

The changes of groundwater chemistry of semi-confined buried valley aquifer during one decade of water exploitation

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Abstract This article presents the analysis of the temporal changes in water chemistry in a semi-confined aquifer (Wielkopolska Buried Valley aquifer, Poland) during one decade of water exploitation. It is shown that the groundwater contamination, as documented in a previous work, still persists and has led to steady groundwater quality deterioration. The most intensive changes in water chemistry due to contamination are observed in the regions recognized earlier as the most vulnerable parts of the aquifer. The influence of contamination is effective despite implementation of groundwater protection activities. The travails of groundwater quality protection of the confined or semi-confined aquifers were accentuated.

Keywords Groundwater quality deterioration · Groundwater contamination · Confined aquifer protection · Wielkopolska Buried Valley aquifer · Poland

Introduction

The buried valleys are the most attractive sources of groundwater in many parts of Poland. As a result of low vulnerability (large thickness of the aquitard) these aquifers usually accumulate unpolluted groundwater. However, often increasingly, the symptoms of deterioration of water quality are visible in these types of aquifers too (Gorski 1989). It is usually reflected by concentrated increase of groundwater components that are most sensitive to

contamination. The additional factor that increases vulnerability to pollution is groundwater exploitation that causes high downward gradient (Jeong 2001; Lawrence et al. 2000). This gradient activates or intensifies the migration of contaminants from land surface and shallow (usually polluted) aquifers to deeper water systems.

The chemistry of the groundwater in the semi-confined Wielkopolska Buried Valley aquifer (WBV), Poland, was investigated in the year 2000. In spite of very small spatial variations in the chemistry of the groundwater, the hydrochemical zones were classified in order to identify the flow pattern of the groundwater within the aquifer (Dragon and Górski 2009). Furthermore, the zones of anthropogenic groundwater contamination were identified despite the occurrence of semi-confined conditions (Dragon 2008). For identifying the temporal changes in groundwater chemistry, the wells of the WBV aquifer were tapped and resampled in 2009.

The main objective of this paper is the identification of the temporal variability of groundwater chemistry. Special emphasis is placed on the hydrogeochemical processes initiated or intensified by anthropogenic contamination.

Study area

Hydrogeological setting

The WBV aquifer is classified as one of the Major Ground Water Basins (MGWB—144) in Poland (Kleczkowski 1990). It is an important aquifer that supplies drinking water to many towns and villages of the Wielkopolska region (Fig. 1).

The thickness of water-bearing sediments (mainly sand and gravel) ranges from 20 to 50 m (Fig. 2). The confining

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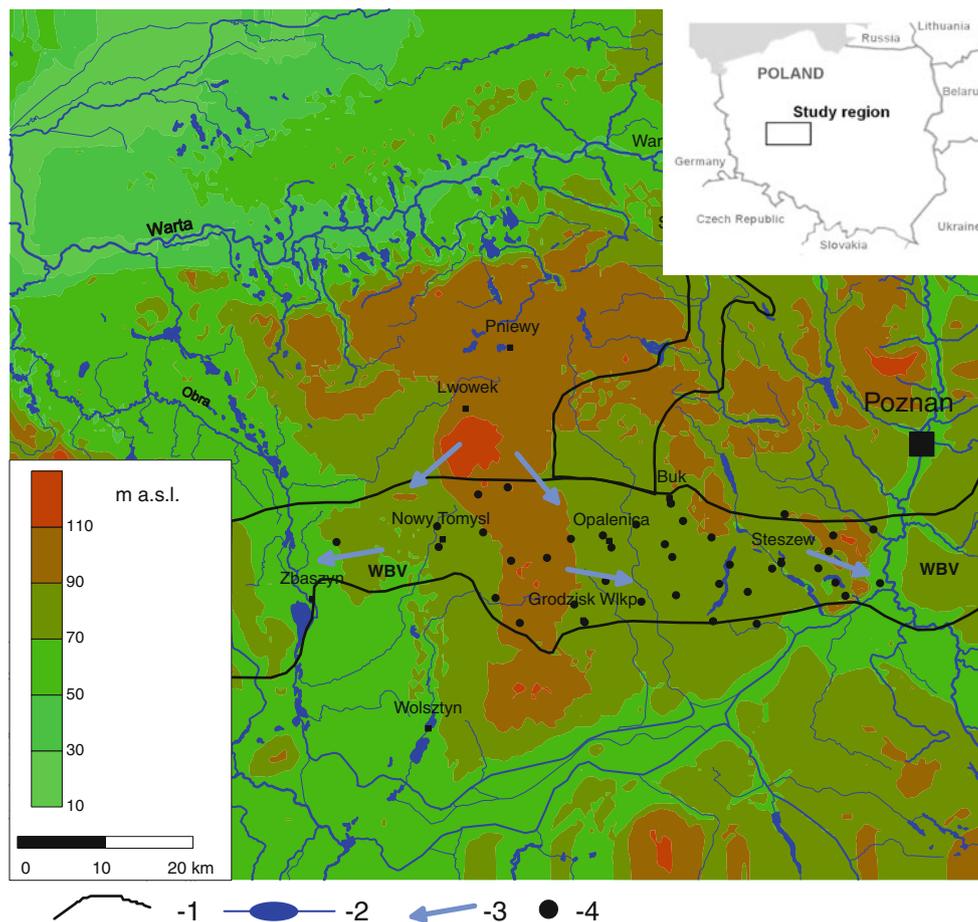


