

CHEMICAL COMPOSITION OF GROUNDWATER FROM THE SE PART OF LAKE GOPŁO CATCHMENT

Summary

The paper outlines the analyses of chemical composition of groundwater from 13 monitoring well located in the vicinity of Lake Gopło. The measurements were performed between 2014 and 2017. We measured the concentrations of NO_3^- , NH_4^+ , PO_4^{3-} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , HCO_3^- as well as electric conductivity and pH. In major analyzed samples the concentrations of the above chemical species fell in the range typical for drinking water. NO_3^- and PO_4^{3-} were enhanced in wells located adjacently to farm buildings and in local depressions and consequently were exposed to delivery of nutrients from anthropogenic sources. The enhanced concentrations of NO_3^- ($>50 \text{ mg NO}_3^- \cdot \text{dm}^{-3}$) were found in two sites located in arable area and prone to surface runoff of biogenic substances.

Key words: groundwater, analyses of chemical composition, Gopło lake, Poland

CHEMIZM WÓD GRUNTOWYCH FRAGMENTU ZLEWNI JEZIORA GOPŁO

Streszczenie

W pracy przedstawiono wyniki analiz chemicznych wód gruntowych pobranych z 13 studzienek piezometrycznych, zlokalizowanych w obniżeniach terenu w rejonie Jeziora Gopło. Prezentowane wyniki analiz laboratoryjnych pochodzą z badań monitoringowych prowadzonych w latach 2014-2017. W pobranych próbkach wody oznaczono stężenie takich składników jak: NO_3^- , NH_4^+ , PO_4^{3-} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , HCO_3^- oraz odczyn i przewodnictwo elektrolityczne. Badane wody gruntowe analizowanego obszaru nie przekraczały znacząco dopuszczalnych stężeń analizowanych substancji. Sytuacje przekroczeń dopuszczalnych stężeń dotyczyły takich substancji jak: azotany i fosforany, dotyczyło to głównie wód pobranych ze studzienek piezometrycznych nr 1, 4, 11, oraz 13, które zlokalizowane były na terenach wiejskich, oraz w śródpolnych obniżeniach terenu, gdzie mogą występować sploty powierzchniowe. Podwyższone stężenia azotanów przekraczające wartość $50 \text{ mg NO}_3^- \cdot \text{dm}^{-3}$ stwierdzono tylko w dwóch studzienkach zlokalizowanych w obniżeniach na granicy pól uprawnych, gdzie możliwy był splot wód powierzchniowych.

Słowa kluczowe: woda gruntowa, analiza chemiczna, jezioro Gopło, Polska

1. Introduction

Owing to crucial environmental and economical functions of water its quality is of major concern to environmental scientists. Many studies have shown [1, 5, 6, 15] that chemical composition of groundwater is strongly influenced by agricultural activity. For effective protection of groundwater it is always essential to recognize the sources of contamination [1]. Delivery of biogenic substances to groundwater fuels eutrophication of surface waters [8, 15]. In addition, the consumption of NO_3^- -enriched water by humans leads to serious illnesses such as methemoglobinemia, thyroid problems etc. These diseases are directly related to fertilization of arable lands which delivers NO_3^- , acting as substrates for denitrification producing toxic NO_2^- species in water.

The current research aimed at assessing chemical composition of groundwater from monitoring wells adjacent to Lake Gopło. We determined the conductance and pH as well as concentrations of NO_3^- , NH_4^+ , PO_4^{3-} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , HCO_3^- in the water samples. The chemical data were used to determine the class of purity of the water according to Decree Law of the Minister of the Environment [12].

2. Materials and methods

The analyses of groundwater from 13 monitoring wells located in the vicinity of Lake Gopło were performed be-

tween 2014 and 2017. The studied lake acts as the largest lake of the Kujawsko-Pomorskie voivodeship and is located in the Gniezno Lake District, 20 km to south of Inowrocław. The biggest town sitting on the lakes is Kruszwica. Lake Gopło is situated in a glacial channel. Its maximum depth is 16.5 m and a mean depth is 3.5 m.

