

Identification of groundwater chemistry origins in a regional aquifer system (Wielkopolska region, Poland)

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Abstract This paper describes the origin of the groundwater chemistry in the regional aquifer located in the Wielkopolska region of western Poland. Factor analysis was used for the identification of geochemical processes that influence the groundwater chemistry. Two groups of processes were identified: anthropogenic (i.e., caused by groundwater contamination) and geogenic (i.e., caused by natural geochemical processes). Based on a background of the natural variations in the groundwater chemistry, the effect of upward groundwater flow from the deep part of the flow system on the groundwater chemistry was identified. The boron concentrations and isotope data allowed for the identification of zones of relatively old groundwater. The spatial distribution of fluoride concentrations allowed for the identification of recharge zones. This study demonstrates the general usefulness of groundwater chemistry differentiation for supporting identification of groundwater flow patterns. It also demonstrates the importance of using chemical data to evaluate the connectivity between different aquifers. These interpretations can be used for better management of water resources on a regional scale.

Keywords Factor analyses · Groundwater chemistry · Hydrochemical zoning · Poland · Regional aquifer system

Introduction

Determining the origin of groundwater chemistry is crucial for effective water resource management and protection (Jeong 2001; Moosavirad et al. 2013; Perea and Rodriguez–Rodriguez 2009; Tweed et al. 2005). Many studies have shown that changes in groundwater chemistry can help in determining the flow pattern occurring in the aquifers (Afsin 1996; Coetsiers and Walraevens 2006; Hendry and Schwartz 1990; Jackson and Lloyd 1984; Ophori and Toth 1989; Ochsenkuhn et al. 1997). This information is particularly important in groundwater systems where the hydrogeology is complex due to the presence of multiple aquifers. In the case of multilayer aquifer systems, the spatial variations in groundwater chemistry can help in determining the vertical interactions of the groundwater between different aquifers (Al-Mashaikhi et al. 2012; Carillo-Rivera et al. 1996; Pilla et al. 2006).

The use of major ions as natural tracers is a common method for identifying flow paths in aquifers (Back 1966). The general approach is to assign water samples to groups (called hydrochemical facies or hydrochemical zones) with similar hydrochemical characteristics, which can then be correlated with locations (Thyne et al. 2004). These facies are a function of chemical processes operating within the lithologic framework and within the flow patterns of the water (Back 1966). The differences between the chemical facies of these groups can provide insight into the aquifer connectivity and the chemical processes controlling the groundwater chemistry.

In the present study, multi-component geochemical tracers in conjunction with physical parameters were used for investigating the flow conditions. Certain trace elements (i.e., boron and fluoride) were used to qualitatively

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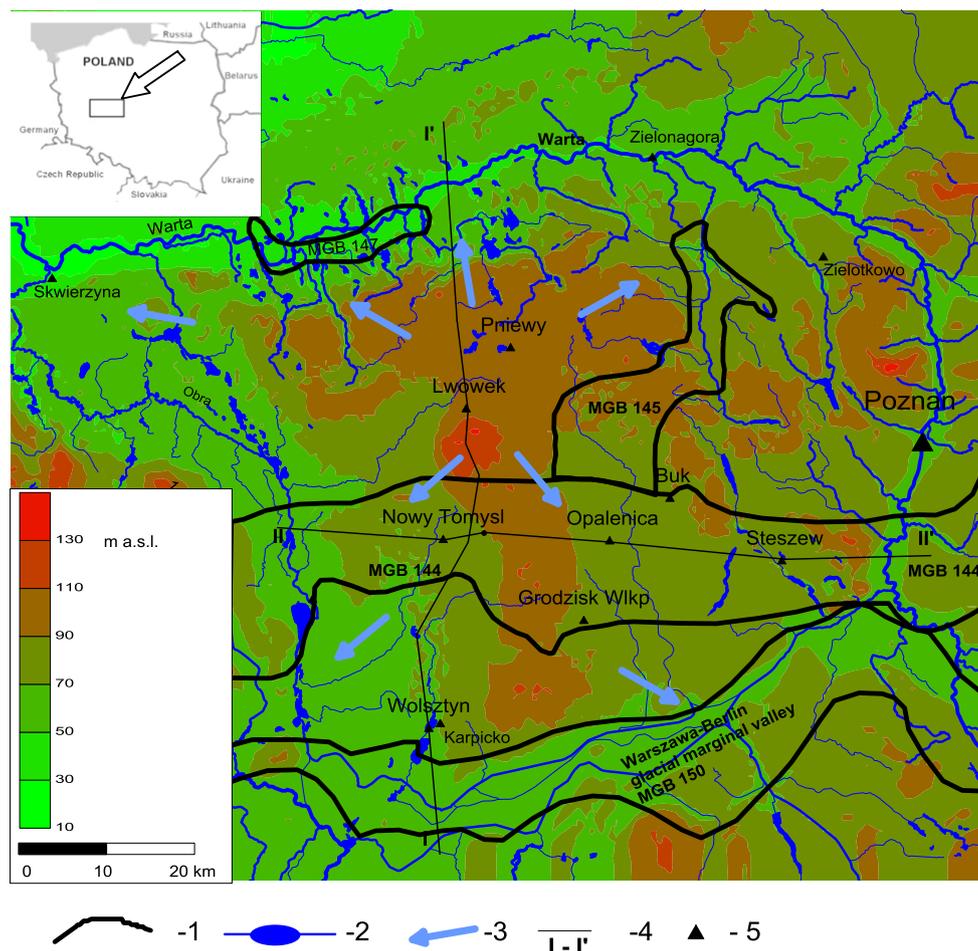


Fig. 1 The location of the study area on a background of the land relief (after Dragon 2013, modified), 1 the boundaries of the major groundwater basins; 2 surface water (lakes and rivers); 3 general

groundwater flow directions; 4 the lines of cross-sections: A cross-section I-I', B cross-section II-II' (Fig. 2); 5 main towns

determination the residence times of water in the groundwater system. For the determination of groundwater chemistry zonation, both conventional techniques and multivariate statistical methods (factor analysis) were used. Factor analysis (FA) was used to simplify and organise the data set to develop useful generalisations and insights. This method can help identify variables that characterise the aquifers present and hydrogeochemical processes occurring in a groundwater system (Drever 1997). This method can also be used to distinguish geogenic and anthropogenic processes that influence the groundwater chemistry (Dragon 2006).

The main objective of this study was to identify the groundwater zones in a regional aquifer system (central Wielkopolska, Poland) that is characterised by relatively few variations in its groundwater chemistry. The specific aims were (i) identification of the vertical (upward) component of groundwater flow and (ii) examination of the groundwater flow systems using hydrochemical data. This

study focused primarily on the natural groundwater processes affecting the groundwater chemistry.

The study area

The study area is located in the western part of the Wielkopolska region, which is in the western Polish Lowlands (Fig. 1). The central part of this region is at an elevation of 138 m a.s.l. (above sea level). From this central location, the ground slopes downward in all directions to ~60 m a.s.l. in the Odra Valley (to the west), Warta Valley (to the east) and Warszawa-Berlin glacial marginal valley (to the south) and to <20 m a.s.l. in the Warta Valley (to the north) (Fig. 1).

