EVOLUTION OF RADIOCARBON IN A SANDY AQUIFER ACROSS LARGE TEMPORAL AND SPATIAL SCALES: CASE STUDY FROM SOUTHERN POLAND

M Dulinski[1,2] • K Rozanski[1] • T Kuc[1] • Z Gorczyca[1] • J Kania[3] • M Kapusta[3]

ABSTRACT. We present the results of a comprehensive study aimed at tracing the evolution of carbon isotopic composition of the TDIC (total dissolved inorganic carbon) reservoir from the unsaturated zone down to the discharge area, in a sandy aquifer near Kraków, southern Poland. A multilevel well penetrating the unsaturated zone in the study area was equipped with horizontally mounted lysimeters with ceramic suction cups to collect samples of pore water and metal probes to collect soil air. Strong seasonal fluctuations were observed of soil pCO_2 extending down to the water table, coupled with distinct, well-defined depth profiles of $\delta^{13}C_{TDIC}$ reaching approximately −10‰ at 8 m depth and almost constant radiocarbon content in the TDIC pool, comparable to $^{14}CO_2$ levels in the local atmosphere. Simple models (closed/open system) do not account for the observed depth variations of carbon isotopic composition of the TDIC pool. This suggests that the TDIC reservoir of pore waters is evolving under conditions gradually changing from an open towards a closed system. In order to explain ^{13}C and ^{14}C content of dissolved carbonates in groundwater in the recharge area of the studied aquifer, additional sources of carbon in the system are considered, such as organic matter decomposition accompanied by reduction of dissolved nitrates and sulfates. The piston-flow ^{14}C ages of groundwater in the confined part of the studied system were calculated using 2 approaches: 1) the correction model proposed by Fontes and Garnier (1979) was used to calculate groundwater ages, utilizing the chemical and carbon isotopic data available for the sampled wells; and 2) inverse geochemical modeling was performed for selected pairs of wells using NETHPATH code. The calculated ^{14}C ages of groundwater range from approximately 0.6 to 37.5 ka BP. Although both methods appeared to be in a broad agreement, NETHPATH calculations revealed that isotopic exchange processes between TDIC pool and solid carbonates present in relatively small amounts in the aquifer matrix play an important role in controlling the ^{13}C and ^{14}C signatures of the dissolved carbonate species in groundwater and should be taken into account when ^{14}C ages are calculated.

INTRODUCTION

Although radiocarbon is perhaps the most often used tracer to quantify timescales of groundwater flow in the age range from approximately 10^3 to 4×10^4 yr, its usage has been plagued by numerous uncertainties related to non-conservative behavior of carbon in groundwater systems and changing boundary conditions (e.g. Clark and Fritz 1997; Cartwright 2010; Blaser et al. 2010). These difficulties have 3 major roots: 1) the formation of the total dissolved inorganic carbon (TDIC) pool in groundwater, which is usually a subject of ^{14}C dating, may proceed under different geochemical conditions (open- or closed-system behavior with respect to soil CO_2) resulting in large differences in the initial ^{14}C activity of this pool, thus complicating the ^{14}C dating procedure; 2) carbon is essentially a non-conservative element in groundwater systems, particularly when the matrix contains a significant fraction of carbonate minerals; and 3) in double-porosity systems ^{14}C, like any other tracer, is subject to retardation effects, which lead to the delay of tracer movement when compared to the velocity of groundwater flow (Małoszewski and Zuber 1991; Sanford 1997). Notwithstanding those persisting difficulties, ^{14}C was and still remains the tracer of choice for quantifying groundwater ages on millennial timescales.

Here, we present the results of a comprehensive study aimed at tracing the evolution of carbon isotopic composition of the TDIC reservoir in a sandy aquifer near Kraków, southern Poland, from the unsaturated zone down to the discharge area. Over the past 2 decades, the studied aquifer has been

---

[1] AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Kraków, Poland.

[2] Corresponding author. Email: Marek.Dulinski@fis.agh.edu.pl.

[3] AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Kraków, Poland.

Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 905–919

a test ground for various tracer methods being applied to define timescales of groundwater flow and to calibrate 3D numerical flow and transport models (Zuber et al. 2005; Witczak et al. 2008). Physical and chemical parameters (temperature, pH, Eh, major and trace ions) as well as concentrations of various environmental tracers including tritium, SF_6, freons, stable isotopes of oxygen and hydrogen in water, ^{85}Kr, ^{39}Ar, heavy noble gases, ^{3}He/^{4}He ratio, and ^{13}C and ^{14}C content of TDIC, have been analyzed in more than 40 wells. We focus here on the processes controlling carbon isotope composition of pore waters in the unsaturated zone of the studied aquifer and decipher the chemical and isotope evolution of this reservoir, with the central aim of providing quantitative information on timescales of groundwater flow in the confined part of the studied system.

THE STUDY AREA

The Bogucice Sands aquifer (49°59′–50°03′N; 19°58′–20°17′E) is located in southern Poland, at the outskirts of the Kraków agglomeration (Figure 1). It consists of quartz sands, loose sandstones, and silts of the Badenian deltaic basin located at the northern boundary of the flysch Carpathians (Porębski and Oszczypko 1999). The main part of the Bogucice Sands aquifer belongs to the national category of Major Ground Water Basins (MGWB), with the boundaries of the MGWB-451 chosen at transmissivity exceeding 10 $m^2\,hr^{-1}$ (Kleczkowski et al. 1990). The lithology of the aquifer is very irregular, with 2 permeable layers representing 20–80% of the profile (Figure 2), and carbonate content in the range of 3–10% in sands, partly as calcareous shell debris, and 25–29% in sandstones, mainly as carbonate cement. The marine origin of the carbonate phase in the aquifer matrix was confirmed through analyses of its carbon isotopic composition ($\delta^{13}C \cong 0$, lack of ^{14}C).

The Bogucice Sands aquifer is recharged mainly by precipitation at the outcrops partly covered by Quaternary sediments. Some recharge is also possible via downward seepage through the aquitard in the areas where extensive abstraction caused significant drops of water pressure. The general direction of groundwater flow is towards the Vistula River valley in the north (Figure 1), with natural drainage by upward seepage in most of the confined area. Intensive exploitation of the aquifer started in the second half of the past century, with a current total withdrawal of about 11,000 $m^3\,d^{-1}$ (Kulma et al. 2001).

The hydrochemistry of Bogucice Sands aquifer was briefly outlined in Zuber et al. (2005) and discussed in detail by Witczak et al. (2008). In the recharge area, both water-bearing layers contain water of HCO_3-Ca or HCO_3-SO_4-Ca types, with slightly elevated Na^+, Cl^-, and NO_3^- contents of anthropogenic origin in the most western and eastern parts. Elevated SO_4^{2-} contents (up to 200 mg L^{-1}) are regarded as resulting mainly from acid rain and atmospheric deposition of industrial dust from a nearby large metallurgical plant. In the confined area, deeper within both aquifer layers, elevated Fe^{2+}, Mn^{2+}, and NH_4^+ contents are observed. In the most northern part of the aquifer, water is of HCO_3-Ca-Na and HCO_3-Na types with TDS values in some cases slightly exceeding 1 g L^{-1}.

