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Isotope characterisation of deep aquifers in the Gwda catchment, northern Poland

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Abstract

We present the results of isotope measurements (δ^{18}O, δ D, δ^{13}C$_{DIC}$ and ^{14}C) and chemical analyses (TDS, TOC, HCO$_3^-$, SO$_4^{2-}$, Cl$^-$, NO$_3^-$, NH$_4^+$, Ca^{2+}, Mg^{2+} Na$^+$ and K$^+$) conducted on groundwater samples collected from deep Cenozoic aquifers. These aquifers are the basic source of drinking water at numerous localities within the study area in northern Poland. Most of the δ^{18}O determinations are characterised by low variability (i.e., > 70 per cent of δ^{18}O are between –9.5‰ and –9.2‰). In most cases tritium activity was not detected or its content slightly exceeded the uncertainty of measurement (from ±0.3 T.U. to ± 0.5 T.U.). On average, ^{14}C activity is twice higher than that under similar conditions and in hydrogeological systems. The δ^{13}C$_{DIC}$ values fall within the –13.6‰ to –12.8‰ range. A slight variability is observed when considering all isotope and chemical data within the study area and under these hydrogeological conditions. In general, the results of isotope and chemical analyses seem to be homogeneous, indicating the presence of closely similar groundwaters in the system, irrespective of geological formation. It is likely that there is a significant hydraulic connection between shallow and deep aquifers in the Gwda catchment, which indicates the potential for seepage of pollutants from shallow Pleistocene to deep Miocene aquifers. This can endanger the latter by e.g., high concentrations of NO$_3^-$, SO$_4^{2-}$ and Cl$^-$ ions from shallow aquifers within the Gwda catchment.

Keywords: Cenozoic aquifers, groundwater dating, stable isotopes, radiocarbon

1. Introduction

The Miocene aquifer in the catchment of the River Gwda (northern Poland), is part of an extensive reservoir of good-quality groundwater (II and III classes, according to Rozporządzenie, 2008) with a range that is much greater than the catchment area discussed (Kotowski & Satora, 2012). This aquifer is the basic source of drinking water at numerous localities. The present paper discusses results of isotope measurements and chemical analyses performed for groundwater samples taken mainly from the Miocene aquifer and locally from the Lower Pleistocene aquifer. Until now, analysis of δ^{13}C and ^{14}C was never conducted for the Miocene aquifer in the River Gwda catchment area.

The existing knowledge of the Miocene aquifer in the Gwda catchment comprises regional and cartographic works or those related to the documentation of groundwater intakes. These previous papers (e.g., Kachnic & Kotowski, 2004a, b) focused on a draft description of the abundance and dynamics of Miocene aquifers and also on the assessment of their quality and related threats.

A preliminary analysis of groundwater circulation systems and hydrodynamic conditions using hydrodynamic cross sections in the western part of the Gwda catchment was presented by Kotowski & Śmietański (2010). Later, processes affecting the chemical composition of groundwater in the southeastern part of this catchment were studied by Kotowski & Kachnic (2007). These studies were

supplemented by Kotowski & Burkowska (2011), who discussed issues related to the genesis of sulphates in the Lower Pleistocene aquifer in the area of a buried valley near Wysoka. An analysis of groundwater pollution has shown that a significant number (> 30 per cent) of shallow aquifers within the Gwda catchment are anthropogenically polluted (Kotowski, 2009).

Taking the mutually noted observations into account within the context of water management and supply, these aquifers have been poorly examined, which is why it is important to understand in detail the groundwater conditions within the study area. Determination of the isotope composition of groundwaters from deep and shallow aquifers is significant for our understanding of the groundwater circulation system within the area. Another key research task is to estimate of the age of groundwater in deep aquifers. This can be significant in the future because the shallow aquifers are significantly polluted by man on a local level. Overall, the primary twofold aim of the present study is to investigate the connection between shallow and deep aquifers and to describe its isotope variability.

2. Geology and hydrogeology of the study area

The Gwda catchment (4,943 km²) is located in western Pomerania (northern Poland). Groundwater flow in deep aquifers generally takes place towards the south (with the exception of the Gwda valley), in the direction of the mouth of the River Gwda where it flows into the Noteć River.

A map of the groundwater level for deep aquifers is presented in Fig. 1. Unfortunately, there are no reliable data to determine the groundwater level within the deep aquifers in the western and northern parts of the study area. The research was conducted on deep aquifers – mainly the Miocene and Lower Pleistocene ones; locally, the latter has a direct connection with the Miocene aquifer (Fig. 2).

