, the mean tritium residence time is much longer than the duration of the H-bomb era, which is caused by the presence of flow lines with tracer transit times at a scale of hundreds of years.

Generally, in the southern part of the area mudstones dominate, whereas in the northern part sandstones and conglomerates prevail. Higher tritium ages of the groundwater of the southern zone might also result from the tritium retardation caused by matrix diffusion in the mudstones. The effect of molecular diffusion is expected to be higher in the mudstones than in the conglomerates and sandstones of northern zone.

The difference between zones might also be conditioned and reinforced by a lithological barrier. In the lower part of the Zagórzyn Member, an interbed of bituminous shales and mudstones of about 150 metres thickness occurs (Text-fig. 2). This stratum strikes WNW–ESE, and is situated between wells 7 and 8. The bituminous shales are less weatherable than the adjacent rocks, and their outcrops form a marked feature in the terrain. This lithological barrier might impede hydraulic contacts between groundwater in the catchment of the Sokołowiec stream and groundwater in the Ścinawka catchment in vicinity of Unisław Śląski. Furthermore, several faults are inferred between Sokołowsko and Unisław Śląski (Text-fig. 1). The characters of these faults have not been fully determined, but it is possible that some of faults might also restrain hydraulic contacts.

Radiocarbon age of sulphate mineral water

Dating of groundwater using radiocarbon was first proposed by Münnich (1957), and is usually applied to tritium-free groundwater. Radiocarbon dating of groundwater requires knowledge of: (1) initial (input) ^{14}C activity (N_0) in groundwater recharging the hydrogeological system, (2) final (output) ^{14}C activity (N) measured at some point(s) of the system, and (3) chemical reactions affecting the radiocarbon activity along the flow path. The presence of multiple source and sink carbon phases in atmosphere, biosphere and geosphere (e.g., atmospheric and soil CO_2, live and dead organic matter, mineral phases) and interactions between them make radiocarbon dating of groundwater methodologically very complicated.

Most of the radiocarbon in the atmosphere is of cosmogenic origin, and its production is related to changes of the solar activity and the Earth's magnetic field. For instance, a slight decrease in atmospheric ^{14}C activity from ca. 30 000 years BP (BP means before 1950) has been documented by the study of tree rings and marine corals (Pearson *et al*. 1986; Bard *et al*. 1993). The increasing use of fossil fuels resulted in large amounts of CO_2 being emitted into the atmosphere, especially since about 1890. Because the fuels (e.g., coal, petroleum) have been predominantly very old and radiocarbon-free, the ^{14}C activity in the atmosphere was reduced. This tendency has been called "the industrial effect" and continued until the 1950s. Apart from the cosmogenic, other sources of ^{14}C in atmosphere are weapons testing and the activity of nuclear reactors. Thermonuclear flux of radiocarbon emitted into the atmosphere during nuclear tests, mainly in the 1950s and the 1960s, disrupted the natural ^{14}C cycle and increased the ^{14}C content in the atmosphere. The maximum activity of ^{14}C in the atmosphere noted in 1963–1965, was nearly 100% greater than before H-bomb tests (e.g., Levin and Kromer 2004; Hua and Barbetti 2004). Since the mid 1960s, radiocarbon activity has systematically decreased and at present is only about 5% greater than before H-bomb tests.

To avoid the industrial effect, wood grown in 1890, and extrapolated for decay to 1950 AD, was initially used as the modern radiocarbon reference standard. At present, oxalic acid standards correlated with the activity of the 1890-wood standard are usually used. Radiocarbon concentration is conventionally is expressed in percent of modern carbon (pmC) (Stuiver and Polach 1977). 100 pmC is defined as 0.9500 activity of oxalic acid.

Despite atmospheric ^{14}C activity variations documented for Pleistocene and Holocene, for interpretation of groundwater recharged in the pre H-bomb era, the ^{14}C activity in atmospheric CO_2 usually is assumed to be constant, and about 100 pmC. The H-bomb tritium impulse is widely used in hydrogeology. However, due to many methodological difficulties, the H-bomb radiocarbon impulse is currently not used in hydrogeological interpretation.

