Impact of human activity on groundwater chemistry (Wielkopolska region, Poland)

Krzysztof Dragon

Abstract The article identifies the effects of human activity on groundwater chemistry in the regional aquifer system located in the Wielkopolska region (western Poland). It was documented using statistical methods, that the main process influencing the groundwater chemistry is connected to contamination. The impact of contamination is evident in regions without sewers and where the aquitard is relative thin. Chloride and sulphatewere found most influenced by pollution from surface sources. Total hardness is also sensitive, but its behavior is controlled by geogenic processes as well. Factor analyses are a reliable tool for recognizing contamination's impact on groundwater chemistry, especially for cases with a relatively low contamination level, when contamination is related to natural occurring water components. This research is important for implementing groundwater protection plans at the regional scale. These interpretations may be used to manage water resources better at the regional scale.

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INTRODUCTION

Groundwater is the main source of water for the population and industrial uses in Poland. Contamination leads to deterioration in groundwater quality. Therefore, groundwater pollution can cause both health and economic consequences (Choi *et al.* 2005). Contamination increases the cost of water treatment and influences the effectiveness of equipment used to extract, treat and distribute water. In extreme cases, impurities can lead to closures of water infrastructure (Dragon & Gorski 2008).

Groundwater is increasingly contaminated due to human activities all over the world. This effect is particularly apparent in shallow, unconfined aquifers. However, evidences of contamination are also observed in deeper aquifers covered by a thick aquitard. It is important factor for groundwater management strategies because it is common tendency to relocate water exploitation to deeper aquifers due to shallow groundwater contamination (Jeong 2001).

Therefore, recognizing the impact of human acti-

vity on groundwater chemistry is critical (Lawrence *et al.* 2000; Jeong 2001; Cronin *et al.* 2003) and should be the starting point for implementing groundwater protection zoning (Nel *et al.* 2009; Jime´nez-Madrid *et al.* 2012). For such actions to be effective, they should be undertaken even at sites with low levels of anthropogenic change to groundwater chemistry.

Recognizing the first symptoms of anthropogenic contamination is a difficult scientific research problem, especially when the contamination concerns only naturally occurring groundwater components such as Cl and SO_4 ions. In this case, an assessment of anthropogenic impact must be performed based on recognizing natural geochemical processes, hydrochemical zoning and natural background concentrations.

For groundwater chemistry recognition due to the cost of establishing not specially dedicated monitoring boreholes but pre–existing pumping wells are typically used (Netzer *et al.* 2011). The depth and degree at which contaminants penetrate aquifers remain poorly understood among other factors due to a lack of depth–specific sampling (Cronin *et al.* 2003).
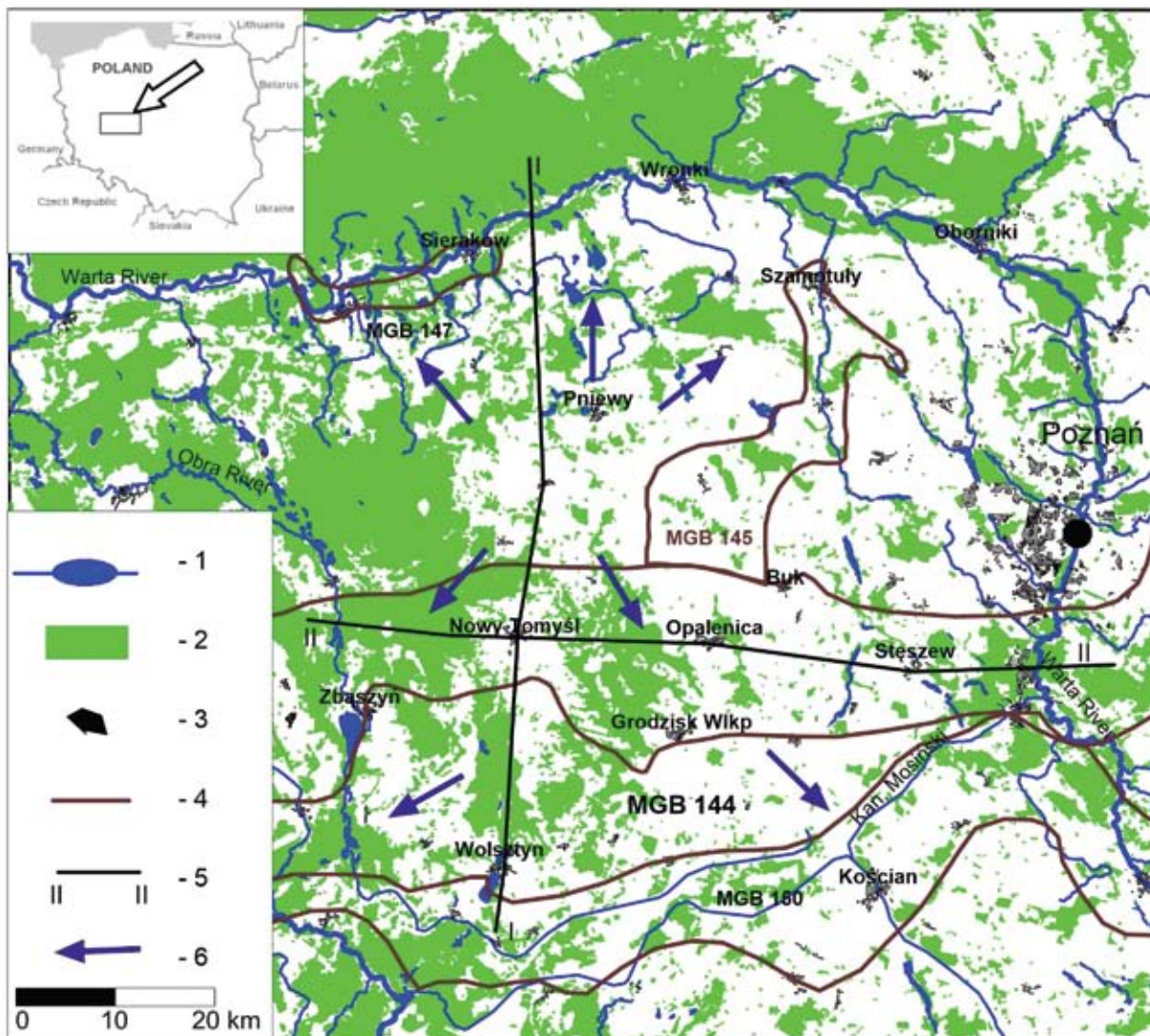
The main goals of this study include the following: (1) investigating human activity on the groundwater chemistry of a regional aquifer system located in the Wielkopolska region (Poland); (2) assessing the depth to which contaminants influence groundwater chemistry; (3) identifying the groundwater components reflected first stage of contamination. This research is performed on background of natural groundwater chemistry recognition (Dragon & Gorski 2015).