The Miocene aquifer occurs within strata assigned to the Krajenka and Adamów formations, which are primarily represented by terrestrial deposits (Piwocki & Ziembińska-Tworzydło, 1997). The rock matrix of the Miocene aquifer consists of quartz sands and silts, usually with abundant mica flakes and coal dust. The Pleistocene aquifer is sit-
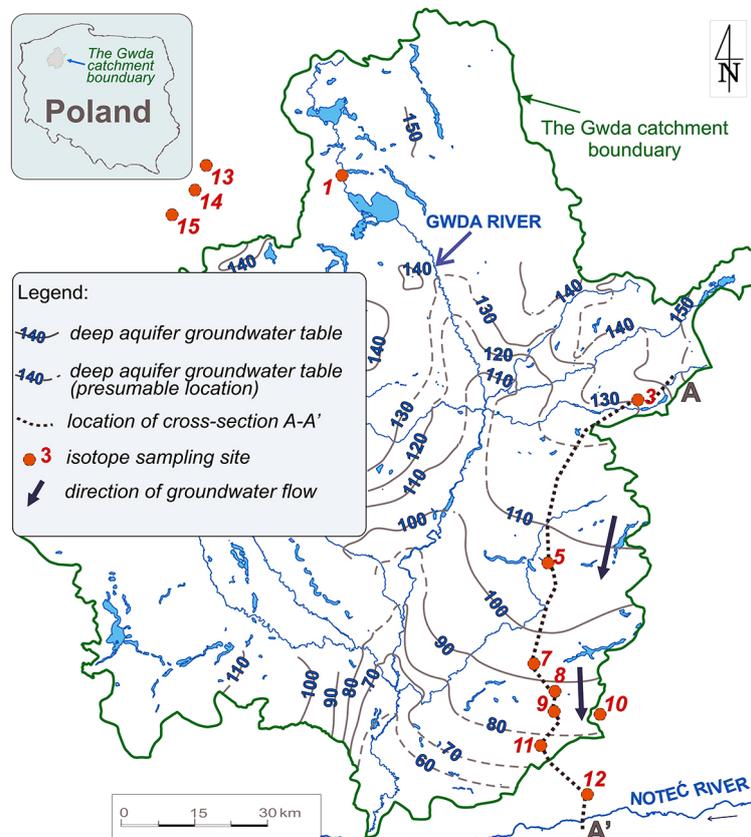

Fig. 1. The deep-aquifer, piezometric level and location of isotope sampling sites (modified from Kotowski & Śmietański, 2010).

uated in glaciofluvial sands and gravels as well as glaciolacustrine sands and silts. Calcite content in Pleistocene sediments (tills) is about 10–14 per cent (Górska, 2002). Despite the distinct lithology and genesis of aquifer deposits the deep Pleistocene aquifer was considered together with the Miocene one as a common element in the groundwater circulation system. Irrespective of variable thicknesses, the Miocene aquifer is characterised by a significant extent and continuity. It extends across almost the entire study area with the exception of a deeply eroded, buried valley. Locally, Miocene deposits have been completely or almost completely removed and replaced with sandy Pleistocene deposits. There are numerous erosion-buried valleys in the entire study area (Fig. 3). In most cases, these valleys allow groundwater flow between different aquifers. There are numerous glaciotectonic structures (deformation), which may merge with various aquifers in the northern part of the study area. A broader description of hydrogeological conditions within the study area was presented in previous papers on this region (e.g., Kotowski & Kachnic, 2007).The formative processes of chemical composition of the deep aquifers (Miocene and Lower Pleistocene) are of natural geological character and are conditioned by the current groundwater circulation system. These processes are related to mineral dissolution and percolation of groundwaters from shallow aquifers (Middle and Upper Pleistocene) to deeper ones, without substantial change in chemical composition (Kotowski & Śmietański, 2010). The ascent of groundwaters from the Mesozoic aquifers is the major process responsible for increased Cl^- ion concentration in the Miocene and deep Pleistocene aquifers (Kotowski & Kachnic, 2007). Pyrite oxidation is the major process responsible for an increase of SO_4^{2-} and Ca^{2+} ions within a study area. For a more detailed discussion of groundwater chemistry in the study area, reference is made to Kotowski (2011).

3. Material and methods

3.1. Hydrochemical data

The chemical composition of groundwater was estimated on the basis of the outcome of the analysis of groundwater samples collected during implementation of the Hydrogeological Map of Poland (HMP), scale 1:50,000. Electric conductivity and pH were measured *in situ*. The HCO_3^- ion concentration was measured directly in the field by titration using 0.1M HCl, in the presence of a WTW pH indi-

cator. Samples collected for chemical analyses were immediately passed through a 0.45-µm membrane filter into polyethylene bottles and kept refrigerated until analysed. Sample for cations (acidification using a few drops of concentrated HNO_3), anions, alkalinity and TOC (Total Organic Carbon) analyses were preserved in bottles (collectively about 250 dm^3). Chemical analyses were conducted between 2003 and 2010, by the accredited laboratory of the Polish Geological Institute at Warsaw.

The major dissolved elements were analysed (analytical uncertainty up to ± 15 per cent) by ICP-OES (inductively coupled plasma optical emission spectrometry) method with an iCAP 6500 DUO (Thermo-Scientific) or Panorama V (Jobin-Yvon). Concentrations of anions were analysed (analytical uncertainty up to ± 15 per cent) by high-performance liquid chromatography HPLC (high-performance liquid chromatography with UV, conductivity, fluorescence and diode array detection) method with an Ion Chrom or Aliance (Waters). TOC was determined by Pastel UV with Oxi UV 50 (Secomam) (analytical uncertainty up to ± 15 per cent).

