DOI: 10.2428/ecea.2018.25(2)16 ECOL CHEM ENG A. 2018;25(2):197-205

Beata MALCZEWSKA[1*], Stanisław CZABAN[1]
and Bartosz JAWECKI[2]

CHANGES IN THE PHYSICO-CHEMICAL QUALITY OF DRINKING WATER FROM WELLS IN SELECTED RURAL HOUSEHOLDS

ZMIANY WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH WODY ZE STUDNI W WYBRANYCH WIEJSKICH GOSPODARSTWACH DOMOWYCH

Abstract: Presented research concerned on the quality of drinking water from private-supply wells in selected locality in a households in the close vicinity to copper ore tailings facility. Groundwater quality and its suitability for drinking purpose were examined by various physico-chemical parameters such as: pH, electrical conductivity, total hardness, calcium, magnesium, sodium, potassium, sulfate, chloride and total dissolved substances. These parameters were used to assess the suitability of groundwater for domestic purpose. In some of the collected samples, the concentrations of these parameters exceed the permissible limits, but overall concentrations of major ions (calcium, magnesium, sodium, potassium) as well as the values of the parameters: pH, temperature, hardness do not exceed the values recommended by Polish standard relating to drinking water. At the same time evaluated water characterized by the low mineralization therefore it can not be recommended for drinking purpose.

Keywords: macroelements, drinking water, well water, water quality, major constituents of water

Introduction

Drinking water from various water intakes contains many minerals, among which macroelements are of great importance. The human body, in order to function correctly, needs not just water but also substances dissolved in it. Mineral substances dissolved in water can be divided into two major categories: main components (macronutrients – macroelements), secondary components and microelements (microcomponents). Macronutrients such as sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{2+}) and magnesium (Mg^{2+})

[1] Institute of Environmental Engineering, Wroclaw University of Environmental and Life Sciences, pl. Grunwaldzki 24, 50-363 Wroclaw, Poland, phone: +48 71 320 66 65, email: beata.malczewska@upwr.edu.pl, Stanislaw.czaban@upwr.edu.pl, bartosz.jawecki@upwr.edu.pl

* Corresponding author: beata.malczewska@upwr.edu.pl

as well as anions e.g. (Cl^-) and (SO_4^{2-}) are essential to human life. Sodium, calcium and magnesium deficiencies can be supplemented by drinking water, but potassium is seldom find in natural water [1–3]. In case of magnesium (Mg^{2+}) and calcium (Ca^{2+}), they occur naturally in water since they are quite common alkaline-earth metals. Their concentration can be correlated with the type of land use in the catchment areas [1, 4, 5]. Calcium and manganese can be present in the environment in exceeded concentration as an effect of anthropogenic impact, e.g. they can originated from mines [6]. The magnesium compounds are usually predominant in natural waters and the recommended magnesium concentration in drinking water is between 30 and 125 mg · dm^{-3}. At the same time, calcium concentration is not standardized [5]. Both metals in water determines its hardness. In Poland in accordance with applicable law, the hardness of water intended for human consumption must be within 60 and 500 mg$CaCO_3$ · dm^{-3} [2, 7]. Calcium and magnesium salts enter the water as a result of carbon dioxide contained in the water contact with soil and rocks containing limestone and magnesite. Then limestone and magnesite, which are hardly soluble in water, turn into water-soluble bicarbonates of calcium and magnesium [2]. The hardness can be divided into two main categories: carbonate hardness (transient, perishable) – which is generated by bicarbonates and non-carbonate hardness (persistent) that is generated by the salts of other acids, mainly chlorides, but also sulphates, nitrates and others [8].

Chlorine and sulfate ions are commonly found in natural water as well. Their concentration vary depending on the catchment areas. And their presence especially chlorine in surface waters may results as an uncontrolled discharges from mines [9]. The EPA Secondary Drinking Water Regulations recommend the maximum concentration of 250 mg · dm^{-3} for chloride ions and 250 mg · dm^{-3} for sulfate ions (expressed as Cl^- and SO_4^{2-}, not as $CaCO_3$) [10]. Polish standards with respect to limit ranges for chloride and sulfate ions values are the same [7].