Fig. 1 The location of the study area on background of the land relief. 1 boundary of the aquifer, 2 surface water (lakes and rivers), 3 general groundwater flow directions, 4 location of the sampling sites. WBV Wielkopolska Buried Valley aquifer

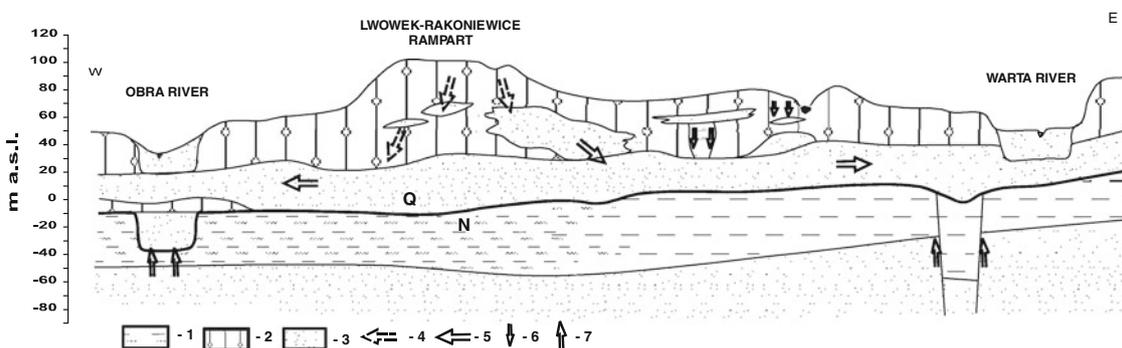


Fig. 2 Schematic cross-section and conceptual model of the aquifer recharge (after Dragon and Górski 2009, simplified) 1 and 2—confining layers (1 clays, mud and silts; 2 glacial tills), 3 water-bearing sediments (sands and gravels), 4 preferential flow through

glacial tills, 5 groundwater flow direction in the aquifer, 6 leakage of contaminated water from surface and shallow aquifers, 7 upward flow from deeper flow system, Q Quaternary, N Neogene

layer has a thickness between 20 and 50 m and is composed of glacial tills. A layer of Neogene clay occurs at the aquifer bottom and isolates the WBV aquifer from the Neogene aquifers. The main recharge area is located in the region of the Lwówek-Rakoniewice Rampart from where

the groundwater flows east to the Warta River and west to the Obra River (Fig. 1). The principal source of the recharge is the percolation of groundwater through glacial tills and upper-intertill aquifers (Fig. 2). There is also recharge owing to the inflow from the intertill aquifers