The identification of human impact on groundwater chemistry that is still at low (initial) level was performed for semi–confined aquifers (mainly buried valleys). It is poorly identified matter particularly in case of the relative deep aquifers covered by layer of glacial tills that are the most attractive water supply aquifers in Polish lowland area. This is important subject matter for implementation of groundwater protection activities instantaneously at low groundwater contamination level.
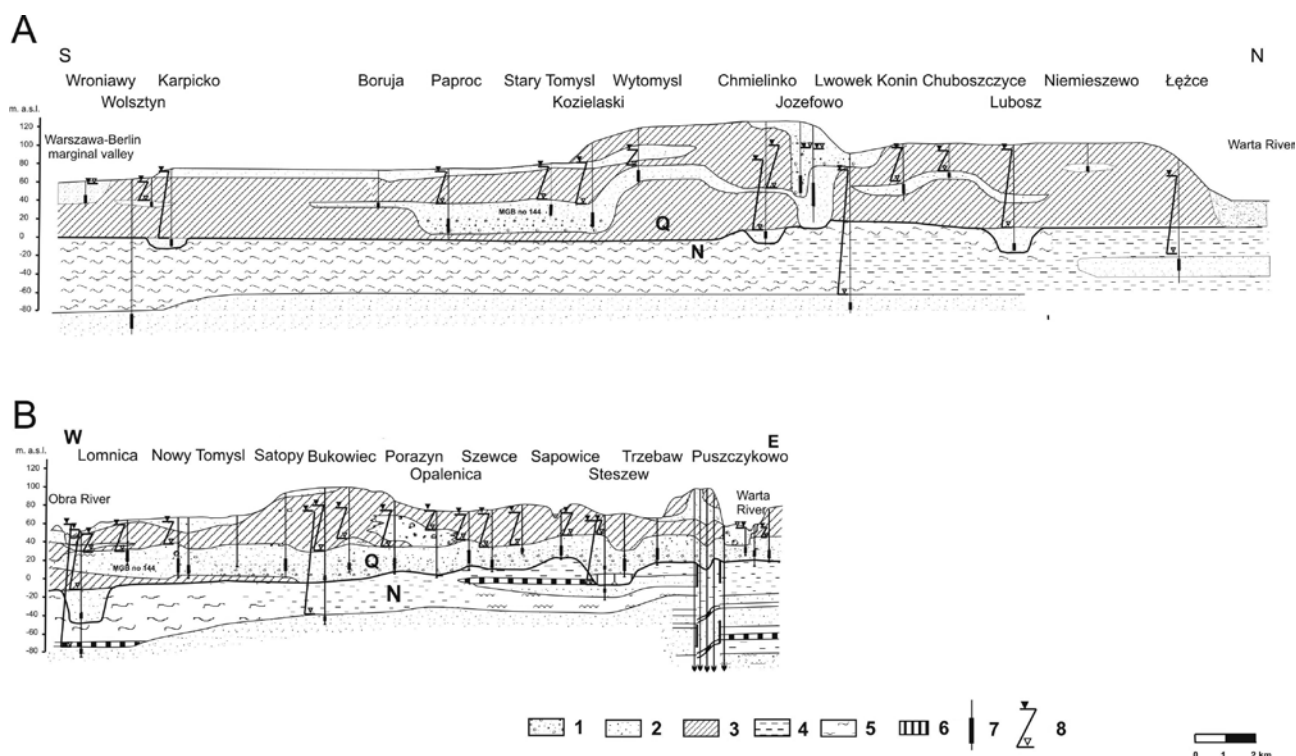
STUDY AREA

The study area is located in the Wielkopolska region, the western part of the Polish Lowlands (Fig. 1). The thickness of the Quaternary sediments is greater than 130 m in the central part of the study area, declining to about 60 m in the Warszawa–Berlin glacial ice-marginal valley less than 40 m in the Warta valley (north part of the study area) (Fig. 2). The Quaternary lithology is represented by glacial and fluvioglacial deposits. The fluvioglacial sands and gravels form aquifers in some regions and generate a multilayer aquifer system.

The aquifers associated to the Wielkopolska buried valley aquifer system (WBV) are located in the central part of the study area. These aquifers thickness ranges between 30 and 40 m. The lithology is dominated by sand (fluvial origin) in the upper part of the aquifer and by sand and gravels (fluvioglacial origin) in the deeper portions. The aquifers which are in

Fig. 1 The location of the study area on a background of the land use. 1 – surface water (lakes and rivers); 2 – forests; 3 – settlement areas >1000 inhabitants (towns with > 5000 inhabitants are marked with town name); 4 – the boundaries1 of the Major Groundwater Basins (MGB); 5 – lines of cross-sections (Fig. 2); 6 – groundwater flow directions. The areas outside the settlement without forest are usually used as arable land

Fig. 2 The hydrogeological cross-sections (after Dragon, Gorski 2015, modified). 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

contact with the WBV from the north and south have thicknesses between 5 and 20 m; and they are mainly composed of fine and medium sand. The deepest aquifers thickness is approximately 20-30 m and they are mainly composed of fine sand. This type of aquifer was discovered only locally in the part of the region where shallow aquifers do not exist.

The confining layers that cover the shallow aquifers contain glacial till between 15 and 30 m thick. The WBV aquifer system is covered by a thick aquitard (between 15 and 45 m), while the deepest aquifers are buried under an aquitard more than 60 m thick (Fig. 2).

The regional recharge area is situated in the central part of the studied region (Lwowek–Rakoniewice Rampart). The regional discharge areas are located in the river valleys surrounding the studied region: the Warta valley from the east and north, the Obra valley from the west and the Warszawa–Berlin glacial marginal valley from the south (Fig. 1).

The WBV aquifer system is classified as Major Groundwater Basin (MGB) no. 144 and 145 (Kleczkowski, Ed. 1990). Moreover, the Miedzychod–Sierakow aquifer and Warszawa–Berlin glacial ice-marginal valley aquifer are classified as Major Groundwater Basins no. 147 and 150, respectively (Fig. 1).

The groundwater system in the eastern part of the studied region (Warta valley zone) has been studied by Gorski (1989), who assessed the natural hydrochemical background of the main water component concen-

trations. The groundwater chemistry differentiation of the WBV aquifer (MGB 144) was recognized by Dragon (2006) with use of multivariate analysis to separate anthropogenic and geogenic processes that control the groundwater chemistry. The hydrochemical zonation in the WBV aquifer was recognized by Dragon & Gorski (2009). Moreover, a contamination that still existed at low (initial) levels was discovered (Dragon 2008) but leads to a steady deterioration in groundwater quality with time (Dragon 2012). The ground water chemistry of the recharge zone of the studied aquifer system was examined relative to nitrate migration (Dragon 2013).

These works have demonstrated that the groundwater chemistry of the WBV aquifer originates largely from the influx of groundwater from aquifers located north of the WBV aquifer. Therefore, this work was extended to cover the whole aquifer system (regional recharge area surrounded by discharge areas).

