



Chemical variations in mine water of abandoned pyrite mines exemplified by the Colorful Lakes in Wieściszowice, Sudetes Mountains, Poland

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ABSTRACT

Study region: This article contributes to understanding processes occurring in long-time abandoned, shallow and unremediated mining lakes exemplified by the Colorful Lakes near Wieściszowice, Southwest Poland.

Study focus: Temporal and spatial water chemistry variation and stable isotopic composition has been investigated in two sampling campaigns in wet and dry seasons. Novelty relating to these Lakes is that for the first time, depth and temporal dependent samples were studied chemically and isotopically. Water samples from various depths of the lakes and drainage water were analyzed for main ions, trace and semi-metals as well as sulfur and water isotopes. Data were interpreted statistically and with the chemical-thermodynamic code PHREEQC.

New hydrological insights for the region: Processes in the lakes are similar, resulting from rain and groundwater infiltrating the rocks and mine residues and leaching efflorescent salts. Differences result from the lakes' depth, altitude, and source of inflow. They cause the Blue Lake to be in the Al- and the Yellow and Purple Lakes in the Fe-buffer-range. These lakes' characteristics result either in stratification, evaporation influence or a well-mixed pit lake identified by the isotope variability. Isotope results further identified bacterial sulfate reduction throughout the lake water column during spring and summer. Saturation indices show an undersaturation in relation to most phases, and the species distribution in the lakes mirrors their individual buffer environment.

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1. Introduction

Abandoned flooded mine sites are places where the full spectra of geochemical processes affecting water quality and the environment can be studied, particularly in pit lakes, which often create a picturesque landscape but with a potentially harmful content. Numerous accidents are related to tourists swimming in low pH water, including instagrammers or influencers being injured after posing in the Spanish Monte Neme lake (Zlotnick, 2019). To minimize the effects of such events, it is critical to know the water chemistry and processes in post-mining lakes of touristic interest in as many locations as possible (e.g. Molenda and Kidawa, 2020). This is also a crucial issue in case of the Colorful Lakes (Kolorowe Jeziora) presented in this article, one of the most popular touristic attractions in southern Poland (Kolorowe Jeziora, 2021).

In the past two decades, the complexity of post-mining lakes has been described in four comprehensive monographs. They provide an outlook on former metal, lignite, and hard coal open-pit mines (Castendyk and Eary, 2009; Geller et al., 2013, 1998; McCullough, 2011) that are often affected by acid mine drainage (AMD). In these books, guidelines for investigations, management, remediation, and prediction of the water chemistry and potential environmental impacts of pit lakes are given and supported by relevant case studies. A comprehensive study on potential after-usage of open-pit lakes was published by McCullough et al. (2020).

Abandoned open-pit mines, ultimately resulting in pit-lakes, are common wherever easy-accessible, shallow mineral resources occur. Some of the best-explored open pit-lakes are in Germany, Australia, Spain, Portugal, USA, Canada, and Poland. Focusing on European examples, German pit lakes are mostly related to lignite mining in the 19th and at the beginning of the 20th century. Nearly 500 lakes located in six German districts cause substantial environmental and reclamation challenges (Benthaus et al., 2020; Schultze et al., 2009), with over 140 lignite mining pits belonging to the Central German District (Schultze et al., 2010). Most of these lakes are highly acidic and need long term remediation measures. In Poland, similar lakes near the German border are part of the Łuk Mużakowa Geopark. Publications about Polish lignite mine pit lakes focus on their chemistry and biology (Gąsiorowski et al., 2021; Lutyńska and Labus, 2015; Oszkini-Golon et al., 2020; Sienkiewicz and Gąsiorowski, 2016), while those about German pit lakes focus on identifying the chemical processes, reclamation methods or mine water reuse (Benthaus et al., 2020; Nixdorf et al., 2010; Schultze et al., 2018).

One of the World's most prominent cases for acid rock and mine drainage is the Spanish and Portuguese Iberian Pyrite Belt. Dozens of lakes are highly acidic, and their hydrochemistry and limnology has extensively been characterized (Gomes et al., 2019; Sánchez-España et al., 2009, 2005). In addition, their microbial diversity (Santofimia et al., 2013) and biogeochemistry were studied in detail (Falagán et al., 2014). A common feature of these lakes and the Colorful Lakes is that they are the remnants of pyrite mining. Yet, the Iberian Pyrite Belt's pit lakes are larger and deeper compared to the Colorful Lakes, and their geological as well as climatic background is different.

These differences make the Colorful Lakes a stimulating site for hydrogeological and isotopic investigations. Groundwater research of the lakes' vicinity initially focused on regional aspects followed by studies of the chemistry. Michniewicz (1981) identified a hydrogeochemical anomaly, and based on these results, a model of mineral transformation in the sulfide oxidation zone of the silicate metamorphic rocks was developed. Further research provided knowledge on the origin and chemical composition and evolution of groundwater (Jezierski, 2002; Koniecznyńska, 2007; Marszałek and Wąsik, 2001; Mickiewicz and Marszałek, 2016). The water of the Colorful Lakes has been characterized by several authors, of which the first one presents aluminum solubility in the pit lakes' water (Dobrzyński, 1995). Parafiniuk and Dobrzyński (1995) investigated the relationship between groundwater and surface water, and Pocięcha et al. (2018) described the rotifer diversity in the lakes, while the physicochemical background has been analyzed by Fedak and Lindner (1966). So far, the latest investigation of the baseline and the pit lake chemistry has been provided by Costa et al. (2021).

This investigation aims in understanding temporal and spatial changes in the chemistry (main and trace elements) and stable isotope composition in shallow pit lakes, exemplified by the Wieściszowice Colorful Lakes. None of the previous studies of the Colorful Lakes conducted investigations in potential lake stratification and the chemical mechanisms occurring in different seasons. Therefore, this study supplements the knowledge about long time abandoned (nearly 100 years) shallow and unremediated metal mining lakes. Preliminary results of this research were published by Konsencjusz et al. (2012b) and are extended and interpreted in more detail here. The goal of this paper is to characterize chemical processes, understand vertical spatial changes in the lakes' chemistry, and answer whether these changes fit seasonal patterns.

2. Materials and methods

2.1. Study area

Colorful Lakes near the village of Wieściszowice (formerly *Rohnau*), Poland is a common name for a set of four abandoned mining lakes located in the Rudawy Landscape Park and Rudawy Janowickie Natura 2000 area (Fig. 1). Around the lakes, the 3-ha-large area has been intensively transformed by historical opencast and underground mining of pyrite performed from the end of the 18th to the beginning of the 20th century. After mining and sulfuric acid production ceased in 1925 (Pietryga, 1962), the Mienica and its tributaries (Rdzawy Potok – “Rusty Brook” [formerly *Ockerbach*] – and several unnamed streams) flooded the mine excavations, and four artificial lakes formed: Yellow, Purple, Blue and Green (periodical). All these lakes are situated in the lower part of the Wielka Kopa (871 m a.s.l., formerly *Scharlachberg*) at an altitude of 560 – 730 m a.s.l. (Fig. 2). The higher parts of Wielka Kopa (Blue Lake) are dominated by coniferous pine-spruce forests with a small admixture of deciduous trees, while at lower altitudes (Purple Lake and Yellow Lake) deciduous trees with a high proportion of birch dominate, meaning that more leaves are in the brooks and lakes and settle to the bottom, where they decompose.



Fig. 1. Images of the three Colorful Lakes, SW Poland. From left to right: Blue, Purple and Yellow Lakes.

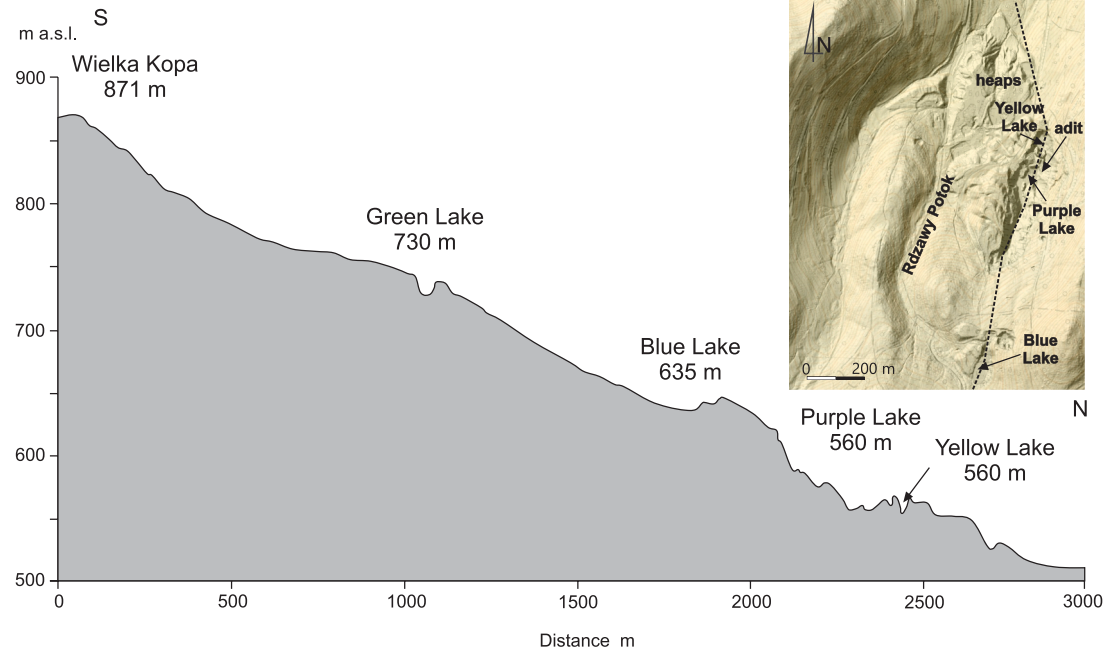


Fig. 2. Cross section of the Colorful Lakes region and a Lidar map of the Rdzawy Potok valley (www.geoportal.gov.pl).

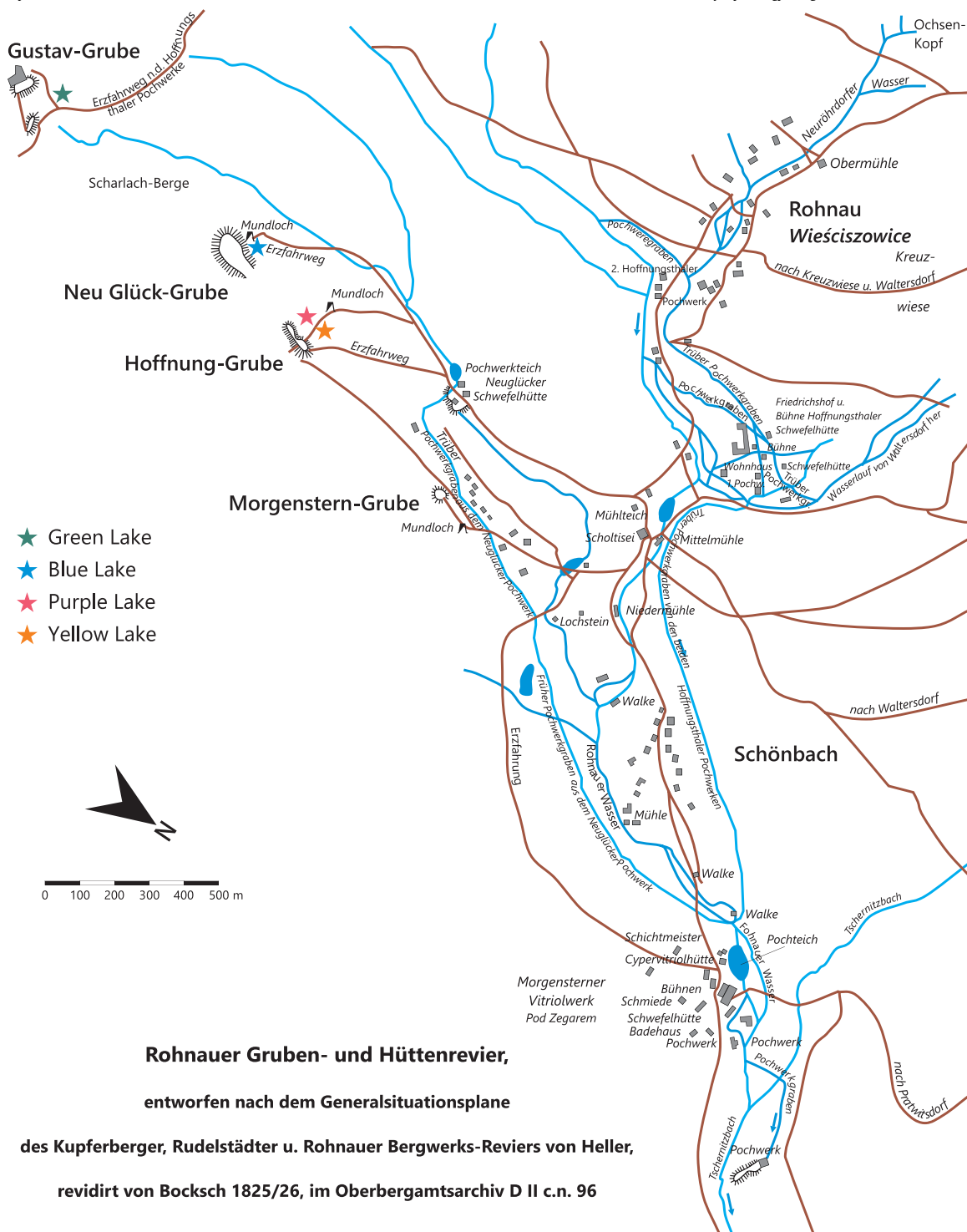


Fig. 3. Historical, German map of the Rohnau (Wieściszowice) pyrite mining area (after Fechner, n.d., map h), providing an impression of the mining area at that time. Situation and identification of the locations in the text. Location of the four lakes superimposed on the historical map.