The distribution of monitoring wells is depicted in Fig. 1. The wells were established east of the lake. The wells no. 1, 2, 9, 10, 11, 12 and 13 were located in the midst of arable lands in small open depressions drained by Lake Gopło. Wells no. 3 and 4 were situated within the glacial channel of the lake while the remaining were along the Warta-Gopło canal, in the south of the lake (Tab. 1).

The groundwater samples were taken 5-10 cm below the water table with quarterly resolution in different seasons. In total we analyzed 104 water samples. Electric conductivity and pH were measured potentiometrically. PO_4^{3-} and NO_3^- were determined spectrophotometrically with ammonium molybdate and brucine sulphate, respectively. NH_4^+ was analyzed using Nessler method. Cl^- was titrated with AgNO_3 using potassium chromate as indicator. HCO_3^- was titrated with HCl . Na^+ , K^+ and Ca^{2+} were analyzed using atomic emission spectrometry (EAS) and Mg^{2+} using atomic absorption spectrometry (AAS).

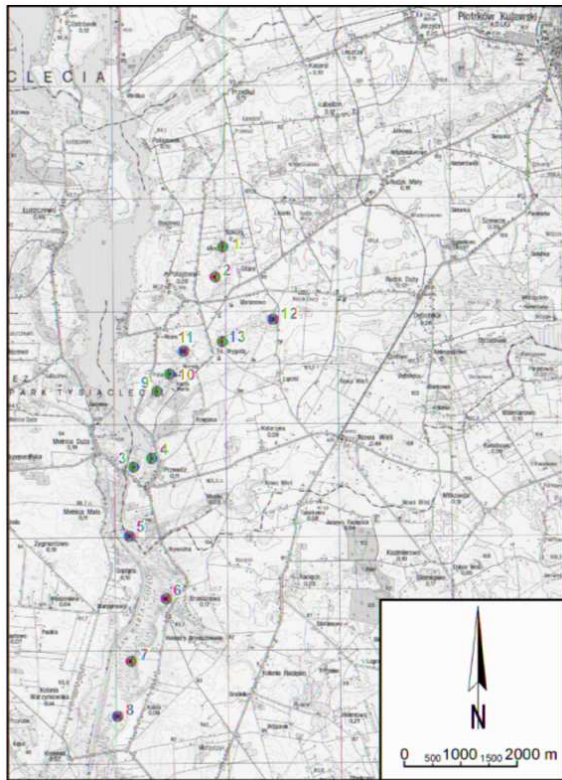


Fig. 1. Topographic map of the vicinity of Lake Gopło and distribution of monitoring wells

Rys. 1. Szkic topograficzny z rozmieszczonymi studzienkami piezometrycznymi w rejonie jeziora Gopło

Tab. 1. Physiographic conditions of monitoring wells

Tab. 1. Warunki fizjograficzne lokalizacji studzienek piezometrycznych

No.	Location of monitoring wells	Number of monitoring wells
1	Open depression drained by Lake Gopło	1, 2
2.	Lake Gopło glacial channel	3, 4
3.	Lake Gopło glacial channel along the Warta-Gopło canal	5, 6, 7, 8,
4.	Open depression drained by Lake Gopło	9, 10, 11
5.	Closed depression near Marianowo village	12, 13
Total		13

Source: own work / Źródło: opracowanie własne

3. Results and discussion

The results obtained during the study were summarized in Figures 2-5.

Chemical composition of groundwater is determined by many factors among which mineralogy and chemical composition of soil matrix, soil structure and the intensity of agricultural activity act as the most important. In addition, water regime and drainage conditions play a non-negligible role.

The highest concentrations of PO_4^{3-} of 0.20 and 0.21 mg $PO_4^{3-} \cdot dm^{-3}$ (Fig. 2) were observed in wells no. 2 and 11 located in depressions adjacent to villages and farm buildings. Consequently, these sites could be influenced by agricultural activity likewise the groundwater sampled in the vicinity of Lake Niepruszewskie [15]. The lowest PO_4^{3-} occurred in wells no. 3 and 12 and the mean concentrations were between 0.07 and 0.21 mg $PO_4^{3-} \cdot dm^{-3}$. The minimum value was 0.02 mg $PO_4^{3-} \cdot dm^{-3}$. On the basis of concentra-

tions of PO_4^{3-} the samples analyzed were numbered along the 1st class of water quality [7, 11, 15].