MATERIALS AND METHODS

A multilevel well located few kilometers north of the studied system (cf. Figure 1) and penetrating the unsaturated zone was used to study isotope and chemical evolution of the TDIC pool and soil CO_2 during the infiltration process. The well (1.1 m diameter, 8 m deep) was originally constructed to track the migration of pollutants from the nearby steel factory through the unsaturated zone. The well was equipped with horizontally mounted lysimeters with ceramic suction cups to collect pore waters for chemical analyses (Karpińska-Rzepa et al. 2005; Operacz 2009). Later on, horizontally mounted metal probes were added to collect soil air from different depth intervals within the profile. The lysimeters and metal probes extended ~90 cm into the unsaturated zone profile and were posi-

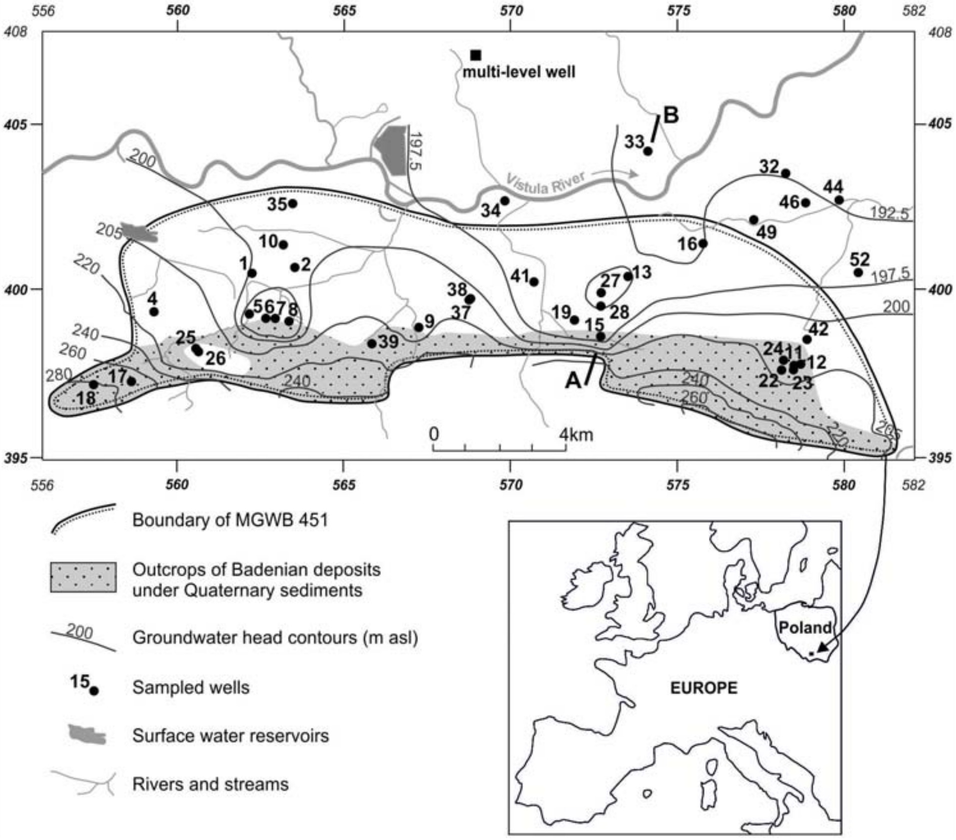

Figure 1 Location and hydrogeological map of the studied aquifer system, Bogucice Sands, southern Poland

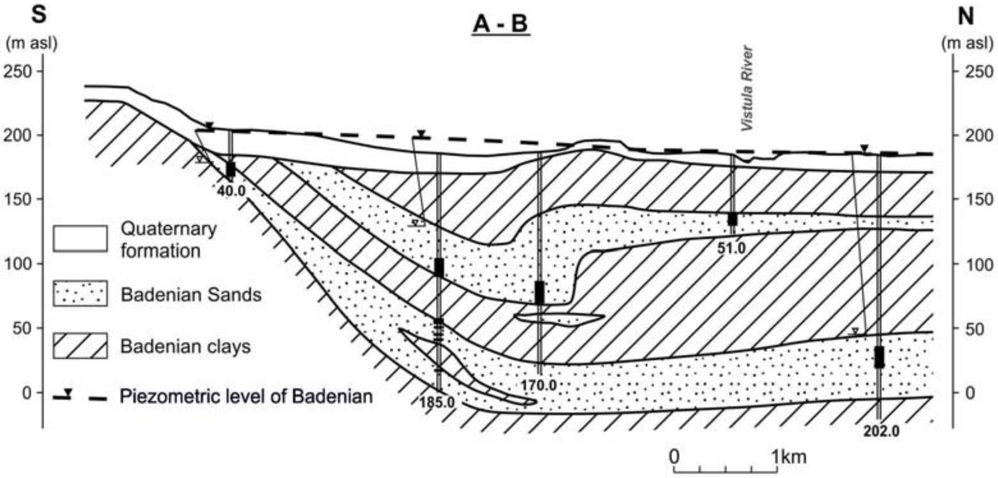

Figure 2 Hydrogeological cross-section through the Bogucice Sands aquifer along the A-B transect in Figure 1, with the projection of some wells and their screened parts.

tioned at different horizontal angles, in order to avoid a shadowing effect. They were properly sealed to assure sampling from the predefined depth interval within the profile. Characteristics of the unsaturated zone in this area (loess, ~8 m depth) are similar to those prevailing over the recharge area of the Bogucice Sands aquifer.

Samples of pore water and soil air were collected during several sampling campaigns; pH and temperature of pore waters were measured *in situ*. The chemistry (major ions) of the pore waters was analyzed in the Hydrogeochemical Laboratory of the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Kraków using ICP-MS. Carbon dioxide was extracted from samples of pore waters using an acidification technique similar to that described by Atekwana and Krishnamurthy (1998). Its ^{14}C content was measured in the Poznań AMS Radiocarbon Laboratory, while the ^{13}C content was determined in the mass spectrometry laboratory of the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology in Kraków using the conventional dual-inlet IRMS technique. Samples of soil air (approximately 3–5 L) were collected from different depth intervals in the unsaturated zone using a membrane pump and inflatable polyvinyl fluoride bags (Cole-Parmer Int.). The CO_2 was cryogenically extracted from the soil air in the laboratory and its ^{14}C and ^{13}C content was measured using miniature gas proportional counters (Gorczyca 2003) and dual-inlet IRMS, respectively. Dissolved carbonates in analyzed groundwater samples were precipitated in the field from ~60 L of water following the established procedure (Clark and Fritz 1997). ^{14}C content in those samples was measured using benzene synthesis followed by liquid scintillation spectrometry (Florkowski et al. 1975) while ^{13}C content was measured using the dual-inlet IRMS technique.

