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## ANALYSIS OF THE SPATIAL VARIABILITY OF THE CONCENTRATIONS OF Na<sup>+</sup> AND K<sup>+</sup> IONS IN THE GROUNDWATER SOURCED IN SOUTHERN POLAND

Differences in the spatial variability of Na<sup>+</sup> and K<sup>+</sup> ion concentrations in the groundwater sourced in Southern Poland have been analysed. The study was based on selected hydrogeological environments differing in the lithology and geometry of aquifer rock voids. The hydrogeochemical background for Na<sup>+</sup> and K<sup>+</sup> ions was determined for various hydrogeological environments as well. The hydrogeochemical background ranges obtained do not deviate significantly from the background ranges for groundwater observed in other areas of Poland. The analyses conducted indicate the presence of anomalous concentrations of Na<sup>+</sup> and K<sup>+</sup> ions in all hydrogeological environments often accompanied with significantly elevated concentrations of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions. Owing to the fact that the data analysed exhibit a distribution deviating considerably from a normal one, non-parametric methods of statistical inference were used. The results obtained indicate statistically significant differences between the variabilities of Na<sup>+</sup> and K<sup>+</sup> ion concentrations in various hydrogeological environments. The factors responsible for such differences are lithological variability and different groundwater circulation systems.

### 1. INTRODUCTION

Sodium and potassium are very abundant elements in the Earth's crust. They are involved in the hypergenic processes related to the circulation of elements and also play important parts in physiological processes. The primary source of Na<sup>+</sup> and K<sup>+</sup> ions in groundwater are the products of the chemical weathering of commonly occurring igneous rock minerals. A secondary source of these ions may be the inflow of water with a high content of Na<sup>+</sup> and K<sup>+</sup> ions. The increased content of these ions in groundwater may be the result of geogenic and/or anthropogenic processes.

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Within Southern Poland, groundwater is often the primary source of drinking water. Therefore, owing to the fact that standard groundwater treatment methods (aeration and filtration) do not eliminate  $\text{Na}^+$  and  $\text{K}^+$  ions, it is important to study the differences in the variability of  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations in the area under consideration. According to the law currently in force (Journal of Laws [Dz. U.] No. 72 of 20 April 2010 item 466 in conjunction with related acts), the maximum permissible concentration of  $\text{Na}^+$  ions in drinking water is  $200 \text{ mg/dm}^3$ . This concentration is exceeded in groundwater in many cases. The maximum permissible concentration of  $\text{K}^+$  ions has not been stipulated but an excess of potassium in the body may cause heart problems [1].

By using 150 results of chemical analyses of groundwater sampled from wells drilled in the Southern Poland Province that source groundwater from (Cenozoic and Paleozoic) formations of different ages, an attempt was made to determine the variability of, and the factors affecting the concentrations of sodium and potassium ions in selected hydrogeochemical environments.

## 2. GEOLOGICAL AND HYDROGEOLOGICAL CONDITIONS

The study area covers the Southern Poland province, which includes diverse geological structures such as the Silesia-Cracow Monocline and the Miechów Trough, the Silesia-Kraków and Carpathian Foredeep and the Outer and Inner Carpathians. Porous and fractured porous aquifers occur mainly in Quaternary, Miocene, Paleogene and Upper Cretaceous (flysch), Permian and Carboniferous clastic sediments. Fractured porous and fractured karst aquifers occur mainly in carbonate Cretaceous (Miechów Trough), Jurassic, Triassic and Devonian layers. The locations of individual aquifers and the numbers of wells analysed within them are shown in Fig. 1.

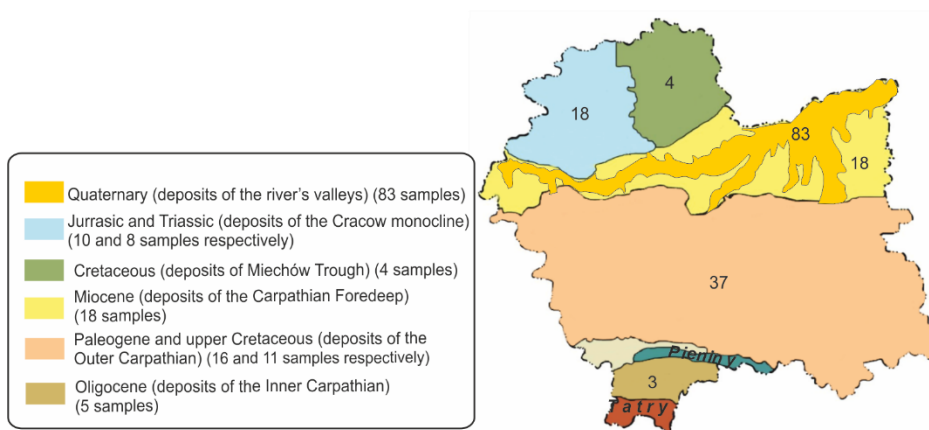


Fig. 1. Location of multiaquifer formations and the number of wells analysed

As concerns the lithology and differences in the geometry of aquifer rock voids, the following main types of hydrogeological environments can be distinguished:

Type A. Quaternary and Miocene formations of the Carpathian Foredeep – clastic rock, loose with dominant detrital material content, sometimes interbedded with compact rock (porous, occasionally fractured porous aquifers).

