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ORIGINAL ARTICLE

Groundwater geochemical evolution under the influence of polymetallic deposit in Czarnów (Western Sudetes, SW Poland)

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Abstract Water environment in the vicinity of Czarnów (Rudawy Janowickie Mts., Western Sudetes) is characterized by an occurrence of rich variety of trace elements affecting its quality directly. Based on the analyses of chemical composition of waters supported by geochemical modeling using PHREEQC code the significant influence of either natural geological conditions or former and contemporary mining activity has been confirmed. The results of inverse modeling suggest the contribution of carbon dioxide dissolution, pyrite oxidation, carbonates and plagioclases dissolution and ionic exchange between Ca^{2+} and Na^{+} as major chemical processes influencing water chemistry evolution. The anomalous concentration of arsenic in several locations as a result of probable desorption from iron oxide–hydroxides under the elevated pH conditions can be observed. The evaluation of changes in waters chemical composition during the past three decades indicates the tendency of their self-purification.

Keywords Geochemical modeling · Geochemical evolution · Groundwater · Western Sudetes · Poland

Introduction

The mining activity in the Rudawy Janowickie Mts. range (Western Sudetes) has reached the medieval times. The very first records of mine workings in the area are dated from the thirteenth century and can be considered as one of the oldest in Europe. The earliest stage of exploitation regarded only gold exploration until the middle of the eighteenth century when the 'Evelinens Glück' mine ('Eveline's Luck' mine) was launched and the workings focused on arsenic and copper ores exploitation. At the beginning of the twentieth century the exploitation in Czarnów was conducted on 12 exploitation levels and the production came up to 1000 t of ore annually (Dziekoński 1972). The operation of the 'Evelinens Glück' mine was finished in 1925 considering its unprofitability. Currently the mine is closed and unavailable for entry. The remainings of its former activity in the form of shafts, adits and mine tailings have still a huge impact on the entire environment and play a significant role in the evolution of water chemistry in the study area. The additional influence on the waters exerts the present exploitation of dolomitic marbles in open-pit mine in Rędziny.

Rudawy Janowickie Mts. has been the point of interest for a few last decades considering its interesting geological structure and mining history. The scientific investigations in the Czarnów area regarding the aspects of geology, mineralogy and tectonics were conducted by many Polish scientists (i.a. Zimnoch 1985; Cymerman 1996; Mazur and Aleksandrowski 2001; Mazur 2003; Kozdrój 2003; Mochnacka et al. 2009; Mikulski 2010). The latest description of mining history and heritage in Rudawy Janowickie can be found in several articles in the monograph 'Mining history—element of European culture heritage (Zagozdzon and Madziarz 2009). Also a few papers

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describing the interactions between water and ore mineralization in Rudawy Janowickie has been published (Balcerzak et al. 1992; Marszalek and Wasik 2001; Konieczyńska 2006). So far the subject of geochemical evolution of waters in Czarnów area has not been commented in the literature.

The aim of the paper is identification of main factors affecting the chemical composition of waters in the area of former arsenic and copper exploitation in Rudawy Janowickie Mts. and recognition of their geochemical evolution based on geochemical modeling using PHREEQC code.

Geological and hydrogeological background

Geologically the study area is a part of Rudawy Janowickie metamorphic complex located in Western Sudetes (northern part of the Bohemian Massif). The unit is composed mostly of crystalline rocks represented the eastern shield of Variscan granitoid intrusion covered partly with Intrasudetic Basin sediments. Predominant rocks in the area are metamorphic schists, amphibolites, gneisses and dolomitic marbles (Fig. 1). The origin of polymetallic ore is associated with Variscan hydrothermal activity of granite intrusion as well as early Paleozoic magmatic and volcanic activity in Rudawy Janowickie (Mikulski 2010). The mineralization, mainly arsenopyrite (FeAsS), is present in a form of veins and lenses between silicate and carbonate rocks. The other minerals including pyrrhotite (FeS), pyrite (FeS_2), marcasite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS) and bornite (Cu_5FeS_4) are also present.