The concentrations of NO_3^- in groundwater varied in a broad range. Considerable differences, evidenced by the very high coefficient of variation of 6110%, occurred throughout the whole study area and in each station. The minimum concentration was 0.6 mg $NO_3^- \cdot dm^{-3}$ and occurred in wells number 6, 7, 10 and 12 (Fig. 2). The highest concentrations obtained in well no. 1 were 192.2 mg $NO_3^- \cdot dm^{-3}$. The second highest NO_3^- of 133.6 mg $NO_3^- \cdot dm^{-3}$ was in well 13 (Fig. 2). These wells were located in small depressions in the midst of arable lands and consequently the enhanced delivery of nutrients to ground waters was highly likely [5, 11, 15]. With respect to concentrations of NO_3^- , the studied groundwater falls into the 1st quality class, except for well no. 1 and 13 representing 4th and 2nd class. As it was mentioned the latter stations could be affected by surface nutrient runoff from the adjacent farms. Mazurek [8] obtained NO_3^- concentrations between 0.0 and 73.0 mg $NO_3^- \cdot dm^{-3}$. In turn, Grześ et al. [3] measured 26.2 – 80.8 mg $NO_3^- \cdot dm^{-3}$ and Zbierska et al. [15] obtained 0.0 -177.0 mg $NO_3^- \cdot dm^{-3}$. According to Komisarek [7] the enhanced concentrations of nitrates are alarming, because the enrichment in NO_3^- in groundwater can initiate accelerated eutrophication of surface waters.

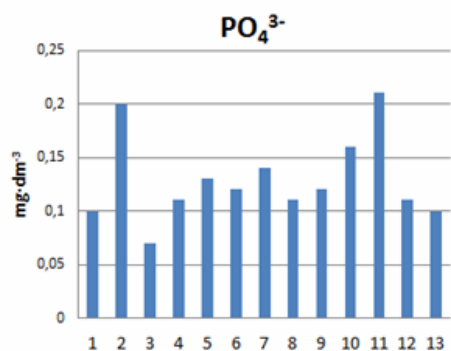
Chlorides act as principle components of groundwater from deeper circulation. The concentration of Cl^- in our samples were highly variable and the coefficient of variation was 14-86%. The mean values were between 13.1 (well no. 8) and 100.8 mg $Cl^- \cdot dm^{-3}$ (well no. 4) (Fig. 3). Major analysed samples represented 1st class of water quality. The sample no. 4 was classified as 3rd class and samples from well no. 9, 12, and 13 was numbered among 2nd class. Similar results (17.8-159.8 mg·Cl⁻) were obtained by Czajkowska [2]. Komisarek [7] established that the variability in Cl^- concentrations is primarily controlled by the origin of parent material in soils as well as the high rate of water exchange in vadose zone of small thickness.

The studied samples displayed increased concentrations of HCO_3^- and the mean concentrations were between 152.2 and 544.6 mg $HCO_3^- \cdot dm^{-3}$ (Fig. 3). Only one sample (no. 1) was classified as 1st quality class. The remaining represented 2nd, 3rd and 4th classes. Our results seem high compared to Jonczak [6] and Czajkowska [2], who reported concentrations of bicarbonates between 127-247 and 48.7-334.7

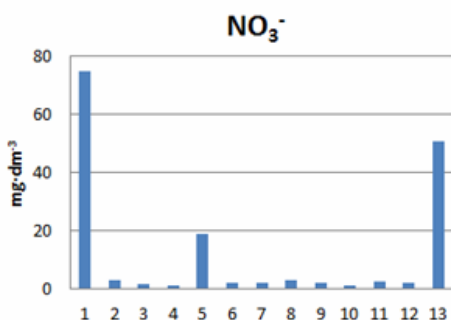
6 mg $HCO_3^- \cdot dm^{-3}$. Some authors [4, 9] argue that the enhanced concentrations of HCO_3^- in groundwater result from anoxic conditions and availability of organic matter which creates favorable conditions for microbial degradation of organic compounds.