Type B. Paleogene (including Inner Carpathian Oligocene) and Outer Carpathian Cretaceous – fissured solid flysch with dominant detrital material content (fractured porous aquifers).

Type C. Cretaceous and Jurassic and Triassic formations of the Silesia-Cracow Monocline – fissured carbonate rocks, with highly developed karst processes in places (fractured karst aquifers).

### 3. GROUNDWATER CHEMISTRY

The weathering of aluminosilicates (e.g. albite) is the major source of  $\text{Na}^+$  ions in groundwater. Ion exchange processes may be another source of sodium. The mixing of fresh groundwater and heavily saline groundwater, e.g. as a result of the dissolution of evaporites, is also a significant source of  $\text{Na}^+$  ions in groundwater. In the case of potassium, a significant source of  $\text{K}^+$  ions in groundwater is the weathering of aluminosilicates that are rich in potassium (such as orthoclase, muscovite, and biotite). Despite their considerable chemical affinity,  $\text{Na}^+$  and  $\text{K}^+$  ions behave differently in the soil-water environment. Potassium ions are very rapidly adsorbed in the soil-water environment by clay minerals, soil colloids and plants. Additionally,  $\text{K}^+$  ions are often not involved in ion exchange processes as they are very strongly bound by clay minerals [2]. Therefore groundwater concentrations of  $\text{K}^+$  ions are usually fairly low, clearly lower than the coincident concentrations of  $\text{Na}^+$  ions. A high content of  $\text{K}^+$  ions in groundwater often points to anthropogenic pollution.

According to the law currently in force, the maximum permissible concentration of  $\text{Na}^+$  ions in drinking water is  $200 \text{ mg}\cdot\text{dm}^{-3}$ . For the A hydrogeological environment, 14% of observations exceeded this threshold. For the B and C environments, the threshold  $\text{Na}^+$  ion concentration of  $200 \text{ mg}\cdot\text{dm}^{-3}$  was exceeded in 3.4% and 4.6% of observations, respectively.

The research materials used in this paper were made available by the Carpathian Branch of the Polish Geological Institute with its seat in Kraków. They consisted of the data contained in the “Hydro” Regional Hydrogeological Data Bank of the PGI in electronic form. These materials include, *inter alia*, the results of chemical analyses of groundwater sampled from 150 wells drilled, constructed and operated in Southern Poland from 1950 to 2004. These wells source groundwater from clastic Quaternary (83), Miocene (18), Paleogene (16), Oligocene (3), Cretaceous flysch (11), Miechów Trough Cretaceous (4), Jurassic (10) and Triassic (8) layers (see Fig. 1). In the paper, the variability

of pH and total dissolved solids (TDS) values as well as the variabilities of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations were analysed. In order to identify hydrochemical water types, the widely used classification proposed by Back and Hanshaw [3] was adopted.

Groundwaters from Quaternary and Miocene aquifers (the A hydrogeological environment) exhibit considerable differences in terms of their hydrochemical properties. These are both ordinary groundwaters that include 2 or 3 ions ( $\text{Ca-HCO}_3$  or  $\text{Ca-HCO}_3\text{-SO}_4$ ) as well as groundwaters that include 4 or 5 ions, with clearly higher mineral content and high  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  ion concentrations. Most are fresh groundwaters (sometimes also mineral ones) with dry residue ranging from 135 to  $4509 \text{ mg}\cdot\text{dm}^{-3}$  and pH ranging from 6.2 to 8.5. Groundwaters with higher TDS ( $>1000 \text{ mg}\cdot\text{dm}^{-3}$ ) are abundant in Pleistocene sediments. The increased TDS of these groundwaters is most often associated with the processes of Mesozoic groundwater ascent or with intense human pressure. For Miocene sediments, another likely cause is the dissolution of gypsum, which results in the presence of elevated  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ion concentrations and generally in high TDS.