The transformation of groundwater chemical composition is impacted by the pH and the redox potential. The pH value, water hardness and other elements have a direct impact on maintaining the ecological balance in water. Polish regulations for permissible ranges of pH values specify the value of 6.5–9.5 [7]. And this parameter should be taken into account when assessing the aggressive corrosive properties of water.

Total dissolved substances (TDS) usually describes the presence of salt from sulfate sodium potassium magnesium and other cations. This parameter allows to assess the overall salinity of water. The dissolved substances in inland waterways should not exceed 1200 mg · dm^{-3}. The permitted concentration of dissolved substances in drinking water and commercial water is 800 mg · dm^{-3} [11].

The water provided by the waterworks is under permanent control. However its quality my by affected by many factors, for example raw water (soil, basin), water treatment techniques (sedimentation, filtration, disinfection), network (materials, biofilm), and use (flow) [1]. In the face of diminishing drinkable water resources and increasing demand for it, research on its quality and efficient way of treatment is being carried out. The natural environment's resources, including private-supply well should be also taken into account. Increasing the charges for water use may inadvertently incentivize the consumers to reuse the wells that are no longer in use. And since such water is not subject to continuous monitoring it may pose a significant risk to users.

The main objective of this paper is the description of changes in chemical composition of the Quaternary aquifer in private-supply well located in close vicinity of the cooper tailings ponds.

Study area

The study presents the results of investigation carried out between 1999 and 2015 (with the frequency of two years) in region of the LGOM area (Lubin, Polkowice, and Glogow districts) in Lower Silesia, Poland. This is an area where the tailing pond Zelazny Most and its wastes from copper ore mines is located, that covers an area of about 1,400 ha, and the volume of waste stored in it is ca. 500 mln m^3 [12]. Samples were randomly collected from 11 location (Bytkow, Dabrowa, Grodowiec, Grodziszcze, Juszowice, Komorniki, Krzydlowice, Rudna, Rynarcice, Tarnowek and Zelazny Most) and analyzed in accordance with the analytical reference method and under the regulation of the Polish Minister of Health (13.11.2015) on the quality of water intended for human consumption (Dz.U. 2015 poz. 1989).

Sampling points have been selected to include the whole area analyzed (Fig. 1). The drinking water is fed by the waterworks into the distribution network in this area. But