Land use and urbanization

The eastern part of the study area (east to the line of Grodzisk Wielkopolski, Opalenica and Pniewy) is predominantly agricultural, while forested lands prevail to the west (Fig. 1). There are also developed areas including several towns (5 000−15 000 inhabitants) and many villages. In the biggest towns there are usually sewage systems with each connected to a central sewage treatment station. These systems are relatively new; they were mostly constructed or

expanded over the last decade. Previously, the sewage systems often covered only the town's center. The remaining communities in the area usually have no central sewage systems. Domestic sewage is usually stored in septic tanks that are often poorly constructed, as well as poorly maintained or used. This situation may cause the leakage of sewage waste into the ground, in some cases seeping directly into the groundwater. The zones outside the rural and urban areas are dominated by agricultural activity. Chemical fertilizers and manure spread on the land are also potential sources of groundwater contamination.
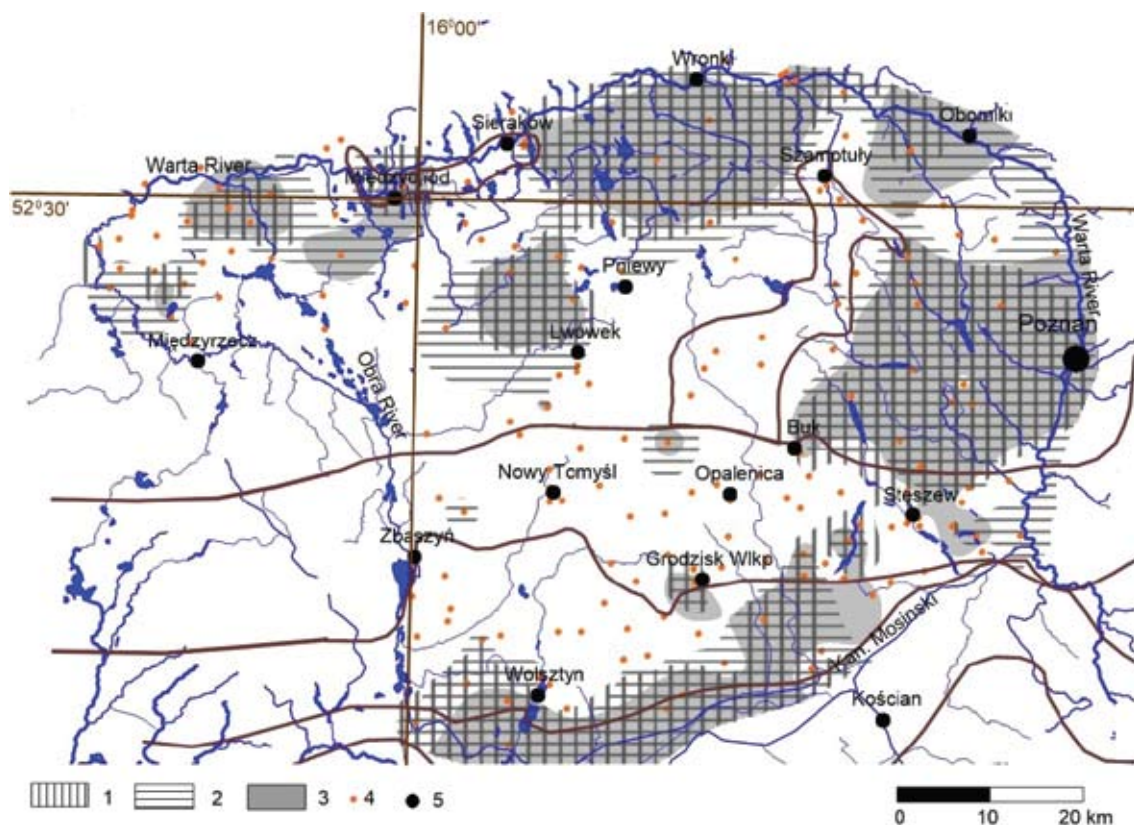
MATERIAL AND METHODS

Sample collection and analysis

The examination of the groundwater chemistry was performed using data from groundwater sampling performed during summer 2009. 185 continuously pumped production wells were sampled (Fig. 3 and Fig. 5). The water samples were taken into 100–ml HDPE bottles. For nutrient analyses separate samples were taken (treated with chloroform), as well as for iron and manganese (treated with HNO_3). All bottles were completely filled to prevent degassing. The water samples were stored in a portable refrigerator and the same day transported to the laboratory. Water temperature, electrical conductivity, colour,

pH and alkalinity were measured in the field. Chemical analyses were performed at the Adam Mickiewicz University in Poznan (Institute of Geology) using a Compact IC 881Pro ion chromatograph. The ion- balance error was calculated for quality control. The calculated error did not exceed 3 %.

Data processing

To characterize and interpret the data, conventional techniques, including the interpretation of maps, diagrams and cross–sections, as well as multivariate statistics were applied. Factor analysis (FA) was used to separate groups of correlated elements from the initial data set. The procedure was performed using the methodology presented in a previous work (Dragon 2006; Dragon & Gorski 2015). The statistical software package Statistica 10 (StatSoft Inc., 2004–2011) was used for the calculations. Before the analysis, the initial data set was standardized using the criteria presented by Davis (1973). This operation allowed the analysis of parameters that occur in different concentration ranges (macro– and microelements), as well as the parameters that were measured in different units (chemical components concentrations and aquifer thickness). As an extraction technique the principal component analysis was used (Davis 1973). This procedure generates new groups of variables from the initial data set (called the factors). The factor load-

Fig. 3 Generalized map of the groundwater chemistry (after Dragon, Gorski 2015, modified). 1 – Cl > 40 mg/l; 2 – SO$_4$ >60 mg/l; 3 – total dissolved salts (TDS) > 500 mg/l; 4 – location of the sampling sites; 5 – main cities. Remaining explanations are similar to Fig. 1

ings reveal how the factors characterize the variables (e.g., ion concentration). High factor loadings (close to 1 or –1) indicate a strong relationship (positive or negative, respectively) between the variable and the factor that describe this variable. The factor scores were calculated for each sample. Dalton & Upchurch (1978) have demonstrated that the factor scores for each sample may be related to the intensity of the chemical process described by the factor and subsequently used to recognize the hydrochemical zones origin. Positive factor scores (>+1) indicate the zones most affected, and negative scores (<–1) reveal the zones unaffected by the chemical process characterized by the factor. Near–zero scores reflect zones affected by the process (or factor) to an average degree. For example, a set of physico–chemical parameters correlated in a particular factor may be described with a chemical process (anthropogenic or geogenic), leading to the variability in the data set.

The weakness of FA is the difficulty of distinguishing the processes characterized by similar differentiation of groundwater chemistry (Olmez *et al*. 1994). Moreover, a priori knowledge of hydrogeological processes affecting the studied environment is required to effectively apply FA (Lawrence & Upchurch 1983).

RESULTS

Previous work revealed that groundwater chemistry in the studied area displays little variation (Table 1). However, zones with high concentrations of some components are evident (Dragon & Gorski 2015). These zones are mainly connected to water components that are the most influenced by water contamination. The spatial distribution of some ion concentrations is presented on the map (Fig. 3).

