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Estimation of inorganic carbon sources in groundwater recharge by inverse geochemical modelling (Carboniferous aquifer, the Intra-Sudetic Basin, SW Poland)

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Geochemical modelling was applied in quantification of chemical reactions responsible for the chemistry of groundwater in the recharge zone of a Carboniferous aquifer (the Sudety Mts., SW Poland). Calculation of the contribution of dissolved inorganic carbon (DIC) sources allowed estimation of the initial radiocarbon activity in the recharge to groundwater. The ^{14}C activity calculated upon the results of geochemical modelling is consistent with the ^{14}C activity measured in groundwater. Geochemical modelling can be applied for estimation of the initial ^{14}C activity in recharge water as well as the ^{14}C activity in groundwater along the flow path. Methods of geochemical modelling have an advantage over empirical methods because they combine the effects of various chemical reactions occurring in the geochemical system.

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Key words: Poland, Sudety Mts., inverse geochemical modelling, radiocarbon activity, groundwater chemistry.

INTRODUCTION

In Carboniferous and Permian sedimentary rocks in the area of Unisław Śląski–Sokołowsko (the Intra-Sudetic Basin, the Sudety Mts., SW Poland) different groundwater chemical types occur (Dobrzyński, 2007*a*). Locally, groundwater is exploited for drinking-water supply in the town of Wałbrzych. Chemical and isotopic research was carried out to decipher the origin of the chemical composition and the "age" of the groundwater. Estimation of the radiocarbon-age of groundwater requires recognition and quantification of the reactions in the water-rock system that affected ^{14}C activity. The processes occurring during groundwater recharge in vadose zone, and those occurring in the saturated zone of the aquifer have to be accounted for. Therefore, a correction is required for the initial ^{14}C activity (N_0) in the recharge groundwater and for chemical reactions that affected the ^{14}C activity (N) measured along the flow path. The initial ^{14}C activity relates to the value in freshly recharged groundwater off the influence of seasonal fluctuations. The activity of ^{14}C in infiltrating water changes during percolation through the vadose zone due to soil CO_2 and carbonate mineral dissolution, reactions with organic matter, *etc*. The trend is towards lowering of the ^{14}C activity in water. Various empirical approaches and models have been proposed to estimate the appropriate values of N_0 (Clark and Fritz, 1997; Geyh, 2000; Kalin, 2000). Usually, these approaches consider the influence of single processes. Geochemical modelling allows one to combine the effects of numerous reactions. In this paper, methods of inverse geochemical modelling are applied for quantifying:

— processes which are responsible for the chemistry of groundwater in the recharge zone of the aquifer studied;
— the contribution of particular inorganic carbon sources;
— the initial ^{14}C activity (N_0) in the recharge groundwater.

METHODS

Groundwater field parameters were measured (pH, T, Eh, SEC, H_2S, O_2) and groundwater was analysed for chemical and isotopic (tritium, ^{14}C) composition. Water samples were filtered through 0.45 μm membrane filters and stored in LDPE bottles. Anions in groundwater were determined by spectrophotometric and volumetric methods, and the main cations and

trace elements were determined by ICP-AES (Inductively Coupled Plasma–Atomic Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma–Mass Spectrometry) methods. Tritium was analysed in the Institute of Nuclear Chemistry and Technology (Warszawa) by liquid scintillation spectrometry. Radiocarbon activity was determined by the Accelerator Mass Spectrometry (AMS) method in the Poznań Radiocarbon Laboratory. Geochemical modelling was executed using the PHREEQC code (Parkhurst and Appelo, 1999) with a thermodynamic data base — phreeqc.dat. Inverse geochemical modelling calculations were performed between wet deposition and groundwater in the recharge zone. The chemical composition of wet deposition is taken after Dobrzyński (1997). The chemical composition of groundwater from water supply well (no. 2) located in the unconfined part of the aquifer is considered as typical of the recharge zone. Groundwater in well 2 was sampled during a dry period to minimize the effect of precipitation on groundwater chemistry.

