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QUALITY OF GROUNDWATER IN RURAL HOMESTEADS AND AGRICULTURAL LAND IN THE CATCHMENT OF LAKE MIEDWIE

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Abstract

The paper presents the impact of pollutants from areas intensively used for agriculture on the quality of shallow groundwater in the drainage basin of Lake Miedwie, which is the main source of potable water for the city of Szczecin. This groundwater, due to the poor insulation against the penetration of contaminants from the surface, is a good indicator of the environmental pressure level from agriculture. The aim of the study was to analyze the chemical composition as well as the pH and electrolytic conductivity of waters of the first Quaternary aquifer in the catchment area of Lake Miedwie, located in the municipality of Warnice, which is characterized by intensive farming. The results indicate that there has been a noticeable improvement over the last ten years in the quality of groundwater, and periodic increases in the levels of certain chemical parameters such as ammonium nitrogen (6.070 mg dm^{-3}), nitrate nitrogen (225.1 mg dm^{-3}), phosphate phosphorus (2.635 mg dm^{-3}) or potassium (452.0 mg dm^{-3}) can be explained by negligence or insufficient knowledge of farmers with respect to manure storage and rational use of mineral fertilizers. Correlation analysis of the sum of chemical parameters regarding conductivity demonstrated a virtually absolute relationship (r = 0.948 at p = 0.001), confirming a close relationship of groundwater's chemical parameters with the properties of the physical parameter such as specific electrolytic conductivity. Moreover, it was shown that the specific electrolytic conductivity of groundwater of 8 piezometric intakes tested was mainly shaped by the concentrations of sodium (Na), potassium (K) and magnesium (Mg) for all chemical parameters analyzed.

Keywords: groundwater, nitrates, ammonia, phosphates, potassium, sodium, magnesium, calcium, pH, electrolytic conductivity.

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INTRODUCTION

Pollution of the aquatic environment causes many adverse changes in aquatic ecosystems and in all environmental components that make use of their resources. There is a long-term tendency observed of groundwater quality deterioration (SAPEK 1996, PIETRZAK, SAPEK 1998, BROERS, VAN DER GRIFT 2004, DRAGON 2006, ONORATI et al. 2006), particularly the waters located in the shallowest layers and poorly insulated by soil formations from contamination sources.

A major challenge for Poland as well as for whole Europe is how to protect water resources from contamination with biogenic compounds, particularly nitrates from agricultural sources (SAPEK 1996, PIETRZAK, SAPEK 1998, MIODUSZEWSKI et al. 2008, SAPEK 2014). Actions needed in this aspect are regulated by the Nitrates Directive, which obliges the European Union Member States to identify waters vulnerable to pollution by nitrates from agricultural sources, i.e., characterized by the content of nitrates above 50 mg dm^{-3} (waters contaminated with nitrates), or within 40-50 mg dm^{-3} (waters endangered with pollution), and subsequently to implement repair programs where the occurrence of sensitive waters was found (the so-called Nitrate Vulnerable Zones) (91/676/*Council Directive*... 1991).

The adoption of the Nitrates Directive, established for the protection of waters against nitrate pollution from agricultural sources (*Council Directive*... 1991), in Polish law necessisated designation of Nitrate Vulnerable Zones (NVZ) in Poland (*Regulation*... 2002). In 2004, 21 such areas were established in 6 regions of Poland (representing 2% of the country's area). In the following years, during regular evaluations of the degree of water pollution, 19 NVZs were established in 2008-2012 (1.480% of the country's area), and 48 NVZs in 2012 (4.460% of the country's area). The catchment of Lake Miedwie has been considered a nitrate vulnerable zone from agriculture sources throughout the whole period (since 2004). This is important because the waters of Lake Miedwie have been used since 1976 to supply the inhabitants of the city of Szczecin with drinking water.

Studies carried out thus far in the catchment area of Lake Miedwie focused on determining the load of pollutants flowing into surface waters and the relationship between the chemical potential brought to the area and water pollution. The results of these studies showed a significant impact of agriculture in the area on water quality, as reflected by a high content of biogenic compounds in the tested waters (WORONIECKI, RUMASZ-RUDNICKA 2008, BRYSIEWICZ et al. 2013). Therefore, measures have been taken to monitor groundwaters within the NVZ by the Institute of Technology and Life Sciences (ITP) under the Multiannual Programme – Action 1.3, which involves the assessment of the chemical status of groundwater and trends of changes in it.