This map was created using the kriging interpolation method (Kitanidis 1997). Subsequently, the areas of high concentration of each water component were separated. The zones visible on the map represent areas where the concentration of ions is higher than natural hydrochemical background assessed in a previous work (Gorski 1989). The zones where the Cl concentrations exceeded 40 mg/l and the SO_4 concentrations exceeded 60 mg/l generally occurred in the regions to the north and south of the WBV aquifer system. In these regions, the total hardness (TH) is usually high (TH > 6 meq/l), and the TDS usually exceeds 500 mg/l (Fig. 3). The zone with high TH and low Cl and SO_4 occupy the MGB 145 area and its vicinity. Additionally, in the eastern portion of the WBV aquifer, there is a zone with high TH (low Cl and SO_4). That zone represents the inflow of groundwater from the aquifers contacted north to the WBV aquifer (Dragon & Gorski 2009). There are also small areas with high concentration of Cl and SO_4 in the WBV aquifer. These zones occur in the areas characterized by the thinnest aquitard (Dragon 2008). In these zones, the most intensive changes in the groundwater chemistry were observed over the last decade of water extraction (Dragon 2012). The maximum nitrate concentra-

Table 1 Statistical characteristics of the data set (after Dragon, Gorski 2015)

	Unit	Frequency	Average	Median	Min.	Max.	Standard deviation
Colour	mg Pt/l	180	14	10	0	120	14
pH		184	7.45	7.42	6.88	8.29	0.22
Alkalinity (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	1180	179
Electrical conductivity	μS/cm	185	652	618	210	1606	233
Cl		185	34.2	24.6	6.9	236.5	31.1
SO_4		185	76.7	56.2	3.3	317.6	68.8
Ca		185	109.1	103.6	34.0	248.0	37.2
Mg		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	mg/l	161	2.7	2.5	0.0	9.8	1.7
Mn		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		185	1.47	0.01	0.005	57.80	5.32
NO_2		185	0.031	0.005	0.005	1.199	0.124
NH_4		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

tion is 57.8 mg/l, however high nitrate concentration occurs only in several water samples taken from shallow wells.

The statistical analyses enabled more quantitative data interpretation. The results of the FA are presented in Fig. 4 and Table 2. No apparent trend was documented in the spatial distribution of the water types; moreover, the spatial changes of calcium and magnesium was very similar within the data set. Consequently, these water components were omitted and replaced by total hardness (TH), which enable to reduce the number of variables being considered.

Three calculated factors explain 59.2% of data set's variance. In Factor 1 the highest factor loadings of Cl, SO_4, TH, TDS and Mn to some extent were documented and low factor loadings of the remain-

ing parameters. The thickness of the aquitard and the pH also had relatively high, although negative, factor loadings. The concentration of these parameters (especially the Cl and SO_4 content) increased during well exploitation (Dragon 2013). Moreover, these ions' low concentrations are attributed to the unpolluted confined aquifers located in the Wielkopolska region (Gorski 1989). Relative high (negative) factor loading of the aquitard thickness indicates that less protected shallow aquifers are most sensitive to pollution. The form of this factor suggests that these parameters have an anthropogenic origin; therefore, this factor is labeled "anthropogenic".

Factor 2 contains the highest factor loadings of oxygen consumption, Fe, alkalinity and pH (negative). The water's colour and NH_4 content are also
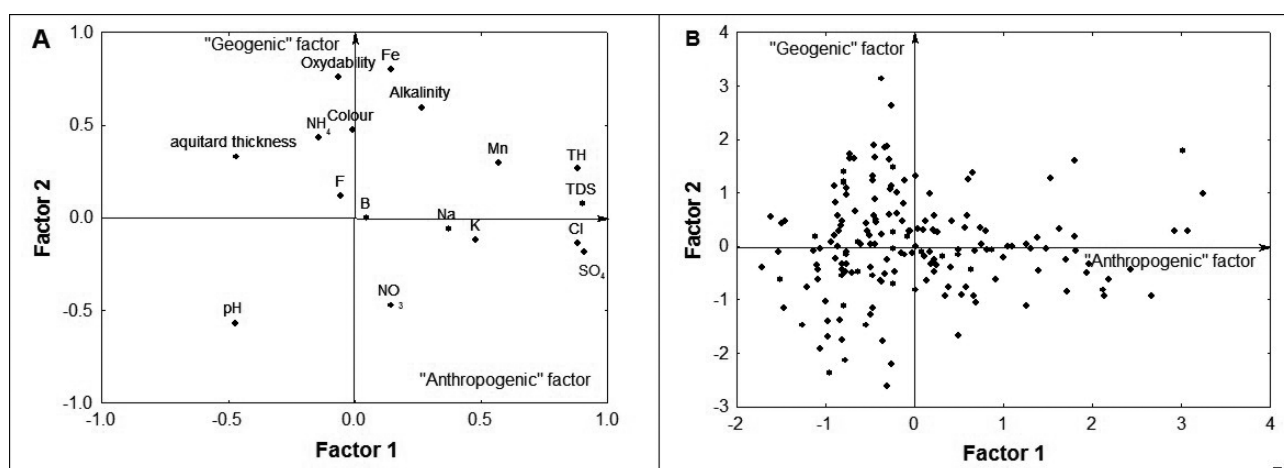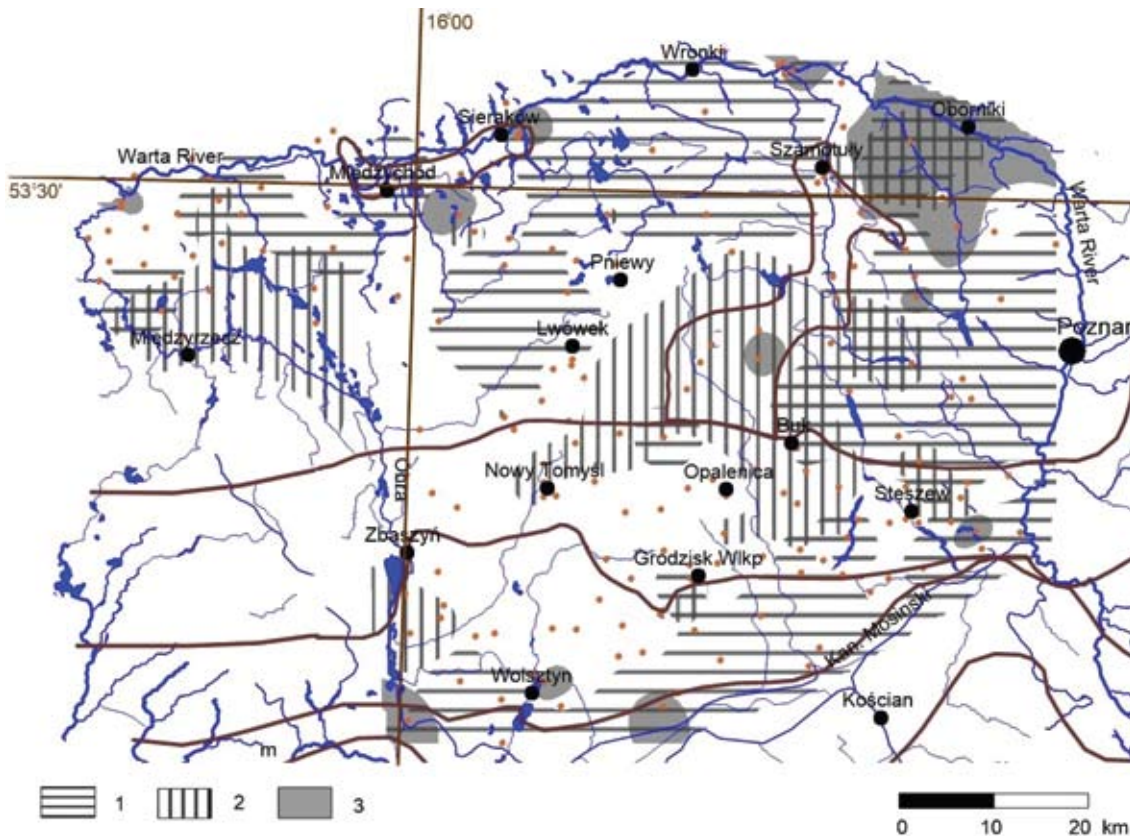