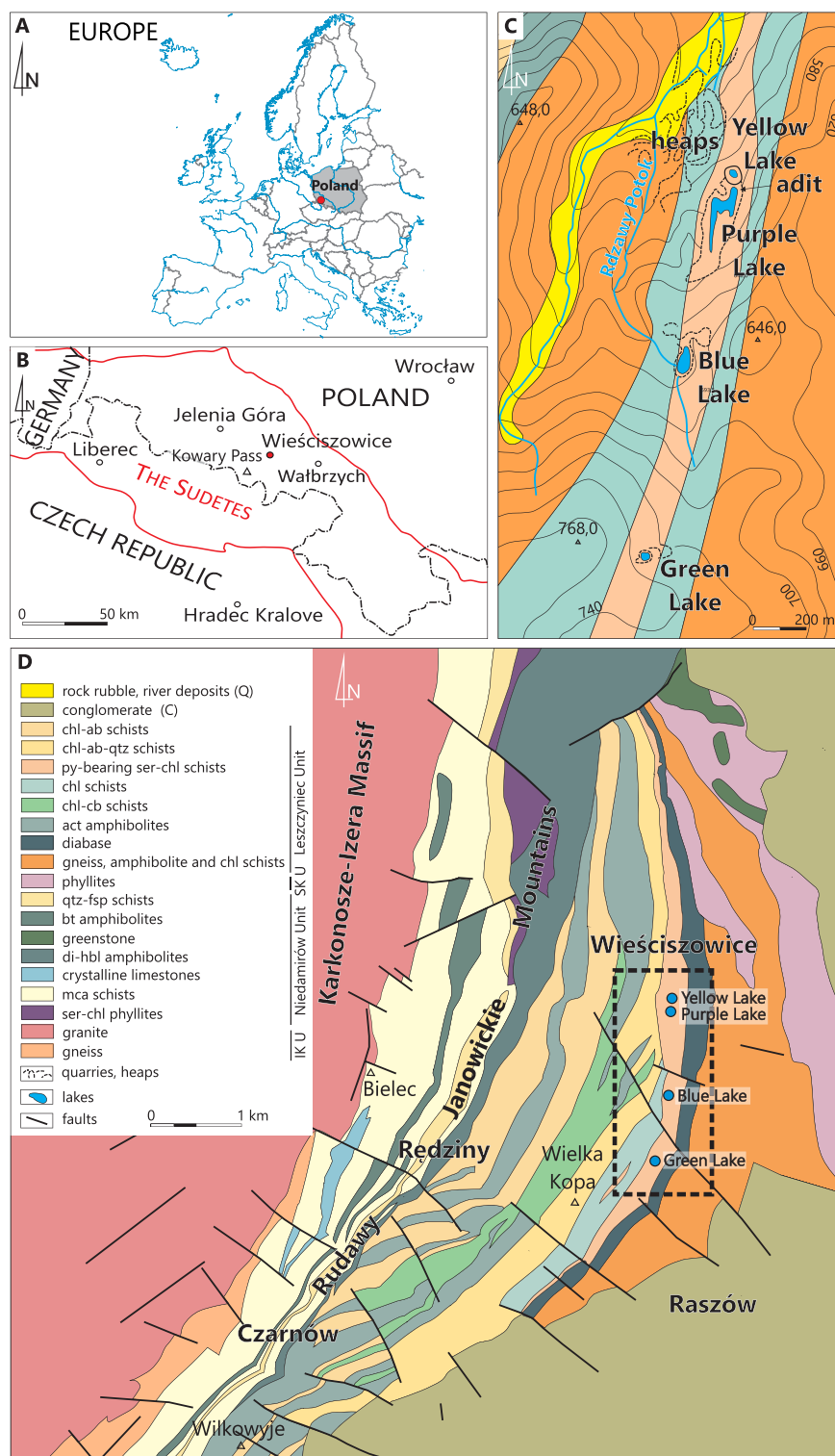


Fig. 4. Geological setting of the Leszczyniec Unit (D; modified after [Szałamacha and Szałamacha, 1988](#)) and geological map of the Wieściszowice deposits in the Leszczyniec Unit (C; modified after [Berg \(1913b\)](#)). Abbreviations: C: Carboniferous, Q: Quaternary, act: actinolite, ab: albite, bt: biotite, cb: carbonate minerals, chl: chlorite, di: diopside, fsp: feldspar, hbl: hornblende, mca: mica, py: pyrite, qtz: quartz, ser: sericite, IK U: Izera Kowary Unit, SK U: Southern Karkonosze Unit.

Green Lake (also known as Green Pond, Black Lake) was created during the *Gustav Grube* mine excavation (Fig. 3), which started operation in 1796. This lake is located at an altitude of 730 m a.s.l. and appears rarely, only after intense rainfall. Usually, it dries out quickly, disappearing again for many years. During the 2011 and 2012 sampling campaigns, this lake was dry and, therefore, could not be sampled.

Blue Lake (also known as Emerald, Turquoise, Azure, formerly *Grüner See*) is a remnant of the abandoned *Neues Glück* mine, which started operation in 1793. Located at an altitude of 635 m a.s.l., the lake is 150 m long, 30–50 m wide and 7–8 m deep. There are two old adits in its close vicinity, the first one 45 m long and partially flooded, while the other one is only about 10 m long.

Purple Lake (also known as Orange or Red Lake) is another remnant of the *Hoffnung* mine at an altitude of 560 m a.s.l. This lake has dimensions of about 430×110 m, a highly variable shoreline and its depth depends substantially on rainfall, ranging from 0.5 to 3 m. Around the lake, the height of rock faces measured from the water level reaches 30–150 m. Moreover, there is a former, currently flooded mine gallery with a length of 132 m, a width of 1.5 m and a height of 1.7 m.

Yellow Lake (also known as Yellow Pond) is in the oldest and northern part of the *Hoffnung* mine, which started mining in 1785 (Berg, 1913a, 1913b; Fedak and Lindner, 1966; Jaskólski, 1964; Krajewski, 1949; Nielubowicz, 1958; Nielubowicz and Jaskólski, 1957). This lake is located at an altitude of 560 m a.s.l. and formed between the mined heaps about 20 years ago. After heavy rainfall, rainwater draining from the hill slopes fills it with yellowish water. Greatly depending on the amount of rain, its depth ranges between 0.5 and 4 m. In dry, low precipitation years, the lake disappears and leaves an indistinguishable depression from its surroundings. For none of the lakes or streams, hydrographs exist, so that precipitation–flow relationships can currently not be provided. This also holds true for bathymetric data about the lakes.

Hydrological, hydrogeological and detailed meteorological studies in the area around the lakes could not be found in the published literature. In principle, the hydrogeological conditions of the Rudawy Janowickie can be considered similar to those in other crystalline massifs of the Sudetes (Marszałek, 1996; Staško, 2010). Groundwater occurs in three depth zones: within a weathering cover in the upper part of the fractured crystalline rocks, in deeper fractured rocks and the deep tectonic faults. These zones are often connected with each other but can also form independent and isolated hydrodynamic systems (Mickiewicz and Marszałek, 2016). The first zone, from which the lakes' water supply originates, is related to a porous-fissured aquifer composed of the weathering zone of fissures with a saprolite up to 25–30 m thick. It is recharged by precipitation and melting snow. In general, the fracture density was observed to decrease with depth. Pumping tests identified that the hydraulic conductivity of the fissured zone is low and amounts to $0.08–0.1 \text{ m d}^{-1}$ on average (Marszałek and Wąsik, 2005). Springs draining hard rocks discharge mostly from 0.1 to 1.0 L/s (Marszałek and Wąsik, 2001).

Various geological studies were conducted around Wieściszowice, with initial scientific activities primarily related to mineral exploitation dating to the 18th century, when pyrite deposits were found (Fechner, 1900). Three separate mines were established there at that time (Fig. 3): the *Hoffnung* mine in 1785, the *Neues Glück* mine in 1793 and the *Gustav Grube* mine in 1796 (Fechner, 1900). Subsequent geological research related to an attempt to resume sulfide mining after the world wars, but exploitation was finally abandoned. First publications in the 20th century were conducted by German geologists and subsequently by Polish ones (Petrascheck, 1933; Schneiderhöhn, 1958). Exploitation concerned only pyrite, the source of raw material for sulfuric acid production and lasted continuously until 1923 (closure of the mine) and 1925 (closure of the ore processing plants; Aleksandrowski, 2003; Fedak and Lindner, 1966; Kądziołko-Hofmokr et al., 1998; Kryza et al., 1995; Kryza and Mazur, 1995; Mayer et al., 2012; Mazur, 1995; Mazur et al., 2006; Mazur and Aleksandrowski, 2001; Mroczkowski, 1992; Pietryga, 1962; Szalamacha and Szalamacha, 1991; Werner et al., 2000).

Geologically, the study area belongs to the Leszczyńiec unit, which is made up of metabasites and gneisses (Fig. 4) and has been described in several publications. Numerous geologists, using geochemical and isotopic analyses, have also studied the tectonic position, origin of metamorphic rocks and the geological age of rocks belonging to the Rudawy Janowickie Mountains (Kryza and Mazur, 1995). Generally, the metamorphic part of the Karkonosze-Izera Massif has been interpreted as a succession of four structural units (Fig. 4): the Izera-Kowary, the Ještěd, the Southern Karkonosze, and the Leszczyńiec Units (Mazur and Aleksandrowski, 2001). The metaigneous Leszczyńiec Unit is located in the uppermost position of the Karkonosze-Izera Massif's structural units. This formation is composed of fine-grained, schistose and medium-grained, massive metabasites as well as metagranites (felsic gneisses) and metadiorites (hornblende gneisses), the latter two forming several, large igneous bodies within the metabasites (Oberc-Dziedzic et al., 2011). In the northern part of the Leszczyńiec Unit, near Wieściszowice, the metaigneous rocks are accompanied by pyrite-bearing schists, representing the only metasedimentary rocks in that unit (Jaskólski, 1964). All the remaining rocks are a mineralogically variable series of quartz-sericite-chlorite schists (Kryza and Mazur, 1995).

The pyrite bearing sericite-chlorite schists spread over a length of 4 km, from the Kowary Pass through Czarnów to Wieściszowice. On the surface, they outcrop from about 200 m south of Wieściszowice up to Wielka Kopa, gradually wedging out and disappearing, with the Colorful Lakes being in this zone (Fig. 4). Three 5–12 m thick zones of high-quality pyrite ore were found during exploitation (Nielubowicz, 1958), and further research found that the central zone is the richest part of the deposit (Parafiniuk and Siuda, 2006). On average, the deposit's pyrite concentrations were 10%, reaching 30% in some locations (Oberc-Dziedzic et al., 2011; Parafiniuk et al., 2016; Petrascheck, 1933; Piastrzyński and Salamon, 1977; Teisseyre, 1973).

Based on the literature, the main ore mineral is pyrite, besides chalcopyrite, tennantite, galena, pyrrhotite, arsenopyrite, marcasite, sphalerite, boulangerite, jamesonite, bournonite, tetrahedrite, limonite, and siderite (Balcerzak et al., 1992). On these rocks and in the heaps, a weathering zone with a wide range of secondary efflorescent minerals formed. Among these are components of the pyritic shale (quartz, sericite, chlorite), secondary minerals (illite, kaolinite, goethite; Balcerzak et al., 1992; Parafiniuk, 1996, 1991; Parafiniuk et al., 2016, 2010; Parafiniuk and Dobrzyński, 1995) and a rich paragenesis of secondary sulfate minerals: melanterite, fibroferite, copiapite, pickeringite, slavkite, epsomite, alunogen, and gypsum (Balcerzak et al., 1992; Parafiniuk and Dobrzyński, 1995; Uzarowicz et al., 2012, 2011, 2008).

Geochemical research showed that intense pyrite weathering in the abandoned excavations and heaps resulted in a specific

geochemical environment and the creation of a local hydrogeochemical anomaly (Parafiniuk and Siuda, 2006), commonly referred to as acid rock drainage (ARD). Due to this highly acidic environment and well-developed ARD and AMD, also schwertmannite precipitates were found (Balcerzak et al., 1992; Costa et al., 2021; Parafiniuk, 1996; Parafiniuk and Dobrzyński, 1995; Uzarowicz et al., 2012, 2011, 2008).

Relating to the weathering processes in the oxidation zone of the Wieściszowice pyrite-bearing shale, the surrounding rocks control the chemistry of the water and weathering products (Balcerzak et al., 1992). Mining resulted in the rocks' disintegration, increasing the thickness of the aeration and oxidation zone as well as the water ingress and, consequently, the weathering process. Iron-(di)sulfide oxidation releases iron and chalcophile metals, protons, and sulfate, turning the water and environment acidic. Consequently, further geochemical reactions in the weathering zone intensify the hydrolytic breakdown of additional minerals (Balcerzak et al., 1992), being responsible for the characteristic chemical composition of the lakes' water.

