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ORIGINAL PAPER

Temporal fluctuations in water contamination from abandoned pyrite Wieściszowice mine (Western Sudetes, Poland)

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Abstract Production of acid mine drainage may occur during mining operations and may continue for many years after closure. In some cases, especially when host rock is capable of reacting with acidic drainage, metal concentrations may decrease over time and distance. Seasonal variations in water flow rate also play an important role in metals concentration both in surface and groundwater. The present study evaluates the contamination of an abandoned pyrite mining area (Wieściszowice, SW Poland) and the temporal variation of the water contamination in selected locations of 2 sampling campaigns (2000 and 2015). The mining surrounding Rudawy Janowickie Mountains range is well known for the rich mining history and is considered as one of the oldest in Europe. The Wieściszowice pyrite mine was exploited for several hundreds of years and processed Fe and Cu sulfides, and sulfur. This mine was closed in 1925 because of the high competition of pyrites from Spain. Results show clearly that water samples collected in the mining area are mainly Ca–SO_4 and acid/high metal, while spring water and surface water samples, representing the local geochemical background, are Ca–HCO_3 and neutral-low metal. The analysis of data shows an improvement in water quality from 2000 to 2015 as well as a decreasing of water risk assessment for human use. This improvement can be related to the fact that 2015 was a very dry year, with over 60% less flow than in 2000, leading to less water contamination.

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Introduction

Acid mine drainage (AMD) formation occurs by interaction of surface and/or groundwater with minerals enriched in metal sulfides accumulated in tailing piles or underground. Production of AMD may occur during mining operations and may continue for several years after mine closure (Tabelin et al. 2020). In sulfide mining districts, AMD pollution longevity can be extremely long (Bigham and Nordstrom 2000). This extreme longevity is due to the amount of pyrite and other sulfides remaining in the galleries (Caraballo et al. 2016) and by the production of "juvenile acidity" (Younger 1997; Tabelin et al. 2020) due to the dissolution of these sulfides. This process is particularly important in above-drainage underground mines where seasonal flow fluctuations and variability of available oxygen are high (Demchak et al. 2004). In some cases, especially where ore host rock is capable of reacting with acidic drainage, metal concentrations may attenuate over time and distance. Important attenuation processes at mining sites include pH buffering and acid neutralization, adsorption at the mineral-water interface, mineral precipitation, and dilution/dispersion. A primary control on the metal attenuation process in mining-impacted sites is acid neutralization (Ali et al. 2016; Berger et al. 2000) predominantly from carbonate minerals (calcite and dolomite) once most of the non-carbonate minerals associated with metalliferous deposits (e.g. aluminosilicates) react extremely slow to influence pH values (Jambor et al. 2000). As pH increases, aqueous metal species tend to precipitate as hydroxide, oxyhydroxide, or hydroxysulfate minerals (Nordstrom 1982; Nordstrom and Alpers 1999). In addition, dissolved metals may co-precipitate or adsorb onto surfaces of these secondary minerals, or in other surfaces such as organic matter or clay minerals, contributing to the attenuation of contaminants from mining effluents (Casiot et al. 2005; Hammarstrom et al. 2005; Sánchez-España et al. 2005). Commonly high aluminum and silica concentrations are found in mine effluents as a result of weathering of aluminosilicate minerals at low pH.

The present study aims to evaluate the natural attenuation capacity of the abandoned pyrite Wieściszowice mine, SW Poland, by (a) determining chemical elemental concentration together with pH and electrical conductivity (EC) determination in stream and groundwaters; (b) determining water saturation state taking in consideration the mineral phases and conditions for mineral precipitation/dissolution; (c) calculating waters risk assessment for human consumption; (d) identifying temporal changes of physicochemical water characteristics by comparing different time periods data in the same region; and (e) evaluating the present water quality.

Study area

Location and history

The study area is located in Wieściszowice, in the Rudawy Janowickie Mountains, within the Western Sudetes, SW Poland. The first records of mining operations reach the medieval era (thirteenth century). The deposit was exploited, and materials processed for Fe and Cu and S for the production of sulfuric acid [H_2SO_4]. Between 1852 and 1925, the local production reaches 200 511 tons of concentrate with 47% sulfur (Krajewski 1947). The mine closed in 1925. The present legacy of the mine is 3 main quarries and several adits and dumps, being a tourist attraction mainly due to the colourful lakes (Fig. 1). Drainage mine waters are not used for any purposes. They feed the right tributary of the Mienica stream (Fig. 3) that is used for irrigation and animals drinking and downstream merges with Bóbr River, an important river which carries water from the north of the Czech Republic to the Southwest of Poland.

Geological setting

Geologically the study area is part of the Rudawy Janowickie metamorphic complex located in the Western Sudetes (NE of the Bohemian Massif, Poland). The unit represents the eastern cover of a Variscan granitoid intrusion. Lower Paleozoic crystalline rocks with Quaternary alluvial sediments in river valleys are also present. The predominant

Fig. 1 **a** Purple Lake located in the Wieściszowice mine area; **b** Blue Lake located in the Wieściszowice mine area

metamorphic rocks of the area are quartz-chlorite schists, sericite-chlorite schists, chlorite schists, chlorite schists with carbonate intercalations, quartz-feldspar schists, mica schists, amphibolites, metadiabases, gneisses, phyllites and greenstones (Fig. 2) (Szałamacha 1956; Szałamacha and Szałamacha 1988). The pyrite mineralization occurs within the chlorite-sericite schists (Piestrzyński and Salamon 1977) forming a ~ 250-m-wide and 4-km-long belt (Szałamacha 1979). Major and predominant ore mineral is pyrite which concentration in rock can reach 80% (Piestrzyński and Salamon 1977). The minor minerals in the deposit are chalcopyrite [$CuFeS_2$], bornite [Cu_5FeS_4], sphalerite [(Zn, Fe)S] and galena [PbS] present as inclusions in pyrite (Jaskólski 1964).

The isotopic analyses of S in pyrite indicate its hypogene source and the hydrothermal origin of the deposit (Parafiniuk 1996). In the whole mining area intensive processes of sulfides oxidation can be observed (Parafiniuk 1996). The pyrite weathering zone is rich in sulphate minerals paragenesis, such as gypsum [$CaSO_4.2H_2O$], melanterite [$FeSO_4{\cdot}7H_2O$], copiapite [$Fe^{2+}Fe^{3+}{}_4(SO_4)_6(OH)_2{\cdot}20(H_2O)$], fibroferrite [$Fe^{3+}(SO_4)(OH){\cdot}5H_2O$], schwertmannite [$Fe_8O_8(OH)_6(SO_4){\cdot}nH_2O$], epsomite [$MgSO_4{\cdot}7H_2O$], pickeringite [$MgAl_2(SO_4)_4{\cdot}22(H_2O)$], slavikite [$NaMg_2Fe^{3+}{}_5(SO_4)_7(OH)_6.33(H_2O)$], and alunogen [$Al_2(SO_4)_3{\cdot}17H_2O$] (Parafiniuk 1996; Balcerzak et al. 1992; Parafiniuk and Siuda 2006). From the group of minerals some of them are common (fibroferrite, magnesocopiapite and gypsum), some as slavikite, pickeringite and schwertmannite—rather common, but others such as melanterite, alunogen and epsomite occur rarely (Borkowski et al. 2013).

Climate and hydrogeological conditions

The study area is located within the Sudetic climatic region characterized by altitudinal zonality and thus variability in seasonal conditions. The average annual temperature at 450–600 m above sea level (asl) is 6.5 °C and the annual mean precipitation 700 mm. At 600–800 m asl, the mean precipitation is 820–840 mm, and above 800 m maximum temperature of 4.5 °C with 1100 mm mean precipitation (Kwiatkowski and Hołdys 1985).

The Rudawy Janowickie Mountains form the elevated hydrogeological massif built of fissured metamorphic rocks covered by rather thin weathering residuals and alluvial deposits in river valleys. Considerable anisotropy of fissured hard rocks influences the variable water-bearing capacity. In vertical profile, there are mostly 1–3 water-bearing zones up to the depth of 100 m. The first one is related to porous-fissured aquifer composed of weathering zone of fissures with saprolite up to 25–30 m thick. Fracture density decreases with depth. The values of fissured hydraulic conductivity estimated by pumping tests are low and amount 0.1–0.8 m d^{-1} in average (Marszałek and Wąsik 2005). The average transmissivity of hard rocks in Western Sudetes is mainly within