3.2. Isotope data

Wells were sampled under pressure to avoid sample degassing. For sampling groundwater, sampling system for He concentration measurement has been used. During the collection of groundwater samples, the dissolved oxygen (O_2) concentration in the groundwater was measured so as to check the air tightness of the sampling system. A detailed descriptive diagram of the system for groundwater sampling was presented by Najman & Śliwka (2013), to which reference is made. Groundwater samples ($\delta^{18}O$, δD and tritium) were collected in polyethylene vessels with a capacity of 1.5 dcm^3, filled to the top, with no headspace, no sample filtration or preservation. During sampling, storage and transportation to the laboratory, we were careful not to expose samples to the atmosphere or evaporation. Groundwater samples for $d^{13}C_{DIC}$ and ^{14}C analyses were collected in polyethylene bottles with a capacity of 30 dcm^3, with no headspace. We added about 50 cm^3 of carbonate-free concentrated NaOH to raise the pH of the sample and avoid contamination of the sample by atmospheric CO_2.

Determinations of groundwater samples were conducted in the laboratory of the Faculty of Physics and Applied Computer Science AGH-UST at Kraków in 2006–2008. The isotope composition of samples ($\delta^{18}O$, δ^2H and $\delta^{13}C_{DIC}$) was determined on a Finnigan MAT 251 Ratio Mass Spectrometer. The
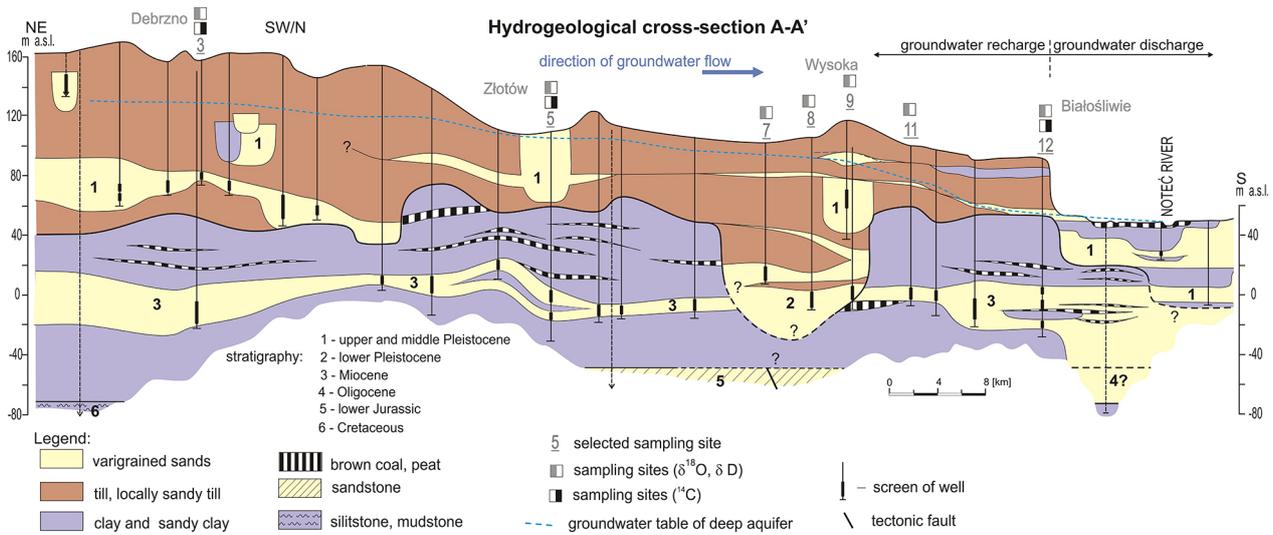
Fig. 2. Hydrogeological cross section of the study area (modified from Kotowski & Najman, 2015).
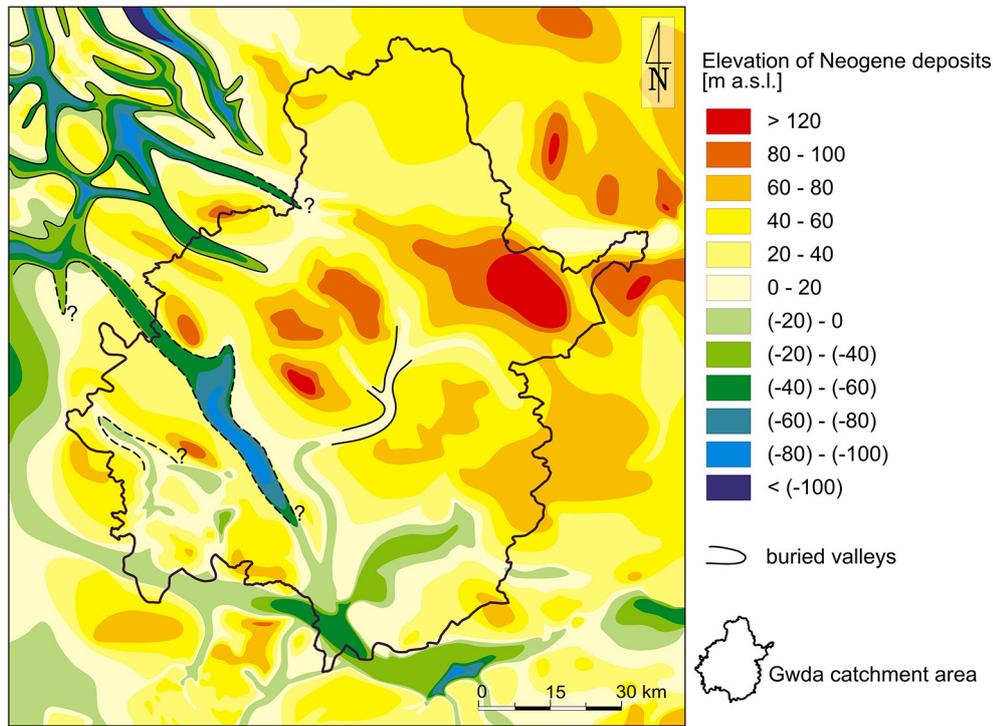