Electric conductivity of groundwater, which is mainly dependent on mineralization, was characterized by the appreciable variability. The lowest conductivity of 409 $\mu S \cdot cm^{-1}$ was measured in well no. 1 and the maximum value (2482 $\mu S \cdot cm^{-1}$) was obtained in well no. 11 (Fig. 5). The conductivities of the studied samples fall within the reference range for natural waters (100-1000 $\mu S \cdot cm^{-1}$) and drinking water (2500 $\mu S \cdot cm^{-1}$). The groundwater which migrates through the thick layers of glaciolacustrine deposits dissolve more ions than surface runoff waters. The groundwater from Złotniki area had conductivities between 648 and 1480 $\mu S \cdot cm^{-1}$ [3]. Zbierska et al. [15] obtained conductivities between 734 and 2650 $\mu S \cdot cm^{-1}$, and Rzepa et al. [13] measured 900-5200 $\mu S \cdot cm^{-1}$.

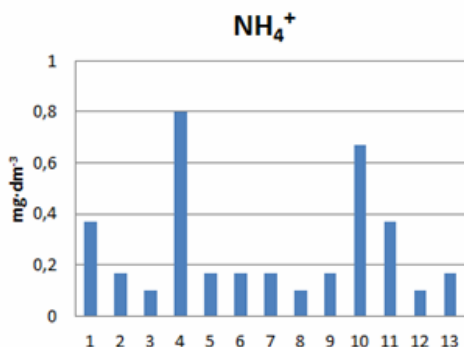
No.	Min.	Max.	Average	Variation coefficient
1	0.05	0.16	0.10	44
2	0.11	0.31	0.20	53
3	0.02	0.14	0.07	66
4	0.09	0.12	0.11	13
5	0.07	0.25	0.13	62
6	0.04	0.25	0.12	85
7	0.11	0.19	0.14	26
8	0.09	0.13	0.11	15
9	0.06	0.16	0.12	40
10	0.06	0.28	0.16	56
11	0.17	0.26	0.21	19
12	0.02	0.22	0.11	95
13	0.08	0.14	0.10	27



No.	Min.	Max.	Average	Variation coefficient
1	31.8	192.2	74.8	105
2	1.9	5.0	2.9	49
3	0.7	2.7	1.5	55
4	0.7	1.6	1.2	31
5	16.0	26.7	19.0	27
6	0.6	3.7	2.4	55
7	0.6	4.0	2.4	59
8	1.8	4.5	3.2	41
9	0.8	3.2	2.3	47
10	0.6	3.5	1.5	92
11	2.4	2.8	2.6	6
12	0.6	5.0	2.3	82
13	8.7	133.6	50.5	110



No.	Min.	Max.	Average	Variation coefficient
1	0.3	0.4	0.4	16
2	0.1	0.2	0.2	35
3	0.1	0.1	0.1	0
4	0.5	0.9	0.8	30
5	0.1	0.2	0.2	35
6	0.1	0.2	0.2	35
7	0.1	0.2	0.2	35
8	0.1	0.1	0.1	0
9	0.1	0.2	0.2	35
10	0.3	0.9	0.7	48
11	0.3	0.4	0.4	16
12	0.1	0.1	0.1	0
13	0.1	0.2	0.2	35



Source: own work / Źródło: opracowanie własne

Fig. 2. Concentration of phosphates, nitrates, ammonium in the analyzed samples ($\text{mg} \cdot \text{dm}^{-3}$)

Rys. 2. Koncentracja fosforanów, azotanów, amoniaku w analizowanych próbkach

However, the latter values were representative for groundwater affected by municipal waste dump.

pH of water was between 6.2 and 8.2 (Fig. 5) and major samples had neutral pH. This feature is representative for the 1st class of water quality. The pH of groundwater is controlled by HCO_3^- and CO_2 contents, however parent rock composition is essential for determining pH. Komisarek [7], Jonczak [6] and Zbierska et al. [15] reported pH values similar to our results (6.5-8.0).