The Quaternary sediments are more than 130 m thick in the central part of the region, thinning to ~60 m in the Warszawa-Berlin glacial margin valley area and to <40 m in the Warta Valley (northern part of the study area)

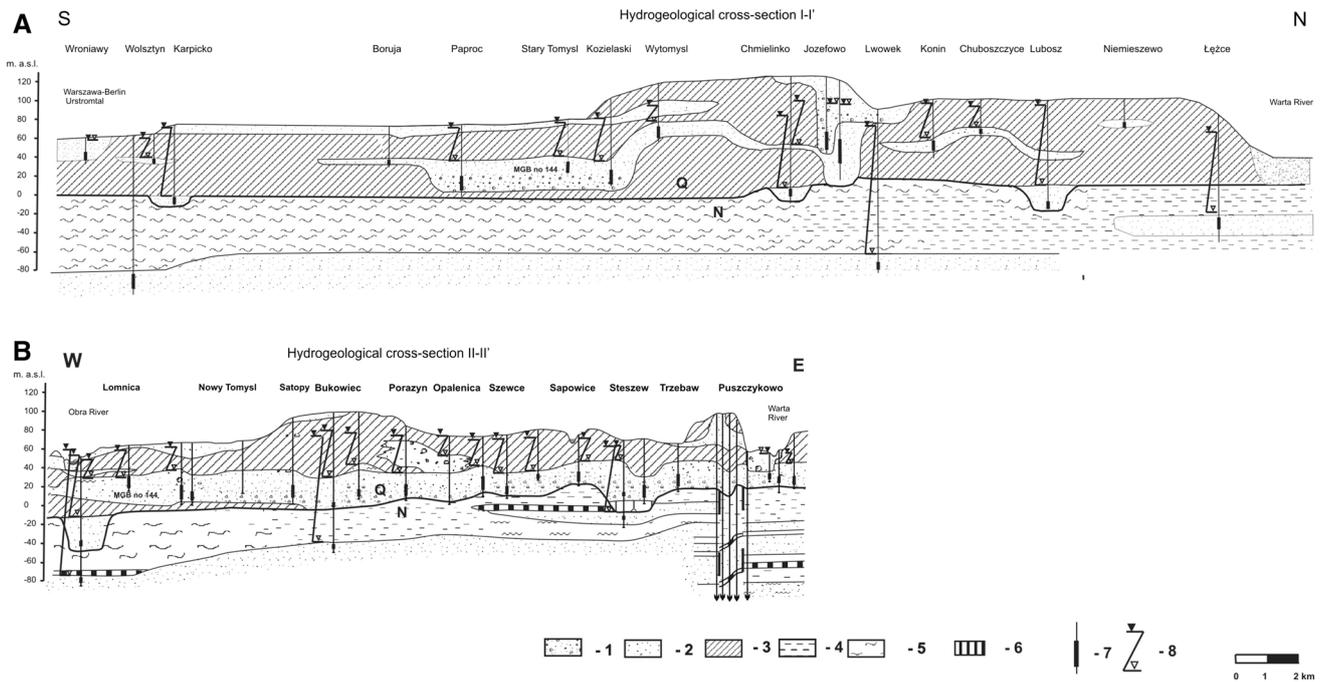


Fig. 2 The hydrogeological cross-Sects. 1 coarse sand and gravel, 2 medium and fine sand, 3 till, 4 clay, 5 silt, 6 brown coal, 7 the location of the well screen, 8 ground water level, Q quaternary, N neogene

(Fig. 2). The lithology is dominated by glacial and fluvioglacial deposits. The fluvioglacial sands and gravels comprise the aquifers, which consist of a multilayer system in certain areas. The deepest aquifers are ~20–30 m thick and are primarily composed of fine sands. These deep aquifers were discovered only locally in the part of the region where there are no shallow aquifers. The shallow aquifers are connected to the Wielkopolska buried valley (WBV) aquifer system, which is located in the central part of the study area. These aquifers vary from 30 to 40 m thick. The lithology is dominated by fine and medium sands of fluvial origin in the upper parts of the aquifers and by coarse sands and gravels of fluvioglacial origin in the deeper parts. The upper part locally contains fine sand with dispersed organic matter. The aquifers in contact with the WBV aquifer system on the north and south are between 5 and 20 m thick and are composed primarily of fine and medium sands. The shallower part of the groundwater system consists of intertill aquifers that are ~5–20 m thick and primarily composed of fine sands occurring within glacial tills. These aquifers have fluvial and fluvioglacial origin (buried sandur deposits and buried valleys). The confining layers bounding these aquifers are composed of glacial tills of variable thickness (Fig. 2).

The general groundwater flow lines follow the main morphologic features (Fig. 1). The main recharge area is located in the area of the highest elevations (Lwowek-Rakoniewice Rampart). The main discharge areas are located in the valleys surrounding the study area: the Warta

Valley on the east and north, the Obra Valley on the west and the glacial margin Warszawa-Berlin Valley on the south. The greatest downward groundwater gradient is located in the central part of the study area. The difference between the piezometric levels of the deepest and shallowest aquifers is more than 14.0 m locally (Chmielinko well—Fig. 2a). The greatest upward gradient is located in the discharge areas. The difference between the groundwater levels of the deepest and shallowest aquifers in the Obra River Valley is 8 m.

The WBV aquifer system were designated Major Groundwater Basins (MGB) no. 144 and 145 (Kleczkowski ed. 1990). The Miedzychod-Sierakow aquifer and Warszawa-Berlin glacial marginal valley aquifer were designated Major Groundwater Basins no. 147 and 150, respectively (Fig. 1).

The groundwater system in the eastern part of the study area (Warta Valley region) was studied by Gorski (1989), who described the natural hydrochemical background characteristic of the Quaternary aquifers. The groundwater chemistry of the WBV aquifer (MGB 144) was studied by Dragon (2006), who used multivariate statistics to separate the anthropogenic and geogenic processes influencing the groundwater chemistry. The hydrochemical zonation of the WBV aquifer was described by Dragon and Gorski (2009). In addition, a contaminant impact on the groundwater that is still present at small (initial) levels was discovered (Dragon 2008). Further work performed after one decade documented that the impacted groundwater is still present

and has led to steady groundwater quality deterioration over time (Dragon 2012). The hydrogeochemical processes occurring in the recharge zone of the aquifer system under investigation were examined in the context of nitrate migration (Dragon 2013). The movement of nitrate plumes to the deepest parts of the flow system that is initiated or intensified by water extraction were documented.

These previous studies documented that the groundwater chemistry of the WBV aquifer originated largely with the inflowing groundwater from aquifers located north of the WBV aquifer. For this reason, this study was extended to the entire aquifer system (regional recharge area and associated discharge areas).

Materials and methods

This investigation of the groundwater chemistry was performed using data from groundwater sampling completed in the summer of 2009. A total of 185 productive, continuously pumped wells were monitored. The sampling locations are shown in Figs. 4 and 6. The water samples were poured into 100-ml HDPE polyethylene bottles. Separate samples were taken for nutrient analyses (treated with chloroform) and for iron and manganese analysis (treated with HNO_3). All of the collected bottles were

rinsed three times and filled completely to prevent degassing. The samples were stored at cold temperatures ($\sim 4\text{--}6\text{ }^\circ\text{C}$) in a portable refrigerator and immediately (the same day) transported to the laboratory, located in Poznan, Poland. The water temperature ($T\text{ }^\circ\text{C}$), colour (mgPt/L), alkalinity (mg HCO_3/l), electrical conductivity (EC $\mu\text{S}/\text{cm}$) and pH were directly measured using a portable meter in the field. The field sampling was performed in accordance with relevant ISO 5667-11 method standards (ISO 5667-11 1993). The chemical analyses were performed at the Institute of Geology of Adam Mickiewicz University, Poznan, using a Compact IC 881Pro ionic chromatograph. The ionic error balance was calculated as a quality control measure, and the calculated error did not exceed 3 %.

The levels of stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in seven water samples were determined and expressed in terms of the $\delta\text{V-SMOW}$ (Standard Mean Ocean Water). These water samples were also analysed for C^{14} (reported as Percent Modern Carbon—pmc). The tritium content was measured in ten water samples and expressed in TUs (tritium units). The isotope analyses were performed in the laboratory of the University of Science and Technology (Faculty of Physics and Applied Computer Science) in Cracow, Poland. The results of isotope analyses presented by Dragon and Gorski (2009) were also used in the data interpretation.