2.2. Isotopes

Until present, no publication dealt with isotopic research about the Colorful Lakes. From general studies it is known that sulfate is not subject to isotopic exchange processes and, therefore, the sulfur isotopic composition is only determined by its origin and redox reactions, which are primarily controlled by the biosphere (Clark and Fritz, 1999; Kendall and McDonnell, 1998). Consequently, $\delta^{34}\text{S}$ (SO_4^{2-}) results from the isotopic composition of sulfate from different sources. Each source has its distinct isotopic characteristic as well as isotopic fractionation factor related to the transition of sulfur to different oxidation states with the largest variations resulting from kinetic effects accompanying the biochemical cycling of sulfur (Krouse and Grinienko, 1991). The most relevant process modifying the sulfate isotopic composition is bacterial sulfate reduction, which enriches the heavier sulfate isotope ^{34}S , because sulfate reducing bacteria prefer the light sulfur isotope ^{32}S (Jędrysek, 2002; Kendall and McDonnell, 1998).

Sulfur fractionation is also associated with photosynthetic reduction of sulfate by plants during the incorporation of sulfur into the amino acid structures (Kendall and McDonnell, 1998). Plants preferentially use ^{32}S , but the isotopic effect is less pronounced as in bacterial sulfate reduction (Mandernack et al., 2000), even considered negligible by some authors (Fritz et al., 1989).

Similarly, the sulfate oxygen isotopic composition in lacustrine water predominantly depends on biological processes: sulfate reduction and reoxidation of reduced sulfur. In spite of a slow rate of thermodynamic isotopic exchange between sulfate and water, $\delta^{18}\text{O}(\text{SO}_4^{2-})$ is clearly related to $\delta^{18}\text{O}(\text{H}_2\text{O})$. This relationship results from the equilibrium isotopic exchange of sulfate oxygen with water oxygen during bacterial sulfate reduction in cells ($\text{D}_{\text{SO}_4^{2-}-\text{H}_2\text{O}} \approx 25\text{‰}$; Brunner et al., 2005). This process is bidirectional and can accompany the reduction of sulfate to sulfide and subsequently their reoxidation. An isotopic equilibrium is therefore reached between sulfate oxygen and water oxygen during these gradual successive transformations. Thus, $\delta^{18}\text{O}(\text{SO}_4^{2-})$ results from: the water isotopic composition, the equilibrium oxygen isotopic fractionation factor in the system, the kinetic isotopic effect that occurs during reoxidation of reduced sulfur phases, and the ratio of the rate of sulfate reduction to the rate of their re-formation during oxidation processes (Schiff et al., 2005). During sulfate formation, water oxygen or molecular oxygen dissolved in the water are used as oxygen sources. $\delta^{18}\text{O}$ of the formed sulfate therefore depends on the ratio of water oxygen and the oxygen from dissolved molecular oxygen, both of which are a function of the available dissolved oxygen, the type of enzymes catalyzing the oxidation reaction, and Eh, pH, and temperature (Carmody et al., 1998).

2.3. Methods

Sampling in the Colorful Lakes was performed twice: on 2011–09–29 and 2012–06–20 (Konsencjusz et al., 2012a). Weather conditions (temperature, precipitation) were like those recorded in previous years. In the Blue Lake, samples were taken at depths of 0 m, 1.5 m, 2.5 m, 3.5 m, 4.5 m, 5.5 m (only on 2011–09–29), 6.5 m, and 7.5, in the Purple Lake at 0 m, 1.5 m, and 2.5 m, and in the Yellow Lake at 0 m, 2.0 m, and 3.5 m below the lake surface. As the green lake was dry during the sampling campaigns, it could not be sampled. Samples were taken from the central part of each lake using a pontoon and a Ruttner type sampler (KC Denmark A/S). A 5-liter cylindrical acrylic probe that closed at the desired depth was used. Collection of water from the sampler was done through a dew valve located at the lower part of the sampler. Flow in Rdzawy Potok and the Neues-Glück-adit was measured volumetrically with the bag and stopwatch method.

pH, Eh (redox potential, corrected to standard hydrogen electrode) and EC (electrical conductivity) were measured in the field with an Elmetron CPC-401 multi-parameter instrument and IJ44C, CD-210, CT2B-121 and ERPt-13 electrodes. Main and trace element concentrations (detection limits 0.01 mg/L, other detection limits in brackets) of Cl^- (0.05), SO_4^{2-} , PO_4^{3-} (0.006), NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe_{tot} , Al^{3+} were analyzed photometrically, Mn^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Ba^{2+} , As^{3+} , Pb^{2+} (0.01 $\mu\text{g/L}$) were analyzed by Atomic Absorption Spectrophotometry (AAS) on an Avanta Σ GBC. If compounds exceeded the upper limit of the method, samples were diluted accordingly. Alkalinity was analyzed by titration (PN-EN ISO, 9963–1, 2001) and TDS gravimetrically with 25 mL of sample and drying at 105 °C. Analyses were made at the Chemical Laboratory of the Physical Geography Department of the Wrocław University (Appendix 1).

Oxygen and hydrogen stable isotope samples were collected in 30-mL, tightly sealed amber-glass bottles and analyzed by mass spectrometry. Sulfur (^{34}S , ^{32}S) and sulfate oxygen (^{18}O , ^{16}O) stable isotope samples were collected in acidified (pH 2–3) 1-L HDPE bottles with 10% BaCl solution to precipitate sulfate as BaSO_4 (Gehre, 1996; Gehre et al., 2004; Vinograd and Porowski, 2020) and analyzed at the Institute of Geological Sciences of the Polish Academy of Sciences (ING PAN, Warsaw, Poland, Appendix 1).

Oxygen isotopes (^{18}O) were measured by water- CO_2 gas equilibration using a ThermoFisher Scientific's Gas Bench II system with online continuous flow on evolved CO_2 gas, and hydrogen isotopes (^2H) by water reduction on hot chromium using an automated

Table 1

Summarized results of the chemical and physicochemical parameters of the two sampling campaigns in the Colored Lakes. TDS: total dissolved solids, EC: electrical conductivity, b.d.l.: below detection limit, -: not analyzed, IB error: PHREEQC ion balance error.

	Blue Lake, <i>n</i> = 15				Purple Lake, <i>n</i> = 6				Yellow Lake, <i>n</i> = 6			
	min.	max.	\bar{x}	σ	min.	max.	\bar{x}	σ	min.	max.	\bar{x}	σ
T, °C	11.2	20.4	16.7	2.7	15.7	22.3	18.3	2.7	13.7	19.4	16.4	2.5
pH, –	4.85	5.74	5.14	0.24	2.37	2.88	2.62	0.26	2.25	2.90	2.61	0.31
Eh, mV	479	532	503	20	659	785	717	47	732	792	759	23
pE, –	8.48	9.42	8.91	0.37	11.65	13.88	12.68	0.84	12.94	14.02	13.45	0.41
EC, $\mu\text{S}/\text{cm}$	160	188	180	7	2470	3950	3130	648	1540	1956	1678	161
TDS, mg/L	80	144	114	22	2500	4776	3313	839	1236	1624	1360	141
Cl ⁻ , mg/L	1.54	5.13	3.51	1.55	0.64	2.57	1.43	0.79	1.35	4.54	2.64	1.28
HCO ₃ ⁻ , mg/L	7.93	14.03	10.82	2.02	–	–	–	–	–	–	–	–
SO ₄ ²⁻ , mg/L	62.9	88.8	74.1	6.9	1268	3108	1930	650.1	618.8	837.6	716.1	86.1
NO ₃ ⁻ , mg/L	0.05	4.21	1.10	1.19	7.68	20.79	13.68	4.46	4.14	8.97	5.90	2.05
PO ₄ ³⁻ , mg/L	b.d.l.	0.30	0.08	0.10	0.01	0.45	0.13	0.17	0.01	0.11	0.06	0.05
NH ₄ ⁺ , mg/L	b.d.l.	0.41	0.13	0.15	0.08	1.09	0.54	0.42	b.d.l.	1.31	0.57	0.59
Na ⁺ , mg/L	2.29	3.61	2.98	0.41	2.73	4.77	3.53	0.81	3.24	4.14	3.60	0.37
K ⁺ , mg/L	0.07	0.25	0.14	0.06	0.04	0.16	0.11	0.05	0.15	0.40	0.26	0.11
Mg ²⁺ , mg/L	4.18	6.98	5.66	1.10	67.9	138.2	103.5	29.7	32.62	38.50	35.24	2.12
Ca ²⁺ , mg/L	11.32	25.99	19.80	4.11	179.9	619.5	303.7	161.7	86.25	137.74	112.28	19.88
Mn ²⁺ , mg/L	0.12	0.21	0.17	0.03	1.62	3.31	2.43	0.71	0.39	0.68	0.48	0.11
Fe _{tot} , mg/L	0.06	0.21	0.13	0.06	25.38	109.34	68.82	38.19	12.16	71.74	39.76	29.12
SiO ₂ , mg/L	31.92	36.41	34.82	1.46	86.38	154.73	119.89	26.62	33.27	73.12	54.04	14.59
Al, mg/L	0.40	5.49	2.15	1.73	34.66	84.28	57.42	20.98	10.17	22.80	15.07	4.88
Ag, $\mu\text{g}/\text{L}$	0.01	2.80	0.69	1.09	0.04	2.19	0.55	0.85	0.06	4.60	1.76	2.08
As, $\mu\text{g}/\text{L}$	b.d.l.	2.13	1.10	0.73	37.03	84.83	68.76	20.52	1.61	11.50	7.86	3.81
Ba, $\mu\text{g}/\text{L}$	2.70	10.53	7.15	2.81	6.05	8.77	7.37	1.11	b.d.l.	7.77	4.02	3.28
Cd, $\mu\text{g}/\text{L}$	0.02	0.26	0.14	0.10	0.39	3.81	2.12	1.52	0.13	1.52	0.84	0.46
Co, $\mu\text{g}/\text{L}$	26.17	39.05	33.68	3.48	115.2	1072.0	518.9	384.0	345.7	420.8	370.7	27.4
Cr, $\mu\text{g}/\text{L}$	b.d.l.	0.67	0.20	0.23	49.33	125.04	89.44	32.49	19.80	27.77	23.47	2.79
Cu, $\mu\text{g}/\text{L}$	2.26	3.72	2.96	0.42	24.45	471.35	202.40	194.01	6.97	49.04	27.43	21.15
Mo, $\mu\text{g}/\text{L}$	b.d.l.	2.70	0.68	0.96	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5.13	1.49	2.46
Ni, $\mu\text{g}/\text{L}$	1.82	35.25	11.39	11.25	47.27	327.11	182.60	116.75	26.54	159.37	65.84	53.31
Pb, $\mu\text{g}/\text{L}$	b.d.l.	13.08	4.99	4.79	b.d.l.	4.81	2.09	2.07	b.d.l.	7.89	3.40	3.58
Sn, $\mu\text{g}/\text{L}$	b.d.l.	0.03	0.01	0.01	b.d.l.	0.04	0.02	0.02	b.d.l.	0.06	0.02	0.03
Sr, $\mu\text{g}/\text{L}$	2.56	3.82	3.13	0.47	30.09	44.03	37.45	5.41	16.98	21.99	19.94	1.77
Ti, $\mu\text{g}/\text{L}$	b.d.l.	12.83	4.00	4.81	b.d.l.	19.34	9.50	9.67	11.70	20.82	17.20	4.84
Zn, $\mu\text{g}/\text{L}$	7.47	29.10	11.99	7.13	80.84	839.10	356.19	290.38	22.70	159.80	65.46	52.41
IB error, %	-13.01	3.05	-2.59	4.08	-17.04	7.24	-5.47	10.5	-15.06	25.05	4.79	18.18

ThermoFisher Scientific H-device system. The results of analyses were reported using δ notation with respect to the VSMOW international standard (Gehre, 1996; Gehre et al., 2004; Vinograd and Porowski, 2020). Measurement precision, based on the long-term repeated measurements of international reference materials was $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for $\delta^2\text{H}$. Sulfur and oxygen isotopes of sulfate were analyzed by dynamic flash combustion (TC/EA combined with a Thermo Scientific Delta V Advantage IRMS) on BaSO₄ wrapped in silver capsules (Halas et al., 2007; Mizutani, 1971) and purged in helium to remove water and nitrogen. To analyze the sulfur isotopes, combustion and reduction were carried out in a single reactor filled with tungsten oxide (WO₃) and copper (Cu) as a reducing agent. In the reactor, the 1020 °C helium carrier is enriched in O₂ gas, and the BaSO₄ is thermally decomposed to produce SO₂ for sulfur isotope measurement. For the oxygen isotopes, the samples and glassy carbon were heated to around 1450 °C to produce CO gas from which the oxygen isotopes were measured (Kendall and McDonnell, 1998). The results of analyses were reported using δ notation: $\delta^{18}\text{O}$ with respect to VSMOW, and $\delta^{34}\text{S}$ with respect to VCDT (Carmody et al., 1998; Gehre, 1996; Gehre et al., 2004; Vinograd and Porowski, 2020). The precision of the measurements was $\pm 0.1\text{‰}$ for both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$.

Statistical investigations were conducted with SPSS 27 using the methods discussed in each individual section.

