Geology, Geophysics & Environment 2025, vol. 51 (4): 389–411

Trace elements and rare earth elements in post-mining pit lakes of the Muskau Arch (Poland): AMD-related enrichment and toxicity assessment

Igor Śniady[1], Aleksandra Machowska[2], Maciej Dysierowicz[3], Marcin Siepak[4]

[1] Adam Mickiewicz University, Faculty of Geographical and Geological Sciences, Poznań, Poland, e-mail: igosni@st.amu.edu.pl, ORCID ID: 0009-0002-5651-6324
[2] UiT the Arctic University of Norway, Department of Geosciences, Tromsø, Norway, e-mail: almac4419@uit.no, ORCID ID: 0009-0004-6714-4057
[3] Adam Mickiewicz University, Faculty of Geographical and Geological Sciences, Poznań, Poland, e-mail: macdys@st.amu.edu.pl, ORCID ID: 0009-0001-5309-443X
[4] Adam Mickiewicz University, Faculty of Geographical and Geological Sciences, Poznań, Poland, e-mail: marcin.siepak@amu.edu.pl (corresponding author), ORCID ID: 0000-0002-6364-874X

Received: 7 July 2025; accepted: 27 November 2025; first published online: 29 December 2025

Abstract: This study presents results for trace elements (TEs) and rare earth elements (REEs) in five pit lakes located within the Muskau Arch, one of the largest regions in Central and Eastern Europe affected by acid mine drainage (AMD). Concentrations of TEs (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Th, Tl, U, V, Zn) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were determined using inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS). The highest concentrations were recorded for Fe (0.14–156.9 mg/L), which was the dominant TE in all pit lakes except MA1, where Al was dominant. PCA indicated that TEs such as Al, Be, Co, Fe, Li, Mn, Ni, Rb, Sc, Th, and Zn were strongly associated with pit lakes affected by AMD. Two subgroups were identified: (1) Be, Co, Ni, and Zn, which correlated with Al and low pH, and (2) Fe, Mn, Li, Rb, and Th, which correlated with slightly higher pH and anoxic and more reducing conditions. The toxicity analysis of TEs revealed substantial variation among the pit lakes (from extreme to low toxicity) and indicated that the most important TEs contributing to water toxicity were Al, Mn, Zn, and Ba. Total REE concentrations ranged from 0.15 μg/L to 149.3 μg/L, with by far the highest values recorded in MA2, and their concentrations were strongly influenced by pH. The pit lakes generally exhibited LREE (including La to Eu) enrichment, as well as a weaker MREE (including Sm to Dy) enrichment. Positive Gd anomalies were identified at all sampling points. Additionally, positive Eu anomalies were observed in all pit lakes except MA2, which was the most strongly affected by AMD, and positive Tb anomalies were recorded primarily in samples influenced by AMD.

Keywords: acid pit lake, lignite pit lake, acid mine drainage, LREE enrichment, meromictic pit lake, neutralized pit lakes

INTRODUCTION

Pit lakes, depending on the reclamation strategy adopted or its absence, as well as the local geological structure, can develop highly diverse ecosystems (e.g., Parshley & Bowell 2003, España et al. 2008, Geller 2013, Marszelewski et al. 2017, Chudy et al. 2021, Szafarczyk & Gawałkiewicz 2023, Śniady et al. 2024a, 2024b). One of the greatest threats to the water environment associated

https://doi.org/10.7494/geol.2025.51.4.389 ISSN 2299-8004 | e-ISSN 2353-0790 | Wydawnictwa AGH

with mining and the formation of pit lakes around the world is acid mine drainage (AMD) (Gawor & Lutyńska 2015, Rezaie & Anderson 2020, Lund & Blanchette 2023). The primary cause of AMD is the oxidation of metal sulfides (e.g., pyrite and marcasite), which readily oxidize upon contact with oxygen from infiltrating and atmospheric waters (Akcil & Koldas 2006). The resulting sulfuric acid production initiates a series of chemical reactions, leading to e.g. exceptionally low pH levels in the water, high sulfate (SO_4^{2-}) and iron (Fe) content. Additionally, other trace elements (TEs) and rare earth elements (REEs), often regarded as a distinct subgroup due to their coherent geochemical behavior and characteristic fractionation patterns in natural waters, can also reach very high concentrations in AMD-affected waters (Blowes et al. 2014, Migaszewski & Gałuszka 2015, León et al. 2021). Their study not only enhances the understanding of TE and REE geochemistry in acidic post-mining environments but also, as highlighted by León et al. (2021), may have potential economic significance at exceptionally high concentrations.

However, exceptionally low pH and high concentrations of TEs in the waters of such pit lakes represent a significant limiting factor for the development of aquatic organisms and vegetation (Hogsden & Harding 2012, Roccotiello et al. 2015). Additionally, depending on the region and the resource, AMD and mining-related pollution may also pose a threat to human health (e.g., Simate 2021, Vesković et al. 2023). In areas affected by water shortages, it presents a major challenge to achieving the United Nations' Sustainable Development Goal 6 (Broadhurst 2019, Adeniyi et al. 2022). From a European perspective, the primary concern should be the environmental risks, as well as the potential hazards for tourists visiting acid lakes, which often have an attractive appearance (e.g., Chudy et al. 2021). Nevertheless, these threats have driven the development of research on the toxic effects of AMD-impacted waters worldwide (e.g., Singovszka et al. 2017, Fernández et al. 2018, Atangana & Oberholster 2021, Luo et al. 2022). It should also be emphasized that toxic concentrations of TEs in mining areas are not only detected in waters of pit lakes but are also commonly found in soils (e.g., Yu et al. 2024) and fly ashes (Slavković-Beškoski et al. 2024), further contributing to the overall toxicity risks in such regions.

An example of a region where acidic pit lakes with high touristic attractiveness occur is the Muskau Arch, which is considered one of the largest areas affected by AMD in Central and Eastern Europe (Gąsiorowski et al. 2021) and has been included in the UNESCO Global Geoparks list since 2011 (Koźma & Migoń 2024). This region is referred to as an "anthropogenic lakeland" due to the presence of over 100 lakes formed after the mining of lignite and, to a lesser extent, clays and sands (Jędrczak 1992, Koźma 2016). These lakes originated from mining operations conducted from the second half of the 19th century until 1974, when the last mine, "Babina," was closed (Jędrczak 1992). Following the cessation of mining, the pit typically became directly inundated by groundwater and precipitation, which facilitated the development of AMD (Pukacz et al. 2018).

The chemical composition of the resulting pit lakes is influenced by factors such as age, origin, hydrological and geological conditions, as well as the presence of natural or artificial neutralization processes (Lutyńska & Labus 2015, Sienkiewicz & Gąsiorowski 2016, Pukacz et al. 2018, Oszkinis-Golon et al. 2020, Gąsiorowski et al. 2021). Additionally, at least four pit lakes have been identified as meromictic (Oszkinis-Golon et al. 2020), meaning their waters do not fully mix (Boehrer & Schultze 2006). This phenomenon is relatively common among AMD-impacted pit lakes (Boehrer & Schultze 2006, Schultze et al. 2017). These factors collectively contribute to the high geochemical variability observed across pit lakes in this region (Pukacz et al. 2018, Oszkinis-Golon et al. 2020, Gąsiorowski et al. 2021).

To date, most studies on pit lakes in the Muskau Arch have focused primarily on the concentrations of Al, Fe, and Mn – well-documented and commonly associated with AMD (e.g., Lutyńska & Labus 2015, Pukacz et al. 2018, Sienkiewicz & Gąsiorowski 2018, Gąsiorowski et al. 2021). Furthermore, Sienkiewicz and Gąsiorowski (2017) reported surface water concentrations of Al, Mn, Ni, Fe, and Zn in 69 pit lakes. More comprehensive analyses have so far been limited to individual lakes, e.g., studies by Sienkiewicz et al. (2023) on TEs and Sekudewicz et al. (2024) on heavy metals. Results for REEs have been presented only in a single study (Bauerek et al. 2019), which included five pit lakes, although solely based on surface water samples. Therefore, the present study aims to expand the research on the concentrations of a broad range of TEs (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Th, Tl, U, V, Zn) as well as REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in pit lake waters within the Muskau Arch.

The specific objectives of this study are: (1) to describe the distribution and geochemistry of TEs and REEs in the waters of selected lakes on the Muskau Arch; (2) to assess the potential toxicity of TEs in pit lake waters using selected indices; and (3) to identify anomalies of the detected REEs.

MATERIALS AND METHODS

Study area

The Muskau Arch encompasses a glaciotectonic deformation zone in the shape of a horseshoe, extending across the Lower Lusatia region (Germany) and Lower Silesia (Poland). In its central part, it is divided into the German and Polish sections by the Lusatian Neisse River. The geology of this area primarily consists of Paleogene and Neogene deposits, including lignite, clay, and sand sediments (Koźma 2016). This study focuses on the Polish section of the Muskau Arch (Fig. 1). To describe the geochemical behavior of TEs and REEs in the waters of pit lakes on the Muskau Arch, five pit lakes were selected with different origins, ages and genesis (Table 1, Fig. 1), as well as differing in the presence of artificial or natural neutralization.

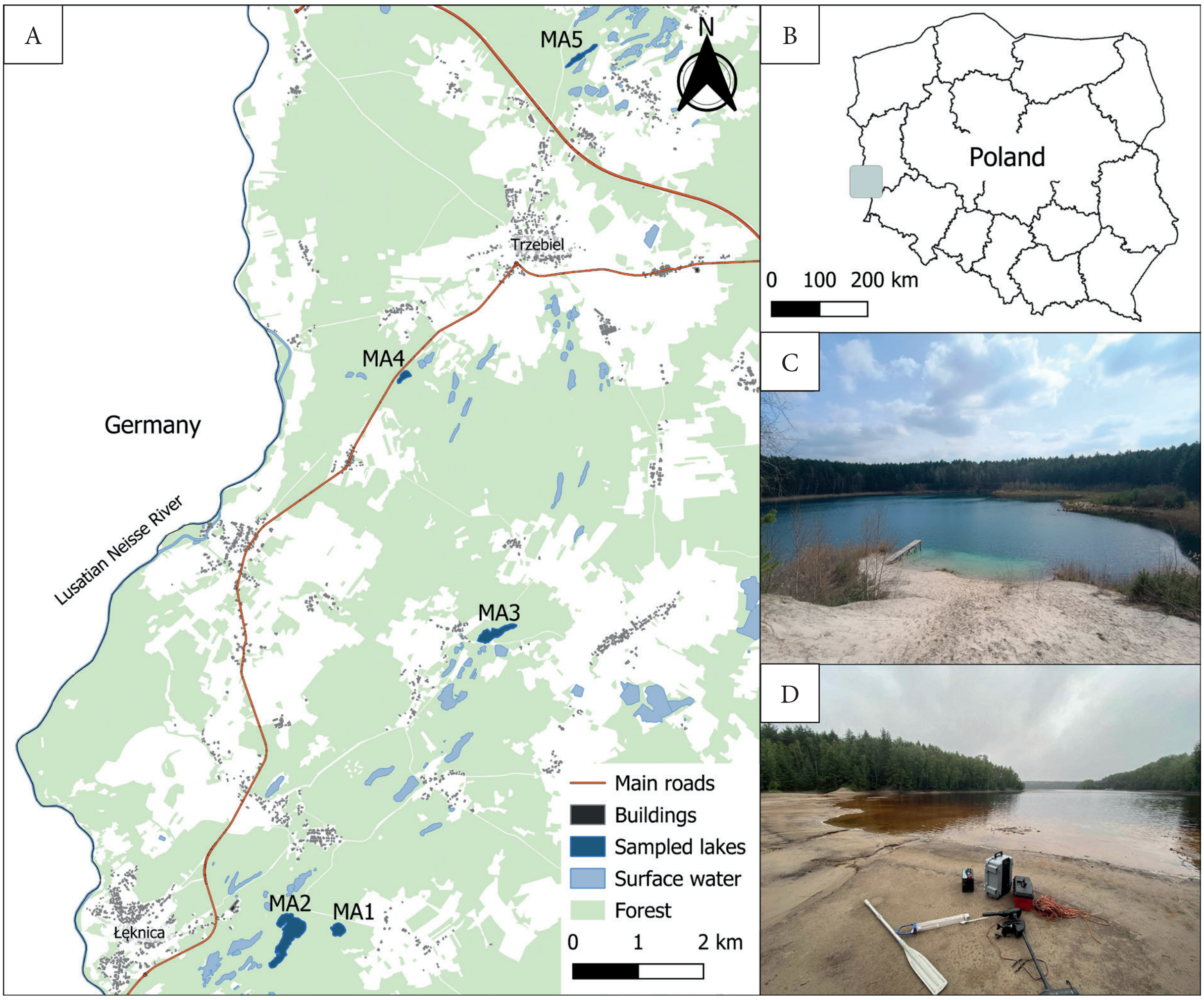

Fig. 1. *Location of studied pit lakes (A), position of Muskau Arch in Poland (B) and photo of studied pit lakes MA1 (C) and MA2 (D)*

Three of them (named thereafter MA2, MA3, MA4) are meromictic. Two of them (MA2 and MA3) were not artificially neutralized, and stratification in them was enhanced by the influx of highly mineralized groundwater (Gąsiorowski et al. 2021). The vertical pH differences in these pit lakes are likely due to oxygen consumption in the bottom zone caused by organic matter decomposition and Fe reduction, which has led to an increase in pH (Gąsiorowski et al. 2021). MA4 was probably limed and wastewater fertilization in the 1980s and 1990s, which led to its eutrophication (Jachimko & Kasprzak 2011). Meromixia in that pit lake, probably developed due to groundwater inflows affected by AMD in the past from a nearby pit lake with a shared aquifer (Jachimko & Kasprzak 2011, Sienkiewicz & Gąsiorowski 2019).

