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TECHNICAL ARTICLE

Hydrochemistry-Based Statistical Model for Sourcing Groundwater Inrush into Underground Mining Works: A Case Study in Eastern Serbia

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Abstract

Discriminant analysis was applied to a baseline groundwater quality data set to develop a model for sourcing groundwater inrush into underground mining works. Such inrush events compromise the safety of the working environment and the feasibility of mining; thus, a comprehensive characterization of the hydrogeological system is required. In this study, a statistical model for groundwater sourcing was developed and validated based on a dataset of 179 groundwater chemical analyses related to the "Čukaru Peki" Cu–Au underground mine in eastern Serbia. The studied groundwaters are primarily of low TDS (235–715 mg/L), with a neutral to slightly alkaline pH, while the mine waters are alkaline ($pH > 9$). The evolution of groundwater chemical composition with depth was observed; Ca–HCO_3 water prevails in the shallow zones, transforming to Na–SO_4 type at depth. Two discriminant functions were delineated by statistical analysis, explaining 65.3% and 31.2% between-group variability, with SO_4^{2-}, Na, Al, pH, Sr, Li, and SiO_2 identified as grouping factors. The resulting discriminant functions were applied to 11 mine water samples to examine their relationship with the main hydrogeological units. Among the examined groundwater inflow samples, three were classified as having a different origin than the lithological unit at the mine from which the water was sampled, bringing valuable information for planning mitigation measures. The demonstrated approach highlights the importance of comprehensive baseline hydrogeological investigations at mine sites to obtain relevant data for controlling groundwater inrushes during development of the declines and shafts.

Keywords Water inrush · Hydrochemical origin · Mining · Statistical modelling · Water quality

Introduction

Growing demand for raw materials in support of the green transition and decarbonization are causing the mining industry to increase the production of critical commodities. Since most of the easily accessible deposits are already exhausted, the mining companies are responding by investing in exploring new deposits, expanding the exploitation of low-grade deposits associated with vast generations of mining waste, and turning toward deeper ore bodies. Both open pits and underground exploitation influence the groundwater system. The exploitation of raw materials, storage of the accompanying mining waste, and the lowering of groundwater levels induced by the dewatering of mining works can affect the availability and the quality of groundwater resources and the environment (Agboola et al. 2020; Tomiyama and Igarashi 2022). Alternatively, if not adequately managed, groundwater can pose a significant risk to the operations by affecting the stability of the mine and thus compromising worker safety in case of sudden water inrush.

Proper assessment and characterization of the hydrogeological system are required to enable feasible and safe mineral exploitation while minimizing environmental impacts. Baseline characterization of groundwater quality prior to the commencement of mining activities is a requirement for new mines. Therefore, reliable groundwater monitoring is necessary to enable accurate identification of the origin of the groundwater samples in order to deduce proper hydrogeological and hydrochemical information (Lapworth et al. 2022; Panagopoulos et al. 2016; Ravenscroft and Lytton 2022). Along with monitoring groundwater levels

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oscillations, hydrochemical data are often used in combination with the multivariate statistical approaches to better understand the groundwater system (Amiri and Nakagawa 2021; Madrigal-Solís et al. 2022; Patel et al. 2023), including recharge discharge relations, aquifer interconnections, and groundwater contamination (Li et al. 2013, 2018; Wang et al. 2023; Xu et al. 2023).

Predicting the influence of mining on groundwater, and vice versa, can be challenging due to markedly altered groundwater flow patterns in exploitation areas. Therefore, in areas affected by mining, multiple parameters are used to assess groundwater inflows-dewatering needs, environmental impacts, and water balance (Atanacković et al. 2022; Li et al. 2019; Mohan 2020; Szczepiński 2019). Site-specific contaminants like total and free cyanide concentrations provides valuable information in assessing leakage from waste heaps and tailings storage facilities into aquifers (Abdelaal et al. 2021). Kurukulasuriya et al. (2022) reviewed the use of environmental water tracers (water quality parameters, major ions, stable isotopes, radioisotopes, and dissolved gases) in evaluating the groundwater flow and surface connections around mines. Influence on water resources at catchments affected by active or abandoned mines was assessed based on major ions and stable isotope composition (Doveri et al. 2021; Guo et al. 2019; Li et al. 2022; Mengistu et al. 2015; Walton-Day and Poeter 2009).

Due to the increasing depth of mining operations, groundwater inrush can be a severe threat to a mine, with catastrophic consequences reflected in a loss of human life and operation feasibility (Li 2018; Wang et al. 2022). Since most of the recently reported mine water inrush accidents are related to coal mines, most of the published studies on sourcing water inrush are focused on underground coal exploitation, usually associated with limestone aquifers (Dong et al. 2021). Groundwater levels, temperature, and hydrogeochemistry have all been used to source water inrush into coal mines (Sun et al. 2016; Wu et al. 2019; Zhang et al. 2019). Various statistical and multi-criteria decision analysis methods (MCDA), including principal component analysis (PCA), hierarchical cluster analysis (HCA), regression, fuzzy logic, and Fisher's discriminant analysis (FDA), have been successfully applied to hydrochemical data in assessing and predicting groundwater inrush into underground coal mines (Bi et al. 2021; Huang et al. 2019; Ju and Hu 2021). Liu et al. (2021) applied HCA and FDA on hydrochemical data to assess the primary source of mine water seepage into an open pit. An improved method for risk assessment of underground mine floor water inrush, based on a combination of the improved analytic hierarchy process (IAHP) and principal component logistic regression analysis (PCLRA), was proposed by Li and Sui (2021). In recent studies, these data have been combined with laser-induced fluorescence technology under a machine learning framework to develop predictive models (Hu et al. 2019; Yan et al. 2023), thus reducing the time needed to develop water management and mitigation measures.

In the present study, a set of 179 baseline groundwater quality analyses collected in the pre-production phase were analyzed to: (i) select representative hydrochemical parameters for groundwater samples grouping, (ii) source groundwater inflows, and (iii) develop a predictive model for tracing the origin of groundwater for future inflows. Although discriminant analysis (DA) has been successfully applied in investigating mine water inrush in active coal mines, the present study applied a stepwise discriminant analysis to a groundwater quality analysis largely composed of baseline data collected before mining at a massive sulfide copper and gold deposit. A stepwise discriminant analysis model was created and applied to the area of the "Čukaru Peki" (CP) copper and gold mine. The deposit is situated in the Bor metallogenic zone of the Cretaceous magmatic Apuseni-Banat-Timok-Srednogorje metallogenic belt (Gallhofer et al. 2015; Janković 1990). In a final step, the established model was tested and validated with data collected during the main underground infrastructure development phase.