The aim of this study was to analyze the chemical status of the first Quaternary aquifer waters of the catchment area of Lake Miedwie, located in the municipality of Warnice, which is characterized by an intensive farming.

MATERIAL AND METHODS

The catchment of Lake Miedwie is located in the mesoregion called the Pyrzycko-Stargard Plains (Durkowski et al. 2004). It is a typical agricultural catchment with intensive methods of farming. Reclamation works, carried out several times in the seventeenth, eighteenth and nineteenth centuries, resulted in significant changes in the hydrology and shape of the lake's basin. The current shape of Lake Miedwie is a product of the reclamation works carried out about 230 years ago. In order to enlarge the area of grasslands, the water level in the lake, which then covered 72 km^2, was lowered, After partial drainage of the area, today's shape of Lake Miedwie was achieved. It is now a flow-through reservoir, with an area of 39.13 km^2, average depth of 19.30 m, maximum depth of 43.80 m, length of 16.20 km and width of 3.200 km. The capacity of the lake basin is about 696.6 million m^3 (Kalisińska et al. 2011). The lake is the fifth largest lake in area and second one in volume of water in Poland. Since 1976, it has been the main source of drinking water for Szczecin, with an average daily intake of about 90 000 m^3.

The municipality of Warnice covers part of the catchment of Lake Miedwie. It comprises very good soils called the Pyrzyce black earths, representing almost 96% of agricultural land, of which 86% is and 14% is grassland. There are no forests in this area. Therefore, the catchment has favorable agroclimate conditions for the cultivation of cereals, such as wheat and barley, and industrial plants like beet and rapeseed. NPK mineral fertilization is in the range of 60-350 kg ha^{-1}. The most popular fertilizers are cattle manure and liquid manure. Natural fertilizers are used in the fertilization of agricultural land in the following doses: manure 30-35 t ha^{-1}, liquid manure 20 m^3 ha^{-1} (Durkowski et al. 2007).

The study was conducted in 2012-2013 and comprised an area used by agriculture in the municipality of Warnice, within the catchment of Lake Miedwie. It was carried out under the framework of the Multiannual Programme – Action 1.3, which is run in this area by the West Pomeranian Szczecin Research Centre of the Institute of Technology and Life Sciences in Falenty. Piezometers from which groundwater was collected for chemical analysis were located on agricultural land and at rural farms (Figure 1). During the study period, water samples were collected from piezometers to polyethylene bottles once a month from April to October. Chemical analyses were conducted at the Research Laboratory of Environmental Chemistry ITP in Falenty.