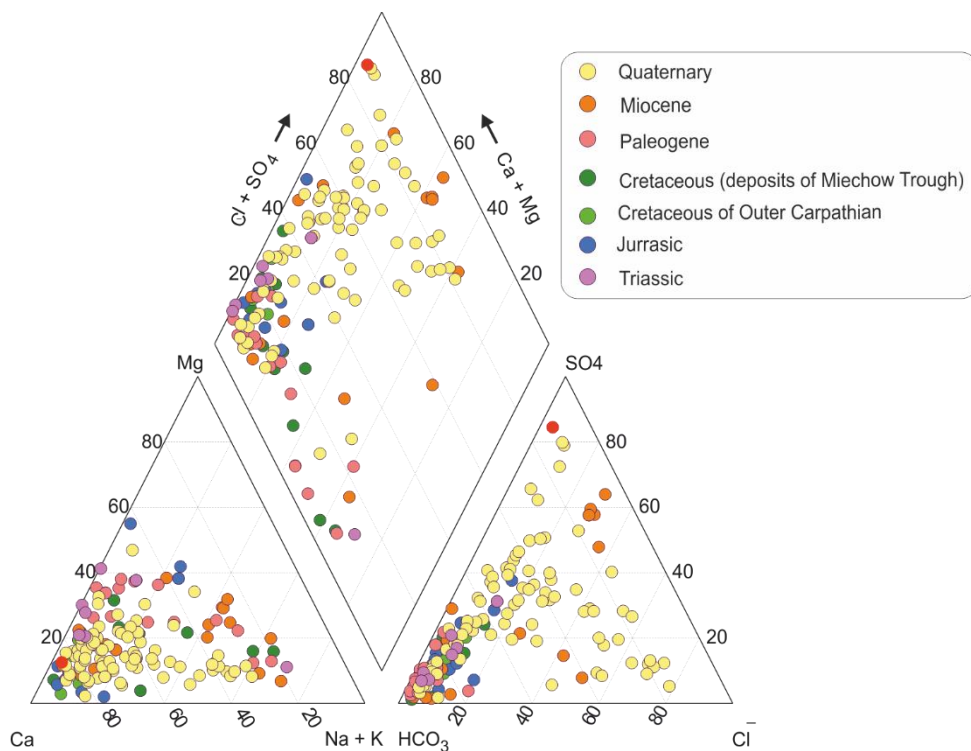


Fig. 2. The Piper diagram

Groundwaters from solid clastic formations (the B hydrogeological environment) are most commonly  $\text{Ca-Mg-HCO}_3$  or similar groundwaters, sometimes with elevated  $\text{Na}^+$  ion concentrations (naturally carbonated mineral waters). These exhibit a smaller diversity of hydrogeochemical types than groundwaters from the Pleistocene and Miocene layers. Most are fresh groundwaters (occasionally mineral ones) with dry residue ranging from 191 to 1262  $\text{mg}\cdot\text{dm}^{-3}$  and pH ranging from 6.3 to 8.4.

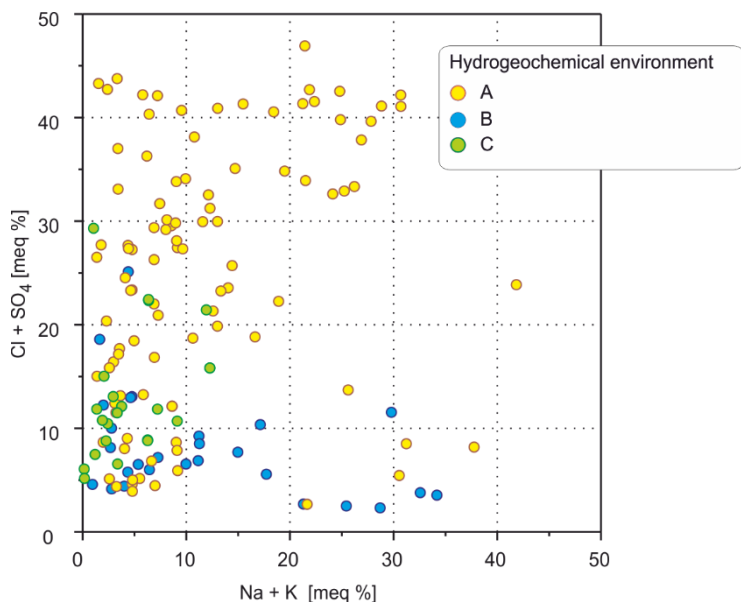


Fig. 3. The Langelier–Ludwig diagram

Groundwaters from carbonate formations (the C hydrogeological environment) are most commonly  $\text{Ca-HCO}_3$  and  $\text{Ca-Mg-HCO}_3$  or similar groundwaters, sometimes with elevated  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations. These are fresh groundwaters with dry residue ranging from 239 to 787  $\text{mg}\cdot\text{dm}^{-3}$ . Their pH values range from 7.5 to 8.5.