Study Area

The" Čukaru Peki" is a world-class copper and gold deposit discovered in 2012 in the vicinity of the "Bor" mining complex in eastern Serbia (Fig. 1). The deposit is situated in the Bor metallogenic zone, with three types of ore mineralization distinguished: porphyry, highsulphidation, and transitional epithermal type (Klimentyeva 2022; Velojić et al. 2020). The mine site is located along a small hill line, which extends towards the southwest with an elevation between 350 and 400 m above sea level. The ridge is flanked to the west by the Brestovac River Valley and to the east by the Borska River Valley. The average annual precipitation in the area is approximately 680 mm, with the highest rainfall during the spring months (April-June) and secondary peaks in November and December.

Geology

The CP site is a part of the Late Cretaceous Timok magmatic complex (TMC), which is a trans-tensional rift system. Volcanism generally started with the emplacement of coarser-textured hornblende-biotite andesite (Phase I andesite), which formed the productive ore-host rocks on the east side of the district and evolved to a finer-grained, pyroxene-bearing (Phase II) andesite (Banješević 2010; Gallhofer et al. 2015; Klimentyeva et al. 2020).

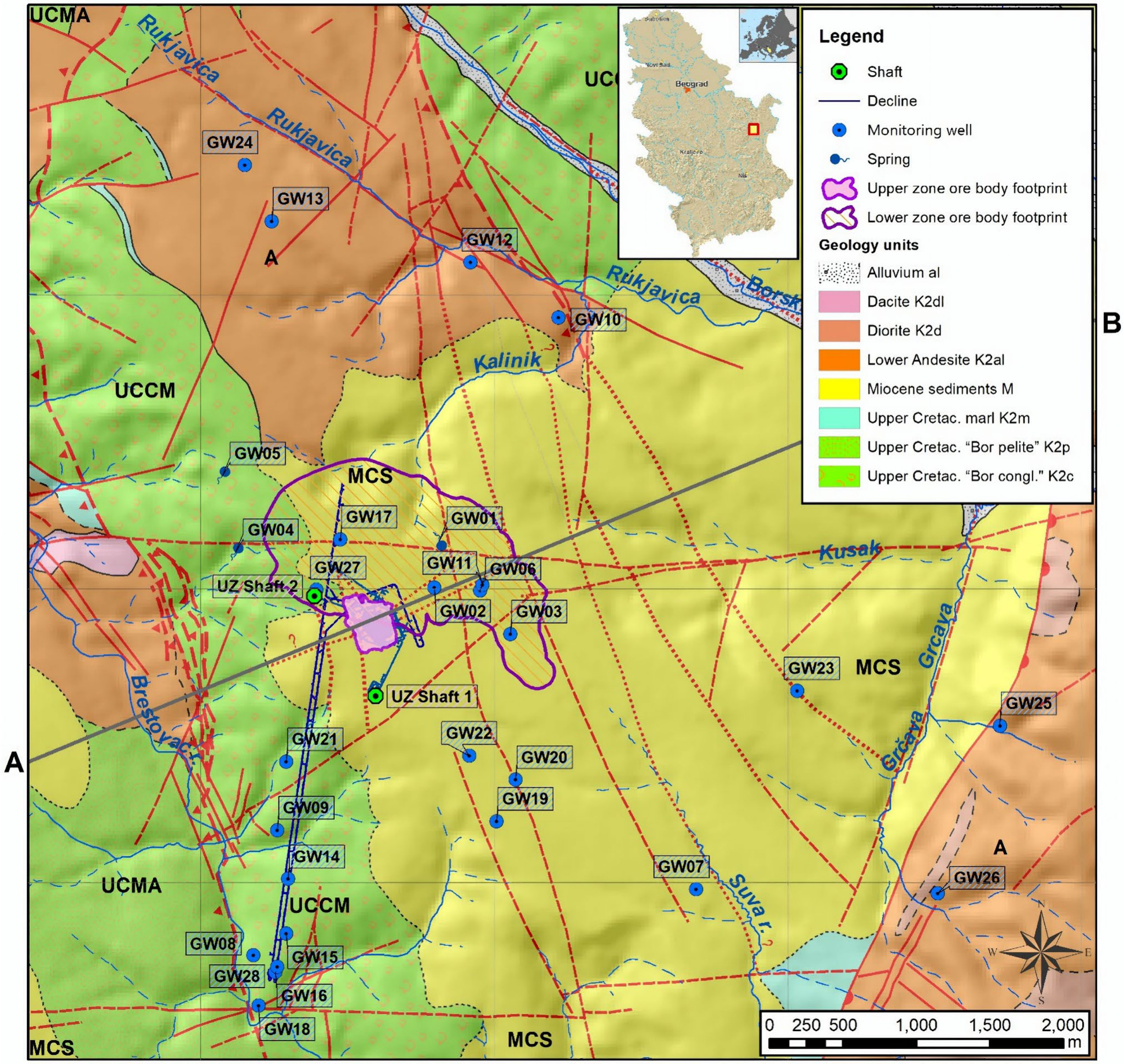

Fig. 1 Geological map of the wider area of the "Čukaru Peki" Cu–Au underground mine, with the locations of the sampled monitoring wells

The copper and gold mineralization of the CP deposit has formed two main ore bodies, the Upper Zone (UZ) and Lower Zone (LZ), at depths between 400 and > 2000 m below the surface. The UZ is a high-sulfidation ore body while the deeper, northwest-plunging LZ is characterized by porphyry-type mineralization. UZ and LZ are hosted by altered Upper Cretaceous volcanic and volcaniclastic rocks, internally labeled as the lower andesite (LA). They are overlain by a relatively unaltered andesitic unit named the upper andesite (UA) by the project geologists. The UA unit is covered by a westwardly dipping Upper Cretaceous sedimentary sequence of conglomerates, sandstones, and marls. The entire volcano-sedimentary succession is unconformably overlain by Miocene conglomerates and sandstones (MCS) of the "Slatina" basin (Velojić et al. 2020). The basement of the TMC comprises the pre-volcanic rocks: Hercynian granite, Paleozoic greenschists and carbonates, and Jurassic to Cretaceous age carbonates. Mesozoic karstified limestones are exposed on the surface of the magmatic complex's east and west margins.