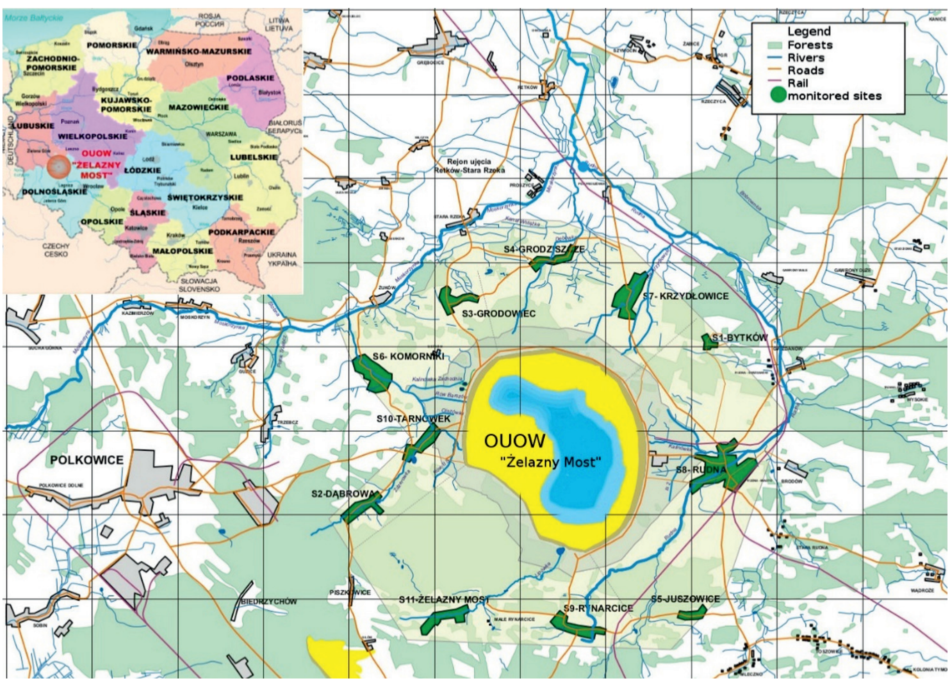

Fig. 1. Location of sampling sites in the study area

despite the development of water supply infrastructure in rural areas, households continue to use an additional water sources such as shallow wells.

The results were statistically evaluated in the Statistica 12.5. The median and range of variability of the tested parameters were determined. The measurements of the central trend (median, average) and variability (e.g. quartiles, standard error or standard deviation) are calculated for each observation group and their values are visualized in box-and-whisker graphs (Fig. 2). In order to confirm which factor determines the dynamics of evaluated quality parameters, the regression analysis was also performed.

Results and discussion

The behavior of major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3, SO_4^{2-}, Cl^{-}) and other organoleptic and physico-chemical parameters such as pH, electrical conductivity (*EC*), total dissolved solids (TDS), and total hardness (TH) in the study area are discussed below. The visualization of data is presented on a box-and-whisker graphs (Fig. 2), where the median (middle quartile) marks the mid-point of the data and is shown by the square, and the upper and lower whiskers represent minimal and maximal value of the data

Figure 2 presents distribution of ions where standard error bars is a line through a point on a graph, parallel to one of the axes, which represents the uncertainty or variation of the corresponding coordinate of the point. The range and standard deviation (*SD*) are used for descriptive error bars the data are spread.

Analyses of water samples carried out for private-supply wells showed that, there is a significant discrepancy in the data. An increased amount of chlorine ions has been reported. The median concentrations of chloride, evaluated in this study ranged from 2.70 and 376.0 mg · dm^{-3}. The maximum concentration of the chlorine ion was recorded in well S11 and it was 376.0 mg · dm^{-3}, and the lowest value was observed for S4 well and it was 2.70 mg · dm^{-3}. The average values of the chlorine ions was 38.84 mg · dm^{-3}. Sapek et al. [13] reported that the most common source of chlorides were natural fertilizers stored in farms. However, only the organoleptic and physicochemical parameters have been taken into account in this study and therefore this observation cannot be verified.

The average pH values of groundwater range from 5.82 to 9.78 with the annual average value of 7.48. This shows that the groundwater of the study area is neutral in nature on average. But the values of pH were found to be significantly scattered. The lowest value of the pH has been recorded for S7 well and the higher one for the S11 well.

Significant differences in conductivity values were also observed in the analyzed private-supply wells water. Values recorded during the surveys for conductivity were from 0.027 to 73.3 with an average of 0.84 and are below the range foreseen for the natural waters (100 – 1000 μS · cm^{-1}) as well as for drinking water (2500 μS · cm^{-1}).

The concentrations of calcium was found to be between 2.48 (for the S7 well) and 1948 mg · dm^{-3} (for S6 well) with an average of 87.30 mg · dm^{-3}, as for the magnesium concentration, the maximum concentration of the Mg^{2+} ion was recorded in well S12