Fig. 3. Relief of Neogene sediments (modified from Kotowski & Satora, 2012).

isotope ratios of sampled groundwater were measured using the CO_2–H_2O equilibration method for oxygen, and the H_2–H_2O equilibration method for hydrogen. Oxygen and hydrogen isotope results are recorded in per mill (‰) relative to VSMOW (Vienna Standard Mean Ocean Water) and normalised (Coplen, 1994) on scales such that oxygen and hydrogen isotope values of SLAP (Standard Light Antarctic Precipitation) were −55.5‰ and −427.5‰, respectively. The combined standard uncertainty was estimated at ±0.02‰ and ±0.3 ‰ for $\delta^{18}O$ and δD, respectively. The activity of tritium was

determined by the electrolytic enrichment method (e.g., Gröning & Rozanski, 2003), the precision of tritium activity measurements was ± (0.3÷0.5). The carbonate stable isotope standard TS-Limestone (NBS–19), with a known $\delta^{13}C_{DIC}$ value (+1.95‰ ±0.2 ‰) and known $\delta^{18}O$(−2.2‰ ±0.2 ‰), were used to calibrate $\delta^{13}C_{DIC}$ measurements (Friedman et al., 1982). Activities of ^{14}C were conducted by using the LSC method (Liquid Scintillation Counting) with GPC (Gas Proportional Counters). The uncertainty was estimated at ±(0.76÷1.33) pmC (depending on the number of counts) (Gorczyca et al., 1998).

4. Results and discussion

A comparison of the basic geochemical parameters of groundwaters from Miocene and Lower Pleistocene as well as Middle and Upper Pleistocene aquifers is presented in Table 1. The chemical composition of groundwater from deep (Miocene and Lower Pleistocene, n=101) and shallow aquifers (Middle and Upper Pleistocene, n=218) is similar. In most cases concentrations of the main ions, i.e., HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+ (and also, to some extent, SO_4^{2-} and Cl^- ions) in groundwater from deep and shallow aquifers within the study area are closely similar. Differences between average values of TDS (Total Dissolved Solids) for shallower and deeper aquifers typically fall within the 5–10 per cent range (difference ratios being 1.01 (mean) and 1.04 (median)). The difference ratios for ions (HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+) fall within the 0.85÷1.19 and 0.88÷1.33 ranges (mean and median, respectively), while those for other major ions (NO_3^-, SO_4^{2-} and Cl^-) fall within the 0.08÷0.41 and 0.22÷0.42 ranges (mean and median, respectively). The primary factor that differentiates groundwater chemistry in these aquifers are the elevated concentrations of SO_4^{2-}, Cl^- and, in part, also NO_3^- ions in shallow aquifers, which are mostly related to the inflow of groundwater polluted by humans. There are numerous areas with high concentrations of SO_4^{2-}, Cl^- and NO_3^- (more than 75, 30 and 10 mg/l, respectively; see Kotowski, 2009).

Results nos. 13–15 (Table 2) apply to isotope analyses carried out in 1997 for the northwestern part of the Gwda catchment and the adjacent area (Wiśniowski, 1998). Detailed characterisations of the wells sampled are presented in Table 2.

Table 1. Comparison of basic geochemical parameters of groundwaters from Miocene and Lower Pleistocene (n=101) as well as Middle and Upper Pleistocene aquifers (n=218).

Aquifer	Uncertainty [%]	Miocene and Lower Pleistocene n=101		Middle and Upper Pleistocene n=218		Differences ratio between aquifers[2] [-]	
Parameters[1]		Mean	Median	Mean	Median	Mean	Median
TDS	–	395	386	391	372	1.01	1.04
TOC	±1.0	2.8	2.2	3.1	2.2	0.90	1.00
HCO_3^-	20	263	261	221	209	1.19	1.25
SO_4^{2-}	±0.5	11.2	6.7	37.7	30.6	0.30	0.22
Cl^-	±0.5	6.8	5.0	16.6	12.0	0.41	0.42
NO_3^-	±0.01	0.12	0.07	1.57	0.20	0.08	0.35
NH_4^+	±0.05	0.24	0.16	0.11	0.04	2.18	4.00
Ca^{2+}	±0.1	73.4	72.2	78.3	75.0	0.94	0.96
Mg^{2+}	±0.1	9.2	8.1	8.2	7.4	1.12	1.09
Na^+	±0.5	7.1	5.8	8.4	6.6	0.85	0.88
K^+	±0.1	1.7	1.6	1.9	1.2	0.89	1.33

[1] The Total Dissolved Solids (TDS), Total Organic Carbon (TOC) and ion concentrations are given in mg/l.
[2] Differences ratios between aquifers are calculated as a value for Miocene and Lower Pleistocene aquifer divided by the value of Upper Pleistocene aquifer.

Table 2. Characteristics of wells that were selected for isotope studies.