Fig. 4 Plots of factor loadings (A) and factor scores (B)

Table 2 The results of the factor analysis (after varimax rotation) (after Dragon & Gorski 2015)

Parameter	Factor 1 "anthropogenic"	Factor 2 "geogenic"	Factor 3 "ascent"
Colour	−0.01	0.48	0.00
pH	−0.48	−0.56	−0.18
Alkalinity (HCO_3)	0.26	0.60	0.59
Oxygen consumption	−0.07	**0.76**	0.24
Fe	0.14	**0.81**	0.17
Mn	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
NO_3	0.14	−0.47	0.16
NH_4	−0.14	0.44	0.60
Na	0.37	−0.06	**0.74**
K	0.48	−0.12	0.43
SO_4	**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

Fig. 5 The distribution of the factor scores of each factors (after Dragon, Gorski 2015, modified): 1 – factor scores of factor 1 ("anthropogenic") > 0; 2 – factor scores of factor 2 ("geogenic") > 0.5; 3 – factor scores of factor 3 ("ascent") > 1

clustered in this factor. These parameters reflect natural ("geogenic") hydrogeochemical processes. The behavior of the parameters that are correlated in this factor is mainly related to organic matter decay under anaerobic conditions causing more intensive dissolution processes. Therefore, this factor is called "geogenic".

Factor 3 is mostly linked to B, Na^+, alkalinity, NH_4^+ and F^-. These parameters reflect the influence of the deep–water circulation on the groundwater chemistry. Nevertheless, the origin of this factor is more complicated to explain than the other factors because it reflects the local variability of the hydrogeochemical conditions. This factor is usually represented by individual wells only in regions where the deepest aquifers were discovered (Dragon & Gorski 2015).

Spatial distributions of the scores for each factor show that the highest factor scores for factor 1 occupy the regions with the highest concentrations of Cl and SO_4 (compare Figs. 3 and 5). There are regions located north and south to the WBV aquifer, where the shallowest aquifers covered by a thin aquitard are used for water supply (Fig. 2).

The contamination is the most intense within these regions, and a steady increase in the Cl and SO_4 content, as well as the TH, is observed. These regions represent the most vulnerable parts of the aquifer system. Moreover, it is expected that these regions would face

the most intensive changes in groundwater chemistry caused by human activity during water extraction in the future. The zone of high TH in MGB 145 is reflected on the map in factor 2 ("geogenic"). Additionally, the inflow's influence on the groundwater chemistry of the WBV aquifer is apparent and is reflected by the factor 2 zone that surrounds the recharge area of the WBV aquifer (the Buk area to the east and the Nowy Tomysl area to the west). The TH behavior reflects that it contributes to both factors ("anthropogenic" and "geogenic"). The results of the FA enabled us to differentiate these processes. The contamination of the groundwater was identified in both urban and rural areas. The most distinct effect was noted in the regions with intense farming (east to line of Grodzisk Wielkopolski, Opalenica and Pniewy) and those historically rural lands without sewers. This type of pollution source has remained an influence dating back even to the last centuries (beginning of settlement). In the forested areas contamination usually occurs at a low level (compare Figs. 1 and 5). This observation allowed to conclude that the groundwater contamination caused by sewage effluents is connected not only to rapidly developing cities (Lawrence *et al*. 2000; Rajesh & Murthy 2004), but also to old settlement areas without sewage systems and areas where the sewage systems are relative new.

The changes in the concentrations of some param-

eters with depth are presented in Fig. 6 for parameters influenced mainly by "anthropogenic" processes (parameters grouped in factor 1). To construct these plots, the entire data set was divided into subsets based on the aquitard's thickness (10 m interval). The plots reveal the differentiation between these groups. On the graph, there is very clear decrease in each water component relative to depth. This behavior is reversed relative to the changes in the water components influenced by "geogenic" processes that usually increase with depth (Dragon & Gorski 2015). This fact is confirming the anthropogenic origin of the analyzed ions and its dependence on human impact.

For a quantitative interpretation of the groundwater chemistry changes as a function of depth, the FA was performed for the subsets of data divided according to the thickness of the aquitard (four subgroups, 15 m intervals). Two factors were obtained for each data group (Table 3). The obtained structure of the factors is similar to the analysis performed using the entire data set (compare Table 2 and 3).

However, the identification of the aquifer depth's influence was exposed. In the data subset containing the smallest thickness of the aquitard (< 15 m), Factor 1 has very similar structure to the analyses performed for entire data set except that the participation of Na^+,

K^+ and B in the "anthropogenic" factor was more obvious. This result reveals their anthropogenic origin (in the shallowest wells). The structure of the second ("geogenic") factor is very similar to the examination of the whole data set. The second data subgroup (thickness of the aquitard between 16 and 30 m) shows a structure where both factors are very similar to the analysis of the entire data set. In the next subgroup of data (thickness of the aquitard between 31 and 45 m), the basic structure of the factors is similar to the previous one, except that the first factor (the most significant) indicates a "geogenic" origin and the second factor indicates an "anthropogenic" origin. This evidence reveals that human activity in this data subset is less effective. The most important processes that influence the groundwater chemistry have a "geogenic" origin. The structure of the factors obtained for the last subset (thickness of the aquitard more than 46 m) indicates a "geogenic" origin for both factors. The composition of the first factor (most significant) is very similar to that of factor 3 ("ascent") obtained for the entire data set. The second factor has a configuration very similar to the "geogenic" factor obtained for the whole data set. The structure of these factors indicates that the anthropogenic influence on the groundwater chemistry is insignificant in the deepest part of

Table 3 Results of the factor analysis (after varimax rotation) performed for the data subsets allocated according to different aquitard thickness (after Dragon & Gorski 2015)

Parameter	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
	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)	
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**
Alkalinity (HCO₃)	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	−0.09	**0.82**	0.42	0.54	**0.73**	−0.24	−0.17	0.67
Mn	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
NO₃	0.47	−0.37	−0.03	−0.04	0.06	0.48	−0.25	0.14
NH₄	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
SO₄	**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