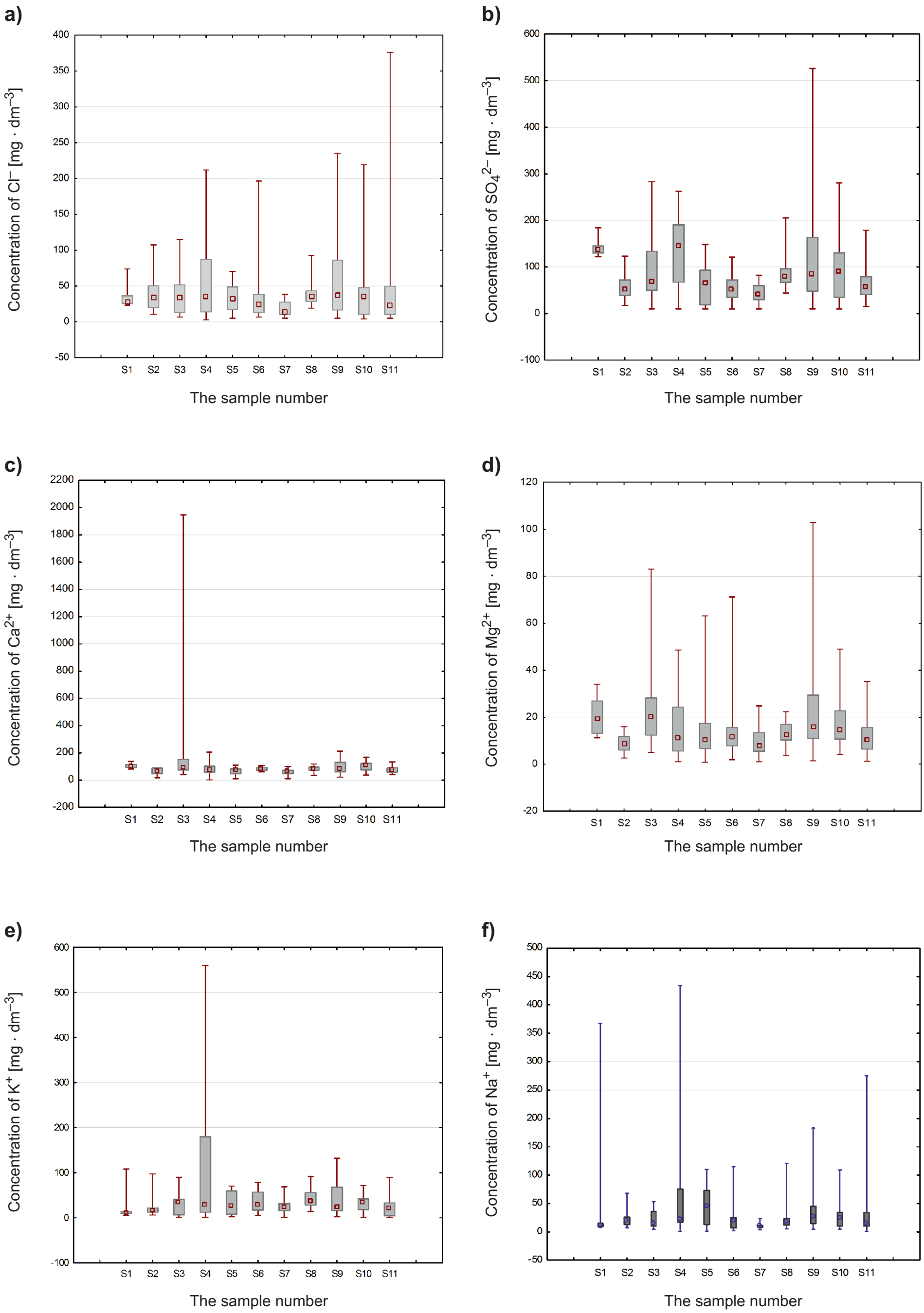

Fig. 2. The visualization of the distribution of the evaluated ions concentration a) Cl^-, b) SO_4^{2-}, c) Ca^{2+}, d) Mg^{2+}, e) K^+, f) Na^+ in groundwater for the study area

and it was 103 mg · dm^{-3}, and the lowest value was observed for S8 well and it was 0.9 mg · dm^{-3}. The average values of the Mg^{2+} in analyzed wells was 15.39 mg · dm^{-3}. Compared to the applicable standard (30–125 mg · dm^{-3}), the analyzed water can be described as magnesium-poor. Although most of the samples had concentrations below limits, but their concentration is significantly spread out from the mean value for each tested well. Neither WHO nor Polish guidelines did not specify a permissible limit for calcium in drinking water.