The chemical composition of the groundwaters analysed is shown in the Piper diagram (Fig. 2). One can see considerable variation in the chemical composition of groundwater from the Pleistocene and Miocene layers and much less variation in the chemical composition of groundwater in other aquifers.

The analysis of groundwater chemistry incorporating stratigraphic divisions is made very difficult by the small sample sizes for some aquifers (see Fig. 1) and the complex hydrogeological conditions in the study area. Therefore the classification of the types of hydrogeological environment (A–C) rather than the stratigraphic division was used in further studies. The chemical composition of groundwater is additionally presented in the Langelier–Ludwig diagram (Fig. 3).

Considerable variation can be observed with respect to the concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions within the A hydrogeological environment while a significantly lower variation is observed in the concentrations of these ions in the other hydrogeological environments (B and C). A significant percentage of observations demonstrate that elevated concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions are often accompanied by considerably elevated levels of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions, particularly in the A hydrogeological environment.

#### 4. METHODS AND RESULTS

To evaluate the distribution of analysed data, the statistical tests were used (Statistica ver. 10.0). The Chi-square and Kolmogorov–Smirnov tests with the Lilliefors correction as well as the Shapiro–Wilk tests were conducted for sets of results of physical and chemical analyses from all hydrogeological environments (A, B and C). Test results indicate that all

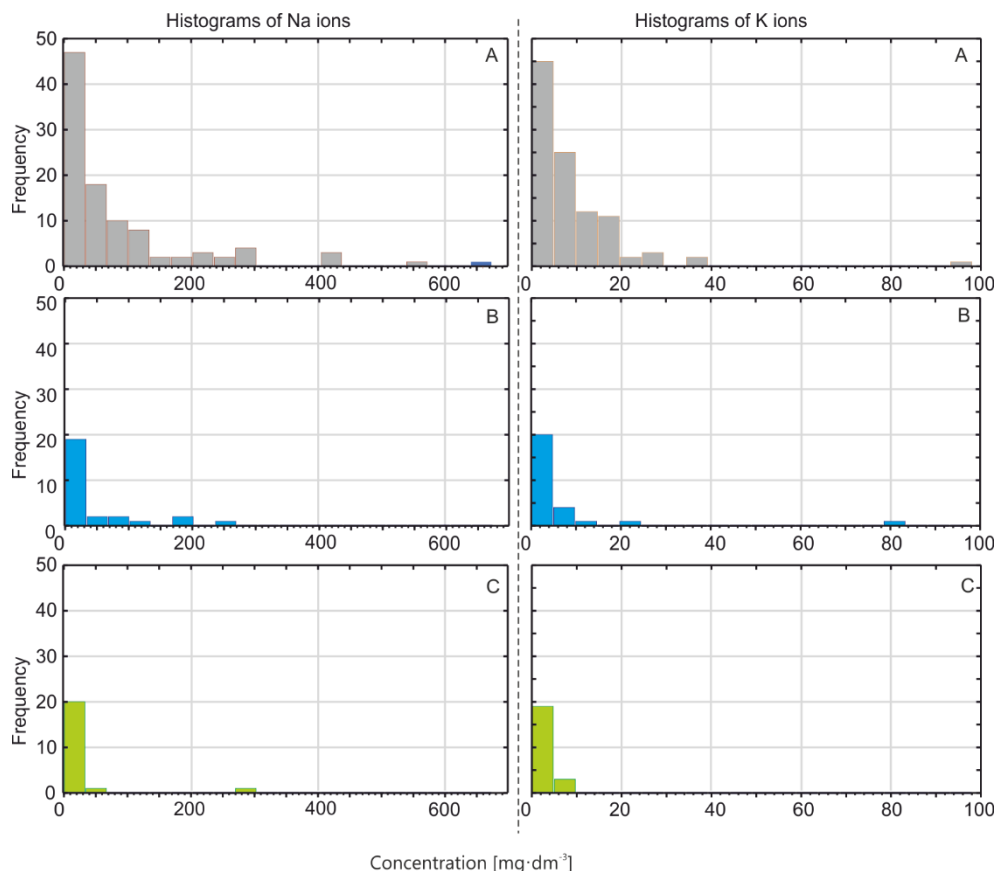


Fig. 4. Histograms for  $\text{Na}^+$  and  $\text{K}^+$  ions

data sets exhibit a distribution significantly deviating from a normal one at the level of significance adopted  $\alpha = 0.05$ . This is also clearly visible in the histograms presented (Fig. 4).