The hydrogeological conditions in the Rudawy Janowickie are similar to those in other crystalline massifs of the Sudetes (Marszałek 1996; Staśko 2010). Groundwater occurs in three depth zones: within weathering cover with upper part of fractured crystalline rocks, in deeper fractured rocks and the deep tectonic faults. These zones are often connected; however they can also form the independent and isolated hydrodynamic systems. The research area is entirely drained by small mountainous streams (Fig. 1) starting in springs and flowing through the abandoned mining area as well as through the active dolomite mine. The surface waters are exposed to the contamination with trace elements all the way from springs to the stream outlet.

The presence of carbonate rocks in the complex of metamorphic series creates a specific type of alkaline groundwater environment with pH above 8, clearly different from mainly acidic groundwater occurring in other parts of the crystalline massif of the Western Sudetes.

Methods

The geochemical characteristics of groundwater within the study area was carried out based on chemical analyses of water samples collected in January 2013 at 10 sampling locations (Fig. 1). The water was sampled from the local springs, household dug wells and streams. Each of the water samples has been preserved in dark HDPE bottles after previous filtration using 0.45 μm membranes. The samples intended for the analyses of cations were additionally acidified with nitric acid. Eight basic ions (HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+) were determined using HPLC technique and 7 trace elements (As, Cu, Fe, Mn, Ni, Pb, Zn) using ICP-MS technique. In March 2013 additional analyses of basic chemical composition of water were carried out in five sampling locations to extent the recognition of water chemistry. Also the repetition of basic chemical analyses in five sampling locations was performed to exclude analyses errors.

Measurements of basic physico-chemical parameters of water such as temperature, pH, electrolytic conductivity (EC) and redox potential (Eh) were carried out on-site using calibrated portable WTW 340 multiparametric meter with precision of measurements: 0.01 μS/cm for EC and 0.01 for pH. Inverse geochemical modeling with PHREEQC version 3 was used to identify water–rock interaction processes controlling the geochemical evolution of groundwater. The geochemical model was based on the calculation of the distribution of species and the values of saturation index (SI) for selected minerals.

Results and discussion

The groundwater in the Czarnów area is characterized by low TDS (total dissolved solids) rarely exceeding 100 mg/L. The spatial distribution of total mineralization reveals the tendency to increase with the distance from the springs. The highest values of mineralization are recorded in the streams of the rural areas due to local pollution from agricultural holdings. The other factor affecting the increment of water mineralization is the presence of mine tailings and dolomite mine. The preceding tendency is confirmed by the measurement of electrolytic conductivity of water ranging from 59 μS/cm in springs to 295 μS/cm in the stream water. The highest value of EC measured in groundwater was 378 μS/cm (Table 1).

Based on the measured pH values the waters of the study area can be classified as acidic, slightly acidic and slightly alkaline. The pH ranges from 4.2 to 8.2. The groundwater has also wide ranges of hardness fluctuating from 0.15 to 2.05 meq/L. The highest values of both pH and hardness