The concentrations of Na^+ were relatively low and varied between 6.0 and 80.9 $\text{mg Na}^+ \cdot \text{dm}^{-3}$ (Fig. 3) and the average values were 6.5-73.3 $\text{mg Na}^+ \cdot \text{dm}^{-3}$ respectively. These values were in line with published data [11]. The studied samples, except for sample no. 4, represented 1st class of water quality. In temperate climate sodium is only weakly bound by the soil matrix, and consequently is very mobile in groundwater [7].

K^+ behaves similarly to Na^+ . The lowest concentrations of 0.4 $\text{mg K}^+ \cdot \text{dm}^{-3}$ were obtained in well no. 5, located in a local depression in the east of Warta-Gopło canal. The highest con-

centrations were 13.6 $\text{mg K}^+ \cdot \text{dm}^{-3}$ and occurred in sample no. 4 (Fig. 4), major analyzed samples can be numbered among the 1st quality class. Sample no. 4 was the only exception. Our values are similar to the data reported by Grześ et al. [3] obtained from cultivated lessive soils where there was 6.1-38.0 $\text{mg K}^+ \cdot \text{dm}^{-3}$, however lower than 1.3-38.0 $\text{mg K}^+ \cdot \text{dm}^{-3}$, obtained by Pawęska et al. [11].

Ca^{2+} changed from 53.8 in well no. 1 to 510.1 $\text{mg Ca}^{2+} \cdot \text{dm}^{-3}$ in well no. 11 (Fig. 4). On the basis of mean concentrations of Ca^{2+} none of the samples analyzed could be classified as the 1st quality class. Jonczak [6] measured 8.9-39.7 $\text{mg Ca}^{2+} \cdot \text{dm}^{-3}$ and Czajkowska [2] obtained 20.0-196.4 $\text{mg Ca}^{2+} \cdot \text{dm}^{-3}$. In turn, Siciński and Kuszneruk [14] reported 70.0-100.0 $\text{mg Ca}^{2+} \cdot \text{dm}^{-3}$. The Ca^{2+} ion predominates in fresh weakly mineralized water and decreases in favor of other species with increasing mineralization. The changes in the concentrations of Ca^{2+} are used to trace the delivery of groundwater from deeper aquifers [10].

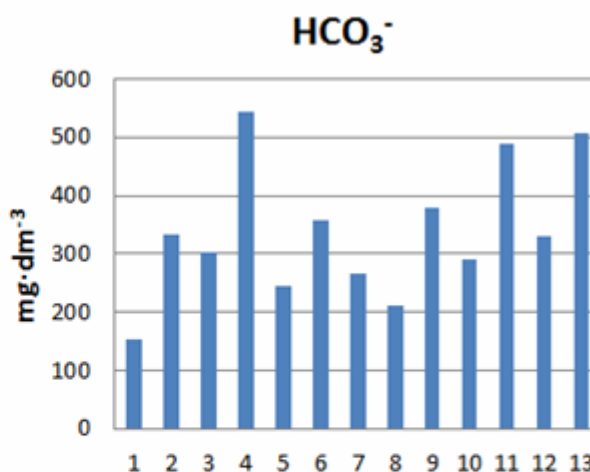
Mg^{2+} ranged from 3.4 to 63.4 $\text{mg Mg}^{2+} \cdot \text{dm}^{-3}$ (Fig. 4) which indicated 1st – 3rd class of quality. According to Komisarek [7] the enrichment of ground waters in Mg^{2+} can be

due to the occurrence of Ca-Mg carbonates in soil matrix. These minerals are prone to chemical weathering and are easily leached to groundwater.