The ^{13}C content in the soil CO_2 and in the TDIC pool of the pore waters and the analyzed groundwater samples is expressed as per mil deviation ($\delta^{13}C$) from the internationally accepted standard, V-PDB (Coplen 1996), while ^{14}C content is expressed in percent of modern carbon (pMC), following recommendations of Stuiver and Polach (1977) and Mook and van der Plicht (1999). Typical uncertainty of ^{14}C concentration in the TDIC pool of the pore waters, measured by the AMS technique, was in the order of 0.3–0.4 pMC, while for soil CO_2 gas, where ^{14}C content was measured using miniature gas proportional counters, this uncertainty was larger, about 0.6–0.8 pMC. Typical uncertainty of ^{14}C analyses of the TDIC pool in groundwater samples collected in the recharge area and in the confined part of the studied aquifer was ~ 0.7 pMC, while typical reproducibility of $\delta^{13}C$ determinations was ~0.1‰.

The $\delta^{13}C_{TDIC}$ values observed in the pore waters of the studied unsaturated zone as well as carbon isotope composition (^{13}C and ^{14}C content) of the TDIC pool in groundwater samples collected in the recharge area were modeled using PHREEQC (v 2.18) geochemical code (Parkhurst and Appelo 1999). Piston-flow ^{14}C ages of groundwater in the confined part of the studied system were calculated using the correction model of Fontes and Garnier (1979). In parallel, for the selected pairs of wells, apparent ^{14}C ages of groundwater were calculated using NETHPATH code (Plummer et al. 1994).

CARBON ISOTOPE COMPOSITION OF PORE WATERS IN THE UNSATURATED ZONE

Depth profiles of carbon isotope composition of TDIC reservoir in the pore waters and of the soil CO_2 were measured during several sampling campaigns carried out in 2005 and 2006. The results are summarized in Table 1 and shown in Figure 3.

As seen in Figure 3a and Table 1, the concentration of CO_2 in the soil air reveals strong seasonal fluctuations. It varies between approximately 4000–6000 ppmv during summer months and 500–

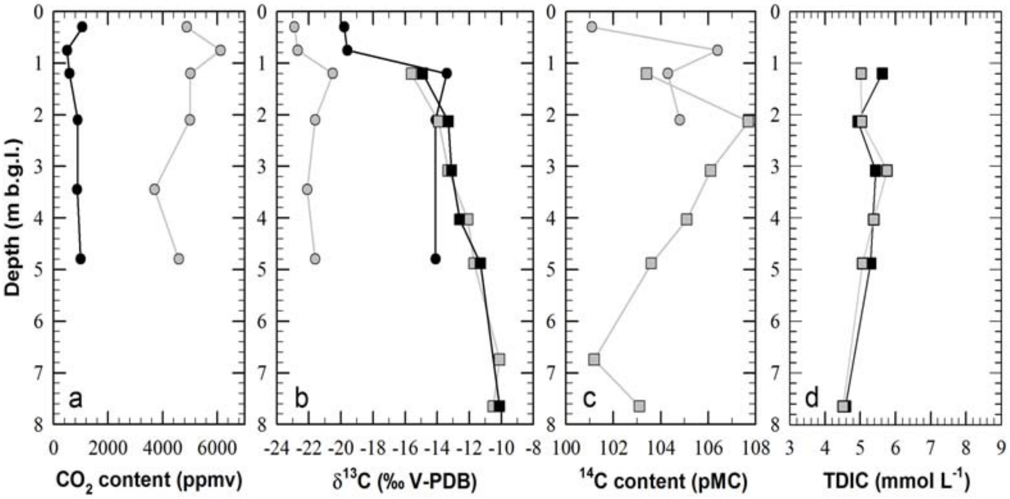

Figure 3 Unsaturated zone depth profiles of soil CO_2 concentration (a), $\delta^{13}C$ (b), and ^{14}C (c) content in soil CO_2 and TDIC pool of the pore waters. Shown are also depth profiles of TDIC concentration (d). Black symbols – winter profile (19 December 2005); gray symbols – average summer profile (cf. Table 1); circles – soil CO_2; squares – total dissolved inorganic carbon (TDIC) pool.

1000 ppmv during winter. For comparison, the atmospheric CO_2 concentration measured in Kraków during 2005–2006 was about 370–380 ppmv (Chmura et al. 2008). Also, the ^{13}C content in soil CO_2 varies with the season (Figure 3b). During summer, the measured $\delta^{13}C$ values ranged from approximately –23‰ in the upper part of the profile (down to 1 m depth) to about –21.5‰ in middle and lower part, with a small maximum around 1.2 m. Such values are expected considering the fact that plant cover and organic matter in the soil of this region has $\delta^{13}C$ values ranging from –25 to –27‰ (Gorczyca 2003). Apparent enrichment in ^{13}C of the soil CO_2 with respect to the source organic matter observed along the profile stems from isotope fractionation associated with diffusive transport of carbon dioxide from the soil to the atmosphere (Dörr and Münnich 1980; Amundson et al. 1998). During winter months, $\delta^{13}C$ of soil CO_2 dropped significantly; values were recorded from –19.7‰ in the upper part of the profile down to –14.1‰ at 4.8 m depth. These results should be compared with $\delta^{13}C$ values of CO_2 in the Kraków atmosphere recorded during this period (between approximately –9.7 and –10.7‰, as reported by Kuc et al. 2007). A substantial increase of $\delta^{13}C$ of soil CO_2 during winter may result from some admixture of atmospheric CO_2 in the soil air (Dudziak and Halas 1996), facilitated by a significantly reduced soil-atmosphere CO_2 concentration gradient during this time of the year and/or by some unidentified leakages in the sampling system.

^{14}C content in soil CO_2 has been measured in the samples collected during the June 2005 campaign in the upper part of the profile (Figure 3c). It varied between 101.1 pMC (0.30 m) and 106.4 pMC (0.75 m). A similar range of ^{14}C concentrations was observed by Carmi et al. (2009) in the CO_2 collected in the unsaturated zone of the coastal aquifer in Israel. The ^{14}C content in atmospheric CO_2 measured in Kraków during summer 2005 was fluctuated around 104 pMC (Kuc et al. 2007). The fact that ^{14}C content in the soil CO_2 collected in the upper part of the profile is similar to that observed in the local atmosphere suggests that root respiration was an important source of the soil CO_2 sampled in June 2005. However, it should be noted that decomposition of soil organic matter of appropriate age structure may also lead to ^{14}C levels of soil CO_2 similar to $^{14}CO_2$ levels recorded in the local atmosphere (Gorczyca et al., these proceedings).

The TDIC concentration in the pore waters decreases slightly with depth (Figure 3d), from approximately 5.5 mmol L^{-1} recorded in the upper part of the profile down to 4.5 mmol L^{-1} at 7.6 m depth, suggesting partial degassing of the solution and precipitation of carbonate phase in the lower part of the profile. The ^{13}C content in the TDIC pool gradually increases with depth, from about –15‰ at 1.2 m to –10‰ at 7.65 m, irrespective of season (Figure 3b). ^{14}C content in the TDIC reservoir was measured only in the samples of pore waters collected during the September 2006 campaign. It remains high (>100 pMC) along the profile, with a small maximum at 2.13 m (107.7 pMC) and a gradual decrease down to 101–103 pMC in the lower part of the profile (Figure 3c).

