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SUMMARY OF THE DOCTORAL DISSERTATION

# Spatio-temporal changes of the chemical composition of sulfide water in Busko-Zdrój and Solec-Zdrój regions

In the region of Busko-Zdrój and Solec-Zdrój, in the south-eastern part of the Szczecin-Łódź-Miechów synclinorium, a particular type of groundwater has been identified — sulphide water, which have been known and appreciated since the fourteenth century due to their medicinal properties.

The purpose of this study was to analyze the variation of the chemical composition of sulfide water in the Busko-Zdrój and Solec-Zdrój regions in a spatial and temporal system. The dissertation presents various methods applied during the physico-chemical studies of these water.

Data from 15 wells and 5 springs of sulphide water come from:

- the Miocene aquifer — a Dar Natury intake and springs: Piestrzec and Senisławice;
- the Upper Cretaceous (Cenomanian + adjacent carbonate layer) — intakes: B-4b, B-8b, B-13, B-16a, B-17, Busko C-1, LW-1, LW-2, Shaft Solecki, Solec 2 Karol, Solec 2B, Dobrowoda G-1, Cudzynowice GT-1 and springs: Gadawa and Owczary;
- the Upper Jurassic — Wełnin intake and Szczerbaków spring.

The work was based on a review and analysis of documentary materials, published articles and books as well as the collection, verification and study of the archival chemical analyses and chemical components and physical properties of sulfide water of the Busko-Zdrój and Solec-Zdrój region from a period 1871–2017. A number of 601 results of analysis has been collected. Additionally, the author performed the research in the years 2012–2018 determining the content of macro- and micro components in waters from the analyzed intakes and springs (83 analyzes in 14 series). Totally, the results of 684 physico-chemical analyses of sulphide water were collected and used. Petrographic analysis of sandstone, limestone and limestone-marly conglomerates has also been carried out. For testing of rock, samples were taken from two selected wells: Busko-C1 and Las Winiarski LW-1.

The first part of the work describes the geological structure and hydrogeological conditions of the study area and presents the general hydrogeochemical characteristics of the sulfide water. These water were of different chemical types, depending on lithology and mineral composition of aquifers that originate from different periods: Miocene, Upper Cretaceous and Upper Jurassic. Using the exploration procedure available in the PS Imago Pro/IBM SPSS Statistics program, a statistical analysis was performed for the basic parameters characterizing the studied sulfide water (i.e. pH, TDS, ions: $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$, S(II), $I^-$, $F^-$ and $Fe^{2+}$). Individual outliers were identified in the data, which may primarily result from a change in the laboratory which carried out the chemical analyzes, and thus from a change in their sampling methodology and testing methodology.

The next part of the work presents a detailed assessment of the variability of the chemical composition of sulphide water based on the results of physicochemical analyzes from the last 10 years (2009–2018). Basing on the analysis of control charts of individual measurements (made in the PS Imago Pro program) and analysis of trends in changes of main and specific components (using the GWSDAT v. 2.1 program), an analysis of changes of the chemical composition of the examined waters over the time was carried out. The analysis generally showed the stability of the chemical composition of the examined waters in relation to selected physicochemical parameters.

For the analysis of changes of the chemical composition of the examined sulphide water in the spatial system, one of the methods of multidimensional data analysis was used — analysis of the main components — PCA (Principal Component Analysis) also performed in the PS Imago Pro program. Two main components were distinguished, describing the chemical composition of the discussed sulphide water of Busko-Zdrój and Solec-Zdrój. Based on the analysis of the graph of the relationship between the extracted factors, an assessment of the similarity between the sulfide water wells and springs was performed. The obtained results confirmed the sense of analysis of these waters separately for 3 aquifers from which these water originate: Miocene, Upper Cretaceous and Upper Jurassic. The analysis of the variability of the chemical composition of the examined water in the spatial system was also made by the graphic method, using Udluft charts and Piper diagrams.

Additionally, a geochemical modelling was carried out using the PHREEQC v. 3 program. In the first step, speciation analysis of the main ions and specific components of water from the discussed sulfide water wells and springs was performed. Based on the results of the calculations, the actual chemical composition of these water was determined, as well as the ion speciation. Trends of the changes of speciation over time were identified and dominating forms in given water were indicated. The analysis showed that the concentrations of all speciation can be considered stable over time. The interpretation of the cumulative graphs, which took into consideration the forms of occurrence of the discussed ions in concentrations above 0.5% mmol/kg $H_2O$, clearly showed the differences between the discussed aquifers, which are reflected by a different percentage of the dominant forms of a given element in water. The largest differences occur with respect to speciation for sulfur (VI) compounds. In water from the Miocene aquifer, the dominant speciation are: $SO_4^{2-}$ and $CaSO_4$, while the speciation of $MgSO_4$ and $NaSO_4^-$ are present in negligible concentrations. In the Upper Cretaceous water, $SO_4^{2-}$ is also the main sulfur (VI) speciation, while the content of other speciation is at a similar level. $SO_4^{2-}$ ions are also the dominant speciation in the Upper Jurassic waters. The waters of this aquifer also have high concentrations of $NaSO_4^-$ ions, while the content of $MgSO_4$ and $CaSO_4$ ions is slightly lower.

An assessment of the hydrogeochemical balance of the sulphide water of the examined area in the water-mineral phase system was also carried out. Based on the analysis of the SI (Saturation Index) value of the analysed sulfide water, it was found that it is formed mainly by the phases of carbonate minerals (calcite and dolomite) and a group of feldspars (mainly albite and adular). It is associated with lithology and mineralogical composition of aquifers in the majority of the research area, and also shows the connection of sulphide water with the crystallinic bedrock. This confirms the great importance of the impact of the rock environment on the formation of the chemical composition of groundwater. The obtained results allow to claim that the processes of carbonate rock dissolution have a significant impact on the hydrogeochemical equilibrium state of the examined sulphide water. The examined water show a state of hydrogeochemical equilibrium with respect to sulphate minerals (mainly with gypsum) and clay mineral — illite. On the other hand, most of these sulphide water show a state of unsaturation in relation to gypsum. Negative SI values suggest no tendency to precipitate and the possibility of dissolution under favourable thermodynamic conditions. This shows the relationship of the tested aqueous solutions with the overburden rocks, which form gypsum and clay deposits of the Neogene (Miocene). It also confirms the origin of hydrogen sulfide formation in the studied water — the origin of $H_2S$ from the reduction of sulphates derived from dissolution of gypsum with the participation of hydrocarbons in the presence of sulphur bacteria (Zuber et al., 1996, 1997, 2010; Chowaniec et al., 2009). In addition, the sulphide water of Busko-Zdrój and Solec-Zdrój region show supersaturation with respect to quartz, pyrite and clay minerals. Positive SI values suggest the possibility of precipitation of new minerals under appropriate thermodynamic conditions and indicate a high resistance of minerals to dissolution.

The results presented in the dissertation significantly supplement and broaden the knowledge on the hydrogeochemical problems of sulfide water in the Busko-Zdrój and Solec-Zdrój regions.