Sodium concentration in groundwater samples ranges from 0.70 to 434.0 mg · dm^{-3} with an average of 27.79 mg · dm^{-3}. According to WHO (2011) guidelines, the maximum admissible limit is 200 mg · dm^{-3} [1]. Groundwater samples of all samples show concentration of Na^{+} lower than the permissible limit. Sodium concentration in the analyzed samples was also low (in relation to values standard 200 mg · dm^{-3}) and ranged from 6.60 to 434 mg · dm^{-3}.

Potassium concentrations are relatively low with values varying between 1.0 and 560.0 mg · dm^{-3}. The annual average concentration of potassium ions exceeds 37.65 mg · dm^{-3}. Potassium ions content in groundwater samples are lower than recommended values [14].

There were significant variations ($p < 0.05$) in total hardness of all water sources with concentration in shallow ground waters ranged from 107.2 to 682.3 mg · m^{-3} (the weighted mean of 15.18 mg · m^{-3}).

Average sulfate concentrations in analyzed water samples were in the following range: between 10.0 and 526.0 mg · dm^{-3}. There was a significant variations in minimum values, which ranged from 10.0 to 122 mg · dm^{-3}. Highest concentration values of sulphates varied between 82.3 and 526.0 mg · dm^{-3}.

On average the ion concentration was within the legally determined standard, but in an individual cases it has been exceeded. At the same time, the analyzed ion concentration were characterized by a large variation of concentrations.

Additionally, the Principal component analysis (PCA) so called multivariate statistical analysis was implemented in order to obtain the graphical representation of high-dimensional data sets.

Some studies have proven that multivariate analysis help to identify the factors contributing to the environmental pollution [15]. Figure 3 shows plot of variables and distribution of components in analyzed water samples. Each of the variables is represented in Fig. 3 as a vector. The direction and length of the vector determines the extent to which each variable influences the individual main components. Such vectors are called loadings. When two of variables are located close to each other on the graph, it means that they are strongly positively correlated with each other (e.g. variables Na and Cl). When variables are orthogonal to each other, this means that there is no correlation (e.g. pH and Ca). There are not strongly negatively correlated variables since they are not located on the opposite side.

The piper diagram is a visualization of the chemistry of water sample. According to Przybysz [13] 67 % of Poland's territory is medium-hard water, 25 % soft water and hard water about 8 %.

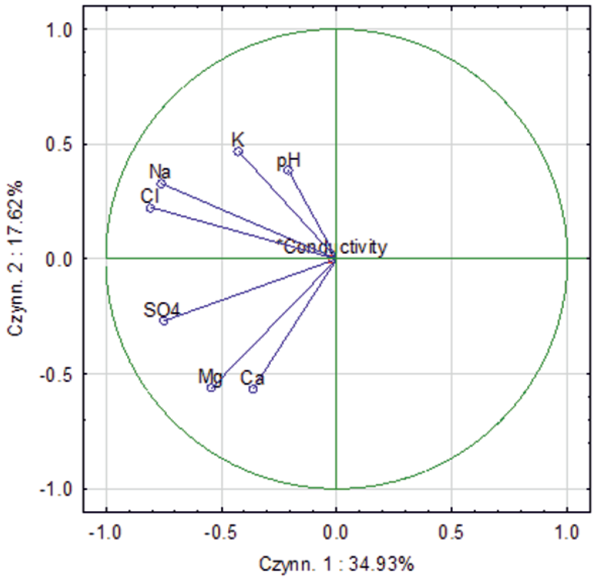

Fig. 3. Plot of variables. Location of load vectors towards two principal components