Table 1 Measured depth profiles of the selected parameters of pore waters and soil CO_2.

Pore waters			Soil CO_2			
Depth (m bgl)	$\delta^{13}C_{TDIC}$ (‰ V-PDB)	^{14}C content (pMC)	Depth (m bgl)	pCO_2 (ppmv)	$\delta^{13}C$ (‰ V-PDB)	^{14}C content (pMC)
Summer[a]:			Summer[a]:			
1.20	–15.6	103.4	0.30	4884	–22.9	101.1[b]
2.13	–13.9	107.7	0.75	6125	–22.7	106.4[b]
3.08	–13.3	106.1	1.20	5012	–20.5	104.3[b]
4.03	–12.1	105.1	2.10	4999	–21.6	104.8[b]
4.88	–11.7	103.6	3.45	3697	–22.1	n.a.[c]
6.74	–10.1	101.2	4.80	4589	–21.6	n.a.
7.65	–10.5	103.1				
Winter[d]:			Winter[d]:			
1.20	–14.9	n.a.	0.30	1057	–19.8	n.a.
2.13	–13.3	n.a.	0.75	500	–19.6	n.a.
3.08	–13.1	n.a	1.20	584	–13.4	n.a.
4.03	–12.6	n.a.	2.10	886	–14.1	n.a.
4.88	–11.3	n.a.	3.45	869	n.a	n.a.
6.74	n.a.	n.a.	4.80	989	–14.1	n.a.
7.65	–10.1	n.a.				

[a] Average values of the parameters measured during sampling campaigns carried out on 8 June 2005, 1 August 2006, and 13 September 2006.
[b] Measured in the samples collected during sampling campaign carried out on 8 June 2005.
[c] n.a. – not analyzed.
[d] Sampling campaign carried out on 19 December 2005.

The depth profile of $\delta^{13}C_{TDIC}$ measured in June 2005 was modeled using the PHREEQC geochemical code. In addition to isotopic data, also physico-chemical parameters of pore waters collected during this sampling campaign (temperature, pH, concentration of major ions) were used in model calculations. Starting from the measured $\delta^{13}C$ values of soil CO_2 along the profile and assuming open-system conditions (unlimited supply of CO_2), with full chemical and isotope equilibrium maintained between soil CO_2 and the TDIC pool, the $\delta^{13}C$ content of the dominant carbon species in the pore waters (dissolved CO_2 and HCO_3^- ions) was calculated. $\delta^{13}C_{TDIC}$ was then calculated as a weighted mean of these 2 components and compared with the measured values (Figure 4).

Qualitative agreement between the measured and modeled $\delta^{13}C_{TDIC}$ values was obtained. Both measured and modeled $\delta^{13}C_{TDIC}$ values decrease with depth, from –14.5‰ at 1.2 m to about –11.8‰ at 4 m. Below that depth, the measured values suggest a further increase of $\delta^{13}C_{TDIC}$, which is not the case for the model results. It seems that the interaction of gaseous CO_2 and pore waters in the unsaturated zone is a more complex process than the simple open-system model implies. On the scale of

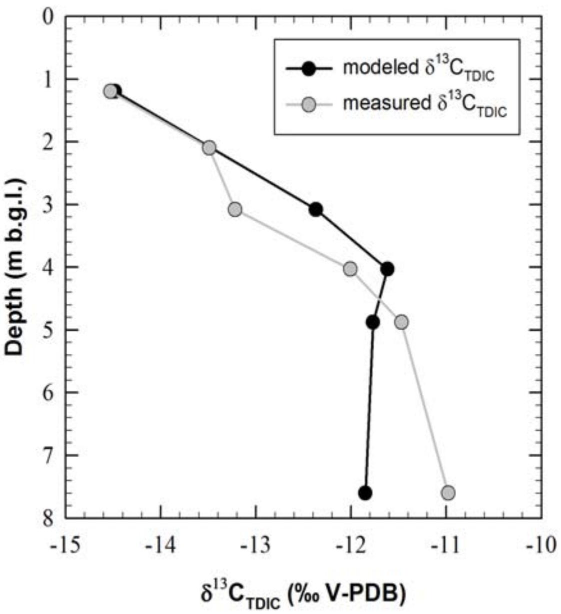

Figure 4 Comparison of measured and calculated depth profiles of $\delta^{13}C_{TDIC}$ of pore waters in the studied unsaturated zone. The measured values represent the June 2005 sampling campaign.

single centimeters, pore waters may temporarily lose contact with soil CO_2. This would mean switching from open- to closed-system conditions, which would lead to higher $\delta^{13}C_{TDIC}$ values observed in the pore waters. Without detailed studies it is not possible to quantify the fraction of time that pore waters may spend under open- and closed-system conditions. It is also not known whether the general assumption about chemical and isotopic equilibrium holds also on such small scales along the profile. The apparent evolution from open- to closed-system conditions in the lower part of the profile should lead not only to higher $\delta^{13}C_{TDIC}$ values but also to a reduction in ^{14}C content in the TDIC reservoir. Indeed, ^{14}C concentration in the TDIC reservoir drops from 107 pMC at ~2 m to 102 pMC at 7.5 m depth. This evolution towards closed-system conditions might be facilitated by decreasing air porosity with increasing depth in the unsaturated zone.

ISOTOPIC COMPOSITION OF TDIC RESERVOIR IN GROUNDWATER OF STUDIED AQUIFER

In total, 36 wells have been sampled for δ^{13}C and ^{14}C analyses of the TDIC pool, both in the recharge and confined zone of the studied aquifer, a number of them several times over the period from 1987 until 2011. The relationship between ^{14}C and δ^{13}C content of the TDIC reservoir in the analyzed groundwater samples is presented in Figure 5. Two categories of data points are shown in the figure: 1) those representing groundwater in the recharge area, and 2) those representing groundwater in the confined zone of the studied aquifer. The first group was identified via measurable amounts of anthropogenic tracers present in those waters, mainly tritium and SF_6 (Zuber et al. 2005). A distinct evolution in the carbon isotopic composition along the flow paths is apparent in Figure 5. A reduction of ^{14}C content is accompanied by gradual evolution of ^{13}C content towards less negative $\delta^{13}C_{TDIC}$ values, reaching –8.5‰ for groundwater with trace amounts of ^{14}C.

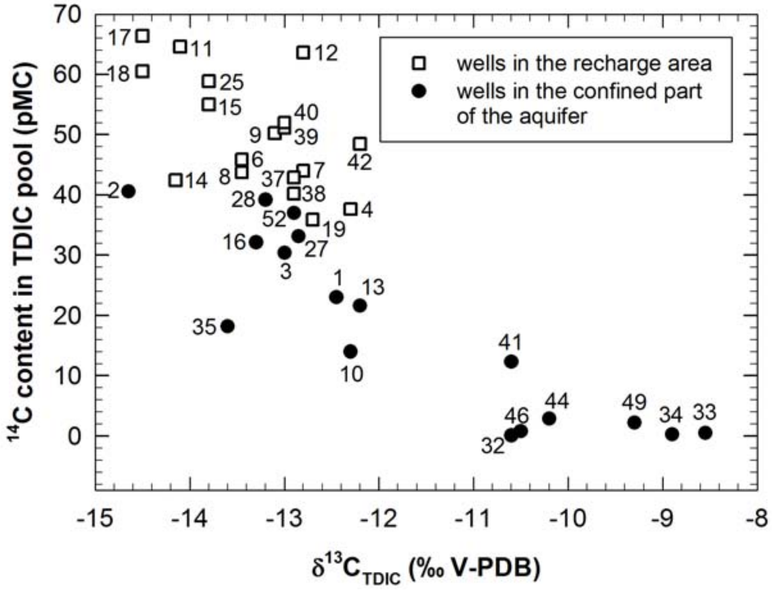

Figure 5 Relationship between ^{14}C and ^{13}C content of the TDIC pool in samples collected in the studied aquifer system. The wells are identified by numbers (cf. Figure 1).