Table 1
Characteristics of the studied pit lakes on the Muskau Arch

Parameter	Lake number				
	MA1	MA2	MA3	MA4	MA5
Age [years]*	56	56	94	120	124
Area [ha]*	2.63	17.87	6.53	1.84	2.87
Max. depth [m]	9.7	21.0	15.7	9.1	3.1
Origin*	lignite, clay	lignite	clay	lignite	lignite, clay
Genesis*	open-cut	open-cut	open-cut	sink hole	sink hole, open-cut

* After Pukacz et al. (2018), updated.

Depending on the study, the MA1 was characterized as dimictic or polymictic and showed slow natural neutralization (Jędrczak 1992, 1996, Najbar & Jędrczak 1998, Oszkinis-Golon et al. 2020), which has not yet exceeded a 4.5 pH, the effect of rapid degradation of an acidic unique ecosystem (Brugam & Lusk 1986). Lake MA5 is relatively shallow and old, and it may have been acidified in the past, as indicated by its origin. However, it probably became neutralized as a result of liming and being fertilized with wastewater in the 1980s and 1990s (Oszkinis-Golon et al. 2020). Thus, this lake may be an example of a neutralized pit lake with a common operating condition used by people. In addition, these pit lakes differ in terms of their geological structure, as illustrated in detail in Figure 2.

Samples collection

Sample collection took place on August 29–30, 2023. Three vertical profile samples were taken from each pit lake (surface, transitional, bottom), except for MA5 where two samples were taken due to the shallow depth. A Water Sampler USB 50015 (UWITEC GmbH, Mondsee, Austria) was used for this purpose. Water samples of 500 mL were collected in polyethylene bottles (HDPE) by Nalgene®. Samples used for chemical analyses were fixed *in situ*. The samples for major ion analyses were treated with chloroform to prevent the growth of microorganisms and to maintain a stable ionic composition, and, for TEs and REEs testing, were treated with HNO_3 (Merck, Darmstadt, Germany). After collection, the samples were taken to a chemical laboratory in a mobile refrigerator at a temperature of 4°C ±2.5°C. Additionally, *in situ* measurements of basic water parameters such as pH, temperature, optical dissolved oxygen (ODO), electrical conductivity, and redox potential (Eh) were conducted. A ProDSS Multiparameter Digital Water Quality Meter by YSI (Ohio, USA) was used for this purpose.

Chemical analysis

Water samples were analyzed for their cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (Cl^- and SO_4^{2-}) using a Metrohm ion chromatograph (IC), model 881 Compact IC Pro (Metrohm, Switzerland). During IC assays, standard solutions from Merck (Merck, Darmstadt, Germany) and CPAchem (C.P.A. Ltd., Stara Zagora, Bulgaria) were used. The mobile phase for cations and anions was prepared using Fluka reagents (Sigma-Aldrich, Steinheim, Switzerland). Alkalinity was measured by *in situ* titration with HCl (0.1 N) using methyl orange as an indicator. As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed ±3%.

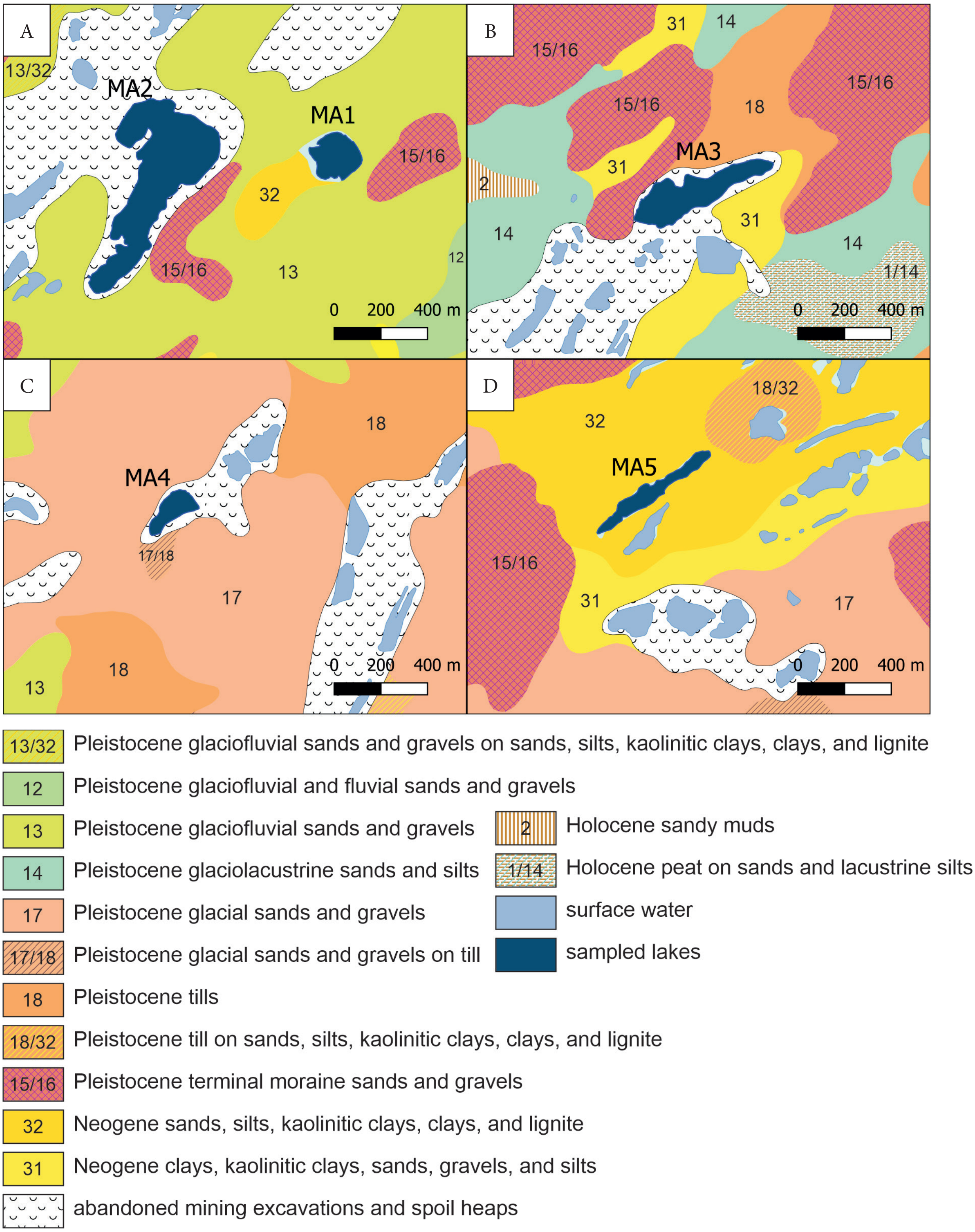

Fig. 2. *Geological structure of the areas around the studied pit lakes. The geological data are based on the Detailed Geological Map of Poland in scale 1:50,000 (Bartczak & Gancarz 1998)*

Concentrations of TEs (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Th, Tl, U, V, Zn) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were determined by inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ-MS 8800 Triple Quad, Agilent Technologies, Tokyo, Japan). Assays using the ICP-QQQ-MS technique were performed using calibration curves obtained from the diluted stock multi-element standard at 100 μg/mL (VHG Labs, Manchester, NH, USA). The operating parameters of the ICP-QQQ-MS instrument and the analytical procedures are described in the works of Siepak and Sojka (2017), Siepak et al. (2020), and Mikoda et al. (2024). All reagents used were ultrapure, and water was deionized to a resistivity of 18.2 MΩ·cm in a Direct-Q® UV3 Ultrapure Water System apparatus (Millipore, France). The analytical quality control was verified by the analysis of certified reference materials, i.e., SRM 1640a (National Institute of Standards and Technology, Gaithersburg, MD, USA), SPS-SW2 (Spectra pure Standards As, Oslo, Norway), RAIN-97, and PERADE-09 (Environment Canada). High compliance with reference values was found.

Statistical analysis

To identify the sources and assess the geochemical behavior, a chemometric approach based on principal component analysis (PCA) was applied to the obtained TE and REE data (Onjia et al. 2022). For this purpose, the data were first centered log-ratio (clr) transformed and then standardized. Additionally, the PCA included basic physicochemical parameters of water as additional variables: pH, Eh, electrical conductivity, temperature, and ODO. The analysis was conducted using the vegan package version 2.6–6.1 (Oksanen et al. 2024). The results were visualized as biplots using the ggvegan package version 0.1.999 (Simpson & Oksanen 2023). All analyses were performed using R version 4.3.0 (R Core Team 2023).

Trace metal toxicity assessment

The trace metal toxicity load (TMTL) was applied to quantify toxic TE concentrations in the pit lakes of the Muskau Arch and to assess their potential impact on human health (Saha & Paul 2019, Yakovlev et al. 2022). TMTL is determined by multiplying the studied content of trace elements in water (C_i) by their total hazard score (HIS_i) assigned by the *Substance Priority List* prepared by the Agency for Toxic Substances and Disease Registry (ATSDR 2022). It is calculated according to Equation (1):

$$\mathrm{TMTL} = \sum_{i=1}^{n} C_i \times \mathrm{HIS}_i \qquad (1)$$

This allowed us to consider the toxicity of all the trace elements examined, with the exception of Bi, Fe, Li, Mo, Rb, and Tl. These elements were not included in the ATSDR (2022) list, and therefore it is assumed that they do not exhibit significant toxicity at concentrations typically found in natural waters. A scale following Yakovlev et al. (2022) was adopted for quality assessment using TMTL: 0–100 – low toxicity; 100–300 – moderate toxicity; 300–500 – high toxicity; 500–1,000 – very high toxicity, and above 1,000 – extremely high toxicity.

The trace metal evaluation index (TMEI) (Śniady et al. 2024a) was used to present direct exceedances of metal concentrations in water according to the standards of the Regulation of the Minister of Infrastructure for surface waters (Rozporządzenie 2021). It is expressed as the ratio of the monitored metal concentration (TM_{conc}) to its maximum permissible concentration (TM_{MPC}). It was therefore calculated for Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Tl, V, Zn according Equation (2):

$$\mathrm{TMEI} = \sum_{i=1}^{n} \frac{\mathrm{TM_{conc}}}{\mathrm{TM_{MPC}}} \qquad (2)$$

For the purpose of assessing trace metal contamination, 1.0 was used as a threshold value. Results above 1.0 indicate poor lake condition and results below 1.0 indicate good lake condition in terms of trace metals included in the analysis.

REE division, normalization, and anomaly calculation

For the purposes of data analysis, the rare earth elements (REEs) were divided into two conventional subgroups: (1) light REEs (LREEs) including elements from La to Eu, and (2) heavy REEs (HREEs) including elements from Gd to Lu (Migaszewski et al. 2016). Additionally, a third subgroup, the middle REEs (MREEs), was distinguished, comprising elements from Sm to Dy (Grawunder et al. 2014, Bauerek et al. 2019).

To eliminate the REEs "zigzag" pattern and perform further calculations, normalization to the NASC (North American Shale Composite) standard (Haskin et al. 1968, Gromet et al. 1984) was applied. To examine the depletion or enrichment of REE subgroups, ratios of La_{NASC}/Yb_{NASC}, La_{NASC}/Sm_{NASC} and Sm_{NASC}/Yb_{NASC} were calculated, where the subgroups are represented by: LREE (La), MREE (Sm), and HREE (Yb) respectively (Migaszewski et al. 2016). Ratio values below 0.8 indicate depletion, whereas those above 1.2 indicate enrichment of the respective REE subgroup (Grawunder et al. 2014).

Anomalies were also calculated for the most commonly selected REEs: Ce/Ce_{NASC}, Eu/Eu_{NASC}, Gd/Gd_{NASC}, and Tb/Tb_{NASC}. The formula proposed by Bau and Dulski (1996) was used for this purpose, as expressed by:

$$\frac{Ce}{Ce_{NASC}} = \frac{Ce_{NASC}}{\left(0.5La_{NASC} + 0.5Pr_{NASC}\right)} \tag{3}$$

where Ce_{NASC} represents the background concentration, whereas La_{NASC} and Pr_{NASC} are the NASC-normalized La and Pr concentrations, respectively.

For Eu/Eu_{NASC}, Gd/Gd_{NASC}, and Tb/Tb_{NASC}, modified formulas were applied due to the presence of pronounced Eu, Gd and Tb anomalies (Migaszewski et al. 2016, Bauerek et al. 2019):

$$\frac{Eu}{Eu_{NASC}} = \frac{Eu_{NASC}}{\left(0.5Sm_{NASC} + 0.5Dy_{NASC}\right)} \tag{4}$$

$$\frac{Gd}{Gd_{NASC}} = \frac{Gd_{NASC}}{\left(0.5Sm_{NASC} + 0.5Dy_{NASC}\right)} \tag{5}$$

$$\frac{Tb}{Tb_{NASC}} = \frac{Tb_{NASC}}{\left(0.5Sm_{NASC} + 0.5Dy_{NASC}\right)} \tag{6}$$

where $Eu/Gd/Tb_{NASC}$ represents background concentrations, whereas Sm_{NASC} and Dy_{NASC} are the NASC-normalized Sm and Dy concentrations, respectively.