Table 1 Principal hydrogeological units in the CP area with representative hydraulic conductivity values derived from in-situ packer injection tests

Hydrogeology unit	Lithology	Aquifer type	Geo mean Kf (m/s)	Relative permeability	Thickness (m)
Miocene sediments (MCS)	Clay, silt, marl, sand, gravel, siltstone, sandstone, conglomerate	Intergranular/fractured/aquitard	2.7×10^{-7}	Low-moderate	0–450
Upper Cretaceous “Bor” clastics (UCCM)	Conglomerate and sandstone	Fractured	4.2×10^{-8}	Low	0–650
Upper Cretaceous marls (UCMA)	Marl	Fractured/aquitard	3.1×10^{-9}	Low	
Andesite and Volcanoclastic (A)	Andesite, andesitic breccia, epiclastic	Fractured	1.3×10^{-7}	Low-moderate	< 3500
Mesozoic sedimentary rocks	Limestone, marl, sandstone, breccia	Fractured/karst	–	Moderate-high	500–800
Magmatic rocks	Diorite	Fractured, unconfined and confined	–	Low	–

The mine area occurs on the contact between two tectonic sub-units: the Timok sub-unit to the west and the Tupižnička sub-unit to the east, divided by the Bor fault. The structural setting of the Čukaru Peki area is dominated by a system of reverse NNW striking faults, with movement of the upthrown blocks to the east (Toljić 2016).

Hydrogeology

According to the rock type and hydraulic properties derived from in-situ testing, six hydrogeological units have been distinguished, shown in Table 1.

In this complex geological and hydrodynamic settings, the following aquifer types are defined: an unconfined intergranular aquifer (unconsolidated alluvial and Miocene sediments); an unconfined to semi-confined fractured aquifer (consolidated Miocene sediments and “Bor” clastics); and a semi-confined to confined fractured aquifer (volcanic and volcanoclastic rocks). Layers of fine-grained Miocene sediments and UC marls are interpreted as aquitards. On the flanks of the volcanogenic complex, there are thick Upper Jurassic and Cretaceous deposits of carbonate rocks, which host karst aquifers that are naturally drained via a series of karst springs. The current assumption is that Mesozoic sedimentary rocks form the base of the volcanic complex where the “Čukaru Peki” copper and gold mineralization is deposited (Fig. 2).

Still, no hydrogeological data exists for limestone below the ore body due to the depth (anticipated ≈ 3000 m below the ground surface). To characterize the hydrogeological system and collection of baseline groundwater data prior to mining, an extensive groundwater monitoring network was installed, comprising 112 hydrogeological installations ranging in depths from 15 m up to 2000 m.

Mine Development

The Upper Zone ore body is accessed from the southwest by twin decline (two parallel tunnels) that serve as the main mine development infrastructure object, driven at a length of ≈ 2500 m, with cross-cuts every 300 m. Additionally, two vertical shafts (O–1 and O–2) were simultaneously skunked to a depth of 648 and 493 m, respectively. The 6.5 m diameter shafts are a part of the mine ventilation system. The decline tunnels are supported by shotcrete, while the shafts are lined with free-draining concrete rings. The mine is now fully owned and operated by the Zijin Mining Group (ZMG). Access to the underground mining works were driven through Miocene clastics (MCS), UC clastic, and marl (UCCM and UCMA), ultimately reaching the andesite and volcanoclastic (A) host rocks.

Materials and Methods

Hydrogeological and groundwater quality data were collected by the geological service of the ZMG mining company, with support from the University of Belgrade. Groundwater quality monitoring data from 28 monitoring wells and 11 mine water samples collected from the face and walls of the underground mining works were used in the study. The sampled monitoring wells range from shallow (15–50 m) to deep, with depths up to 500 m. The groundwater quality data used in the study were collected in the four-year period prior to the commencement of the mining works. The sampling was performed monthly or quarterly, thus covering entire hydrological cycles. Among the examined monitoring sites, nine are tapping Miocene aquifer (MCS), 11 are related to the Bor conglomerates and sandstones (UCCM), and eight monitoring wells are screened within the volcanic unit (A).