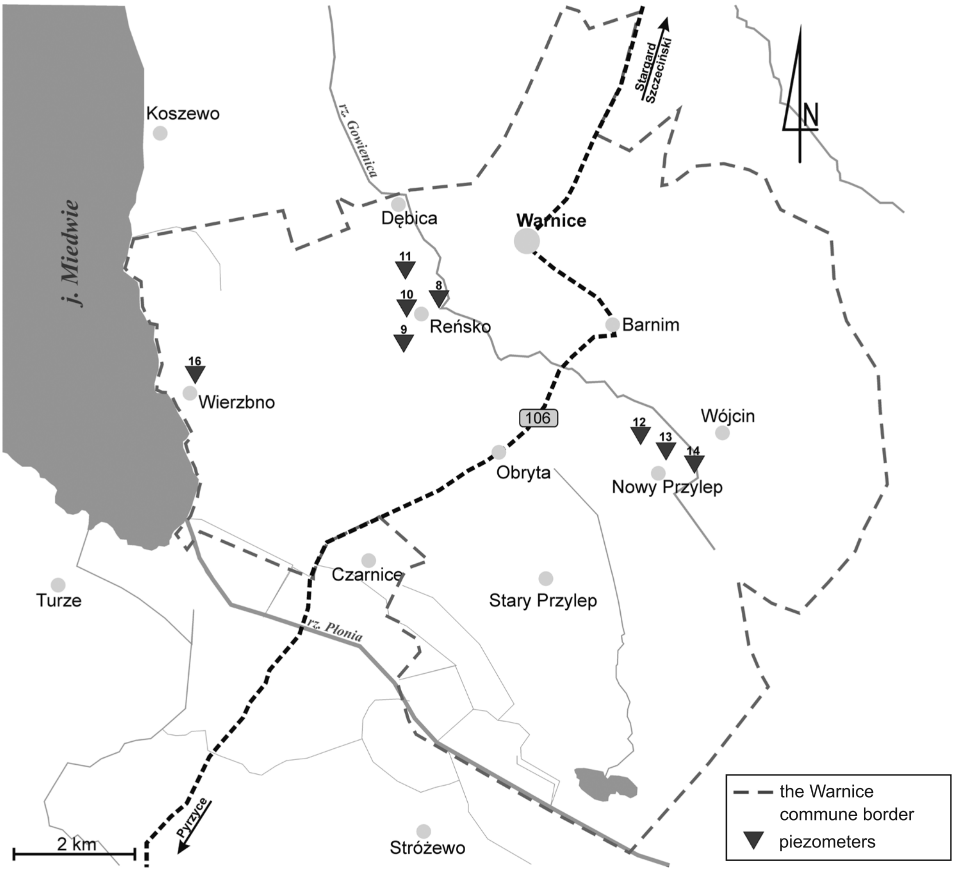

Fig. 1. Location of piezometers in the municipality Warnice

Water quality parameters were determined by the following methods: pH – potentiometrically; EC electrolytic conductivity (μS cm^{-1}) – conductometrically, in both cases a SevenMulti instrument (Metter Toledo) was used. Nitrogen ($N\text{-}NO_3$, $N\text{-}NH_4$) and phosphate phosphorus ($P\text{-}PO_4$) were determined by colorimetry with segmented flow analysis (SFA) using a SKALAR measuring instrument, according to the methodology described by the manufacturer (SKALAR). Potassium (K), sodium (Na), magnesium (Mg) and calcium (Ca) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo Scientific spectrometer. Results for nitrogen and phosphorus are expressed as the concentration of elements.

Statistical analysis was performed using Statistica software (StatSoft Inc., version 10). The Shapiro-Wilk test was used to evaluate the distribution of variables. The results were logarithmized (log10) in order to obtain a normal distribution. Differences in the parameters between the two study periods analyzed were determined using one-way Anova. The relationships between the studied parameters were determined by the *Pearson's* correlation coefficient (*r*).

RESULTS AND DISCUSSION

Groundwater sampled from piezometers located in the municipality of Warnice in two years (2012-2013) had neutral pH with an increasing tendency to become slightly alkaline (Table 1). At that time, the pH ranged from 6.780 - 8.280 and low standard deviations *SD* possibly indicated a significant stability of the pH of these waters. Higher pH values close to 8 were recorded in August of 2012 and 2013, while slightly lower pH values (approximately 7) were recorded in July. In addition, differences were observed in the water pH between the two years, i.e., slightly lower average pH values oscillating in the range of 7.100-7.600 were recorded in 2012, while slightly higher values in the range of 7.390-8.160 were measured in the consecutive year. These differences were statistically significant ($p < 0.05$) for waters from piezometers 9 and 10.

The electrolytic conductivity of groundwaters sampled for analysis varied throughout the entire period (2012-2013) – Table 1. The highest mean value of 3003 μS cm^{-1} was recorded in 2012, in a water sample collected from piezometer 9, located at a farm, near livestock buildings. The values of this parameter exceeded 3000 μS cm^{-1}, and classified this groundwater to the fifth (last) quality class of groundwaters (*Regulation*… 2008). In 2013, groundwater collected from the same piezometer (No. 9) was characterized by lower electrolytic conductivity, 2284 μS cm^{-1} on average, which corresponds to the third class of groundwater quality. Statistical analysis confirmed that the waters tested in piezometers 9 and 14 had significantly ($p < 0.05$) higher conductivity values in 2012 than in 2013. Paradoxically, a reverse situation was observed in the waters of piezometric wells 10 and 13, and these results were also statistically significant. In 2013, the highest average value of specific conductivity for the entire period of the study was observed in the groundwater collected from piezometer 13 (3792 μS cm^{-1}). Well number 13 was located on intensively fertilized arable land. The resulting value of this parameter classified the water to the fifth quality class (Table 1). In contrast, low electrolytic conductivity was found in piezometer 12, located at a dairy farm near a barn and close to a manure plate, liquid manure tank and manure water. Conductivity values of groundwater from that piezometer were: 1164 μS cm^{-1} in 2012 and 1280 μS cm^{-1} in 2013, which meant that the grandwater belonged to the second class of quality (*Regulation*… 2008).