PHREEQC 3.6.2 (Parkhurst and Appelo, 2013) with the phreeqc.dat database was used to conduct chemical-thermodynamic modeling of the Colorful Lakes' mining influenced water. All the parameters that can be calculated with this database were included in the solution_spread input file. Concentrations under the detection limit were used with half of the detection limit.

3. Results

3.1. General

It can clearly be seen that the water in the three lakes is either in the Fe or in the Al buffer range (Table 1), and according to the Furtak and Langguth (1965) classification, all sampled waters are of the normal earth alkaline with prevailing sulfate type. While the Blue Lake, with pH values from 4.9 to 5.7 shows the characteristics for water in the Al buffer range with lower electrical conductivities, the Purple and Yellow Lakes, with pH between 2.3 and 2.9 is in the Fe buffer range and has higher electrical conductivities. This

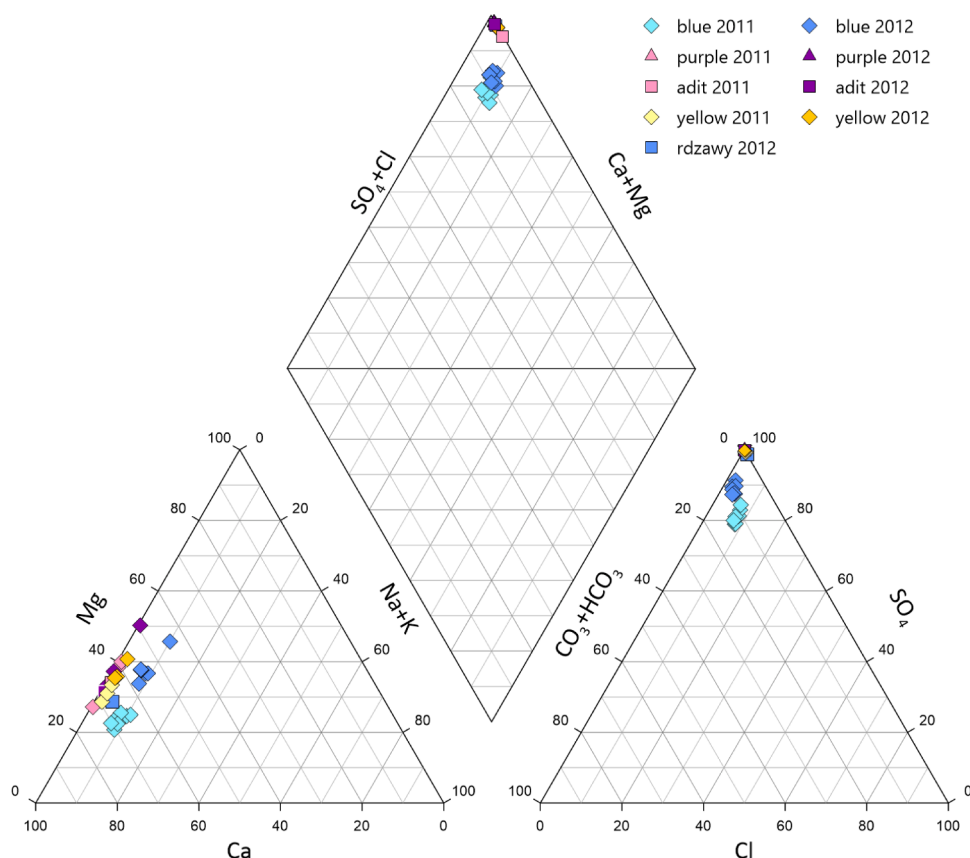


Fig. 5. Piper diagram of the Wieszcziszowice Colorful Lakes water samples.

characteristic influences the lakes' chemistry and therefore, a conclusive discussion needs to consider these differences. Hierarchical cluster analysis (Ward method), using the parameters with a score above 0.5 from principal cluster analysis of all samples showed that each lake falls into its own cluster, indicating that the individual chemistry of the three lakes differs statistically significantly, and that they can be discussed individually (Appendix 2). First the physicochemical and isotopic characteristic of each individual lake and thereafter a summarizing discussion will be given.

Principal component analysis (Appendix 3) showed that 74% of the water chemistry's variance is covered by the first three components. 50% of the variance is in the first component, which consists of the electrical conductivity, Mg, Sr, SO_4 , NO_3 , SiO_2 , Mn, the proton activity, Ca, Fe, Eh and some minor constituents. The second component, accounting for 16% of the variance, is dominated by Na and NH_4 , while the 3rd component, which accounts for 8% of the variance, is dominated by Ba. The first component is indicative of pyrite weathering and the dissolution of efflorescent minerals from the waste rock, while the second component seems to be primarily indicative for rain and snow influence of the lakes' waters. Rain and snow in the southern part of Poland contains 0.3 – 11.4 mg/L of NH_4 , 0.6 – 4.3 mg/L of Cl, and 0.6 – 2.5 mg/L of Na as well as 0.3 – 1.1 mg/L of K (Błaś et al., 2008; Dore et al., 1999; Stachurski and Zimka, 2002; Żelazny, 2005). As no other source of ammonia that could correlate with Na exists in the vicinity of the lakes, the rain and snow source is the most likely in that case. Ba is abundant in the pyrite-bearing host rocks with up to 786 mg/kg (Oberc-Dziedzic et al., 2011) and could originate from there.

Calculation of the sample's ion balances with PHREEQC showed values between +25.0 and –19.2% (Table 1), which are not pH dependent, but show a high positive correlation with the electrical conductivity imbalance (ratio between measured and calculated electrical conductivity). In the Blue Lake, the absolute values are generally lower than in the Yellow and Purple Lakes which have lower pH values. Because the lab used an uncommon method to calculate the ion balances, this error was not noted before the detailed analysis with PHREEQC, which is based on the species rather than the equivalent concentration of the individual analytes. All the interpretations in this paper have been done with this imbalance in mind.

3.2. Blue Lake

Samples of the Blue Lake (Table 1, Fig. 4), were taken at eight depths. It is the deepest of the lakes and it has the lowest TDS. Among the three lakes, it has the highest pH, ranging from 4.85 to 5.74, decreasing with depth. The vertical distribution of selected chemical indicators is shown in Figs. 5–9 and in Appendix 1.

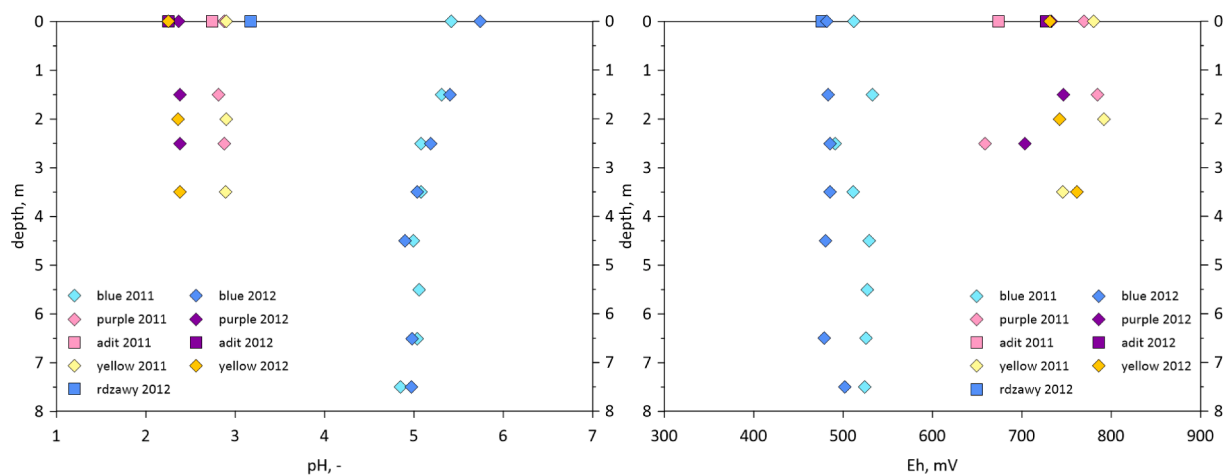


Fig. 6. Depth distribution of pH (left) and Eh (right) in the Wieściszowice Colorful Lakes.

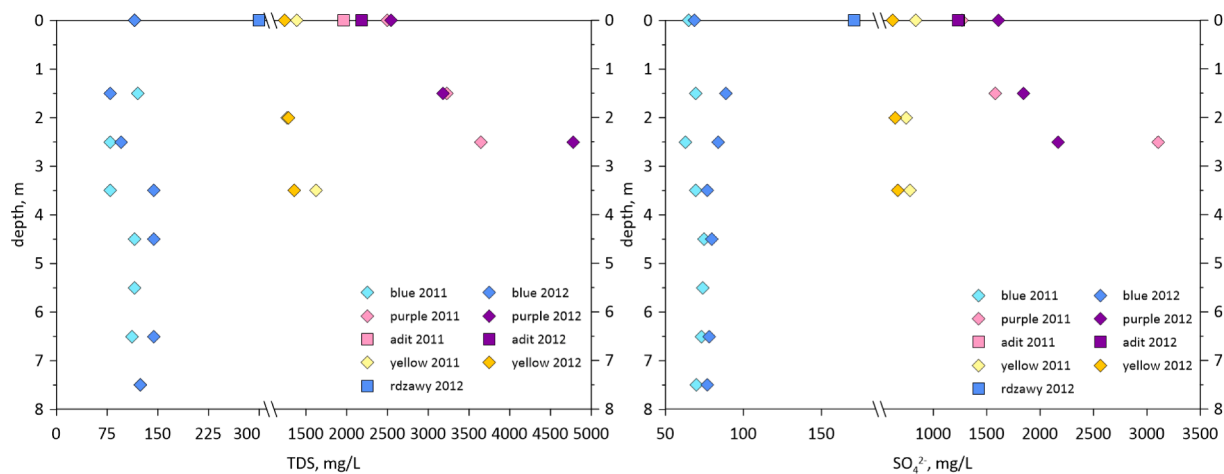


Fig. 7. Depth distribution of TDS and sulfate concentrations in the Wieściszowice Colorful Lakes.

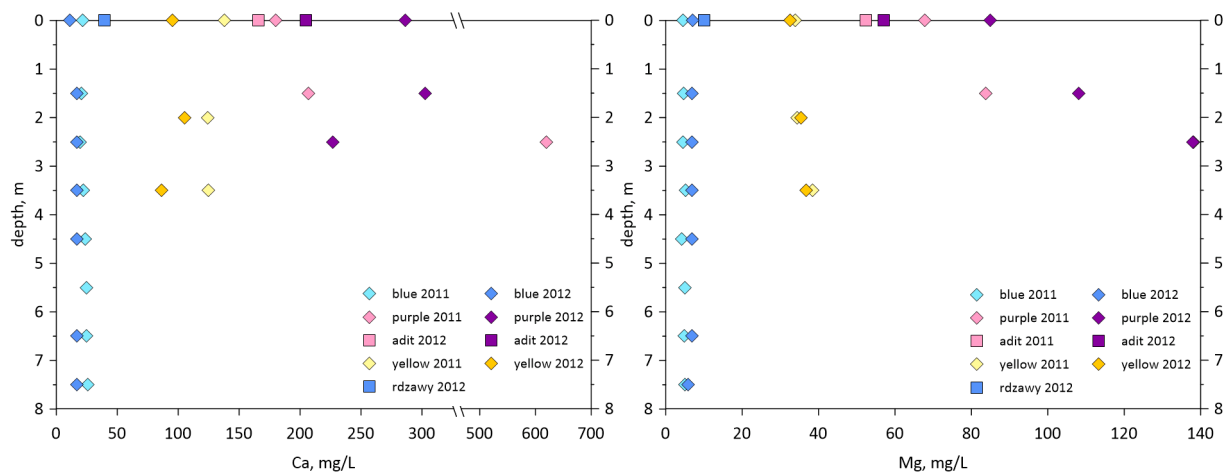


Fig. 8. Depth distribution of Ca^{2+} and Mg^{2+} concentrations in the Wieściszowice Colorful Lakes.