Defining the initial ^{14}C activity (N_0) in groundwater recharging the hydrogeological system is difficult. The initial ^{14}C activity (N_0) is taken to be the value of ^{14}C activity without the influence of seasonal fluctuations. Two theoretical models of the formation of carbon isotopic composition in groundwater during infiltration through the recharge zone are mainly presented in the hydrogeological literature: a model of an open system with respect to soil CO_2 and a model of a closed system (e.g., Clark and Fritz 1997). They illustrate the extreme theoretical conditions. In real hydrogeological systems, transitional conditions are often found (Clark and Fritz 1997).

Radiocarbon dating is methodologically complicated hence radiocarbon does not behave as a conservative tracer in groundwater. Numerous physicochemical reactions might affect radiocarbon activity in water during percolation throughout the vadose zone and during flow in the saturation zone. Usually, the trend is towards reduction in the ^{14}C activity in water along the flow path. Radiocarbon dating of groundwater demands that these reactions be recognized and quantified. Numerous empirical approaches and models were derived to estimate the appropriate values of initial ^{14}C activity. These generally comprise mixing approaches, isotope exchange approaches, and mass balance approaches (Kalin 2000). Methods of radiocarbon age correction are summarized, e.g., by Clark and Fritz (1997), Geyh (2000), Kalin (2000). Mixing models (like the Pearson or Tamers models) assume simple mixing between two carbon sources: soil CO_2 and carbonate minerals. Isotope exchange models (e.g., models of Fontes and Garnier, Mook, etc.) involve reactions of isotope exchange between solute and/or solid carbon species. Plummer (1977) first applied a mass balance/mass transfer model for correcting the radiocarbon age. Mass balance models use extensive water chemistry and isotopic data. Correction of the initial ^{14}C for effects of carbon source and sink phases by mass transfer calculations was presented by Plummer *et al*. (1983). Gallagher *et al*. (2000) after comparative analysis of several commonly used models for the same aquifers stated that the results of some mixing and isotope exchange models closely correspond to estimations made by using mass balance models. However, inverse mass balance models provide the most complete analysis and produce the best estimates for the initial radiocarbon activity (Zhu and Murphy 2000).

Interactions affecting radiocarbon activity depend mainly on aquifer mineralogy. Conventionally, two types of aquifers are distinguished: siliceous aquifers and carbonate aquifers. In siliceous aquifers devoid of carbonates and organic matter, radiocarbon content might change only in the soil due to reaction with soil CO_2 and dead organic matter. In carbonate aquifers, radiocarbon activity actually changes along the whole flow path as a consequence of carbonate minerals dissolution and/or precipitation, and isotope exchange between dissolved and solid carbonates. Decomposition of organic matter, e.g. due to sulphate reduction, or an influx of magmatic or metamorphic CO_2, might additionally complicate the geochemistry of carbon isotopes in the aquifer. Even a small amount of carbonate minerals in an aquifer can influence carbon isotope activities.

Mass balance modelling is the most efficient method of correction for the effects of water-rock interactions, because it combines all known chemical reactions which occur in the hydro-geochemical system. This approach was expanded after development of the first mass balance geochemical codes (like PHREEQE (Parkhurst *et al*. 1980), BALANCE (Parkhurst *et al*. 1982), NETPATH (Plummer *et al*. 1991)), but is not widely applied in radiocarbon dating of groundwater. The method was used e.g., by Plummer *et al*. (1990), Van der Kemp *et al*. (2000), Plummer and Sprinkle (2001). The mass balance approach needs both the hydrochemistry and mineralogy to be well known in the recharge zone and along the flow path.

In Poland, radiocarbon is not commonly using for groundwater dating. The method was applied for dating, e.g., mineral and thermal waters in the Sudetes (Dowgiałło *et al*. 1974; Ciężkowski *et al*. 1985, 1992; Zuber *et al*. 1995), Mazovian Basin (Zuber *et al*. 2000), Tertiary sandy aquifers (Kania *et al*. 2003, 2005; Witczak *et al*. 2007), and a Jurassic limestone aquifer (Zuber *et al*. 2004). Correction for the effect of water-rock-gas interactions in these studies was usually done by applying the so-called Pearson's correction (Clark and Fritz 1997; Zuber 2007).

In the present studies, mass balance geochemical modelling was used in radiocarbon dating of the sulphate mineral water from Sokołowsko. In Poland, correction of radiocarbon dating from inverse mass balance modelling has not been applied before.