Table 1 Statistical characteristics of the hydrochemical parameters

Parameter (unit)	Min.	Max.	Average	Median	Standard deviation	Skewness
2000 sampling survey						
Colour (mg Pt/l)	5	70	22	20	12.9	1.6
pH	6.98	7.85	7.44	7.40	0.20	0.32
Oxygen consumption (mg O ₂ /l)	1.5	7.0	3.1	3.0	1.17	1.49
Electrical conductivity (μS/cm)	293	869	577	560	147	0.2
Total hardness (TH) (mval/l)	2.8	8.9	6.0	5.8	1.4	-0.1
Alkalinity (HCO ₃) (mval/l)	2.6	6.9	5.2	5.5	1.1	-0.5
TDS (mg/l)	205	573	394	385	94	0.04
Cl (mg/l)	8.0	70.0	22.9	18.0	16.7	1.4
SO ₄ (mg/l)	0.0	120.0	40.1	33.0	29.9	0.8
N-NO ₃ (mg/l)	0.0	6.0	0.16	0.0	0.94	6.3
N-NH ₄ (mg/l)	0.00	0.50	0.17	0.16	0.15	0.44
Fe (mg/l)	1.2	13.1	4.3	3.8	2.4	1.6
Mn (mg/l)	0.08	0.57	0.18	0.18	0.09	2.24
Ca (mg/l)	48.5	143.0	93.1	91.5	24.1	0.1
Mg (mg/l)	4.3	29.1	16.6	17.4	5.6	-0.1
Na (mg/l)	5.2	66.0	12.8	10.5	9.4	4.6
K (mg/l)	1.4	14.0	3.5	3.1	2.2	3.3
2009 sampling survey						
Colour (mg Pt/l)	5	50	14	15	10.3	1.1
pH	7.18	7.84	7.40	7.38	0.16	0.52
Oxygen consumption (mg O ₂ /l)	0.7	5.5	2.2	1.9	1.1	1.1
Electrical conductivity (μS/cm)	314	1315	527	599	196	1.1
Total hardness (TH) (mval/l)	3.2	14.9	6.7	6.3	2.1	1.4
Alkalinity (HCO ₃) (mval/l)	2.7	7.3	5.5	5.6	1.2	-0.5
TDS (mg/l)	130	922	396	353	152	0.99
Cl (mg/l)	8.3	140.0	29.0	19.8	26.1	2.5
SO ₄ (mg/l)	3.6	249.0	48.9	36.9	46.9	2.2
N-NO ₃ (mg/l)	0.0	7.5	0.28	0.01	1.2	5.6
N-NH ₄ (mg/l)	0.03	0.78	0.31	0.33	0.19	0.28
Fe (mg/l)	0.8	9.8	3.2	2.9	1.8	1.3
Mn (mg/l)	0.09	0.47	0.20	0.19	0.07	1.61
Ca (mg/l)	54.4	240.0	106.8	100.9	32.7	1.7
Mg (mg/l)	6.1	36.3	17.1	17.2	6.9	0.3
Na (mg/l)	5.5	26.7	12.9	12.4	5.8	0.7
K (mg/l)	1.0	9.7	3.4	3.5	1.8	1.8

Frequency *n* = 41

located to the north of the WBV aquifer. It was documented with the use of hydrochemical data (Dragon and Górski 2009).

Land use

The examined area is used for various purposes. The eastern part of this region (to the east of Grodzisk Wielkopolski and Opalenica) is dominated by agriculture, whereas forested lands prevail in both the central (recharge

area of WBV aquifer) and the western parts. Besides, rural and urban built-up areas occur. There are five towns (5000–15000 inhabitants) located in the investigated region.

Sources of pollution typical for the whole Wielkopolska region are present in the studied area. The most significant source of pollution is the untreated sewage from both rural and urban lands: a long-standing problem that has not been solved since the centuries past. It should be underlined that very long time of influence is characteristic for this

