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## DIVERSIFICATION OF MAIN ION CONCENTRATION IN UNDERGROUND WATERS, BASED ON ION DISTRIBUTION TYPE

The influence of ion distribution type on diversification of the main ion concentrations expressed as mean and median values in underground waters is presented. The following ions:  $\text{HCO}_3$ ,  $\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{Fe}$ ,  $\text{Mn}$ ,  $\text{NH}_4$ ,  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{NO}_2$  and  $\text{NO}_3$  have been analysed in underground water occurring in water-bearing layers of Quaternary, Miocene, Paleogene, Cretaceous of flysch and Nida, Jurassic and Triassic found in the area of Lesser Poland voivodeship. Low difference values, from several to over a dozen per cent, exist for  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{HCO}_3$  ions and a total mineralization of Cenozoic waters as well as for  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{K}$ ,  $\text{HCO}_3$  ions and a total mineralization of Mesozoic waters. Depending on the expression of general ion values in the form of mean or median value, the hydro-chemical water type has changed in some waters.

### 1. INTRODUCTION

Popular, shortened forms of presenting chemical contents of underground waters, such as the Udluft graphs or the Kurłow formulas [1]–[5], used in hydro-chemical analysis require the definition of a representative average value in the case of determining the quota of chemical contents (ions) in the selected area, tectonic unit, level or water-bearing layer. Analyzing over a dozen of research results and determining one representative value of particular chemical contents of underground waters in terms of a distribution type, the mean value or the median value of results can be calculated. The mean value is recommended [7] in the case of normal distributions or distributions similar to them, and the median value – in the case of the asymmetric ones. The aim of our research was to determine the ionic content of underground waters occurring in rock layers diversified both stratigraphically and lithologically in the area of Lesser Poland voivodeship.

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## 2. METHODS

### 2.1. AREA CHARACTERISTICS

Lesser Poland voivodeship is located in southern part of Poland and consists of 19 land districts, 3 magistrate districts and 182 communes. These districts are as follows: Olkusz, Chrzanów, Oświęcim, Miechowice, Proszowice, Kraków, the city of Kraków, Wadowice, Sucha Beskidzka, Myślenice, Wieliczka, Bochnia, Brzeg, Dąbrowa, Tarnów, the city of Tarnów, Limanowa, Nowy Sącz, the city of Nowy Sącz, Gorlice, Nowy Targ and Tatra.

Based on morphological characteristics the area of the voivodeship can be divided into the following units: the Śląsk-Kraków Uplands, the Miechowice Uplands, the Proszowice Plateau, the Oświęcim Valley, the Kraków Gate, the Sandomierz Valley, the Wieliczka Foothills, the Beskids, the Pieniny Rock Belt, the Podhale Valley and the Tatra Mountains.

From a geological point of view, within the limits of Lesser Poland voivodeship approximately 80% of over 15,000 sq. km are covered by the structures connected with the Carpathian Arc and its foreground, which consist of the Inner Carpathians, the Pieniny Rock Belt and the Outer Carpathians. In the middle part of the voivodeship, the Carpathians border on the Forecarpathian Cavity from the north, and further in north direction there are Mesozoic structures: the Miechowice Basin and the Silesian-Cracovian Monocline as well as Paleozoic structure: the Upper Silesian Cavity, partly covered with Miocene sediments of the Forecarpathian Cavity [6]. Stratigraphically, the underground Oligocene waters are connected with flysch structures of the Outer Carpathians; the waters of the Upper Cretaceous and Paleogene – with flysch of Outer Carpathians; the Miocene waters – with the Forecarpathian Cavity; the Cretaceous Nida waters – with the Miechowice Basin; the Jurassic and Triassic waters – with Silesian-Cracovian Monocline; and the Permian, Carboniferous and Devonian waters – with the Upper-Silesian Cavity.