Fig. 3 Piper diagram

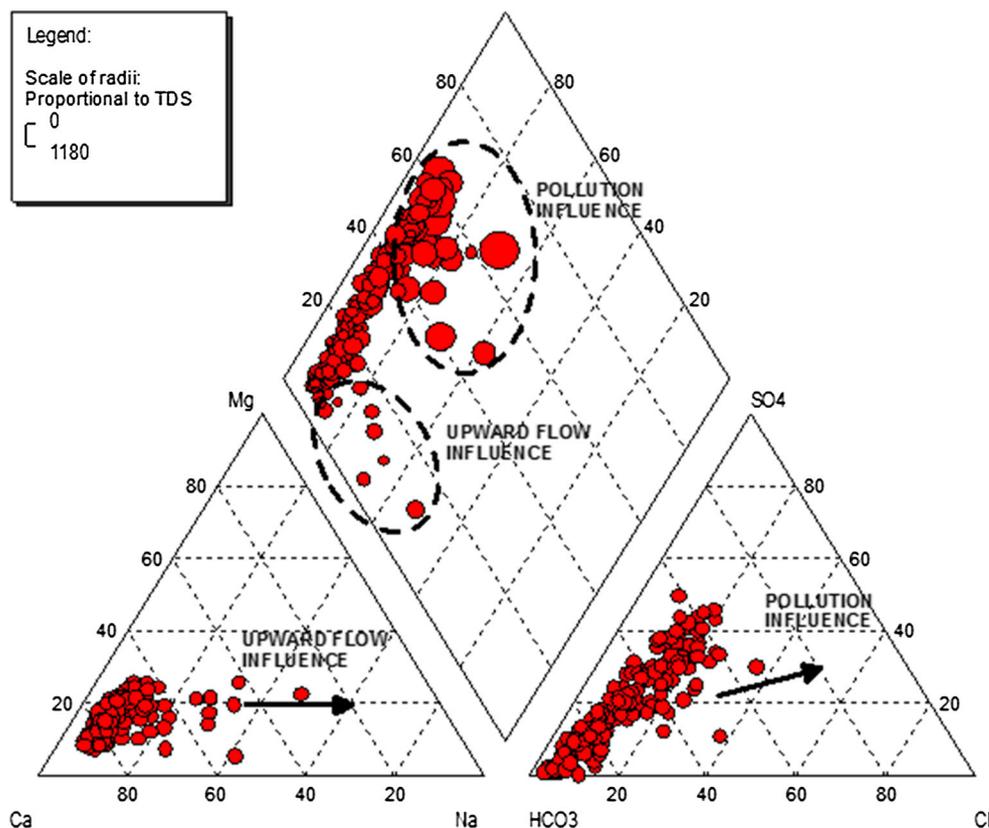
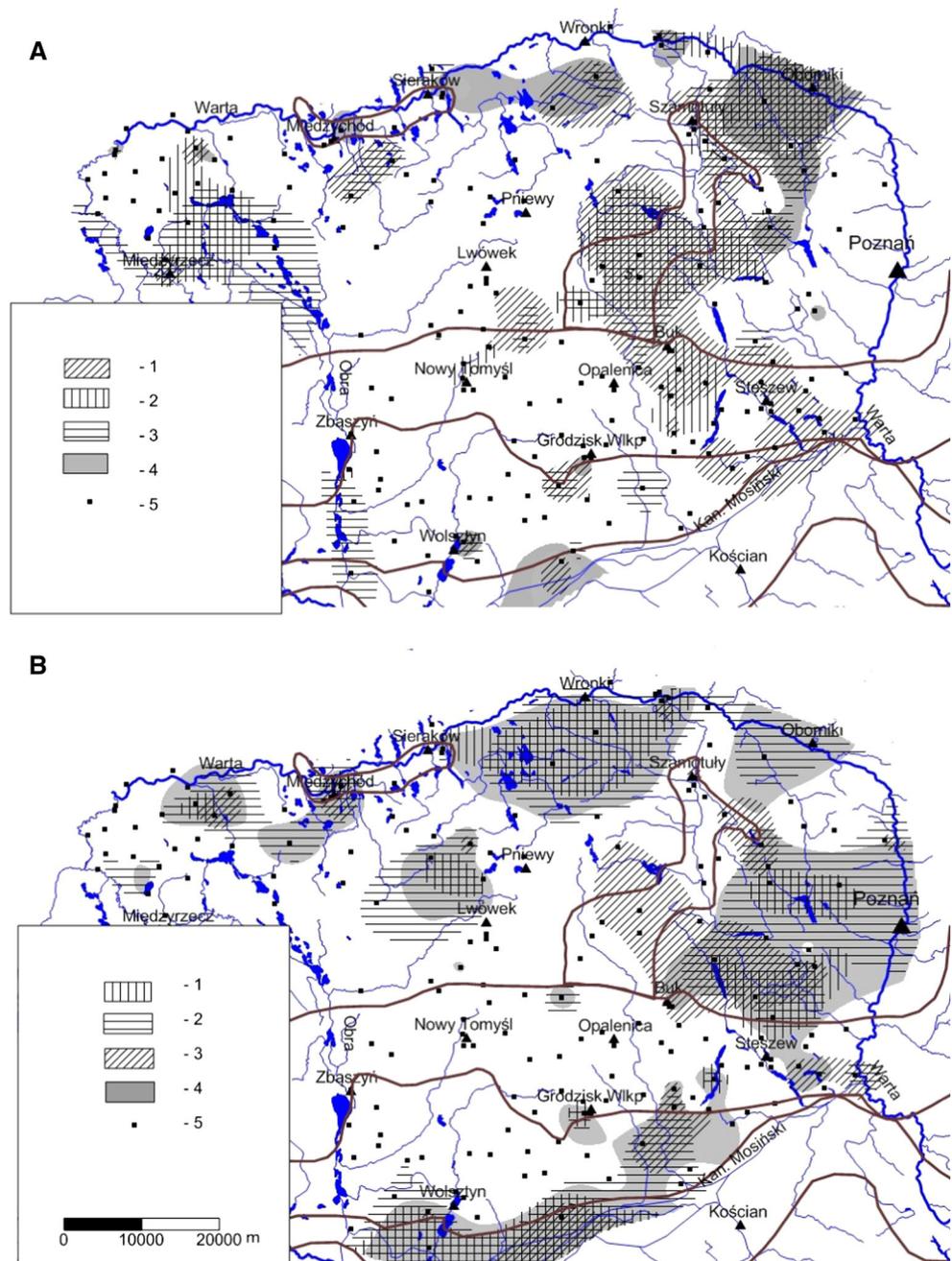


Fig. 4 Generalized map of groundwater chemistry. **a** 1 alkalinity (HCO_3^-) > 6 meq/l; 2 Fe^{2+} > 4 mg/l; 3 NH_4^+ -N > 0.6 mg/l; Na^+ > 30 mg/l. **b** 1 Cl^- > 60 mg/l; 2 SO_4^{2-} > 100 mg/l; 3 total hardness (TH) > 8 meq/l; 4 TDS > 500 mg/l. **a** and **b** 5 location of the sampling sites. Remaining explanations like on Fig. 1. The interpolation was made with use of kriging method



For the characterisation and interpretation of groundwater chemistry, two methods were used: conventional techniques (interpretation of maps, cross sections and diagrams) and multivariate statistics. Factor analysis (FA) was used to generate groups of correlated elements from the initial data set. These groups were included in the principal factor analysis and used to evaluate the processes occurring in the investigated environment. The identification of these factors enabled the genetic interpretation of the environment.