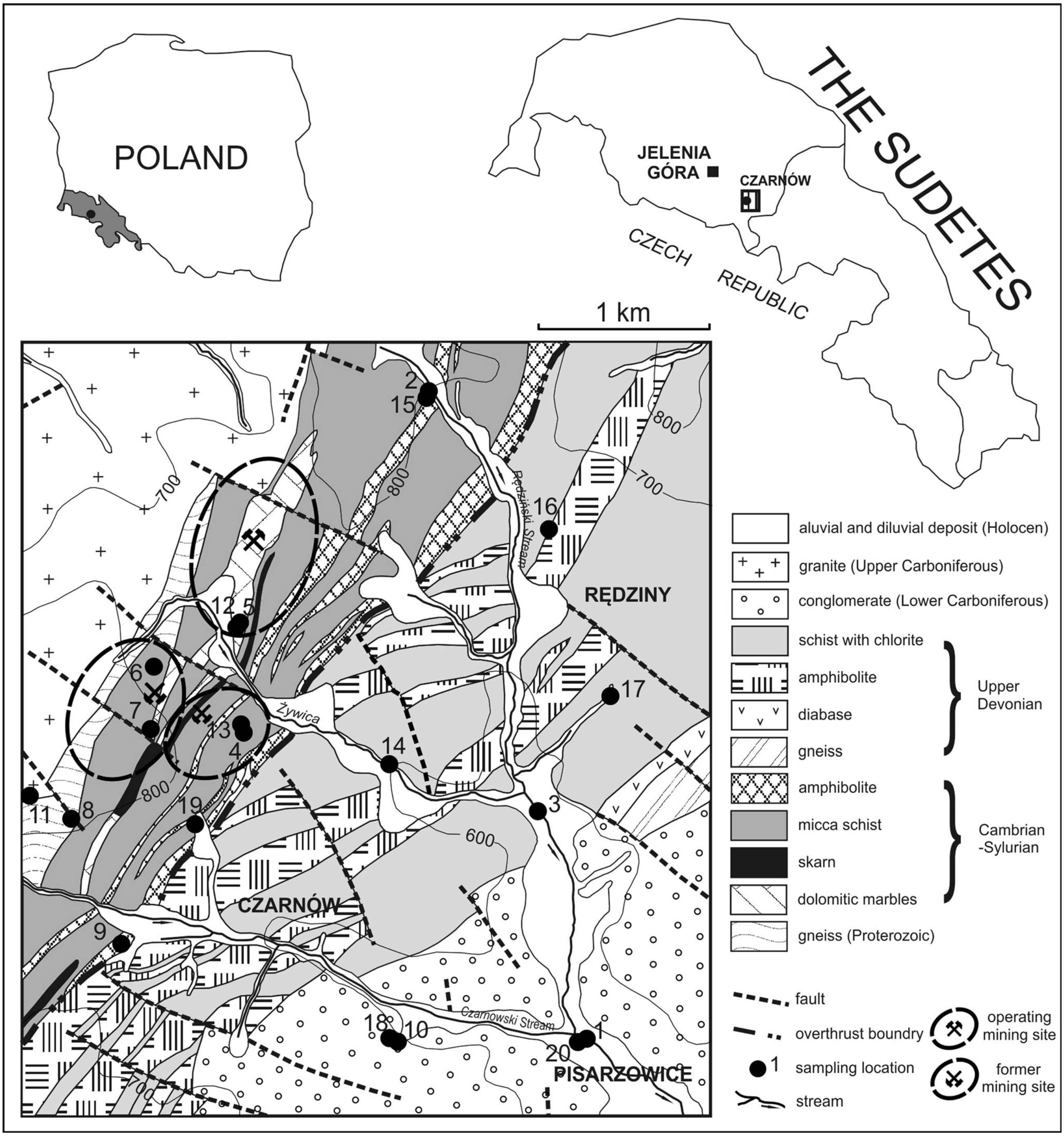


Fig. 1 Location of the sampling waters points on the geological background of the study area

are directly related to weathering of carbonates in the adjacent sites.

Temperature of groundwater, measured at the water outflow, is largely affected by atmospheric conditions. At the time of field measurements in winter period the temperature of water ranged from 2.1 to 5.2 °C. The low values of water temperature indicate the direct influence of atmospheric temperature and respectively the shallow and fast water flow within rock environment.

