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

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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, more and more often the symptoms of water quality deterioration become visible also in this type of aquifers (Gorski, 1989). 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 investigation of groundwater chemistry of the semi-confined buried valley aquifer (Wielkopolska Buried Valley aquifer -WBV, Poland) was performed in 2000 year. The classification of hydrochemical zones was performed and used for identification of groundwater flow pattern within the aquifer (Dragon and Gorski, 2009). Also the zones of groundwater anthropogenic contamination were identified even though the semi-confined conditions occur (Dragon, 2008). For identification of temporal groundwater chemistry changes wells tapping WBV aquifer were resampled in 2009 year.

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

STUDY AREA

WBV aquifer is very important for drinking water supply of many towns and villages in Wielkopolska region (Fig. 1).

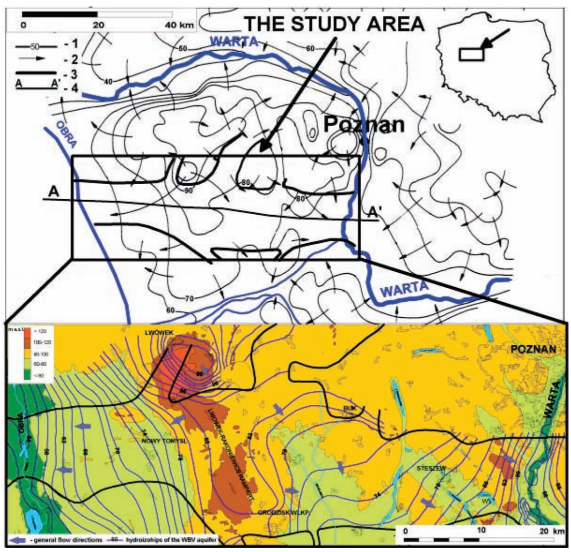

Figure 1. Location map of the study area on the background of the groundwater flow system of the Quaternary aquifers (after Dragon, Gorski, 2009). 1 – hydroizohips of the Quaternary aquifers; 2 – general groundwater flow directions; 3 – boundary of the Wielkopolska Buried Valley aquifer; 4 – line of cross-section (Fig. 2).

The thickness of the aquifer (composed mainly by sand and gravel) ranges from 20 to 50 meters (Fig. 2). The confining layer has thickness between 20 and 50 m and is composed of glacial tills. The main recharge area is located in the region of the Lwówek-Rakoniewice Rampart. The principal source of the recharge is the percolation of groundwater through glacial tills and upper intertill aquifers (Fig. 2). The recharge by the inflow from the intertill aquifers, located to the north of the WBV aquifer, also takes place. It was documented with use of hydrochemical data (Dragon and Gorski, 2009).

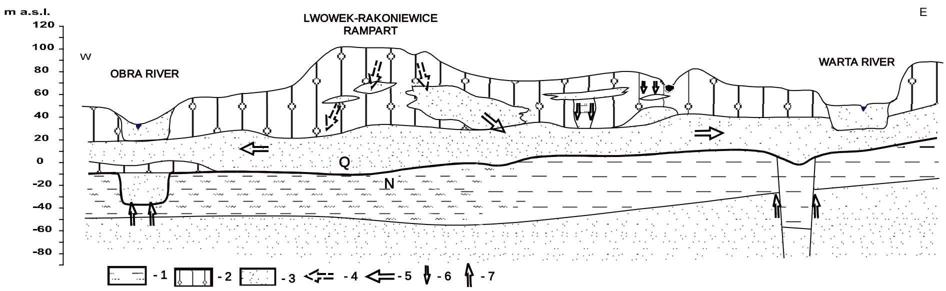

Figure 2. Schematic cross-section and conceptual model of the aquifer recharge (after Dragon, Gorski, 2009, simplified) 1 and 2 – confining layers (1 – clays, muds and silts; 2 – glacial tills); 3 - water bearing sediments (sands and gravels); 4 – preferential flow through glacial tills; 5 – groundwater 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.

Sources of pollution typical for the Wielkopolska region are present in the study area. The most significant source of pollution is the untreated sewage from both rural and urban lands – a long-lasting problem that has not been solved since the last centuries. It should be underlined that very long time of influence is characteristic for this 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 other 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 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 of 61 wells sampled in 2000. Unfortunately some of wells sampled in 2000 were closed down before 2009. Water samples were taken from productive, continuously pumped wells. For quality control measures the ionic error balance was calculated and does not exceed 3%. Moreover, archival physico-chemical analyses from the period of wells construction and performed during wells exploitation were use.