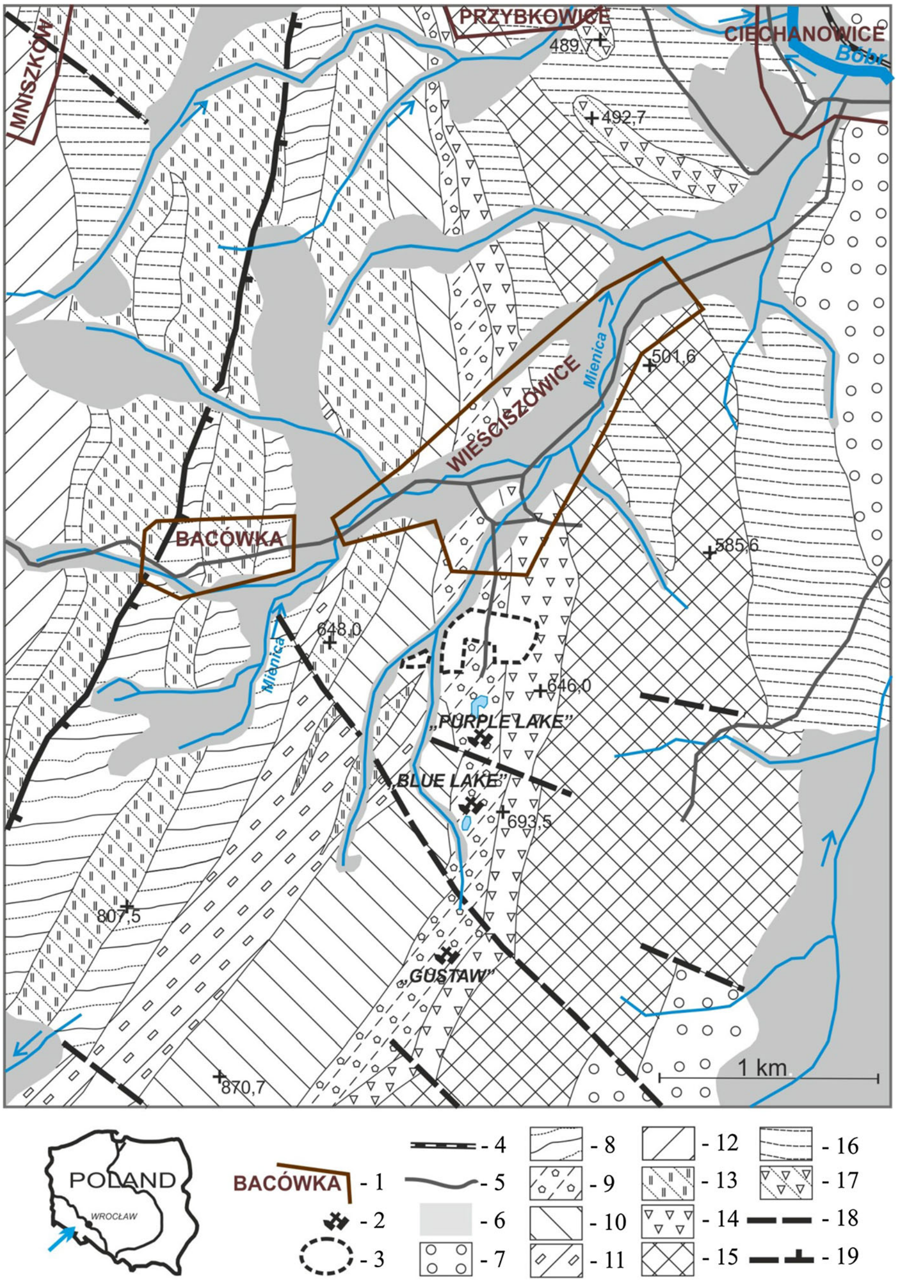


Fig. 2 Geological map (adapted from Szałamacha (1956); Szałamacha and Szałamacha (1988)). 1—village, 2—mine workings, 3—dump, 4—railroad line, 5—road, 6—sands, gravels, clays (Quaternary), 7—conglomerates (Lower Carboniferous), 8—quartz-chlorite schists (8–17 Lower Paleozoic), 9—pyrite-bearing sericite-chlorite schists, 10—chlorite schists, 11—chlorite schists with carbonate intercalations, 12—quartz-feldspar schists and mica schists, 13—amphibolites, 14—metadiabases, 15—mylonite complex (amphibolites, chlorite schists and gneisses), 16—phyllites, 17—greenstones, 18—faults, 19—thrusts

1–40 $m^2 d^{-1}$ and rarely reaches 100 $m^2 d^{-1}$ (Marszałek, 2007). The wells have discharges in the range of 0.5–5.0 $m^3 h^{-1}$. The high recharge from precipitation and intensive fissuring of the crystalline massif in near-surface sector leads to the main renewable groundwater resources there. The groundwater runoff, formed by spring and bed rivers drainage is of 5–10 L s^{-1} km^2). The most springs have discharges in the range of 0.1–0.5 L s^{-1}. The different depth of groundwater circulation influences their specific physicochemical properties. Groundwater has rather low mineralization with total dissolved solids (TDS), rarely exceeding 100 mg L^{-1} (Marszałek, 2007). Higher values of groundwater TDS occur in mining and urban areas.

Materials and methods

Sampling, sample preparation and physicochemical analysis

The fieldwork (November 2015) included the identification and sampling of 10 water samples (Fig. 3): 2 acid mine effluents from mine dumps (sample 8 and 9), 3 samples from lakes related to mine exploitation (sample 5, 6 and 10), one sample from a spring (sample 4), 3 stream water samples—one above Blue Lake (sample 7), other about 350 m downstream last mine dump (sample 3), and another about 3 km below the same dump (sample 1), and one stream water sample from Mienica stream, representative of background water quality (sample 2). Sampling locations 3, 4, 5, 8 and 10 were also sampled in November 2000 (Marszałek and Wąsik 2001). The 2 sampling campaigns were performed under different hydrological conditions.

During the 2015 sampling campaign, for cations and trace elements analysis, water samples were filtered in situ with syringe and a 25-mm disposable disk filter of cellulose acetate membrane with a pore size of 0.20 µm. After filtration into 100-ml polyethylene bottles, samples were acidified with HNO_3 to pH less than 2.0 (ASTM 1984). For the analysis of major anions and alkalinity, samples were collected into 1 l polyethylene bottles and filtered through a 0.45 µm acetate cellulose membrane only in the moment of the sample analyze preparation. Field blanks for assessing possible contaminations were prepared with de-ionized water in the field. Water samples were returned in a cooled box to the laboratory and stored at 4 °C until analyses.

Temperature (T), pH, and electrical conductivity (EC) parameters were measured in situ using a portable WTW 340 multiparametric meter (precision: EC ± 0.01 µS cm^{-1}; pH ± 0.01).

Concentrations of Cl^-, NO_3^- and SO_4^{2-} were determined in unacidified samples by ion chromatography (IC) using a Dionex® 1000i workstation with a Dionex AS4-SC column and an isocratic elution with a sodium bicarbonate/sodium carbonate solution. The HCO_3^- concentration was estimated by volumetric titration with sulfuric acid on laboratorial filtered unacidified samples. A suite of 18 major cations and trace elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and U, V, Zn) were analyzed in acidified waters by ICP-MS at Geosciences Department of Aveiro University. The detection limits of Ca, Cl, K, Mg, Na, NO_3 and SO_4 were less than 1 mg L^{-1}. The detection limits for trace elements were: 0.01 µg L^{-1} for U; 0.02 µg L^{-1} for Co and V; 0.05 µg L^{-1} for Cd; 0.1 µg L^{-1} for Ba, Cr, Cu and Pb; 0.2 µg L^{-1} for Ni; 0.5 µg L^{-1} for As, Mn and Zn; 1 µg L^{-1} for Al; and 10 µg L^{-1} for Fe. A rigorous water data quality control was conducted by inserting reagent blanks, duplicate samples and standard reference materials (WASTWATER3) into each batch to check the validity and reproducibility of the results (Ramsey and Thompson 1987). Typical uncertainties including error sources were below 6% for all the trace elements, whereas for major anions, the uncertainties lie between 2 and 7%, depending to the concentration levels.

The November 2000 sampling campaign and analysis are described in Marszałek and Wąsik (2001).

Data analysis

Data basic statistical analysis was carried out using the Statistica 9.0 software®.

Piper diagram was used to define the hydrogeochemical facies of each water sample and group in terms of similarities related to major ions percentage, expressed in milliequivalents per liter (Piper 1944). Freeze and Cherry (1979) describe more detailed information on the plot procedures. Plot of data in the Piper diagram was done using AquaChem software®.

In order to interpret variations in drainage water chemistry, Ficklin diagram (Plumlee et al. 1992) was created, based on pH and the sum of the base metals (Zn + Cu + Pb + Cd + Co + Ni). These parameters were selected rather than more common metals such as Fe, Al, and Mn since have proven to be the