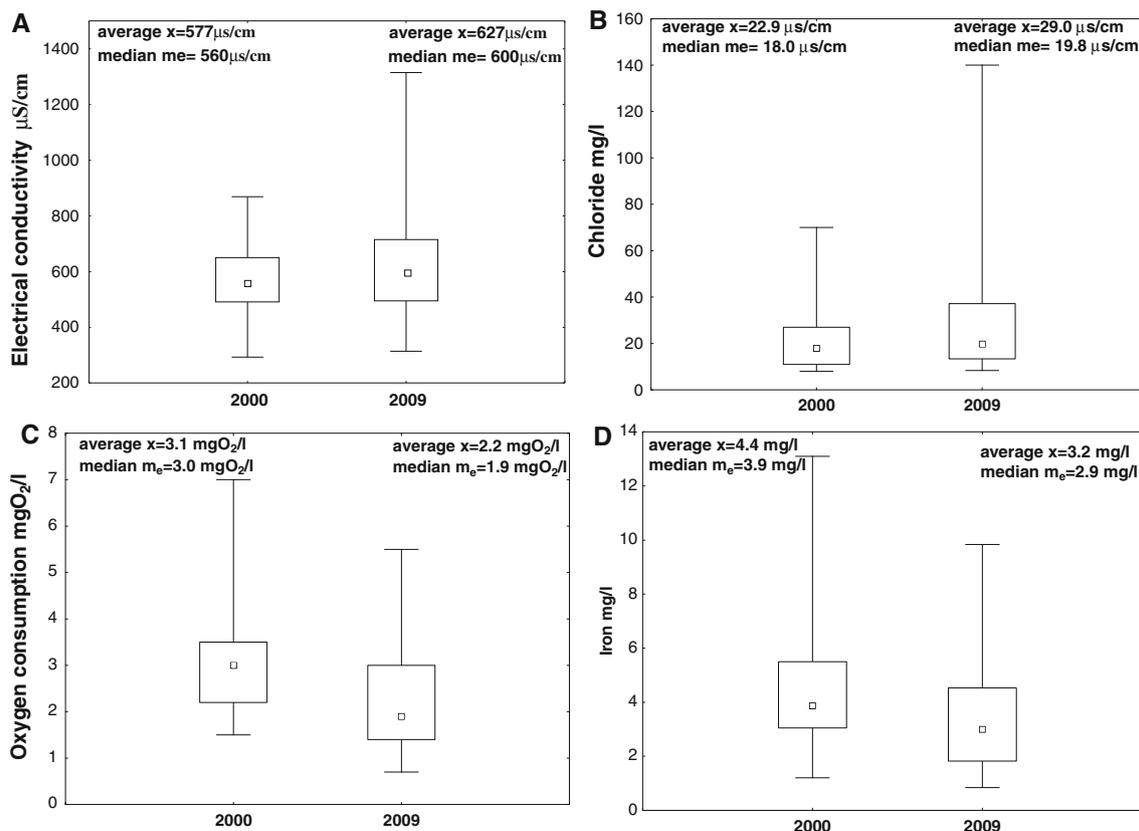


Fig. 3 Variability of groundwater chemistry (example parameters) during period between 2000 and 2009 years (whole data set, number of samples $n = 41$) Explanations: \square Median \square 25%–75% \perp Min–Max

type of contaminant sources, dating back to the beginning of the settlement. Another most important source of contamination, connected with agriculture are livestock farms. Livestock manure is in most cases spread on the fields. The main risk concerning a cultivated land is an excessive usage of fertilisers.

Materials and methods

The study of temporary hydrogeochemical evolution of groundwater accumulating within WBV aquifer has been made based on a comparative analysis of data obtained in two surveys performed in 2000 and in 2009. The sampling survey performed in 2000 consists of 61 sampling sites (Dragon 2006; 2008). In the 2009 sampling program, water samples were taken from 41 wells from among 61 wells sampled in 2000. Unfortunately, some of wells sampled in 2000 were closed down before 2009. The location of the sampling sites is presented in Fig. 1.

Water samples were taken from productive and continuously pumped wells. The water colour, alkalinity, electrical conductivity, pH and temperature were measured directly in the field. The list of parameters measured in the

laboratory with detection limit and precision (in brackets) is listed below: oxygen consumption: 0.7 mgO_2/L (5%), N-NH_4 : 0.04 mg/L (10%), N-NO_3 : 0.1 mg/L (20%), Na and K: 0.1 mg/L (5%), Cl and Mg: 5 mg/L (5%), SO_4 : 10 mg/L (5%), Fe: 0.001 mg/L (10%), Mn: 0.003 mg/L (10%), Ca: 2 mg/L (5%), Total hardness (TH): 0.36 mval/L (5%), TDS (determined by evaporating): 1 mg/L (5%). The analyses were performed in the Adam Mickiewicz University, Poznan, with use of an ionic chromatograph Dionex DX-120 (anions) and an atomic absorption spectrometer Perkin Elmer Analyst 300 (cations). For quality control measures the ionic error balance was calculated. The calculated error does not exceed 3%. Moreover, archival physico-chemical analyses from the period of wells' construction and performed during wells' exploitation were used.

Results and discussion

Basic statistics of the hydrogeochemical parameters measured during 2000 and 2009 sampling surveys are presented in Table 1. The results of chemical analysis show relatively small water chemistry variation over time.