### 2.2. METHODOLOGY OF RESEARCH

Archival geological material used in the elaboration has been shared by the Carpathian Station of National Geological Institute with its seat in Kraków. It was an electronic form of data collected in the Regional Bank of Hydro-geological Data "Hydro" PIG. This material includes, among others, the results of extended chemical analyses of the samples of underground water taken during test pumping from 346 drilled wells, made and exploited in the area of Lesser Poland voivodeship over the period of 1950–2004.

The material of interest comprises the concentrations of such ions as: bicarbonates, sulfates, chlorides, calcium, magnesium, sodium, potassium, iron, manganese, nitrates,

nitrites and ammonium nitrogen. These results have been classified, depending on the age of the waters taken. The Quaternary waters (Holocene and Pleistocene together), Miocene, Paleogene of outer and inner flysch (Oligocene), flysch Cretaceous, Nida Cretaceous, Jurassic, Triassic, Permian, Carboniferous and Devonian have been separated. Because of a small number of analyses (to 6) the Oligocene and Paleozoic waters have not been analyzed thoroughly.

Determining a chemical content of waters that contained only alkaline cations, a missing sodium ion concentration is calculated [5] using the following dependence:

$$rNa^+ = \Sigma rA - (rCa^{2+} + rMg^{2+}) \quad (1)$$

determined based on:

$$\Sigma rA = \Sigma rK, \quad (2)$$

where:

A – anions, K – cations, r – cations and anions calculated as mval·dm<sup>-3</sup>.

Formula (2) has been used to verify the correctness of chemical analyses. It enables the conversion of ion concentration from weight form (mg dm<sup>-3</sup>) to equivalent form (mval·dm<sup>-3</sup>) [3], [4], which has been used after converting it to per cent share (mval·dm<sup>-3</sup>). This share can be used for the Kurlow formula or the Udluft graph [5], taking both anion and cation concentrations as 100%. If the equivalent cation sum has not been equal to anion sum, then the correction was made in order to eliminate this difference. In the first series of calculations, the mean value for each ion has been determined. In the second series, the distribution of a given ion has been analysed. If the distribution has been normal or similar (lognormal, for example), then the mean value can be calculated, and if it has been asymmetrical (exponential or other), the median value is calculated. Summing up all average concentrations of the ions tested, i.e. bicarbonates, sulfates, chlorides, nitrates, nitrites, calcium, magnesium, sodium, potassium, iron, manganese and ammonium nitrogen, both in the form of the mean value alone, or the mean value and the median value, the value of dry mineral residual has been obtained, being the so-called total mineralization of water. Comparing the ionic chemical content and mineralization of underground waters, expressed by the mean value alone, of the stratigraphically determined water-bearing level with ionic chemical content and mineralization of the same waters expressed, depending on the distribution type, by mean value or median value, the diversification of ion concentrations and total mineralization have been determined as a percentage value.

The distributions of the cations and anions present in waters of various age have been determined using Statistica program. The concentration frequency of each ion is represented by a histogram, and the hypothesis regarding the distribution type has been tested. We have checked that the distributions obtained follow the normal distribution, using the Shapiro–Wilk test. The other distributions, i.e. exponential or log-

normal, have been checked based on  $\chi^2$  test [7], [8]. If the test of goodness of fit is in conformity with a theoretical distribution, a graph of hypothetical density function is plotted along with the histogram. If no conformity with any of typical distributions has been obtained, only its asymmetry is defined.

### 2.3. RESULTS AND THEIR DISCUSSION

346 water samples taken from drilled wells were analysed. In 99 cases, the wells have underground Quaternary waters; in 40, Miocene waters; in 22, Paleogene waters; in 45, Nida Cretaceous; in 26, flysch Cretaceous; in 92, Jurassic waters and in 22, Triassic waters. The concentrations of such ions as: bicarbonates, sulfates, chlorides, nitrates, nitrites, calcium, magnesium, sodium, potassium and ammonium nitrogen were determined. These concentrations, expressed by weight for underground waters of defined age, are given in tables 1 and 2 in two columns in the form of mean value and median value. In the third column, there is a difference in the concentration values of mean value and median value of particular ions expressed as a percentage.