RESULTS

Basic physico-chemical parameters

The analyzed pit lakes exhibited significant variability in physico-chemical parameters depending on the parameters assessed. Only pit lake MA1 showed no substantial changes in parameter values along the vertical profile. In contrast, MA2, MA3, and MA4 displayed pronounced stratification of the measured parameters, whereas MA5, due to its shallow depth, exhibited a slight decrease in most parameters with increasing depth. Acidic pH values were recorded in pit lakes MA2, MA3, and MA1, with surface values of 2.58, 2.92, and 4.07, respectively. With increasing depth, the pH in MA2 and MA3 significantly increased, reaching 4.77 and 6.46 near the bottom, respectively (Fig. 3A). The pH of MA4 and MA5 was slightly alkaline, ranging from 7.09 to 7.86.

Surface water temperature across the pit lakes ranged from 20.6°C to 22.6°C. A distinct thermal stratification was observed in MA2, MA3, and MA4, characterized by a temperature decline between 3 m and 6 m. Below 6 m, temperature stabilization was evident in these pit lakes (Fig. 3B). MA1 and MA5 exhibited a generally stable temperature profile, although MA5 showed a typical slight temperature decrease with depth (Fig. 3B).

In pit lake MA1, ODO remained stable throughout the water column, except for a measurement taken near the bottom, while MA5 showed a linear decline in ODO with depth (Fig. 3C). MA2, MA3, and MA4 exhibited clear stratification, with MA4 showing a marked ODO decline between 3 m and 5 m. In contrast, MA2 and MA3 displayed a sudden increase in ODO at a depth of 5 m, followed by a subsequent decline (Fig. 3C).

The highest electrical conductivity was recorded in MA2, increasing from 2,078.0 μS/cm at the surface to 3,313.3 μS/cm at the bottom. MA3 showed a gradual increase in electrical conductivity, with distinct rises at 9 m and near the bottom, reaching a maximum of 2,170.3 μS/cm. The other pit lakes exhibited relatively uniform electrical conductivity throughout the water column (Fig. 3D), except for MA4, where electrical conductivity sharply increased near the bottom, reaching 778.2 μS/cm.

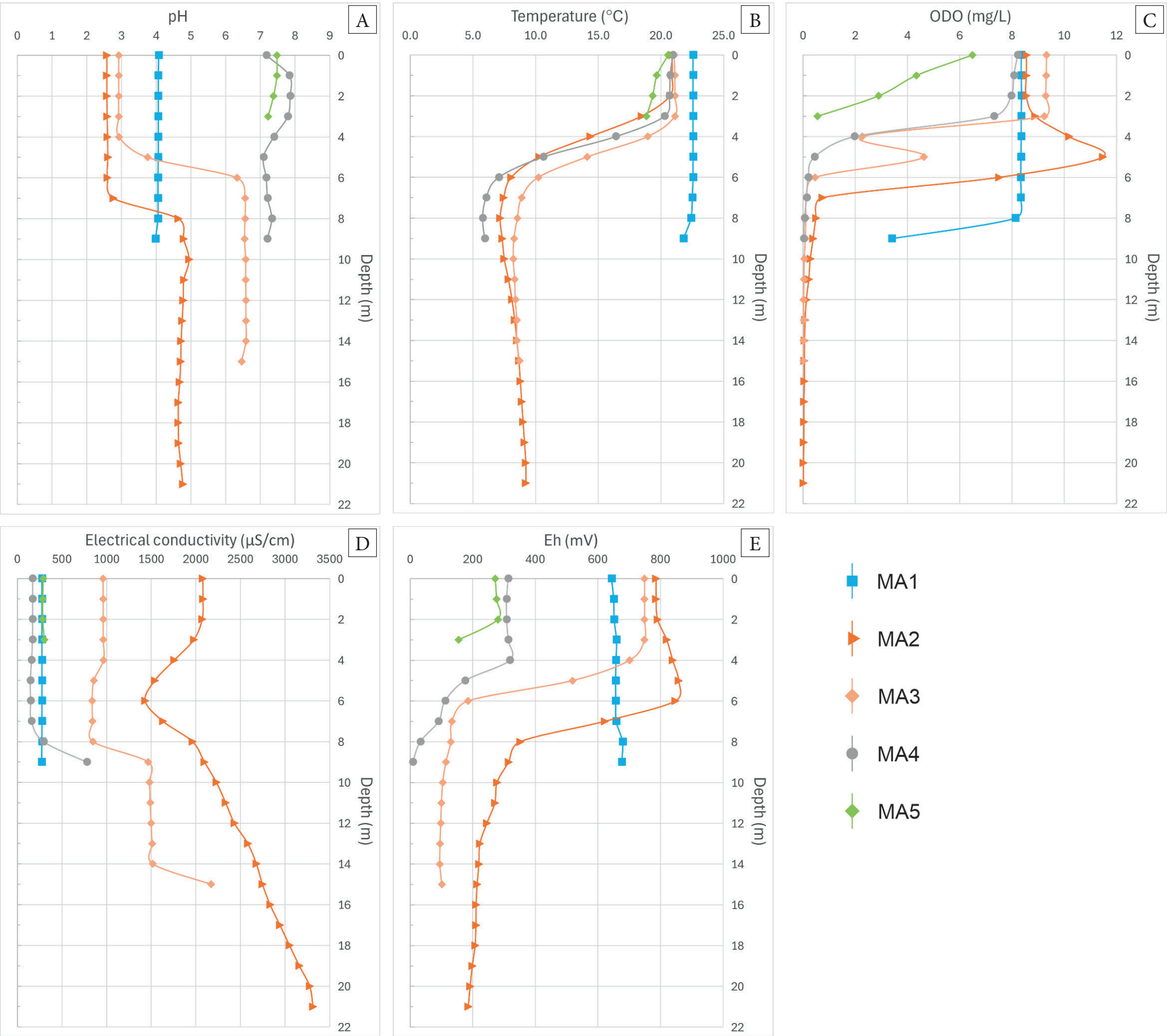

Fig. 3. The basic physical and chemical parameters for the studied pit lakes on the Muskau Arch: A) pH; B) temperature; C) optical dissolved oxygen (ODO); D) electrical conductivity; E) redox potential (Eh)

Redox potential (Eh) exhibited pronounced stratification in MA2, MA3, and MA4, with substantial variability in values (Fig. 3E). MA1 and MA5 showed lower variability, with only a noticeable Eh decrease near the bottom in MA5 (Fig. 3E).

Major ions

Based on the analysis of major ions, the pit lakes studied can be categorized into two distinct groups. In MA1, MA2, and MA3, the dominant anion was SO_4^{2-} (Fig. 4), with the highest concentrations recorded in MA2, ranging from 1,176.9 mg/L at the surface to 1,705.3 mg/L at the bottom. Similar SO_4^{2-} concentrations were observed in MA3 at the bottom (1,282.2 mg/L), but its surface concentration was significantly lower at 369.5 mg/L. Pit Lake MA1 exhibited generally lower concentrations of major ions, with SO_4^{2-} levels ranging between 109.7 mg/L and 111.8 mg/L. The Cl^- concentrations in MA1, MA2, and MA3 did not exceed 13.5 mg/L, while HCO_3^- levels remained below 18.3 mg/L. The dominant cation in these pit lakes was Ca^{2+}, which reached particularly high concentrations in MA2 and MA3, ranging from 121.8 mg/L to 309.4 mg/L.

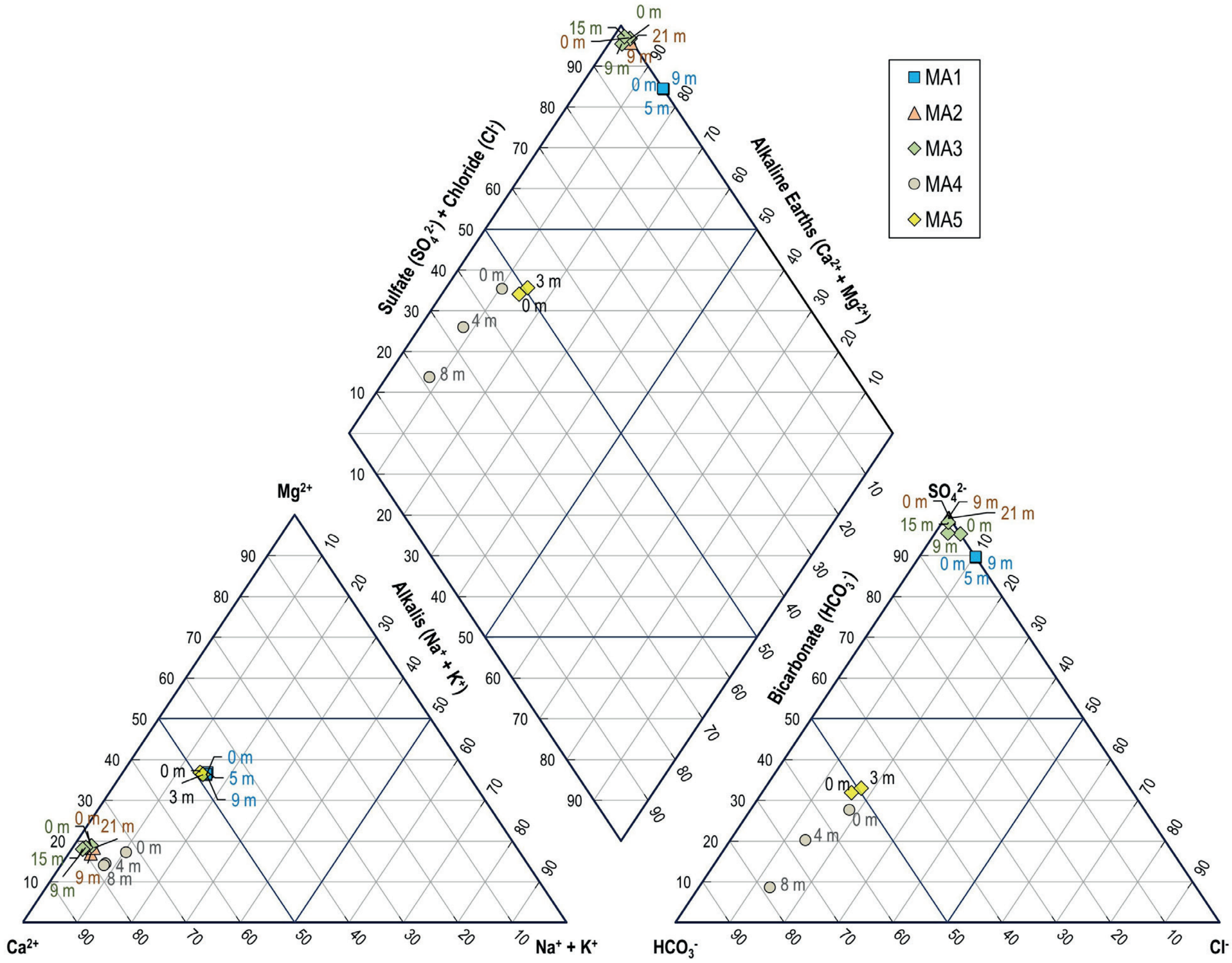

Fig. 4. *Piper chart for major ions in the waters of the studied pit lakes on the Muskau Arch*

In contrast, MA1 had lower Ca^{2+} concentrations, between 23.8 mg/L and 24.2 mg/L. The concentrations of other cations in MA1, MA2, and MA3 ranged as follows: Mg^{2+} from 11.0 mg/L to 42.3 mg/L, Na^+ from 3.60 mg/L to 6.06 mg/L, and K^- from 3.80 mg/L to 15.1 mg/L.

Pit lakes MA4 and MA5 exhibited similar Ca^{2+} and HCO_3^- concentrations (Fig. 4), with ranges of 26.4–39.9 mg/L and 61–122 mg/L, respectively. MA5 was characterized by higher concentrations of Mg^{2+}, Na^+, and K^+, as well as elevated levels of Cl^- and SO_4^{2-}. Additionally, it should be noted that MA4 was the only pit lake that exhibited pronounced vertical variability in major ion composition (Fig. 4).

TE concentrations, spatial and vertical variability, and PCA relationships

In general, pit lake MA2 exhibited the highest concentrations of TEs, with Fe levels (characteristic of AMD influence) reaching 317.2 mg/L. Additionally, pit lake MA3 also displayed exceptionally high TE concentrations, with surface values of 13.5 mg/L and bottom concentrations reaching 284.1 mg/L. In pit lake MA4, only the monimolimnion exhibited very high Fe concentrations, reaching 40.4 mg/L, while surface levels were significantly lower at 1.33 mg/L. The remaining two pit lakes (MA1 and MA5) recorded Fe concentrations ranging from 0.14 mg/L to 0.36 mg/L.

Notably, MA1 was the only pit lake where Fe was not the dominant TE; instead, the highest concentrations were recorded for Al, with a maximum of 0.5 mg/L. Compared to the other pit lakes, MA1 and MA2 showed significant enrichment in Co, Ni, Zn, Be, and Mn. Only in the monimolimnion of MA3 did Zn and Mn reach comparable concentrations. Additionally, MA2 exhibited exceptionally low Ba concentrations compared to the other pit lakes, whereas As levels were the highest in MA2 and MA5. The mixolimnion of MA2 also displayed markedly elevated concentrations of Sc, Cr, Cd, Ag, Se, Th, and U, significantly exceeding the values recorded in the other pit lakes. In detail, the results for TEs are shown in Figure 5 and Table S1 (available online as a supplementary file to the article).