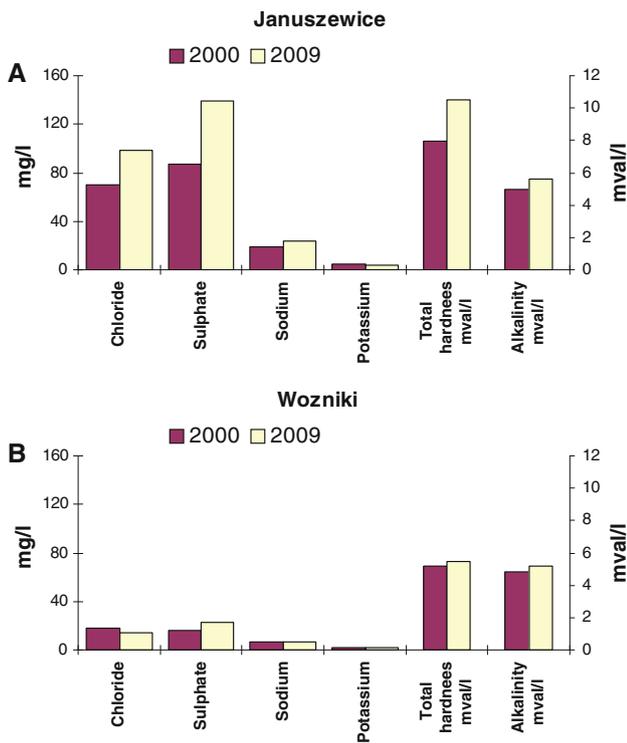


Fig. 4 The typical variation of groundwater chemistry in period between 2000 and 2009. **a** example well located in zone of anthropogenic input, **b** example well located in zone of lack of anthropogenic input

Nonetheless, in the case of some parameters, increase of concentrations over time is observed (Fig. 3a and 3b). The most intensive increase is visible in cases of chloride and sulphate (reflected by electrical conductivity); thus, the parameters reflect water anthropogenic contamination (Dragon 2008). Interestingly, some parameters (oxygen consumption, iron and water colour) show decrease of concentrations over time (Fig. 3c and 3d). It is connected with intensification of the water circulation within the

aquifer owing to exploitation, which causes shorter water residence time in the aquifer.

The typical changes in the groundwater chemistry in the zones of anthropogenic input and in the remaining parts of the aquifer are presented in Fig. 4. The most intensive increase of water components concentrations is visible in the zones documented earlier as the most vulnerable in the aquifer (Dragon and Górski 2009). Figure 4a shows typical groundwater chemistry changes in this zone. The increase of concentrations of chloride, sulphate and total hardness is clearly visible, whereas in the remaining parts of the aquifer, these concentrations are stable during wells' exploitation (Fig. 4b). These groundwater components were identified as the most sensitive indicators of anthropogenic input (Dragon 2008). Their concentrations are incomparably higher than those of the whole data set (compare Fig. 3 and 5); moreover, the steady increase of its concentrations over time was documented. It is clearly visible in some wells. Figure 6 presents water chemistry changes in the well located in Grodzisk Wielkopolski town during the period of water extraction between 1960 (well construction) and 2002 (well liquidation). During the period of well construction, all groundwater components (include indicators of water pollution) were at the level of the natural hydrogeochemical background. The systematic increase of chloride (from the range of the natural hydrogeochemical background—10 mg/L to more than 80 mg/L) and sulphate (increase to more than 175 mg/L) as well as total hardness is visible during wells exploitation. It should be underlined that before starting of water exploitation the contamination was not observed and appear with stable tendency later. This is characteristic also for other wells tapping the WBV aquifer. It should be suspected that the mechanism, which activates or increases effective migration of contaminants from the surface, is water exploitation that can create high downward gradient. Water exploitation over a long period of time (like in case

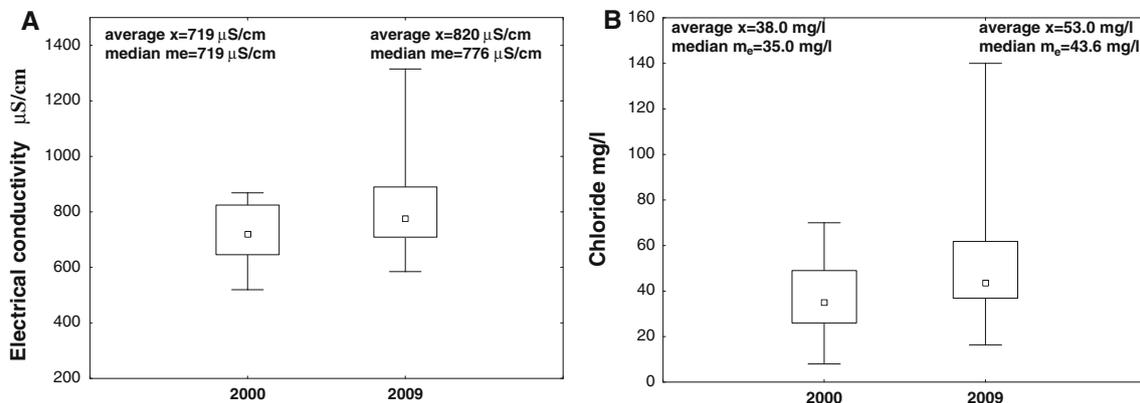


Fig. 5 Variability of groundwater chemistry (example parameters) during period between 2000 and 2009 years (zone of anthropogenic input, number of samples $n = 14$) Explanations: □ Median □ 25%–75% ⊥ Min–Max