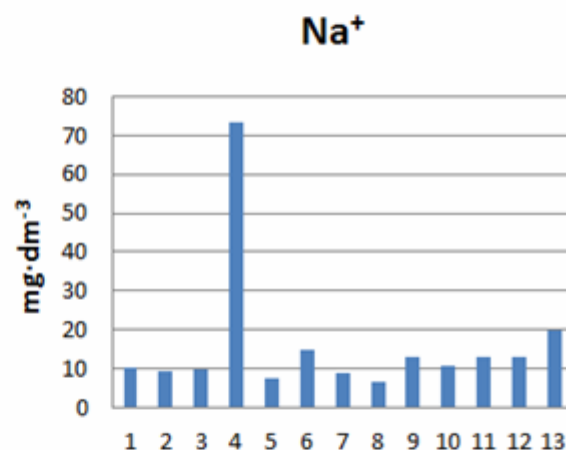
NH_4^+ was low and varied from 0.1 to 0.9 $\text{mg NH}_4^+ \cdot \text{dm}^{-3}$ (Fig. 2). In sites no. 4 and 10 we found higher NH_4^+ than

allowable limits for drinking water. However, the high values of the coefficient of variation (33-48%) reflect considerable variance of the concentrations. Pawęska et al. [11] argued that the low concentrations of NH_4^+ indicate lack of contamination with organic substances.

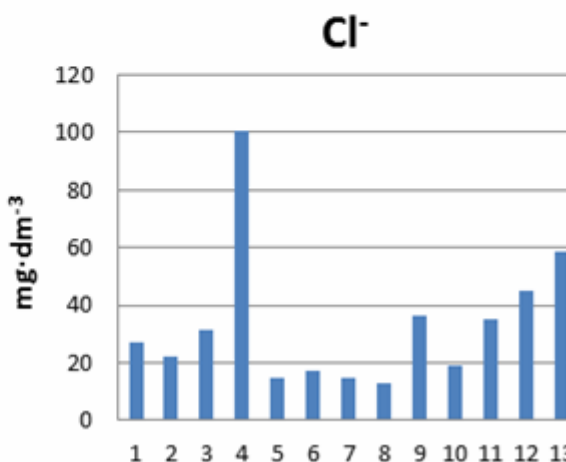
No.	Min.	Max.	Average	Variation coefficient
1	76	262	152	52
2	216	432	334	27
3	254	393	304	21
4	360	664	545	24
5	218	270	245	9
6	292	433	359	16
7	233	338	267	18
8	176	241	213	13
9	280	441	380	18
10	242	368	289	20
11	320	656	488	28
12	287	369	329	10
13	474	538	506	5



No.	Min.	Max.	Average	Variation coefficient
1	6.4	15.9	10.1	43
2	8.5	10.1	9.3	9
3	9.1	10.3	9.7	5
4	65.3	80.9	73.3	9
5	6.9	8.5	7.4	10
6	11.3	19.1	14.9	23
7	8.4	9.8	9.1	8
8	6.0	7.0	6.5	7
9	9.8	19.5	12.8	35
10	8.7	13.1	10.9	21
11	12.3	14.2	13.2	6
12	11.9	16.6	13.3	17
13	12.9	29.3	20.1	34



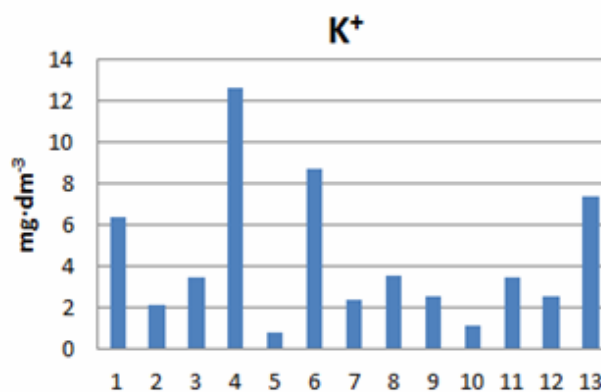
No.	Min.	Max.	Average	Variation coefficient
1	12.4	43.7	26.9	48
2	16.0	31.0	22.3	33
3	24.2	36.7	31.2	17
4	71.6	153.6	100.8	37
5	11.9	19.6	14.7	24
6	11.7	23.8	17.5	38
7	11.2	20.0	14.7	28
8	9.7	17.6	13.1	25
9	19.9	72.1	36.1	67
10	12.8	25.0	18.9	29
11	29.2	41.2	35.2	14
12	25.3	80.1	45.0	57
13	16.2	129.1	58.7	85