Determining the appropriate value of initial ^{14}C activity plays a crucial role in accurate radiocarbon dating. As a first step, before correcting for the effects of chemical reactions along the flow line in the saturation zone, the initial ^{14}C activity in the groundwater recharging the system should be determined. The ^{14}C activity of soil CO_2 is 100.5 pmC (Clark and Fritz 1997). The ^{14}C activity of dissolved inorganic carbon (DIC) in soil waters depends on various factors, e.g., fractionation and kinetic effects, CO_2 pressure, temperature, soil humidity, etc., and shows seasonal and spatial variations. Duliński *et al*. (2007) documented variations of ^{14}C in the DIC of soil waters between 101 pmC and 108 pmC, and a decrease in $^{14}C_{DIC}$ down the unsaturated zone profile.

In a system open to soil CO_2 in the absence of C-source phases in the bedrock (conditions of a siliceous aquifer) the initial ^{14}C activity of DIC in groundwater recharging the system should theoretically amount to 102.3 pmC (e.g., Clark and Fritz 1997). The aquifer studied, which is dominated by detritical siliceous material, contains carbonate minerals as interlayers, intercalations and fissure fillings. Carbonate minerals occurring in the recharge zone of an aquifer dissolve and dilute ^{14}C concentration in water recharging the system. In a system fully closed with respect to soil CO_2 in the presence of ^{14}C-free carbonate mineral (usually calcite), groundwater should be saturated with the mineral, and according to the equation (5) should have half the ^{14}C activity of $^{14}C_{DIC}$ in an open system, i.e. about 51 pmC. Therefore, reasonable values for the initial water ^{14}C activity range from circa 50 pmC to circa 100 pmC. This range introduces a considerable uncertainty in the groundwater ages, namely one half-life of carbon-14, i.e. about 5,700 years.

The measurement of ^{14}C in the recharge zone groundwater is important in determining the isotopic composition of recharge water for use in the age correction of waters along the flow path in the confined part of the aquifer.

In inverse geochemical modelling for the sulphate water, fresh groundwater from well 2 was taken as initial (input) water (Table 6). Groundwater in well 2 contains 59.39 pmC of ^{14}C (Table 4). It indicates that in the groundwater of well 2 conditions of a system not fully closed (semi-closed) with respect to the soil CO_2 (Dobrzyński 2008) are occurring.

Calculation of radiocarbon age of the sulphate mineral water has been made for two variants: (1) assuming the initial ^{14}C activity (N_0) in groundwater recharge of 51 pmC (fully closed system), and (2) “field” N_0 of 59.39 pmC (semi-closed system).

Transfer of C-bearing phases affects the concentration of dissolved carbon and the activity of radiocarbon in groundwater. The next step was the correction of initial ^{14}C activity for reactions taking place along the flow path in the saturation zone. The results of inverse mass balance modelling for the sulphate water (see chapter Sulphate mineral water) were used in the radiocarbon correction. Model no. 1 (Table 9) has been chosen as more reliable for explaining the origin of the chemistry of the sulphate mineral water. According to this model, carbon is released into the solution during dissolution of carbonates (dolomite, etc.) and decomposition of organic matter. Meanwhile, some amount of carbon is sinking in precipitating calcite.

In the sulphate water, the redox potential is low and hydrogen sulphide occurs (Table 3). Sulphide solute originates from sulphate reduction with the decomposition of organic matter mediated by microorganisms in accordance with equation (2). The model found requires precipitation of pyrite. Precipitation of every mole of pyrite according to the formula (in *wateq4f.dat* database used during geochemical modelling):

$$Fe^{2+} + 2HS^{-} = FeS_2 + 2H^{+} + 2e^{-} \quad (7)$$

consumes two moles of sulphide and goes together with the formation of four moles of dissolved inorganic carbon. Pyrite formation indirectly affects the balance of carbon solutes and this process should be also taken into account in the correction of radiocarbon activity. The radiocarbon activity of dissolved carbonates and organic matter was taken as zero pmC.

Geochemical modelling indicated that groundwater sampled in well 5p is the mixture of two components: 65% of older sulphate mineral water (OSW) and 35% of modern fresh groundwater (MTW) (Dobrzyński 2007b). The radiocarbon activity measured in the groundwater from well 5p was 26.94 ±0.19 pmC (Table 4). The mixing ratio allowed estimation of the ^{14}C activity in the sulphate water component ($a^{14}C_{OSW}$): $a^{14}C_{OSW} = (26.94 - 0.35\ N_0)/0.65$, where N_0 is the assumed initial ^{14}C activity in the groundwater recharge. The $a^{14}C_{OSW}$ amounts to 13.98 pmC for variant no. 1 ($N_0 = 51$ pmC), and to 9.47 pmC for variant no. 2 ($N_0 = 59.39$ pmC). Both these $^{14}C_{OSW}$ values, corrected for the mixing effect, were used in further calculation as new final (output) ^{14}C activities (N) in the sulphate mineral water.