PCA for TE identified two main components influencing the distribution of TE in water samples. PC1 and PC2 account for 42.8% and 22% of the variance, respectively (Fig. 6). A group of elements, including Al, Be, Co, Fe, Li, Mn, Ni, Rb, Sc, Zn and to a lesser extent Th, is negatively correlated with PC1. Within this group, a distinct separation into two subgroups is observed: the first subgroup (Al, Be, Co, Ni, Zn) is strongly negatively correlated with PC2, while the second subgroup (Fe, Li, Mn, Rb, Sc, and to a lesser extent Th) is strongly positively correlated with PC2.

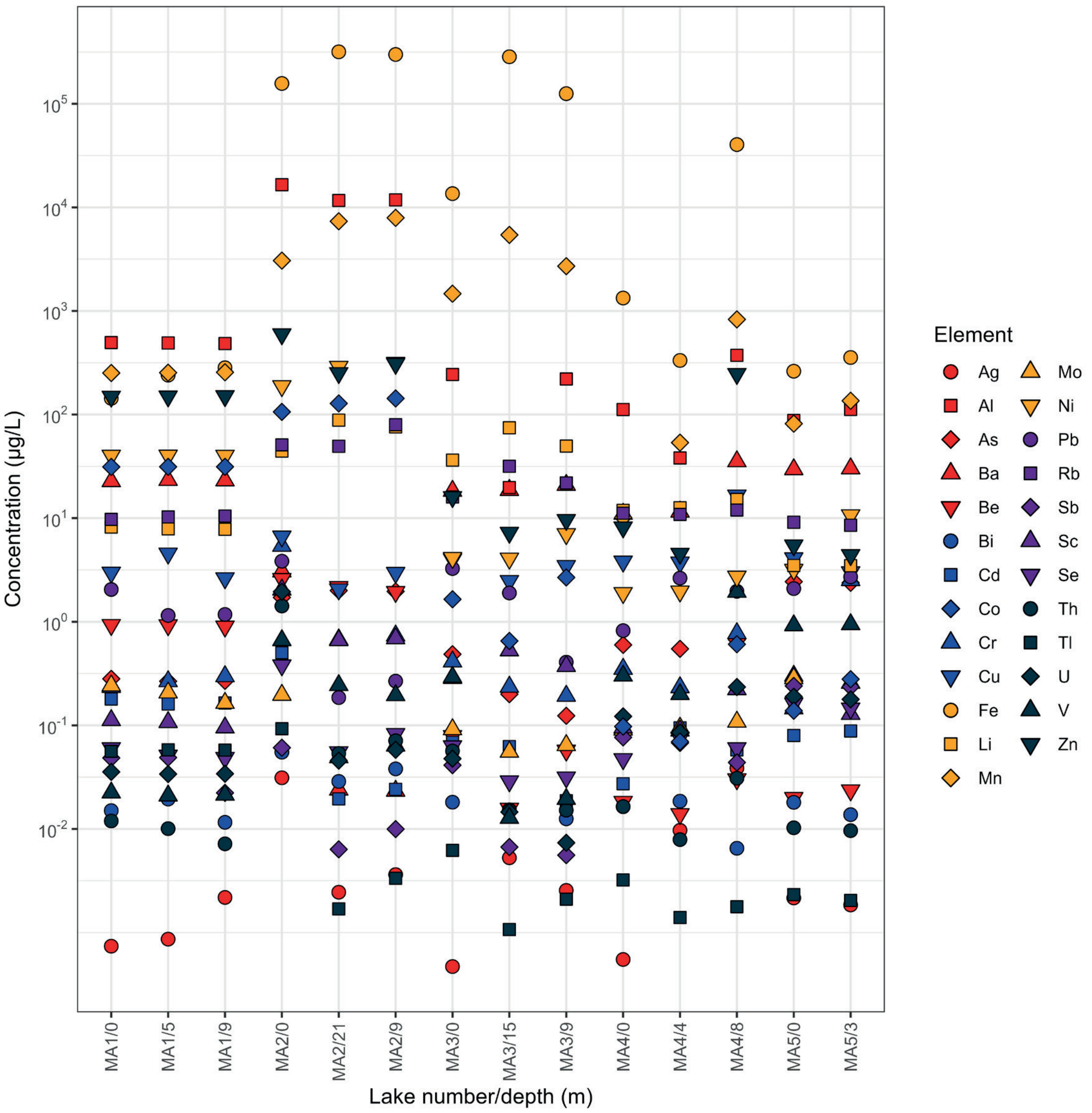

Fig. 5. *Concentrations of trace elements (TEs) in pit lakes on the Muskau Arch*

The first subgroup (Al, Be, Co, Ni, Zn) is located in the same region as the mixolimnion sample from Lake MA2 and samples from pit lake MA1 and is characterized by a moderate positive correlation with Eh. The second subgroup (Fe, Li, Mn, Rb, Sc, Th) is located in the same region as samples with noticeably higher pH from the chemocline and monimolimnion of pit lakes MA2 and MA3, and is characterized by a positive correlation with electrical conductivity and a negative correlation with ODO, temperature, and Eh. Additionally, Tl exhibits a strong negative correlation with PC2 and correlates with pit lake MA1. The set of elements including As, Bi, Cr, Cu, and V generally show correlations among themselves and are characteristic of the pit lake MA4 and also shows a strong positive correlation with pH. Se, Pb, and U display a strong positive correlation with PC1 and samples from pit lake MA5. It should also be noted that Cd, Mo, and Sb distinctly stand out from the other samples and are positively correlated with PC1.

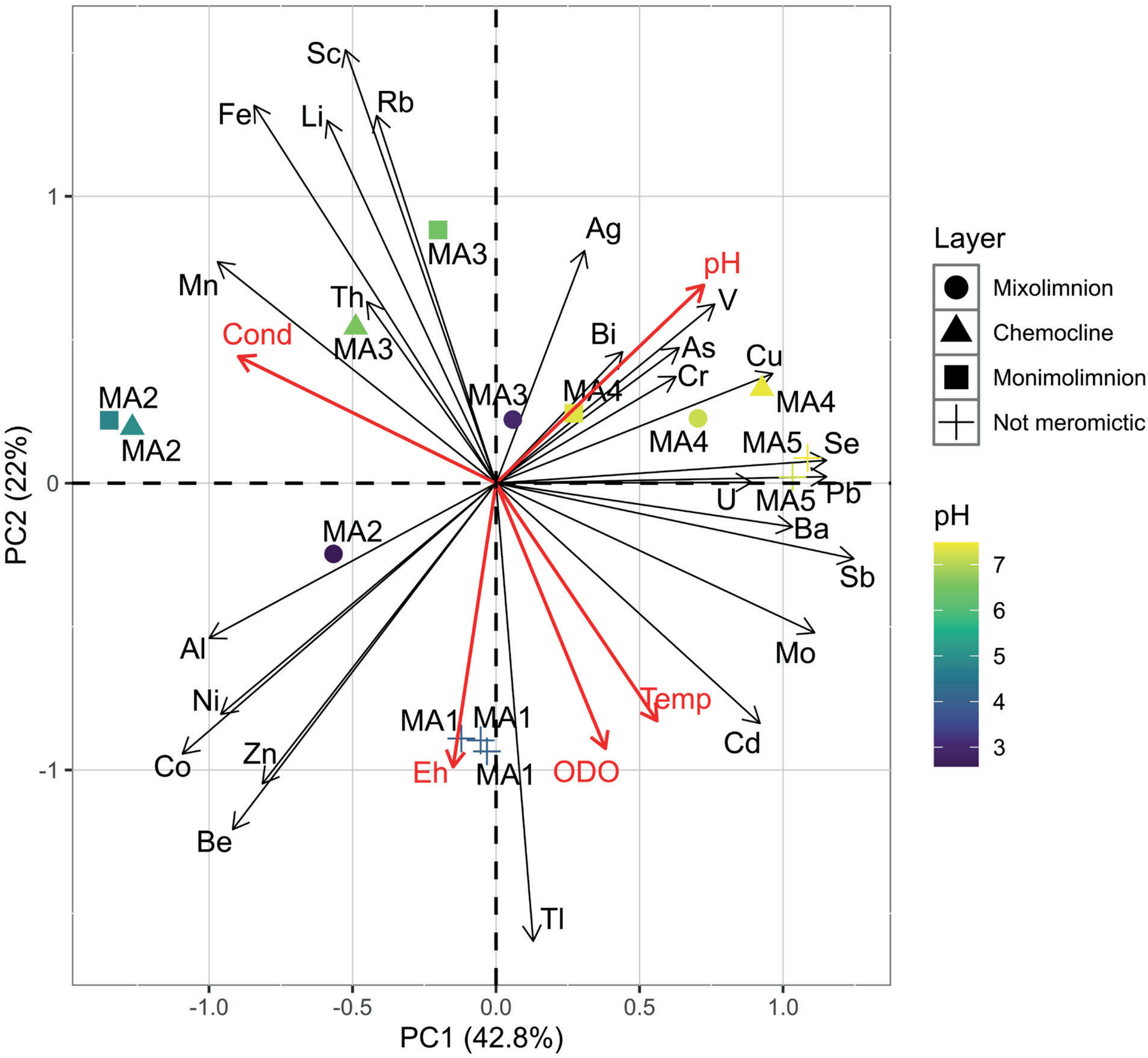

Fig. 6. PCA biplot for trace elements (TEs) and their correlations with basic physico-chemical water parameters: pH, Eh, temperature (Temp), electrical conductivity (Cond), and optical dissolved oxygen (ODO)

Trace metal toxicity assessment

The highest metal toxicity, expressed using TMTL, was recorded in pit lake MA2 (Table 2). These values exceed the threshold for extreme contamination by about 15 times, ranging from 14,498 to 15,171. Pit lake MA1 has a very high TMTL result, with slight vertical variability, and values ranging from 771 to 775. Pit lake MA3 indicates extreme toxicity throughout the profile. In MA3, TMTL values are lowest at the surface (1,384) and increase with depth, reaching 4,375 in the monimolimnion. Pit lake MA4 has moderate and low metal toxicity in the mixolimnion and chemocline, respectively, but reaches extreme toxicity in the monimolimnion with a TMTL of 1,195. Lake MA5 has moderate TMTL values throughout its profile, with the highest value of 239 at the bottom. The primary contributors to the TMTL values were elevated concentrations of Al, Mn, and Zn, and additionally Ba in all pit lakes except MA2. In pit lakes MA1 and MA2, the high TMTL values were further influenced by elevated Co and Ni concentrations, whereas in MA5 they were driven solely by Ni.

The TMEI, based on values set by Regulation of the Minister of Infrastructure (Rozporządzenie 2021), indicates that all pit lakes exceed the standards (Table 2).

Table 2
Results of TE toxicity assessment in pit lakes waters using TMEI and TMTL

Lake number	Depth [m]	TMEI	TMEI quality	TMTL	TMTL toxicity
MA1	0	17	poor lake condition	775	very high
	5	16		774	
	9	16		771	
MA2	0	104		14,652	extremely
	9	115		15,171	
	21	107		14,498	
MA3	0	5		1,384	extremely
	9	3		2,351	
	15	3		4,375	
MA4	0	2		109	moderate
	4	4		93	low
	8	5		1,195	extremely
MA5	0	4		169	moderate
	3	7		239	

Pit lake MA2 has the highest TMEI, exceeding the standards by over 100 times. Lake MA1 also significantly exceeds the TMEI standards, by more than 15 times. Although MA3 has higher TMTL values than MA1, its TMEI values are lower, ranging from 3 to 5. Lake MA4 shows a gradual increase in TMEI with depth, with values of 2, 4, and 5 from the surface to the bottom. Lake MA5 has a TMEI of 4 at the surface and 7 at the bottom.

REE concentrations, spatial and vertical variability, and PCA relationships

Lake MA2 exhibits the highest REE concentration, with a value of 149.27 μg/L at the surface, decreasing to 59.6 μg/L at the bottom. Lake MA1 shows slightly higher REE values compared to the other lakes, ranging from 5.72 μg/L to 5.46 μg/L (Table 3). The remaining lakes have significantly lower REE concentrations. Similar to MA2, Lake MA3 has the highest REE concentration at the surface (1.65 μg/L), which decreases with depth to 0.96 μg/L in the chemocline and 0.15 μg/L in the monimolimnion. Lake MA4, however, shows the highest values in the monimolimnion at 1.99 μg/L, decreasing to 0.22 μg/L in the chemocline and 0.45 μg/L in the mixolimnion. The pit lake MA5 has the lowest overall REE concentrations, ranging from 0.45 μg/L to 0.51 μg/L. In detail, the results for REEs are shown in Table S2 (available online as a supplementary file to the article).

All of the lakes, except for the bottom sample from MA3, exhibit a LREE enrichment relative to HREE (Table 3). LREE enrichment relative to MREE (expressed by the La_{NASC}/Sm_{NASC} ratio) was found in pit lakes MA1, MA2, chemocline of MA3, monimolimnion of MA4 and surface sample of MA5. The most pronounced LREE enrichment is observed in the chemocline and monimolimnion of MA2, as well as in the chemocline of MA3 and the monimolimnion of MA4. The sample from the monimolimnion of MA3 is the only one to show LREE and MREE depletion. Additionally, lakes MA2, MA3, MA4, and MA5 exhibit MREE enrichment, with the exception of the mentioned sample from MA3 and the deepest sample from MA4 (Table 3). The highest MREE enrichment is found in the mixolimnion of MA4.