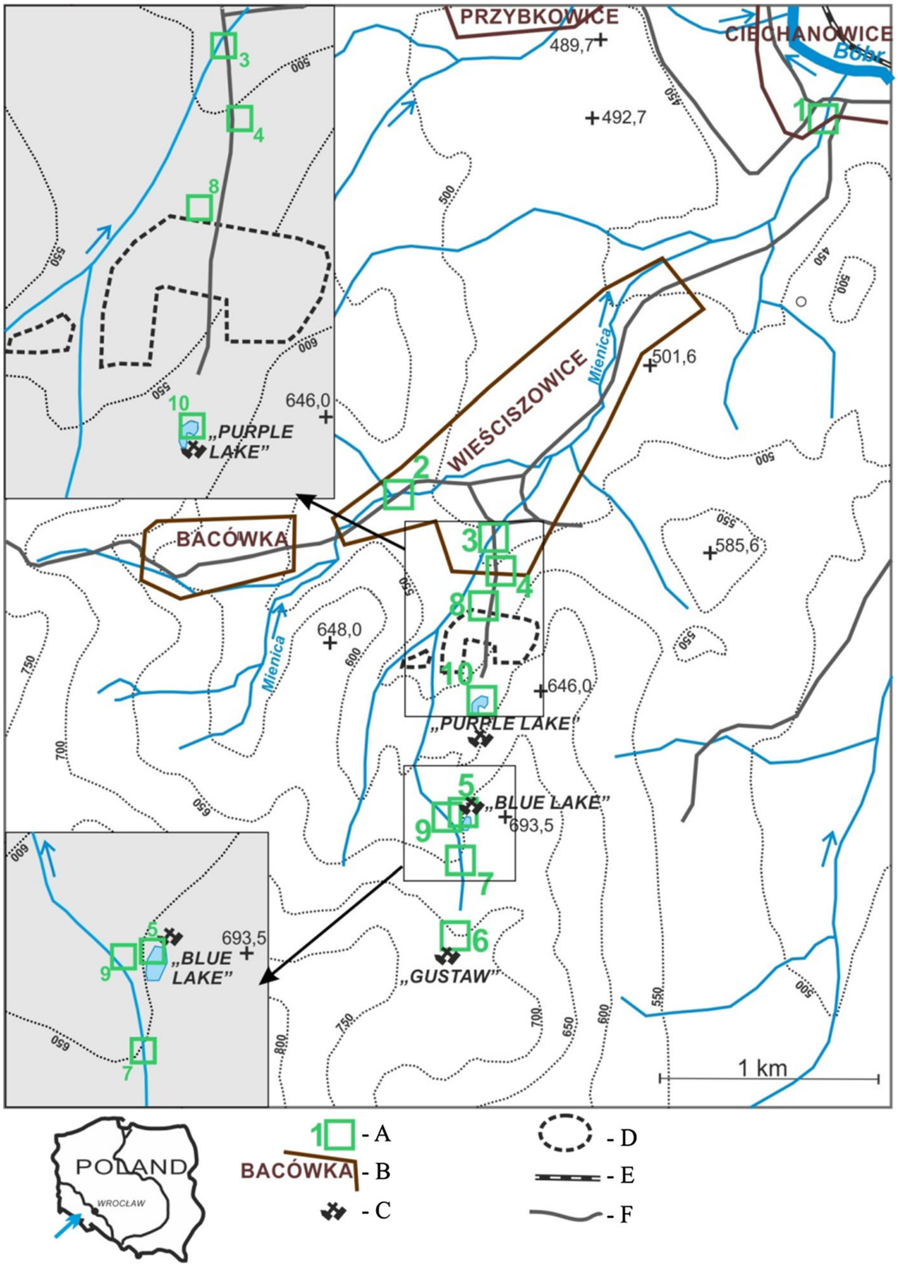


Fig. 3 Location of water samples collection. A-sampling point of water samples (from 2015), B—village, C—mine workings, D—dump, E—railroad line, F—main road. Water samples: 1—Mienica stream, at the outlet to Bóbr River, Marciszów-Ciechanowice: 2—Mienica stream, Wieściszowice; 3—nameless stream from Colourful Lakes, Wieściszowice; 4—Spring next to the road, outflow through the pipe, Wieściszowice; 5—Colourful Lakes–Blue Lake; 6—Colourful Lakes–Emerald Pond; 7—small stream above the Blue Lake; 8—outflow from dump adit in Purple Lake, Wieściszowice; 9—outflow from the adit next to the Blue Lake, below the dump; 10—Colourful Lakes—Purple Lake

most diagnostic in identifying different geologic controls (INAP 2009).

The geochemical speciation model PHREEQC (Parkhurst and Appelo 1999) was used to calculate the distribution of species and the values of saturation indices (SI) for several minerals. The geochemical modeling software PHREEQC code is based on the ion-association aqueous model and is able to describe chemical reactions and transport processes in waters based on equilibrium chemistry of aqueous solutions with minerals, gases, solid solutions, exchangers, and sorption surfaces. Among others, PHREEQC is a speciation program used to calculate SI and the distribution of aqueous species (Parkhurst and Appelo 2013). It uses the temperature, pH, Eh, DO, and alkalinity water parameters, in addition to the chemical analysis, computing the distribution of aqueous species, ion activities, and mineral SI that specify the propensity of a water to dissolve or precipitate a set of minerals (Drever 1998; Nordstrom and Munoz 1986). The speciation results are used to examine the tendency of water to reach mineral solubility equilibrium as a constraint on interpreting the chemistry of waters. These results are a helpful implement used for reaction modeling with the PHREEQC software (Ball and Nordstrom 1991). The SI indicates if a solution is in equilibrium with a solid phase or if it is undersaturated or supersaturated (Alpers and Nordstrom 1999; Nordstrom and Alpers 1999). Equilibrium was defined as 0. If SI is below 0, the solution is undersaturated on the corresponding mineral and water still has the ability to dissolve that mineral phase. When SI exceeds 0, then the solution is oversaturated in that mineral and has the tendency to precipitate the mineral phase.

The human health non-cancer risk assessment was based on the assumption that residents, both children and adults, are directly exposed (exposure time of 6 h) to waters through 3 main pathways (a) ingestion; (b) dermal absorption and (c) inhalation. Reference toxicity values were estimated as given in (RAIS 2018). For each element and pathway, the non-cancer toxic risk was estimated by computing the Hazard Quotient (HQ), also known as non-cancer risk for systemic toxicity. Non-cancer health risk is expressed as hazard index. Values of $HQ > 1$ suggest that non-carcinogenic effects might occur. To estimate the overall developing hazard of non-carcinogenic effects, it is assumed that toxic risks have additive effects. Therefore, it is possible to calculate the cumulative non-carcinogenic hazard index (HI), which corresponds to the sum of HQ for each pathway. Values of $HI < 1$ indicate that there is no significant risk of non-carcinogenic effects, while values of $HI > 1$ imply that there is a probability of occurrence of non-carcinogenic effects, being enhanced with increasing HI values.

Results and discussion

Physicochemical data of water samples from pit lakes, dump adits, streams and spring

Statistical summary is presented in Table 1, for a total of 26 variables. In order to points out each variable behavior along the sampling sites major trend and dispersion measures were extracted.

According to Table 1 results, pit lakes and adits reveal the highest values for the EC, SO_4, Mg, Ca, Al, Fe, Mn and Zn and the mean value is higher than the median value showing clearly the influence of outlier values. The streams have lower values than pit lakes and adits showing a dilution effect by uncontaminated water input. According to the statistical results, the distributions of the variables EC, SO_4, Mg, Ca, Al, Cd, Cu, Fe, Mn, Ni, Pb, V and Zn are mostly positively skewed. Spring groundwater does not exhibit metal contamination and has an alkaline pH and the highest bicarbonate concentration meaning that it is not affected by mine influence.

Hierarchical cluster analysis (HCA) was used to find homogeneous groups of samples (Mode Q) of their geochemical compositions (Mode R). In this study, dendrogram charts (Fig. 4) were obtained using the Ward's method for the successive aggregation, whereas the 1-Pearson r distance was used for regrouping of samples.

According to the mode R results (Fig. 4a), it is possible to identify 2 main clusters. According to mode Q results (Fig. 4b), it is possible to separate the waters in 2 groups: one group representing waters from uncontaminated areas or less impacted, and other group that represents contaminated waters by mining activities.

Table 1 Statistical summary of water samples analyzes

Variables	Unit	Stream (*n* = 4)				Pit lakes (*n* = 3)				Adits (*n* = 2)				Spring
		Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	
Temp	°C	3.4	3.6	2.5	3.9	2.03	1.7	1	3.4	5.45	5.45	3.9	7	8.1
Cond	μS cm^{-1}	578	364	247	1338	1092	423	223	2630	2111	2111	661	3560	398
Eh	mV	19.5	7	− 108	172	66	141	− 154	210	191	191	178	204	-21
pH		4.9	5.1	3.1	6.3	3.8	3.6	2.8	5.1	3.0	3.0	2.8	3.2	5.5
HCO_3	mg L^{-1}	40	39	0	83	4.6	0	0	13.8	0	0	0	0	159
Cl	mg L^{-1}	4.7	5.1	2.5	6.4	1.8	2.4	0.5	2.6	1.6	1.6	0.5	2.7	3.8
NO_3	mg L^{-1}	3.8	3.6	0.5	7.6	2.0	0.5	0.5	5.0	0.5	0.5	0.5	0.5	5.6
SO_4	mg L^{-1}	227	122	38	625	528	108	78	1398	1198	1198	232	2163	51
Na	mg L^{-1}	4.9	4.5	4.4	6.3	3.5	4.0	2.4	4.1	4.7	4.7	4.1	5.4	4.6
K	mg L^{-1}	2.05	2.17	0.58	3.30	1.26	0.71	0.51	2.56	0.83	0.83	0.72	0.93	0.70
Mg	mg L^{-1}	19.6	12.2	7.1	47.0	29.1	7.7	5.2	74.4	74.4	74.4	12.2	136.5	13.8
Ca	mg L^{-1}	57	50	24	105	65	22	9.3	164	153	153	34	273	67
Al	μg L^{-1}	3824	743	8.2	13,804	11,776	5324	200	29,805	22,831	22,831	3740	41,921	28
As	μg L^{-1}	0.6	0.2	0.2	1.6	0.7	0.8	0.2	1.0	0.6	0.6	0.2	1.0	0.8
Ba	μg L^{-1}	19.9	21.4	12.5	24.2	23.2	22.3	4.4	43.0	16.6	16.6	7.5	25.8	4.0
Cd	μg L^{-1}	0.71	0.55	0.05	1.67	1.46	0.93	0.05	3.41	3.50	3.50	0.49	6.51	0.05
Co	μg L^{-1}	38	15	0.2	122	72	24	8.9	182	179	179	26	333	0.3
Cr	μg L^{-1}	1.7	0.26	0.04	6.3	13	3.80	0.10	37	21	21	1.6	41	0.21
Cu	μg L^{-1}	59	5.5	2.4	222	343	31	2.1	995	481	481	43	919	0.7
Fe	μg L^{-1}	6876	360	14	26,768	27,520	4029	49	78,483	63,002	63,002	5635	120,369	59
Mn	μg L^{-1}	634	258	4.4	2013	697	488	192	1411	1926	1926	334	3517	5.1
Ni	μg L^{-1}	23	11	0.5	68	62	29	7.0	149	113	113	15	211	0.3
Pb	μg L^{-1}	0.5	0.5	0.5	0.5	1.6	0.5	0.5	3.7	1.7	1.7	0.5	3.0	0.5
U	μg L^{-1}	0.13	0.04	0.01	0.42	0.20	0.03	0.01	0.57	0.53	0.53	0.04	1.02	0.16
V	μg L^{-1}	0.13	0.07	0.02	0.36	0.47	0.43	0.09	0.89	0.37	0.37	0.09	0.64	0.16
Zn	μg L^{-1}	301	103	17	979	130	106	19	265	270	270	53	487	8.5