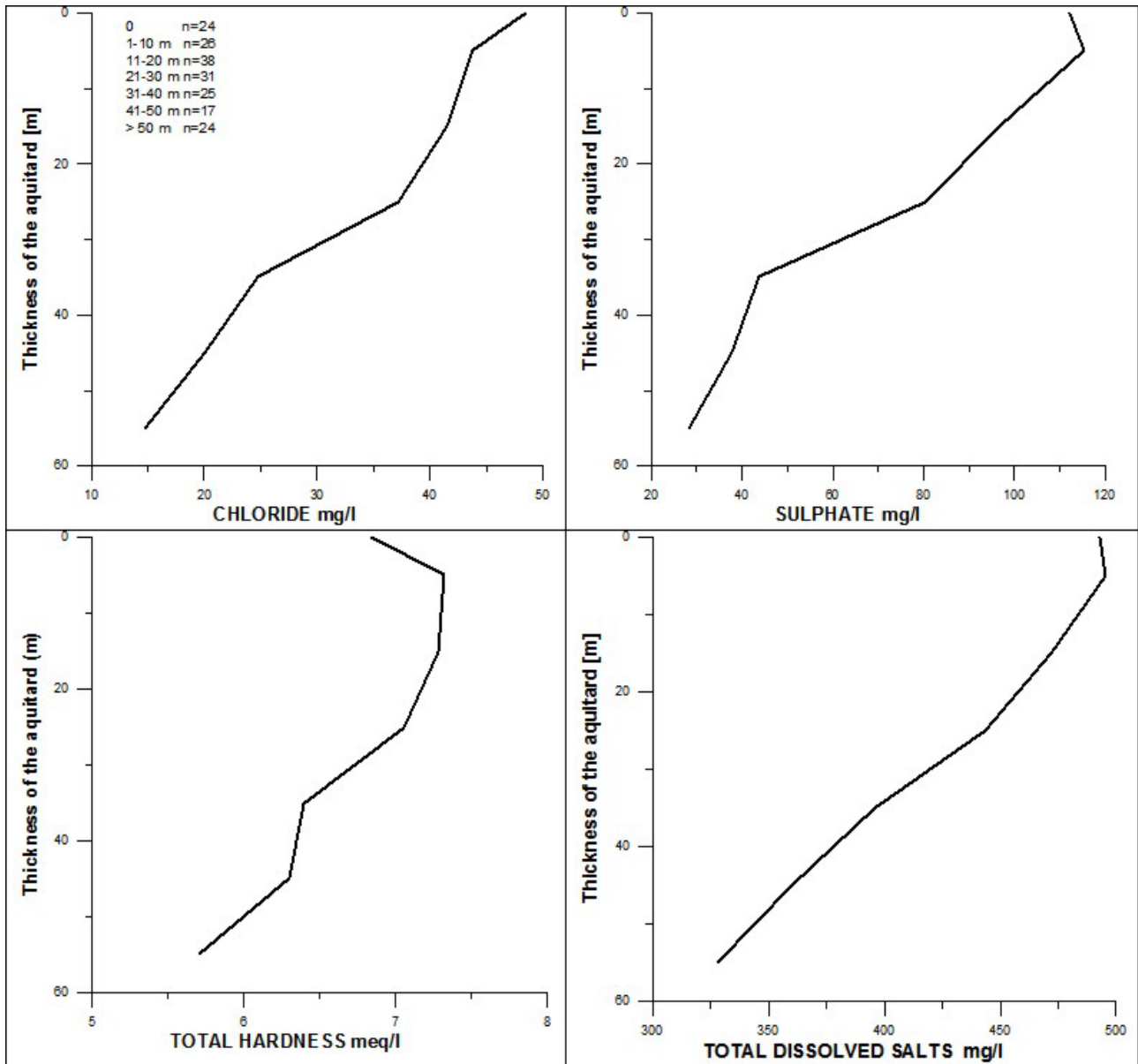Factor loadings >0.7 are marked by bold font

Fig. 6 The changes of choosing parameters concentration with depth

the flow system. The chemistry of this water depends mainly on the natural processes; it is not influenced by pollution.

DISCUSSION

The results of the FA indicate that human activity considerably influences the groundwater chemistry. Moreover, in a distinct portion of the study area, the "geogenic" and "anthropogenic" processes overlap. To identify the parameters most influenced by contamination, the subset of data that characterized natural groundwater chemistry was separated. Subsequently, this data subset was compared to the whole data set using correlation and regression analyses (Fig. 7). The factor scores for factor 1 ("anthropogenic") were used for the separate data sets that

represented natural groundwater chemistry. The regions with high factor score values revealed to the most noticeable anthropogenic transformations of the groundwater chemistry, as well as to the regions with the highest groundwater vulnerability. In that case the factor score values could be used to indicate contamination. First, the subset of the analysis characterized by the factor scores <0 for the first "anthropogenic" factor were distinguished. Next, all water samples that contained nitrate were removed. After this procedure, the data subset containing 68 analyses (36 % of the entire data set) that characterized "natural" groundwater chemistry was attained. The remaining data set characterizes the groundwater chemistry that is influenced by anthropogenic contamination.