No.	Localization	Stratigraphy	Depth of well [m]	Depth of aquifer top[1] [m]	Depth of well screen center [m]
1	Spore	Miocene	220	174	185
3	Debrzno	Miocene	194	149	177
5	Złotów	Miocene	146	126	133
8	Bądecz	Pleistocene	116	103	108
9	Wysoka	Pleistocene	80	40	67
10	Młotkowo	Pleistocene	93	70	84
12	Białośliwie	Miocene	115	82	96
13	Górki	Pleistocene	138	127	134
14	Stary Chwalim	Pleistocene	42	20	36
15	Barwice	Miocene	111	83	103

[1] Depth of top of shallow Pleistocene aquifer is below 100 m.

Table 3. Results of determinations of δ^{18}O, δ^2H and activity of tritium.

No	Sampling date	Localization	O$_2$ [mg/l]	T [^{o}C]	δ^{18}O [‰] V-SMOW	δD [‰] V-SMOW	Tritium activity [T.U.]
1	04.06.07	Spore (1)	0.79	11.6	–9.3	–64.6 –64.9	not measured
3	29.05.07	Debrzno	0.59	10.0	–9.4 –9.4	–66.0	not measured
5	03.11.06	Złotów	0.20	10.5	–9.4	–65.8 –64.9	0 ± 0.3
5	29.05.07	Złotów	–	–	–9.2	–67.9	not measured
8	03.11.06	Bądecz	–	–	–8.9	–64.2 –63.7	0 ± 0.3
9	20.11.07	Wysoka	0.30	10.5	–9.4	–66.1	0 ± 0.3
10	03.11.06	Młotkowo	–	–	–9.6	–67.1 –67.3	0.5 ± 0.3
12	29.05.07	Białośliwie	0.35	11.0	–8.1 –8.2 –8.2	–62.8 –61.9	not measured
13	23.05.97	Górki	–	–	–9.3 –9.3	–64.8 –65.0	1.2 ± 0.5
14	23.05.97	Stary Chwalim	–	–	–9.4 –9.4	–65.4 –65.6	0.1 ± 0.5
15	23.05.97	Barwice	–	–	–9.4 –9.5	–64.6 –64.3	0.2 ± 0.5

Results of δ^{18}O determinations (Table 3; Fig. 4) indicate the presence at considerable depths (>100 m) of groundwater with an isotope composition that is indicative of infiltration during the Holocene.

Results of δ^{18}O and δ D for samples nos. 1, 3 and 5 (δ^{18}O also in sample 13) are very similar to average values of the isotope composition of infiltration water recharged in this area during the Holocene (–9.6 and –65.7, respectively; see d'Obyrn et al., 1997).

The δ^{18}O determinations are characterised by low variability (excepting for samples 8 and 12). A small difference in δ^{18}O is likely to have resulted from the infiltration of water during different climatic periods, with a *c.* 0.5–1.0 degree amplitude of long-term average temperatures.

In the graph (Fig. 5), δ^{18}O and δ D in most cases are concentrated around the WMWL (World Meteoric Water Line) line as determined by the equation:
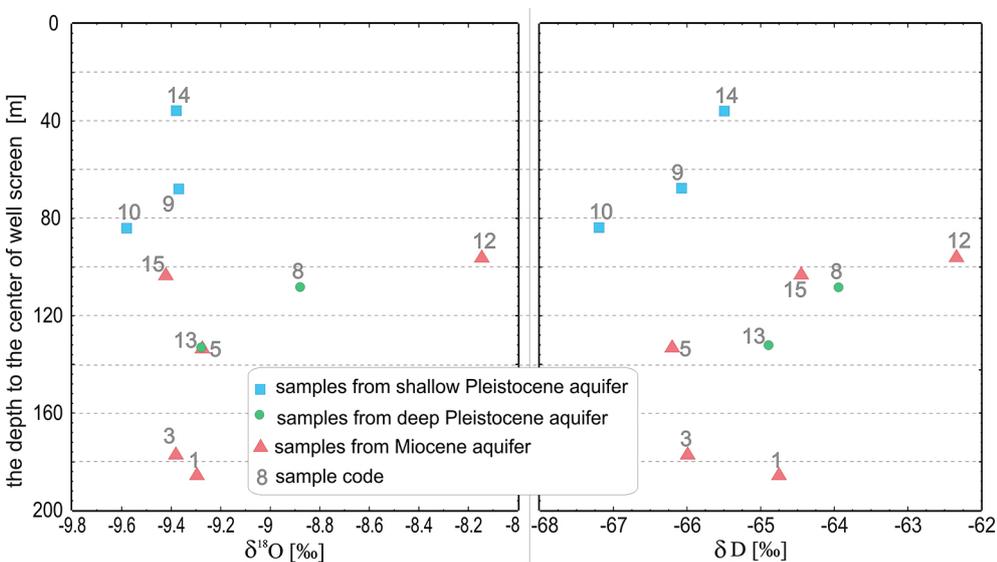