According to Reimann and Filzmoser [4], geochemical data sporadically exhibit a normal or near-normal (log-normal) distribution. Concentrations of  $\text{HCO}_3^-$  or  $\text{Ca}^{2+}$  ions as well as TDS are those parameters that exhibit a normal or near-normal distribution most frequently. However, no such case was observed for the data analysed. An attempt to normalise the distributions of the data analysed using generally applied logarithmic transformations failed.

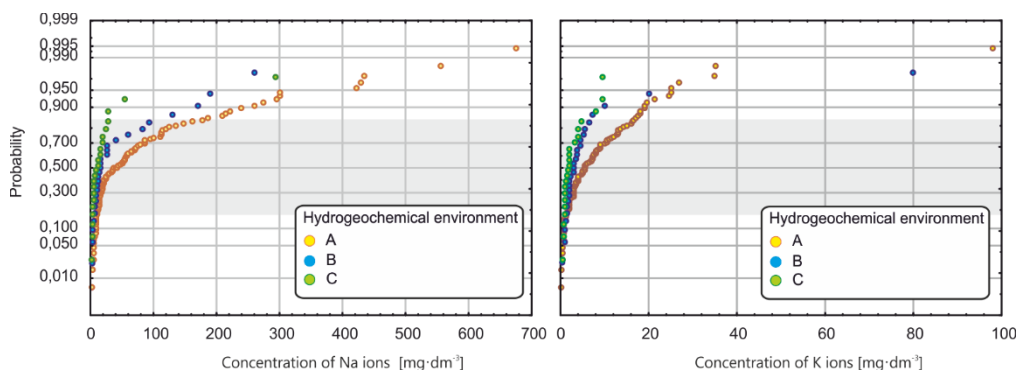


Fig. 5. Hydrogeochemical background of  $\text{Na}^+$  and  $\text{K}^+$  ions within the A, B and C hydrogeological environments

Taking the above observations into account when determining hydrogeochemical background values for  $\text{Na}^+$  and  $\text{K}^+$  ions in the selected hydrogeological environments, percentile values rather than standard deviation were used as a measure of dispersion. The probability of observations in which  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations correspond to values between the 16 and 84 percentiles is indicated by the grey area in Fig. 5. This range covers 68% of the data population and for a normal distribution, it is identical as the  $x_{av} \pm \sigma$  range using the standard deviation recommended [5]. Boundary values for  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations for the grey area in the figure determine the range of hydrogeochemical background values for these ions in the hydrogeological environments A–C.

For  $\text{Na}^+$  ions in the C hydrogeological environment, the upper background limit does not exceed  $40 \text{ mg}\cdot\text{dm}^{-3}$ , for the B environment it is approximately  $100 \text{ mg}\cdot\text{dm}^{-3}$ , and  $180 \text{ mg}\cdot\text{dm}^{-3}$  for the A environment. These wide background ranges for the A and B environments result from a large number of observations with very high concentrations of  $\text{Na}^+$  ions in the population analysed.

For  $\text{K}^+$  ions, the upper background limits are ca.  $16.6$  and  $5 \text{ mg}\cdot\text{dm}^{-3}$  for the A, B and C hydrogeological environments, respectively. This wide background range in the

An environment results from a large number of observations with very high concentrations of  $K^+$  ions in the population analysed.

The hydrogeochemical background ranges for  $Na^+$  and  $K^+$  ions observed in the study area were compared to the background ranges for these ions obtained by other authors for various major groundwater basins (MGBs) in Poland (Fig. 6). In order to make the figure more legible, the MGBs analysed were divided according to the dominant type of flow, analogously as in the classification of hydrogeological environment types adopted in this paper.

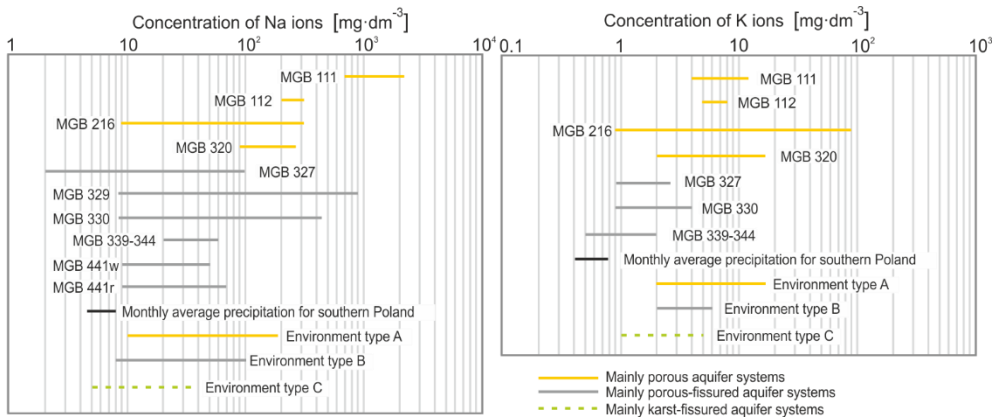


Fig. 6. Hydrogeochemical background of  $Na^+$  and  $K^+$  ions within the selected major groundwater basins in Poland (after Macioszczyk [6], modified)