The resulting differences in ion concentration per cent in underground waters in the area of Lesser Poland voivodeship, expressed in the form of the mean value and the median value depending on the distribution type, are quite substantial and vary in the range from 0.76% in the case of nitrite ions in Paleogene waters to 4012.8%, also in the case of nitrite ions in Jurassic waters. In the prevailing number of cases, the ion concentrations expressed by the mean value have been higher than the ion concentrations expressed by the median value (except bicarbonate ions of Quaternary waters, calcium in Miocene waters, calcium, magnesium and potassium in Paleogene waters, sodium and potassium in Nida Cretaceous waters, calcium, magnesium and potassium in Jurassic waters and bicarbonates in Triassic waters). In Quaternary waters, the biggest difference of 905.4% was observed in the concentration of nitrites, and the slightest one of 1.42% – in the concentration of bicarbonates. In Miocene waters, the biggest difference of 820.55% was revealed in manganese, and the slightest one of 2.4% in the nitrite concentration; in Paleogene waters, the biggest difference of 835.26% was noticed in the ammonium nitrogen and the slightest one of 0.76% in the concentration of nitrites, in chalk of flysch the biggest difference of 482.39% concerned the concentration of nitrites, and the slightest one of 2.89% the concentration of calcium and magnesium, in Cretaceous of Nida the biggest difference of 1929.5% was observed in nitrites and the slightest one of 2.64% in ammonium nitrogen and manganese. In Jurassic waters, the biggest difference of 4012.79% was in nitrites and the slightest one of 1.35% in bicarbonates, and in Triassic waters the biggest difference of 938.38% was revealed in ammonium nitrogen and the slightest one of 3.84% in calcium, magnesium and potassium.





The biggest difference in the concentrations of calcium ions in the form of mean value and median value being 9.9% occurred in Quaternary waters and the slightest one of 2.89% in the Cretaceous of flysch waters, in the case of magnesium ion the biggest difference of 24.99% occurred in Miocene waters and the slightest of 2.89% in the Cretaceous of flysch waters. For sodium ions the biggest difference of 275.38% occurred in Quaternary waters and the slightest one of 2.64% in the Cretaceous of Nida waters. Potassium had the biggest concentration difference of 797.53% in Miocene waters and the slightest one of 2.64% in the Cretaceous of Nida waters. Iron had the biggest difference of 308.72% in the Cretaceous of flysch waters, and the slightest one of 20.7% in Miocene waters, while manganese had the biggest concentration difference of 835.26% in Paleogene waters and the slightest one of 2.64% in Nida Cretaceous waters. Ammonium nitrogen reached the biggest concentration difference of 1841.87% in Jurassic waters and the slightest one of 2.64% in the Cretaceous of Nida waters, bicarbonates had the biggest concentration difference of 12.51% in the Cretaceous of flysch waters and the slightest one of 1.35% in Jurassic waters. Sulfates had the biggest concentration difference of 82.05% in Miocene waters, and the slightest one of 2.68% in the Cretaceous of Nida waters. Chlorides had the biggest concentration difference of 159.80% in Quaternary waters, and the slightest one of 3.08% in Jurassic waters. In nitrates, the biggest concentration difference of 550.81% was noted in Quaternary waters and the slightest one of 25.31 in Jurassic waters. Nitrites had the biggest concentration difference of 4012.79% in Jurassic waters and the slightest one of 0.76 in Paleogene waters. A total mineralization reached the biggest concentration difference of 25.33% between the mean value and the median value in Quaternary waters and the slightest one of 2.23% in Jurassic waters. Thus, in Quaternary waters, there was observed the biggest concentration differences of total mineralization and of Ca, Na, Cl and NO<sub>3</sub> ions, in Miocene waters – of Mg, K, Mn and SO<sub>4</sub> ions, in the Cretaceous of flysch waters – of Fe and HCO<sub>3</sub> ions, in Jurassic waters – of Mn and NH<sub>4</sub> ions. In Paleogene waters, the Cretaceous of Nida waters and Triassic waters, we did not observe any biggest concentration differences in all ions.