The predominant ions in groundwater are bicarbonates HCO_3^- (9.15–122.04 mg/L), sulfides SO_4^{2-} (8.84–29.20 mg/L), calcium Ca^{2+} (1.94–25.63 mg/L) and natrium Na^+ (3.66–11.55 mg/L) (Table 1). The higher concentrations of chlorides Cl^- (1.23–27.32 mg/L) and nitrogen compounds

Table 1 Chemical composition of surface and groundwater of the study area

Water	SC µS/cm	pH –	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^+ mg/L	K^+ mg/L	HCO_3^- mg/L	SO_4^- mg/L	Cl^- mg/L	NO_3^- mg/L	NO_2^- mg/L
Surface											
Min	59.00	6.6	6.88	0.88	4.28	0.15	33.56	9.86	1.23	1.28	0.03
Max	295.00	8.1	32.31	9.47	21.14	23.00	118.99	43.34	27.32	35.90	0.10
Average	199.19	7.4	22.64	4.42	8.77	4.41	79.78	24.17	8.41	8.70	0.08
Ground											
Min	57.90	4.7	1.94	0.68	3.66	0.27	9.15	8.84	0.95	0.00	0.08
Max	378.00	8.2	25.63	9.92	11.55	1.89	122.04	29.20	3.90	9.35	0.12
Average	140.32	6.6	14.39	2.68	6.65	0.67	46.73	18.79	1.89	2.24	0.10

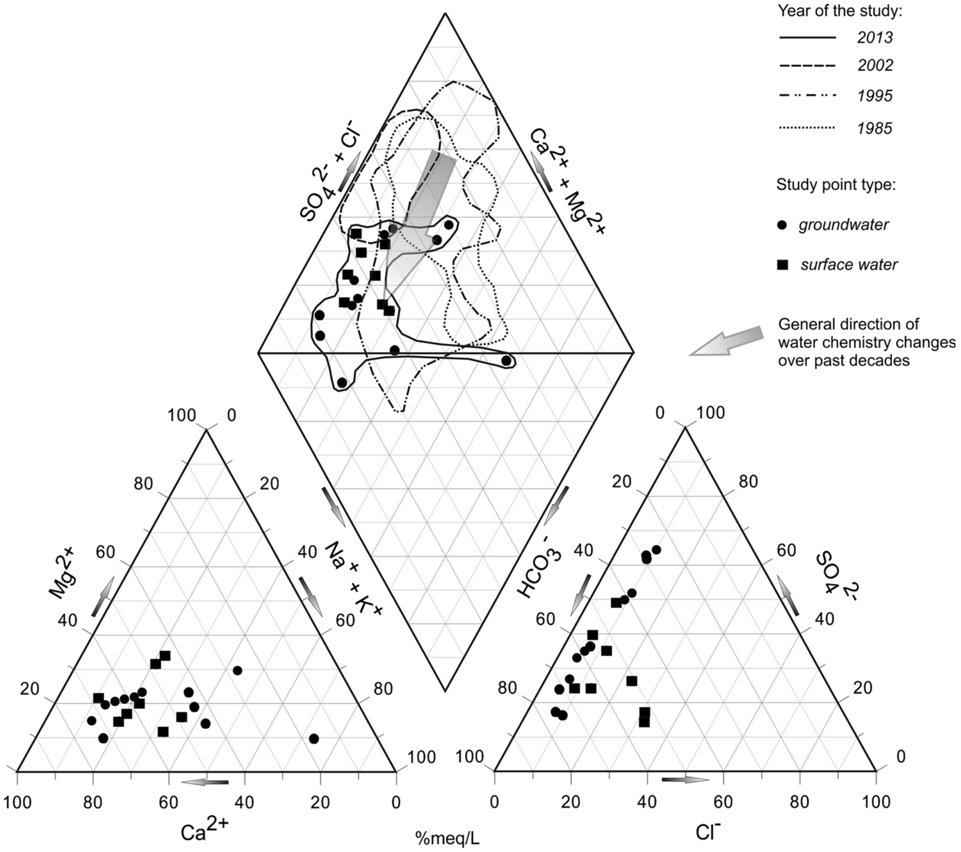
occur in surface water (Table 1) wherein the amount of NO_3^- and NO_2^- ions reach the maximum values of respectively 35.9 and 0.12 mg/L.