The A, B and C hydrogeological environments selected include various MGBs present in the study area. 23 MGBs are present in Southern Poland (of which 8 basins in their entirety and 15 in part). The background ranges obtained for  $Na^+$  and  $K^+$  ions for all hydrogeological environments do not differ significantly from the background ranges for these ions for individual MGBs. It can be observed that  $Na^+$  ion background ranges are shifted relative to environments A–C.  $K^+$  ions reveal similar relationships, but these are not as clear as in the case of  $Na^+$  ions.

The  $Na^+/K^+$  hydrogeochemical ratio was analysed as well. The results of this analysis are presented in Fig. 7. According to Płochniewski and Bidzińska [7], the  $Na^+/K^+$  ratio in Pleistocene aquifers in the Polish Lowlands ranges from 0.2 to 0.9, while for groundwaters with high TDS it usually ranges from 30 to 200. Within the study area, in groundwaters from Pleistocene aquifers (the A environment) the  $Na^+/K^+$  did not exceed the 0.9 threshold in just 2 cases. Almost 88% of  $Na^+/K^+$  ratios were in the 0.9–30 range. This concerned both ordinary groundwaters and those with higher TDS ( $>1000 \text{ mg}\cdot\text{dm}^{-3}$ ). The remaining  $Na^+/K^+$  ratio measurements (8.4%) exceeded the 30 threshold. In the remaining hydrogeological environments (B and C), the 0.9 threshold for the  $Na^+/K^+$



ratio was exceeded in 92.6% and 95.2% of observations, respectively. On the other hand, the 30 threshold for the Na<sup>+</sup>/K<sup>+</sup> ratio was exceeded in 7.4% and 4.8% of observations, respectively. Apart from the outliers, the variabilities of the Na<sup>+</sup>/K<sup>+</sup> ratio in the A and B environments can be described as similar.

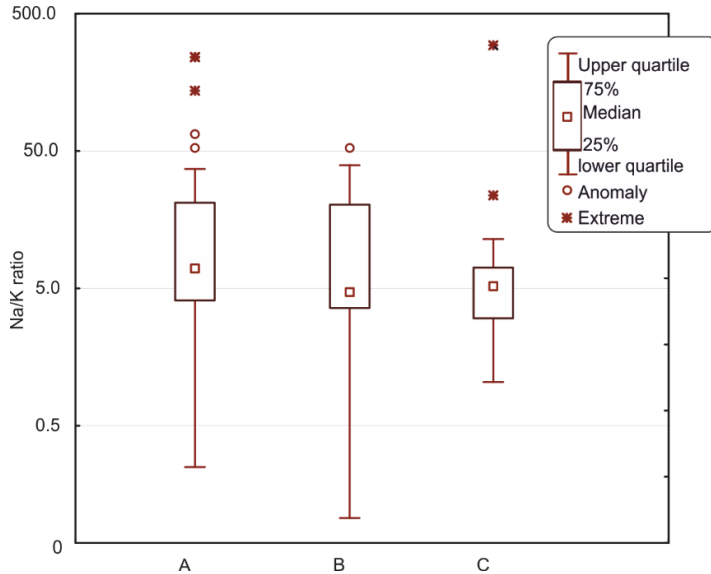


Fig. 7. Na<sup>+</sup>/K<sup>+</sup> ratios for various hydrogeochemical environments

The high values of the Na<sup>+</sup>/K<sup>+</sup> ratio, exceeding 30, observed in the study area are due to the considerable number of cases with high Na<sup>+</sup> ion concentrations (Figs. 4, 5). Such high Na<sup>+</sup>/K<sup>+</sup> ratios often indicate significant anthropogenic pollution associated with leaky sewerage systems or septic tanks [8] or leachate from landfills [9].