Recharge Area

The evolution of carbon isotopic composition of the TDIC pool in the recharge area has been modeled using PHREEQC geochemical code. Two contrasting scenarios of this evolution have been considered: 1) open-system model where the TDIC pool is formed under unlimited supply of soil CO_2 at constant conditions (soil temperature, partial pressure of soil CO_2, and its ^{13}C and ^{14}C content); and 2) closed-system conditions where the infiltrating water saturated with CO_2 leaves the soil zone and interacts with carbonate matrix further down in the aquifer, acquiring the observed alkalinity. The data-model comparison is shown in Figure 6 where the ^{14}C and δ^{13}C content of the TDIC pool is plotted as a function of its size, both for open- and closed-system conditions. It is obvious from Figure 6 that simple open- and closed-system models cannot explain the measured concentration and carbon isotopic composition of the TDIC pool. This is particularly the case for ^{14}C content (Figure 6a). Apparently, some additional processes are at work in the studied groundwater system that influence both the isotopic composition and the size of the TDIC reservoir.

Additional supply of carbon to the evolving TDIC reservoir may occur via decomposition of organic matter dissolved in the infiltrating water, perhaps with some contribution from decomposition of organic matter incorporated in the aquifer matrix in contact with the flowing water. The ^{14}C content in the total organic carbon (TOC) pool of groundwater samples collected in the recharge area has not been measured. Organic matter incorporated in the aquifer matrix is most probably ^{14}C-free. It has been assumed in the model calculations that the ^{14}C content of the source organic matter subject to decomposition varies between 50 and 20 pMC. Also, 2 different concentrations of ^{13}C in this organic matter were assumed ($\delta^{13}C_{OM} = -25$ and -20‰). The results of model calculations are summarized in Figure 7a and b. Several consecutive steps in the evolution of the TDIC pool were considered.

Initially, the solution is evolving under open-system conditions at full contact with soil CO_2, and reaches the prescribed degree of saturation equal 1 or 50% (points “a” in Figure 7a and 7b). Further

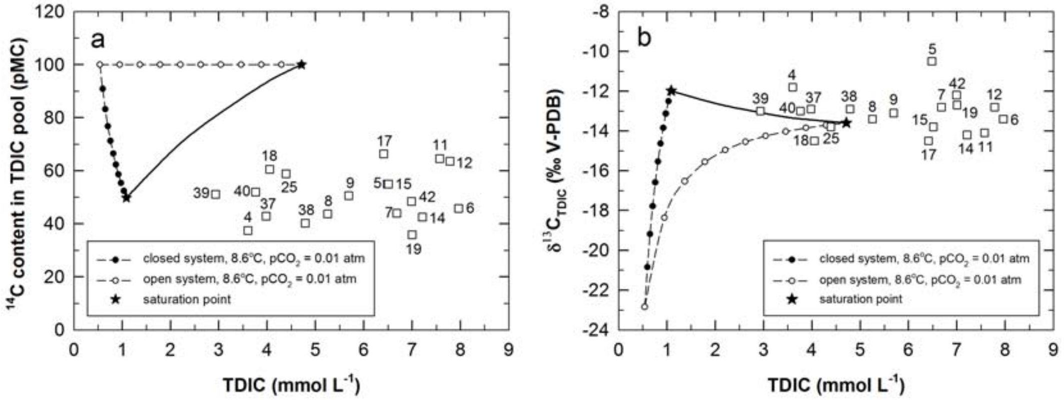

Figure 6 Model-data comparison for the relationship between ^{14}C (a) and ^{13}C (b) content and the size of the TDIC reservoir in the analyzed groundwater samples representing the recharge area of the studied aquifer (squares). Model calculations were performed for open- and closed-system conditions using PHREEQC geochemical code. The solid lines connecting the points corresponding to saturation under open- and closed-system conditions (stars) represent the locus of the end points of isotope and chemical evolution, with degree of contact of soil CO_2 during dissolution of carbonate phase changing from no contact for the closed-system conditions to full contact for the open-system conditions.

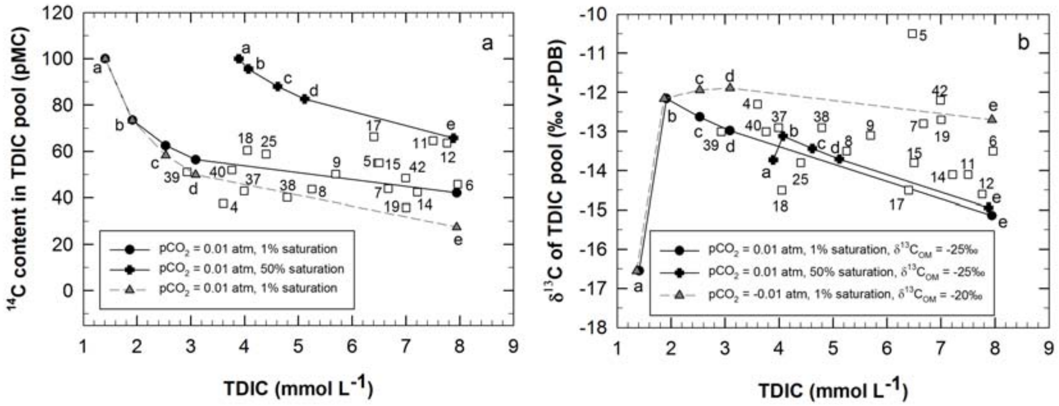

Figure 7 Model-data comparison for the relationship between ^{14}C (a) and ^{13}C (b) content and the size of the TDIC pool in analyzed groundwater samples representing the recharge area of the studied aquifer. Model calculations were performed using PHREEQC geochemical code (open squares = measured values). The ^{14}C content of the source organic matter was assumed to be 50 and 20 pMC (black symbols and gray triangles, respectively, in Figure 7a). The ^{13}C content of the source organic matter was taken as −25‰ and −20‰ (black symbols and gray triangles, respectively, in Figure 7b). See text for details.

down along the flow paths, the evolution proceeds under closed-system conditions until saturation is reached ("b" in Figure 7a and 7b). Then, additional CO_2 resulting from decomposition of source organic matter is supplied to the solution, with oxygen dissolved in water being consumed in this process. The new saturation point is reached when the dissolved O_2 is exhausted ("c" in Figure 7a and 7b). Further decomposition of source organic matter proceeds as a result of nitrate reduction until a new equilibrium is reached ("d" in Figure 7a and 7b). Finally, decomposition of organic matter continues as a result of sulfate reduction until the size of the TDIC reservoir reaches the prescribed value of ~8 mmol L^{-1} ("e" in Figure 7a and 7b). The initial NO_3 concentration in the infiltrating water was set at 20 mg L^{-1} (Witczak et al. 2008). The amounts of SO_4 consumed in the oxidation process varied between about 90 and 150 mg L^{-1}, depending on the assumed degree of saturation. SO_4 concentrations up to 500 mg L^{-1} were observed in the pore waters of the investigated unsaturated zone (Operacz 2009).