RESULTS AND DISCUSSION

The results of chemical analysis show relative small water chemistry variation over time. Nonetheless in case of some parameters increase of concentrations over time is observed. The most intensive increase is visible in case of chloride and sulphate (and is reflected by electrical conductivity – Fig. 3), thus the parameters reflecting water anthropogenic contamination (Dragon, 2008).

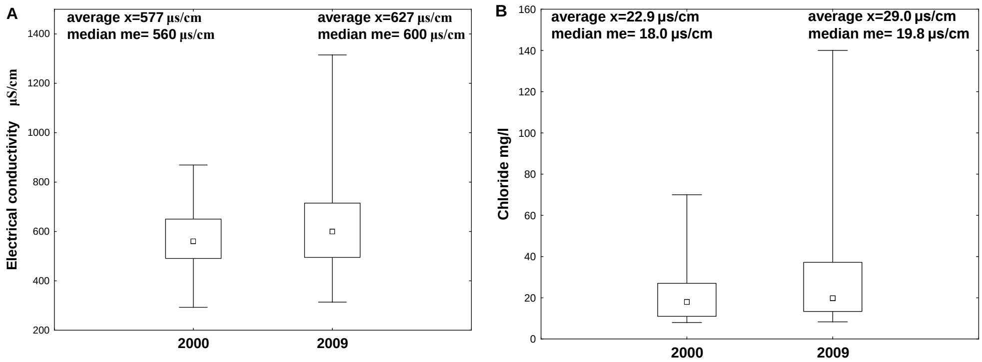

Figure 3. Variability of groundwater chemistry (example parameters) during period between 2000 and 2009 years (whole data set, number of samples n=41). Explanations: □ Median ⎕ 25%-75% ⊥ Min-Max.

The typical changes of groundwater chemistry in the zones of anthropogenic input and in the remaining parts of the aquifer are presented on Fig. 4. The most intensive increase of concentrations is visible in the zones identified using factor analysis as the most vulnerable parts of the aquifer (Fig. 4A) (Dragon and Gorski, 2009). The increase of concentrations of chloride, sulphate and total hardness is clear visible while in the remaining parts of the aquifer concentrations of these parameters 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 in whole data set (compare Fig. 3 and 5), moreover the steady increase of its concentrations over time was documented.

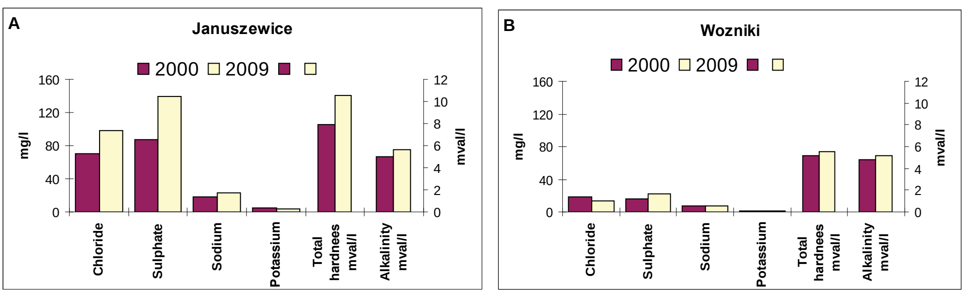

Figure 4. The typical variation of groundwater chemistry in period between 2000 and 2009. A — example well located in zone of anthropogenic input; B — example well located in zone of lack of anthropogenic input.

It is clear visible in case of some wells. Fig. 6 presents water chemistry changes in well located in the Grodzisk Wielkopolski town during period of water extraction between year 1960 (well construction) and year 2002 (well liquidation). At the period of well construction all groundwater components (include indicators of water pollution) were at level of 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 at the beginning of water exploitation the contamination was not observed and appear with stable tendency later.