Table 1

Results of the Kruskal–Wallis test for Na<sup>+</sup> and K<sup>+</sup> ions ( $n = 150$ )

Dependent variable Type of hydrogeological environment	N of valid	Rank total	Rank average
Na <sup>+</sup> ions, $H = 19.17$ , $p = 0.0001$			
A	101	8644.5	85.59
B	27	1716	63.56
C	22	964.5	43.84
K <sup>+</sup> ions, $H = 13.78$ , $p = 0.0010$			
A	101	8493.5	84.09
B	27	1755.5	65.02
C	22	1076.0	48.91

Owing to the fact that the data analysed exhibit distribution deviating considerably from a normal one, non-parametric methods of statistical inference were used. The Kruskal–Wallis test was applied. This test is the non-parametric equivalent of one-way analysis of variance (ANOVA) and enables, *inter alia*, comparison of populations of various sizes. The interpretation of its result is based on the ranks calculated. The results of the Kruskal–Wallis test for the  $\text{Na}^+$  and  $\text{K}^+$  ions present in the three types of hydrogeological environments are shown in Table 1.

The value of the Kruskal–Wallis test ( $H$ ) and the level of probability ( $p$ ) allow us to reject the null hypothesis that assumes that there are no significant statistical differences between the variabilities of the concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions in different hydrogeological environments (Table 1). In other words, the variabilities of  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations for different hydrogeological environments (A, B and C) differ significantly in statistical terms.

The median test was also applied (Table 2). This is a less accurate version of the Kruskal–Wallis ANOVA test. This statistic tests the null hypothesis that all samples come from populations with identical medians.

Table 2

Median test for  $\text{Na}^+$  and  $\text{K}^+$  ions ( $n = 150$ )

Na <sup>+</sup> ions, overall median = 24.0, $\chi^2 = 9.67$ , $df = 2$ , $p = 0.0079$				
Median	A	B	C	Total
≤Observed	43.0	16.0	17.0	76.0
Expected	51.17	13.68	11.15	
Observed – expected	–8.17	2.32	5.85	
>Observed	58.0	11.0	5.0	74.0
Expected	49.83	13.32	10.85	
Observed – expected	8.17	–2.32	–5.85	
Total observed	101.0	27.0	22.0	150.0
K <sup>+</sup> ions, overall median = 4.0, $\chi^2 = 12.97$ , $df = 2$ , $p = 0.0015$				
≤Observed	44.0	18.0	18.0	80.0
Expected	53.87	14.4	11.73	
Observed – expected	–9.87	3.6	6.27	
>Observed	57.0	9.0	4.0	70.0
Expected	47.13	12.6	10.27	
Observed – expected	9.87	–3.6	–6.27	
Total observed	101.0	27.0	22.0	150.0

The results of the median test (with the probability  $p$  clearly below 0.05) indicate that the null hypothesis can be rejected (Table 2), since the median concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions differ. In other words, the hypothesis that concentration variabilities are the same (identical medians) for different hydrogeological environments is rejected. Additionally, an analysis of multiple (two-sided) comparisons was performed (Table 3).

This statistic consists of multiple comparisons of average ranks for each pair of groups. Column headers show average ranks ( $R$ ) for individual types of hydrogeological environments. For each comparison, post-hoc probabilities (adjusted for the number of comparisons) are calculated for two-sided significance tests.

Table 3

Multiple comparison test for Na<sup>+</sup> and K<sup>+</sup> ions ( $n = 150$ )

Hydrogeochemical environment (Na)	Probability $p = 0.0001$		
	A R: 85.59	B R: 63.56	C R: 43.84
A	–	0.0577	0.00013
B	0.0577	–	0.342
C	0.00013	0.342	–
Hydrogeochemical environment (K)	Probability $p = 0.001$		
	A R: 84.09	B R: 65.02	C R: 48.91
A	–	0.128	0.0017
B	0.128	–	0.590
C	0.0017	0.590	–

For these tests, we once again reject the null hypothesis ( $p = 0.0001$  for Na<sup>+</sup> ions and  $p = 0.001$  for K<sup>+</sup> ions) that there is no difference in the variability of Na<sup>+</sup> and K<sup>+</sup> ion concentrations in different types of hydrogeological environments. The analysis of the results indicates that a statistically significant difference in the variability of Na<sup>+</sup> and K<sup>+</sup> ion concentrations ( $p = 0.00013$  and  $p = 0.0017$ , respectively) is present between the A and C environments while the difference in the variability of Na<sup>+</sup> and K<sup>+</sup> ion concentrations between the remaining environments is statistically insignificant.

#### 4. CONCLUSIONS

Clearly elevated concentrations of Na<sup>+</sup> and K<sup>+</sup> ions can be observed in all hydrogeological environments, and particularly in the Pleistocene and Miocene aquifers (the A environment). In the remaining hydrogeological environments (B and C), the anomalously high concentrations of these ions observed are significantly lower and not as frequent. A considerable number of observations with clearly elevated, anomalous concentrations of Na<sup>+</sup> and K<sup>+</sup> ions significantly affect the upper limit of the range of hydrogeochemical background values for the A and B hydrogeological environments. On the other hand, when anomalous values are rejected, the hydrogeochemical background ranges obtained for Na<sup>+</sup> and K<sup>+</sup> ions for all hydrogeological environments do

not differ significantly from the backgrounds for these ions obtained by other authors for different aquifers in Poland.