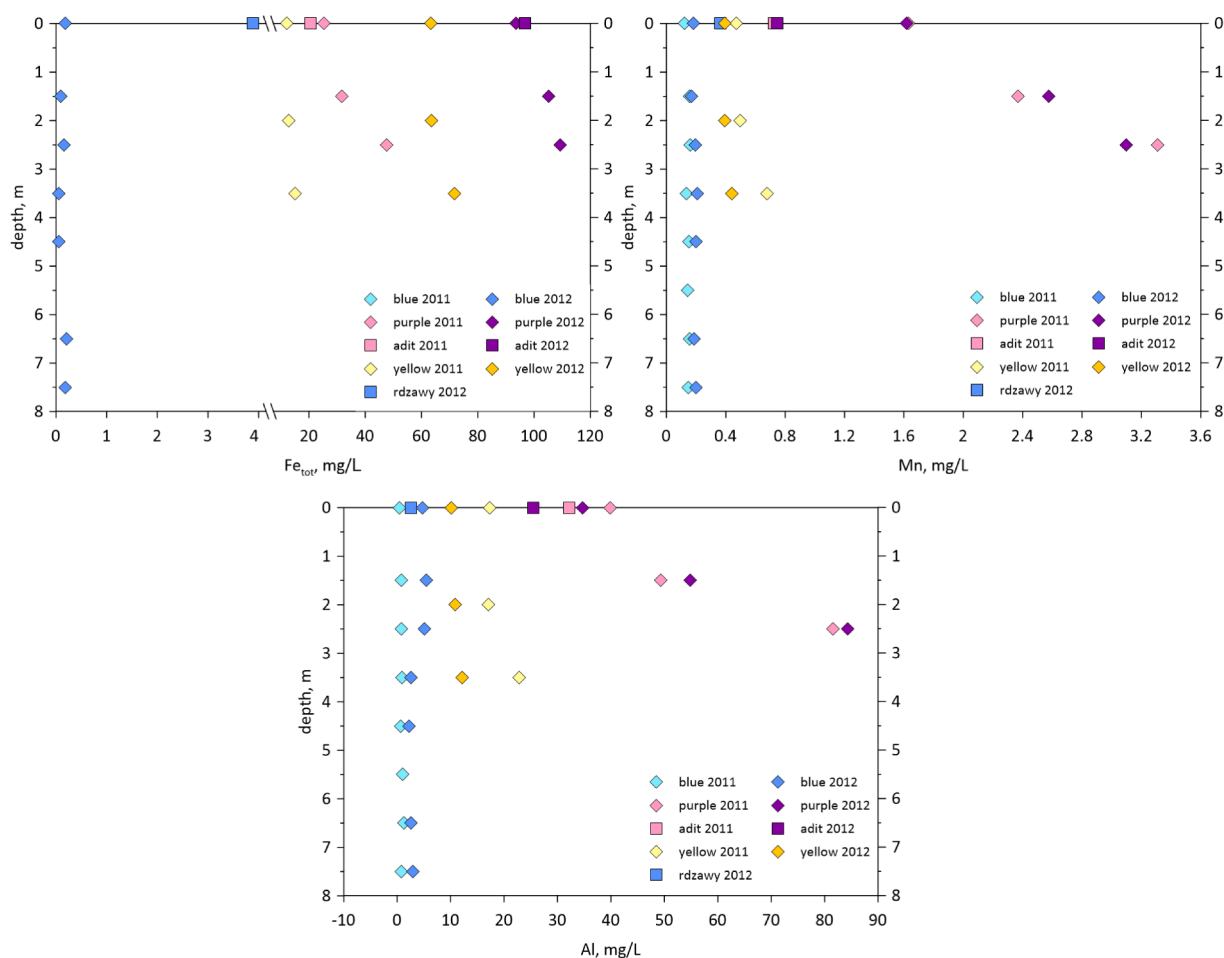


Fig. 9. Depth distribution of Fe_{tot} , Mn and Al concentrations in the Wieściszowice Colorful Lakes.

From the west, the intermittent Rdzawy Potok with a discharge of 0.1 L/s flows into the Blue Lake. Field observations show that the brook is fed from seepage water from waste rock heaps after snow melt or longer rainfall. In June 2012, the samples were acid (pH 3.17), with 2.5 times higher TDS (300 mg/L) concentrations than the Blue Lake. Consequently, most of the other parameters show also higher concentrations, such as 2.5 times more SO_4^{2-} (170 mg/L) or 4 times more Ca^{2+} (29.5 mg/L). The largest difference was found for Fe_{tot} , with a more than 20 times higher concentration, reaching 3.88 mg/L. Main ion concentrations (Cl^- , Na^+ , K^+) are like those of the Blue Lake, especially in its lower parts. Rdzawy Potok water is of the SO_4 -Ca-Mg type (Appendix 1).

3.3. Purple Lake

Of all the lakes, the Purple Lake shows the most variable shoreline and a maximum depth of 2.5 – 3.0 m in its center. Compared to the Blue Lake, the water's mineralization is higher and acid, though it has the same SO_4 -Ca-Mg water type (Table 1). The vertical distribution of selected chemical indicators is shown in Fig. 5 to Fig. 9 and in Appendix 1.

Apart from rainwater and snowmelt, the Purple Lake is recharged from acid mine water discharging from the abandoned mine adit. pH ranged from 2.3 to 2.7, TDS from 2180 to 1960 mg/L, and Fe_{tot} from 20 mg/L to 97 mg/L in June and September, respectively. All these values are in the same range as those of the lake's surface, indicating a relationship between the adit and the lake water.

3.4. Yellow Lake

Yellow Lake is the shallowest of the three lakes with the smallest water volume. Chemically, the lake's water is similar to the Purple Lake, and it is also of the SO_4 -Ca-Mg type (Table 1) as well as acid (2.25 – 2.9; Fig. 6), with TDS concentrations in the range of 1236 – 1384 mg/L (Fig. 7). The vertical distribution of selected chemical indicators is shown in Fig. 5 to Fig. 9 and in Appendix 1.

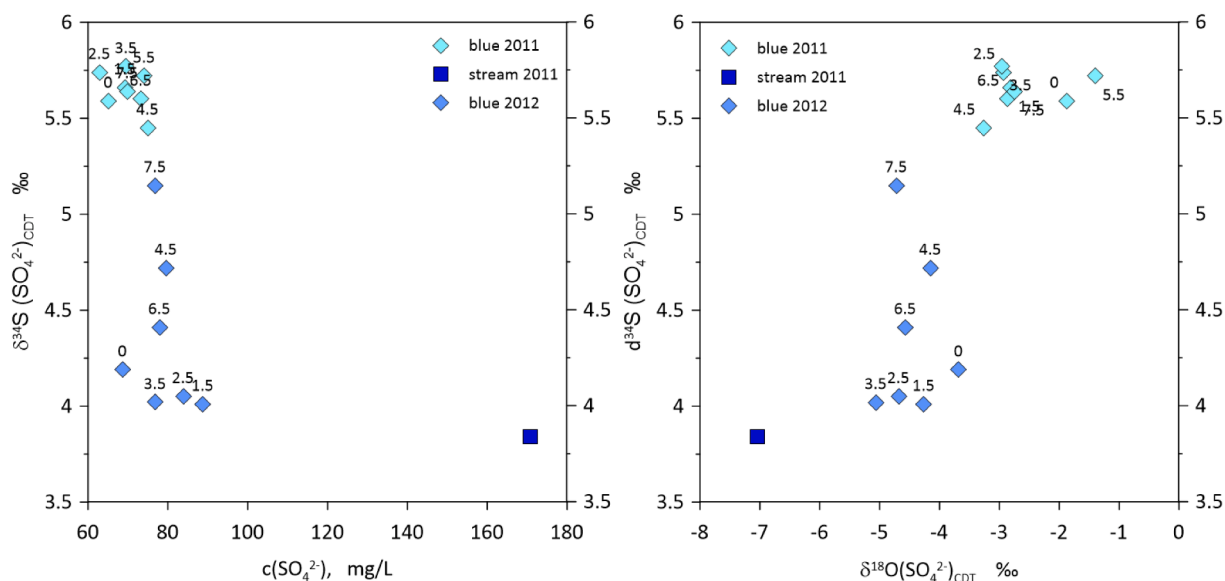


Fig. 10. Sulfur isotopic composition vs. SO_4^{2-} -concentration and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ in the Blue Lake; small numbers indicate the sample depths.

Table 2

Results for the isotopic composition of $\delta^{34}\text{S}(\text{SO}_4^{2-})$, $\delta^{18}\text{O}(\text{SO}_4^{2-})$, $\delta^2\text{H}(\text{H}_2\text{O})$, and $\delta^{18}\text{O}(\text{H}_2\text{O})$ in the lakes' waters, nuclides in ‰; RP: Rdzawy Potok, n.a.: not analyzed.

Lake	Depth, m	September 2011				June 2012			
		$\delta^{18}\text{O} \text{ H}_2\text{O}$	$\delta^2\text{H} \text{ H}_2\text{O}$	$\delta^{18}\text{O} \text{ SO}_4^{2-}$	$\delta^{34}\text{S} \text{ SO}_4^{2-}$	$\delta^{18}\text{O} \text{ H}_2\text{O}$	$\delta^2\text{H} \text{ H}_2\text{O}$	$\delta^{18}\text{O} \text{ SO}_4^{2-}$	$\delta^{34}\text{S} \text{ SO}_4^{2-}$
Blue	RP	n.a.	n.a.	n.a.	n.a.	-9.9	-69.0	-7.0	3.8
	0	-9.6	-64.4	-1.9	5.6	-9.6	-64.1	-3.7	4.2
	1.5	-9.5	-64.2	-2.8	5.7	-9.6	-64.8	-4.3	4.0
	2.5	-9.5	-64.9	-2.9	5.7	-9.8	-60.4	-4.7	4.1
	3.5	-9.4	-65.1	-3.0	5.8	-9.1	-61.8	-5.1	4.0
	4.5	-9.6	-64.7	-3.3	5.5	-10.0	-64.9	-4.2	4.7
	5.5	-9.5	-65.7	-1.4	5.7	n.a.	n.a.	n.a.	n.a.
	6.5	-9.6	-65.4	-2.9	5.6	-10.0	-64.4	-4.6	4.4
	7.5	-9.5	-65.6	-2.7	5.6	-9.9	-69.5	-4.7	5.2
Purple	0	-8.0	-57.4	-8.1	3.4	-8.4	-60.1	-12.0	3.0
	1.5	-9.2	-63.9	-9.6	3.4	-9.3	-64.9	-12.5	2.9
	2.5	-9.8	-65.1	-9.3	3.5	-10.0	-65.3	-12.9	2.6
Yellow	adit	-10.0	-65.9	-10.2	3.4	-10.2	-67.8	-13.0	2.9
	0	-9.5	-64.9	-9.6	2.6	-9.2	-71.4	-11.7	2.9
	2	-9.4	-63.5	-9.5	4.0	-9.6	-73.5	-11.7	2.8
	3.5	-9.5	-65.5	-9.6	3.1	-9.8	-74.4	-12.4	2.8

3.5. Isotopic composition

3.5.1. Blue Lake

Results from the Blue Lake show seasonal variations of the SO_4^{2-} concentrations, $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ (Fig. 10, Table 2). Source of the SO_4^{2-} in this lake is mainly surface runoff containing sulfate and oxidized organic sulfur, while sulfate originating from direct oxidation of pyrite, commonly found in dispersed form in the adjacent rock formations and spoil tips, is missing. SO_4^{2-} from direct pyrite oxidation would be characterized by negative $\delta^{34}\text{S}(\text{SO}_4^{2-})$ values, ranging from about -4.5‰ to about -3.5‰ , and in extreme cases up to -15‰ (Balcerzak et al., 1992), but was not observed in the vicinity of the Colored Lakes. It can therefore be assumed that the SO_4^{2-} in the lakes originates from sulfide oxidation in the adjacent spoil tips surrounding this water body. Such processes were found in the oxidation zone of pyrite-bearing shales near Wieściszowice (Mandernack et al., 2000). In September 2011, compared to June 2012, lower concentrations of SO_4^{2-} as well as smaller differences in $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ were found. In September 2011, with lower rainfall and therefore probably lower surface runoff, less SO_4^{2-} discharged into the lake. In June 2012, higher rainfall was recorded, and increasing surface runoff of oxidized sulfur species into the lake caused a small increase in the SO_4^{2-} concentrations. This runoff probably “activated” an additional SO_4^{2-} source and hence the greater differences in $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$. Results of the SO_4^{2-} oxygen and sulfur isotopic composition from the Rdzawy Potok shows a twice as high SO_4^{2-} concentration compared to the lake. No depth dependency was observed for the SO_4^{2-} concentrations, $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$, which is an

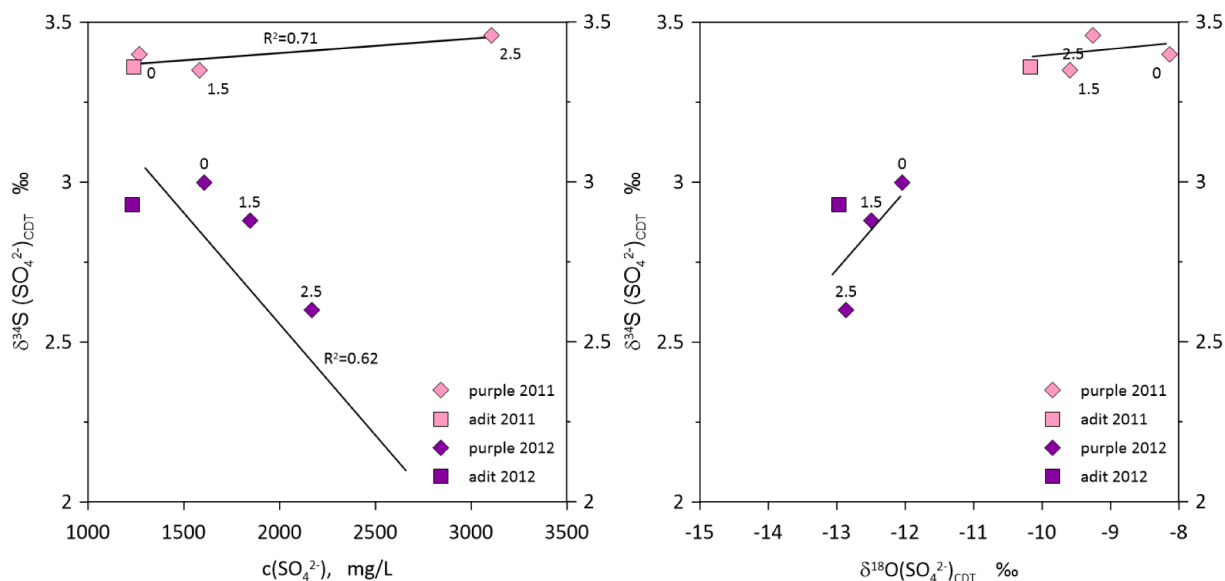


Fig. 11. Sulfur isotopic composition vs. SO_4^{2-} -concentration and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ in the Purple Lake; small numbers indicate the sample depths.