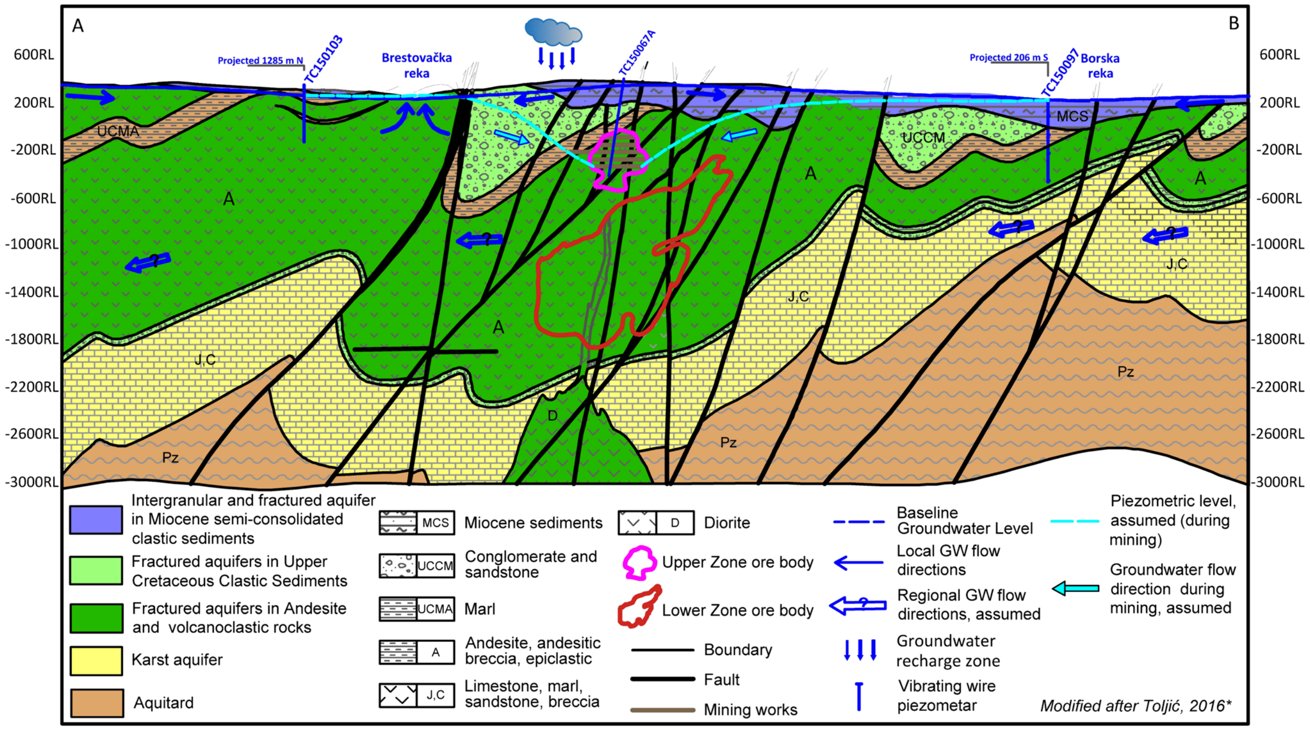

Fig. 2 Conceptual hydrogeological cross-section of the "Čukaru Peki" deposit

With the commencement of the mining works, particularly with the construction of the twin decline and two ventilation shafts, groundwater inflows started to appear. During advancement of the mining works, samples of mine water were collected by the ZMG at the points of inflow and from the mine dewatering system. To better understand the main source of inflows, the hydrochemistry of the mine water samples was compared with the groundwater quality data collected before mining, using the Piper chart and analyzing basic hydrochemical parameters. Discriminant analysis was applied to establish relevant discriminant functions to understand the relationship of water inflows with the main aquifers. These functions can be further used to classify the mine water samples in terms of the groundwater origin, relative to the aquifers and corresponding main hydrogeological units. The predictive ability of the statistical model was further tested with a validation set composed of 11 mine water samples that were not used for model development. All relevant steps of the applied research methodology are summarised in a flow chart (Fig. 3).

Sampling and Field Measurements

Depending on the monitoring wells' depth and groundwater levels, passive (grab samples with bailer) and low flow sampling techniques (low flow submersible pumps) were applied, following the ISO 5667-11:2009 and corresponding SRPS ISO 5667-11:2019 standards for groundwater sampling (ISO 2019). The mine water samples were collected directly from the face and the walls of the mining works or from the dewatering system. The following parameters were measured in situ: temperature, pH, electrical conductivity (EC, in µS/cm), redox potential (Eh, in mV), and dissolved oxygen (DO, in mg/L), using a multiparameter probe.

Laboratory Analysis

Laboratory analyses included the determination of physical and chemical parameters (pH, EC at 20 °C, dry residue at 105 °C), macro and micro-components, and selected organic compounds. Determination of total and composite alkalinity was performed volumetrically, following the European norm SRPS EN ISO 9963-1:2007 (ISO 2007a). At the same time, inorganic ions (sulfate, chloride, nitrate, fluoride, and orthophosphate) were analyzed using ion chromatography in accordance with the EPA 300.1 method (EPA 1993). The concentrations of dissolved metals were determined using the ICP-OES technique, as per the EPA 200.7 method (EPA 1998). Contents of organic compounds (AOX, TOC, aromatic hydrocarbons etc.) were determined using guidelines for the determination of adsorbable organically bound halogens – AOX (ISO 2008), total organic carbon – TOC (ISO 2007b), and for gas-chromatographic determination of monocyclic aromatic hydrocarbons (ISO 2009). The

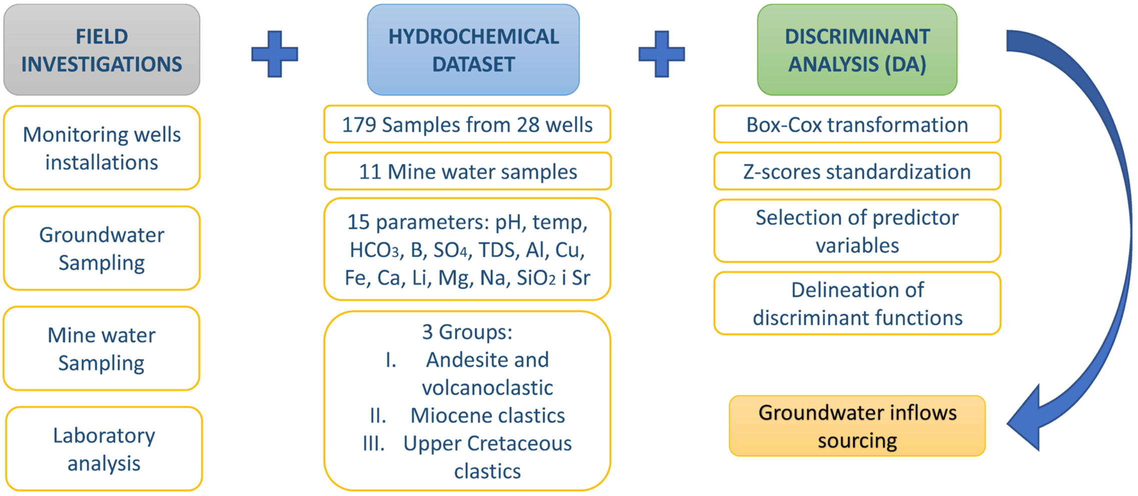

Fig. 3 Flow chart of the applied methodology

software package Aqua-Chem 10.0 (Waterloo Hydrogeologic) was used to process the hydrochemical data.

Statistical Analysis

The initial dataset comprised 220 groundwater chemical analyses, with a substantial number of physical and chemical parameters determined. Descriptive statistics (mean, median, range, variance, standard deviation, etc.) gave insight into the data structure and allowed for the identification of potential outliers, which were later excluded. Also, the complete chemical analyses and individual chemical parameters contained many values below the detection limit or missing values, which were excluded from further calculations. The remaining data were Box-Cox transformed (Box and Cox 1964) and z-score standardized, as these are prerequisites for DA (Asante and Kreamer 2015). The final dataset considered for the DA consisted of 179 chemical analyses of groundwater samples from 28 monitoring wells; the results of 15 physical and chemical parameters were used in calculations: pH, temp (°C), TDS (mg/L), HCO_3^- (mg/L), SO_4^{2-} (mg/L), Na (mg/L), Ca (mg/L), Mg (mg/L), B (mg/L), Al (mg/L), Cu (mg/L), Fe (mg/L), Li (mg/L), Sr (mg/L), and SiO_2 (mg/L). The model testing phase also considered 11 chemical analyses of mine waters.