All samples from this study are relatively high in sulfate, as indicated by their locations on a Piper diagram (Fig. 4). Due to concentration of cations and anions the evaluated sample of water might be classified as Sulphate type. At the same time, Krasny and Sharp [17] reported that the dominant ions in groundwater are bicarbonate

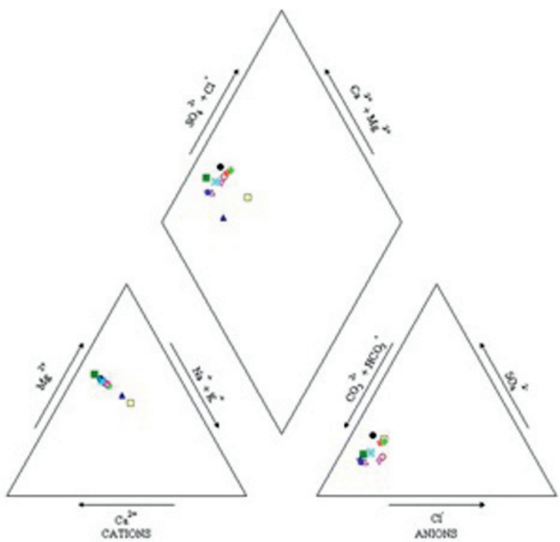

Fig. 4. Piper diagram of the ionic composition of studied samples

and calcium and that the decrease in dissolved solids concentration and pH might be the result of rain contamination.

Comparisons with standards for drinking water, indicate that the private-supply wells water in the studied area are not suitable for drinking purposes. However, further studies should be conducted, as the demands on the quality of water intended for human consumption is determined not only by the allowable amount of macronutrients in water, but also the presence of microorganisms and parasites and chemical substances in quantities that threaten the humans health.

Conclusions

Assessing the content of selected parameters suggests that the evaluated water is not suitable for drinking purpose. There are cases where the limit value is exceeded and where ions concentration is below limits. The chemical composition of groundwater is changing in every sampling year. This indicate the needs to monitor the water for future chemical status change.

The conducted statistical analysis does not allow to classify the tested water as drinkable. It is proposed that additional tests should be carried out at increased frequency. In addition, it is recommended to extend the study to other parameters that determine the chemical and microbiological requirements applicable to water intended for human consumption.

References

[1] WHO. Guidelines for drinking-water quality. Recommendations, 2nd edition. Geneva: WHO; 1993. https://www.who.int/water_sanitation_health/publications/gdwq2v1/en/

[2] Ingegerd Rosborg I, Nihlgĺrd B, Ferrante M. Mineral Composition of Drinking Water and Daily Uptake, Drinking Water Minerals and Mineral Balance. Cham: Springer International Publishing; 2015. ISBN 978-3-319-09592-9.

[3] Raczuk J, Królak E, Biardzka E. Percentage of drinking water in estimated average requirement for calcium and magnesium of youth and adults. Probl Hig Epidemiol. 2015;96(2):529-533.

[4] Potasznik A, Szymczyk S. Magnesium and calcium concentrations in the surface water and bottom deposits of a river-lake system. J Elem. 2015;20(3):677-692. DOI: 10.5601/jelem.2015.20.1.788.

[5] Goncharuk VV. Drinking Water: Physics, Chemistry and Biology. Springer International Publishing; 2014. ISBN 978-3-319-04334-0

[6] WHO. Calcium and Magnesium in Drinking-water Public health significance. Spain. World Health Organization; 2009. https://www.who.int/water_sanitation_health/publications/publication_9789241563550/en/

[7] Rozporządzenie Ministra Zdrowia z dnia 13 listopada 2015 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi Dz.U. 2015 poz. 1989 (Regulation of the Minister of Health of November 13, 2015 on the quality of water intended for human consumption). http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20150001989

[8] WHO. Hardness in Drinking-water, Background document for development of WHO, Guidelines for Drinking-water Quality, World Health Organization, Geneva; 2011. https://apps.who.int/iris/handle/10665/70168

[9] Sapek A. Contemporary chloride sources in environment of inland waters. Ochr Środ Zasob Natur. 2009;40:455-464.