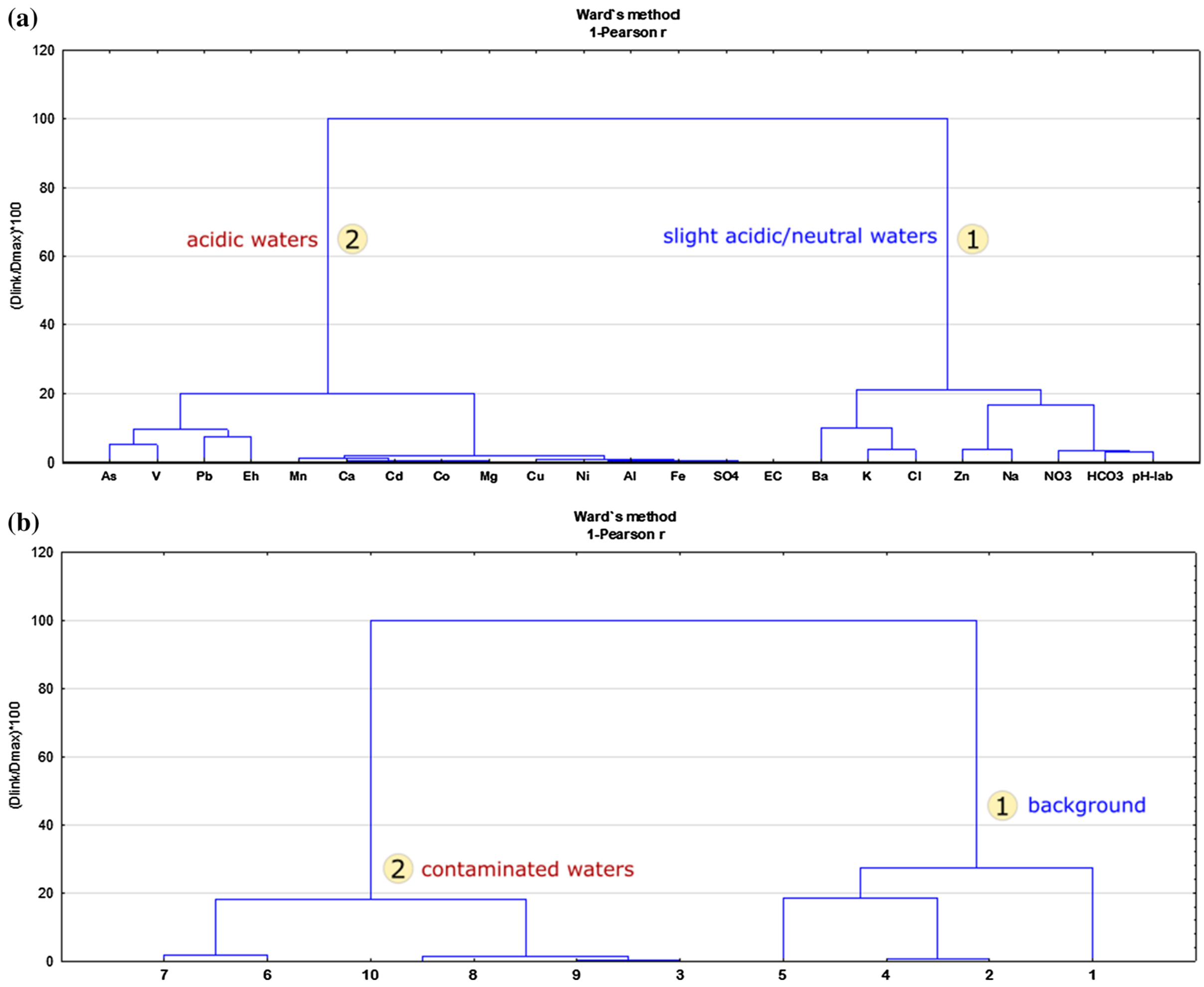


Fig. 4 Hierarchical cluster analysis of geochemical data of analyzed water samples. 1—Mienica stream, at the outlet to Bóbr River, Marciszów-Ciechanowice: 2—Mienica stream, Wieściszowice; 3—nameless stream from Colourful Lakes, Wieściszowice; 4—spring next to the road, outflow through the pipe, Wieściszowice; 5—Colourful Lakes-Blue Lake; 6—Colourful Lakes–Emerald Pond; 7—small stream above the Blue Lake; 8—outflow from dump adit in Purple Lake, Wieściszowice; 9—outflow from the adit next to the Blue Lake, below the dump; 10—Colourful Lakes–Purple Lake. **a** Mode R results; **b** Mode Q results

Cluster I

(Ba, K, Cl, Zn, Na, NO_3, HCO_3, pH): related mainly with sites representing the local geochemical background or slightly contaminated.

The first group is represented by samples 1, 2, 4 and 5. Surface water (sample 2) from Mienica stream, upstream mine influence, with a pH of 5.9, EC 247 µS cm^{-1}, and low SO_4, Al, Fe, Mn, Ni and Zn, is representative of background conditions. Spring groundwater (sample 4) collected near surface acidic water (sample 3), with the highest HCO_3 (153 mg L^{-1}), does not show the contribution of the sulfide minerals to the water hydrogeochemistry, suggesting a completely different circulation. Blue Lake water (sample 5) revealed the lowest mineralization in the study area.

Cluster II

(As, V, Pb, Eh, Mn, Ca, Cd, Co, Mg, Cu, Ni, Al, Fe, SO_4, EC): corresponding mainly to the acidic waters associated with very high contaminated sites. Water analysis results suggest that most of the samples

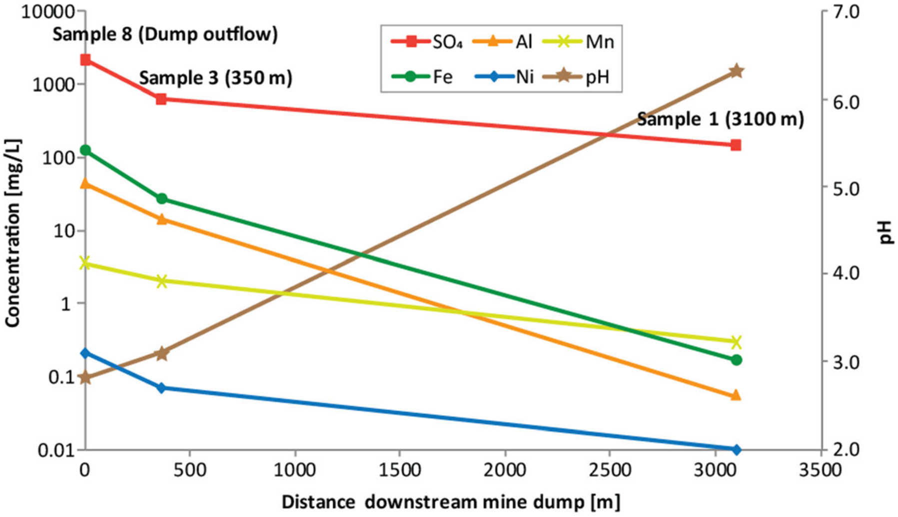


Fig. 5 Evolution of stream water chemistry with distance, from outflow from dump adit in Purple Lake (sample 8), to 350 m downstream (sample 3), until the mouth of Mienica stream, about 3 km downstream (sample 1)

included in this cluster have high EC (> 500 µS cm^{-1}) when compared with local geochemical background samples).

This second group include samples 3, 6, 7, 8, 9 and 10. Sample 10 from Purple Lake and sample 8 from the dump adit show both acidic pH values (both with pH 2.8), and the highest EC (2630 and 3560 µS cm^{-1}), Al (30 and 42 mg L^{-1}), SO_4 (1400 and 2160 mg L^{-1}), Fe (78 and 120 mg L^{-1}), Mn (1410 and 3517 µg L^{-1}), Ni (149 and 211 µg L^{-1}), and Zn (265 and 487 µg L^{-1}), respectively. Sample 6 (Emerald Pond) reveals the "Gustaw" shaft mining exploitation effect on water quality by the acidic pH (3.6) and high contents of SO_4–Al–Fe–Mn. EC result (423 µS cm^{-1}) suggests a moderate mineralization probably due to its location in the creek of the watershed. Sample 9 (dump adit above Blue Lake) has similar physicochemical characteristics with a slight increase in EC (661 µS cm^{-1}) explained by the downstream position. Stream water sample above Blue Lake (sample 7) is ~ 580 m distant of Emerald Pond, with acidic pH (4.4) and low mineralization (267 µS cm^{-1}), being SO_4 (92 mg L^{-1}) and Al (1433 µg L^{-1}) predominant.