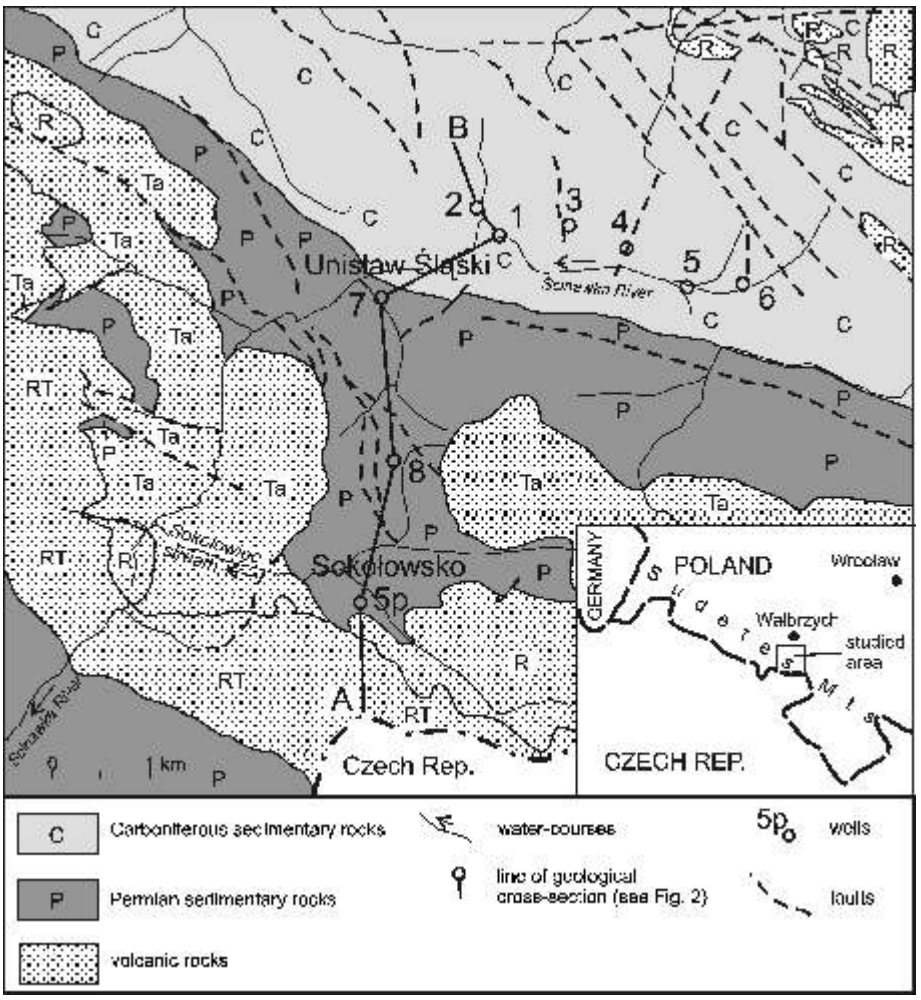

Fig. 1. Geological map of the Unisław Śląski area (after Grocholski, 1971; Bossowski *et al*., 1994; Awdankiewicz, 1999)

R — rhyolites, RT — rhyolitic tuffs, Ta — trachyandesites

GEOLOGICAL SETTING AND HYDROGEOLOGY

The area studied is situated in the uppermost part of the Ścinawka River catchment, in the Kamienne and Wałbrzyskie Mts. Geologically, the area is located in the Intra-Sudetic Basin (central part of the Sudety Mts., SW Poland), and is composed of Upper Carboniferous and Lower Permian sedimentary and volcanic rocks (Fig. 1). Groundwater occurs in fissured sedimentary rocks, mainly clastic rocks (conglomerates, sandstones and mudstones), partly interbedded with clays and limestones. The sedimentary rocks were deposited in alluvial and lacustrine environments in a hot arid/semi-arid climate (Bossowski and Ihnatowicz, 1994), and are classified as lithostratigraphic units, namely the Ludwikowice Member (upper Stefanian), and Krajanów and Zagórzyn members (lower Autunian) (Fig. 2). In the vicinity of Unisław Śląski groundwater is usually abstracted from clastic rocks of the Ludwikowice Member, which outcrops north of Unisław Śląski village.