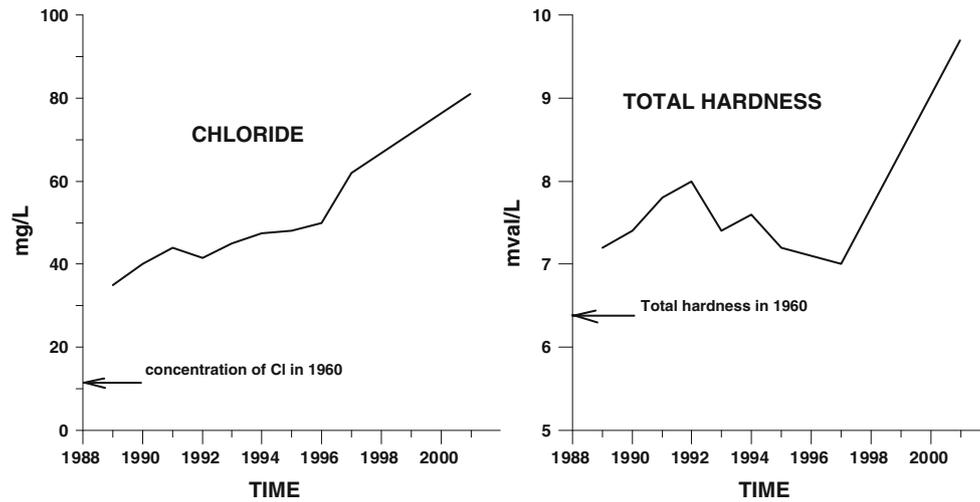


Fig. 6 The variations of the contamination indicators concentrations with time in well located in Grodzisk Wielkopolski town

Table 2 Comparing of the results of the factor analysis (after *varimax* rotation) performed for data sets from 2000 to 2009 sampling surveys

	2000 sampling survey			2009 sampling survey		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Colour	-0.17	0.00	0.87	-0.36	0.54	0.47
pH	-0.38	-0.82	-0.01	-0.42	-0.74	-0.15
Oxygen consumption	-0.12	0.40	0.55	-0.12	0.80	0.14
Total hardness (TH)	0.70	0.63	-0.07	0.91	0.35	0.07
Alkalinity (HCO ₃)	0.27	0.91	0.12	0.41	0.83	0.09
Cl	0.90	0.02	0.17	0.94	0.03	0.04
SO ₄	0.77	-0.13	-0.28	0.93	-0.20	0.04
N-NH ₄	0.07	0.77	0.18	0.17	0.79	-0.17
Fe	-0.11	0.69	-0.14	0.12	0.66	0.10
Mn	0.55	0.16	-0.48	0.14	-0.01	0.88
Na	0.55	-0.07	0.67	0.73	0.41	0.15
K	0.65	0.36	-0.18	0.56	0.29	0.60
Total dissolved solids (TDS)	0.84	0.52	0.02	0.90	0.30	0.09
Percentage of variance	30	27	15	37	29	11