Ammonia nitrogen (N-NH_4). The results of chemical analyzes conducted in 2012 - 2013 of waters collected from eight piezometers for the content

Table 1

Annual average pH values on the Sorensen scale, electrolytic conductivity (EC) and concentrations of potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), ammonium nitrogen (N-NH_3), nitrate nitrogen (NO_3-N) and phosphate phosphorus (P-PO_4) in groundwaters from the area of the municipality Warnice in 2012-2013

Site No.	Locality	Year	Average annual value																	
			pH		EC (µS cm^{-1})		K (mg dm^{-3})		Na (mg dm^{-3})		Mg (mg dm^{-3})		Ca (mg dm^{-3})		N-NH_4 (mg dm^{-3})		N-NO_3 (mg dm^{-3})		P-PO_4 (mg dm^{-3})	
			mean	SD	mean	SD	mean	SD	mean	SD	Mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
8	Reńsko	2012	7.480	0.460	1205	87	17.90	4.500	39.60	5.800	43.60	3.400	77.60	25.40	0.690[a]	0.320	1.190	1.410	0.129	0.099
		2013	7.700	0.360	1182	116	19,00	6.500	45.80	23.00	46.80	3.100	77.10	17.10	0.260[a]	0.150	1.210	1.120	0.156	0.234
9	Reńsko	2012	7.360[a]	0.190	3003[a]	147	206.0	27.80	128.1	21.70	72.70	5.000	139.4[a]	15.80	0.370	0.440	225.1	94.32	0.117	0.094
		2013	7.770[a]	0.370	2284[a]	596	173.3	83.50	127.1	74.70	59.70	18.00	102.9[a]	26.50	0.220	0.200	205.6	21.30	0.092	0.083
10	Reńsko	2012	7.100[a]	0.350	1157[a]	65	35.40[a]	17.70	23.60	18.30	29.10	8.100	125.9	39.60	1.770	2.200	18.62	13.82	0.096	0.084
		2013	7.650[a]	0.420	1534[a]	392	74.60[a]	29.70	14.80	12.00	27.00	8.000	123.7	41.80	0.170	0.110	46.10	35.84	0.049	0.037
11	Reńsko	2012	7.210	0.310	2105	381	137.5[a]	55.20	88.60[a]	18.40	64.10[a]	20.00	58.00	31.50	6.070[a]	3.150	3.330	1.710	0.231	0.164
		2013	7.550	0.440	2438	525	403.0[a]	100.1	154.6[a]	42.10	45.30[a]	7.600	48.00	25.70	0.220[a]	0.200	23.05	17.88	0.287	0.196
12	Nowy Przylep	2012	7.160	0.320	1164	185	3.500	2.100	24.30	13.20	28.90[a]	4.300	137.4	72.50	1.020	0.430	3.630	4.760	0.139	0.139
		2013	7.390	0.200	1280	86	4.300	4.700	15.50	5.800	36.30[a]	3.200	121.7	57.50	1.100	1.290	1.370	1.560	0.041	0.033
13	Nowy Przylep	2012	7.390	0.340	1300[a]	718	6.800[a]	4.300	37.90[a]	44.70	65.30	42.80	104.7[a]	52.80	0.560[a]	0.860	16.61	8.040	0.112	0.077
		2013	7.590	0.230	3792[a]	783	452.0[a]	217.7	178.5[a]	57.70	113.3	20.50	35.90[a]	15.00	0.410[a]	0.360	5.700	5.370	0.033	0.036
14	Nowy Przylep	2012	7.600	0.470	1819[a]	133	12.90	1.500	113.4	18.00	146.1	15.50	29.30	8.800	1.390[a]	1.160	1.100	0.870	0.186	0.157
		2013	7.810	0.430	1541[a]	156	16.00	8.300	127.4	42.60	129.1	17.10	25.60	10.70	0.280[a]	0.210	1.260	1.110	0.057	0.050
16	Wierzbno	2012	7.490	0.460	1282	262	206.0	94.30	31.30	15.20	20.60	4.400	81.90	29.00	5.160	6.040	4.540	2.950	2.635	1.127
		2013	8.160	0.290	1152	315	169.7	105.5	26.10	15.50	20.90	3.500	79.00	18.80	2.260	3.460	4.010	3.560	2.045	0.511