The Ludwikowice Member is composed of polymictic conglomerates and sandstones, rarely with mudstones and shales. The main mineralogical features of these rocks comprise the presence of numerous fragments of volcanic rocks (rhyolites, trachyes) 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).

Groundwater in sedimentary rocks forms the fissured aquifer. There are generally confined conditions in the aquifer, only in well no. 2 is there a free water table. The Ścinawka River is the main base level of groundwater drainage in the area studied. Groundwater occurring in the vicinity of Unisław Śląski is exploited for drinking-water supply in the town of Wałbrzych.

CONCEPTUAL GEOCHEMICAL MODEL

Water from well 2 represents the chemistry of groundwater in the recharge zone. The groundwater has low mineralization. Bicarbonate, sulphate and calcium ions prevail (Table 1), and the Ca-HCO_3-SO_4 hydrochemical type dominates.

Determination of unstable isotopes reveals the presence of radiocarbon (^{14}C) and tritium (^{3}H) in groundwater from well 2 (Table 1). Radiocarbon activity (59 pmC) indicates the present-day "age" of the groundwater. Tritium data were used for estimation of groundwater tritium-"age" by applying the

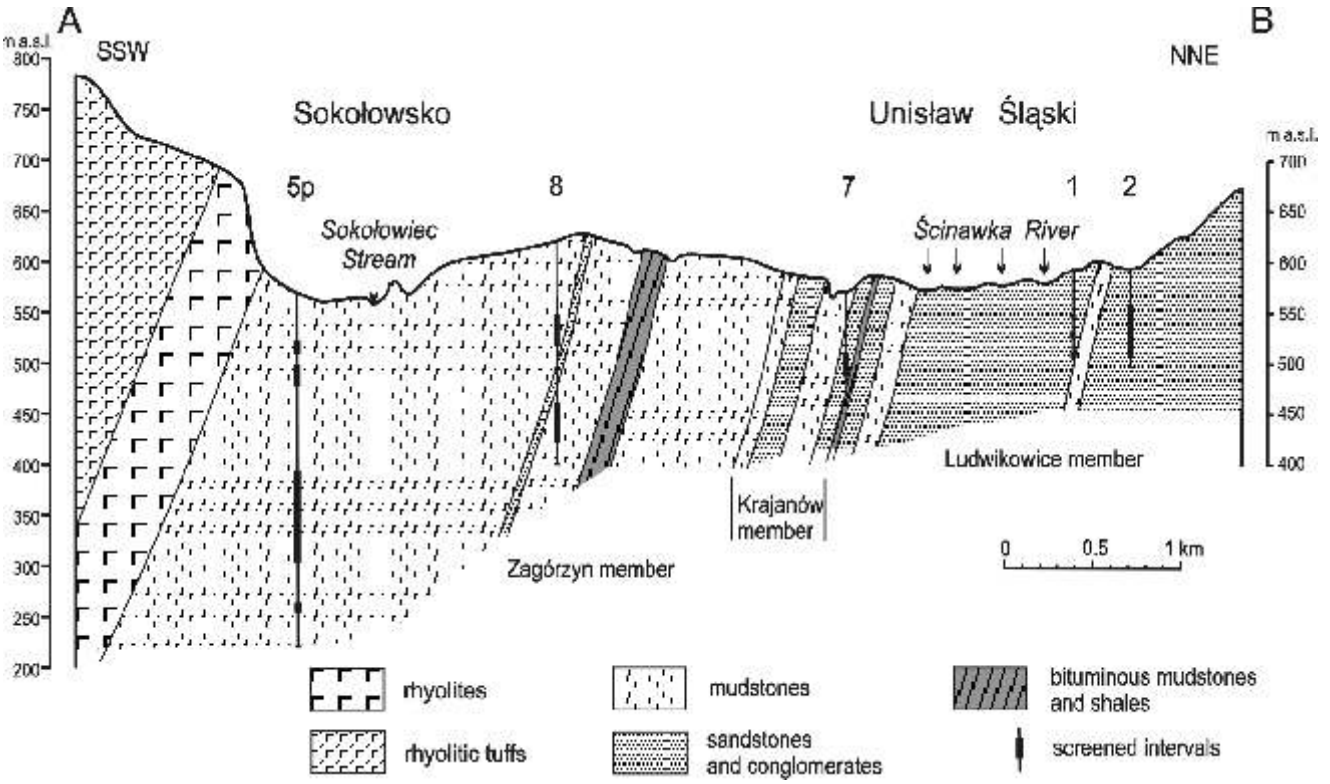

Fig. 2. Schematic geological cross-section (after Dobrzyński, 2007*a*)