Stepwise discriminant analysis (Afifi et al. 2004; Fisher 1936) was used to examine the differences in groundwater quality between three representative hydrogeological units (A – andesite and volcanoclastics, MCS – Miocene clastics, and UCCM – Upper Cretaceous "Bor" clastics), in order to classify future mine water samples of an unknown source. This classification was achieved by determining which parameters, known as predictors, contribute most to the predictive power of the discriminant functions. The linear combination of predictor variables constitutes the discriminant function (i.e. equation), which enables the prediction of the group membership of samples. The mean value of the discriminant function scores for each group represents a group centroid, and all samples with scores near a particular centroid are classified into that group. Ultimately, the percentage of correctly classified groundwater samples is calculated by the "leave one out" classification (only for those cases used in the DA), where each case is classified by the functions derived from all cases other than that case. This procedure serves as a cross-validation of the discriminant functions' predictive accuracy (Panagopoulos et al. 2016). IBM SPSS Statistics 25.0 software was used for data processing.

Results and Discussion

Baseline Groundwater Chemistry

The assessment of physical and chemical parameters has revealed the diverse hydrochemical composition of groundwaters from three representative hydrogeological units (Table 2, Fig. 4).

Reported pH levels indicate mildly acidic to mildly alkaline conditions in samples from Miocene sediments – MCS unit (median 7.1), while alkaline conditions prevail in the Bor clastics – UCCM unit (median 7.3) and especially in the andesite – A unit (median 7.4) (Fig. 4a). Both MCS and UCCM units are characterized by low TDS (< 500 mg/L in most of the samples), while groundwater from andesite feature moderately elevated TDS values (median 715 mg/L) (Fig. 4b). A similar consistency was observed with the sulfate concentrations; median

Table 2 Physical and chemical parameters of baseline groundwaters and mine waters – mean and median values

Parameter	A (N = 43)		MCS (N = 66)		UCCM (N = 70)		Mine waters (N = 11)	
	Mean	Median	Mean	Median	Mean	Median	Mean	Median
pH	7.5	7.4	7.1	7.1	7.4	7.3	9.0	9.5
Temp (°C)	13.5	13.3	11.8	12.6	13.1	12.8	25.8	26.4
TDS (mg/L)	671.91	715.00	316.15	235.00	450.31	440.00	816.84	210.00
HCO_3^- (mg/L)	359.80	357.00	241.54	125.15	333.40	312.75	49.16	54.60
Cl^- (mg/L)	14.18	13.40	15.16	13.00	10.09	6.45	25.85	9.75
SO_4^{2-} (mg/L)	201.16	169.00	40.34	37.30	84.18	74.10	425.31	46.70
Ca (mg/L)	104.77	77.00	53.43	34.30	94.19	98.00	49.97	2.40
Mg (mg/L)	21.98	20.30	11.88	5.63	16.75	15.10	3.26	0.05
Na (mg/L)	82.91	43.10	30.53	11.70	28.64	17.20	219.55	76.90
SiO_2 (mg/L)	24.37	24.00	21.54	18.95	19.33	19.00	20.86	17.90
Al (mg/L)	0.745	0.120	0.618	0.161	0.162	0.032	0.134	0.071
Cu (mg/L)	0.0150	0.0075	0.0167	0.0145	0.0099	0.0075	0.0059	0.0038
Fe (mg/L)	0.565	0.225	0.358	0.194	0.247	0.023	0.379	0.023
Li (mg/L)	0.0111	0.0100	0.0075	0.0075	0.0093	0.0075	0.0123	0.0121
Sr (mg/L)	0.2271	0.1500	0.1143	0.1300	0.3068	0.1500	0.5884	0.0159
B (mg/L)	0.058	0.070	0.049	0.038	0.046	0.038	0.249	0.230

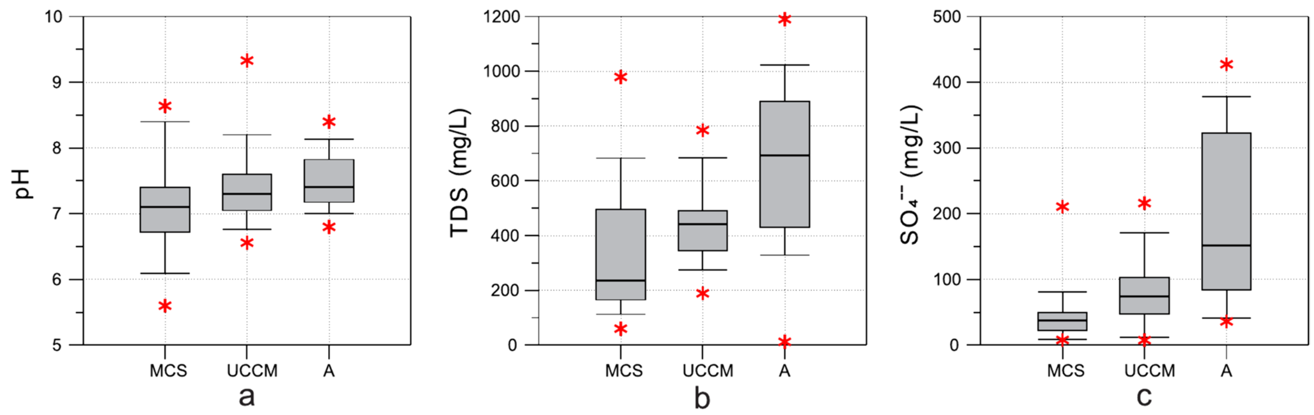

Fig. 4 Box-plot diagrams showing the diverse groundwater chemistry of the principal hydrogeological units

SO_4^{2-} concentrations < 100 mg/L characterize groundwater from the Miocene and Upper Cretaceous sediments while groundwater from volcanic and volcanoclastic rocks are distinguished by a higher sulfate content (median 169 mg/L, with maximum values > 300 mg/L in several samples) (Fig. 4c).