Downstream, stream water (sample 3) revealed an acidic pH (4.4), being SO_4 (625 mg L^{-1}), Al (13,804 µg L^{-1}), Fe (26,767 µg L^{-1}), Mn (2013 µg L^{-1}), and Zn (179 µg L^{-1}), the most important ions in solution. Near the confluence of this stream into Bóbr River (sample 1), pH rises to near-neutral (6.3) while EC decreases (461 µS cm^{-1}) as well as other ions (Fig. 5), with the exception of Zn with the higher concentration of the study area (~ 1 mg L^{-1}), what can be explained by the high mobility of Zn in water (Oyewo et al. 2020; Stumm and Morgan 1996). Zn is also reported by Mayes et al. (2010) as the most common contaminant released from England and Wales abandoned metal mines.

According to Piper diagram (Fig. 6), the collected waters samples are classified as Ca–SO_4 with the exception of sample 4 (spring water) and sample 2, a surface water representing the geochemical background, both classified as Ca–HCO_3.

According to the Ficklin diagram (Fig. 7), samples of the Purple Lake (samples 8 and 10) are classified as acid with high metal concentration, while Emerald Pond (sample 6), Blue Lake adit (sample 9), stream above colourful Lakes (sample 3), Blue Lake (sample 5) and stream above Blue Lake (sample 7) are classified as acidic but with low metal concentration, probably due to dilution effects and weathering of carbonate intercalations present in chlorite schists. Surface water background (sample 2) and surface water collected downstream, near stream and Bóbr River confluence (sample 1), are classified as near neutral with low metal concentration. The same occurs with spring water (sample 4), suggesting a groundwater flow with different flow not affected by the

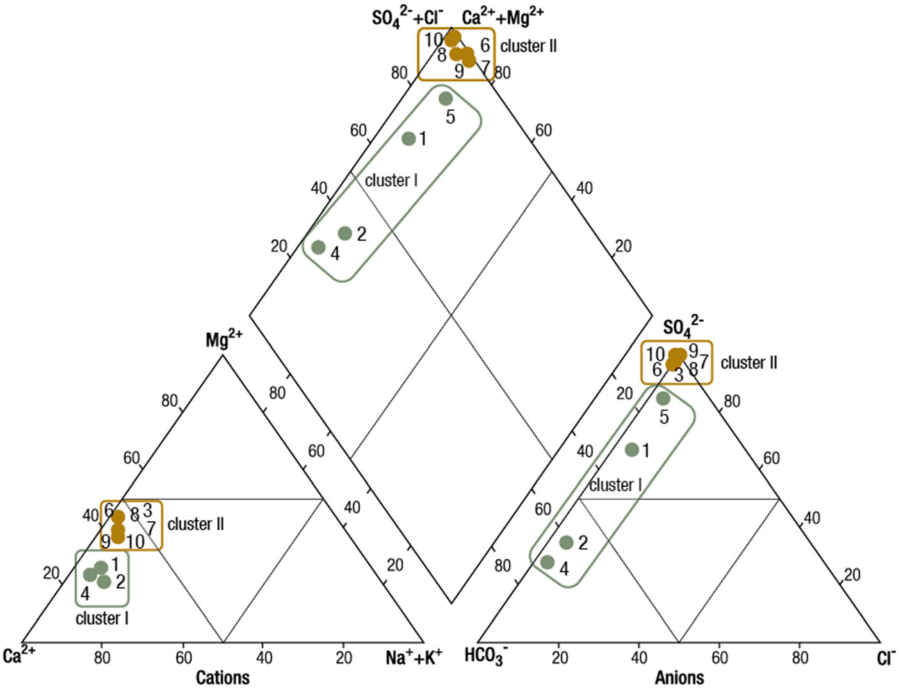


Fig. 6 Plot of 2015 water samples in the Piper diagram. Cluster I and Cluster II are represented. 1—Mienica stream, at the outlet to Bóbr River, Marciszów-Ciechanowice: 2—Mienica stream, Wieściszowice; 3—nameless stream from Colourful Lakes, Wieściszowice; 4—spring next to the road, outflow through the pipe, Wieściszowice; 5—Colourful Lakes–Blue Lake; 6—Colourful Lakes–Emerald Pond; 7—small stream above the Blue Lake; 8—outflow from Dump adit in Purple Lake, Wieściszowice; 9—outflow from the adit next to the Blue Lake, below the dump; 10—Colourful Lakes–Purple Lake

weathering of sulfide minerals. The negative correlation between pH and SO_4, Al and Fe (Fig. 7b, c and d, respectively) shows that water–rock interaction with sulfide minerals in abandoned mining areas is responsible for the lower pH and high SO_4, Al and Fe concentrations.

The very high correlation coefficient between Fe and SO_4 ($r = 0.996$, $p < 0.05$) suggests a common source for these ions and supports previous interpretation (Fig. 8).

Water saturation indices

The PHREEQC program was used to calculate the distribution of aqueous species and saturation indices (SI) of selected minerals (Table 2).

Samples: 1—Mienica stream, at the outlet to Bóbr River, Marciszów-Ciechanowice: 2—Mienica stream, Wieściszowice; 3—nameless stream from Colourful Lakes, Wieściszowice; 4—spring next to the road, outflow through the pipe, Wieściszowice; 5—Colourful Lakes-Blue Lake; 6—Colourful Lakes-Emerald Pond; 7—small stream above the Blue Lake; 8—outflow from under the dump, Wieściszowice; 9—outflow from the adit next to the Blue Lake, below the dump; 10—Colourful Lakes-Purple Lake.

Saturation conditions in Emerald pond water (sample 6) indicate hematite and barite oversaturation while other Fe oxi-hydroxides are undersaturated, suggesting that dissolution conditions are still present. At Purple Lake (sample 10), dump adit from Blue Lake (sample 9) and Purple Lake (sample 8), saturation conditions point to close to equilibrium with barite, but undersaturation in all Fe oxi-hydroxides. The Blue Lake water sample revealed an oversaturation in iron oxi-hydroxides (goethite and hematite) and carbonate species (calcite, aragonite and dolomite), what helps to understand the Blue Lake water low mineralization. Mienica stream water saturation state indicates conditions for precipitation of Fe-hydroxides, observed by the orange staining on the margins and bottom of the stream (Fig. 9).

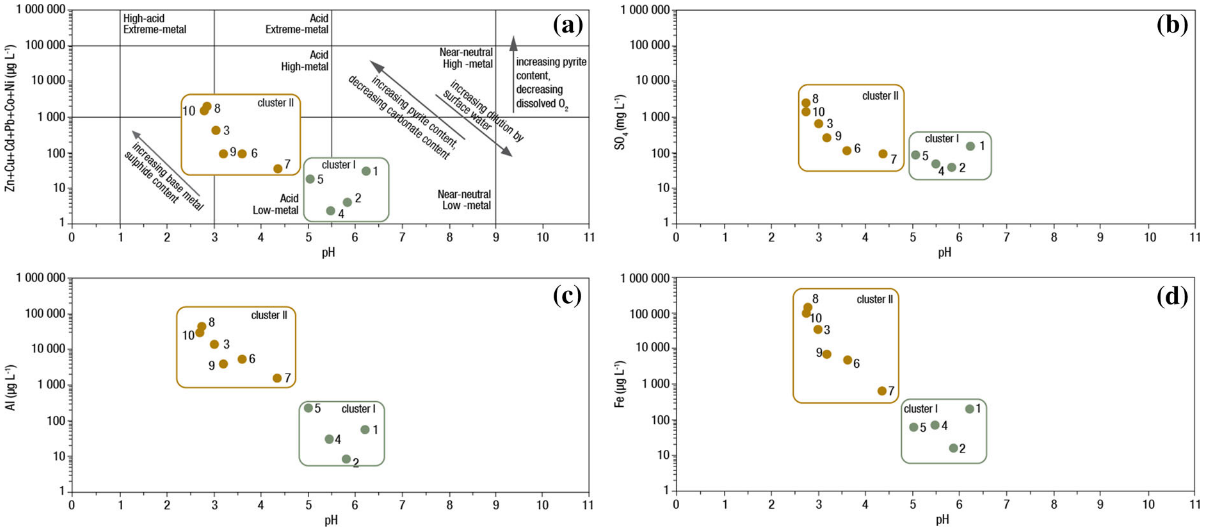
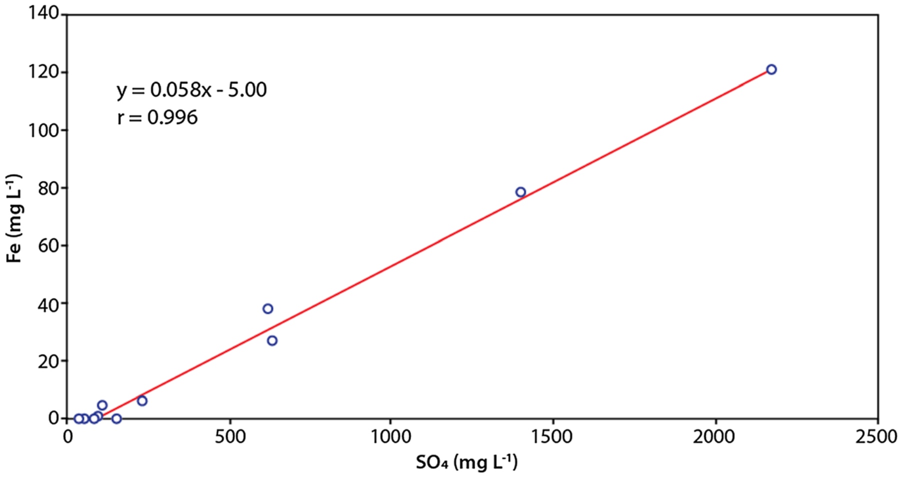


Fig. 7 **a** Ficklin diagram of 2015 water samples; water pH versus **b** SO_4, **c** Al, and **d** Fe concentrations. Cluster I and Cluster II are represented

Fig. 8 Correlation coefficient between SO_4 and Fe



The streams affected by acidic mine drainage (samples 7, 3 and 1) are oversaturated in iron hydroxides and barite. Spring water (sample 4) is oversaturated in iron hydroxides and carbonate minerals.