It is apparent from Figure 7a that the measured ^{14}C content and the size of TDIC pool in the analyzed groundwater samples can be reproduced by the model reasonably well with the prescribed conditions in the unsaturated zone (mean partial pressure of soil CO_2 equal to 1%, degree of saturation varying between 1 and 50%) and the ^{14}C concentration of the source organic matter undergoing decomposition equal to 50 pMC. Still, the measured ^{14}C concentrations in a number of wells (39, 4, 37, 38, 8, 19) are lower than those predicted by the model. Reducing the assumed ^{14}C content in the source organic matter to 20 pMC significantly improves the model-data comparison.

Modeling of the $\delta^{13}C$ content in the TDIC pool provides an additional constraint on the source organic matter being utilized in the process. It is clear from Figure 7b that the measured $\delta^{13}C_{TDIC}$ values cannot be reproduced with a single $\delta^{13}C$ value of the source organic matter. The calculated trajectories in the $\delta^{13}C_{TDIC}$-TDIC space cover most of the data points only if $\delta^{13}C_{OM}$ varies between –25 and –20‰. Such a range of $\delta^{13}C_{OM}$ values is acceptable in light of past climatic evolution of the study area, with a varying influence of C_3 and C_4 plants.

Confined Zone

The evolution of the TDIC reservoir in the confined zone of the studied aquifer has been studied with the focus on assessing the age of groundwater in the sampled wells. Two approaches were used: 1) the geochemical correction model of Fontes and Garnier (1979) was applied to evaluate ^{14}C ages of TDIC reservoir in the confined zone; and 2) NETPATH code was used to calculate ^{14}C age differences between selected pairs of wells.

The piston-flow age of the analyzed groundwater sample can be expressed as

$$t = -8267 \cdot \ln\left(\frac{^{14}C}{q \cdot {}^{14}C_o}\right) \tag{1}$$

where ^{14}C and $^{14}C_o$ represent ^{14}C content in the TDIC reservoir of the analyzed groundwater sample and in the soil CO_2 of the recharge area(s), respectively. The latter is usually assumed to be equal to 100 pMC. q stands for the correction factor accounting for various ^{14}C-dilution processes active in the system.

Since the recharge area of the studied aquifer extends over a large distance (cf. Figure 1), it was split into 5 sectors (A, B, C, D, E; cf. Table 2). The average values of chemical and isotopic parameters characterizing groundwater in each sector (pH, temperature, major ion content, alkalinity, $\delta^{13}C$ content of TDIC pool) were calculated using PHREEQC code on the basis of chemical and isotopic data available for the sampled wells (Kapusta 2012). Those average parameters were then used to calculate the correction factor q for a given well in the confined area, following the Fontes and Garnier (1979) approach. The apparent ^{14}C age of groundwater in this well was then calculated using Equation 1. The calculated ^{14}C ages are summarized in Table 2. The initial ^{14}C content reported in Table 2 for each sector represents the mean value of ^{14}C concentration measured in each individual well.

The uncertainties of the apparent ^{14}C ages calculated using Fontes and Garnier's (1979) correction model (Equation 1) were estimated in accordance with the uncertainty propagation law. It was assumed that typical uncertainty of ^{14}C concentration in the soil CO_2 reservoir is about 5 pMC, whereas the correction factor q can be determined with a relative uncertainty of ~10%. The value 0.7

Table 2 ^{14}C ages of groundwater samples collected in the confined part of the studied aquifer, calculated using the Fontes and Garnier (1979) correction model (see text for details).

		TDIC pool		
Recharge area[a]	Well nr	$\delta^{13}C_{TDIC}$ (‰ V-PDB)	^{14}C content (pMC)	Modeled ^{14}C age[b] (ka BP)
Sector A	4	−12.3	37.7	2.9
wells 17, 18, 25, 26	1	−12.5	23.1	9.1
$\delta^{13}C_{TDIC}$ = −14.3‰, ^{14}C = 62.6 pMC	2	−14.6	40.6	5.1
	10	−12.3	14.0	14.5
	35	−13.6	18.2	14.4
Sector B	10	−12.3	14.0	15.0
wells 5, 6, 7, 8	35	−13.6	18.2	16.0
$\delta^{13}C_{TDIC}$ = −13.2‰, ^{14}C = 47.2 pMC				
Sector C	37	−12.9	42.9	6.6
wells 9, 39	38	−12.9	42.0	6.4
$\delta^{13}C_{TDIC}$ = −13.1‰, ^{14}C = 55.0 pMC	34	−8.9	0.3	>30.3
	33	−8.3	0.2	>30.3
Sector D	41	−10.6	12.3	14.4
wells 15, 19	34	−8.9	0.3	>28.7
$\delta^{13}C_{TDIC}$ = −13.2‰, ^{14}C = 45.1 pMC	28	−13.2	39.2	4.9
	27	−12.8	33.2	10.0
	13	−12.2	19.1	9.3
	33	−8.3	0.2	>28.7
Sector E	16	−13.3	32.2	6.4
wells 11, 12, 22, 23, 24	33	−8.3	0.2	>31.6
$\delta^{13}C_{TDIC}$ = −13.4‰, ^{14}C = 64.1 pMC	42	−12.2	48.5	2.0
	32	−10.6	0.1	>31.6
	46	−10.5	0.8	>31.6
	49	−9.3	2.2	25.7
	44	−10.2	2.9	24.4
	52	−12.9	37.0	3.2

[a] Identified by wells that contain measurable amounts of anthropogenic tracers (mainly tritium and SF_6).

[b] Calculated using Equation 1 and the correction model of Fontes and Garnier (1979).

pMC was adopted in the calculations as a standard uncertainty for ^{14}C content measured in TDIC pool. The calculated uncertainties (1σ) vary from approximately 800 to 1000 yr for the age range up to 10 ka BP and increase to about 3 ka for the age range 25–35 ka. For some wells with measured ^{14}C content below the assumed detection limit of 1.4 pMC (wells 32, 33, 34, 46), only the lower age limit could be established.

In parallel to ^{14}C age determinations based on Equation 1, the age differences between selected pairs of wells were calculated using the NETPATH code (Table 3). First, for each final well the expected ^{14}C concentration in TDIC reservoir resulting only from geochemical processes occurring along the flow path connecting the selected pair of wells was calculated using NETPATH. The chemical and isotopic parameters established for the initial well were used as a starting point for chemical evolution of the TDIC reservoir. Then, the difference between the calculated and measured ^{14}C concentration in each final well was converted to ^{14}C age. Since the initial well was always selected in the recharge area, the calculated age differences are equivalent to ^{14}C ages and can be directly compared with the ages listed in Table 2. Such a comparison is presented in Figure 8.