Aluminum and iron concentrations are higher in samples from volcanic rocks and Miocene sediments (max 7.98 mg/L aluminum and max 3.97 mg/L iron, both in MCS unit), as opposed to groundwater from the Bor clastics (Table 2), where these metals were under the limit of detection in more than 50% of the samples. Additionally, the highest strontium concentration (1.21 mg/L) was recorded in a sample from the andesite unit.

Groundwaters in the andesite unit formed under the influence of two hydrogeochemical processes: hydrolysis of silicate minerals and oxidation of sulfide minerals (Kretić 2022). Hydrolysis of aluminosilicate minerals, primarily andesine, pyroxene, and hornblende, takes place in unaltered andesite rocks and generates HCO_3–Ca waters, with generally low metal concentrations (aluminum, iron, strontium, etc.). With increasing depth, Ca ions are replaced by Na ions, and in addition to the hydrolysis of silicate minerals, the process of sulfide mineral oxidation occurs. These two processes are characteristic of hydrothermally altered andesite rocks. As a result, SO_4, HCO_3–Na waters are formed, mildly alkaline and with elevated metal concentrations. The altered zones are also characterized by lower filtration coefficients due to kaolinization and filling of open fractures, resulting in slower water exchange and favoring the formation of groundwater with higher TDS values. The described vertical hydrochemical zonation is a general characteristic of the Timok Magmatic Complex (TMC), i.e. the wider area of the "Čukaru Peki" Cu–Au underground mine (Dragišić and Milenić 1997).

Two hydrogeochemical processes are dominant in groundwaters from the Miocene sediments and "Bor" clastics: hydrolysis of silicate minerals and dissolution of carbonate minerals. The latter primarily involves calcite, present in conglomerates, sandstone, etc. Elevated concentrations of microelements (iron, aluminum, etc.) in a certain number of samples from the MCS unit can be interpreted as a result of the hydrolysis of fragments of andesitic rocks contained in the Miocene clastics. The pronounced presence of strontium in a number of groundwater samples from the Bor clastics is probably caused by the dissolution of carbonate minerals (in which strontium replaces calcium) or the carbonate matrix of sedimentary rocks (Brand et al. 1999).

Mine Water Chemistry

The chemical composition of mine water samples was evaluated and compared with baseline groundwater chemistry. Most of the analyzed inflows are alkaline (Table 2), with pH values substantially higher than recorded in any baseline groundwater sample, and in sharp contrast to the surrounding underground copper and gold mines within the same metallogenic zone, where sulfide oxidation and associated acid mine drainage (AMD) have been present for decades (Stanković et al. 2021). The reported high pH is partly attributed to the application of shotcrete and concrete lining for physical stabilization of the decline and the shaft's walls. Also, in the early stage of construction of the ore access drives, AMD formation was not observed. The mine waters have low mineralization (median TDS 210 mg/L), except for two mineralized samples (1186 mg/L and 5800 mg/L) from the UZ ore body. Their sulfate contents are similar to those of the andesite groundwaters but with even higher 90th percentile values and with a maximum of 3300 mg/L of SO_4^{2-}. Mine water metal concentrations are generally less than in baseline groundwaters, often under the limit of detection, but the boron concentrations are notably higher, with a maximum of 0.75 mg/L.

Analysis of the dominant water types (Fig. 5) revealed a certain similarity between the groundwaters from the three principal hydrogeological units. Upper Cretaceous clastics primarily contain Ca, Na–HCO_3 waters, with smaller portions of SO_4^{2-} ions in some samples. Miocene sediments are dominated by Ca–HCO_3, SO_4 waters, along with a small group of Na–HCO_3 type samples. Groundwaters from andesite are characterized by a mixed ionic composition, predominantly Ca, Na–HCO_3, SO_4 waters. On the other hand, mine waters (Fig. 5) are Na–SO_4 water type, with only a few samples featuring HCO_3^- ions.

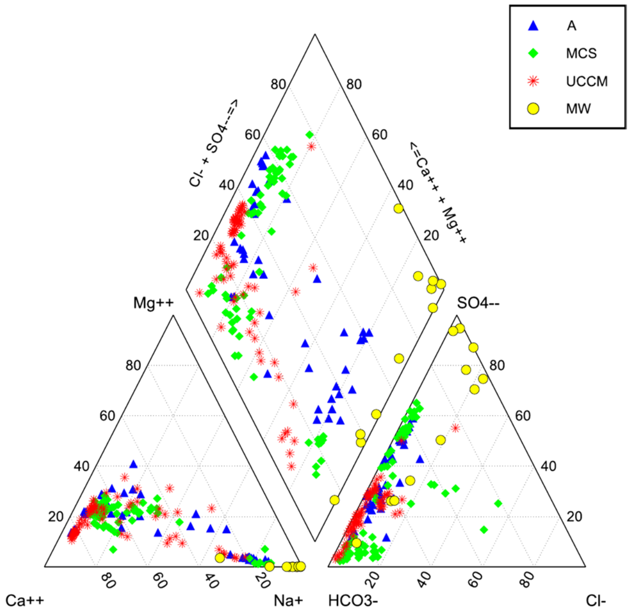

Fig. 5 Piper chart of groundwaters from the three principal hydrogeological units and mine waters from the underground workings

Due to insufficiently pronounced differences in the dominant water types, classification of waters from different hydrogeological units was not possible based only on the Piper diagram (Fig. 5). Thus, the use of discriminant analysis was required for a more comprehensive delineation.