Factor loadings >0.7 are marked by *bold* font

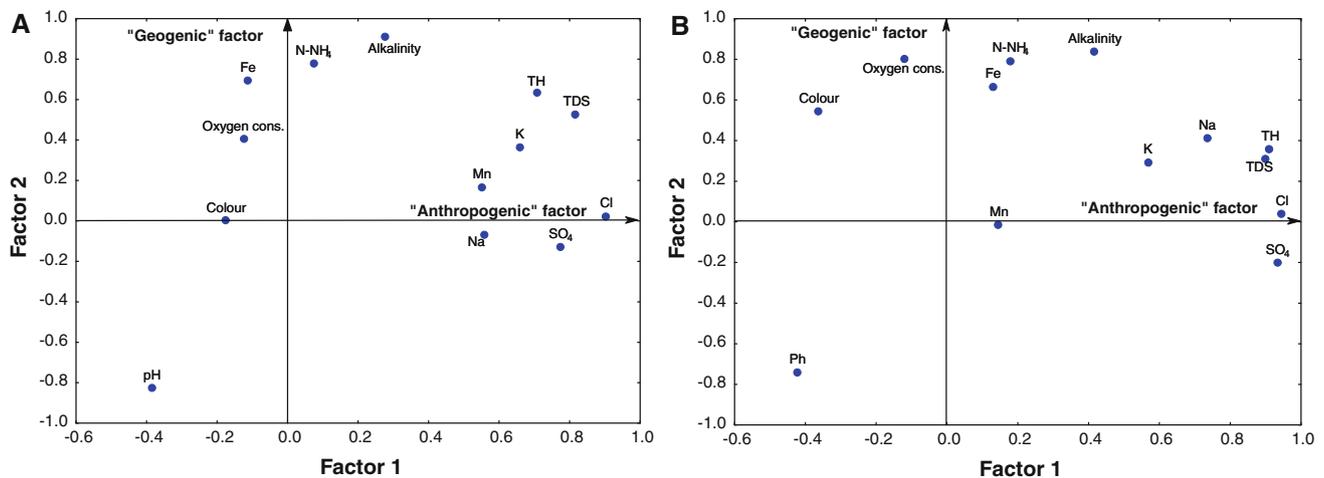


Fig. 7 Plot of factor loadings. **a** 2000 sampling survey; **b** 2009 sampling survey

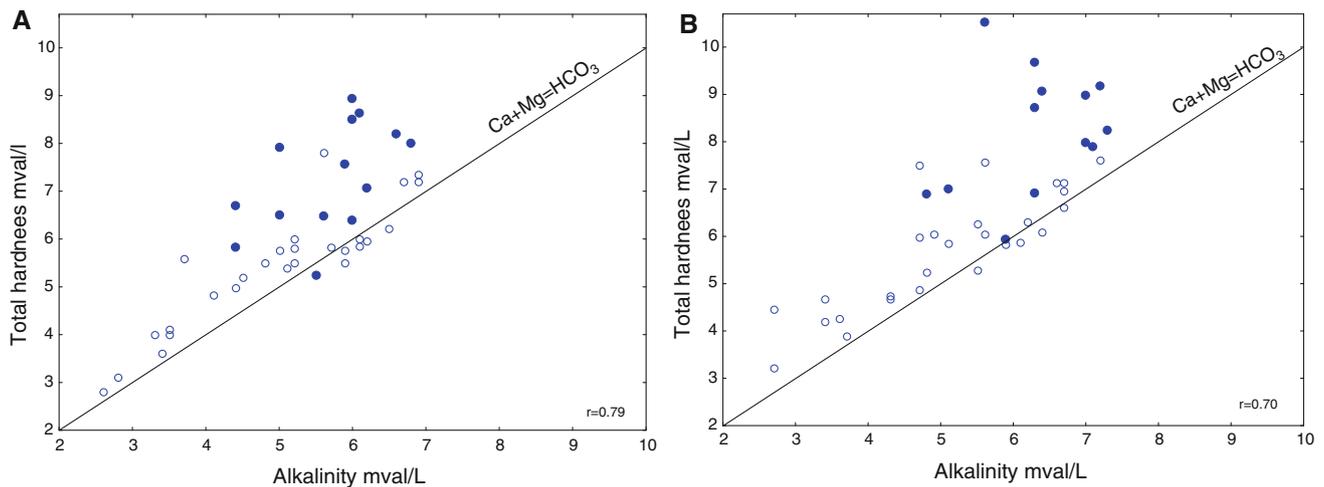


Fig. 8 Scatter diagram of the alkalinity vs. total hardness for the data of 2000 sampling survey (a) and 2009 sampling survey (b) Marked points are located in the zone of anthropogenic contamination

of Grodzisk Wielkopolski town) can cause the shift of the groundwater divide.

The influence of anthropogenic contamination on groundwater chemistry confirms the results of the factor analysis (FA). The analysis was performed using a method presented in a previous work (Dragon 2006). The purpose of FA is to reduce analytical data of each sample (initial data set) to a smaller set of factors that are interpretable. These factors can be associated with a specific source or process (anthropogenic or geogenic) responsible for the change in groundwater chemistry. The principal component analysis was applied as the extraction technique. This operation transforms original variables into a smaller set of independent variables (factors). The factor loading matrix was rotated on an orthogonal simple structure in accordance with the *Varimax* rotation. Following this operation, high factor loadings were obtained for the variables correlated with the factor (close to 1 or -1) and low factor loadings (close to 0) for the remaining variables. In order to establish the number of factors, the Kaiser criterion was applied. Factors that best describe the variance of the analysed data (eigenvalue > 1) and which can be reasonably interpreted were accepted for further analysis (Drever 1997).