The analysis clearly demonstrated that observed relationships between the variables of the entire data
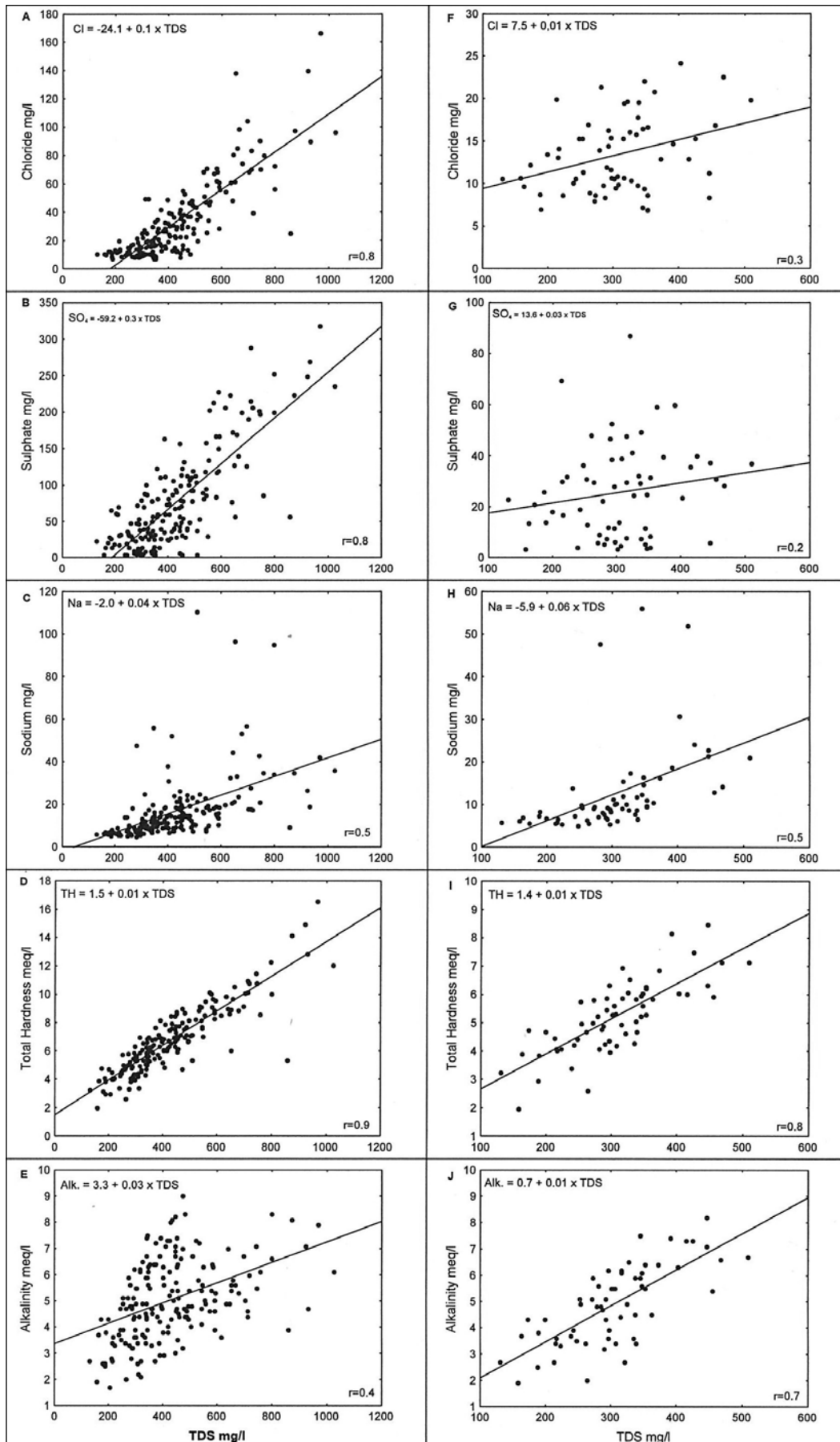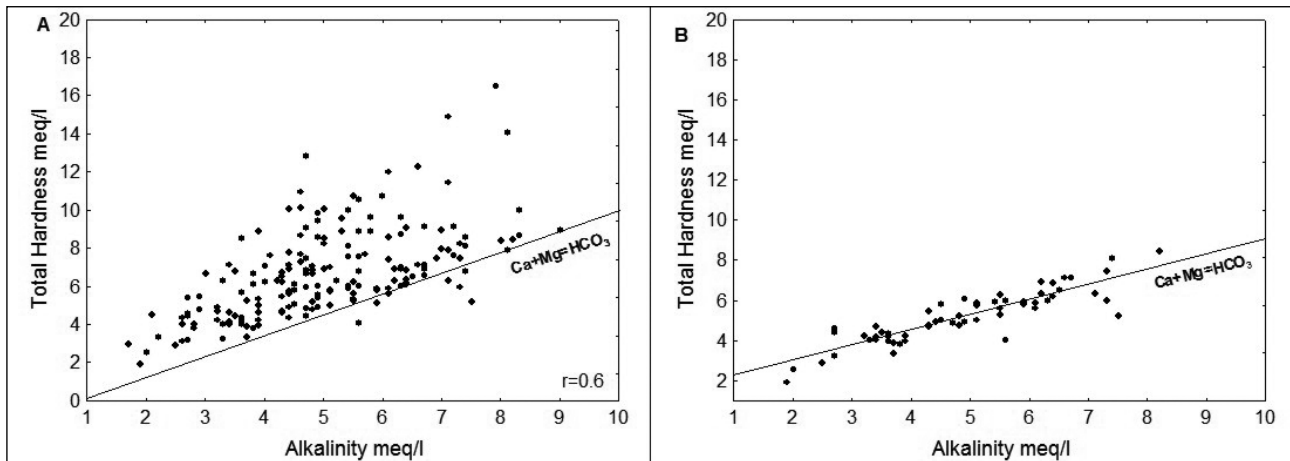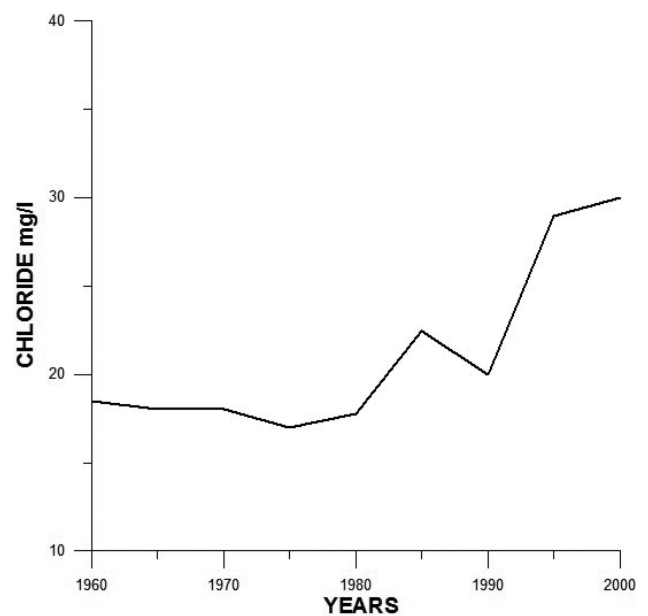
Fig. 7 The scatter diagrams of the hydrochemical parameters (whole data set – left graphs, n=185; "natural" groundwater – right graphs, n=63; α=0.05)

Fig. 8 The scatter diagrams of alkalinity and total hardness (A – whole data set, n=185; B – "natural" groundwater, n=63); α=0.05

set are different from those characterizing the "natural" groundwater chemistry. The relationship of each major ion to TDS is presented in Fig. 7. A strong relationship between the Cl, SO_4 and TH with TDS is apparent for the whole data set. The alkalinity correlates with TDS to smaller extent in this data group. Notably, in the subgroup characterizing natural groundwater chemistry, Cl, SO_4 do not correlate with TDS but TH and alkalinity correlate very well. The plot of TH vs. alkalinity indicates that majority of the data samples is placed above the equal line ($Ca+Mg=HCO_3$) (Fig. 8A), indicating a surplus of TH (i.e., Ca and Mg) relative to alkalinity (i.e., HCO_3) for the entire data set. Higher TH values (relative to alkalinity) are characteristic for the data samples with high Cl and SO_4 concentrations. This observation suggests that the occurrence of non–carbonate hardness is balanced by high SO_4 concentration. For the "natural" groundwater chemistry TH and alkalinity are balanced and most of the data points fall near the equal line ($Ca+Mg=HCO_3$) (Fig. 8B).