Groundwater Inflow Sourcing

Stepwise discriminant analysis was conducted as a first step of the model development for groundwater inrush sourcing. The primary goal of this multivariate statistical method was predicting the affiliation of groundwater samples to the three described principal hydrogeological units (i.e. three groups of cases): (1) A – andesite and volcanoclastic rocks; (2) MCS – Miocene sediments, and (3) UCCM – Upper Cretaceous "Bor" clastics. A stepwise approach enabled us to find the best combination of predictors among the 15 physical and chemical parameters used to characterize the analyzed groundwaters. Based on the significant (at $p<0.01$) F and Wilks' lambda values and significant differences between group means, the following seven predictors were chosen: SO_4^{2-}, Na, Al, pH, Sr, Li, and SiO_2. The DA produced two discriminate functions (equations) that consider the three case groups. The canonical correlations indicated that function F1 explained 65.3% of the between-group variability, while function F2 accounted for 31.2%. The Wilks' lambda values for each discriminant function were significant (at

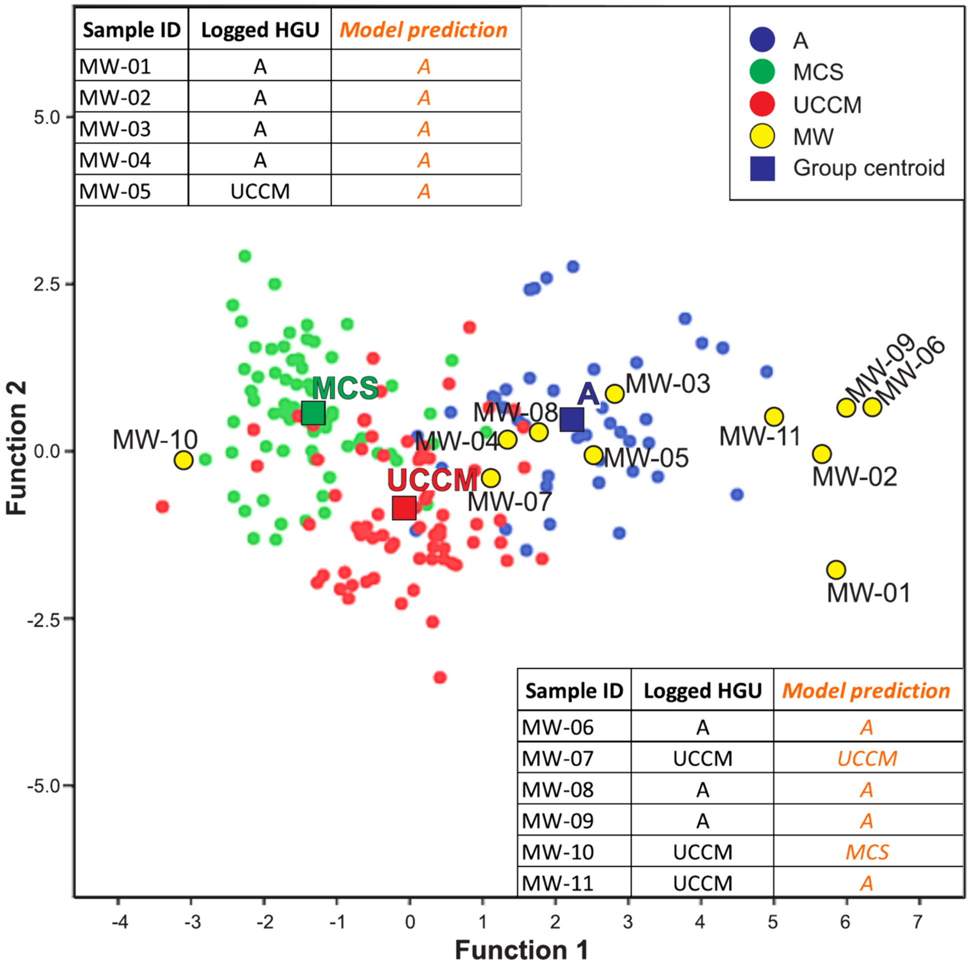

Fig. 6 Scatter plot of the discriminant function scores for functions F1 and F2, the group centroids for the A, MCS, and UCCM units, and the new mine water samples

Sample ID	Logged HGU	*Model prediction*
MW-01	A	*A*
MW-02	A	*A*
MW-03	A	*A*
MW-04	A	*A*
MW-05	UCCM	*A*

Sample ID	Logged HGU	*Model prediction*
MW-06	A	*A*
MW-07	UCCM	*UCCM*
MW-08	A	*A*
MW-09	A	*A*
MW-10	UCCM	*MCS*
MW-11	UCCM	*A*

$p < 0.01$), verifying their importance. Analysis of the structure matrix allowed for the identification of the predictors with the largest discriminant loadings, i.e. the highest relative importance for each function: for F1–SO_4^{2-} (0.604) and Na (0.345), and F2–Al (0.579) and Sr (−0.506). The rest of the predictors had lower loadings and were considered less important variables. In similar studies of mine water inflows, the DA and regression models were applied to a set of hydrogeochemical data mostly restricted to the main ions (Bi et al. 2021; Huang et al. 2019; Zhang and Yao 2020). Results of this study suggest that along with major ions (SO_4^{2-} and Na^+), trace elements are significant in the analysis of groundwater origin. In the examined case, aluminum, strontium, and lithium concentrations were shown to be essential for delineating groundwater samples between principal aquifers.

The unstandardized canonical discriminant function coefficients were used to create the following discriminant functions (equations):

$$F1 = (1.629 \times \mathrm{pH}) + \left(1.313 \times \mathrm{SO}_4^{2-}\right) + (0.105 \times \mathrm{Al}) + (0.934 \times \mathrm{Li}) + (0.342 \times \mathrm{Na}) + \left(0.137 \times \mathrm{SiO}_2\right) + (-0.376 \times \mathrm{Sr}) - 13.285 \tag{1}$$

$$F2 = (-0.867 \times \mathrm{pH}) + \left(0.178 \times \mathrm{SO}_4^{2-}\right) + (0.260 \times \mathrm{Al}) + (-3.397 \times \mathrm{Li}) + (0.467 \times \mathrm{Na}) + \left(0.385 \times \mathrm{SiO}_2\right) + (-1.195 \times \mathrm{Sr}) - 10.447 \tag{2}$$

Each sample's discriminant scores (F1 and F2) were computed by entering measured values (i.e. raw data) for pH, SO_4^{2-}, Al, Li, Na, SiO_2, and Sr into the above equations. Group centroids were obtained by calculating the discriminant scores (F1 and F2) for each of the three groups based on the predictors' means (as opposed to individual values for each sample).

The visual representation of the effectiveness of the computed discriminant functions is given in Fig. 6. The scatter plot illustrates the distribution of the discriminant scores for each principal hydrogeological unit (A, MCS, and UCCM), as well as the position of the unit's centroids.