Various hydrochemical types of waters (from 3 to 5 main ions) can be distinguished (Fig. 2). Among the basic ions bicarbonates, sulphates, calcium, sodium and magnesium are always prevalent. In hydrochemical terms the surface waters are mainly of the $Ca–HCO_3–SO_4$, $Ca–HCO_3–Cl$ or $Ca–Na–HCO_3–SO_4$ type. In case of groundwater such 4-ions hydrochemical types as $Ca–Na–HCO_3–SO_4$ or $Ca–Na–SO_4–HCO_3$ predominate.

Predomination of bicarbonates is typical for low-mineralized shallow groundwater and surface water of temperate climatic zone (Macioszczyk and Dobrzynski 2002). The occurrence of sulphate ions in groundwater is an effect of the sulfide minerals presence in adjacent rocks and their transformations in chemical processes. The high concentration of calcium (up to 25.63 mg/L) and magnesium (up to 9.92 mg/L) cations in groundwater can be related to the weathering of Mg-rich carbonate rocks and the high concentration of sodium cation (up to 11.55 mg/L) to the weathering of plagioclases commonly occurred in rocks.

Based on the analyses of the changes in waters chemical composition during the past three decades the visible tendency of water enrichment with bicarbonates in relation to

Fig. 2 Chemical composition of waters in Czarnów region presented on the Piper's diagram



sulphates can be observed (Fig. 2). Such situation is very common in the Sudetes and indicates the slow waters self-purification and their return to original chemical balance disturbed by environmental disaster in the 1980s as a result of intense acid rains caused by the large-scale burning of fossil fuels on the border of Poland, Germany and Czech Republic. There are no evident differences in total mineralization of waters observed during the past decades. Chemical changes manifest only as variations in proportion between basic ions concentrations.

The chemical analyses of trace elements revealed the presence of anomalous arsenic concentration in waters. Elevated arsenic concentration exceeding the safe limit for drinking water (10 µg/L according to Polish and WHO regulations) was found in waters of four study sites (Nos. 1, 3, 4 and 5) in the closest vicinity of mine tailings and dolomite mine and also in the surface water of streams. The highest values of arsenic ranged 18.27–158.77 µg/L (Fig. 3). Out of the analyzed heavy metals the trace amounts of iron, copper, zinc and nickel were also detected (Fig. 3). Due to the very toxic properties of arsenic and its elevated concentrations in water only this element can be a particular health concern for local community.

Except of arsenic, out of the group of seven analyzed trace elements increased concentrations of Ni were registered in studied water samples (maximum values of 3.11 µg/L for surface water and 3.96 µg/L for groundwater) (Fig. 3). Such elevated contents can be associated with presence of Ni-bearing rocks like amphibolites and serpentinites occurring in Rudawy Janowickie metamorphic unit. The positive correlation between nickel and arsenic as well as nickel and zinc is also observed (Table 2) which may indicate the common origin of these elements.

The chemical composition of groundwater in Czarnów area strictly depends on chemical reactions occurring in water–rock environment. The inverse geochemical modeling with PHREEQC version 3 allowed creating the most probable model of geochemical evolution of groundwater in the study area represented by following chemical processes:

1. Carbon dioxide dissolution,
2. Pyrite oxidation by O_2 with iron oxide-hydroxide precipitation,
3. Carbonates dissolution,
4. Plagioclases dissolution with kaolinite precipitation,
5. Ionic exchange between Ca^{2+} and Na^{+}.