Table 1

Chemical composition of groundwater in the recharge zone (well 2)

Parameter	Value	Parameter	Value
T [°C]	11.2	Na	6.0
pH	7.73	K	1.1
Eh[1] [mV]	357	Al	0.004
SEC[2] [µS/cm]	249	Ba	0.127
O_2	4.47	Fe	0.005
H_2S	0.00	Mn	0.0005
SiO_2	17.0	NH_4	<0.05
SO_4	38.8	Sr	0.086
HCO_3	84	Zn	0.016
Cl	7.12	^3H [TU][3]	10.18 (±0.37)
F	0.11	^3H [TU][4]	10.04 (±0.42)
NO_3	8.11	^3H [TU][5]	9.59 (±0.38)
Ca	33.5	^{14}C [pmC][6]	59.39 (±0.23)
Mg	5.8		

Concentrations in mg/L; [1] — redox potential corrected with respect to SHE after Nordstrom (1977), [2] — specific electric conductivity compensated to 25°C, [3] — September 2004, [4] — March 2005, [5] — October 2007, [6] — measured value

FLOWPC code (Małoszewski and Zuber, 1996). Tritium input function was prepared using precipitation records from the station in Mieroszów, which is located *ca*. 5 km from the studied area. The exponential (EM) and exponential-piston-flow (EPM) models were the most suitable for hydrogeological conditions in the recharge area of well no. 2. Estimated mean tritium residence time in groundwater of well 2 is 10.6 years for the EM model (Σ = 0.20 TU), and 11.2 years for the EPM model (η = 1.05, Σ = 0.22 TU).

The aim of inverse geochemical modelling was defining and quantifying chemical reactions in the recharge zone. The weighted mean chemical composition of wet deposition (Table 2) represents the chemistry of the water entering the topsoil. Before the start of inverse geochemical modelling, the chemical composition of wet deposition was equilibrated with atmospheric CO_2 (pCO_2 = 3.5) by using the PHREEQC geochemical code. Gaseous phases (CO_2, O_2, N_2) and abroad range of solid phases are included in the conceptual model. Solid phases comprise carbonate (calcite, dolomite, siderite, smithsonite, rhodochrosite), sulphate (gypsum, celestite), silicate (albite, chlorite, illite, kaolinite) and halogen (halite, fluorite) minerals. Due to the lack of data on carbonate and gypsum geochemistry, trace elements (Fe, Mn, Zn, Sr) are considered in the conceptual model as pure end-member solid phases (siderite, rhodochrosite, smithsonite, celestite). Siderite is assumed as a likely iron source phase, because groundwater in well 2 is undersaturated with respect to this mineral (SI = –4.78) and considerably supersaturated with respect to iron (oxy)hydroxides, such as goethite, FeOOH or ferrihydrite, $Fe(OH)_3$, SI = 6.76 and 1.38, respectively.

Halite and fluorite play the role of hypothetical phases only, and were used in the modelling to balance chlorides and fluorides. Chloride and fluoride anions in groundwater likely originate from the atmospheric deposition. The mean groundwater "age" in the recharge area estimated from the tritium data is

Table 2

Monthly weighted mean chemical composition of wet deposition in the Kamienne and Wałbrzyskie Mts. (central part of the Sudety Mts.) in the early 1990's (after Dobrzyński, 1997)

Parameter	Value
pH	4.79
Ca	2.7
Mg	1.2
Na	0.6
K	1.6
HCO_3	7.2
SO_4	14.7
Cl	5.1
F	0.05
PO_4	0.07
Al	0.0581
SiO_2	0.227