In the groundwater studied, bicarbonates predominate in the DIC. The isotopic enrichment of ^{13}C between inorganic carbon solutes and precipitating $CaCO_3$ solid depends e.g., on the precipitation rate (Turner 1982) and magnesium substitution (Jimenez-

	Mole transfer			Variant 1. (closed system)	Variant 2. (semi-closed system)
	Mean	Minimum	Maximum	^{14}C [pmC]	
DIC in MTW[1]	1.3733E-03			51.0	59.39
Carbonates dissolution	1.2024E-03	1.1007E-03	1.2881E-03	0	0
Calcite precipitation	1.150E-03	1.065E-03	1.239E-03	14.21	9.70
CH_2O dissolution	4.754E-04	3.779E-04	4.896E-04	0	0
Pyrite precipitation	4.524E-05	1.555E-05	4.724E-05	–	–

1 – dissolved inorganic carbon (DIC) in the MTW component, i.e. groundwater from well 2

Table 13. Data used in radiocarbon activity correction for water-rock interactions, after inverse mass balance model no.1 (Table 9)

Lopez *et al*. 2006). In this study, the enrichment between HCO_3^- during precipitation of $CaCO_3$, $\varepsilon^{13}C_{CaCO_3/HCO_3^-}$, is assumed to be ≈ +1‰ (after Clark and Fritz 1997). Fractionation of ^{14}C is 2.3 times greater than that of ^{13}C due to the mass effect, and the ^{14}C of calcite precipitates changes by ≈ +2.3‰, i.e. ≈ +0.23 pmC, compared with sulphate groundwater. Therefore, the ^{14}C of neoformed calcite might be estimated as 14.21 pmC (13.98 + 0.23), and 9.70 pmC (9.47 + 0.23), for variant no. 1 and variant no. 2 respectively.

Using the results of mass balance modelling, and assuming isotope equilibrium between species, the initial ^{14}C activity (N_0) in groundwater recharge was corrected for chemical reactions accordingly to:

$$N_0 = \frac{\alpha_{MTW} a14C_{MTW} + \alpha_{Carb} a14C_{Carb} + \alpha_{CH_2O} a14C_{CH_2O}}{\alpha_{MTW} + \alpha_{Carb} + \alpha_{CH_2O} + 4\alpha_{Pyrite} - \alpha_{Calcite}} + \\ + \frac{4\alpha_{Pyrite} a14C_{CH_2O} - \alpha_{Calcite} a14C_{Calcite}}{\alpha_{MTW} + \alpha_{Carb} + \alpha_{CH_2O} + 4\alpha_{Pyrite} - \alpha_{Calcite}} \quad (8)$$

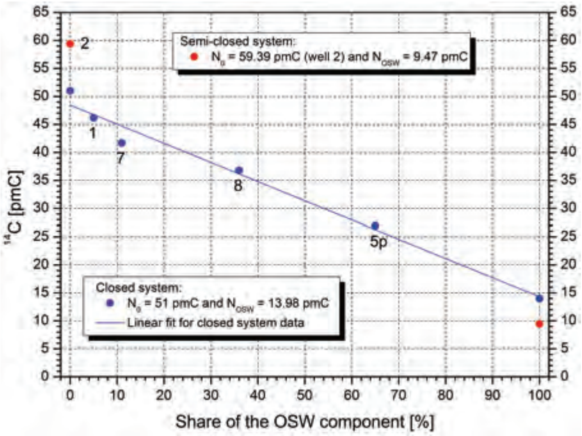
where: α – carbon source mole transfer (α_{MTW} – mole concentration of DIC in fresh groundwater from well 2; α_{Carb}, α_{CH_2O}, α_{Pyrite}, $\alpha_{Calcite}$ – mole transfers for dissolved carbonates and organic matter, precipitating pyrite and calcite, respectively). a14C – radiocarbon activity in species.

Mole transfer of dissolved carbonates is the sum of mole transfers for dolomite, siderite, rhodochrosite, smithsonite, and strontianite. Data used in radiocarbon correction are given in Table 13.