Temporal evolution of water geochemistry from 2000 to 2015

A study published by Marszałek and Wąsik (2001) carried out in November 2000 in the colorful lakes area allows to understand the contamination fluctuation over the years, when compared with the 2015 samples. Five samples are coincident on both studies: (a) samples 5, 8 and 10 related to the old mining area;

Table 2 Saturation indices for Colourful Lakes, stream and spring water samples calculated with PHREEQC code

	Sample	Barite $BaSO_4$	Calcite $CaCO_3$	Aragonite $CaCO_3$	Dolomite $CaMg(CO_2)_2$	Gypsum $CaSO_4$	Goethite $FeO(OH)$	Hematite Fe_2O_3
Colourful Lakes water	6	0.59	–	–	–	− 2.29	− 0.39	1.11
	5	0.24	0.39	0.23	0.29	− 2.03	7.18	16.24
	10	− 0.06	–	–	–	− 0.48	− 1.70	− 1.50
	9	0.43	–	–	–	− 1.52	− 1.19	− 0.46
	8	0.20	–	–	–	− 0.21	− 1.36	− 0.81
Stream and spring water	7	0.26	–	–	–	− 1.94	7.95	17.80
	3	0.50	–	–	–	− 0.83	− 0.63	0.65
	1	0.36	–	–	–	− 1.41	5.31	12.51
	2	− 0.39	–	–	–	− 2.11	2.11	6.12
	4	− 0.94	0.25	0.09	− 0.10	− 1.85	4.15	10.23

Fig. 9 Right tributary of the Mienica stream, Wieściszowice

(b) sample 3, surface water collected on the stream above colorful Lakes; and (c) sample 4, groundwater from a spring close to the lakes. The comparison of the 2000 and 2015 samples analytical results reveals a difference on the SO_4, Al, Co, Cu, Fe, and Zn concentrations (Table 3; Fig. 10).

When compared to the 2000 sampling geochemical results, the stream water below colourful lakes (sample 3) reveal, in 2015, a decrease in contamination: (a) a minor pH increase (2.9 to 3.1), a decrease in SO_4 (< 28%), Al (< 29%) and in trace elements in general, particularly As and Pb; (b) the outflow from under the dump (sample 8) decreased ∼ 52% in SO_4 and ∼ 22% in Al; (c) Purple Lake water (sample 10) decreased ∼ 30% in SO_4 and ∼ 43% in Al; and (d) Blue Lake (sample 5), SO_4 decreased 17% and Al 50%. Additionally, there is a decrease in the SO_4 concentration in lakes and in the stream and a raise of about 10% in spring water (sample 4). The different behavior of spring groundwater suggests that spring flow path is not affected by mining circulation and that natural processes of water–rock interaction should be responsible for the higher EC (263 to 398 $\mu S\ cm^{-1}$) over time. There is a general improvement in the water quality in comparison with the 2000 water samples results, what can be associated to different hydrological and hydrometric conditions. The comparison of the annual sums of precipitation in the 2 weather stations located near the study area (IMGW-PIB 2020) suggests that 2015 was a dryer year: the annual precipitation was of 473 mm in Jelenia Góra and 544 mm in Kowary station respectively (Table 4). The lower rainfall recharge caused a decrease in river flow. The flow of the Bóbr River in the Jelenia Góra gauging-section during the day of water sampling (November 29, 2015) was 2.37 $m^3\ s^{-1}$ (IMGW-PIB 2020) over 60% lower than during the sampling campaign in November 2000 (6.20 $m^3\ s^{-1}$). The comparison of the flow values of the Jedlica River in Kowary showed even greater differences in the river

Table 3 Physicochemical data of the 2000 and 2015 water sampling campaigns

Station ID	Units	Sample 3		Sample 4		Sample 5		Sample 8		Sample 10	
Year		2000	2015	2000	2015	2000	2015	2000	2015	2000	2015
EC	µS cm^{-1}	1229	1338	263	398	243	223	3830	3560	2110	2630
pH		2.9	3.1	5.3	5.5	4.1	5.1	2.8	2.8	2.5	2.8
SO_4	mg L^{-1}	868	625	46	51	94	78	4470	2163	1995	1398
Na	mg L^{-1}	5.3	4.4	4.3	4.6	3.8	4.0	4.0	5.4	5.5	4.1
K	mg L^{-1}	0.7	3.3	0.3	0.7	0.3	0.7	1.3	0.7	0.2	0.5
Mg	mg L^{-1}	58.4	47.0	13.4	13.8	7.3	7.7	131.9	136.5	115.5	74.4
Ca	mg L^{-1}	124	105	52	67	22	22	312	273	251	164
Al	mg L $-^{1}$	19.4	13.8	0.3	0.0	0.4	0.2	54.1	41.9	51.9	29.8
As	µg L^{-1}	28	bdl	35	0.799	29	bdl	bdl	0.947	bdl	0.777
Co	µg L^{-1}	147	122	bdl	0.3	12	8.9	637	333	219	182
Cr	µg L^{-1}	9.0	6.3	bdl	0.2	bdl	0.1	25	41	69	37
Cu	µg L^{-1}	330	222	57	0.7	17	2.1	1560	919	1443	995
Fe	mg L^{-1}	57	27		0.06	0.2	0.0	676	120	160	79
Pb	µg L^{-1}	40	bdl	17	bdl	bdl	bdl	16	2.976	bdl	bdl
Zn	µg L^{-1}	208	179	bdl	8.5	24	19.1	1396.0	487	351	2650

Samples: 3—nameless stream from colourful lakes, Wieściszowice; 4—spring next to the road, outflow through the pipe, Wieściszowice; 5—Colourful Lakes-Blue Lake; 8—outflow from under the dump, Wieściszowice; 10—colourful lakes-Purple Lake; bdl—below detection limit

discharge in the corresponding periods of water sampling in 2000 (0.35 m^3 s^{-1}) and 2015 (0.06 m^3 s^{-1}). The lower flow in 2015 can contribute to smaller contaminants transport downstream, as concluded by Demchak et al. (2004) in above-drainage mines were discharge during dry periods has improved water quality due to lower rain waters infiltration leading to a smaller production of acidity (Caraballo et al. 2016). These conditions occurred in the outflow from under the dump (sample 8), and Blue Lake (sample 5). The presence of efflorescent salts in dry periods, such as gypsum, melanterite, copiapite, fibroferrite, schwertmannite, epsomite, pickeringite, slavikite, and alunogen, reported by Parafiniuk (1996), Balcerzak et al. (1992), and Parafiniuk and Siuda (2006) in the region, also support this geochemical behavior. These efflorescent salts constitute a transient storage of acidity and metals during dry season (Hammarstrom et al. 2005). However, in some cases, namely in Purple Lake (sample 10) and in stream below colourful lakes (sample 3), EC and pH rises in 2015 even with the decrease of SO_4, Al, Co, Cu, Fe, and Zn, what can be linked with the higher concentration of K, and Cl, due to lower recharge rate and lower dilution.

Water quality guidelines and human health non-cancer risk

The water quality for human consumption, according to polish legislation (Rozporządzenie Ministra 2017), in stream water downstream colourful lakes (sample 3) is classified as acidic (pH 3.1), and highly mineralized (EC 1338 µS cm^{-1}), typical of waters impacted by acidic pollutants. Concentration of Fe is 134 times above the guideline for human consumption. Also, Al (69 times), Mn (40 times), Ni (3.4 times) and SO_4 (2.5 times) are above Polish guidelines.

The stream water sample near the confluence with the Bóbr River (sample 1) reveals all parameters below guidelines, with the exception of Mn, 6 times above.