Table 3
Measured total concentrations [μg/L] for selected REE subgroups and REE ratios for pit lakes on the Muskau Arch

Lake number	Depth [m]	ΣREE	ΣLREE	ΣMREE	ΣHREE	La_{NASC}/Yb_{NASC}	La_{NASC}/Sm_{NASC}	Sm_{NASC}/Yb_{NASC}	Ce/Ce_{NASC}	Eu/Eu_{NASC}	Gd/Gd_{NASC}	Tb/Tb_{NASC}
MA1	0	5.46	4.81	0.626	0.654	1.95	1.92	1.02	0.98	2.25	1.93	1.95
MA1	5	5.69	5.02	0.648	0.669	2.25	2.02	1.11	0.98	2.22	2.08	1.70
MA1	9	5.72	5.07	0.634	0.657	2.10	1.94	1.08	1.00	1.96	1.93	1.66
MA2	0	149.3	134.0	15.5	15.3	2.36	1.69	1.40	1.11	1.03	1.91	1.34
MA2	9	70.3	65.3	5.05	4.98	6.15	3.93	1.57	0.91	0.98	2.36	1.49
MA2	21	59.6	55.3	4.36	4.32	5.98	3.83	1.56	0.90	0.95	2.36	1.42
MA3	0	1.65	1.45	0.226	0.202	1.27	1.01	1.25	1.16	3.50	1.58	1.50
MA3	9	0.96	0.87	0.106	0.092	3.42	2.75	1.24	0.96	6.06	2.27	1.72
MA3	15	0.15	0.11	0.045	0.033	0.34	0.68	0.49	1.09	20.6	1.52	2.59
MA4	0	0.45	0.39	0.079	0.057	2.59	1.08	2.41	0.99	5.08	1.36	0.95
MA4	4	0.22	0.19	0.050	0.034	1.55	1.17	1.33	0.98	10.4	1.21	1.71
MA4	8	1.99	1.84	0.191	0.150	3.07	2.66	1.16	1.83	7.68	2.54	1.47
MA5	0	0.45	0.40	0.085	0.047	1.68	1.37	1.23	0.99	15.5	1.62	1.12
MA5	3	0.51	0.45	0.097	0.058	1.59	0.92	1.73	1.20	10.1	1.45	0.93

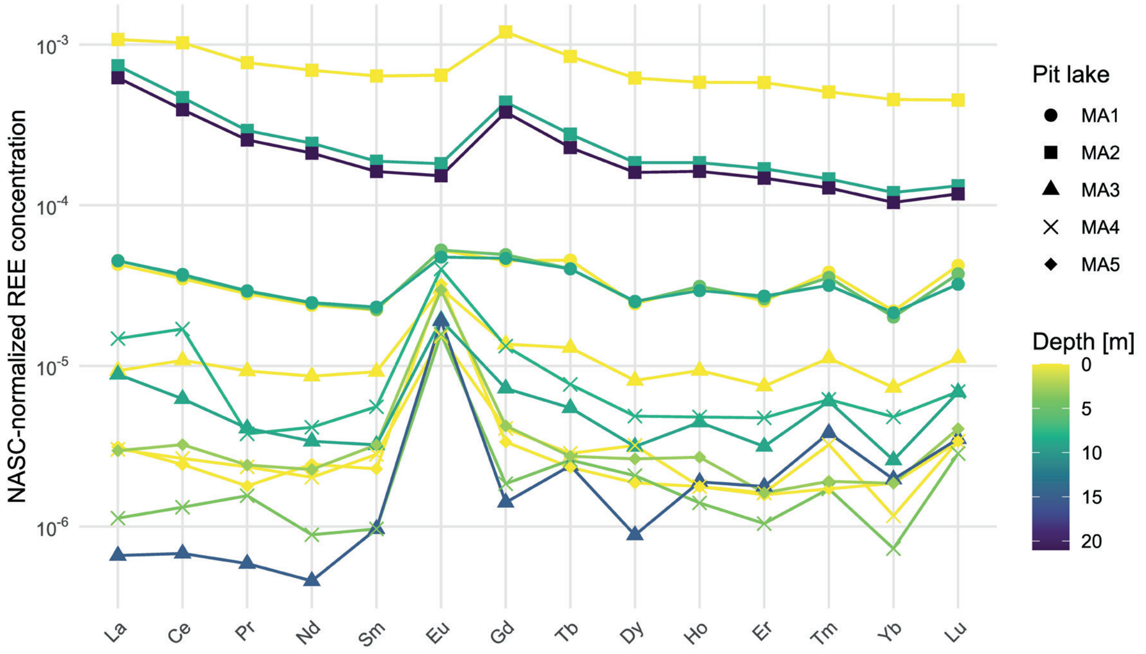

Fig. 7. *NASC-normalized REE pattern for pit lakes on the Muskau Arch*

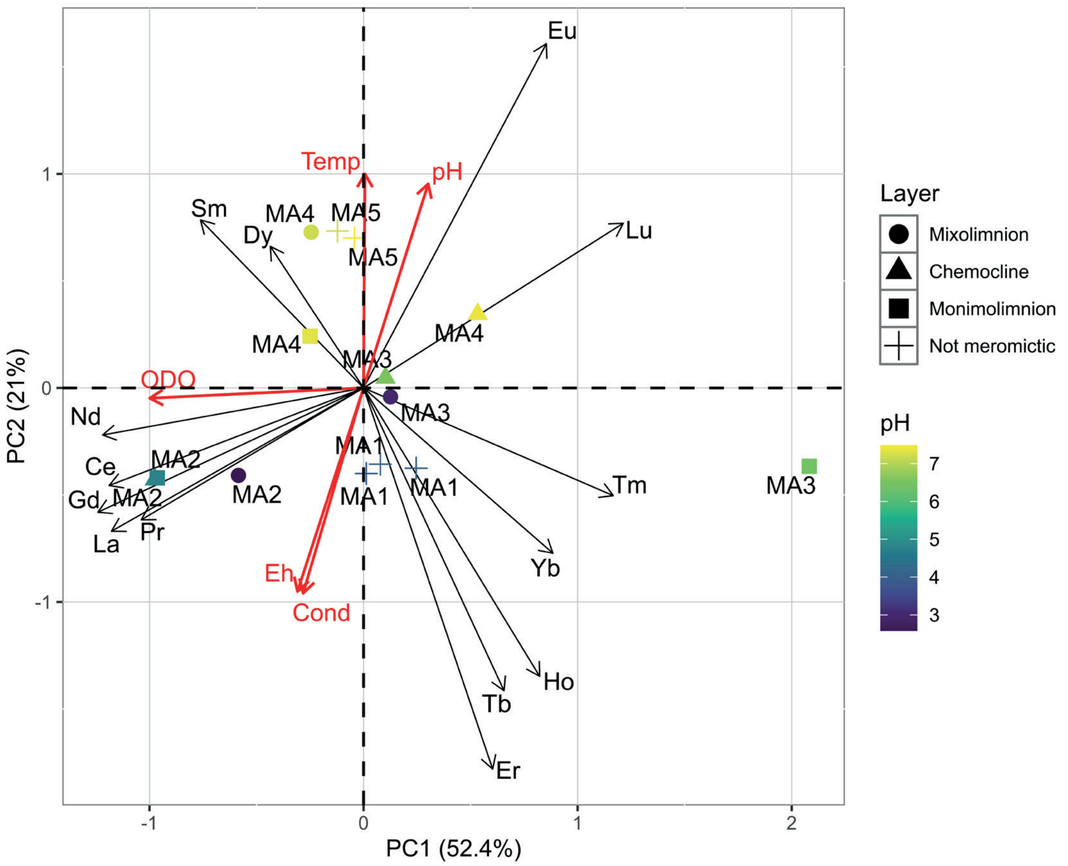

Fig. 8. *PCA biplot for rare earth elements (REEs) and their correlations with basic physico-chemical water parameters: pH, Eh, temperature (Temp), electrical conductivity (Cond), and optical dissolved oxygen (ODO)*

Among the studied REE anomalies, all lakes exhibited a positive Gd anomaly, and a positive Eu anomaly was observed in all lakes except MA2 (Table 3). Positive Gd anomalies were relatively consistent across all lakes. However, Eu anomalies were exceptionally high in lakes MA3, MA4, and MA5. Positive Tb anomalies were observed in all samples except those from lake MA5 and the surface sample of MA4. Similar to Gd anomalies, Tb anomalies were relatively consistent, ranging from 1.34 to 2.59. Positive Ce anomalies were only found in two bottom samples from lakes MA4 and MA5. The REE pattern for the analyzed pit lakes is shown in Figure 7.

PCA for REE identified two main components, PC1 and PC2, which explain 52.4% and 21% of the variance, respectively (Fig. 8). The group of elements Ce, Gd, La, Nd, and Pr shows a strong negative correlation with PC1 and correlates with samples from pit lake MA2. This group shows weak correlations with Eh, electrical conductivity, and ODO. Sm and Dy also exhibit a negative correlation with PC1, but unlike Ce, Gd, La, Nd, and Pr, they show a positive correlation with PC2. Additionally, Sm and Dy correlate with points of higher pH. Eu and Lu demonstrate a strong positive correlation with PC1, although Lu shows a slightly smaller correlation with PC2 compared to Eu. Eu is the only element that shows a strong positive correlation with pH. The group consisting of most HREE including Er, Ho, Tb, Tm, and Yb exhibits a positive correlation with PC1 and a negative correlation with PC2. This group also shows a negative correlation with pH in relation to PC2.

DISCUSSION

Due to its unique character in Central and Eastern Europe and its high environmental variability, the Muskau Arch has been the subject of numerous studies (e.g., Jędrczak 1992, 1996, Najbar & Jędrczak 1998, Jachimko & Kasprzak 2011, Sienkiewicz & Gąsiorowski 2016, 2017, 2018, 2019, Pukacz et al. 2018, Bauerek et al. 2019, Oszkinis-Golon et al. 2020, Gąsiorowski et al. 2021, Sekudewicz et al. 2024). The ongoing neutralization of pit lakes (Sienkiewicz & Gąsiorowski 2016, Oszkinis-Golon et al. 2020), the establishment of the UNESCO Global Geopark (Koźma & Migoń 2024) and information on human use of pit lakes (Pukacz et al. 2018, Sienkiewicz & Gąsiorowski 2019) have created a dual imperative: on one hand, the need to advance research on the unique ecosystems that have developed in this area before they undergo degradation, and on the other hand, an increased necessity to assess potential toxicity risks for individuals utilizing these pit lakes. TEs and REEs in acidic pit lake environments affected by AMD are complex and intriguing subjects of study due to the substantial variability between lakes, which results primarily from differences in geological structure, reclamation strategies, and human impact (Blowes et al. 2014). Consequently, pit lakes can exhibit very different TE and REE patterns among themselves even within a small area, as is the case with the Muskau Arch (Sienkiewicz & Gąsiorowski 2017, Bauerek et al. 2019, Gąsiorowski et al. 2021). The diversity of the studied pit lakes was further supported by the analysis of basic physico-chemical parameters and major ions. In particular, the major ion composition revealed a clear division into two groups (Fig. 4): the first includes MA1, MA2, and MA3, which are characteristic of AMD-affected lakes (Jędrczak 1992), whereas the second group, comprising MA4 and MA5, exhibits features more typical of neutralized lakes (Jędrczak 1992, Pukacz et al. 2018).

Trace elements distribution and toxicity

PCA suggests that Al, Be, Co, Ni, Zn, Fe, Li, Rb, Sc, Mn, and Th show the strongest correlation with pit lakes severely affected by AMD, with Al, Co, Fe, Mn, Ni, and Zn being most typical for AMD (Blowes et al. 2014). Among these elements, two subgroups can be distinguished. The first group (Al, Be, Co, Ni, Zn) includes Al and correlates with points characterized by low pH, which suggests high mobility of these elements under acidic conditions. This relationship is further emphasized by the negative correlation of pH with this group of TEs in the PCA (Fig. 6), as well as by their generally positive correlation with Eh. The second subgroup (Fe, Mn, Li, Rb, Th) comprises Mn and Fe and correlates with deeper sampling points characterized by higher pH in pit lakes. It also shows a negative correlation with ODO and Eh, indicating their association with increased solubility under anoxic and more reducing conditions (Gąsiorowski et al. 2021). These groups are therefore likely differentiated based on the rate at which elements undergo sorption or precipitation into sediment due to changes in the physico-chemical parameters of the water (Takeno 2005). Detailed attempts to describe these relationships for selected TEs have been undertaken, for example, by Lee et al. (2002). However, such studies should be extended in the future to a larger sample of pit lakes within the Muskau Arch. It is also worth noting that Tl shows a strong correlation with the waters of lake MA1, which may be attributed to the local characteristics of the deposit (Koźma 2016, Koźma & Migoń 2024). The study conducted by Cánovas et al. (2022) confirms the association of Tl with AMD and its mobility under acidic pH. Additionally, it should be emphasized that the PCA indicated a strong positive correlation of Tl with Eh and a negative correlation with pH (Fig. 6), which is typical for acidic conditions and contributes to the high mobility of Tl (Zhuang & Song 2021).