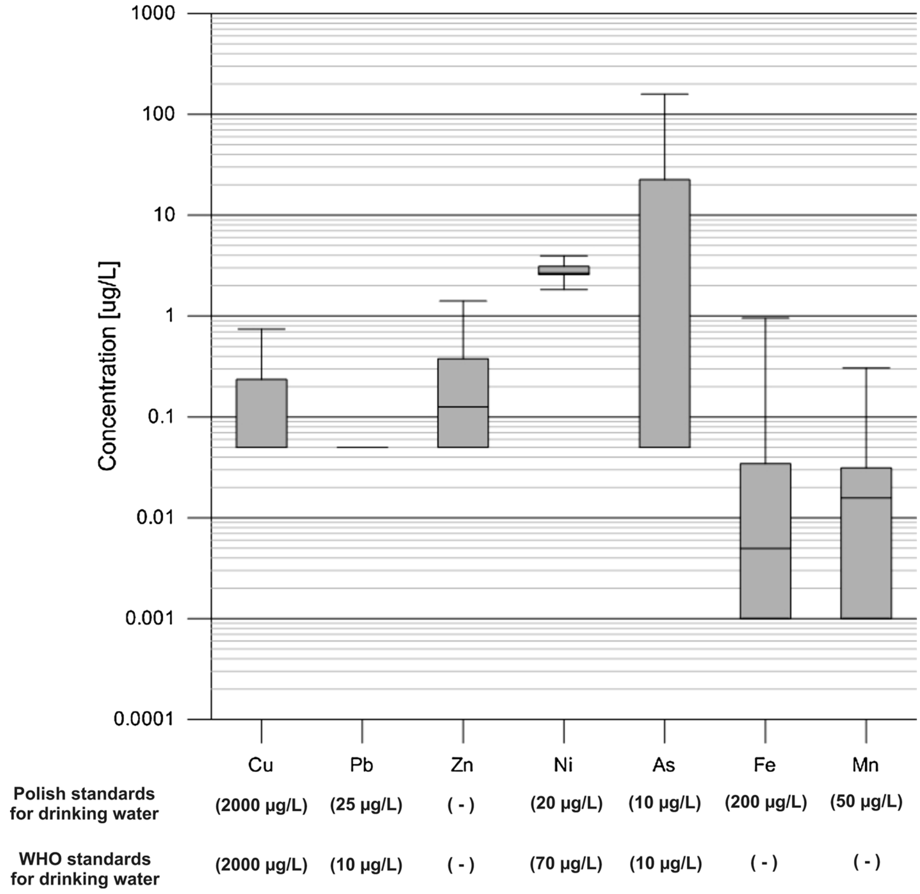


Fig. 3 Selected statistical parameters of trace elements concentrations in waters of the study area

Table 2 Correlation table for selected physico-chemical parameters and chemical components of water in the studied area

	Temperature	pH	SC	Alkalinity	SO_4^{2-}	Cl	NO_3^-	NO_2^-	Ca^{2+}	Na^+	Mg^{2+}	K^+	Cu	Pb	Zn	Ni	As	Fe	Mn
Temperature	1																		
pH	0.132	1																	
SC	0.089	0.770	1																
Alkalinity	0.215	0.794	0.902	1															
SO_4^{2-}	0.481	0.535	0.597	0.534	1														
Cl	0.225	0.381	0.300	0.394	0.212	1													
NO_3^-	0.231	0.542	0.470	0.501	0.833	0.005	1												
NO_2^-	−0.394	−0.132	0.001	−0.098	−0.285	−0.819	−0.011	1											
Ca^{2+}	0.513	0.790	0.769	0.912	0.713	0.393	0.644	−0.262	1										
Na^+	−0.182	0.182	0.571	0.558	0.394	−0.008	0.350	0.235	0.362	1									
Mg^{2+}	−0.136	0.734	0.943	0.895	0.365	0.320	0.348	0.088	0.660	0.616	1								
K^+	0.225	0.325	0.220	0.331	0.188	0.986	0.016	−0.840	0.336	−0.044	0.255	1							
Cu	0.103	−0.169	0.017	0.029	0.096	0.785	−0.150	−0.721	0.022	0.087	0.013	0.771	1						
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1					
Zn	−0.021	−0.765	−0.376	−0.584	−0.134	−0.037	−0.321	−0.137	−0.592	−0.094	−0.437	0.005	0.495	0.000	1				
Ni	−0.246	−0.884	−0.686	−0.662	−0.733	−0.104	−0.715	0.036	−0.737	−0.253	−0.570	−0.082	0.372	0.000	0.661	1			
As	0.137	0.580	0.592	0.589	0.815	−0.015	0.982	0.069	0.666	0.451	0.490	−0.017	−0.170	0.000	−0.328	0.728	1		
Fe	−0.152	−0.476	−0.364	−0.259	−0.528	−0.182	−0.257	0.453	−0.403	0.046	−0.166	−0.132	0.020	0.000	0.260	0.563	−0.252	1	
Mn	−0.082	−0.379	−0.312	−0.163	−0.476	−0.173	−0.174	0.447	−0.295	0.055	−0.111	−0.113	−0.056	0.000	0.143	0.452	−0.174	0.985	1