The non-cancer health effects associated to chronic exposure to contaminants include dermatologic, neurologic, reproductive, genotoxic, cardiovascular, respiratory, and learning disabilities. The human health non-cancer risk was estimated both for child and adults in the 2015 samples (Fig. 11a), and for the 5 corresponding samples of the 2 sampling campaigns (Fig. 11b). Results in Fig. 11 represent the total risk calculated based on the risk posed by Al, Co, Cu and

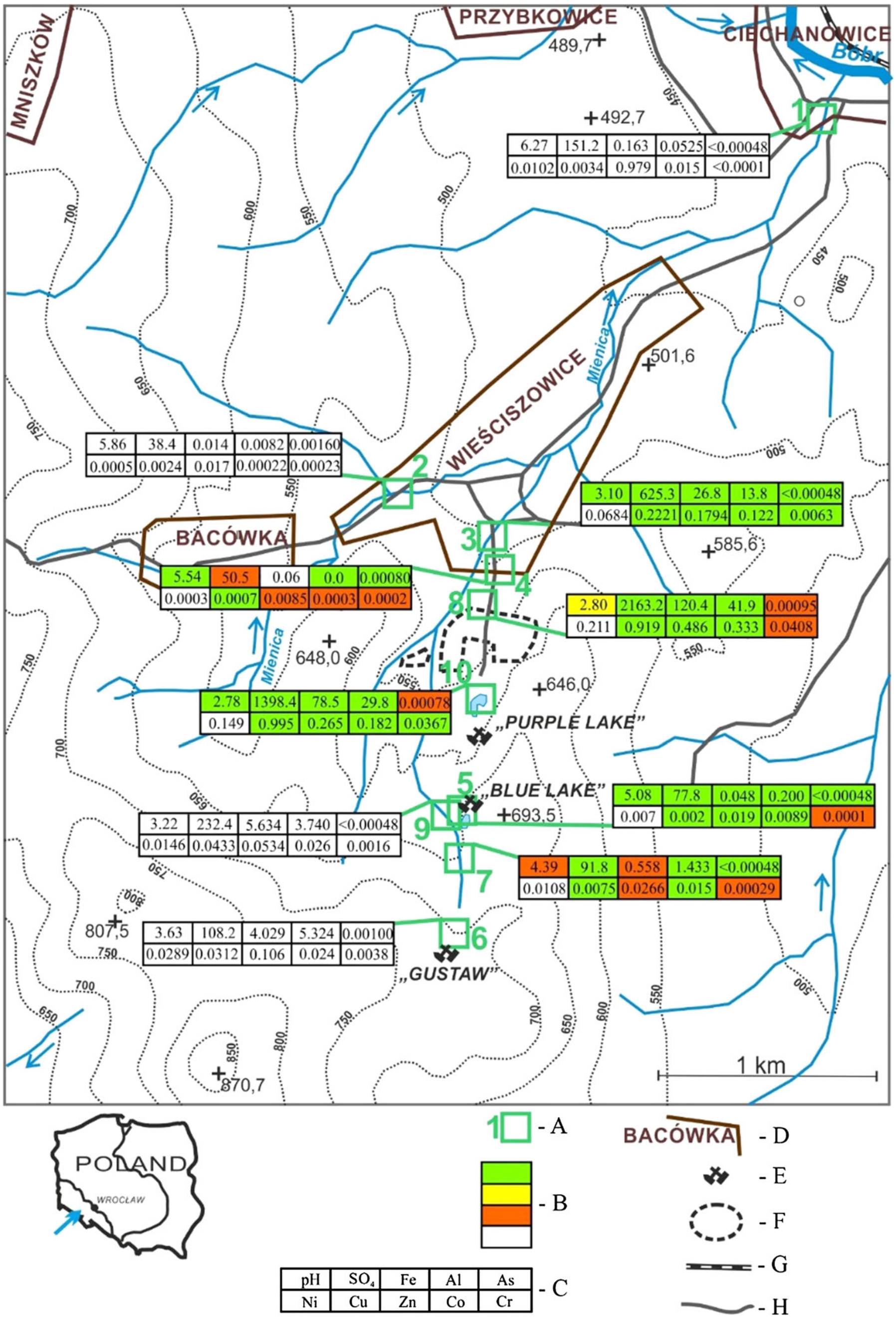


Fig. 10 Spatial distribution of selected chemical components of 2015 samples. Comparison with the 2000 campaign results. A-water sampling location; B-tendency of chemical changes: green-pH increase and drop of ions concentration; yellow-constant pH; orange-pH drop and increase of ions concentration; and white-no 2000 campaign data; C–pH and concentration of selected ions [mg L^{-1}]; D-village; E-abandoned mining area; F-dump; G-railroad line; and H-main road

Fe for each sample location. These elements were chosen due to their potential toxicity when in high concentration, thus with a high potential to induce non-cancer effects. According to Fig. 11, total risk of the selected elements is decreasing from the year 2000 to 2015, for both children and adults.

Sampling site 8 poses the higher risk if humans consume directly or indirectly these waters. This

Table 4 Annual precipitation on the surroundings of the study area between 1999 and 2015 (IMGW-PIB 2020)

	Annual precipitation [mm]																
	1999	**2000**	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	**2015**
Jelenia Góra	613	**700**	885	800	483	630	749	795	704	610	787	984	666	760	853	813	**473**
Kowary	712	**760**	954	822	575	688	860	850	853	778	903	1189	764	887	1007	893	**544**

2000 and 2015 (in bold) are the years compared in this study

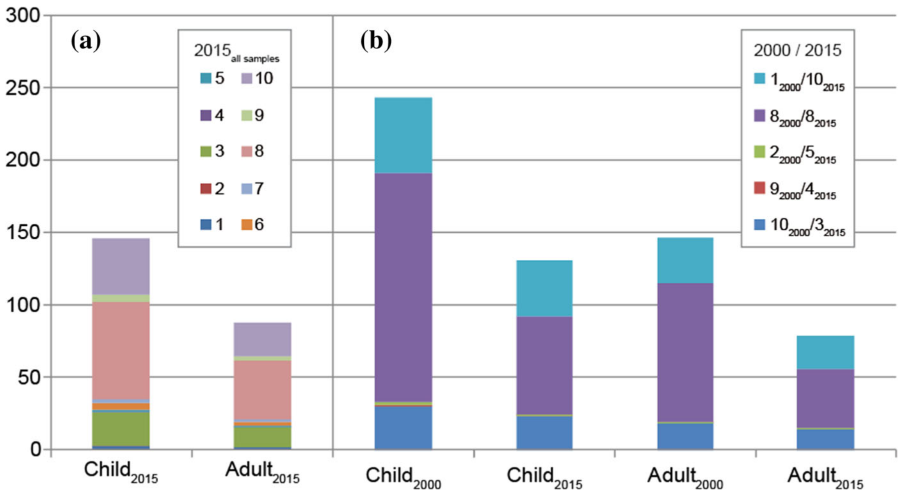


Fig. 11 Cumulative total human health non-cancer risk (HI) both for children and adults in **a** total samples of 2015; **b** the correspondent samples locations of 2000 and 2015. Values above 1 imply that there is a probability of occurrence of non-carcinogenic effects, being enhanced with increasing HI values. Scale represents the cumulative hazard 1 based index

sample was collected in an outflow from under the dump (Fig. 3). Location site 10, in Purple Lake, decreased considerably its potential human health risk from 2000 to 2015. Location site 5, in Blue Lake, does not represent a risk, as well as the spring water from sampling site 4. Stream water located ~ 350 m below the last dump (location site 3) still represents a potential risk, but lower than in 2000. The human health non-cancer risk in Mienica stream, at the outlet to Bóbr River (sample 1) in 2015, was also diminished.

Conclusions

The chemical analysis of the waters that outflows at Bóbr River from Wieściszowice mining area, taking in consideration stable geochemical conditions, reveals an appropriate water quality for human use, except for Mn concentration, 6 times above Polish legislation. The dominant water types are Ca–SO_4 type. Results from HCA analysis suggest that most of the fluctuations are explained by the anthropogenic pollutants and the evolution of water characteristics along the stream. Saturation conditions of water in comparison with mineral phases, in particular oversaturation with Fe oxi-hydroxides, can be contributing to the contaminants retention by adsorption and/or co-precipitation of metals and metalloids. The hydrochemical results indicate a general decrease in metal and SO_4 anthropogenic contributions compared to the year 2000. The human health non-cancer risk of the selected elements Al, Co, Cu and Fe decreased in comparison with the year 2000. Results of the study provide data that can be important for the water resource management in the Wieściszowice area and similar locations, particularly in what concerns to anthropogenic stress in streams. Long-term monitoring of water quality is crucial to document the seasonality of metal concentrations and develop adequate remediation schemes for abandoned mines.

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Compliance with ethical standards

Conflicts of interest There are none.

References

Ali, M. M., Ali, M. L., Islam, S., & Rahman, Z. (2016). Preliminary assessment of heavy metals in water and sediment of Karnaphuli river, Bangladesh. *Environmental Nanotechnology Monitoring and Management, 5,* 27–35. https://doi.org/10.1016/j.enmm.2016.01.002.

Alpers, C. N., & Nordstrom, D. K. (1999). Geochemical modeling of water–rock interactions in mining environments. *Rev Econ Geol, 6A,* 289–323.

ASTM. (1984). American society for testing materials, annual book of ASTM standards. *Water Environmental Technology, 11,* 01.

Balcerzak, E., Dobrzyński, D., & Parafiniuk, J. (1992). The effects of mineral alterations in the weathered zone of pyrite-bearing schists in Wieściszowice. the Rudawy Janowickie Mts., W Sudetes Poland. . *Annales Societatis Geologorum Polonoae, 62,* 75–93.

Ball, J.W., Nordstrom, D.K. (1991). User's manual for WATEQ4F with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters, US Geological Survey Open-File Report, 91–183.