The statistical analysis was performed using the method presented in the previous work of Dragon (2006). The statistical software package Statistica 10 (StatSoft Inc. 2004–2011) was used for the calculations. Prior to the analysis, the initial data set was standardised using criteria presented by Davis (1973). This operation enabled the analysis of parameters of various concentration ranges (macro and micro elements) and parameters that are expressed in different units (aquifer thickness and chemical parameter concentrations). The principal component

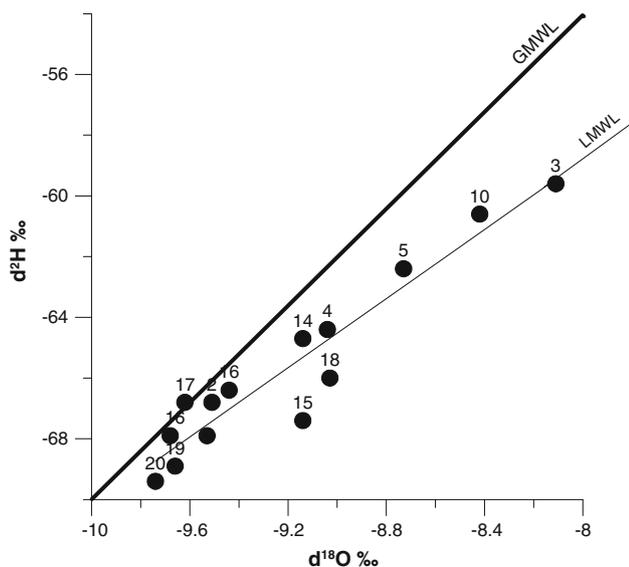


Fig. 5 Isotope composition of groundwater. Numbers identify samples according to Table 2. LMWL: $d^2H = 5.6 * d^{18}O - 13.8$

extraction technique (Davis 1973; Stat-Soft Inc. 2004–2011) was the starting point of the FA to generate new groups of variables from the initial data set (the so-called factors). The factor loadings indicate correlations between the factors and the variables (e.g., ion concentration). High factor loadings (near 1 or -1) indicate a strong correlation (positive or negative, respectively) between the variable and its associated factor. The factor scores of each sample were calculated. Dalton and Upchurch (1978) found that the factor scores of a sample can be related to the intensity of the associated chemical processes and may then be used to interpret the hydrochemical facies origin. Extremely positive factor scores (>1) indicate the areas that are most affected, and extremely negative scores (<-1) indicate the

areas unaffected by the chemical process represented by a factor. Scores near zero indicate areas affected by a process or factor to an average degree. For example, a set of physico-chemical parameters correlated with a particular factor can be explained by a chemical process (anthropogenic or geogenic), which can lead to the variability observed in the data set.

One disadvantage of FA, however, is the difficulty of distinguishing the processes that cause similar variations in the groundwater chemistry (Olmez et al. 1994). In addition, a priori knowledge of the hydrogeologic processes affecting the environment under investigation is required for an effective application of FA (Lawrence and Upchurch 1983).

Results and discussion

The Piper diagram (Fig. 3; Table 1) shows that the groundwater chemistry generally exhibits relatively little variation. The plotted points of the samples in the diagram indicate the fresh character of the water (Appello and Postma 1994). Most of the samples are classified as $Ca^{2+}-HCO_3^-$ and $Ca^{2+}-Mg^{2+}-HCO_3^-$ water types. The evident linear scatter type of the water sample distribution is evident in the trend of the diamond-shaped diagram toward the $Ca^{2+}-HCO_3^-SO_4^{2-}$ water type. Moreover, a distinct shift of the water sample point plots is evident in both the cation and anion triangles. In the anion diagram, several of the sample points are shifted toward the Cl^- apex. These samples all contain high TDS concentrations. In the cation diagram, in turn, the samples are shifted toward the Na^+ apex. These samples contain TDS concentrations typical of the entire data set.

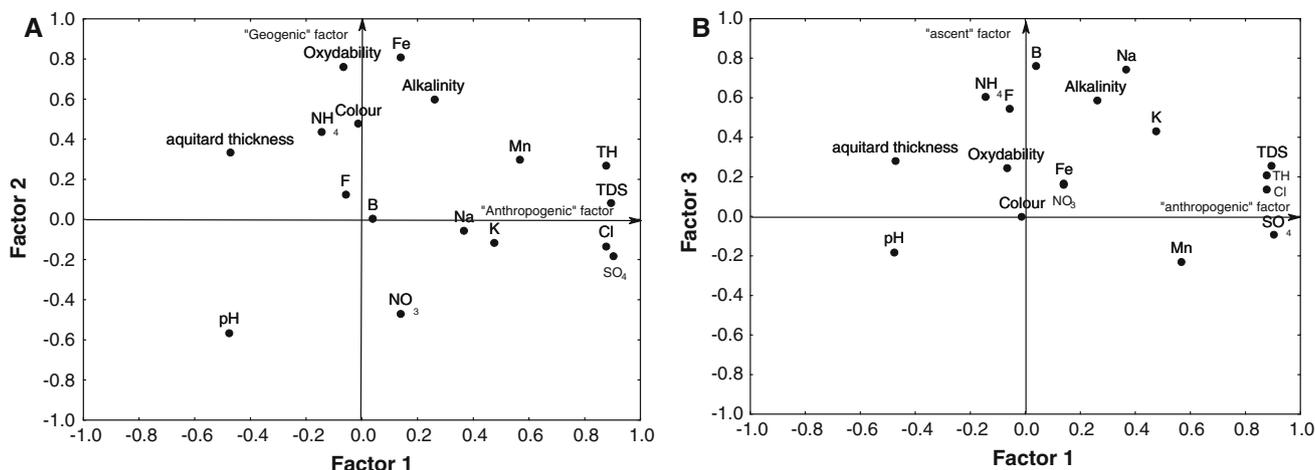


Fig. 6 Plots of factor loadings

Table 1 Statistical characteristics of the data set

	Unit	Frequency	Average	Median	Min.	Max.	SD
Colour	mg Pt/l	180	14	10	0	120	14
pH		184	7.45	7.42	6.88	8.29	0.22
HCO ₃ ⁻	meq/l	185	5.1	4.9	1.7	9.2	1.5
Total hardness (TH)		185	6.7	6.4	1.9	16.5	2.4
TDS	mg/l	185	433	402	130	1,180	179
Electrical conductivity (EC)	μS/cm	185	652	618	210	1,606	233
Cl ⁻	mg/l	185	34.2	24.6	6.9	236.5	31.1
SO ₄ ²⁻		185	76.7	56.2	3.3	317.6	68.8
Ca ²⁺		185	109.1	103.6	34.0	248.0	37.2
Mg ²⁺		185	16.1	15.6	2.6	50.6	7.7
Na ⁺		185	17.5	13.0	4.6	120.6	16.7
K ⁺		185	4.0	3.1	0.7	70.3	7.3
Fe ²⁺		161	2.7	2.5	0.0	9.8	1.7
Mn ²⁺		176	0.2	0.2	0.0	2.1	0.2
B		166	0.038	0.021	0.005	0.347	0.055
F ⁻		185	0.35	0.34	0.13	0.76	0.10
NO ₃ ⁻ -N		185	1.47	0.01	0.005	57.80	5.32
NO ₂ ⁻ -N		185	0.031	0.005	0.005	1.199	0.124
NH ₄ ⁺ -N		185	0.45	0.33	0.00	5.93	0.64
Oxygen consumption	mg O ₂ /l	174	2.1	1.8	0.5	8.3	1.3

The spatial distribution of the primary water components are presented on the maps (Fig. 4). To create these maps, interpolation was performed using the kriging method. Then, the areas with a high concentration of each water component were delineated. The zones where the Cl⁻ concentrations exceed 60 mg/l and the SO₄²⁻ concentrations exceed 100 mg/l are shown on the maps. In these zones, the total hardness (TH) is typically high (TH >6 meq/l), and the TDS level typically exceeds 500 mg/l. There are also zones of high TH (TH >8 meq/l) where the TDS, Cl⁻ and SO₄²⁻ concentrations are low. However, high alkalinity (Alk. >6 meq/l), high Fe²⁺ (Fe²⁺ > 4 mg/l) and high ammonia (NH₄⁺ > 0.6 mg/l) was found in these zones. The zone of high alkalinity and ammonia occupies a distinct part of MGB no. 145 and the vicinity. A relatively high concentration of Na⁺ is evident in these zones. This characteristic is primarily associated with the deepest aquifers located primarily in the discharge areas (river valleys). This type of groundwater typically contains high levels of ammonia, high alkalinity and low TDS. These zones are not easily discernible on the maps because they are small zones restricted to the areas around certain wells. A more detailed characterisation of these zones is presented later in the text. There are also zones of high Na⁺ concentration and high Cl⁻, SO₄²⁻ and TDS concentrations (e.g., in the vicinity of Wronki).