[a] – the same letters indicate statistically significant differences at $p < 0.05$

of ammonium nitrogen (April-October) were distinctly varied and ranged from 0.170 to 6.070 mg dm^{-3} (Table 1). Significantly higher values of average ammonia nitrogen concentrations were recorded in the waters of piezometers 11 and 16 in 2012 (6.070 and 5.160 mg dm^{-3}, respectively) than in 2013, when the concentrations were 0.220 and 2.260, mg dm^{-3}, respectively (Table 1). High concentrations of ammonia nitrogen in the waters from the piezometers tested can be partly explained by the fact that piezometer 11 was located in a heavily fertilized arable area, while piezometer 16 was installed in a farmyard, near a manure plate. The study carried out in this area by researchers headed by Durkowski (2004) in 2001-2003 showed high concentrations of this parameter reaching 69.00 mg dm^{-3}. Having compared the maximum average ammonium nitrogen concentrations (6.070 mg dm^{-3}) from the two years we analyzed (2012 and 2013) with the maximum average value (29.40 mg dm^{-3}) calculated by the above team, a marked improvement in the quality of groundwater in this area was noticed. Statistical analysis of the two consecutive years (2012 and 2013) confirmed significant ($p < 0.05$) improvement of water quality in terms of nitrate nitrogen concentrations determined in samples collected from piezometers 8, 11, 13 and 14. Many authors (Rossa 2003, Durkowski et al 2006, 2007, Burzyńska 2011) demonstrated experimentally that high concentrations of ammonium ions in groundwaters were found near places of livestock manure storage. Lower average concentrations of ammonia nitrogen for the period between April and October were determined in groundwaters collected in 2013 from piezometers 8, 9, 10, 11 and 14, where they reached 0.260, 0.220, 0.170, 0.220 and 0.280 mg $N\text{-}NH_4$ dm^{-3}, respectively. Fairly high average concentrations of ammonia nitrogen in groundwater obtained in 2012 from piezometers 11 and 16 qualified the groundwater to the fifth quality class (concentrations above 2.330 mg dm^{-3} by the limit value calculated for the fifth class of groundwater quality, specified in the Journal of Law of 2008 No. 143, Item 896, while the $N\text{-}NH_4$ concentrations in the waters from the remaining piezometers were mostly within the first class quality for groundwaters.

Nitric nitrogen ($N\text{-}NO_3$). Annual average concentrations of nitrate nitrogen in the waters of all piezometers for the period from April to October were: 1.100-225.1 mg dm^{-3} in 2012, and 1.210-205.6 mg dm^{-3} in 2013. In the two-year study period (2012-2013), the highest average concentration of nitrate nitrogen was found in the water from intake 9 located near livestock buildings, where it equalled 225.1 mg dm^{-3} in 2012 and 205.6 mg dm^{-3} in 2013. The values of $N\text{-}NO_3$ concentrations in water from piezometer 9 exceeded 22.59 mg dm^{-3}, corresponding to the last, fifth class of groundwater quality. The waters from wells 11 and 13 located in arable lands, and well 10 located at a farm were also of the lowest class. Studies of Sapek (1996), Wiater, Skowrońska (2001), Durkowski (2004), Mioduszewski (2008), and Burzyńska (2011) confirmed that the largest groundwater pollution, particularly with nitrates, occured in areas of rural homesteads and intensively farmed arable lands.