### 3. SUMMARY

A thorough analysis of the percentage difference in ion concentration and mineralization of underground waters related to the rocks from Quaternary, Miocene, Paleogene, Cretaceous of flysch and Nida, Jurassic and Triassic periods, i.e. Cenozoic and Mesozoic eras, presented in the form of the mean value and the median value, indicates its substantial dispersion in the range from 0.76 to 4012.79%. Small differences of several or over a dozen per cent exist in Ca, Mg, HCO<sub>3</sub> ion concentration and in the total mineralization of Cenozoic waters and Ca, Mg, K, HCO<sub>3</sub> ions and in the total mineralization of Mesozoic waters. The chemical components of underground waters occur in the highest concentrations and influence, to the great-

est extent, the hydro-chemical content of the waters tested. Thus, an insignificant difference between the mean value and the median value only slightly influences the assumed values of generalized ion concentration and the total mineralization calculated on the basis of these values. A total mineralization is only slightly affected by the difference between the mean value and the median value, which is proved by a slight difference between the total mineralization expressed as the mean value and the median value ranging from 2.23 to 25.33%.

Depending on whether generalized values of ions are expressed in the form of the mean value or the median value, the hydro-chemical type of water can change. This is especially evident in the case of the Paleogene waters, whose mean value is associated with the  $\text{HCO}_3\text{-Ca-Mg-Na}$  water type, and the median value with  $\text{HCO}_3\text{-Ca-Mg}$  water type. In Cretaceous flysch, the mean value is associated with  $\text{HCO}_3\text{-Ca}$  and the median value with  $\text{HCO}_3\text{-Ca-Mg}$ , while in Triassic waters, the mean value is connected with  $\text{HCO}_3\text{-SO}_4\text{-Ca-Mg}$ , and the median value with  $\text{HCO}_3\text{-Ca-Mg}$ . For other stratigraphic types of underground waters the hydro-chemical water types are the same, regardless of what value has been used.

In the case of presenting a ionic chemical content of water in a shortened form, e.g. the Udluft graph, it will be reasonable to show it in the form of the mean value exclusively, because the analysis performed indicates that the biggest differences expressed as percentage values are observed for ions that occur in small amounts in water and while expressed in % mvals per cubic dm, their proportion very seldom is higher than 1%  $\text{mval dm}^{-3}$ .

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**ZRÓŻNICOWANIE STĘŻEŃ GŁÓWNYCH JONÓW  
WYSTĘPUJĄCYCH W WODACH PODZIEMNYCH W ZALEŻNOŚCI OD TYPU ROZKŁADÓW**

Przedstawiono wpływ typu rozkładów na procentowe zróżnicowanie w stężeniach głównych jonów wód podziemnych. Te jony to  $\text{HCO}_3$ ,  $\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{Fe}$ ,  $\text{Mn}$ ,  $\text{NH}_4$ ,  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{NO}_2$  i  $\text{NO}_3$ , których stężenia wyrażono w postaci wartości średniej i mediany. Główne jony były związane z ujętymi wodami podziemnymi pochodzącyymi z wodonośnych warstw czwartorzędowych, mioceńskich, paleogeńskich, kredy flisz i Nidy, jurajskich i triasowych, a występującymi w województwie małopolskim. Małe wartości różnicy rzędu kilku lub kilkunastu procent występują przy jonach  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{HCO}_3$  i mineralizacji ogólnej wód kenozoicznych oraz jonach  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{K}$ ,  $\text{HCO}_3$  i mineralizacji ogólnej wód mezozoicznych. W zależności od tego, czy uogólnione wartości jonów były wyrażone w postaci średniej czy mediany, w przypadku niektórych wód zmieniał się ich typ hydrochemiczny.