The stable isotope analysis indicates that the groundwater originates from modern infiltration (Table 2). The

δ¹⁸O and δ²H values are characteristic of the isotopic composition of meteoric water of the Holocene region of Poland (Rozanski et al. 1993). The Local Meteoric Water Line (shifted right to the Global Meteoric Water Line) presented in Fig. 5 indicates evaporation prior to recharge observed earlier in the Polish Lowland (Zuber et al. 2000). The observed ranges of δ¹⁸O and δ²H values are similar to those found in other aquifer systems located in the Wielkopolska region of Poland (Gorski 1989; Dragon and Gorski 2009).

The ¹⁴C-calculated “age” of the groundwater also indicates its recent origin, which is consistent with the tritium analysis. The youngest ¹⁴C calculated “age” of the groundwater was observed in the upper intertill aquifers located in the recharge area (recent water—Table 2). The oldest water is present in the discharge zone of the WBV aquifer (wells no. 16 and 17—Table 2) and in wells screened in the deepest parts of the flow system (wells no. 3, 5 and 6—Table 2), located in the regional discharge area (water older than 1,000 years).

A relatively high tritium content was measured in several of the samples, indicating post-1951 recharge of the aquifer. This value is characteristic primarily of the shallowest wells (wells no. 5, 7, 11, 12, 13, 20 and 21—Table 2) located in the recharge area (Lwówek-Rakoniewice Rampart). The depths of these wells do not exceed 50 m. In the deepest wells, the tritium content does not exceed 1 TU. A tritium content of 3.6 TU was documented

Table 2 Results of the isotopes analyses

Lp.	Location	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Tritium (T.U)	^{13}C (‰) V-PDB	^{14}C (pmc)	Groundwater calculated "age"
The isotope analysis obtained in recent work							
1	Józefowo 1 bis	−9.68	−67.4	3.6 ± 0.3	−11.8	51.8 ± 1.0	"recent" groundwater
2	Zbąszyń	−9.51	−66.9	0.0 ± 0.3	−12.8	52.0 ± 1.0	"recent" groundwater
3	Skwierzyzna 7	−8.11	−59.3	–	−13.0	42.6 ± 1.0	1,600
5	Skwierzyzna 1	−8.73	−62.8	2.7 ± 0.3	−12.8	45.2 ± 1.0	1,000
4	Ławica	−9.04	−64.5	–	−12.3	55.4 ± 1.0	"recent" groundwater
6	Karpicko	−9.53	−67.8	–	−13.8	28.2 ± 1.0	5,500
7	Grodzisk Wlkp. (Basen)	–	–	10.0 ± 0.6	–	–	–
8	Grodzisk Wlkp. AKSUW	–	–	0.6 ± 0.3	–	–	–
9	Grodzisk Wlkp. (Chopina)	–	–	0.2 ± 0.3	–	–	–
10	Kunowo	−8.42	−60.6	0.1 ± 0.4	−12.9	60.0 ± 1.0	"recent" groundwater
11	Bolewice	–	–	5.1 ± 0.4	–	–	–
12	Grońsko	–	–	4.4 ± 0.4	–	–	–
13	Pniewy	–	–	4.0 ± 0.4	–	–	–
The isotope analysis obtained in previous work (Dragon and Gorski, 2009)							
14	Wąsowo	−9.14	−64.7	0.4 ± 0.5	−13.8	62.4 ± 1.0	"recent" groundwater
15	Porążyn	−9.14	−67.4	0.0 ± 0.5	−13.1	55.2 ± 1.0	"recent" groundwater
16	Jastrzębsko Stare	−9.44	−66.4	0.2 ± 0.5	−13.6	53.1 ± 1.0	200
17	Prądówka	−9.62	−66.8	–	−11.8	46.4 ± 1.0	150
18	Grodzisk Wlkp (Chopina)	−9.03	−66.0	0.4 ± 0.6	–	–	–
19	Grodzisk Wlkp (AKSUW)	−9.66	−68.9	1.0 ± 0.6	–	–	–
20	Porążyn (PKP)	−9.74	−69.4	5.0 ± 0.8	−12.5	64.7 ± 1.0	"recent" groundwater
21	Słocin	−9.63	−67.6	15.2 ± 0.9	–	–	"recent" groundwater

in only one deep well (more than 80 m deep; well no. 1—Table 2). This well is located in the central part of the recharge area, in an area of unconfined aquifer conditions. The factor responsible for the deep circulation of young groundwater in this area is groundwater extraction (Dragon 2013).

For more quantitative data interpretation, statistical methods were used. The results of the factor analysis are presented in Table 3 and Fig. 6. The three factors that explain 59.2 % of the total variance were extracted using the principal components extraction technique and then rotated using the varimax method. The factor (with extremely positive factor loadings) that explains 29.5 % of the variance involves the high loadings of Cl^- , SO_4^{2-} , TH, TDS and Mn^{2+} to some extent; there is a corresponding low factor loading associated with the aquitard thickness and pH. The composition of this factor suggests an anthropogenic origin of these parameters. The concentrations of these parameters usually increase during wells exploitation (Dragon 2012). Moreover, their low concentrations are characteristic of uncontaminated confined aquifers in the Wielkopolska region (Gorski 1989). The low factor loading associated with the aquitard thickness demonstrates that the shallow aquifers are those most vulnerable to contamination. The low factor loading

associated with the pH indicates that water contamination caused the decrease in the pH. This factor is associated with the influence of human activity on the groundwater chemistry, and this factor is therefore classified as anthropogenic.

The oxygen consumption, Fe and alkalinity are clustered in the second factor. Moreover, a highly negative factor loading associated with the pH is evident. The water colour and NH_4^+ are also correlated with this factor. These parameters reflect natural (geogenic) hydrogeochemical processes. The behaviour of the parameters grouped together in this factor is primarily associated with the decay of organic matter under anaerobic conditions and an increase in the intensity of dissolution processes. Therefore, this factor is classified as geogenic.

The third factor is associated primarily with the concentrations of B, Na^+ , NH_4^+ and F^- and the alkalinity. These parameters reflect the influence of deep water circulation (and relatively long residence time) on the groundwater chemistry. However, the origin of this factor is more difficult to explain than are the others, primarily due to its local occurrence. This factor is typically present in proximity to individual wells only in the areas where the deepest aquifers are present.

Table 3 The results of the factor analysis (after varimax rotation)

parameter	Factor 1 “anthropogenic”	Factor 2 “geogenic”	Factor 3 “upward flow”
Colour	−0.01	0.48	0.00
pH	−0.48	−0.56	−0.18
HCO₃	0.26	0.60	0.59
Oxygen consumption	−0.07	0.76	0.24
Fe²⁺	0.14	0.81	0.17
Mn²⁺	0.57	0.30	−0.23
B	0.04	0.00	0.76
F[−]	−0.06	0.12	0.54
Cl[−]	0.88	−0.13	0.14
NO₃[−]-N	0.14	−0.47	0.16
NH₄⁺-N[−]	−0.14	0.44	0.60
Na⁺	0.37	−0.06	0.74
K⁺	0.48	−0.12	0.43
SO₄^{2−}	0.90	−0.18	−0.10
Total hardness (TH)	0.88	0.27	0.21
Total dissolved solids (TDS)	0.90	0.08	0.25
Thickness of the aquitard	−0.47	0.33	0.28
Percentage of variance (%)	29.5	19.6	10.1

Factor loadings >0.7 are marked by bold font

Note that it is difficult to develop explanations for the origins of factors 2 and 3, because the same set of parameters (alkalinity, NH₄⁺, and aquifer thickness) is observed in association with both of these factors. This overlap is an example of one of the disadvantages of using FA (Olmez et al. 1994).