It is also noteworthy that PCA indicated a correlation between many TEs and waters with higher pH. Their presence in water is probably less pH-dependent, as confirmed by studies that have shown that some TEs (such as As, Mo, Sb, Se and U) can be present in AMD-affected water at high concentrations even at neutral pH (Shevenell et al. 1999, Nordstrom 2011). This is also confirmed by the results of the calculated toxicity indices (Table 2), which showed that the toxicity of TEs was not directly correlated with low water pH, and thus with the intensity of AMD. An example of such a situation is the confirmed extreme toxicity of the monimolimnion of MA4, where the current pH is close to neutral. It may be suspected that the migration of TEs to this pit lake occurred through a shared aquifer with a nearby pit lake that had been affected by AMD in the past (Jachimko & Kasprzak 2011, Sienkiewicz & Gąsiorowski 2019). Additionally, it should be noted that although all pit lakes showed significant exceedances of TMEI, not all posed a toxicological threat according to the calculated TMTL, which confirms the need for similar studies to enable objective assessment. A good example is the confirmed very high toxicity in MA1, despite low pH and proximity to MA2, compared to the extreme toxicity of MA3, which exhibits higher pH in the lower layers. Moreover, it should be emphasized that some of the studied pit lakes are used by humans. MA3 is used as a water intake point for firefighting purposes, while pit lakes MA4 and MA5 are used for fishing (Pukacz et al. 2018, Sienkiewicz & Gąsiorowski 2019). It is also worth noting that the extremely high TMTL values were primarily driven by TEs typical of AMD, mainly Al, Mn, and Zn. In all pit lakes except MA2, Ba concentrations also had a significant influence on overall toxicity. Additionally, Ni contributed to elevated toxicity in pit lakes MA1, MA2, and MA5, while Co played an important role only in MA1 and MA2. Therefore, when considering potential remediation strategies for currently utilized pit lakes, priority should be given to methods aimed at removing these TEs (Saha & Paul 2019).

Additionally, the applied toxicity assessment does not account for metals such as Li, Rb, and Fe, which are generally not considered toxic. Li and Rb reach concentrations too low to pose a threat to humans and the environment (Aral & Vecchio-Sadus 2008, US EPA 2016), whereas exceptionally high Fe concentrations, as observed in MA2, may have toxic effects on aquatic organisms (Cardwell et al. 2023). Consequently, severe Fe contamination, when considered separately, may also contribute to a reduction in biodiversity in AMD-affected areas.

Furthermore, the concentrations of TEs in the Muskau Arch reach values comparable to those observed in areas undergoing progressive neutralization, where pit lakes with varying pH levels have been studied, such as in the Lusatian Lignite District in Germany (Friese et al. 1998) or post-mining metal extraction pit lakes in Northern Sweden (Thomas et al. 2022). However, the recorded concentrations are significantly lower than those found in areas severely impacted by AMD, such as the Iberian Pyrite Belt in Spain (España et al. 2008). A detailed comparison with locations in Poland and worldwide is presented in Table 4.

Table 4
Comparison of the results obtained with other locations affected by AMD in Poland and worldwide

Study area	pH	Electrical conductivity [μS/cm]	SO_4^{2-} [mg/L]	Fe [mg/L]	Al [mg/L]	ΣREE [μg/L]	Comment	References
Muskau Arch	2.58–7.86	145.0–3313.3	10.5–1,705.3	0.1–317.2	0.02–16.5	0.15–149.3	–	This publication
Wiśniówka mining area (Poland)	2.2–3.5	1,080–5,570	534–3,978	5.2–860	10.1–86.02	94.85–992.88	Analysis of two acid pit lakes, one pit sump and tailings acid pond	Migaszewski et al. (2016)
Abandoned pyrite Wieściszowice mine (Poland)	2.8–5.1	223–2,630	78–1,398	0.049–78.5	0.2–29.8	–	Analysis of three pit lakes	Costa et al. (2021)
Upper Silesia Coal Basin (Poland)	2.4–3.0	11,300–12,400	3,270–5,630	197–500	63.3–227	478.53–1,831.97	Investigations of acidic runoff waters near an active coal mining waste pile	Bauerek et al. (2019)
Lusatian Lignite District (Germany)	2.55–8.12[1]	–	–	0.09–190[1]	0.006–20[1]	267–329.2[2]	[1]Analysis of 13 pit lakes [2]Mine Lake 111 analysis	[1]Friese et al. (1998) [2]Bozau et al. (2004)
Northern Sweden	2.53–9.33	30–3,800	–	<0.1–240	–	–	Analysis of 27 pit lakes after metal extraction (Au, Cu, Pb, Zn)	Thomas et al. (2022)
Iberian Pyrite District (Spain)	1.2–7.2[3]	1,159–55,600[3]	940–41,900[3]	0.4–36,675[3]	1–1,919[3]	702–3,672[4]	[3]Analysis of 22 pit lakes [4]San Telmo pit lake complex	[3]España et al. (2008) [4]Fuentes-López et al. (2022)

REE distributions, NASC-normalized pattern, and anomalies

REE concentrations in the Muskau Arch exhibit significant variability among the studied pit lakes, with exceptionally high concentrations observed only in MA2. However, the obtained values are lower than those reported from other areas in Poland that are severely affected by AMD, such as the Upper Silesian Coal Basin (Bauerek et al. 2019) or the Wiśniówka mining area (Migaszewski et al. 2016), as well as from sites worldwide, e.g., the San Telmo pit lake complex in the Iberian Pyrite District (Fuentes-López et al. 2022) or Mine Lake 111 in the Lusatian Lignite District (Bozau et al. 2004) (Table 4). The conducted research indicates that the main factor controlling REE concentrations in the water is pH, which is consistent with other studies (e.g., López-González et al. 2012, Obregón-Castro et al. 2023). Additionally, it should be noted that areas affected by AMD often exhibit MREE enrichment (Grawunder et al. 2014), whereas the pit lakes in the Muskau Arch show distinct LREE enrichment. Similar results, also for lignite, were obtained by Bozau et al. (2004) in Lower Lusatia, Germany.

PCA of REE indicates that most LREEs (Ce, La, Pr, Nd) and Gd are strongly associated with the acidic waters of pit lake MA2. It should be emphasized that the distribution of REE in AMD-impacted waters is primarily influenced by the characteristics of the parent rock (Grawunder & Merten 2012). However, as noted by Migaszewski and Gałuszka (2015), no general pattern of REE distribution in AMD-affected waters can be established. It is worth noting that, in contrast to LREE, most HREE exhibit somewhat weaker correlations with AMD-impacted pit lakes (Fig. 8). The weak correlation of this group may be related to the high Fe and Al concentrations in the studied pit lakes, as these elements tend to strongly adsorb HREE rather than LREE upon precipitation (Obregón-Castro et al. 2023). As highlighted by the studies of Gammons et al. (2005), significant REE precipitation occurs when the pH rises above 6. It can therefore be assumed that the pronounced LREE enrichment in the pit lake waters of the Muskau Arch is, on the one hand, a consequence of the characteristics of the parent rock, and on the other hand, a result of the preferential precipitation of HREE together with Al and Fe into the sediment during the neutralization process.

The conducted studies indicate that all pit lakes are characterized by positive Gd anomalies, almost all by positive Tb and Eu anomalies, while positive Ce anomalies were present only in MA4 and MA5 bottom samples (Table 3). As indicated by Olías et al. (2005), Ce at low pH and high Fe concentrations can be characterized by absent or negative anomalies due to preferential fractionation of Ce in Fe oxyhydroxides. The positive Ce anomalies observed at the bottom of MA4 and MA5 may result from a shift in water column conditions from oxidizing to reducing, which can lead to the remobilization of Ce (German & Elderfield 1989). In addition, it should be noted that positive Tb anomalies occurred in all samples except pit lake MA5 and mixolimnion of MA4, which were not affected by AMD. It can therefore be assumed that Tb may serve as one of the indicators of AMD in the Muskau Arch; however, due to the occurrence of a positive Tb anomaly in the chemocline of MA4, where water mixing with the monimolimnion is considerably limited under typical meromictic conditions (Boehrer & Schultze 2006), this issue requires further investigation.

It should also be noted that exceptionally high Eu anomalies were recorded in all pit lakes except MA2. In pit lake MA1, Eu anomalies were positive but relatively moderate, reaching a maximum of 2.25, whereas in the pit lake most strongly affected by AMD (MA2), the values ranged narrowly between 0.95 and 1.03 and were similar to those reported by Bauerek et al. (2019), who obtained a value of 1.00. It is also worth noting that groundwater in the vicinity of MA2 exhibits, similarly to the waters of this pit lake, strong acidity and oxidizing conditions (Gontaszewska et al. 2007). The very high positive Eu anomalies observed in most neutralized pit lakes (MA3, MA4, MA5) may potentially be related to their recharge by groundwater, which has a near-neutral pH (Dembiec 2010). Positive Eu anomalies in waters are generally inherited from the parent rock and are attributed to the preferential dissolution of feldspar minerals enriched in Eu (Chen et al. 2017, Li et al. 2025). The highest Eu anomalies were found in samples where Eh was the lowest, and the occurrence of positive Eu anomalies under near-neutral pH and moderately low Eh may reflect the geochemical characteristics of the parent rock (Migaszewski et al. 2014, Sojka et al. 2019). It should also be noted that Eu in the PCA exhibited a positive correlation with pH, which is not typical for REEs in acidic conditions (Fig. 8). However, studies conducted by Migaszewski et al. (2014) showed that groundwater surrounding the acidic Podwiśniówka pond also exhibited positive Eu anomalies, similarly to the parent rock and AMD sediments. Due to the exceptionally high Eu anomaly values, the conclusions drawn require verification in future studies, and their interpretation should be approached with caution.

CONCLUSION

The conducted studies on the Muskau Arch aimed at investigating a broad range of TEs (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Th, Tl, U, V, Zn) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in pit lakes of the Muskau Arch led to the following conclusions:

1. The analysis of major ions showed that the studied pit lakes can be generally divided into two groups. The first group consists of MA1, MA2, and MA3; is characteristic of AMD-affected waters with high SO_4^{2-} content, reaching up to 1,705.3 mg/L in pit lake MA2. The second group, consisting of MA4 and MA5, is typical of neutralized waters.
2. The investigated pit lakes differed significantly in concentrations of TEs and REEs depending on the occurrence of artificial or natural neutralization and, consequently, on their differing pH levels. Additionally, important factors controlling the geochemical behavior of TEs and REEs in water included ODO and Eh, as well as the complex geological structure of the study area resulting from glaciotectonic deformation.
3. The pit lakes analyzed were characterized by high concentrations and pronounced spatial variability of TEs, particularly those typical of AMD, such as Fe, Al, Mn, and Zn. The highest concentrations were recorded for Fe, ranging from 0.14 mg/L to 156.9 mg/L, and it was the dominant TE in all pit lakes except MA1, where Al was dominant.
4. PCA indicated that TEs such as Al, Be, Co, Fe, Li, Mn, Ni, Rb, Sc, Th, and Zn were strongly associated with pit lakes affected by AMD. Two subgroups were identified: (1) Be, Co, Ni, and Zn, which correlated with Al and low pH, and (2) Fe, Mn, Li, Rb, and Th, which correlated with slightly higher pH and anoxic and more reducing conditions.
5. The conducted toxicity analysis showed that all investigated pit lakes on the Muskau Arch exceeded the TMEI threshold value. However, not all of the pit lakes exhibited extreme toxicity, as indicated by the TMTL, and this toxicity was not directly related to water pH. TMTL indicated extreme toxicity in MA2 and MA3, whereas the lowest recorded toxicity (moderate) was observed in MA5. The greatest vertical variability in toxicity was found in MA4 (ranging from low to extreme), which is a consequence of the occurrence of meromixis. High TMTL values were primarily driven by elevated concentrations of Al, Mn and Zn, and additionally by Ba in all pit lakes except MA2.
6. The ΣREE concentrations in the waters showed substantial variability among the pit lakes, with MA2 exhibiting by far the highest values (up to 149.3 μg/L), followed by elevated concentrations in MA1 (up to 5.72 μg/L). In contrast, MA3, MA4, and MA5 were characterized by markedly lower ΣREE concentrations.
7. The pit lakes generally exhibited LREE enrichment, as well as a weaker MREE enrichment relative to HREE. Positive Gd anomalies were identified at all sampling points. Additionally, positive Eu anomalies were observed in all pit lakes except MA2, which was the most strongly affected by AMD, and positive Tb anomalies were recorded primarily in samples influenced by AMD.

The authors would like to express their sincere thanks to Krzysztof Pleskot for his help with fieldwork, statistical analysis, and all the valuable advice. The authors would also like to thank Karolina Leszczyńska for her consultation and helpful suggestions. The research was funded by Aleksandra Machowska's individual L. Austin Weeks Undergraduate Grant from the AAPG Foundation.

REFERENCES

Adeniyi A.G., Emenike E.C., Iwuozor K.O., Okoro H.K. & Ige O.O., 2022. Acid mine drainage: The footprint of the Nigeria mining industry. *Chemistry Africa*, 5(6), 1907–1920. https://doi.org/10.1007/s42250-022-00493-3.

Akcil A. & Koldas S., 2006. Acid mine drainage (AMD): Causes, treatment and case studies. *Journal of Cleaner Production*, 14(12–13), 1139–1145. https://doi.org/10.1016/j.jclepro.2004.09.006.

Aral H. & Vecchio-Sadus A., 2008. Toxicity of lithium to humans and the environment – A literature review. *Ecotoxicology and Environmental Safety*, 70(3), 349–356. https://doi.org/10.1016/j.ecoenv.2008.02.026.

Atangana E. & Oberholster P.J., 2021. Using heavy metal pollution indices to assess water quality of surface and groundwater on catchment levels in South Africa. *Journal of African Earth Sciences*, 182, 104254. https://doi.org/10.1016/j.jafrearsci.2021.104254.