The most significant process is sulfides oxidation reaction occurring in the presence of oxidants such as oxygen and in most cases catalyzed by bacteria activity. The considerable contribution of this process for the total water mineralization can be also visualized as a positive correlation between SO_4^{2-} ions and EC values (Fig. 4). The basic process of pyrite oxidation runs according to the chemical reaction (Appelo and Postma 2005; Rimstidt and Vaughan 2003):

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

The effect is release of iron, SO_4^{2-} and H^+ ions and precipitation of iron oxide-hydroxides in the form of reddish deposit in certain springs and wells. The process explains the low concentration of iron in the solution in most of the sampling sites.

The carbonates present as dolomitic marbles are dissolved by free H^+ ions. The result of foregoing process is the increase of groundwater alkalinity, hardness and pH. The buffering role of dissolving carbonates favors the precipitation of iron oxide-hydroxides. In the investigation points where the water is oversaturated with calcium and magnesium sulphates the secondary minerals such as gypsum may precipitate. The silicate minerals (plagioclases) are also dissolved with the precipitation of kaolinite.

The arsenic is not present in most of the analyzed water samples due to its probable adsorption on iron oxide–hydroxides. The highest concentrations of arsenic are registered only at the sites of elevated pH of water (Fig. 5). It is unusual situation considering the fact that the alkaline aqueous environment favors adsorption of arsenic from water solution into the structure of iron precipitates. In alkaline waters the decrease of positive charge on the surface of mineral phases can be observed (Dobrzynski and Stepien 2009). Results of modeling with PHREEQC version 3 confirmed that the prevalent arsenic species in water solution are H_3AsO_3 and H_2AsO^{3-}. H_3AsO_3 species has no electric charge therefore there it has no exchange capacity at all. H_2AsO^{3-} as an ion with negative charge is not adsorbed on negatively charged surfaces of mineral phases. This situation explains the remaining of high concentrations of arsenic in studies waters. The phenomenon concerns also the other trace elements occurred in the studied water samples (Fig. 6).

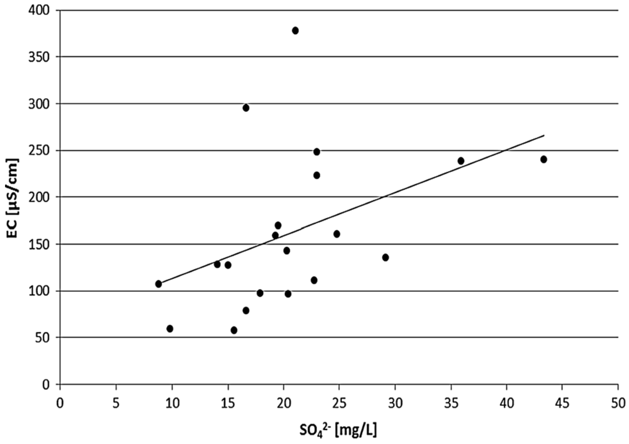


Fig. 4 Concentration of SO_4^{2-} ions versus electrolytic conductivity values (EC) of the studied water samples