In both variants, correction of the N_0 was performed for mean, minimum, and maximum mole transfers, which include uncertainty assumed in mass balance modelling (Table 9).

Carbon isotopes, ^{13}C and/or ^{14}C, have been successfully used as an indicator of the groundwater mixing process (e.g., Lawrence *et al*. 1976; Mazor *et al*. 1986; Landmeyer and Stone 1995).

The pattern of radiocarbon activity in the groundwater studied results from both the mixing of the MTW and OSW components, and from the radioactive decay. The measured ^{14}C activities in the groundwater were compared with the share of the OSW component (estimated from the mixing modelling), and with the corrected values of initial (N_0) and final (N) ^{14}C activities, in order to prove the applicability of radiocarbon as an indicator of the groundwater mixing process in the system studied. The radiocarbon data fit the mixing results much better assuming N_0 and N activities for the closed system, than for the semi-closed system (Text-fig. 25). It both verifies the correctness of mixing modelling and indicates that the radiocarbon age of the sulphate groundwater should be more reliable when calculated for closed system conditions. Inverse mass balance modelling corroborated that the chemistry of the sulphate waters was formed in a system closed with respect to carbon dioxide (Table 9). The results also prove that, after correction for water-rock interactions, radiocarbon might be effectively used as an indicator of groundwater mixing processes.



Text-fig. 25. Radiocarbon activity in groundwater versus water mixing ratio

The radiocarbon age (t_t) of the groundwater was calculated from:

$$t_\tau = \frac{\tau}{\ln 2} \ln \frac{N_0}{N} \qquad (9)$$

where, τ – half-time of radiocarbon decay (5730 years); N_0 – initial (input) ^{14}C activity in groundwater; N – measured (output) ^{14}C activity in groundwater.

The N_0 was corrected for chemical reactions based upon the results of inverse geochemical modelling, and the N was corrected for the mixing effect. The systematic decrease in atmospheric ^{14}C, with some fluctuations, is well documented for the period since about 24 ka. Radiocarbon ages for the internationally accepted half-life (5730 years) have been re-calculated to correct for variations of atmospheric ^{14}C in the Holocene. Calibration was performed by applying the OxCal program, ver. 4.0.5 (http://c14.arch.ox.ac.uk) and IntCal04 curve (Reimer *et al*. 2004). The calculated (5730-years) and calibrated radiocarbon ages of the sulphate mineral water are compared in Table 14.

Uncertainty in the groundwater ages is mainly caused by uncertainty in: (1) radiocarbon determination in water(s), and (2) mass transfer in mass balance model(s). In the sulphate mineral water studied, differences evoked by mole transfer uncertainty (between 690 and 270 years) for calibrated radiocarbon ages are higher than the uncertainty caused by radiocarbon determination (between 170 and 110 years) (Table 14). Correcting for variations of atmospheric ^{14}C in the Holocene should be involved in radiocarbon groundwater dating. Differences between the 5730 half-life ^{14}C ages and the calibrated ^{14}C ages are higher than the uncertainty evoked by ^{14}C analysis or by mole transfer calculation, and are about 790–920 years, and 1750–1880 years, for variant 1 and variant 2 respectively.

Conditions of the CO_2 closed system seem to be more reliable for the sulphate groundwater. Therefore, radiocarbon ages calculated for variant 1 are considered to be more acceptable. The calibrated age of the sulphate mineral waters might be estimated at from 5.6 ka BP to 7.2 ka BP, with a mean age of 5.9 ka BP. It responds to the so-called Mid-Holocene Climatic Optimum, usually taken as 7 ka to 5 ka BP. In this period, due to astronomical factors, the climate was warmer than today, but only in summer in the Northern Hemisphere, whereas winters in the Northern Hemisphere and tropics were colder than today (Ganopolski *et al*. 1998; Hewitt and Mitchell 1998).

The calculated radiocarbon age should be interpreted as a travel time, not as an absolute age, because it refers to the time elapsed between water entering the saturated zone of the system and reaching the sampling point. The time of water travelling throughout the unsaturated zone is probably very short compared to the uncertainties mentioned above and, in the case of the system studied, the difference between travel time and absolute age is negligible.