ATSDR (Agency for Toxic Substances and Disease Registry), 2022. *Substance Priority List*. https://www.atsdr.cdc.gov/programs/substance-priority-list.html?CDC_AAref_Val=https://www.atsdr.cdc.gov/spl/index.html#cdc_program_profile_overview-background [access: 16.03.2024].

Bartczak E. & Gancarz A., 1998. *Szczegółowa mapa geologiczna Polski 1:50 000. Arkusze 645 – Łęknica (M-33--18-A), 646 – Trzebiel (M-33-18-B)*. Państwowy Instytut Geologiczny (Polish Geological Institute), Warszawa. https://bazadata.pgi.gov.pl/data/smgp/arkusze_skany/smgp0646.jpg [access: 20.03.2025].

Bau M. & Dulski P., 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Research*, 79(1–2), 37–55. https://doi.org/10.1016/0301-9268(95)00087-9.

Bauerek A., Bebek M., Białecka B., Mitko K. & Thomas M., 2019. Contents of rare earth elements in acidic waters linked to mining of coal and lignite (Upper Silesia and Muskau Bend, Southern Poland). *Rocznik Ochrona Środowiska – Annual Set The Environment Protection*, 21(2), 1040–1060.

Blowes D.W., Ptacek C.J., Jambor J.L., Weisener C.G., Paktunc D., Gould W.D. & Johnson D.B., 2014. The geochemistry of acid mine drainage. [in:] Holland H.D. & Turekian K.K. (eds.), *Treatise on Geochemistry (Second Edition). Volume 11: Environmental Geochemistry*, Elsevier, Amsterdam, 131–190. https://doi.org/10.1016/B978-0-08-095975-7.00905-0.

Boehrer B. & Schultze M., 2006. On the relevance of meromixis in mine pit-lakes. [in:] Barnheisel R.I. (ed.), *Proceedings of the 7th International Conference on Acid Rock Drainage (ICARD), St. Louis, USA, 26–30 March 2006*, American Society of Mining and Reclamation, Lexington, 200–213. https://doi.org/10.21000/JASMR06020200.

Bozau E., Leblanc M., Luc Seidel J.L. & Stärk H.-J., 2004. Light rare earth elements enrichment in an acidic mine lake (Lusatia, Germany). *Applied Geochemistry*, 19(3), 261–271. https://doi.org/10.1016/S0883-2927(03)00150-1.

Broadhurst J., 2019. The contribution of mining to clean water and sanitation (SDG 6): Case studies from South Africa. [in:] Nagao M., Masinja J. & Alhassan A. (eds.), *Sustainable Development in Africa*, Spears Media Press, Denver, 213–226.

Brugam R.B. & Lusk M., 1986. Diatom evidence for neutralization in acid surface mine lakes. [in:] Smol J.P., Battarbee R.W., Davis R.B. & Meriläinen J. (eds.), *Diatoms and Lake Acidity*, Dr W. Junk Publishers, Dordrecht, 115–129.

Cánovas C.R., Basallote M.D., Macías F., Olías M., Pérez-López R. & Nieto J.M., 2022. Thallium in environmental compartments affected by acid mine drainage (AMD) from the Iberian Pyrite Belt (IPB): From rocks to the ocean. *Earth-Science Reviews*, 235, 104264. https://doi.org/10.1016/j.earscirev.2022.104264.

Cardwell A.S., Rodriguez P.H., Stubblefield W.A., DeForest D.K. & Adams W.J., 2023. Chronic toxicity of iron to aquatic organisms under variable pH, hardness, and dissolved organic carbon conditions. *Environmental Toxicology and Chemistry*, 42(6), 1371–1385. https://doi.org/10.1002/etc.5627.

Chen L., Ma T., Du Y. & Xiao C., 2017. Dissolved Rare Earth Elements of different waters in Qaidam Basin, northwestern China. *Procedia Earth and Planetary Science*, 17, 61–64. https://doi.org/10.1016/j.proeps.2016.12.031.

Chudy K., Worsa-Kozak M., Wójcik A., Wolkersdorfer C., Drzewicki W., Konsencjusz D. & Szyszka D., 2021. Chemical variations in mine water of abandoned pyrite mines exemplified by the Colorful Lakes in Wieściszowice, Sudetes Mountains, Poland. *Journal of Hydrology: Regional Studies*, 38, 100974. https://doi.org/10.1016/j.ejrh.2021.100974.

Costa M.R., Marszałek H., da Silva E.F., Mickiewicz A., Wąsik M. & Candeias C., 2021. Temporal fluctuations in water contamination from abandoned pyrite Wieściszowice mine (Western Sudetes, Poland). *Environmental Geochemistry and Health*, 43(8), 3115–3132. https://doi.org/10.1007/s10653-021-00809-1.

Dembiec T., 2010. *Baza danych GIS Mapy hydrogeologicznej Polski 1:50 000. Pierwszy poziom wodonośny – jakość wód, arkusz 646 – Trzebiel (M-33-18-B)*. Państwowy Instytut Geologiczny (Polish Geological Institute, Warszawa. https://bazadata.pgi.gov.pl/data/hydro/mhp/ppw/wj/mapy/mhpppwwj0646jw.jpg [access: 15.11.2025].

España J.S., Pamo E.L., Pastor E.S. & Ercilla M.D., 2008. The acidic mine pit lakes of the Iberian Pyrite Belt: An approach to their physical limnology and hydrogeochemistry. *Applied Geochemistry*, 23(5), 1260–1287. https://doi.org/10.1016/j.apgeochem.2007.12.036.

Fernández M.R., Martín G., Corzo J., de la Linde A., García E., López M. & Sousa M., 2018. Design and testing of a new diatom-based index for heavy metal pollution. *Archives of Environmental Contamination and Toxicology*, 74(1), 170–192. https://doi.org/10.1007/s00244-017-0409-6.

Friese K., Hupfer M. & Schultze M., 1998. Chemical characteristics of water and sediment in acid mining lakes of the Lusatian Lignite District. [in:] Geller W., Klapper H. & Salomons W. (eds.), *Acidic Mining Lakes: Acid Mine Drainage, Limnology and Reclamation*, Springer, Berlin, Heidelberg, 25–45. https://doi.org/10.1007/978-3-642-71954-7_3.

Fuentes-López J.M., Olías M., León R., Basallote M.D., Macías F., Moreno-González R. & Cánovas C.R., 2022. Stream-pit lake interactions in an abandoned mining area affected by acid drainage (Iberian Pyrite Belt). *Science of The Total Environment*, 833, 155224. https://doi.org/10.1016/j.scitotenv.2022.155224.

Gammons C.H., Wood S.A., Pedrozo F., Varekamp J.C., Nelson B.J., Shope C.L. & Baffico G., 2005. Hydrogeochemistry and rare earth element behavior in a volcanically acidified watershed in Patagonia, Argentina. *Chemical Geology*, 222(3–4), 249–267. https://doi.org/10.1016/j.chemgeo.2005.06.002.

Gawor Ł.P. & Lutyńska S., 2015. Assessment of water quality of degraded anthropogenic reservoirs situated in the area of the former Rozbark Coal Mine in Bytom. *Geology, Geophysics and Environment*, 41(3), 249–256. https://doi.org/10.7494/geol.2015.41.3.249.

Gąsiorowski M., Stienss J., Sienkiewicz E. & Sekudewicz I., 2021. Geochemical variability of surface sediment in post-mining lakes located in the Muskau Arch (Poland) and its relation to water chemistry. *Water, Air, & Soil Pollution*, 232(3), 108. https://doi.org/10.1007/s11270-021-05057-8.

Geller W., 2013. Case studies and regional surveys. [in:] Geller W., Schultze M., Kleinmann R. & Wolkersdorfer C. (eds.), *Acidic Pit Lakes: The Legacy of Coal and Metal Surface Mines*, Springer, Berlin, Heidelberg, 265–436. https://doi.org/10.1007/978-3-642-29384-9_3.

German C.R. & Elderfield H., 1989. Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin. *Geochimica et Cosmochimica Acta*, 53(10), 2561–2571. https://doi.org/10.1016/0016-7037(89)90128-2.

Gontaszewska A., Kraiński A., Jachimko B. & Kołodziejczyk U., 2007. Budowa geologiczna i warunki hydrogeologiczne zbiornika antropogenicznego w okolicach Łęknicy (Łuk Mużakowa) [Geological structure and hydrogeological conditions of anthropogenic reservoir in the environs of Łęknica (Muskau Arc)]. *Zeszyty Naukowe. Inżynieria Środowiska – Uniwersytet Zielonogórski*, 134(14), 33–40.

Grawunder A. & Merten D., 2012. Rare earth elements in acidic systems – biotic and abiotic impacts. [in:] Kothe E. & Varma A. (eds.), *Bio-Geo Interactions in Metal-Contaminated Soils*, Soil Biology, 31, Springer, Berlin, Heidelberg, 81–97. https://doi.org/10.1007/978-3-642-23327-2_4.

Grawunder A., Merten D. & Büchel G., 2014. Origin of middle rare earth element enrichment in acid mine drainage-impacted areas. *Environmental Science and Pollution Research*, 21(11), 6812–6823. https://doi.org/10.1007/s11356-013-2107-x.

Gromet L.P., Dymek R.F., Haskin L.A. & Korotev R.L., 1984. The North American shale composite: Its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta*, 48(12), 2469–2482. https://doi.org/10.1016/0016-7037(84)90298-9.

Haskin L.A., Wildeman T.R. & Haskin M.A., 1968. An accurate procedure for the determination of the rare earths by neutron activation. *Journal of Radioanalytical Chemistry*, 1(4), 337–348. https://doi.org/10.1007/BF02513689.

Hogsden K.L. & Harding J.S., 2012. Consequences of acid mine drainage for the structure and function of benthic stream communities: A review. *Freshwater Science*, 31(1), 108–120. https://doi.org/10.1899/11-091.1.

Jachimko B. & Kasprzak M., 2011. Zmiany składu chemicznego wód kopalnianego zbiornika zapadliskowego [Chemical composition of water in post-mining reservoir of impact origin]. *Rocznik Ochrona Środowiska*, 13, 1753–1766.

Jędrczak A., 1992. *Skład chemiczny wód pojezierza antropogenicznego w Łuku Mużakowskim*. Wydawnictwo Wyższej Szkoły Inżynierskiej w Zielonej Górze, Zielona Góra.

Jędrczak A., 1996. Zbiorniki acidotroficzne. *Zeszyty Naukowe Politechniki Zielonogórskiej. Inżynieria Środowiska*, 114(6), 49–77.

Koźma J., 2016. Anthropogenic landscape changes connected with the old brown coal mining based on the example of the polish part of the Muskau Arch area. *Górnictwo Odkrywkowe*, 57(3), 5–13.

Koźma J. & Migoń P., 2024. Mużaków rampart (Muskau Arch) – the legacy of glacial processes and mining in the UNESCO Global Geopark. [in:] Migoń P. & Jancewicz K. (eds.), *Landscapes and Landforms of Poland*, Springer, Cham, 483–497. https://doi.org/10.1007/978-3-031-45762-3_28.

Lee G., Bigham J.M. & Faure G., 2002. Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Applied Geochemistry*, 17(5), 569–581. https://doi.org/10.1016/S0883-2927(01)00125-1.

León R., Macías F., Cánovas C.R., Pérez-López R., Ayora C., Nieto J.M. & Olías M., 2021. Mine waters as a secondary source of rare earth elements worldwide: The case of the Iberian Pyrite Belt. *Journal of Geochemical Exploration*, 224, 106742. https://doi.org/10.1016/j.gexplo.2021.106742.

Li B., Chen Y. & Hu L., 2025. Characteristics of rare earth elements in groundwater of multiple aquifers and their implications in the Panxie mine area, Huainan Coalfield, China. *Polish Journal of Environmental Studies*. https://doi.org/10.15244/pjoes/203913.

López-González N., Borrego J., Carro B., Grande J.A., De la Torre M.L. & Valente T., 2012. Rare-earth-element fractionation patterns in estuarine sediments as a consequence of acid mine drainage: A case study in SW Spain. *Boletín Geológico y Minero*, 123(1), 55–64.

Lund M.A. & Blanchette M.L., 2023. Closing pit lakes as aquatic ecosystems: Risk, reality, and future uses. *WIREs Water*, 10(4), e1648. https://doi.org/10.1002/wat2.1648.

Luo Y., Rao J. & Jia Q., 2022. Heavy metal pollution and environmental risks in the water of Rongna River caused by natural AMD around Tiegelongnan copper deposit, Northern Tibet, China. *PLoS ONE*, 17(4), e0266700. https://doi.org/10.1371/journal.pone.0266700.

Lutyńska S. & Labus K., 2015. Identification of processes controlling chemical composition of pit lakes waters located in the eastern part of Muskau Arch (Polish-German borderland). *Archives of Environmental Protection*, 41(3), 60–69. https://doi.org/10.1515/aep-2015-0031.

Marszelewski W., Dembowska E.A., Napiórkowski P. & Stolarczyk A., 2017. Understanding abiotic and biotic conditions in post-mining pit lakes for efficient management: A case study (Poland). *Mine Water and the Environment*, 36(3), 418–428. https://doi.org/10.1007/s10230-017-0434-8.

Migaszewski Z.M. & Gałuszka A., 2015. The characteristics, occurrence, and geochemical behavior of rare earth elements in the environment: A review. *Critical Reviews in Environmental Science and Technology*, 45(5), 429–471. https://doi.org/10.1080/10643389.2013.866622.