Uncertainties of ^{14}C ages derived with the aid of NETPATH stem mostly from the uncertainties of physico-chemical parameters measured in groundwater samples collected in the initial and final well. Also, the basic assumption behind the NETPATH approach states that the given parcel of water proceeds from the initial to final well is subject to some uncertainty. Although it is difficult to for-

Table 3 Apparent ^{14}C ages of groundwater in the selected wells located in the confined part of the studied aquifer, calculated using the NETPATH code (see text for details).

Well pairs		^{13}C and ^{14}C content (measured)		δ^{13}C and ^{14}C content (calculated)		Estimated isotope exchange		Modeled ^{14}C age (ka BP)
Initial	Final	$\delta^{13}C_{TDIC}$ (‰ V-PDB)	^{14}C content (pMC)	$\delta^{13}C_{TDIC}$ (‰ V-PDB)	^{14}C content (pMC)[a]	Calcite (mmol L^{-1})	Dolomite (mmol L^{-1})	
38	34	−8.9	0.3	−8.9	28.1	n.e.[b]	n.e.	37.5
37	34	−8.9	0.3	−8.9	21.6	n.e.	0.30	35.3
12	44	−10.2	2.9	−10.2	55.3	0.45	n.e.	24.4
12	52	−12.9	37.0	−12.9	46.6	n.e.	n.e.	1.9
12	16	−13.3	31.8	−13.3	59.8	0.40	n.e.	5.0
12	16	−13.3	31.8	−13.3	59.8	n.e.	0.20	5.0
12	16	−13.3	31.8	−13.3	59.8	n.e.	n.e.	5.5
15	28	−13.2	39.2	−13.2	42.8	n.e.	0.17	0.7
15	28	−13.2	39.2	−13.2	42.1	0.46	n.e.	0.6
15	28	−13.2	39.2	−13.8	44.9	n.e.	n.e.	1.1
25	1	−12.3	23.6	−12.3	47.0	n.e.	0.37	5.9
25	1	−12.3	23.6	−12.3	48.0	0.73	n.e.	5.9
18	1	−12.3	23.6	−12.3	46.5	n.e.	0.25	5.6
18	1	−12.3	23.6	−12.2	46.5	0.50	n.e.	5.6
15	33	−8.6	0.5	−8.5	19.9	1.6	n.e.	30.5

[a] Calculated ^{14}C content of TDIC pool in the end well. Correction for radioactive decay of ^{14}C not applied.

[b] n.e. = no exchange.

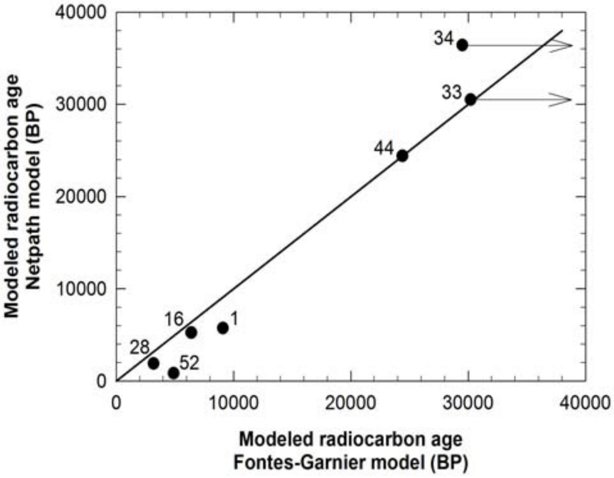

Figure 8 Relationship between piston-flow ^{14}C ages of selected groundwater samples representing the confined part of the studied aquifer, derived using NETPATH code, and the ^{14}C ages derived using Equation 1 and the correction model of Fontes and Garnier (1979). Solid line denotes 1:1 relationship.

mally calculate uncertainties associated with NETPATH inverse calculations, these uncertainties are definitely not larger than those derived from the uncertainty propagation law applied to Equation 1. It should also be noted that the NETPATH approach can accommodate the processes that are not accounted for in the correction model of Fontes and Garnier (1979), such as isotopic exchange in the confined part of the given aquifer system.

The apparent ^{14}C ages of groundwater samples collected in the confined zone of the studied aquifer and calculated using both approaches outlined above vary from approximately 0.6 to 37.5 ka. The largest ages were found in the northern, most distant part of the aquifer. Glacial ages of groundwater in this part of the aquifer suggested by ^{14}C data are confirmed by lower ^{2}H and ^{18}O content and reduced recharge temperatures derived from measurements of noble gas concentrations (Witczak et al. 2008). It is apparent from Figure 8 that ^{14}C ages estimated using 2 different approaches discussed above are in general agreement, although for the lower age range (<10 ka) the NETPATH code provides consistently lower ages when compared to the correction model of Fontes and Garnier (1979). This is most probably due to the fact that NETPATH allows for isotope exchange between the TDIC pool also in the confined part of the groundwater system, which is not the case for the Fontes and Garnier correction model. As shown in Table 3, significant amounts of calcite or dolomite have to be transferred between the solution and the solid carbonate phase present in the aquifer matrix in order to reach agreement between the measured and calculated δ^{13}C values.

CONCLUSIONS

This study reveals a considerable complexity of the processes controlling carbon isotope composition of the TDIC pool in groundwater, both in the unsaturated zone and in the aquifer itself. Under moderate climatic conditions characterized by distinct seasonality in air temperature and the activity of the biosphere, the partial pressure of CO_2 in the unsaturated zone undergoes large variations, with high pCO_2 values during summer months and low values during winter. This leads to repeated outgassing and dissolution of soil CO_2 in the pore waters of the unsaturated zone, inducing isotopic and chemical changes in the solution. As typical travel times of water through the unsaturated zone often exceed several years, in a seasonally varying climate the pore waters will undergo multiple dissolution/outgassing cycles before they enter the water table. The field data and the modeling results presented in this study suggest that the often-made assumption about open-system conditions prevailing in the unsaturated zone may not be fully fulfilled, particularly in deep unsaturated zones. Pore waters during their movement towards the water table may temporarily lose contact with soil CO_2, thus switching to the evolution under closed-system conditions. This may happen many times before they reach water table. More detailed studies are needed to quantify the possible impact of these processes on the chemical and isotope evolution of TDIC pool of pore waters in the unsaturated zone.