Interpreting of radiocarbon residence time between points along the flow path, usually between recharge zone and some point downgradient, also depends on the groundwater flow model. Usually, two approaches are applied for interpreting the radiocarbon age of groundwater: the piston flow model and the dispersion model (Kalin 2000). For radiocarbon age calculation equation (9) is commonly used, but one should remember that using this equation assumes piston flow approximation of groundwater flow. Zuber and Ciężkowski (2002) mention that the piston flow model approximation is often applied in hydrogeological practice without any justification that the simplicity of this model is appropriate for the hydrogeological conditions in question. The piston flow model is generally appropriate for a regional groundwater system, and Kalin (2000) stated that it "would be applied implicitly when calculating the ^{14}C age of groundwater with the geochemical approach of mass balance/mass transfer models".

In the present study, the radiocarbon age of the sulphate mineral water was calculated assuming the piston flow approximation to be acceptable for the OSW component. The acquired data provide evidence that the sulphate mineral water (the OSW component) is mixing with modern fresh groundwater (the MTW

	Radiocarbon age [y] ($t_{1/2}$ = 5730)			Calibrated radiocarbon age [calBP]		
	Total mole transfers			Total mole transfers		
	Minimum	Mean	Maximum	Minimum	Mean	Maximum
Closed (variant 1)	4 790 ±110	5 060 ±110	6 230 ±110	5 580 ±280	5 880 ±290	7 150 ±270
Semi-closed (variant 2)	10 350 ±170	10 520 ±170	11 600 ±170	12 100 ±690	12 350 ±510	13 480 ±320

Table 14. Radiocarbon age of sulphate mineral water from Sokołowsko calculated using 5730 year half-life and calibrated radiocarbon age for both variants of initial ^{14}C activity, at different total mole transfers (upon uncertainty of geochemical mass balance)

component), probably during the ascent into the discharge zone of the Sokołowiec valley.

Another difficulty of the ^{14}C age interpretation is diffusion into the rock matrix and isotopic exchange with carbonate minerals. The process is particularly effective in the microporous matrix of carbonate rocks (Małoszewski and Zuber 1991). In the study area, carbonates occur mainly as an intercalations and fissure fillings, and the process probably does not play a crucial role but it should not be entirely disregarded.

Unstable isotopes (^{3}H, ^{14}C) in the groundwater show a regularity of mixing pattern (Text-fig. 3) – the lower the tritium content, the lower the radiocarbon content. However, samples of sulphate water from well 5p differ slightly from the regular pattern. This might be caused by increased tritium content due to inflow of modern water in the discharge zone. On the other hand, radiocarbon activity might be slightly lowered as an effect of exchange with carbonate phases.

ESTIMATION OF REACTION RATES

The reaction rate (or rate of reaction) is a measure of how fast a particular chemical reaction occurs, and is defined in various ways. Typically, it is measured as the change in concentration of a reactant(s) and/or a product(s) of reaction over unit time.

Combining the mass transfer for mineral phases with the groundwater ages allows determination of the rates of geochemical reactions in the hydrogeological system. This kind of rate is sometimes regarded as an apparent rate because it is not normalized to unit water-rock surface area but to unit volume (or mass) of a solution.

The reaction rate of the main reactive phases, which influence the chemistry of sulphate mineral water, has been calculated using the calibrated radiocarbon age and the results of inverse mass balance modelling. Mole transfer for the main reactive phases included (dissolving carbonates – mainly dolomite, dissolving sulphates – gypsum, precipitating calcite and decomposing organic matter), after model no. 1 (Table 9), and calibrated ages for variant 1 (Table 14) have been used for reaction rate calculations. The results are shown in Table 15.

Dissolution of 2.85 μmol/L/year of gypsum and 0.21 μmol/L/year of carbonate minerals (mainly dolomite) accompanied by precipitation of 0.20 μmol/L/year of calcite have been probably responsible for the formation of the chemistry of the sulphate mineral groundwater in Sokołowsko. The process of sulphate solute reduction probably has consumed about 0.08 μmol/L/year of organic matter (given as CH_2O).

Diffusion exchange of ^{14}C between groundwater and rock matrix leads to a decrease in the ^{14}C activity in the groundwater, and an overestimation of the radiocarbon age. Consequently, the age calculated is the longest that should be expected, and the real reaction rates are probably somewhat higher than the calculated ones.