Berger, A. C., Bethke, C. M., & Krumhansl, J. L. (2000). A process model of natural attenuation in drainage from a historic mining district. *Applied Geochemistry., 15,* 655–666. https://doi.org/10.1016/S0883-2927(99)00074-8.

Bigham, J. M., & Nordstrom, D. K. (2000). Iron and aluminum hydroxysulfates from acid sulfate waters. *Reviews in Mineralogy and Geochemistry, 40,* 351–403.

Borkowski, A., Parafiniuk, J., Wolicka, D., & Kowalczyk, P. (2013). Geomicrobiology of acid mine drainage in the weathering zone of pyrite-bearing schists in the Rudawy Janowickie Mountains (Poland). *Geological Quarterly, 57*(4), 601–612. https://doi.org/10.7306/gq.1115.

Caraballo, M. A., Macías, F., Nieto, J. M., & Ayora, C. (2016). Long term fluctuations of groundwater mine pollution in a sulfide mining district with dry Mediterranean climate: implications for water resources management and remediation. *Science of the Total Environment, 539,* 427–435.

Casiot, C., Lebrun, S., Morin, G., Bruneel, O., Personne, J. C., & Elbaz-Poulichet, F. (2005). Sorption and redox processes controlling arsenic fate and transport in a stream impacted by acid mine drainage. *Science of the Total Environment, 347,* 122–130.

Demchak, J., Skousen, J., & McDonald, L. M. (2004). Longevity of acid discharges from underground mines located above the regional water table. *Journal of Environmental Quality, 33*(2), 656–668.

Drever, J. I. (1998). *The geochemistry of natural waters* (2nd ed.). Prentice-Hall: New Jersey.

Freeze, R. A., and Cherry, J. A. (1979). *Groundwater*. Prentice-Hall (604 pp.).

Hammarstrom, J. M., Seal, R. R., II., Meier, A. L., & Kornfeld, J. M. (2005). Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. Geochemistry of sulfate Minerals: A Tribute to Robert O. Rye. 2. *Chemical Geology, 215,* 407–431.

IMGW-PIB (2020). Meteorological and hydrological database of Institute of Meteorology and Water Management–National Research Institute (IMWM-NRI)–unpublished.

INAP (2009). The International Network for Acid Prevention, Global Acid Rock Drainage Guide (GARD Guide), http://www.gardguide.com/. Accessed December 2018.

Jambor, J. L., Nordstrom, D. K., & Alpers, C. N. (2000). Metal-sulfate salts from sulfide mineral oxidation. *Reviews in Mineralogy and Geochemistry, 40*(1), 303–350. https://doi.org/10.2138/rmg.2000.40.6.

Jaskólski, S. (1964). Złoże łupków pirytonośnych w Wieściszowicach na Dolnym Śląsku i próba wyświetlenia jego genezy. The pyrite-bearing schists deposit in Wieściszowice in Lower Silesia and an attempt to explain its origin. *Rocznik Polskiego Towarzystwa Geologicznego, 34*(1–2), 29–55.

Krajewski, R., & Report on works of the Ore Division for. (1947). *Polish Geological Survey*. Warsaw: Polish Geological Institute.

Kwiatkowski J., and Hołdys T. (1985). Klimat Climate. In: Janh, A. red. Karkonosze Polskie. *Wrocław: Wyd*. Ossolineum, s. 87–116. In Polish.

Marszałek H. (2007). *Kształtowanie zasobów wód podziemnych w rejonie Kotliny Jeleniogórskiej. Forming of groundwater resources in the Jelenia Góra Basin Acta Universitatis Wratislaviensis* No 2993, seria: Hydrogeologia. Wyd. Uniwersytetu Wrocławskiego, Wrocław, pp 234. In Polish.

Marszałek H., Wąsik M. (2001). Hydrogeochemical anomaly in waters of the pyrite deposit area in Wieściszowice

(Western Sudetes Mts., SW Poland). In: Seiler, Wohnlich (eds.)–*New Approaches Characterizing Groundwater Flow*. Swets & Zeitlinger, Lisse.

Marszałek H., Wąsik M. (2005). Wodonośność skał krystalicznych metamorfiku kaczawskiego i izerskiego na podstawie wyników próbnych pompowań. The water-bearing capacity of the crystalline rocks in the Kaczawa and Izera Metamorphic units on the basis of the pumping test results. [W:] Współczesne Problemy Hydrogelogii, tom XII, wyd. UMK Toruń, 491–497. In Polish.

Mayes, W. M., Potter, H. A. B., & Jarvis, A. P. (2010). Inventory of aquatic contaminant flux arising from historical metal mining in England and Wales. *Science of the Total Environment, 408*(17), 3576–3583.

Nordstrom D. K. (1982). *Aqueous pyrite oxidation and the consequent formation of secondary minerals* . In: Acid Sulfate Weathering, Publisher: Soil Science Society of America, Editors: Kittrick JA, Fanning DS, Hosner LR, 37–56.

Nordstrom, D. K. and Munoz, J. L. (1986). *Geochemical Thermodynamics*. Blackwell Scientific Publications.

Nordstrom, D. K., Alpers, C. N. (1999). *Geochemistry of acid mine waters*. In: Plumlee, G. S., Logsdon, M. J. (Eds.), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues, Society of Economic Geologists, Reviews in Economic Geology 6A, 133–156.

Oyewo, O., Adeniyi, A., Bopape, M., & Onyango, M. (2020). Heavy metal mobility in surface water and soil, climate change and soil interactions. *Climate Change and Soil Interactions*. https://doi.org/10.1016/B978-0-12-818032-7.00004-7.

Parafiniuk, J. (1996). Sulfate minerals and their origin in the weathering zone of the pyrite bearing schists at Wieściszowice (Rudawy Janowickie Mts) Western Sudetes. *Acta Geologica Polonica, 46*(3–4), 353–414.

Parafiniuk, J., & Siuda, R. (2006). Schwertmannite precipitated from acid mine drainage in the Western Sudetes (SW Poland) and its arsenate sorption capacity. *Geological Quarterly, 50*(4), 475–486.

Parkhurst, D. L., Appelo, C. A. J. (1999). Users guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water-Resources Investigation Report* 99–4259. U.S. Geological Survey, Denver, Colorado.

Parkhurst, D. L., Appelo, C. A. J. (2013). Description of input and examples for PHREEQC version 3-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: *US Geological Survey Techniques and Methods*, 6(A43).

Piestrzyński, A., & Salamon, W. (1977). New data on polymetallic mineralization of quartz veins in pyrite deposite from Wieściszowice (Lower Silesia). *Kwartalnik Geologiczny, 21,* 25–37.

Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water analyses. *Transcations American Geophysical Union, 25,* 914–923.

Plumlee, G. S., Smith, K. S., Ficklin, W. H., Briggs, P. H. (1992). Geological and geochemical controls on the composition of mine drainages and natural drainages in mineralized areas, *Proceedings 7th Int Water-Rock Interaction Conference,* Park City, Utah, 419–422.

RAIS (2018). *The Risk Assessment Information System*; US Department of Energy's Oak Ridge Operations Office (ORO): Oak Ridge, TN, USA.

Ramsey, M. H., & Thompson, M. (1987). High-accuracy analysis by inductively coupled plasma atomic emission spectrometry using the parameter-related internal standard method. *Journal Analytical Atomic Spectrometry, 2,* 497–502.

Rozporządzenie Ministra (2017). Rozporządzenie Ministra Zdrowia w sprawie jakości wody przeznaczonej do spożycia przez ludzi z dnia 7 grudnia 2017 r. (Dz.U. z 2017 r. poz. 2294). *Regulation of the Minister of Health on the quality of water intended for human consumption*, December 7, 2017. In Polish.

Sánchez-España, J., López Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., & Barettino, D. (2005). Acid mine drainage in the iberian pyrite belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry, 20–7,* 1320–1356.

Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry: chemical equilibria and rates in natural waters* (3rd ed.). London, UK: Wiley.

Szałamacha, J. (1956). *Szczegółowa mapa geologiczna Sudetów w skali 1:25000, ark.* Janowice Wielkie. Geological map of the Sudetes in the scale of 1: 25,000, Janowice Wielkie sheet. Warszawa: PIG. In Polish.

Szałamacha, J. (1979). *Pyrite-bearing schists.* In: Dziedzic K. (ed.)–Mineral deposits of Lower Silesia. Ossolineum, Wrocław.

Szałamacha, J., Szałamacha, M., (1988). *Szczegółowa mapa geologiczna Sudetów w skali 1:25000, ark. Pisarzowice.* Geological map of the Sudetes in the scale of 1: 25000, Pisarzowice sheet. Warszawa: PIG. In Polish.

Tabelin, C. B., Corpuz, R. D., Igarashi, T., Villacorte-Tabelin, M., Alorro, R. D., Yoo, K., et al. (2020). Acid mine drainage formation and arsenic mobility under strongly acidic conditions: Importance of soluble phases, iron oxyhydroxides/oxides and nature of oxidation layer on pyrite. *Journals Hazardous Materials, 399,* 122844. https://doi.org/10.1016/j.jhazmat.2020.122844.

Younger, P. L. (1997). The longevity of mine water pollution: a basis for decision-making. *Science of the Total Environment, 194–195,* 457–466. https://doi.org/10.1016/S0048-9697(96)05383-1.