Concentrations in mg/L

about 11 years. In the region of the Sudetes Mts., studied in the early 1990's the weighted mean concentration of chloride and fluoride in wet atmospheric deposition was 5.1 and 0.05 mg/L (Table 2), respectively. Chemical data on wet deposition refer to sites located in the northern part of the Intra-Sudetic Basin, in the Kamienne and Wałbrzyskie Mts. (Dobrzyński, 1997). Considering an evapotranspiration coefficient of about 2 (Dobrzyński, 1997), concentrations of chloride and fluoride are consistent with groundwater data for well 2 (Table 1). This confirms that the role of Cl and F from source mineral phases in the soil and the bedrock, and local chloride and fluoride contamination sources, seem to be negligible. In the recharge zone there are no point-sources of contamination. The area is forested, and partly occupied by barren land and meadows.

RESULTS AND DISCUSSION

Two models (with a minimum number of phases) were found (Table 3) as a result of inverse mass balance geochemical modelling. According the modelling results, the chemical composition of groundwater in the recharge area arises from dissolution of carbonates, gypsum and silicates. During incongruent dissolution of silicates, secondary clay phases are formed. Dissolution of carbonates and gypsum may bring about a small increase in Fe, Mn, Zn, and Sr concentrations in water during infiltration in the recharge zone.

The main difference between the two models found is in the magnesium source phase (chlorite or dolomite). In fact, both models are possible, but model 2 seems to be more appropriate because it includes carbonate as the Mg source. Magnesium from dolomite is probably more available for reaction than magnesium from the chlorite phase. Model 2 also shows lower total mole transfer of phases than model 1. During the establishing of chemical equilibrium in the geochemical systems, reactions that require smaller mass transfers are thermodynamically preferred. It is conceivable that in the real system both dolomite and chlorite dissolve, and real reactions might be somewhere between model 1 and model 2.

In the recharge zone there are no point-sources of contamination. Infiltrating waters might only be slightly affected by atmospheric deposition. Therefore, the chemical reactions found in the models illustrate natural processes in the bedrock of the recharge zone.

The calculated mass transfer (Table 3) for dissolved inorganic carbon (DIC) sources (soil CO_2, carbonates) allows estimation of the activity of ^{14}C in the recharge groundwater. Carbonate minerals occurring in Carboniferous conglomerates are assumed to be ^{14}C-free. It is likely that only ^{14}C-free carbonates dissolve in the vadose zone water. Saturation indices (SI) for calcite and dolomite in groundwater from well 2 are –0.45 and –1.52, respectively. This means that the formation of modern ^{14}C-bearing carbonates is not thermodynamically possible. During infiltration of rain water, soil CO_2 dissolves that has a ^{14}C activity of 100.5 pmC (Clark and Fritz, 1997).

The activity of ^{14}C in groundwater of the recharge zone depends on the radiocarbon activity in reacting carbon-bearing components (soil CO_2, carbonates, and also atmospheric CO_2). Considering that rain water has a ^{14}C activity the same as that of atmospheric CO_2 (104.3 pmC; Clark and Fritz, 1997) the ^{14}C activity in groundwater can be estimated. The role of atmospheric carbon is smaller than that of other C-sources. The mole concentration of inorganic carbon in wet deposition was $1.18 \cdot 10^{-4}$ mol (Table 2).

Table 3

Geochemical models found (with minimum number of phases)

Phases	Model 1	Model 2
	Mole transfers	Mole transfers
$CO_2(g)$	7.634E-04	5.837E-04
$O_2(g)$	3.031E-04	3.031E-04
$N_2(g)$	6.534E-05	6.534E-05
Calcite	4.952E-04	2.966E-04
Dolomite	–	1.891E-04
Siderite	8.955E-08	8.955E-08
Rhodochrosite	9.103E-09	9.103E-09
Smithsonite	2.448E-07	2.448E-07
Gypsum	2.760E-04	2.760E-04
Celestite	9.817E-07	9.817E-07
Albite	1.416E-04	1.605E-04
Chlorite[1]	3.782E-05	–
Kaolinite	–7.198E-05	–4.362E-05
Illite[1]	–3.290E-05	–3.290E-05
Halite	8.147E-05	7.780E-05
Fluorite	1.725E-06	1.725E-06
Sum of phase transfers	2.062E-03	1.879E-03
Total mole transfer of C-carbonates	4.955E-04	4.860E-04