Demonstrably lower concentrations of nitrates were found in the groundwaters collected from the remaining piezometers (8, 12, 14 and 16). The concentrations of nitrate nitrogen in the waters from these piezometers were mainly within the first and second class of groundwater purity (*Regulation*… 2008). Statistical analysis showed no significant differences ($p < 0.05$) in the concentrations of nitrates in the water samples collected from all the control wells during the study period.

Phosphorus phosphate (P-PO_4). Annual average concentrations of phosphate phosphorus in the groundwaters in all the analyzed piezometers with the exception of piezometers 16, 11 and 14 were low (in the range of 0.033 - 0.156 mg dm^{-3}), and thus falling within the first class of groundwater quality (*Regulation*… 2008). Waters from piezometric intake 16, located in a farmyard, belonged to the fifth class of groundwaters due to the high average concentrations of phosphate phosphorus, such as 2.635 mg dm^{-3} in 2012 and 2.045 mg dm^{-3} in 2013 (>1.630 mg dm^{-3}). These results are consistent with the results reported a few years ago in the same area (Durkowski et al. 2004, 2007), when high concentrations of phosphate in groundwaters were due to negligence in the collection and storage of solid and liquid animal manure. Noteworthy is the noticeable improvement in the quality of water from the intake No. 14 for the parameter discussed. During the two-year period of the study, a decrease in the concentration of P-PO_4 was reported from the average level of 0.186 mg dm^{-3} in 2012 to 0.057 mg dm^{-3} recorded in 2013. However, these differences were not statistically significant ($p < 0.05$). The result achieved in the last year of the study meant that the groundwater belonged to the first class of groundwater quality (*Regulation*… 2008).

Potassium (K). An average annual concentration of potassium in the waters from piezometers (for the April-October period) in the study period (2012-2013) was mostly very high, in the range from 169.7 to 452.0 mg dm^{-3} (Table 1). High levels of potassium were found in the waters collected from piezometers 9, 11, 13 and 16, most of which, except piezometer 13, were located at farms in the vicinity of livestock buildings. Likewise, Rossa (2003), Marcinkowski (2014), Barszczewski et al. (2001) and Woroniecki and Rumasz-Rudnicka (2008) reported in their studies that the proximity of livestock facilities and supporting infrastructure designed for storage of animal manure caused an increase of potassium concentrations in groundwaters, which tended to decline with an increasing distance from such structures. High levels of potassium reported in the waters from these piezometers corresponded to the fifth class of quality. It should also be noted that very low potassium levels were recorded in one piezometer (No. 12) in both 2012 and 2013 (3.500 mg dm^{-3}, and 4.300 mg dm^{-3}, respectively). The concentrations of potassium in piezometer 12 qualified this water to the first class of groundwater purity. The measured potassium level in the waters of piezometer 8 located on arable land was 17.90 mg dm^{-3} in 2012 and 19.00 mg dm^{-3} in 2013. Average values of potassium concentrations in water from the control well were of the fourth class of groundwater quality (*Regulation*… 2008) and were at a slightly lower level than the results of the study conducted previously by DURKOWSKI et al. (2007), which were 20.20-23.50 mg dm^{-3}. The statistical analysis showed significant differences ($p < 0.05$) in potassium levels in the successive years of research for waters derived from piezometric wells 10, 11 and 13, which indicated a clear inflow of this element to groundwaters within the last year of the study. This may have been caused by intense mineral fertilization with fertilizers containing potassium in their composition.

Sodium (Na). Average annual concentrations of sodium (for the period from April to October) in the waters from the eight analyzed piezometers located in the municipality of Warnice were low and ranged from 14.80 to 178.5 mg dm^{-3} (Table 1). The results correspond to concentrations obtained by SZYMAŃSKA-PULIKOWSKA (2008) in experiments carried out in the vicinity of Wrocław. The lowest sodium concentrations, in the range of 14.80-45.80 mg dm^{-3}, were found in the groundwaters collected from piezometers 8, 10, 12 and 16. The measured concentrations were in the first class groundwater quality. Slightly higher sodium levels were recorded in the waters sampled from piezometers 9, 11, 13 and 14, reaching the values of 178.5 mg dm^{-3}, thus within the second class of groundwater quality (*Regulation*... 2008). Control wells number 1 and 13 demonstrated significant differences ($p < 0.05$) in the results of sodium concentrations in water samples collected between the years 2012 and 2013. The average annual concentrations in the waters were as follows: 88.6 mg dm^{-3}, 154.6 mg dm^{-3} and 37.90 mg dm^{-3}, 178.5 mg dm^{-3}.