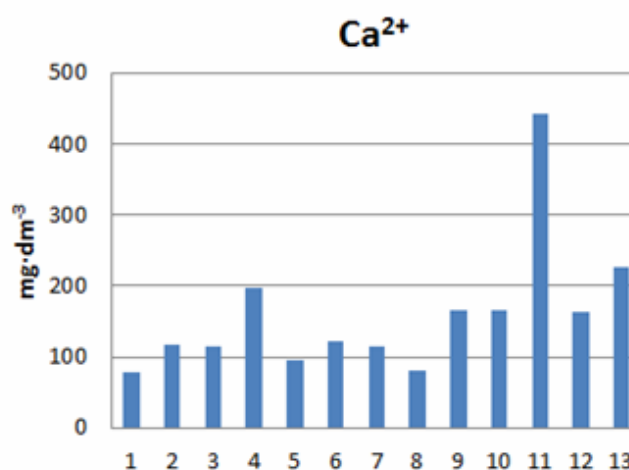
Source: own work / Źródło: opracowanie własne

Fig. 3. Concentration of bicarbonates, sodium, chlorides in the analyzed samples ($\text{mg HCO}_3^- \cdot \text{dm}^{-3}$, $\text{mg Na}^+ \cdot \text{dm}^{-3}$, $\text{mg Cl}^- \cdot \text{dm}^{-3}$)
 Rys. 3. Koncentracja wodorowęglanów, sodu, chlorków w analizowanych próbkach

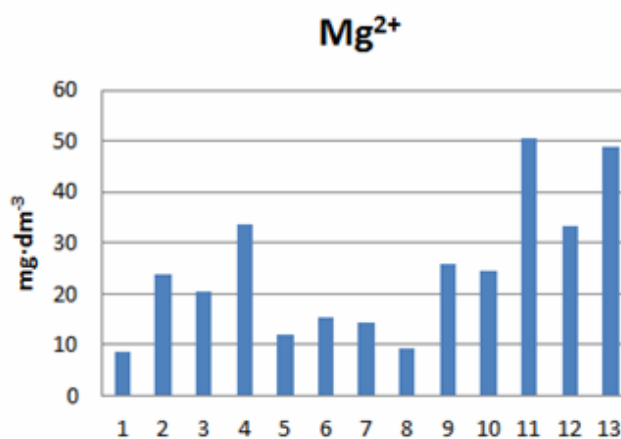
No.	Min.	Max.	Average	Variation coefficient
1	3.8	12.0	6.4	61
2	0.8	4.2	2.2	68
3	2.1	5.8	3.5	48
4	11.9	13.6	12.7	5
5	0.4	1.3	0.8	45
6	7.5	10.5	8.7	15
7	1.8	3.4	2.4	29
8	3.0	4.3	3.6	16
9	1.9	4.0	2.5	40
10	0.6	1.5	1.2	35
11	3.4	3.6	3.5	2
12	2.3	2.9	2.6	10
13	6.3	8.0	7.4	11



No.	Min.	Max.	Average	Variation coefficient
1	53.8	106.2	77.2	30
2	103.1	127.6	117.1	9
3	90.8	128.5	113.7	14
4	178.9	225.6	196.4	11
5	62.0	108.7	94.2	23
6	85.6	163.7	121.3	27
7	94.9	131.0	114.8	13
8	70.2	84.8	79.7	8
9	153.5	176.0	164.3	6
10	117.2	212.1	165.0	29
11	372.6	510.1	441.4	13
12	130.1	226.4	162.6	26
13	199.4	272.4	226.8	14



No.	Min.	Max.	Average	Variation coefficient
1	4.5	14.9	8.5	52
2	22.5	25.6	24.0	6
3	16.4	24.6	20.3	17
4	30.0	35.6	33.6	8
5	3.4	15.9	12.1	49
6	14.6	16.4	15.4	5
7	13.4	15.0	14.4	5
8	8.3	10.6	9.4	10
9	19.3	30.6	26.0	19
10	20.3	30.1	24.5	18
11	37.9	63.4	50.7	20
12	32.7	33.9	33.3	02
13	42.1	60.6	48.9	17