Table 3 Observed categories of the groundwater samples vs. predicted group membership

Principal HGU	Predicted Group Membership			Total
	A	MCS	UCCM	
Original				
Count				
A	36	1	6	43
MCS	3	52	11	66
UCCM	5	12	53	70
%				
A	83.7	2.3	14.0	100
MCS	4.5	78.8	16.7	100
UCCM	7.1	17.1	75.7	100
Cross validated				
Count				
A	35	1	7	43
MCS	3	50	13	66
UCCM	6	12	52	70
%				
A	81.4	2.3	16.3	100
MCS	4.5	75.8	19.7	100
UCCM	8.6	17.1	74.3	100

From the range of the scores on the F1 and F2 axis, it can be noted that function F1 mostly contributes to the separation of samples from andesite relative to the samples from the other two units, and to a certain extent, it facilitates differentiation between the samples from the UCCM and MCS units. Function F2 contributes to the sorting between samples from MCS and UCCM. Overall, more considerable overlaps on the scatter plot suggest less efficient differentiation between groundwaters from the Miocene sediments and "Bor" clastites and relatively good separation of andesite groundwaters. This finding corresponds with the hydrogeological settings, under which MCS and UCCM units have very similar lithology (sandstone, conglomerate, siltstone) and hydraulic properties, both outcropping at the surface. In these conditions, trace elements concentrations proved to be more relevant than major ions for delineating between those two similar groups.

One of the results of the DA is the classification summary (Table 3), which indicates to what extent the predicted group membership of the groundwater samples (the columns of Table 3) matches the original observed data (the rows in Table 3). The cross-validated dataset (the lower part of Table 3), obtained by the "leave one out" classification, showed that samples from the andesite unit were classified with slightly better accuracy (81.4%) than the Miocene sediments unit (75.8%) and "Bor" clastics unit (74.3%). The cross-validation results also revealed that 76.5% of the groundwater samples were correctly classified overall. The results for the MSC and UCCM units are slightly below the accuracy of the methods used for inrush sourcing in similar studies (Bi et al. 2021; Huang et al. 2019; Ju and Hu 2021), which is interpreted to be a consequence of small differences in groundwater quality. Although comprehensive chemical parameters were tested, potential mixing and similarities in groundwater composition limit the accuracy and affect the modeling results. Additionally, groundwater quality data collected in the pre-production phase should be representative for the aquifers present in the mining area, including the deep ones, to enable reliable predictions.

Delineated discriminant functions were used to calculate the discriminant scores (F1 and F2) for the mine water samples in order to compare these new samples with an existing set of samples. Based on the proximity to a group centroid, mine water samples were classified as belonging to one of the three principal hydrogeological units – A, MCS, or UCCM (Fig. 6). Most of the mine water samples were determined to originate from volcanoclastic and andesite units. When comparing these results ("model prediction" in Fig. 6) with the exact location at the mine from which the mine water sample was taken ("logged HGU" in Fig. 6), significant matching was obtained. However, several samples (MW-05, MW-10, and MW-11) were classified into a hydrogeological unit different from the one in which they were sampled. In the case of sample MW-10, this discrepancy was probably due to similar hydrogeological features of the UCCM and MCS units and the fact that distances between MW-10 and these two group centroids are relatively similar. Samples MW-05 and MW-11 were taken from the mining works while advancing through the UCCM unit. However, their chemical composition (i.e. model-predicted group membership) suggests their origin from the andesite rocks. This finding revealed the complexity of the groundwater system, with faults and ungrouted resource holes acting as conduits for groundwater, connecting different hydrogeological units.

Acknowledging the CP deposit mineralogy and analogy with surrounding mines within the same metallogenic zone, it is expected that, with time, AMD will start to form. Since F2 strongly depends on the concentration of SO_4^{2-}, the established model should adequately reflect the change in the chemical composition of mine water. Still, for proper characterization, the mine water samples used in the analysis should be collected from the inflow points rather than from the dewatering system in cases where different water streams are combined.

Sourcing of groundwater inrushes into mine development infrastructure with the application of machine learning algorithms on the pre-mining chemical dataset, combined with groundwater levels data, is a promising perspective for raising the predictive accuracy, as reported in similar studies (Dong and Zhang 2023; Fang 2022; Wu et al. 2022).

Conclusion

The source of groundwater inflows into the construction works of the "Cukaru Peki" massive sulfide Cu–Au underground mine was investigated by interpreting the hydrochemical data collected before mining. A set of 15 chemical parameters from 179 groundwater chemical analyses sampled across multiple seasons were used in the analysis. The chemical fingerprint of groundwater varies with depth and within the main hydrogeological units (Miocene clastic, Upper Cretaceous clastic, and andesite). The Ca–HCO_3 water dominates in the shallow andesite and clastic units while transforming toward Na–SO_4 type groundwater with depth. The mineral alteration zones are distinguished from fresh volcanics by higher clay and sulfide mineral content, which influences the groundwater chemistry by restricting groundwater flow and increasing TDS concentrations. In conditions with pronounced variability of groundwater quality within the aquifers, understanding water inrush sources is difficult. To address this challenge and to compensate for the lack of mine water quality data in the mine construction phase, an approach is proposed for sourcing of mine water inflows into the ore body access underground infrastructure.

This method is based on pre-mining groundwater quality and stepwise discriminant analysis. Within the study, two discriminant functions were delineated, revealing a significant association between three main hydrogeological units and seven chemical parameters – SO_4^{2-}, Na, Al, pH, Sr, Li, and SiO_2, accounting for 65.3% (F1) and 31.2% (F2) of the variability between units. Closer inspection of the structure matrix singled SO_4^{2-} and Na as the most relevant predictors for characterizing the andesite unit. At the same time, Al and Sr were crucial for differentiating the groundwater from the Miocene and the Upper Cretaceous sediments. The cross-validated classification showed that 76.5% of the groundwater samples were correctly classified. Although readily available, basic physical–chemical parameters are prone to influence by the measures taken to physically stabilize the excavations. Also, groundwater sourcing may not fully apply in complex hydrogeological conditions when relying only on major ions. In such circumstances, trace elements like Li, Sr, and Al can be essential in differentiating between aquifers. Thus, the described approach identifies the water quality parameters that contribute most to the separation between hydrogeological units. Based on the described discriminant functions, the origin of subsequently collected mine water samples was determined, indicating that several groundwater inflows originate from hydrogeological units different from the ones in which they were sampled, revealing complex flow paths. The study successfully demonstrates the method for practical application of the groundwater chemistry data acquired in the pre-production period, emphasizing the relevance of the proposed approach in developing new mines.

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