Magnesium (Mg) Average annual magnesium concentrations in the waters from the following eight piezometers: 8, 9, 10, 11, 12, 13, 14 and 16, varied and were in the range from 20.6 to 146.1 mg dm^{-3} (Table 1). Most results are consistent with those present in the available literature (KOZŁOWSKI, KOMISAREK 2013; ORZEPOWSKI, PULIKOWSKI 2008), and the elevated values of this parameter are believed to be related to the local geological structure. The magnesium concentrations in the waters of piezometers 8, 10, 12 and 16 were very low and did not exceed the limit of 30-50 mg dm^{-3}, thereby they were the first and second class of groundwater quality. In the remaining piezometers (9, 11, 13, and 14), the concentration of magnesium in the water fluctuated within the limit range (100-150 mg dm^{-3}) of the third and fourth class groundwater. The statistical analysis showed significant differences ($p < 0.05$) in magnesium levels in the successive years of research for waters derived from piezometric wells 11 and 12. It should be emphasized that the concentration of sodium (Na) and magnesium (Mg) in the waters from these piezometers did not exceed the limit of the fourth (penultimate) class of groundwater quality (*Regulation*... 2008).

Calcium (Ca). Average annual concentrations of calcium in the water from the eight piezometers analyzed, as in the case of magnesium, varied and ranged from 29.30 to 139.4 mg dm^{-3} (Table 1). Calcium values corresponded to the results of studies carried out on groundwaters of the Poznan Lakeland by KOZŁOWSKI and KOMISAREK (2013), and groundwaters from the vicinity of Wrocław investigated by Orzepowski and Pulikowski (2008). The level of calcium in the water from piezometer 14 did not exceed the limit value of 30 mg dm^{-3}, and thus belonged to the first class groundwater quality. In the other piezometers, the concentration of calcium in water did not exceed the limit value of 100-200 mg dm^{-3} for groundwaters, thereby falling within the second and third class of waters. Comparing calcium concentrations in the individual years in which our study was conducted, a distinct reduction was recorded in the last year. Although this trend was observed in all the sites of groundwater sampling, it was statistically significant ($p < 0.05$) only in the waters of piezometers 9 and 13.

The Pearson's correlation analysis (r) was performed in order to determine the relationships between the parameters studied (Table 2) The analysis demonstrated that the specific electrolytic conductivity of groundwater from the eight piezometric intakes tested was shaped mainly by the concentrations of sodium, potassium and magnesium.

Furthermore, a significant correlation ($r = 0.717$) was observed between the concentration of sodium and magnesium, a moderate correlation appeared between potassium and sodium, nitrate nitrogen and potassium, and a significant negative correlation was revealed between sodium and calcium. In addition, a correlation analysis of the sum of chemical parameters regarding conductivity was carried out, which unsurprisingly proved to be a virtually absolute relationship ($r = 0.948$ at $p = 0.001$), confirming a very close relationship of groundwater chemical parameters with the properties of the physical parameter such as specific electrolytic conductivity.

Recaptulating the results of physicochemical parameters, it can be noticed that the groundwaters of the first Quaternary aquifer from the catchment area of Lake Miedwie demonstrate similar parameters to those described by authors conducting research on groundwaters from other Polish regions. In addition, when comparing the results with the data from the past decade, a marked improvement in the quality of these waters can be observed, while periodic increases in the levels of certain chemical parameters can be explained by negligence or insufficient knowledge of farmers with respect to manure storage and rational use of mineral fertilizers.

CONCLUSIONS

1. The pH of groundwaters in all the piezometers was neutral throughout the two-year study period with a slight trend of becoming alkaline.