[10] EPA. Secondary Drinking Water Standards: Guidance for Nuisance Chemicals; 2017. https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals

[11] WHO. Total dissolved solids in drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality. Geneva; 2003. https://www.who.int/water_sanitation_health/dwq/chemicals/tds.pdf
[12] Dobrzański Z, Kołacz R, Czaban S, Bubel F, Malczewski M, Kupczyński R, et al. Assessing Mercury Content in Plant and Animal Raw Materials in an Area Impacted by the Copper Industry. Pol J Environ Stud. 2017;26(2):577-583. DOI: 10.15244/pjoes/66709
[13] Sapek B, Sapek A. Nagromadzenie składników nawozowych w glebie i wodzie gruntowej z zagrody i jej otoczenia w gospodarstwach demonstracyjnych w dwóch gminach województwa kujawsko-pomorskiego (Accumulation of fertilizer components in soil and groundwater from the homestead and its surroundings in demonstration farms in two communes of the Kujawsko-Pomorskie Voivodeship). Wiad Melioracyjne Łąkarskie. 2006;3:137-141.
[14] Tahar N, Ali B. Hydrochemistry and Assessment on Groundwater Quality of the Aquifer of Heliopolis in North of Guelma-Algeria. Int J Scientific Eng Res. 2016;7(11):318-324. https://www.ijser.org/researchpaper/Hydrochemistry-and-Assessment-on-Groundwater-Quality-of-the-Aqui.pdf
[15] Bodrud-Doza Md, Islam ARM, Ahmed F, Das S, Saha N, Rahman MS. Characterization of groundwater quality using water evaluation indices, multivariate statistics and geostatistics in central Bangladesh. Water Sci. 2016;30(1):19-40. DOI.org/10.1016/j.wsj.2016.05.001
[16] Przybysz O. Twardość wody a praca pomp do cyrkulacji cieplnej wody użytkowej (c.w.u.) (Water hardness and the work of pumps for the circulation of hot water). Instal Reporter (online) 2012; 02:26-27.https://www.instalreporter.pl
[17] Krásný J, Sharp J M. Groundwater in Fractured Rocks: IAH Selected Paper Series, CRC Press, Science, IAH Selected Paper Series, 9; 2007. ISBN 9780415414425

ZMIANY WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH WODY ZE STUDNI W WYBRANYCH WIEJSKICH GOSPODARSTWACH DOMOWYCH

Instytut Inżynierii Środowiska,
Uniwersytet Przyrodniczy we Wrocławiu, Wrocław, Polska

Abstract: Artykuł przedstawia wyniki badań dotyczących jakości wody pitnej ze studni zaopatrujących wybrane gospodarstwa domowe znajdujące się w bliskim sąsiedztwie składowiska rud miedzi. Jakość wód gruntowych i ich przydatność do picia badano przy użyciu różnych parametrów fizykochemicznych, takich jak: pH, przewodność elektryczna, twardość całkowita, wapń, magnez, sód, potas, siarczany, chlorki i substancje rozpuszczone ogółem. Parametry te wykorzystano do oceny przydatności wód podziemnych do picia. W niektórych analizowanych próbach stężenie omawianych parametrów przekraczała dopuszczalne normy, generalnie jednak stężenie głównych jonów (wapnia, magnezu, sodu, potasu) oraz wartości parametrów: pH, temperatury, twardości nie przekraczały wartości zalecanych przez polskie regulacje prawne w odniesieniu do wody pitnej. Jednocześnie analizowana wodę charakteryzowała się niską mineralizacją, stąd też nie można jej polecić jako wody nadającej się do spożycia przez ludzi.

Słowa kluczowe: makroelementy, woda pitna, woda studzienna, jakość wody, główne składniki wody