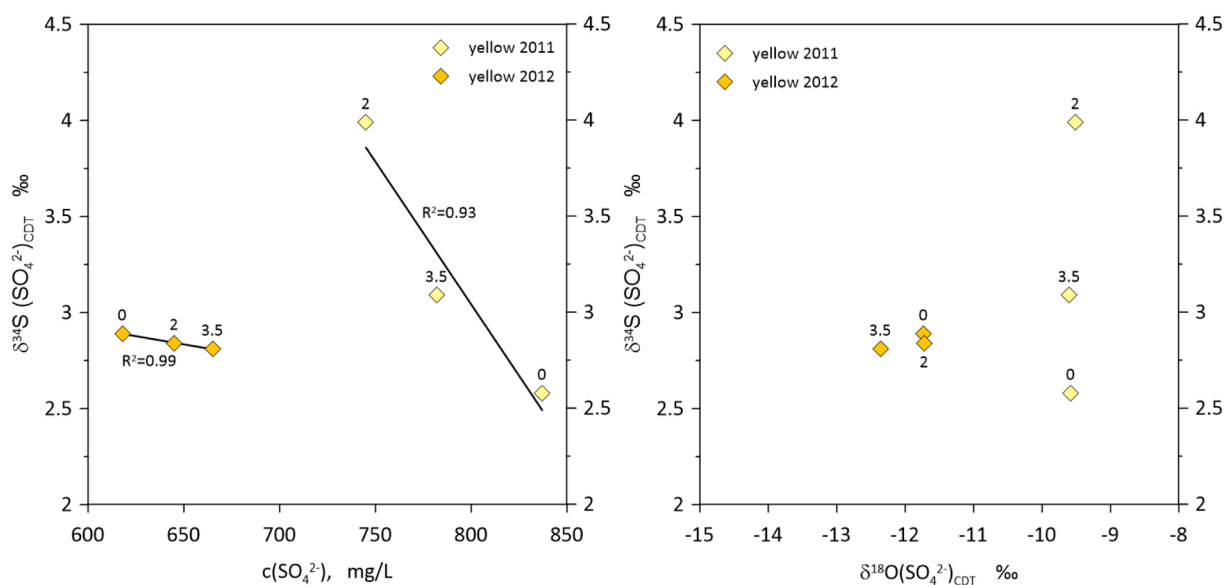


Fig. 12. Sulfur isotopic composition vs. SO_4^{2-} -concentration and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ in the Yellow Lake; small numbers indicate the sample depths.

evidence of mixing and more or less no stratification in this lake.

Results of the oxygen and hydrogen isotopes show small variations in September 2011, confirming one main supply source into the lake (Fig. 13). Larger variations of the isotopic composition were found in June 2012. No relationship between depth and $\delta^2\text{H}(\text{H}_2\text{O})$ or $\delta^{18}\text{O}(\text{H}_2\text{O})$ could be observed, confirming a good mixing processes with respect to $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$.

3.5.2. Purple lake

Sulfate concentrations as well as $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ showed seasonal variations (Fig. 11) and correlations between the sulfate concentrations, $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ with R^2 between 0.6 and 0.7. In September 2011, a larger span of the sulfate concentrations occurred, but very small variations in $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{18}\text{O}(\text{SO}_4^{2-})$ at the same time. It can be assumed that oxidation of reduced organic sulfur occurred accompanied by an increase in sulfate concentration without changing the isotopic composition (Krouse and Grinienko, 1991). This process was most intensive above the sediment because the largest amount of organic matter is accumulated in the bottom sediment. In June 2012, a negative correlation between the sulfate concentration and $\delta^{34}\text{S}(\text{SO}_4^{2-})$ exists,

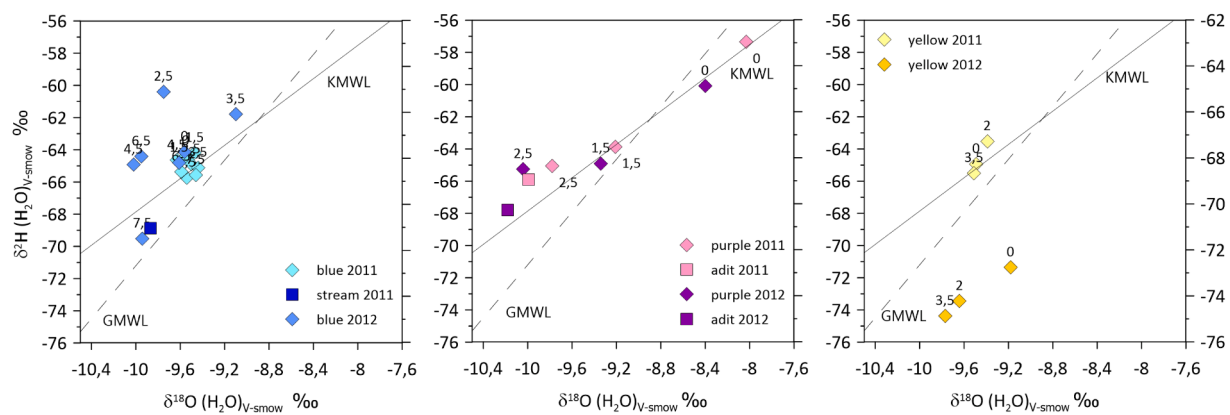


Fig. 13. $\delta^2\text{H}(\text{H}_2\text{O})$ vs. $\delta^{18}\text{O}(\text{H}_2\text{O})$ isotopic composition in the Blue, Purple and Yellow Lakes. GMWL – Global Meteoric Water Line, KMWL – Karkonosze (local) Meteoric Water Line.

indicating bacterial sulfate reduction. This leads to the accumulation of the heavy sulfur isotope, as sulfate-reducing bacteria prefer to process the lighter sulfur isotope (^{32}S) (Cook and Olive, 2012; Noyhouzer et al., 2018). Simultaneously, the sulfate concentration decreases.

In the Purple lake, a correlation between depth and $\delta^2\text{H}(\text{H}_2\text{O})$ as well as $\delta^{18}\text{O}(\text{H}_2\text{O})$ exists (Fig. 13), shifting $\delta^2\text{H}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ to more negative values both in June 2012 and September 2011. One of the main processes driving changes in $\delta^2\text{H}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ is evaporation, indicated by the heavier samples near the lake's surface. With increasing depth, the oxygen and hydrogen isotopic composition was shifted towards negative values. Such a situation was found for both sampling periods, with a similar trend. The main process driving the oxygen and hydrogen isotopic composition in the pond is evaporation. The greatest impoverishment in the light isotopes of oxygen and hydrogen was found in the samples collected from the pond surface. The surface evaporation process loses its importance and at a depth of 2.5 m, the isotopic composition of $\delta^2\text{H}(\text{H}_2\text{O})$, $\delta^{18}\text{O}(\text{H}_2\text{O})$ is similar to that of the adit. It can therefore be inferred that the adit is one of the main sources supplying this lake, which can also be seen by the chemical similarity of adit and lake surface water in both sampling periods.

3.5.3. Yellow Lake

Seasonal changes of sulfate concentrations and $\delta^{34}\text{S}(\text{SO}_4^{2-})$ as well as $\delta^{18}\text{O}(\text{SO}_4^{2-})$ could also be observed for the Yellow Lake (Fig. 12). A strong negative correlation ($R^2 = 0.99$ for September 2011 and $R^2 = 0.93$ for June 2012) exists for $\delta^{34}\text{S}(\text{SO}_4^{2-})$ vs. sulfate concentrations. For both sets of samples, bacterial sulfate reduction seems to occur, being less prominent in September 2011 compared to June 2012, where larger variations of $\delta^{34}\text{S}(\text{SO}_4^{2-})$ exist. As in the Purple Lake, $\delta^2\text{H}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ is controlled by evaporation but with different intensities (Fig. 13). In September 2011, $\delta^2\text{H}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ variations were small and no depth correlation existed, indicating a low evaporation and mixing. In June 2012, evaporation was more intense, affecting the isotopic fractionation, and resulting in an enrichment of heavier isotopes in the upper Lake water body, disappearing with depth. The depth correlation of $\delta^2\text{H}(\text{H}_2\text{O})$ and $\delta^{18}\text{O}(\text{H}_2\text{O})$ indicates an absence of mixing in the lake.

3.6. Chemical-thermodynamic calculations

Most of the normally relevant phases in mine water calculated by PHREEQC are undersaturated in relation to the lakes' water (Appendix 4). This result is similar to that of Dobrzyński (1995), who used WATEQ4F for his calculations. Very likely, this undersaturation results from both the missing concentrations of the chemical analysis and a relatively short reaction time between the efflorescent salts in the abandoned mines' waste rock and the precipitation. Therefore, only for a selected range, controlling phases can be defined. Controlling phases in the Blue Lake are $\text{Al}(\text{OH})_3(\text{a})$, Barite, and $\text{Fe}(\text{OH})_3(\text{a})$, for Al, Ba, and Fe and Chalcedony, Quartz and SiO_2 for the silica. For Al, this differs from Dobrzyński (1995), who identified AlOHSO_4 , respectively Jurbanite ($\text{AlOH}\text{SO}_4 \cdot 5\text{H}_2\text{O}$), as the controlling phase. A reason for this potential discrepancy is the different thermodynamic databases used in both cases. In the Purple and Yellow Lakes, controlling phases are Anhydrite and Gypsum for the sulfate, Barite for Ba and Chalcedony and SiO_2 for silica. These controlling phases do not explain the whole lakes' chemical composition, but all other phases show a high undersaturation, including calcite ($\text{SI} = -4$ to -7) and dolomite ($\text{SI} = -7$ to -13). What can clearly be seen is that the species' distribution and the saturation indices in the three lakes show a pattern which allows to differentiate between the various mining influenced lake waters.

In the Purple and the Yellow Lake, the SI in the three depths are similar, respectively, while in the Blue Lake, the SI shows a slight stratification with a trend to lower SI with increasing depths for most of the relevant phases, possibly indicating evaporation. Exceptions to this stratification are the sulfate phases Anhydrite, Gypsum and Celestine as well as the silicate phases, which have a similar SI throughout the water column. All the carbonate phases, Aragonite, Calcite, Dolomite and Rhodochrosite, show different behaviors in the September and the June sampling. While the SI increases in September, it decreases in June. These results show that the smaller lakes are very likely connected with each other, which can already be seen by the similar chemistry and the fact that the cluster analysis groups them into the same cluster.

Comparing the SI of the two influents into the lakes, it becomes obvious, that the same SI distribution prevails for the Purple and Yellow Lakes, including their inflow. Rdzawy Potok shows the SI signature for the acidic waters, but is quickly buffered once it flows into the Blue Lake, with some of the SI increasing (e.g. $\text{Al}(\text{OH})_3(\text{a})$, $\text{Fe}(\text{OH})_3(\text{a})$, Jarosite-K, Gibbsite), others decreasing (e.g. Anhydrite, Gypsum, Melanterite). This indicates precipitation and mixing reactions occurring once the brook water enters the Blue Lake.

Investigating the species calculated by PHREEQC shows that in all three lakes and the three inflows, SO_4^{2-} dominates, followed by Ca^{2+} (Fig. 14). In the Blue Lake, the next dominating species are H_4SiO_2 and Mg^{2+} . All other species in the Blue Lake contribute to a smaller degree to the total water's chemistry. Between the September and the June samples of the Blue Lake, there is a difference in the concentration of NO_3^- and HCO_3^- , with a higher concentration of HCO_3^- resulting from either carbonate dissolution or evapo-concentration in September and a higher concentration of NO_3^- in June, the latter possibly resulting from precipitation. Though the SI for the Yellow and Purple lakes were similar, this is not the case for the species distribution. H_4SiO_4 concentrations in these acid lakes become less, while the typical AMD phases of Al and Fe show up. Purple lake shows a stratification with increasing concentrations with depth, while the Yellow Lake seems to be better mixed, just showing small variations between the sampling campaigns. In case of the Purple Lake, which is fed by the mine drainage from the adit, one can see that a) evaporation increases the concentrations of the species and b) the TDS increase with depth, discussed above, and results mainly from the SO_4^{2-} and Ca^{2+} -species. Though the inflow into the Blue Lake has SI similar to the acid lakes, the species distribution of the inflow is similar to the Blue Lake's species distribution, indicating that the water in this lake is mainly fed by the inflow and unlikely by additional ground water sources.