2. The highest values of electric conductivity (EC) were determined in groundwaters from piezometers located in rural farms (piezometer No. 9 – 3003 μS cm^{-1}) and intensively fertilized arable land (piezometer No. 13 – 3792 μS cm^{-1}).

Table 2

Results of the correlation analysis (r) between the parameters of water

r	K	Na	Mg	Ca	$N\text{-}NH_4$	$N\text{-}NO_3$	$P\text{-}PO_4$	pH	EC
K		0.464 $p = 0.000$	-0.016 $p = 0.865$	-0.117 $p = 0.219$	0.205 $p = 0.030$	0.428 $p = 0.000$	0.287 $p = 0.002$	0.237 $p = 0.012$	0.608 $p = 0.000$
Na	0.464 $p = 0.000$		0.717 $p = 0.000$	-0.423 $p = 0.000$	0.154 $p = 0.104$	0.046 $p = 0.633$	-0.100 $p = 0.293$	0.041 $p = 0.665$	0.738 $p = 0.000$
Mg	-0.016 $p = 0.865$	0.717 $p = 0.000$		-0.333 $p = 0.000$	0.117 $p = 0.220$	-0.119 $p = 0.212$	-0.352 $p = 0.000$	-0.054 $p = 0.573$	0.532 $p = 0.000$
Ca	-0.117 $p = 0.219$	-0.423 $p = 0.000$	-0.333 $p = 0.000$		-0.092 $p = 0.337$	0.246 $p = 0.009$	0.034 $p = 0.724$	-0.158 $p = 0.096$	-0.186 $p = 0.050$
$N\text{-}NH_4$	0.205 $p = 0.030$	0.154 $p = 0.104$	0.117 $p = 0.220$	-0.092 $p = 0.337$		-0.311 $p = 0.001$	0.087 $p = 0.365$	-0.032 $p = 0.735$	0.255 $p = 0.007$
$N\text{-}NO_3$	0.428 $p = 0.000$	0.046 $p = 0.633$	-0.119 $p = 0.212$	0.246 $p = 0.009$	-0.311 $p = 0.001$		0.012 $p = 0.900$	-0.004 $p = 0.967$	0.304 $p = 0.001$
$P\text{-}PO_4$	0.287 $p = 0.002$	-0.100 $p = 0.293$	-0.352 $p = 0.000$	0.034 $p = 0.724$	0.087 $p = 0.365$	0.012 $p = 0.900$		0.157 $p = 0.099$	-0.233 $p = 0.013$
pH	0.237 $p = 0.012$	0.041 $p = 0.665$	-0.054 $p = 0.573$	-0.158 $p = 0.096$	-0.032 $p = 0.735$	-0.004 $p = 0.967$	0.157 $p = 0.099$		0.027 $p = 0.780$
EC	0.608 $p = 0.000$	0.738 $p = 0.000$	0.532 $p = 0.000$	-0.186 $p = 0.050$	0.255 $p = 0.007$	0.304 $p = 0.001$	-0.233 $p = 0.013$	0.027 $p = 0.780$	

3. There was a demonstrable improvement in the quality of groundwaters observed in the parameters such as ammonium nitrogen ($N-NH_4$) and potassium (K) compared to previous findings by other authors pursuing research programs in the same area.

4. Elevated concentrations of nitrate nitrogen (225.12 mg dm^{-3}) and phosphate phosphorus (2.635 mg dm^{-3}) may indicate the use of excessive doses of fertilizers in the area and improper handling of manure during storage. This indicates the need to make farmers aware about environmental hazards, both locally and globally, resulting from the application of excessive amounts of nitrogen and phosphorus to the environment.

5. Concentrations of the macronutrients potassium (K), sodium (Na), calcium (Ca) and magnesium (Mg) varied in the groundwaters of the study area, but they mostly corresponded to the first quality class of groundwater. Even the highest values of these parameters did not implicate that the groundwaters studied belonged to the worst, fifth quality class.

6. Statistical analysis demonstrated that the specific electrolytic conductivity of groundwaters from the eight piezometric intakes tested was more distinctly shaped by the concentrations of sodium (Na), potassium (K) and magnesium (Mg) than by the other chemical parameters analyzed.

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