Fig. 4. δ^{18}O and δ D values as a function of well filtering depth, n=10 (compare Table 2).
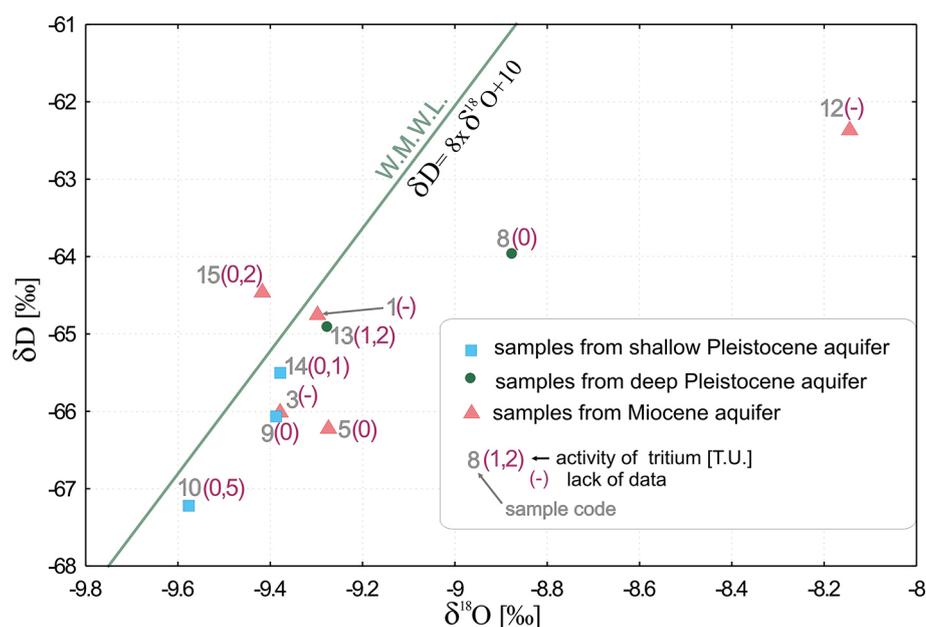
Fig. 5. The δD *vs* δ^{18}O plot and activity of tritium, n=10 (compare Table 1).

δ D = 8*δ^{18}O+10 (Craig, 1961). Only two samples, 8 and 12, are clearly spaced away from that line. This clear enrichment with heavy isotopes of the groundwater from Białośliwie (sample 12) presumably is the result of partial evaporation of this water prior to the infiltration process. This is a phenomenon that is frequently observed for groundwater in Pleistocene aquifers that were recharged during the Holocene (Zuber et al., 1990). The evaporation effect is related to the existence of numerous lakes and marginal areas during the Holocene. Surface waters from such water bodies could have recharged groundwater; they were preserved in large aquifer systems (Zuber et al., 1990).

Values of δ^{18}O and δ D (–8.9‰ and –64.0‰) obtained for sample 8 are similar to those from Lower Jurassic aquifers, which are –8.8‰ (δ^{18}O) and –62.4‰ (δ D), respectively (Krawiec, 2005).

The apparent enrichment in heavy oxygen and deuterium isotopes in sample 8 is the result of partial evaporation of groundwater prior to infiltration, as in sample 12. It should be noted that both samples (8 and 12) come from regions with fossil and/or Recent buried valleys.

In most cases (see Fig. 5), the activity of tritium was either not detected or its activity slightly exceeded the determination uncertainty (±0.5 T.U.). Results of tritium activity measurements indicate are low (≤ 1.2 T.U.) in groundwater from deep aquifers. This signifies a lack of considerable inflow of groundwaters of modern infiltration (<50 years in the aquifer) to deep aquifers.

Determinations of $\delta^{13}C_{DIC}$ values and ^{14}C activity together with the age of groundwater are shown in Table 4 and Figure 6.

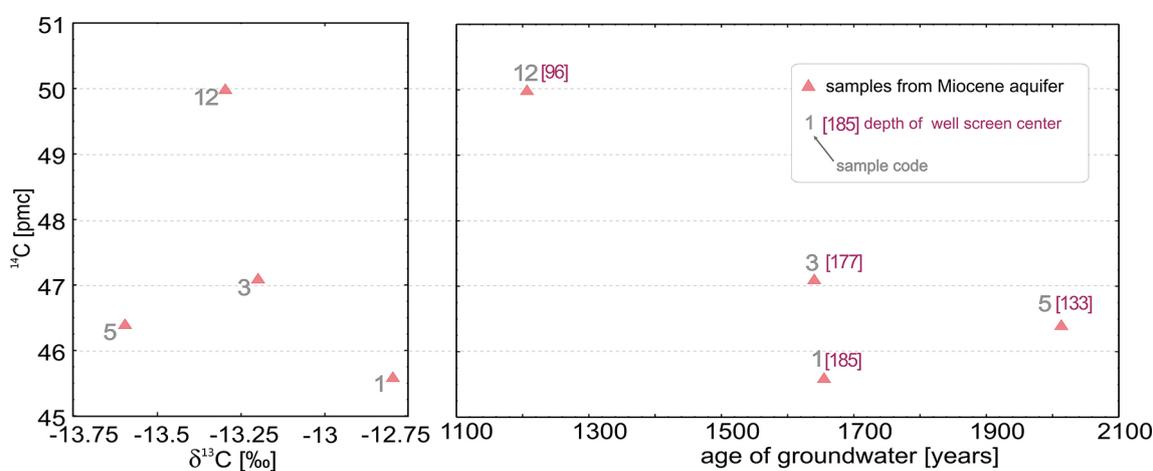**Fig. 6.** Measurements of $\delta^{13}C_{DIC}$ and ^{14}C activity and groundwater ages, n=4 (compare Table 2).