Migaszewski Z.M., Gałuszka A. & Dołęgowska S., 2016. Rare earth and trace element signatures for assessing an impact of rock mining and processing on the environment: Wiśniówka case study, south-central Poland. *Environmental Science and Pollution Research*, 23(24), 24943–24959. https://doi.org/10.1007/s11356-016-7713-y.

Migaszewski Z.M., Gałuszka A. & Migaszewski A., 2014. The study of rare earth elements in farmer's well waters of the Podwiśniówka acid mine drainage area (south-central Poland). *Environmental Monitoring and Assessment*, 186(3), 1609–1622. https://doi.org/10.1007/s10661-013-3478-7.

Mikoda B., Potysz A., Siepak M. & Kmiecik E., 2024. The valorization of flotation tailings in terms of the concept of the circular economy: Characterization, environmental risk assessment, and waste utilization routes. *Geology, Geophysics and Environment*, 50(4), 401–420. https://doi.org/10.7494/geol.2024.50.4.401.

Najbar B. & Jędrczak A., 1998. Stopień zeutrofizowania wód zbiorników „pojezierza antropogenicznego." *Zeszyty Naukowe Politechniki Zielonogórskiej. Inżynieria Środowiska*, 116(7), 19–37.

Nordstrom D.K., 2011. Mine waters: Acidic to circumneutral. *Elements*, 7(6), 393–398. https://doi.org/10.2113/gselements.7.6.393.

Oksanen J., Simpson G., Blanchet F., Kindt R., Legendre P., Minchin P., O'Hara R., Solymos P., Stevens M., Szoecs E., Wagner H., Barbour M., Bedward M., Bolker B., Borcard D., Carvalho G., Chirico M., De Caceres M., Durand S., …, Weedon J., 2024. *vegan: Community Ecology Package. R package version 2.6-6.1*. https://CRAN.R-project.org/package=vegan [access: 12.06.2024].

Obregón-Castro C., Prudêncio M.I., Diamantino C., Carvalho E., Russo D. & Marques R., 2023. Geochemical behaviour of rare earth elements throughout an acid mine drainage passive treatment system in the Lousal mine area, Portugal. *Mine Water and the Environment*, 42(2), 533–545. https://doi.org/10.1007/s10230-023-00954-2.

Olías M., Cerón J.C., Fernández I. & De la Rosa J., 2005. Distribution of rare earth elements in an alluvial aquifer affected by acid mine drainage: The Guadiamar aquifer (SW Spain). *Environmental Pollution*, 135(1), 53–64. https://doi.org/10.1016/j.envpol.2004.10.014.

Onjia A., Huang X., Trujillo González J.M. & Egbueri J.C., 2022. Editorial: Chemometric approach to distribution, source apportionment, ecological and health risk of trace pollutants. *Frontiers in Environmental Science*, 10, 1107465. https://doi.org/10.3389/fenvs.2022.1107465.

Oszkinis-Golon M., Frankowski M., Jerzak L. & Pukacz A., 2020. Physicochemical differentiation of the Muskau Arch pit lakes in the light of long-term changes. *Water*, 12(9), 2368. https://doi.org/10.3390/w12092368.

Parshley J.V. & Bowell R.J., 2003. The limnology of summer Camp Pit lake: A case study. *Mine Water and the Environment*, 22(4), 170–186. https://doi.org/10.1007/s10230-003-0020-0.

Pukacz A., Oszkinis-Golon M. & Frankowski M., 2018. The physico-chemical diversity of pit lakes of the Muskau Arch (Western Poland) in the context of their evolution and genesis. *Limnological Review*, 18(3), 115–126. https://doi.org/10.2478/limre-2018-0013.

R Core Team, 2023. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna. https://www.R-project.org [access: 15.01.2024].

Rezaie B. & Anderson A., 2020. Sustainable resolutions for environmental threat of the acid mine drainage. *Science of The Total Environment*, 717, 137211. https://doi.org/10.1016/j.scitotenv.2020.137211.

Roccotiello E., Marescotti P., Di Piazza S., Cecchi G., Mariotti M.G. & Zotti M., 2015. Biodiversity in metal-contaminated sites – problem and perspective – a case study. [in:] Blanco J., Lo Y.-H. & Roy S. (eds.), *Biodiversity in Ecosystems – Linking Structure and Function*, IntechOpen, 563–582. https://doi.org/10.5772/59357.

Rozporządzenie, 2021. *Rozporządzenie Ministra Infrastruktury z dnia 25 czerwca 2021 r. w sprawie klasyfikacji stanu ekologicznego, potencjału ekologicznego i stanu chemicznego oraz sposobu klasyfikacji stanu jednolitych części wód powierzchniowych, a także środowiskowych norm jakości dla substancji priorytetowych*. Dz.U. 2021 poz. 1475 [Regulation of the Minister of Infrastructure of 25 June 2021 on the classification of ecological status, ecological potential, and chemical status, as well as the method of classification of the status of surface water bodies, and environmental quality standards for priority substances. Journal of Laws of 2021 item 1475]. https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20210001475 [access: 3.03.2025].

Saha P. & Paul B., 2019. Assessment of heavy metal toxicity related with human health risk in the surface water of an industrialized area by a novel technique. *Human and Ecological Risk Assessment: An International Journal*, 25(4), 966–987. https://doi.org/10.1080/10807039.2018.1458595.

Schultze M., Boehrer B., Wendt-Potthoff K., Sánchez-España J. & Castendyk D., 2017. Meromictic pit lakes: Case studies from Spain, Germany and Canada and general aspects of management and modelling. [in:] Gulati R., Zadereev E. & Degermendzhi A. (eds.), *Ecology of Meromictic Lakes*, Ecological Studies, 228, Springer, Cham, 235–275. https://doi.org/10.1007/978-3-319-49143-1_9.

Sekudewicz I., Syczewski M., Rohovec J., Matoušková S., Kowalewska U., Blukis R., Geibert W., Stimac I. & Gąsiorowski M., 2024. Geochemical behavior of heavy metals and radionuclides in a pit lake affected by acid mine drainage (AMD) in the Muskau Arch (Poland). *Science of The Total Environment*, 908, 168245. https://doi.org/10.1016/j.scitotenv.2023.168245.

Shevenell L., Connors K.A. & Henry C.D., 1999. Controls on pit lake water quality at sixteen open-pit mines in Nevada. *Applied Geochemistry*, 14(5), 669–687. https://doi.org/10.1016/S0883-2927(98)00091-2.

Sienkiewicz E. & Gąsiorowski M., 2016. The evolution of a mining lake – from acidity to natural neutralization. *Science of The Total Environment*, 557–558, 343–354. https://doi.org/10.1016/j.scitotenv.2016.03.088.

Sienkiewicz E. & Gąsiorowski M., 2017. The diatom-inferred pH reconstructions for a naturally neutralized pit lake in south-west Poland using the mining and the combined pH training sets. *Science of The Total Environment*, 605–606, 75–87. https://doi.org/10.1016/j.scitotenv.2017.06.171.

Sienkiewicz E. & Gąsiorowski M., 2018. The influence of acid mine drainage on the phytoand zooplankton communities in a clay pit lake in the Łuk Mużakowa Geopark (western Poland). *Fundamental and Applied Limnology*, 191(2), 143–154. https://doi.org/10.1127/fal/2018/1079.

Sienkiewicz E. & Gąsiorowski M., 2019. Natural evolution of artificial lakes formed in lignite excavations based on diatom, geochemical and isotopic data. *Journal of Paleolimnology*, 62(1), 1–13. https://doi.org/10.1007/s10933-019-00069-1.

Sienkiewicz E., Gąsiorowski M., Sekudewicz I., Kowalewska U. & Matoušková Š., 2023. Responses of diatom composition and teratological forms to environmental pollution in a post-mining lake (SW Poland). *Environmental Science and Pollution Research*, 30(50), 110623–110638. https://doi.org/10.1007/s11356-023-30113-7.

Siepak M. & Sojka M., 2017. Application of multivariate statistical approach to identify trace elements sources in surface waters: a case study of Kowalskie and Stare Miasto reservoirs, Poland. *Environmental Monitoring and Assessment*, 189(8), 364. https://doi.org/10.1007/s10661-017-6089-x.

Siepak M., Marciniak M., Sojka M. & Pietrewicz K., 2020. Trace elements in surface water and bottom sediments in the hyporheic zone of Lake Wadąg, Poland. *Polish Journal of Environmental Studies*, 29(3), 2327–2337. https://doi.org/10.15244/pjoes/109847.

Simate G.S., 2021. Environmental and health effects of acid mine drainage. [in:] Simate G.S. & Ndlovu S. (eds.), *Acid Mine Drainage: From Waste to Resources*, CRC Press, Boca Raton, 97–116. https://doi.org/10.1201/9780429401985.

Simpson G.L. & Oksanen J., 2023. *ggvegan: "ggplot2" Plots for the "vegan" Package. R package version 0.1.999.* https://github.com/gavinsimpson/ggvegan.

Singovszka E., Balintova M., Demcak S. & Pavlikova P., 2017. Metal pollution indices of bottom sediment and surface water affected by acid mine drainage. *Metals*, 7(8), 284. https://doi.org/10.3390/met7080284.

Slavković-Beškoski L., Ignjatović L., Ćujić M., Vesković J., Trivunac K., Stojaković J., Perić-Grujić A. & Onjia A., 2024. Ecological and health risks attributed to rare earth elements in coal fly ash. *Toxics*, 12(1), 71. https://doi.org/10.3390/toxics12010071.

Sojka M., Siepak M. & Pietrewicz K., 2019. Concentration of rare earth elements in surface water and bottom sediments in Lake Wadąg, Poland. *Journal of Elementology*, 24(1), 125–140. https://doi.org/10.5601/jelem.2018.23.2.1648.

Szafarczyk A. & Gawałkiewicz R., 2023. An inventory of opencast mining excavations recultivated in the form of water reservoirs as an example of activities increasing the retention potential of the natural environment: A case study from Poland. *Geology, Geophysics and Environment*, 49(4), 401–418. https://doi.org/10.7494/geol.2023.49.4.401.

Śniady I., Orzechowska W., Smardz E. & Siepak M., 2024a. Trace elements in Turkusowe Lake waters and bottom sediments (Wolin National Park, Poland). *Przegląd Geograficzny*, 96(4), 459–471. https://doi.org/10.7163/PrzG.2024.4.3.

Śniady I., Zięba M., Wojciechowska J., Majewski M. & Siepak M., 2024b. Condition of the post-reclamation Przykona reservoir (Turek, Poland): Water and sediment chemistry. *Acta Geographica Lodziensia*, 114, 19–34. https://doi.org/10.26485/AGL/2024/114/2.

Takeno N., 2005. *Atlas of Eh-pH Diagrams: Intercomparison of thermodynamic databases*. Geological Survey of Japan Open File Report, 419. https://www.nrc.gov/docs/ML1808/ML18089A638.pdf.

Thomas R., Mantero J., Cánovas C.R., Holm E., García-Tenorio R., Forssell-Aronsson E. & Isaksson M., 2022. Natural radioactivity and element characterization in pit lakes in Northern Sweden. *PLoS ONE*, 17(3), e0266002. https://doi.org/10.1371/journal.pone.0266002.

US EPA, 2016. *Provisional Peer-Reviewed Toxicity Values for Rubidium Compounds (CASRN 7440-17-7, Rubidium) (CASRN 7791-11-9, Rubidium Chloride) (CASRN 1310-82-3, Rubidium Hydroxide) (CASRN 7790-29-6, Rubidium Iodide).* Superfund Health Risk Technical Support Center, Washington, DC, USA. https://hhpprtv.ornl.gov/issue_papers/Rubidium.pdf [access: 15.06.2025].

Vesković J., Bulatović S., Miletić A., Tadić T., Marković B., Nastasović A. & Onjia A., 2024. Source-specific probabilistic health risk assessment of potentially toxic elements in groundwater of a copper mining and smelter area. *Stochastic Environmental Research and Risk Assessment*, 38(4), 1597–1612. https://doi.org/10.1007/s00477-023-02643-6.

Yakovlev E., Druzhinina A., Druzhinin S., Zykov S. & Ivanchenko N., 2022. Assessment of physical and chemical properties, health risk of trace metals and quality indices of surface waters of the rivers and lakes of the Kola Peninsula (Murmansk Region, North-West Russia). *Environmental Geochemistry and Health*, 44(8), 2465–2494. https://doi.org/10.1007/s10653-021-01027-5.

Yu J., Liu X., Yang B., Li X., Wang P., Yuan B., Wang M., Liang T., Shi P., Li R., Cheng H. & Li F., 2024. Major influencing factors identification and probabilistic health risk assessment of soil potentially toxic elements pollution in coal and metal mines across China: A systematic review. *Ecotoxicology and Environmental Safety*, 274, 116231. https://doi.org/10.1016/j.ecoenv.2024.116231.

Zhuang W. & Song J., 2021. Thallium in aquatic environments and the factors controlling Tl behavior. *Environmental Science and Pollution Research*, 28(27), 35472–35487. https://doi.org/10.1007/s11356-021-14388-2.

Supplementary data associated with this article can be found in the online version at: https://doi.org/10.7494/geol.2025.51.4.389.

Table S1. *Detailed results of trace element concentrations obtained in pit lakes in the Muskau Arch*

Table S2. *Detailed results of rare earth elements concentrations obtained in pit lakes in the Muskau Arch*