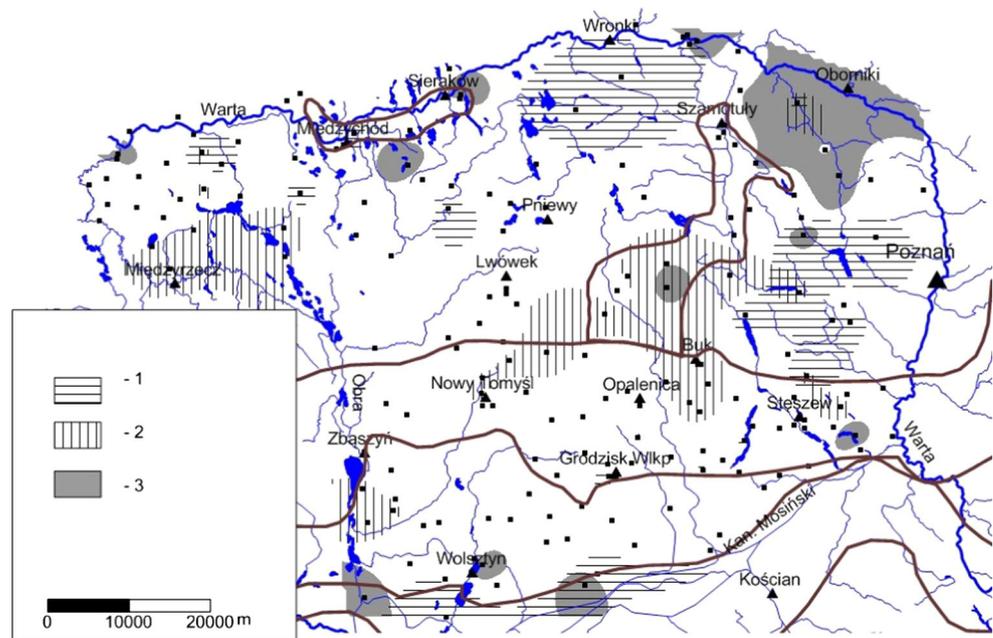
The spatial distribution of each factor is shown in Fig. 7. The highest factor scores of the anthropogenic factor represent the most vulnerable parts of the aquifer system. The contamination is most extensive in these areas. This situation is representative of the shallow parts of the flow system (shallow intertill aquifers—Fig. 2). The distribution of the scores of the geogenic factors shows that a distinct part of the study area, represented by factor 2, is influenced by geogenic processes. This distribution is evident throughout the entire area of MGB no. 145. The distribution of the factor scores in the northern part of the WBV aquifer indicates that the effects of these processes have shifted to the south, following the flow patterns. In this case, a distinct part of the WBV aquifer is influenced by the inflow of water from the area outside the aquifer to the north (Dragon and Gorski 2009). The remainder of the study area, where both factors have low factor scores, constitutes an area of relatively higher potential effects due

to infiltration. There, the processes associated with factor 2 are less evident. The higher potential effects of infiltration cause these areas to be vulnerable to contamination from the ground surface. However, the anthropogenic factor is also less evident in these areas. One explanation is the type of land use, which is generally dominated by forests. The highest factor scores of factor 3 (i.e., upward flow of groundwater) are distributed in the areas where the deepest aquifers are present. These aquifers are located in the areas of regional discharge, i.e., those with the lowest ground elevations, located in river valleys.

The changes in the concentrations of the same parameters with depth are presented in Fig. 8, in which the parameters influenced primarily by natural (geogenic) processes were chosen for display. The increase in alkalinity with depth is clearly visible on the plot. The highest values of alkalinity were observed in the deepest wells. Moreover, the Na⁺ and B concentrations are higher in the deep wells. From the surface to a depth of 50 m, their concentrations are relatively uniform. In the deepest wells, a distinct divergence in the plot is evident. The highest concentration of Na⁺ in the shallowest wells is associated with water contamination, which is also indicated by the first (anthropogenic) factor (Fig. 6). A progressive increase in the fluoride concentration is evident down to a depth of 20 m. Below this depth, its concentration is relatively uniform.

To develop a more detailed interpretation of the groundwater chemistry variations with depth, an FA was performed on the data subsets, subdivided based on the thickness of the aquitard (15 m intervals). This analysis was performed on four data subsets (Table 4). Two factors were obtained from each data group. The observed patterns in these factors are similar to those resulting from the analysis of the complete data set. However, the influence of the aquifer depth became evident. In the data subset of the smallest aquitard thickness (<15 m), the contributions of the levels of Na⁺, K⁺ and B to the anthropogenic factor is clearer (than those observed with the analysis of the complete data set), which constitutes the evidence for their anthropogenic origin. The composition of the second (geogenic) factor is very similar to that observed with the analysis of the complete data set. The second data subgroup (aquitard thickness between 16 and 30 m) displays a pattern very similar to that resulting from the analysis of the entire data set. In the next data subgroup (aquitard thickness between 31 and 45 m), the basic composition of the factors is similar to that of the previous subgroups, although the first factor (the most significant) indicates its geogenic origin, and the second factor indicates its anthropogenic origin. This evidence indicates that contamination from the surface is less evident in this data subset. The most important processes that influence the

Fig. 7 The distribution of the factor scores of each factors: 1 factor scores of factor 1 (“anthropogenic”) > 1; 2 factor scores of factor 2 (“geogenic”) > 1; 3 factor scores of factor 3 (“ascent”) > 1



groundwater chemistry have a geogenic origin. The most interesting finding is the composition of the factors of the data subset characterised by an aquitard thickness of more than 46 m. The composition of the first factor (the most significant) is very similar to that of factor 3 (upward flow) extracted from the entire data set. The most distinct contributions by water colour, oxygen consumption and F^- are evident in this factor (compared with that of the entire data set). The composition of the second factor is very similar to that of the geogenic factor extracted from the entire data set. These factors indicate that the anthropogenic impact on the groundwater chemistry is negligible in the deepest part of the flow system. The chemistry of the groundwater in the deepest part of the flow system is primarily due to the influence of groundwater from deep circulation and from the influence of natural processes related to the decomposition of organic matter, followed by the increase in the solubility of the geologic elements. The spatial distribution of the factors (Fig. 7) indicates that the first process is related to the deepest aquifers located primarily in the regional discharge zones, which is consistent with the results of the isotope analysis. The oldest calculated age of the groundwater was observed in these aquifers (wells located in Karpicko and Skwierzyna). Thus, the isotope analysis confirms the upward-flow origin of this factor (and factor 3 resulting from analysis of the entire data set). The shift of points in the cation triangle in the Piper diagram (Fig. 3) is caused by this process. The second group of processes (geogenic) is related to the remaining part of the data set that is not influenced by contamination.

The results of the FA indicate that contamination from the ground surface considerably influences the groundwater

chemistry. Moreover, in a distinct part of the study area, the geogenic and anthropogenic processes overlap. Consequently, interpreting the natural changes in the groundwater chemistry is difficult. For this reason, the data subset that is influenced by natural geochemical processes (i.e., not affected by human activity) was analysed using the method presented by Dragon (2008). The results of the FA were helpful in distinguishing between uncontaminated and contaminated groundwater. First, the factor scores of each sample were calculated. The subset of the results characterised by factor scores < 0 for the first anthropogenic factor was marked. Then, the results of water samples that contained nitrate were removed. After this procedure, a subset of 68 analytical results (36 % of the complete data set) representing the natural groundwater chemistry was obtained. The remaining part of the data set represents the groundwater chemistry that is impacted by anthropogenic contamination.