The groundwater chemistry changes in the studied region confirm the role of Cl and SO_4 as the principal products of urbanization influencing the groundwater chemistry (Eisen, Anderson 1979; Jeong 2001; Choi *et al*. 2005). They are generally conservative species and consequently reach the aquifer first. Therefore, these parameters may be used as indicators for anthropogenic pollution. The interpretation of TH that reflects both the Ca and Mg concentrations is more problematic because their concentrations are controlled by both "anthropogenic" and "geogenic" processes. However, it is possible to distinguish these groups of processes using statistical methods (e.g., FA). The variability of the groundwater chemistry with time reveals the intensity of anthropogenic contamination. Most apparent is a change in the average concentration of chloride over time that clearly indicates this trend (Fig. 9).
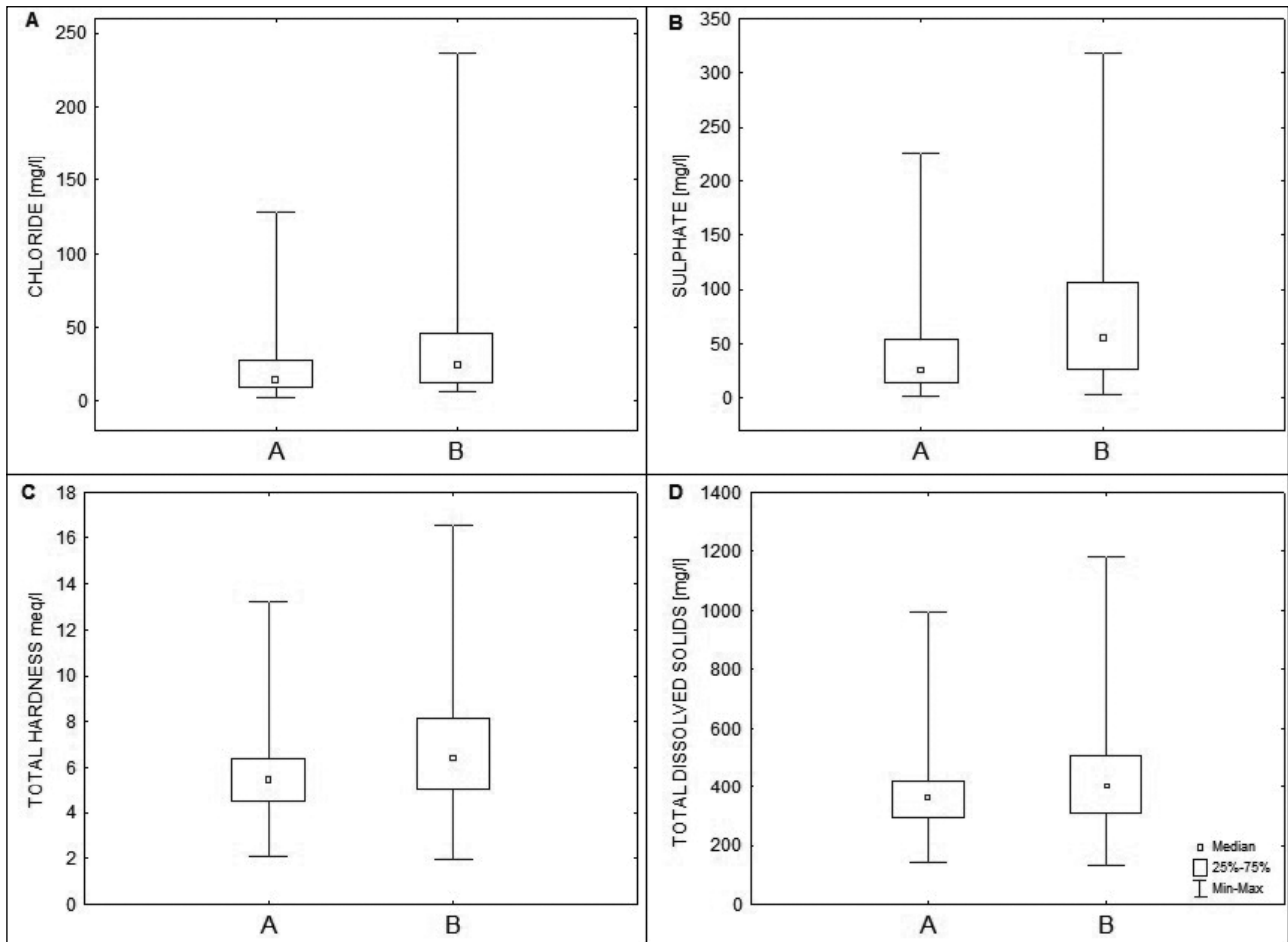

Fig. 9 The variability of chloride concentration over time on the basis of the archival data (chemical analyses from pumping tests period, n=950)

Comparing the groundwater chemistry from period of well construction with recent data (Fig. 10) reveals an increase in the concentration of all parameters grouped in factor 1.

CONCLUSIONS

In the regional aquifer system located in the Wielkopolska region (western Poland), relative stable groundwater chemistry has been documented but distinct zones with high concentrations of some parameters are evident. These zones are mainly connected to the parameters that are most influenced by human impact (Cl, SO_4, TH and TDS). The results of multivariate statistical analyses reveal that the factor responsible for this differentiation is the in-

Fig. 10 Changes of groundwater chemistry over time. A – groundwater chemistry in period of wells construction; B – current state (2009) of groundwater chemistry

put from the surface. The most important factor obtained from the factor analyses (FA) clustered these parameters, indicating an anthropogenic nature. The spatial analyses of the results reveal that the influence of human activity on groundwater chemistry is related to the regions where the aquitard is relatively thin. The factor analyses performed for the data subgroups separated according to the aquitard thickness reveal that the influence of contaminants below 30 m of glacial tills is relative small, and for those with an aquitard of 45 m, the groundwater chemistry is related mainly to natural processes (degradation of organic matter and deep ground water circulation). The regions with the most intensive changes in groundwater chemistry represent the most vulnerable areas of the aquifer system. In these regions, the human impact on groundwater chemistry will likely intensify.

The parameters most influenced by contamination are Cl and SO_4. TH is also influenced by human impact, but its interpretation is more problematic due to the overlap of geogenic and anthropogenic processes. However, statistical analyses (FA) may be helpful for separating these groups of processes and determining

the regions according to their impact on groundwater chemistry.

The nature of groundwater chemistry changes and its spatial differentiation reveals that the main sources of pollution influencing observed water chemistry are the unsewered settlements. The weakest effect caused by human impact was observed on the forested lands. This research show that the groundwater contamination caused by sewage effluents is connected not only to rapidly developing cities, but also to old settlement areas without sewage systems and areas where the sewage systems are relative new. After democratic political changes occurred in Poland, the enforcement of groundwater protection activities (e.g., building of new sewage systems, rationalization of fertilizer use, etc.) has been very successful but the effects related to improving groundwater quality are still not apparent, especially in confined or semi–confined aquifers. The fact that influence of settlement areas without sewage systems is dating back even to the last centuries (beginning of settlement) also should be noted.

The study show that anthropogenic impact on of groundwater is still at low level. The ion concentrations usually do not exceed Polish national limits for

drinking water or WHO recommendations. Nonetheless, the contamination effect is efficient and steady increase over time. It can creates serious hazard for groundwater quality deterioration in the future. This is important if we think about water resources for the next generations.

This study reveals the utility of statistical methods during investigations of human activities on groundwater chemistry, especially at relatively low contamination levels when the pollution is related to naturally occurring water components. This research is relevant for implementing groundwater protection plans at the regional scale. These interpretations may also be used to better manage water resources at the regional scale.

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