Composition of chlorite, $Mg_5Al_2Si_3O_{10}(OH)_8$, and illite, $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ according to *phreeqc.dat* thermodynamic data base; other explanations is in the text

The activity of ^{14}C in groundwater ($a^{14}C_{GW}$) is calculated from the expression:

$$a^{14}C_{GW} = \frac{\alpha C_{CO_{2atm}} \cdot a^{14}C_{CO_{2atm}} + \alpha C_{CO_{2soil}} \cdot a^{14}C_{CO_{2soil}} + \alpha C_{carbonates} \cdot a^{14}C_{carbonates}}{\alpha C_{CO_{2atm}} + \alpha C_{CO_{2soil}} + \alpha C_{carbonates}} \quad [1]$$

where: α — mole transfer of components; $a^{14}C$ — radiocarbon activity in components, in percent of modern carbon [pmC].

Taking the calculated mole transfers (Table 3), $a^{14}C_{GW}$ is 64.66 and 59.75 pmC for model no. 1 and model no. 2, respectively. The values obtained are reasonably consistent with the ^{14}C activity measured in the groundwater (59.39 ± 0.23 pmC; Table 1). Activity calculated for model 2 equals the measured value, providing corroboration that the model with dolomite dissolution is more probable in the real geochemical system. The consistency of calculated and measured ^{14}C activities confirms the correctness of the conceptual geochemical model.

Carbon dioxide and carbonate minerals are the main sources of DIC in the groundwater of the recharge zone. Carbon evolution in many groundwater systems involves dissolution of soil CO_2 and dissolution of carbonate minerals (usually calcite):

$$H_2O + CO_{2(soil)} + CaCO_{3(s)} = Ca^{2+} + 2HCO_3^- \quad [2]$$

At pH found in groundwater of well 2 (pH = 7.73; Table 1) the main form of DIC dissolved in water is the HCO_3^- ion. The presence of H_2CO_3 and CO_3^{2-} might be negligible.

Under conditions of a system closed with respect to CO_2, dissolution of ^{14}C-free carbonates by carbonic acid brings about dilution of the initial ^{14}C originating from soil CO_2. Under ideal closed conditions, according to equation [2] soil CO_2 gives 50% of total molar DIC concentration. In the groundwater studied, 64.0 and 59.1% of molar DIC results from CO_2 (jointly soil and atmospheric) dissolution, for model 1 and model 2 respectively. Under most natural conditions, geochemical systems are transitional between open and closed systems. Also, the hydrogeochemical system of the recharge zone studied can be defined as a transitional, semi-closed one with respect to soil carbon dioxide.

CONCLUSIONS

The radiocarbon activity in groundwater estimated from the results of geochemical modelling is consistent with the measured ^{14}C activity. This corroborates the validity of the geochemical model used. Conditions in the recharge zone of the aquifer studied can be classified as semi-closed with respect to soil CO_2. Calcite saturation is not reached in the system, also indicating the absence of closed system conditions. The results obtained are representative of groundwater in the recharge zone of the hydrogeological system. In the confined part of the aquifer studied, a system closed with respect to CO_2 is present (Dobrzyński, 2007*b*).

The method of inverse geochemical modelling is the tool used for quantification of chemical reactions that occur in the geochemical systems. Furthermore, it may be applied for the estimation of initial ^{14}C activities in the recharge to the groundwater. The same method might also be used for corrections of the effects of reactions on ^{14}C activity along the flow path. Geochemical modelling has an advantage over empirical methods because it simultaneously takes into account the wide range of chemical reactions in the geochemical system.

Application of inverse geochemical modelling methods for correcting the initial ^{14}C activity in the recharge water might be useful especially in that parts of the recharge area which are poorly described hydrogeochemically.

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