To develop an interpretation of the variations in the natural groundwater chemistry, the sum of the major anions and sum of the major cations were separately correlated with each anion and each cation, respectively, in scatter diagrams (Fig. 9). For a better understanding of the relationships between anthropogenic and natural geochemical processes, both groups of data are presented: those data associated with natural geochemical processes and the remaining data (associated with contamination). A well-defined relationship is evident in the HCO_3^- , Ca^{2+} and Mg^{2+} plots of both data subsets presented in the diagrams. The highest concentrations of Ca^{2+} and Mg^{2+} in the contaminated water are evident, indicating the contribution of these parameter concentrations to the groundwater

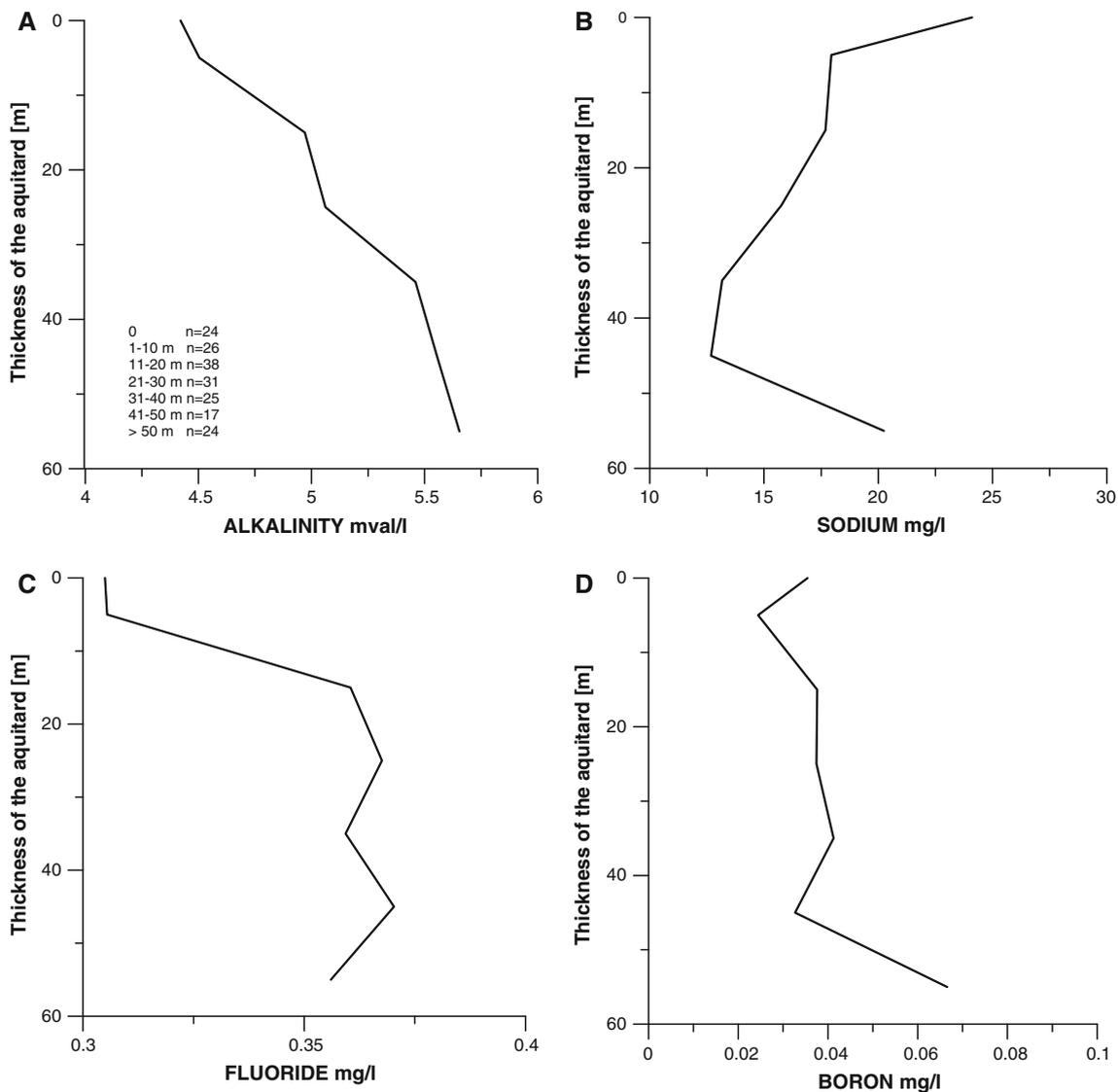


Fig. 8 The variability of choosing parameters concentration with depth ($n = 185$)

mineralisation. This contribution' is reflected in the FA results by the contribution of TH to the first anthropogenic factor (Table 3). In the natural groundwater, the lack of a correlation is evident in the Cl^- , SO_4^{2+} and Na diagrams, whereas in the contaminated water, this relationship is evident, which shows the impact of contamination on the levels of these parameters. The increase in the level of TDS in the contaminated groundwater evident in the Piper diagram (Fig. 3) is due to this process. The distinct shift of certain points in the Na^+ diagram (in a direction toward higher concentrations) and Ca^{2+} diagram (toward lower concentrations) is apparent. These points represent the deepest wells located in the discharge zones (Karpicko, Skwierzyna, Zielonagora and Zielatkowo). The process responsible for this relationship is the cation exchange that occurs in the deepest parts of the flow system. All of these

samples contain the highest concentrations of F^- and B, confirming the oldest age of this groundwater. The locations of these wells in the regional discharge area, where a high upward gradient is present (Fig. 2), indicate that this relationship is caused by the upward flow of water originating from deep water circulation.

The spatial distribution of F^- is shown in Fig. 10. The lowest concentrations (<0.2 mg/l) are present in the recharge area (Lwówek-Rakoniewice Rampart). From there, an increase in the fluoride concentrations in all directions is evident. Thus, the fluoride concentrations clearly follow the flow pattern of the groundwater, and the increases in its concentration coincide with the flow paths. Saxena and Ahmed (2001) concluded that the presence of F^- in groundwater is related to the residence time of the groundwater in the geologic environment. The increase in

Table 4 The results of the factor analysis (after varimax rotation) performed for the data subsets allocated according to different aquitard thickness

Parameter	Aquitard thickness <15 m (n = 71)		Aquitard thickness 16–30 m (n = 47)		Aquitard thickness 31–45 m (n = 39)		Aquitard thickness >46 m (n = 26)	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Colour	0.13	0.71	−0.22	0.50	0.17	0.05	0.77	0.23
pH	−0.62	−0.40	−0.61	−0.10	−0.70	−0.27	0.02	−0.80
HCO ₃ [−]	0.64	0.48	0.57	0.65	0.93	0.22	0.56	0.74
Oxygen consumption	0.13	0.78	−0.06	0.82	0.77	−0.21	0.70	0.50
Fe ²⁺	−0.09	0.82	0.42	0.54	0.73	−0.24	−0.17	0.67
Mn ²⁺	0.45	0.18	0.55	0.18	−0.16	0.39	−0.02	−0.19
B	0.73	0.15	0.25	0.49	0.34	0.17	0.92	0.11
F [−]	−0.08	0.35	0.04	0.41	0.48	−0.09	0.79	−0.06
Cl [−]	0.94	−0.09	0.90	−0.12	0.10	0.89	0.23	0.40
NO ₃ [−] -N	0.47	−0.37	−0.03	−0.04	0.06	0.48	−0.25	0.14
NH ₄ ⁺ -N	0.11	0.66	0.06	0.82	0.77	−0.26	0.69	0.44
Na ⁺	0.82	0.01	0.58	0.54	0.75	0.22	0.95	0.16
K ⁺	0.74	−0.01	0.67	0.32	0.72	0.46	0.68	0.57
SO ₄ ^{2−}	0.78	−0.19	0.91	−0.13	−0.05	0.86	−0.52	0.18
Total hardness (TH)	0.85	0.08	0.96	0.12	0.70	0.65	−0.19	0.90
Total dissolved solids (TDS)	0.91	−0.02	0.95	0.12	0.53	0.79	0.37	0.75
Percentage of variance (%)	36.6	16.9	38.4	16.36	37.4	18.0	41.2	17.8

Factor loadings >0.7 are marked by bold font

the F[−] concentration along the flow path in the present study is related to the relatively longer residence time of the groundwater in the aquifer system. Thus, the distribution of the F[−] concentrations can be helpful for identifying the zones where extensive infiltration occurs (recharge areas).

Conclusions

Based on the statistical analysis and the standard interpretation (analyses of the maps, cross sections and diagrams), the hydrochemical zonation of a regional aquifer system were delineated. Factor analysis was used to identify three primary groups of processes. The most important factors that control the groundwater chemistry are anthropogenic impacts that cause the contamination of groundwater, geogenic processes that increase the dissolution of geological environmental components and the effects of deep water circulation on the groundwater chemistry.