The main features of the geochemical reactions in the sulphate mineral groundwater in the Sokołowsko area are very similar to reactions described for the Madison aquifer by Plummer *et al*. (1990) and Busby *et al*. (1991). In both systems, groundwater quality is determined by the dedolomitization process driven by gypsum dissolution, under conditions of a system closed with respect to carbon dioxide. The mean apparent reaction rates for the Madison aquifer (Plummer *et al*. 1990) calculated from inverse geochemical modelling and radiocarbon groundwater dating are additionally included in Table 15. The reaction rates obtained in the present study are similar to the Madison aquifer rates, despite the significant differences between both hydro-geochemical systems.

In the study area the effect of dedolomitization on groundwater quality was found in a very small aquifer (about 50 square km) with groundwater of low-en-

Phase	Reaction rates[1] for studied aquifer			Mean reaction rates for Madison Aquifer[2]
	Minimum	Mean	Maximum	
Gypsum	2.343 (0.319)	2.849 (0.388)	3.002 (0.409)	0.95
Carbonates[3]	0.175 (0.032)	0.213 (0.039)	0.224 (0.041)	0.24[4]
Calcite	0.167 (0.017)	0.204 (0.020)	0.215 (0.021)	0.59
Organic matter (CH_2O)	0.062 (0.002)	0.075 (0.002)	0.079 (0.002)	0.12

1 – reaction rates in μmol/L/year, in parentheses given reaction rates in mg/L/year; 2 – reaction rates in μmol/L/year, after Plummer *et al.* (1990); 3 – sum of dissolving carbonate phases (dolomite, siderite, rhodochrosite, smithsonite, strontianite); 4 – reaction rate for dissolving dolomite

Table 15. Reaction rate of main reactive phases responsible for chemistry of sulphate mineral water in Sokołowsko

thalpy, at a depth of 100–300 metres. The Madison aquifer is a vast regional system in the states of Wyoming, Montana, South and North Dakota. Groundwater occurs at depths of tens of metres at outcrop, down about 2400 metres in the basin. Groundwater temperature varies from 6˚C to 97.5˚C, and dissolved solids reach up to 6.4 g/L.

The reaction rate for gypsum in the system studied is three times greater than in the Madison aquifer. In the Madison aquifer, at higher temperatures, favouring gypsum dissolution, the groundwater reached saturation with gypsum, which suggests that the reaction rate for this mineral might be underestimated there, due to the high radiocarbon age, up to about 23 ka.

CONCLUSIONS

Comprehensive geochemical investigations revealed that the hydrogeological system studied is chemically and isotopically diversified. The diversity manifests along the dip of beds, but it cannot be explained by the effects of chemical evolution. The mixing of two groundwater components in the active zone of each well appears to be the main process responsible for the observed pattern of aqueous chemistry in the exploited waters. These two water components were recognized and quantified. The first component is the modern, tritium-bearing, fresh groundwater (MTW). The second one is the pre H-bomb, Holocene sulphate mineral water (OSW).

Inverse mass balance modelling was applied to elucidate the origin of the chemistry of both water components. The models obtained are plausible and the assumed reactions exert major controls on the composition of the groundwater.

The chemistry of the fresh groundwater is formed mainly by dissolution of carbonates (limestones and dolomites) and gypsum in the recharge zone. The mean residence time (MRT) of tritium in the fresh groundwater component, estimated using the lumped-parameter models, ranges from 10 years to 200 years. The horizontal zoning of the MTW component is seen in terms of the tritium MRT. In the northern part of the study area, the MRT is 10–20 years, and in the southern part is 100–200 years. This zoning seems to be caused mainly by lithological factors. In the northern part of the area, conglomerates and sandstones prevail, whereas in the southern one mudstones predominate. The tritium retardation caused by matrix diffusion is expected to be higher in fine-grained mudstones. In addition, the 150-metre thick interbed of bituminous shales and mudstones, which occurs in the central part of the area, acts as a potential lithological barrier and impedes hydraulic contacts between both zones.

The main features of the chemistry of the sulphate mineral water are shaped by the process of dedolomitization driven by gypsum dissolution. The dissolution of gypsum is accompanied by the incongruent dissolution of dolomites with calcite precipitation, and the calcium common-ion effects. The radiocarbon-age of the sulphate mineral water is estimated to be of 5.9 ka BP, i.e., it infiltrated during the so-called Mid-Holocene Climatic Optimum.