Table 4. Results of determination of $\delta^{13}C$, ^{14}C, HCO_3^- ions concentrations and age of groundwaters.

No	Sampling data	Localization	$\delta^{13}C$ [‰] V-PDB	^{14}C [pmc]	HCO_3^- [mg/l]	Model	Age of groundwater [years]
1	04.06.07	Spore (1)	–12.8	45.6±1.0	259	piston flow	1700
3	29.05.07	Debrzno	–13.2	47.1±1.0	338	piston flow	1600
5	29.05.07	Złotów	–13.6	46.4±1.0	367	piston flow	2000
12	29.05.07	Białośliwie	–13.3	50.0±1.0	484	piston flow	1200

Ages of groundwater are rounded to the 100 years.

The following equation was applied to calculations of the age of groundwater as based on the ^{14}C content determined (according to Clark & Fritz, 1997):

$$\text{Age [thous. years]} \cong 8300 \cdot \ln\left[\frac{\delta^{13}C_{DIC} - \delta^{13}C_{CaCO3}}{\delta^{13}C_{soil} - \delta^{13}C_{CaCO3}} \cdot \frac{C_o}{^{14}C}\right]$$

where:

C_o = initial ^{14}C content (usually taken as 100 per cent of recnet carbon);

^{14}C = measured value;

$\delta^{13}C_{DIC}$ = value determined for total dissolved inorganic carbon;

$\delta^{13}C_{CaCO3}$ = adopted value (0 ‰) for ^{14}C-free carbon minerals and rocks subjected to dissolution and isotope exchange during the dissolution phase;

$\delta^{13}C_{soil}$ = adopted value (–23 ‰) for soil CO_2 modified by isotope fractionation during diffusional transport, assuming an open system for (soil) CO_2.

A value of $\delta^{13}C_{soil}$ = –23 ‰ was adopted on the basis of results of isotope analyses of soil CO_2 flux (Gorczyca et al., 2003; Gamnitzer et al., 2011). This value includes the effect of, among other factors, the enrichment of soil CO_2 with heavier isotopes during its diffusive migration into the aeration zone. According to some authors, the diffusion process itself may result, at greater depths, in enrichment of soil carbon dioxide with heavier isotopes, reaching levels as high as c. 8.7‰ as compared to the CO_2 present in the stream flowing from the soil (Amundson et al., 1998; Stern et al., 1999). It should be noted that in every case the age of groundwater, calculated using equation 1 and the often assumed value $\delta^{13}C_{soil}$ = –25‰, is c. 692 years less. This result (ca. 700 yrs) is exceeding the potential error related to the accuracy of groundwater age estimation. Assuming uncertainties of ^{14}C to be around ±1 pmC, that of the age of groundwater can be calculated (assuming a piston flow model) to be c. 210 or c. 250 years for uncertainties of $\delta^{13}C_{DIC}$ equal to ±0.1 or ±0.2‰, respectively.

Considering sampling depth (Table 2) and the relatively large distance between the sampling points (Fig. 1), variation of $\delta^{13}C_{DIC}$ and ^{14}C values is low. Differences between ^{14}C values (except for sample 12) slightly exceed the uncertainty (determination error), which is ±1.0 pmC. It should be noted that 1 pmC is the uncertainty that represents the single standard deviation (1σ). The probability is that true values lie in the range ±1σ is c. 66%. For the ±2σ range it rises to 95 per cent. Thus, with a likelihood of 95 per cent, practically all ^{14}C values are identical. The difference between the maximum and minimum values for the $\delta^{13}C$ determinations is only 0.8‰.

Average activity of ^{14}C is twice higher than the activity of ^{14}C determined under similar conditions and hydrogeological systems (e.g., upper Serravallian sands and buried Pleistocene valleys of the Kędzierzyn-Głubczyce Subtrough) where the average activity of ^{14}C is 24.81 pmC (Duliński et al., 2002; Witczak et al., 2007). $\delta^{13}C_{DIC}$ values obtained fall within the –13.6‰ to –12.8‰ range, which, according to Clark & Fritz (1997), possibly indicates contribution from both degradation of organic matter and a carbonate source (50 per cent each). In the Miocene terrestrial strata calcite has not been found or occurs sporadically (merely at brackish levels) and its share usually is a few percent (Stoiński, 2004; Wągrowski, 2005). Despite the small number of samples, the lack of more negative $\delta^{13}C_{DIC}$ values (below –15‰) rather excludes the possibility of carbon isotope modification through decomposition of organic matter in the aquifer. In most cases $\delta^{13}C_{DIC}$ values for different kinds of organic matter are markedly below –20‰ (Gorczyca et al., 2013). Obtained $\delta^{13}C_{DIC}$ values likely indicate moderate levels of organic matter decomposition, mainly of detrital humus and xyloid coal commonly occurring in terrestrial Miocene sedimentary rocks (Kasiński et al., 2002; Piwocki, 2004). Additionally, low organic carbon content – the average TOC being 2.8 mg/l (n=55) – in samples from the Miocene aquifers presumably implies low activity of organic matter decomposition. The average TOC in Miocene levels does not differ much from the average TOC determined for Pleistocene aquifers, the average of which is 3.1 mg/l (n=218).