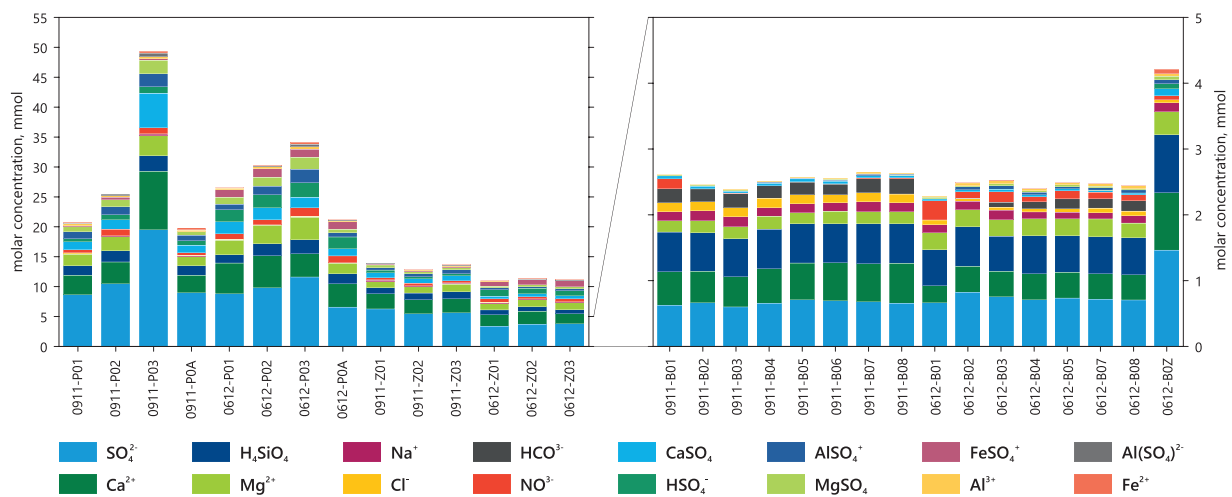


Fig. 14. Distribution of the main species in the Purple (P), Yellow (Z), and Blue (B) Lakes based on the PHREEQC calculation. Note the different scales.

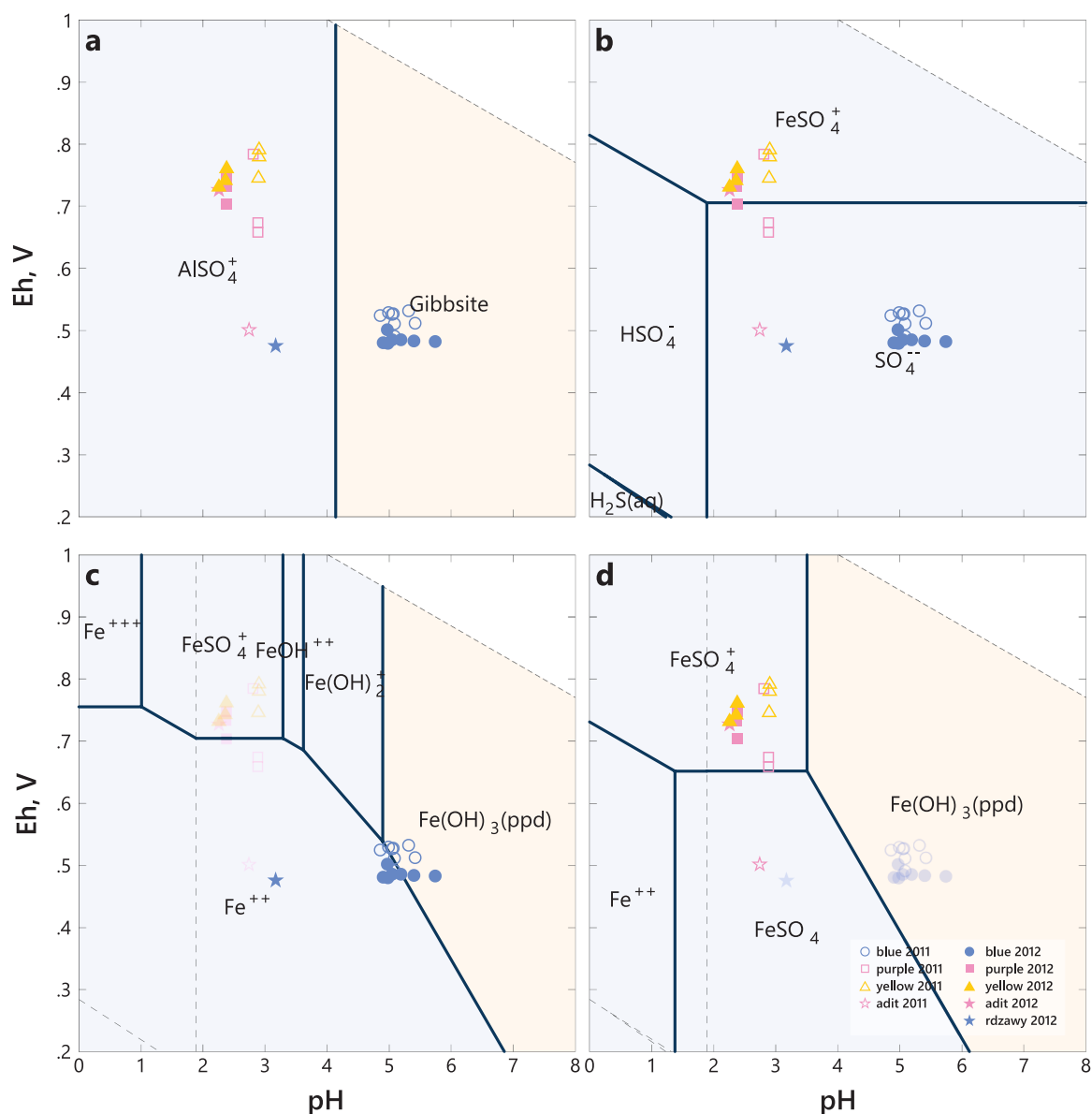


Fig. 15. Pourbaix-diagrams (detail) constructed with Geochemists Workbench. a: $\{Al^{3+}\} = 10^{-3.033}$, b: $\{SO_4^{2-}\} = 10^{-2.025}$, c: $\{Fe^{2+}\} = 10^{-5.633}$, $\{SO_4^{2-}\} = 10^{-3.113}$ Blue Lake, d: $\{Fe^{2+}\} = 10^{-2.914}$, $\{SO_4^{2-}\} = 10^{-1.682}$ Purple and Yellow Lakes. $T = 17^\circ C$, $p = 101.3$ kPa; blue: species, orange: phases.

3.7. Species and controlling processes based on the predominance (Eh-pH) diagrams

Predominance- or Pourbaix-Diagrams are Eh-pH-diagrams that help to understand the predominant species in an analyzed water sample and potential reactions occurring in the system (Pourbaix, 1966; VanLoon and Duffy, 2011; Fig. 15). Though some authors question the usefulness of redox measurements in systems with low concentrations (e.g. Nordstrom and Munoz, 1994), they can be applied in systems, where higher concentrations of redox couples, such as Fe, exist. In case of the Colorful Lakes, the Al and SO_4 -diagrams were plotted based on the average sample chemistry of all the sampled waters, whilst the Fe-diagrams are based on the average of the individual lake essays. Based on the results of the PHREEQC modeling, four representative Pourbaix diagrams for various activities of Al, SO_4^{2-} and Fe were constructed at $17^\circ C$ and 101.3 hPa (Fig. 15).

Al – In the Blue Lake, the Eh and pH falls into the gibbsite field which explains the lower concentrations of Al in the Blue Lake and its pH in the Al-buffer range (Fig. 15 a). This means that the Al-concentration in the Blue Lake is controlled by gibbsite precipitation. As already could be seen earlier (Fig. 6), the pH decreases with depth, while the Eh is relatively stable. The Eh differences between the June and September samples can be neglected, as Eh measurements show a methodological error of ± 50 mV. No controlling Al-phases can be seen in the Purple and Yellow Lakes nor the inflows, which explains why the Al-concentrations in these water samples are

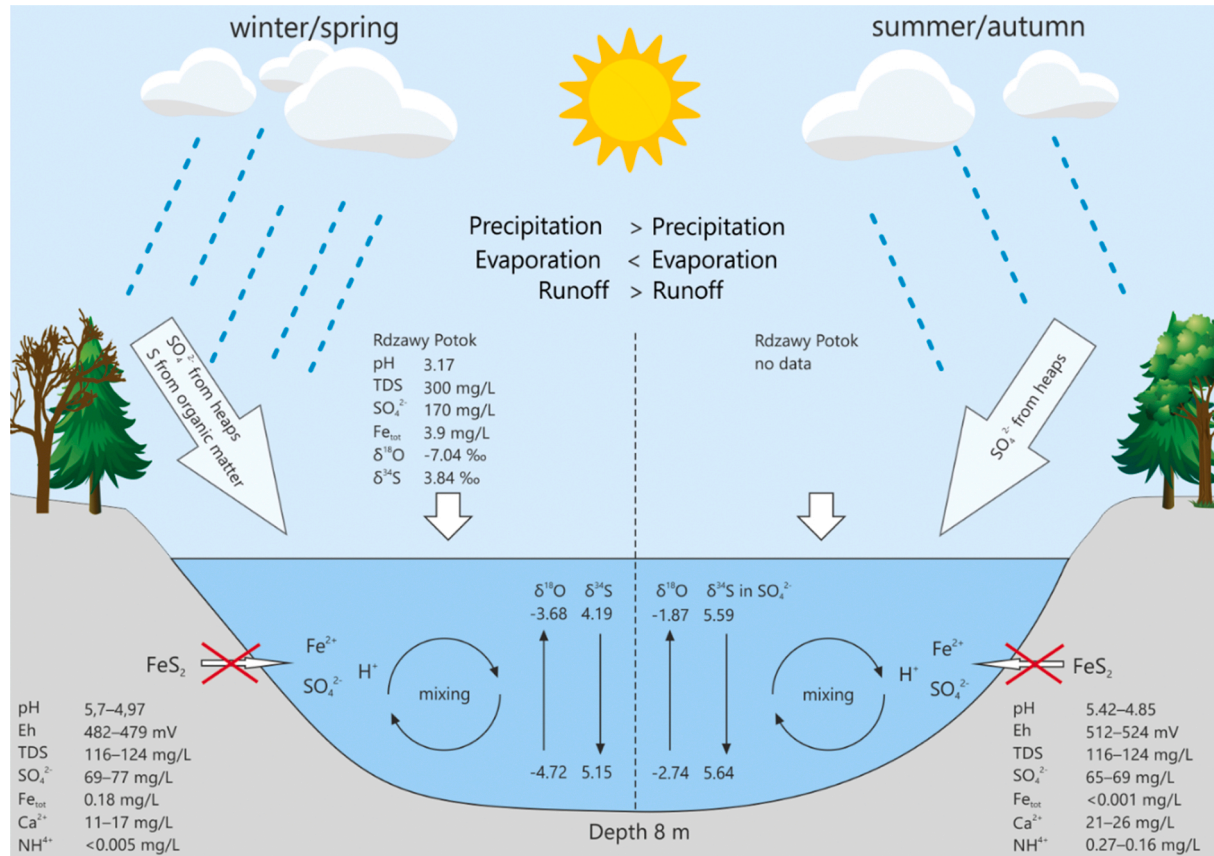


Fig. 16. Schematic diagram of the processes controlling the chemical and physical conditions of the Blue Lake water.

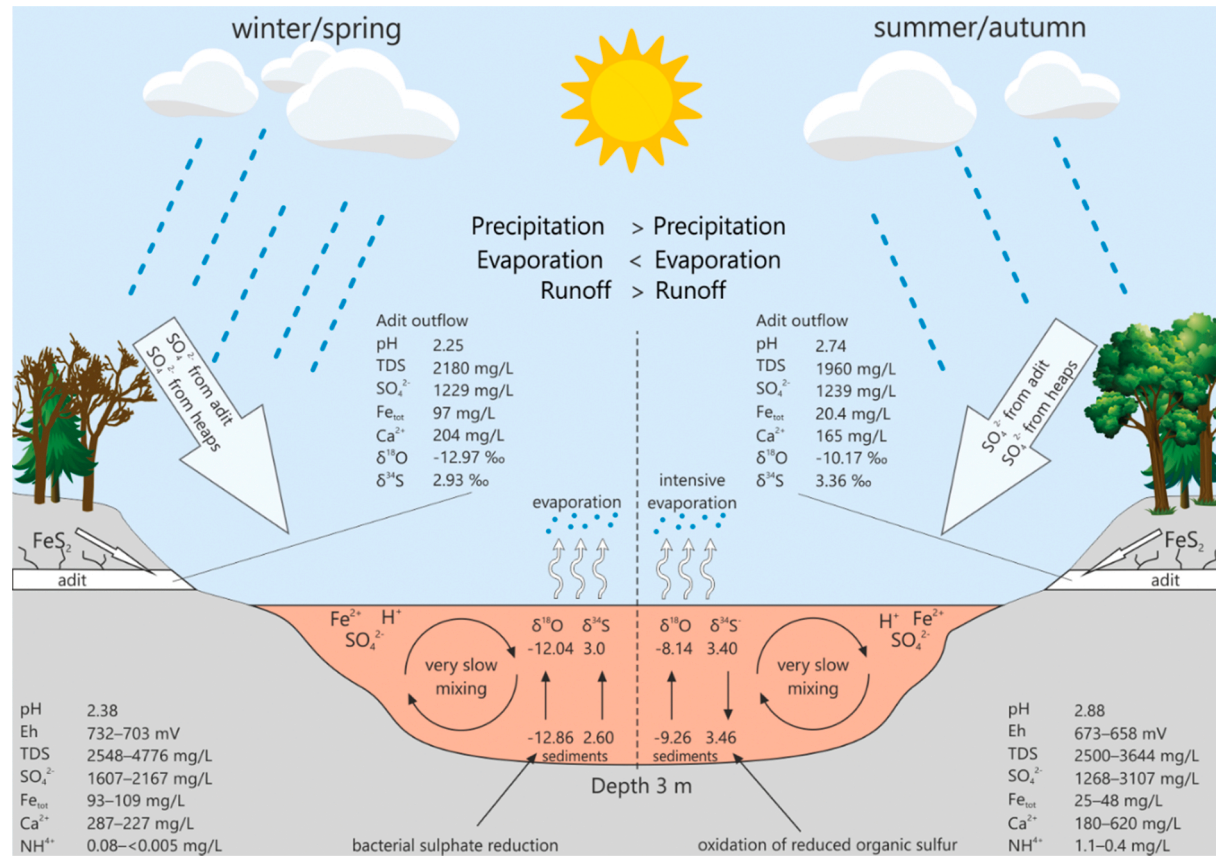


Fig. 17. Schematic diagram of the processes controlling the chemical and physical conditions of the Purple Lake water.

between 7 and 26 times higher than in the Blue Lake. Mine water from Rdzawy Potok seems to be buffered and mixes with lower mineralized surface water once it flows into the Blue Lake.