As demonstrated above, the evolution of carbon chemistry of groundwater along the flow paths can be quite complex even in a relatively simple porous sandy aquifer. In order to explain the size and the carbon isotopic composition of the TDIC pool in the recharge area of the studied aquifer, it was necessary to postulate an additional source of carbon in the system such as decomposition of organic matter, associated with reduction of nitrates and sulfates dissolved in groundwater. A 3-parameter comparison of the measured and modeled quantities (concentration of TDIC pool in groundwater and its carbon isotope composition) provides additional constraints on the source organic matter being utilized in the process. Satisfactory agreement between measured and modeled values could be reached for ^{14}C content of the source organic matter varying between about 20 and 50 pMC with a δ^{13}C value ranging from –20 to –25‰. The NETPATH calculations performed for selected pairs of wells shed light on the role of isotope exchange between the TDIC pool and the solid carbonate phase, present in the aquifer matrix. These processes modify the observed ^{13}C and ^{14}C content of this pool and, as a consequence, the calculated ^{14}C ages of groundwater in the confined part of the aquifer. More studies would be needed to better characterize the dynamics of these exchange processes and their impact on carbon isotope composition of the carbonate interface available for exchange, on timescales comparable with the geological age of the aquifer.

The calculated ^{14}C ages of groundwater in the confined part of the studied aquifer span the entire range of ages accessible by this method (from about 1 to 40 ka). The conservative assessment of uncertainties involved in determination of ^{14}C ages of groundwater presented in this study suggest that uncertainties are in the order of 10% for the age range between about 10 and 35 ka.

ACKNOWLEDGMENTS

Partial financial support of this study through EU research project GENESIS (project no. 226536) and through funds of the Polish Ministry of Science and Higher Education is kindly acknowledged.

REFERENCES

Amundson R, Stern L, Baisden T, Wang Y. 1998. The isotopic composition of soil and soil-respired CO_2. *Geoderma* 82:83–114.

Atekwana EA, Krishnamurthy RV. 1998. Seasonal variations of dissolved inorganic carbon and $\delta^{13}C$ of surface waters: application of a modified gas evolution technique. *Journal of Hydrology* 205:265–78.

Blaser PC, Coetsiers M, Aeschbach-Hertig W, Kipfer R, van Camp M, Loosli HH, Walraevens K. 2010. A new groundwater radiocarbon correction approach accounting for palaeoclimate conditions during recharge and hydrochemical evolution: the Ledo-Paniselian Aquifer, Belgium. *Applied Geochemistry* 25(3):437–55.

Carmi I, Kronfeld J, Yechieli Y, Yakir D, Boaretto E, Stiller M. 2009. Carbon isotopes in pore water of the unsaturated zone and their relevance for initial ^{14}C activity in groundwater in the coastal aquifer of Israel. *Chemical Geology* 268(3–4):189–96.

Cartwright I. 2010. Using groundwater geochemistry and environmental isotopes to assess the correction of ^{14}C ages in a silicate–dominated aquifer system. *Journal of Hydrology* 382:174–87.

Chmura L, Rozanski K, Necki JM, Zimnoch M, Korus A, Pycia M. 2008. Atmospheric concentration of carbon dioxide in southern Poland: comparison of mountain and urban environments. *Polish Journal of Environmental Studies* 17:859–67.

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrogeology.* New York: Lewis Publishers.

Coplen T. 1996. New guidelines for reporting stable hydrogen, carbon and oxygen isotope-ratio data. *Geochimica et Cosmochimica Acta* 60(17):3359–60.

Dörr H, Münnich KO. 1980. Carbon-14 and carbon-13 in soil CO_2. *Radiocarbon* 22(3):909–18.

Dudziak A, Halas S. 1996. Diurnal cycle of carbon isotope ratio in soil CO_2 in various ecosystems. *Plant and Soil* 183(2):291–9.

Florkowski T, Grabczak J, Kuc T, Rozanski K. 1975. Determination of radiocarbon in water by gas or liquid scintillation counting. *Nukleonika* 20:1053–62.

Fontes JC, Garnier JM. 1979. Determination of the initial ^{14}C activity of total dissolved carbon: a review of existing models and a new approach. *Water Resources Research* 15(2):399–413.

Gorczyca Z. 2003. Variability of the isotope composition of the soil CO_2 flux to the atmosphere in the Southern Poland [PhD thesis]. Kraków: AGH University of Science and Technology. 169 p. In Polish.

Gorczyca Z, Kuc T, Rozanski K. 2013. Concentration of radiocarbon in soil-respired CO_2 flux: data-model comparison for three different ecosystems in southern Poland. *Radiocarbon*, these proceedings, doi: 10.2458/azu_js_rc.55.16321.

Kapusta M. 2012. Radiocarbon dating of groundwater—methodology and applications [PhD thesis]. Kraków: AGH University of Science and Technology. 87 p. In Polish.

Karpińska-Rzepa A, Różański K, Witczak SL, Wójcik R. 2005. Transport of anthropogenic pollutants through the unsaturated zone, traced by isotope chemical indicators: a case study from southern Poland. Presented at EGU General Assembly 2005, Vienna, Austria, 24–29 April 2005.

Kleczkowski AS, editor. 1990. *The Map of the Critical Protection Areas (CPA) of the Major Groundwater Basins (MGWB) in Poland*. Kraków: AGH.

Kuc T, Rozanski K, Zimnoch M, Necki J, Chmura L, Jelen D. 2007. Two decades of regular observations of $^{14}CO_2$ and $^{13}CO_2$ content in atmospheric carbon dioxide in central Europe: long-term changes of regional anthropogenic fossil CO_2 emissions. *Radiocarbon* 49(2):807–16.

Kulma R, Haładus A, Kania J. 2001. Hydrodynamic modelling of MGWB 451-Bogucice Sands Aquifer. Internal Report of the Department of Hydrogeology and Water Protection. Kraków: University of Science and Technology. 56 p. In Polish.

Małoszewski P, Zuber A. 1991. Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate rocks. *Water Resources Research* 27:1937–45.

Mook WG, van der Plicht J. 1999. Reporting ^{14}C activities and concentrations. *Radiocarbon* 41(3):227–39.

Operacz A. 2009. Role of soil and vadose zone in self-purification processes existed in groundwater environment degraded by industrial emission near the Arcelor Mittal Steelworks [PhD thesis]. Kraków: AGH University of Science and Technology. 187 p. In Polish.

Parkhurst DL, Appelo CAJ. 1999. User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS, Water-Resources Investigations Report 99–4259.

Plummer LN, Prestemon EC, Parkhurst DL. 1994. An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH. Version 2.0. USGS, Water-Resources Investigations Report 94–4169.

Porębski S, Oszczypko N. 1999. Lithofacies and origin of the Bogucice Sands (Upper Badenian), Carpathian Foredeep *Proceedings of Polish Geological Institute* CLXVIII:57–82. In Polish.

Sanford WE. 1997. Correcting for diffusion in carbon-14 dating of groundwater. *Ground Water* 35:357–61.

Stuiver M, Polach H. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Witczak S, Zuber A, Kmiecik E, Kania J, Szczepańska J, Różański K. 2008. Tracer based study of the Badenian Bogucice Sands aquifer, Poland. In: Edmunds WM, Shand P, editors. *Natural Groundwater Quality*. Malden: Blackwell Publishing. p 335–52.

Zuber A, Witczak S, Różański K, Śliwka I, Opoka M, Mochalski P, Kuc T, Karlikowska J, Kania J, Jackowicz-Korczyński M, Duliński M. 2005. Groundwater dating with ^{3}H and SF_6 in relation to mixing pattern, transport modelling and hydrochemistry. *Hydrological Processes* 19(11):2247–75.