The analysis of the concentrations of the groundwater components with depth revealed certain variations in the Na⁺ and B concentrations. The highest concentrations were observed in the deepest parts of the flow system. The concentrations of these parameters are also higher in the shallowest wells. The factor analysis of the data subgroups was used to divide the data on the basis of the aquitard

thickness and identify the origin of this differentiation. The sharp increases in the concentrations in the deepest part of the flow system are associated with the effect of the upward inflow of groundwater from the deepest part of the aquifer system. This finding is consistent with the isotope analysis, as the oldest water is one characteristic of this groundwater. The high concentrations of Na⁺ and B in the shallow part of the flow system are associated with contamination from the surface.

To develop a more precise interpretation of the natural (geogenic) groundwater chemistry variations, the subgroup of the analytical results not influenced by groundwater contamination was defined. The changes in the groundwater chemistry in the deepest part of the flow system were found to be caused by cation exchange. This process was identified in the deepest wells located in the discharge zones, which led to changes in the water chemistry from one of predominantly Ca²⁺-HCO₃[−] chemistry to one of predominantly Na²⁺-HCO₃[−] chemistry.

The spatial distribution of F[−] shows a clear relationship with the flow pattern. The lowest F[−] concentration was observed in the regional recharge zone, where the highest effective infiltration occurs.

This groundwater chemistry zonation can be helpful in identifying the groundwater flow patterns and in determining the vulnerability of groundwater to contamination. The zones where the geogenic processes are less effective

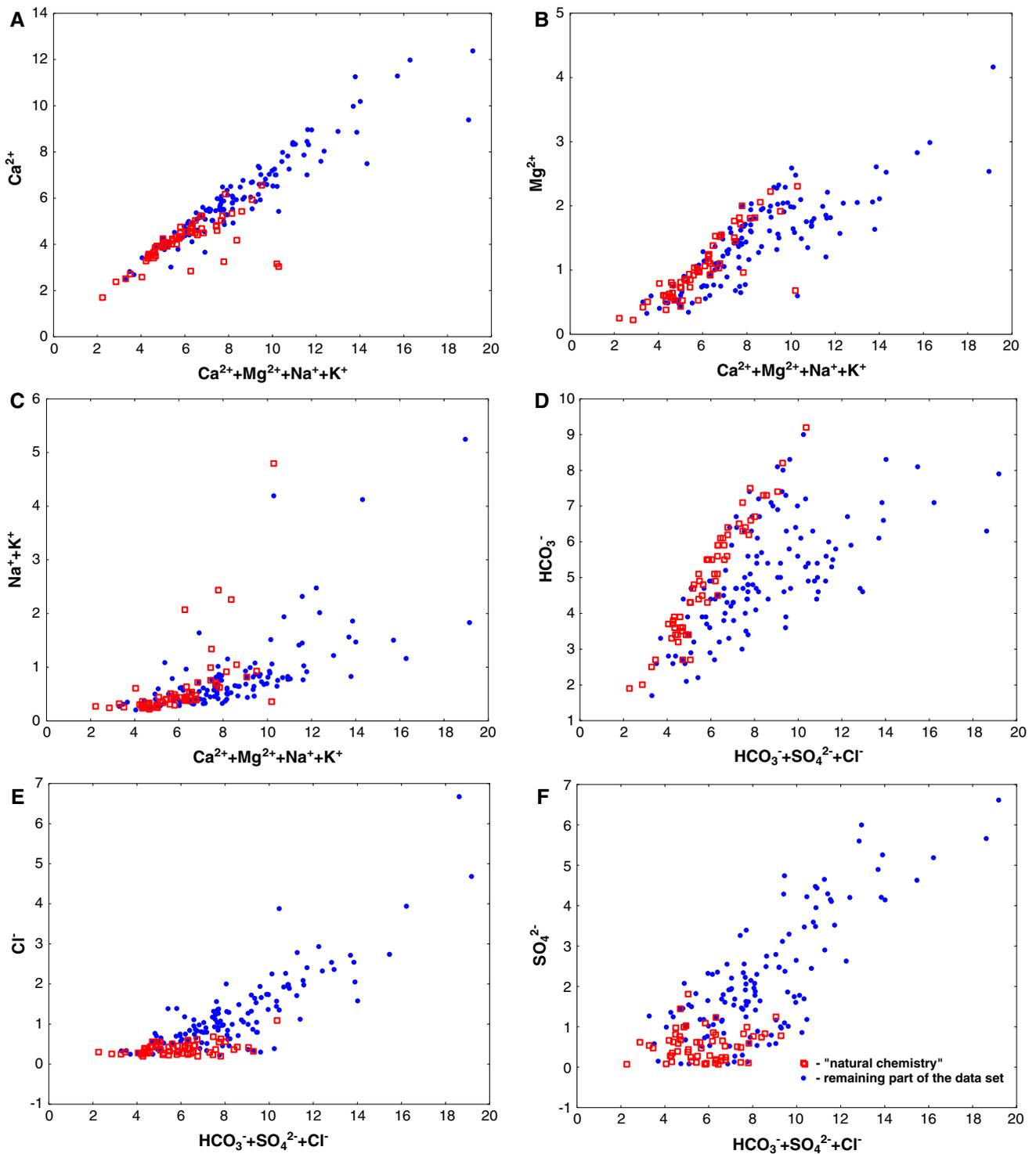


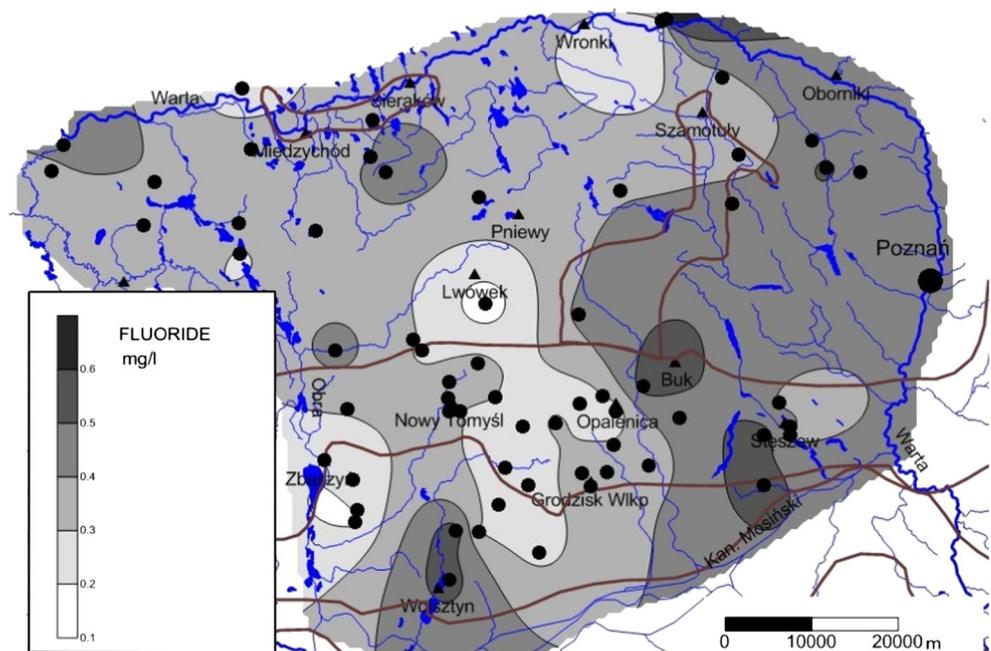
Fig. 9 Plot of sum anions versus each anion and sum of cations versus each cation (concentrations in meq/l)

(identified by the lowest factor scores of the geogenic factor) represent the parts of the flow system where the highest effective infiltration occurs. At this time, these zones are the most vulnerable to contamination from the surface. In contrast, the zones where upward flow of

groundwater influences was identified are those least vulnerable to groundwater contamination.

The present study demonstrates the general usefulness of groundwater chemistry differentiation in support of identification of groundwater flow patterns. It also

Fig. 10 The distribution of fluoride in the part of the data set that is characterized by “natural” groundwater chemistry. By black points the sampling sites from the “natural” data subset is marked



demonstrates the importance of using chemical data to verify the connectivity between different aquifers. These interpretations may be useful for better management of water resources on a regional scale.

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