Anomalous concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions frequently coincide with very high concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions. Given these observations, it can be assumed that anomalous concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions may be related both to the ascent of groundwaters with high TDS from deeper aquifers (e.g. in the area of Kraków) and to increased anthropogenic pollution. Human pressure is particularly relevant in the case of  $\text{K}^+$  ions, since the high content of these ions in groundwater most often indicates anthropogenic pollution. Significant anthropogenic pollution of groundwater in the area analysed has been confirmed by many years of observations. It should be pointed out that in the case of sandy aquifers, the inflow of groundwater with high concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  ions may result in approximately only 5% of the additional  $\text{Na}^+$  ion load remaining directly in groundwater. At the same time, the remaining  $\text{Na}^+$  ions are subject to the ion exchange processes (with  $\text{Ca}^{2+}$  ions) that occur within clay minerals [10]. Taking into account the geological structure of Miocene sediments (lagoon and shallow sea sediments), the highest concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions in the A environment are most likely related to the inflow of groundwaters with high caused by the dissolution of evaporates (i.e. gypsum).

The A hydrogeological environment exhibits the highest concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions and the largest number of observations of high concentrations of these ions. To a large extent, this stems from the manner in which the area where the aquifers are present has been developed; another factor is whether the aquifers are insulated by overlying sediments exhibiting low permeability. For instance, the Pleistocene aquifer in the Vistula River valley is completely devoid of any insulation in many places and contaminants from the surface can penetrate directly into the aquifer. This is confirmed by the analysis results of the  $\text{Na}^+/\text{K}^+$  hydrogeochemical ratio.

The application of the statistical analysis enabled the detection of general regularities present in the data set. All the statistical tests conducted make it possible to reject the null hypothesis that assumes no statistically significant differences between the variabilities of  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations in different hydrogeological environments. The results of multiple comparison tests indicate that a statistically significant difference in the variability of  $\text{Na}^+$  and  $\text{K}^+$  ion concentrations is present between the A and C environments. The factors responsible for this difference are lithological variability and different groundwater circulation systems. The C environment is built of solid carbonate rocks where groundwater flows mainly through fractures while the A environment consists of clastic rocks where groundwater flows primarily through pores. This lithological variability significantly affects the geochemical properties of the rock matrix of the aquifers and thus determines the concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions. The type of groundwater flow (through pores or fractures) is also relevant for the infiltration of water from the surface or the inflow of groundwater from deeper aquifers. In other words, the type

of flow determines the conditions for groundwater circulation and affects the concentrations of Na<sup>+</sup> and K<sup>+</sup> ions.

As concerns the comparison between the A and B hydrogeological environments, no statistically significant difference in the variability of Na<sup>+</sup> and K<sup>+</sup> ions was found. This results mainly from the similar lithologies and types of flow in both environments. The A and B environments consist mainly of clastic rocks (both solid and non-cohesive ones) where groundwater flows mainly through pores (and locally through fractures and pores). It is probably these factors that result in the absence of statistically significant differences in the variability of Na<sup>+</sup> and K<sup>+</sup> ions in these environments. Apart from anomalous values, the lack of difference between the variabilities of Na<sup>+</sup> and K<sup>+</sup> ions in the A and B environments is indirectly indicated by the results of analyses of the Na<sup>+</sup>/K<sup>+</sup> ratio.

It should however be stressed that the application of statistical methods alone does not enable all the processes that shape the chemical composition of groundwater to be detected and identified. For instance, it is difficult to distinguish between geogenic and anthropogenic sources of SO<sub>4</sub><sup>2-</sup> ions which often coincide in high concentrations with the Na<sup>+</sup> and K<sup>+</sup> ions, without performing isotope tests. Therefore the results obtained should be treated as approximate mainly due to the highly variable hydrogeological and geochemical conditions as well as the large study area.

In many cases, the concentration of Na<sup>+</sup> ions permissible in the case of drinking water is exceeded. Where the permissible thresholds are exceeded on a long-term basis for municipal groundwater intakes, this may result in the need for additional, expensive water treatment. In extreme cases, this may even cause an intake to be permanently or temporarily decommissioned. On the other hand, in the case of individual intakes (wells) the inflow or presence of groundwater with the permissible sodium content exceeded constitutes a significant threat to water quality.

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