SO₄ – As expected, most of the sulfate predominates as the SO₄²⁻ species (Fig. 15 b) which was already shown by the PHREEQC chemical-thermodynamic calculations. Only the Purple and Blue Lake samples, with a lower pH and higher Eh, fall into the FeSO₄⁺-field resulting from the high Fe-concentrations in these two lakes compared to the Blue Lake.

Fe – Fe speciation highly depends on the concentrations of the Fe and SO₄ in the system (Garrels and Christ, 1966). To interpret the processes in the three lakes, therefore requires two Eh-pH-diagrams. In the Blue Lake (Fig. 15 c), Fe-concentrations are controlled by the precipitation of the Fe-oxyhydrates in the form of ochre, which can be seen by the coloration of the sediments. Seasonal depth variation play a minor role because all the measured Eh-and pH-values fall into the Fe(OH)₃(ppd) phase field. In case of the Purple and Yellow Lakes (Fig. 15 d), with higher Fe- and SO₄-concentrations and lower pH-values, no carbonates buffer the water. Therefore, the pH stays in the Fe-buffer range, which can be seen by the more or less similar pH-values in each of the two sampling campaigns with more or less no depth dependency. As in the Blue Lake, the controlling phase is still the Fe(OH)₃(ppd), indicated by the parallel course of the sampling dots with the boarder of the predominance field.

Two different behaviors can be recognized for the adits and Rdzawy Potok. The adit water gets oxidized and increases its redox potential, while its pH stays stable as no reactions occur, which could lower the pH through hydrolysis. Because of the similar pH of the adit and lake waters, Fe(OH)₃(ppd) might again be assumed as the controlling phase for this water. Once the adit water enters the lake, it contributes substantially to the lake's chemistry. For Rdzawy Potok the situation differs. It is quickly buffered once it flows into the Blue Lake and increases in its pH-value while the redox potential does not change.

4. Discussion and conceptual model

Blue Lake has the highest altitude and is in an area where mining was deeper but less extensive, leaving steep banks and small heaps above the pit. It is recharged primarily by Rdzawy Potok throughout the year and periodically by precipitation and snowmelt diluting the TDS derived by the stream. Infiltration waters flow through a thin weathered zone with a low hydraulic conductivity (Balcerzak et al., 1992; Costa et al., 2021; Marszałek and Wąsik, 2001; Parafiniuk and Dobrzyński, 1995) and through some heaps, resulting in minor pyrite oxidation (Fig. 16). The brook water has a low mineralization, primarily resulting from SO₄²⁻, Ca, and Mg. Isotope results indicate that sulfate in the lake originates from the advanced oxidation of sulfide to sulfate in the heaps surrounding the reservoir and not from immediate pyrite weathering. Decomposition of organic matter seems to be an additional source of sulfur, especially during the spring (June 2012) sampling. After entering the lake, Rdzawy Potok's water is mixed through the entire profile to a depth of about 8 m, which results in a lack of vertical variability in the lake's chemical composition, and which can be seen by the similar species distribution in both the lake and Rdzawy Potok (Fig. 14). None of the three results, neither the chemical composition, nor the isotopes or the chemical thermodynamic modeling, give indication to a relevant evaporation contribution, which might be due to the lakes higher elevation and lower sun exposure.

Purple Lake is located at a lower altitude, is only 3 m deep and its southern shore is flattened. It is for most of the year fed by the *Neues-Glück*-adit which drains the eastern part of the hills at a flow rate of 0.1 – 0.3 L/s (Fig. 17). During the dryer season (September 2011), mainly from September to November, the adit is commonly dry and its chemical evolution, which is controlled by processes in the mined rocks, has been described in earlier publications (Balcerzak et al., 1992; Costa et al., 2021; Marszałek and Wąsik, 2001; Parafiniuk and Dobrzyński, 1995). Mine water discharging from the adit has a low pH (2.38 – 2.88) and a high concentration of SO₄²⁻, Ca²⁺ and Fe_{tot} with little variability in the two datasets, except Fe_{tot}, which has 5 times higher concentrations in June compared to September. This mine water is the main source for Purple Lake, with additional ions, including H⁺, SO₄²⁻, Fe_{tot}, Ca²⁺ originating from seepage water from the surrounding mine dumps. As could be shown by chemical-thermodynamic modeling, the species composition in this lake is similar to the mine water but substantially different from that in the Blue Lake (Fig. 14).

Evaporation contributes substantially to the lakes chemical composition and its vertical variation, as good sun exposure, extent and a shallow depth result in a higher surface evaporation compared to Blue Lake. It is higher in the 2nd half of the year (summer and autumn). This results in solution concentration, an increase in its density and a slow flow towards the bottom where a twofold increase in mineralization and SO₄²⁻ with very high Fe_{tot}-concentrations are recorded. As indicated by the isotopic results, during spring and summer, a process associated with bacterial sulfate reduction occurs throughout the water column, resulting in an enrichment in the heavy sulfur isotope. Later in the year, the oxidation process of reduced organic sulfur plays a dominant role, increasing the waters' sulfate concentration substantially.

Yellow Lake is the smallest of the three pit lakes and because it is very close to Purple Lake in an identical geological setting, it can be assumed that the processes controlling the lake's chemistry are very similar. There is no inflow of mine drainage, and the feed comes mainly from precipitation and infiltration through the weathered zone of the Wielka Kopa rocks and through numerous mining residues occurring to its north and west (Fig. 18). This can be seen by lower pH values and 5 – 6 times higher Fe_{tot}-concentrations in June 2012, when snowmelt supplies the lake with dissolved efflorescent salts. Due to its poor sun exposure, evaporation is less intense throughout the year, which is evident by the lower mineralization compared to Purple Lake (Fig. 14), but in spring (June) it is higher compared to autumn (September). In deeper parts of the lake, the dominant process seems to be bacterial reduction of sulfate occurring under conditions with lower oxygen availability.

5. Conclusions

Though the Wieściszowice Colorful Lakes are unique for the Sudetes Mountains, due to the outcrop of the pyrite bearing shists, this

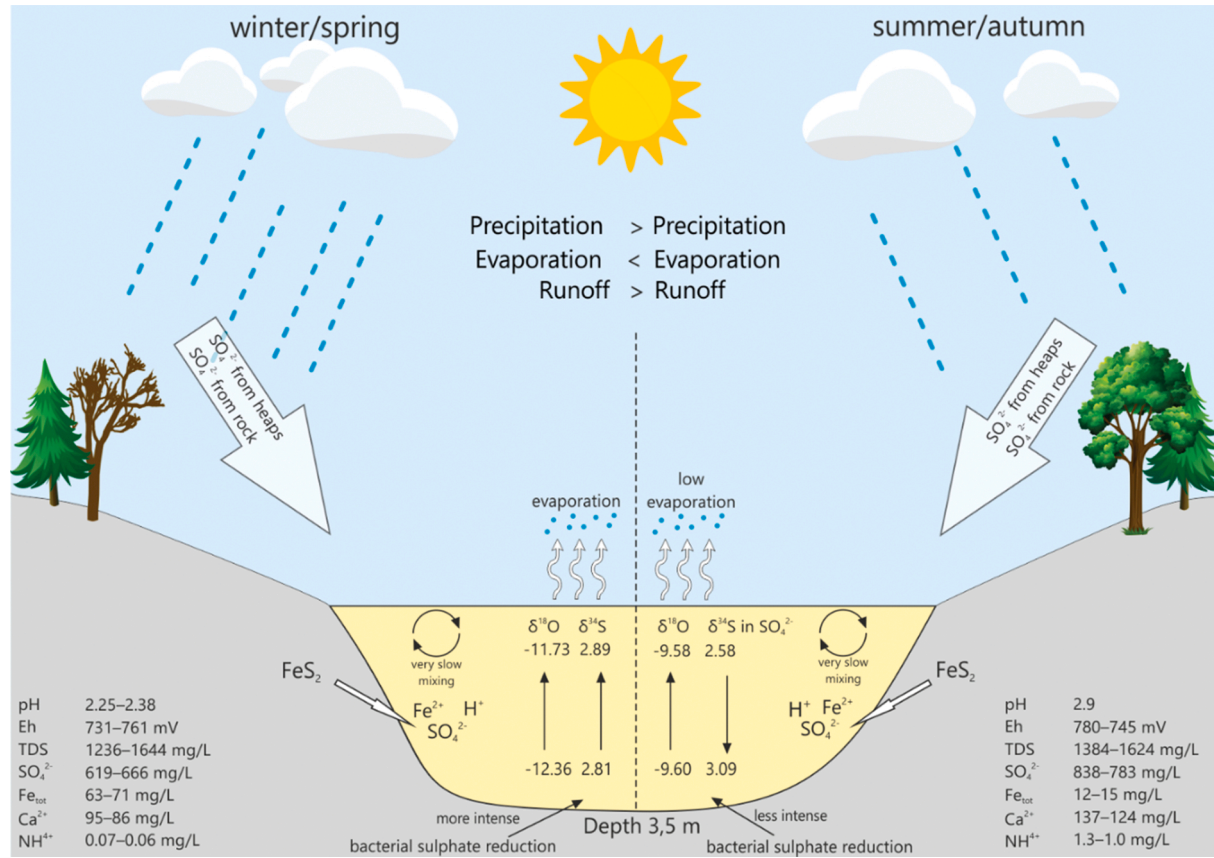


Fig. 18. Schematic diagram of the processes controlling the chemical and physical conditions of the Yellow Lake water.

research extends the knowledge about processes controlling the chemical composition of shallow post-mining lakes in humic meteorological conditions and di-sulfide containing rocks. Until now, research there focused mainly on determining the relevant processes controlling the chemical composition of the water resulting from water–rock-interaction, and the associated phase transformations of the minerals (Costa et al., 2021; Parafiniuk and Dobrzyński, 1995). A second research focus was the influence of efflorescent salts on the water chemistry of the brooks flowing in the Rdzawy Potok valley (Wąsik and Wasowski, 2015). Past pit lakes studies have been limited to samples collected near the banks, which restricts characterization of spatio-temporal developments in the pit lake water strata. In case of the Colorful Lakes, this study, for the first time, also included isotope samples. This investigation, therefore, determined the spatio-temporal variability of water chemistry and isotopic composition. Sampling took place during the wetter season (June 2012), which includes the winter and spring months when snowfall and snowmelt occur, and the dryer season (September 2011), which includes the summer and autumn months with low precipitation and high temperatures associated with insolation.

The results indicate that each of the three pit lakes should be considered separately. Although the general course of processes is similar, there is an obvious difference in the pit lakes' chemical composition resulting from different natural and anthropogenic factors affecting the geochemical conditions of each lake. These similarities result from the inflow water flowing through the weathered mining residues, leaching the efflorescent salts originating from pyrite and rock weathering.

Based on these results and discussions, it can be concluded that only when spatio-temporal samples assisted by isotope investigations are taken and the chemical thermodynamic conditions are studied, investigations of small historical mine pit lakes provide full insight into the relevant processes. Future studies of the Colorful Lakes should sample the waters monthly and measure the flow rates in Rdzawy Potok and the adits regularly to allow for an overall mass balance of the processes occurring in the lakes and the surrounding brooks. Installing a weather station might improve the conclusions that can be drawn.

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CRediT authorship contribution statement

Krzysztof Chudy: Conceptualization, Writing – Original draft preparation, Methodology, Data curation, Formal analysis, Visualization, Investigation. **Magdalena Worsa-Kozak:** Conceptualization, Writing – Original draft preparation, Methodology, Writing-Reviewing and Editing, Funding acquisition. **Agnieszka Wójcik:** Data curation, Writing – Original draft preparation, Visualization. **Danuta Szyszka:** Visualization, Formal analysis, Validation, Writing – Original draft preparation. **Wojciech Drzewicki:** Visualization, Formal analysis, Validation, Writing – Original draft preparation. **Christian Wolkersdorfer:** Validation, Visualization, Writing – Original draft preparation, Writing – Reviewing and Editing, Supervision. **Dominika Konsencjusz:** Investigation, Writing – Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ejrh.2021.100974](https://doi.org/10.1016/j.ejrh.2021.100974).

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