The problem of groundwater pollution with arsenic compounds was recognized and commented wildly all over the world, regarding mostly former mining areas characterized by the occurrence of acid mine drainage (AMD) which favours the remaining of arsenic in water solution. The similar unusual phenomenon as observed in Czarnów region concerning the increase of arsenic in groundwater under neutral or alkaline conditions was described in a few areas in the world e.g. Inner Mongolia (Luo et al. 1997; Zhai et al. 1998; Sun et al. 1999), Chaco-Pampean Plain in Argentina (Nicolli et al. 1989, 2001), Arizona in USA (Robertson 1989), Lagunera in Mexico (Del Razo et al. 1990) and Caldes de Malavella in Spain (Piqué et al. 2010).

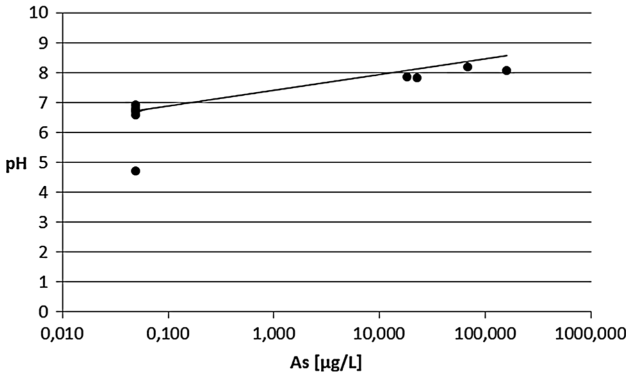


Fig. 5 Concentration of arsenic versus pH values of the studied water samples

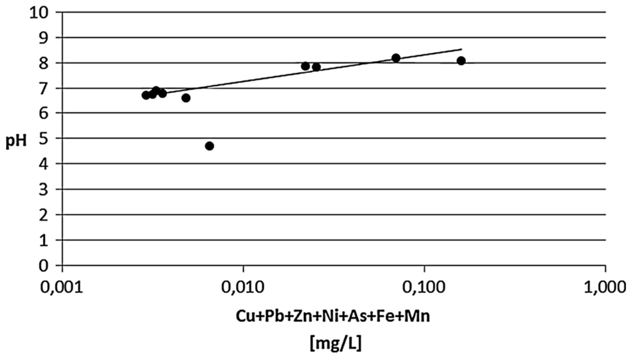


Fig. 6 Total concentration of trace elements versus pH values in the studied samples

Conclusion

The Czarnów area (Rudawy Janowickie Mts., Western Sudetes) is one of the few regions in Poland where the visible impact of long-term mining activity on water environment is observed. The present chemical composition of studied waters is the result of natural geochemical processes occurring within water–rock system intensified strongly by former exploitation of polymetallic deposit and recent exploitation of carbonate rocks. Based on the results of water chemical composition analyses the geochemical model of waters spatial and temporal evolution was created to recognize the most significant chemical reactions controlling water chemistry. The presence of ore (mainly arsenopyrite) mineralization affects the increase of trace metals concentration in the low mineralized waters but neighborhood of carbonate rocks causes alkaline/neutral mining drainage. The content of As reaching 158.77 µg/L and other metals such as iron, copper, zinc and nickel were detected in waters as well. The elevated concentrations of arsenic, because of its toxic properties, should be a particular health concern for local authorities responsible for water management. Regardless of changes in microelements composition during the past three decades the visible tendency of water enrichment with bicarbonates in relation to sulphates is observed. Even though the chemical processes of sulfides dissolution occurring in groundwater of the study area lead to the increase of trace elements concentration in groundwater, the oxidizing conditions are favorable for waters self-purification and self-protection from degradation.

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