The proportion of the OSW component, quantified by geochemical modelling of mixing, in the water inflowing to the wells increases gradually southwards and reaches a maximum of about 65% in the groundwater in the unused well 5p in Sokołowsko. The variation of the mixing proportion involves changes of chemical and isotopic composition. Consequently, the hydrochemical type varies from the Ca-HCO_3-SO_4 type in the recharge zone (well 2) to the Ca-SO_4-HCO_3 and Ca-SO_4 types, to the Ca-Na-SO_4 type in well 5p in Sokołowsko.

Due to the crucial role of mixing in the active zones of the wells, the hydrogeological system studied should be treated as a system of individual flows. The mixing results mainly from long screened intervals and withdrawal of water from different depths. The results obtained showed that both geochemical modelling and radiocarbon determination can be successfully applied for quantifying the effects of groundwater mixing.

The aquifer studied is hydrochemically complex, and two zones might be assigned, both horizontally and vertically. The horizontal zoning of the MTW component mentioned above is conditioned by lithology. The vertical hydrochemical zoning is seen only in the deepest well 5p in Sokołowsko, where four water-bearing horizons are found and screened. Fresh groundwaters occur in shallower horizons (up to 90 m depth), and mineral groundwaters occur in two deeper horizons (below 170 m depth). Both chemical and isotopic data indicate that the Holocene sulphate mineral waters are discharged in the drainage zone of the Sokołowsko valley, and are mixing with modern fresh water. Fresh waters can be schematically attributed to an active groundwater zone, and tritium-free, sulphate mineral waters to a semi-active zone.

The study proved the efficacy of geochemical modelling of groundwater for:

(1) elucidating the origin of groundwater chemistry;

(2) quantifying the effects of groundwater mixing;

(3) correcting the radiocarbon dating of groundwater for chemical reactions which occur along a flow path.

Geochemical modelling of groundwater needs aqueous chemistry and aquifer mineralogy to be determined. Data on the real chemical composition of the mineral phases included in the conceptual model(s), and their isotopic composition, are also very useful. Including the carbon and sulphur stable isotopes in the models allowed a strict chemical mass balance to be verified and specified.

The inverse mass balance modelling can find semi-quantitative data on the chemical composition of reactive phases. On the other hand, knowledge of the real composition of reactive minerals might test the correctness of inverse mass balance modelling. In the present study, good consistency was obtained between the chemistry of the reactive carbonate minerals (inferred from modelling) and the real mineral composition.

Investigations on stable carbon and sulphur isotopes in solutes and solids helped in (1) deciphering the origin of sulphate and carbonate solutes, and (2) verifying the mass balance model for the sulphate mineral water in Sokołowsko.

Unstable isotopes (^{3}H, ^{14}C) have been successfully applied for dating the groundwater studied. The results of the modelling of mixing had a crucial role in quantifying both the tritium and radiocarbon ages. The tritium residence time (so-called tritium age) in the groundwater system was estimated by lumped-parameter models using the FLOWPC code. The radiocarbon age of the sulphate mineral water was quantified by applying a correction for the effects of water-rock interactions to the results of inverse mass balance modelling. The radiocarbon activity correction applied to carbon isotope data is for the effects of: (1) incongruent dissolution of aquifer carbonate minerals (dolomite dissolution with calcite precipitation), (2) decomposition of organic matter, and (3) redox processes (reduction of sulphate solute).

The present study is the first use in Poland of inverse mass balance geochemical modelling for correcting the radiocarbon age of groundwater. The calculated ^{14}C (5730-year half-life) age was also calibrated for the atmospheric variations of radiocarbon activity in the Holocene.

Quantifying the rate of chemical reactions in geochemical systems is a difficult challenge for many reason, e.g., complexity and heterogeneity of the natural systems and, usually, insufficient recognition of its mineralogy and hydrochemistry.

In the present study, the apparent reaction rates for the main reactive phases responsible for the chemistry of the sulphate mineral groundwaters which occur in the area of Sokołowsko were estimated based on phase mole transfers (from geochemical modelling) and radiocarbon dating. This is the first study in Poland of reaction rates in hydrogeochemical systems. The results obtained agree well with the published reaction rates for a vast regional aquifer system (Madison aquifer, USA), where a similar set of geochemical reactions is currently responsible for groundwater quality formation.

Deciphering the origin and age of the sulphate mineral waters which occur in Sokołowsko is very important for the possible, planned use of these waters for curative purposes. The results of geochemical modelling can be helpful for fresh water management in the whole area of Unisław Śląski–Sokołowsko**.**

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