Results of $\delta^{13}C_{DIC}$ and activity of ^{14}C for sample 12 show a slightly different isotope composition in comparison to the remaining determinations. Activity of ^{14}C found in sample 12 is the highest for the samples examined, despite the fact that, given the hydrogeological conditions and the direction of groundwater flow in the Miocene aquifer, one would have expected the lowest value. Modification of $\delta^{13}C_{DIC}$ and activity ^{14}C as a result of isotope exchange between dissolved carbonates and rock matrix carbonates is in this case unlikely, because such exchange leads to a reduction in ^{14}C activity. The $d^{13}C_{DIC}$ in this case is significantly affected by specific hydrogeological and hydrogeochemical conditions. The Miocene and Oligocene aquifers are in full hydraulic connection with aquifers in the Pleistocene sandy sediments that fill the Noteć valley (see Fig. 2). In relation with the above observations, it was assumed that the determined $\delta^{13}C_{DIC}$ and activity ^{14}C in sample 12 are likely the result of mixing groundwater of different origin. Apparently the groundwater from the Miocene aquifer mixed with groundwater from Oligocene and shallow Pleistocene aquifers within the Noteć buried valley area. Considering the slight difference between calibrated and uncalibrated groundwater ages for a range of 1200–2000 years (little below or the same as the precision of dating) the calibration was omitted.

Taking into account the extent of the study area and hydrogeological conditions a weak differentiation is observed when considering all isotope and hydrochemical data. A relatively small variability in the isotope composition of groundwater likely indicates a considerable value of vertical component of the groundwater flow in the recharge zone (in the upland area). It is likely related to significant vertical (or near-vertical) percolation of groundwater into deeper aquifers through confining layers.

5. Conclusions

Groundwater from deep aquifers in our study area could have been affected by anthropogenic pollution (i.e., high concentrations of NO_2^-, NO_3^- SO_4^{2-} and Cl^- ions). It is related to the possibility of inflow of groundwater to deep aquifers, which often are in connection with shallower aquifers and which are polluted by man. Concentrations of the majority ions in shallow and deep aquifers are very similar. The difference ratios for ions (HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ and K^+) fall within 0.85÷1.19 and 0.88÷1.33 ranges (mean and median, respectively). Significant differences between other ions concentrations

(NO_3^-, SO_4^{2-} and Cl^-) for shallower and deeper aquifers are related to anthropogenic pollution. The difference ratios for ions (NO_3^-, SO_4^{2-} and Cl^-) fall within 0.08÷0.41 and 0.22÷0.42 ranges (mean and median, respectively).

Values of $\delta^{18}O$ and δ^2H are similar (–9.6÷–8.1‰ and –67.9÷–61.9‰, respectively) both for Miocene and deep Pleistocene and shallower aquifers. The results of $\delta^{18}O$ determinations indicate the presence at considerable depths (>100 m) of groundwater with an isotope composition that indicates infiltration during the Holocene, with low (*c.* 0.5–1.0 degrees) amplitude of long-term average temperatures. In some cases the enrichment of groundwater with heavy isotopes likely is the result of partial evaporation of this water prior to the infiltration process. In general, results of $\delta^{18}O$ and δD are closely similar to average values of the isotope composition of infiltration water recharged in this part of Poland.

The variability of $\delta^{13}C_{DIC}$ and activity ^{14}C are both very low. Differences in most cases between the latter slightly exceed the determination error.

The difference between the maximum and minimum values for $\delta^{13}C_{DIC}$ determinations amount to only 0.8‰. $\delta^{13}C_{DIC}$ values (–13.6÷–12.8‰) obtained likely indicate partial (50 per cent each) contributions from organic matter degradation and from dissolution of carbonates within the rock matrix of aquifers the majority of which is composed of quartz sands, silts and coal dust. Estimated groundwater ages for Miocene aquifers fall within the range from *c.* 1,200 to *c.* 2,000 years.

Deeply incised river valleys and lakes, as well as deep erosion troughs and buried valleys, in this area significantly facilitate percolation of groundwater into deeper aquifers and are also of considerable importance to the groundwater circulation system. Indirectly, the great intensity of vertical percolation is indicated by the significant depth (*c.* 700 m) of active groundwater exchange zone in the immediate vicinity of the River Gwda catchment.

It can be stated that in most cases groundwaters from deep aquifers are similar to recent groundwater in terms of isotope composition. In general, all results indicate the presence of closely similar groundwaters in the system, irrespective of geological formation.

In consideration of the above observations the results of isotope and chemical analyses presumably indicate a significant hydraulic connection between shallow and deep aquifers of the Pleistocene and Miocene in the Gwda catchment. Such a hydraulic connection between shallow and deep aquifers hints at potential seepage of pollutants from

shallow Pleistocene to deep Miocene aquifers. This can have a negative impact on deep aquifers because over 30 per cent of shallow aquifers within the Gwda catchment are anthropogenically polluted (i.e., high concentrations of NO_3^-, SO_4^{2-} and Cl^- ions). Compared to the anthropogenic contamination classification of groundwater as proposed by Górski (2001), in numerous cases the concentration of those significantly exceeds the limit values (NO_3^- > 10 mg/l; SO_4^{2-}> 100 mg/l and Cl^-> 50 mg/l).

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