Source: own work / Źródło: opracowanie własne

Fig. 4. Concentration of potassium, calcium, magnesium in the analyzed samples ($\text{mg K}^+\cdot\text{dm}^{-3}$, $\text{mg Ca}^{2+}\cdot\text{dm}^{-3}$, $\text{mg Mg}^{2+}\cdot\text{dm}^{-3}$)
 Rys. 4. Koncentracja potasu, wapnia, magnezu w analizowanych próbkach

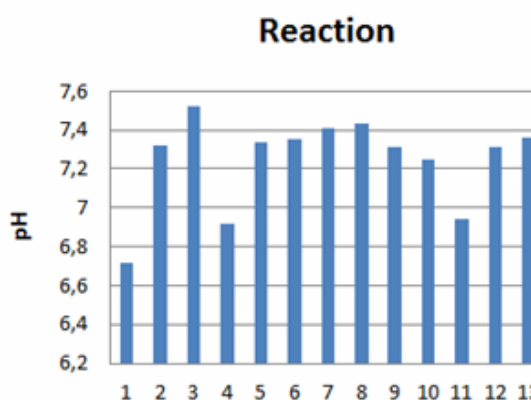
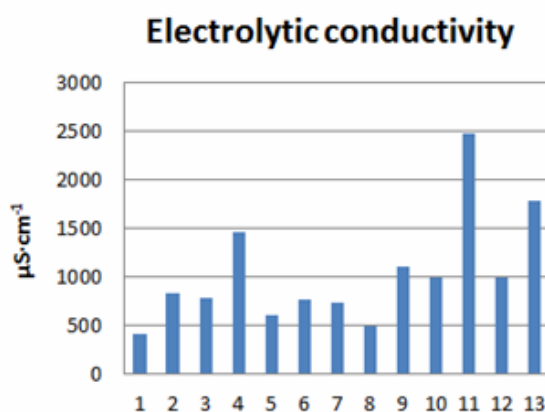
4. Conclusions

1. Chemical composition of the analyzed samples displayed considerable spatio-temporal variability.
2. In major samples the concentrations of analyzed chemical species were within allowable values. Higher concentrations were only obtained in wells located in depressions collecting waters from adjacent arable lands.

3. The concentrations of nitrites of over $50 \text{ mg NO}_3^-\cdot\text{dm}^{-3}$ were only obtained in two sites in the arable lands.
4. The water quality requirements outlined in the Decree Law of the Minister of Environment [12] were not satisfied in majority of samples. Chemical composition of groundwater varied considerably throughout the study period and some species (HCO_3^- , NO_3^- , NH_4^+ , Ca^{2+}) determined fall out of allowable range.

No.	Min.	Max.	Average	Variation coefficient
1	277	756	409	57
2	776	974	832	47
3	750	811	789	51
4	1415	1489	1461	50
5	515	645	608	52
6	725	851	768	48
7	710	783	730	48
8	482	511	495	49
9	967	1430	1115	45
10	738	1601	1000	40
11	2348	2560	2482	50
12	956	1058	993	48
13	1632	2130	1776	46

No.	Min.	Max.	Average	Variation coefficient
1	6.2	7.3	6.7	7
2	6.9	8.2	7.3	34
3	7.1	8.1	7.5	29
4	6.9	7.0	6.9	21
5	7.1	7.8	7.3	15
6	7.2	7.9	7.4	8
7	7.1	8.2	7.4	1
8	7.2	8.0	7.4	5
9	7.0	8.1	7.3	13
10	7.1	7.7	7.3	20
11	6.8	7.0	6.9	29
12	7.1	7.9	7.3	33
13	7.1	7.9	7.4	40



Source: own work / Źródło: opracowanie własne

Fig. 5. Electric conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) and pH values in the analyzed samples

Rys. 5. Przewodność elektryczna właściwa ($\mu\text{S}\cdot\text{cm}^{-1}$) i wartości pH w analizowanych próbkach

5. References

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