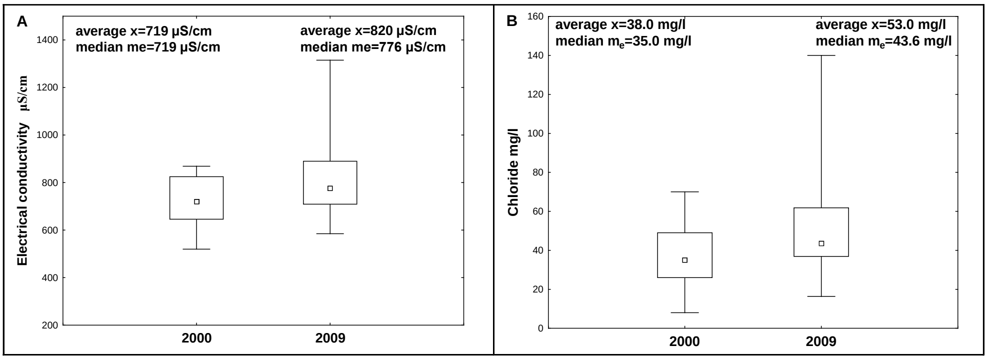

Figure 5. Variability of groundwater chemistry (example parameters) during period between 2000 and 2009 years (zone of anthropogenic input, number of samples n=14). Explanations: □ Median □ 25%-75% ⌶ Min-Max.

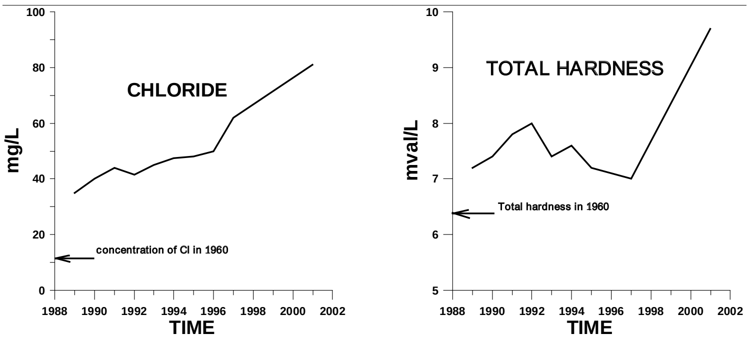

Figure 6. The variations of the contamination indicators concentrations with time in well located in Grodzisk Wielkoposlski town.

This is characteristic also for other wells tapping WBV aquifer. It should be suspected that the mechanism, which activate or increase effectively migration of contaminants from surface, is water exploitation that can create high downward gradient. If the exploitation is performed during long period of time (like in case of Grodzisk Wielkopolski town) it can cause the shift of the groundwater divide. On the map (Fig. 1) the characteristic bent of the hydroisohips in direction of the town is visible. The original location of the water divide was probably in the central part of the Lwowek-Rakoniewice Rampart.

The influence of anthropogenic contamination on groundwater chemistry confirms results of the factor analysis. The analysis was performed using methodology presented in previous work (Dragon, 2006). The results obtained are consistent with previous and moreover shed a new light on groundwater chemistry changes due to contamination. The comparing of the FA results for 2000 and 2009 sampling surveys is presented on Table 1. Three factors were calculated for both data sets. The calculation for 2000 and 2009 sampling surveys explain 72 % and 77 % of variance (respectively). For both data sets Factor 1 was identified as "anthropogenic" because describing variation of parameters identified as contamination indicators, while Factor 2 is recognized as “geogenic” because reflect natural hydrogeochemical processes (Dragon, 2006). The interpretation of factor 3 is difficult because is different in both data sets, but it has relative small importance (explain 15 and 11 % of variance respectively). The comparison of the factor loadings of factor 1 point out that indicators of pollution (Cl, SO_4, TH and TDS) have significantly higher factor loadings in 2009 data set. Moreover, shift of the TDS and TH in direction to “anthropogenic” factor is visible (comparing years 2000 and 2009).

These findings indicate that contamination identified in year 2000 is still effective regardless of enforce of the groundwater protection activities (e.g. building of new sewage systems, rationalization of the fertilizers use, etc.), very effective in Poland after political democratic changes. 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 this type of aquifers we must wait long period of time.

Table 2. Comparing of the results of the factor analysis (after *varimax* rotation) performed for data sets from 2000 and 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
$N\text{-}NH_4$	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
Percent of variance	30	27	15	37	29	11

Factor loadings >0.7 are marked by bold font

CONCLUSIONS

The research presented in the article show that influence of contamination on groundwater chemistry of the Wielkopolska Buried Valley aquifer identified in previous work is still effective. Groundwater contamination lead to deterioration of water quality mainly in case of the parameters identified as the most sensitive to anthropogenic impact (ie 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 of the WBV aquifer 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 thing about water resources for the next generations. It is very important particularly in case of confined or semi-confined aquifers.

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