The results obtained are consistent with the previous calculations performed for the WBV aquifer and moreover shed new light on groundwater chemistry changes owing to contamination. The comparison of the FA results for 2000 and 2009 sampling surveys is presented in Table 2. Three factors were calculated for both data sets. The calculations for 2000 and 2009 sampling surveys explain 72% and 77% of variance, respectively. For both data sets, Factor 1 is identified as “anthropogenic” because describing variation of parameters identified as contamination indicators,

whereas Factor 2 is recognized as “geogenic” because it reflects natural hydrogeochemical processes (Dragon 2006). The interpretation of factor 3 is difficult because it is different in both data sets, but it has relative small importance as compared to factors 1 and 2 (explains 15 and 11% of variance, respectively). The comparison of the factor loadings of factor 1 indicates that the indicators of pollution (Cl , SO_4 , TH and TDS) have significantly higher factor loadings in the 2009 data set. Moreover, on the plot (Fig. 7) shift of the TDS and TH in direction to “anthropogenic” factor is visible (comparing years 2000 and 2009).

The role of chloride and sulphate as the principal products of urbanization that alter groundwater chemistry is well known (e.g. Eisen and Anderson 1979; Jeong 2001; Cronin et al. 2003; Choi et al. 2005). They are generally conservative species; therefore, they reach the aquifer first. The interpretation of the influence of TH, reflecting both Ca and Mg concentrations, is more problematic because their concentration is controlled by both anthropogenic and geogenic factors. However, in some cases it is possible to distinguish between anthropogenic and geogenic sources with use of statistical methods. The results of previous work performed for the studied aquifer show that comparing the whole data to a data set representing natural groundwater chemistry with use of the FA method can help to distinguish between natural and anthropogenic sources of TH (Dragon 2006). Moreover, it is characteristic for the WBV aquifer that TH in natural (unpolluted) groundwater is balanced with alkalinity (reflecting HCO_3 concentration), whereas in contaminated groundwater, TH surplus (relative to alkalinity) occurs (Dragon 2008). This relationship is presented in Fig. 8. It is characteristic for both 2000 and 2009 data sets that in the sampling sites falling

substantially above the $\text{Ca} + \text{Mg} = \text{HCO}_3$ line, higher concentrations of chloride and sulphate were detected. Moreover, most of these sampling sites are located in the area defined as zone of anthropogenic input. This observation may suggest the occurrence of non-carbonate hardness balanced mainly by high sulphate concentrations. Unpolluted water is located in the graphs close to the $\text{Ca} + \text{Mg} = \text{HCO}_3$ line. These observations qualify to treat TH as an indicator of groundwater contamination, particularly if high TH is correlated with high chloride and sulphate concentrations.

The enforcement of groundwater protection activities (e.g. building of new sewage systems, rationalization of fertilizer use, etc.) is very effective in Poland following political democratic changes; however, the findings presented here indicate that the contamination identified in the year 2000 still persists. These findings show the travails connecting with groundwater quality protection of the confined or semi-confined aquifers. It shows that for the visible effects of the water quality protection activities in case of confined and semi-confined aquifers we must wait long period of time (Dragon 2010).

Conclusions

The research presented in the article shows that the influence of contamination on groundwater chemistry of the Wielkopolska Buried Valley aquifer identified in a previous work is still effective. Groundwater contamination leads to deterioration of water quality mainly in case of the parameters identified as the most sensitive to anthropogenic impact (i.e. chloride, sulphate, total hardness and TDS). The contamination is the most effective in the regions identified in previous work as the most vulnerable parts of the aquifer.

The observations presented confirm earlier findings that the intensity of anthropogenic contamination of the WBV aquifer is visible even though the semi-confined conditions occur there. The nature of anthropogenic changes of water chemistry indicates that these water are still at early stages of chemistry transformations (the concentrations usually do not exceed Polish national limits for drinking water and WHO recommendations). However, a distinct and constant increase of water components concentrations over time creates serious hazard for groundwater quality deterioration and its utilities for use in the future. This fact should be taken into consideration if we think about water resources protection for the next generations. It is very important particularly in case of confined or semi-confined aquifers.

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