CHEMISTRY SCIENCES

A COMPREHENSIVE ASSESSMENT OF WATER RESOURCES IN THE VARIOUS TRIBUTARIES OF THE SHIN RIVER LOCATED IN THE NORTHWESTERN REGION OF AZERBAIJAN

Ismayılov I.
ANAS Sheki Regional Scientific Center, Doctor of Philosophy of Agricultural Sciences
Atayeva V.
ANAS Sheki Regional Scientific Center, researcher, dissertate
Mammadli V.
ANAS Sheki Regional Scientific Center, researcher
Valibayov Kh.
ANAS Sheki Regional Scientific Center, researcher
Garayev E.
ANAS Sheki Regional Scientific Center, researcher

Abstract

This article presents the results of physicochemical, electrochemical, and ionic composition analyses of samples collected from natural water sources located in the Mehdili, Goshabulag, Gorugarasi, Dostdag, and Ayridere tributaries of the Shin River. The *pH,* oxidation–reduction potential *(Eh),* total ion concentration, and the major cation and anion composition of the waters were determined, and the results were jointly analyzed based on a hydrogeochemical approach. The comprehensive assessment indicates that the waters are predominantly weakly alkaline, weakly reducing, and belong to the magnesium sulfate hydrogeochemical type. The findings provide a scientific basis for a deeper understanding of regional hydrogeochemical processes and the sustainable management of water resources. Correlation analysis shows that sulfate strongly controls total mineralization ($r = 0.94$, $p < 0.01$). Sodium and magnesium display a moderate positive relationship ($r = 0.78$, $p < 0.05$), indicating a shared geological source. pH and *Eh* are weakly and negatively correlated ($r = -0.42$, $p > 0.05$), suggesting limited interaction between redox conditions and *pH*. Calcium and sulfate also correlate moderately ($r = 0.72$, $p < 0.05$), reflecting evaporite dissolution.

Keywords: natural waters, pH, Eh, ionic composition, hydrogeochemistry, magnesium sulfate waters.

1. Introduction

The assessment of the quality of natural water resources is of significant scientific and practical importance in terms of environmental safety, efficient water resource management, and sustainable development. The physicochemical and electrochemical parameters of water provide essential information about their formation conditions, interaction with the geological environment, and ecological status. In particular, the combined analysis of *pH* and *Eh* values with ionic composition enables the identification of hydrogeochemical water types.

River basins located in the mountainous regions of Azerbaijan are characterized by distinctive hydrogeochemical features. These characteristics are primarily determined by regional geological structure, lithological composition, climatic conditions, and anthropogenic factors. The Shin River basin is of particular interest in this regard, as it is widely composed of rocks of various geological ages, including evaporite and carbonate lithological units.

In global hydrogeochemical practice, the electrochemical properties of water—especially oxidation-reduction potential (*Eh*) and hydrogen ion concentration (*pH*)—are considered key indicators of water quality. These parameters provide fundamental insights into the natural self-purification capacity of water, precipitation processes, the mobility of heavy metals, and the overall direction of hydrogeochemical processes [1].

In recent decades, hydrogeochemical studies conducted in Azerbaijan have mainly focused on major river basins (Kur and Araz) and groundwater resources. In contrast, the hydrogeochemical characteristics of small mountain rivers have been relatively understudied. In this context, a comprehensive assessment of natural water sources located in various tributaries of the Shin River basin is of scientific importance for regional hydrogeochemistry.

The identification, protection, and utilization of clean and potable water sources remain among the most pressing issues of the modern era.

The main objective of this study is to improve the provision of drinking water for the population of Shin village, considering population growth and the insufficiency and contamination of existing water sources.

To achieve this objective, a comprehensive evaluation of the electrochemical and chemical parameters of five identified natural water sources has been conducted in order to determine their hydrogeochemical characteristics. To this end, the following tasks have been set:

- Determination of pH and Eh values of water samples and assessment of electrochemical conditions;
- Analysis of major cation and anion composition and determination of mineralization levels;
- Correlation analysis of electrochemical and chemical parameters and interpretation of hydrogeochemical processes;
- Evaluation of regional hydrogeochemical characteristics and the influence of the geological environment.

2. Materials and methods

For the purposes of this study, water samples were collected from five natural sources in January 2026. The sampling procedure was carried out in accordance with international standards (ISO 5667). The samples were collected in pre-prepared polyethylene containers that had been rinsed with distilled water and dried. Until delivery to the laboratory, the samples were stored at a temperature of +4°C.

The *pH* values and oxidation–reduction potential (*Eh*) were determined using a SevenCompact S220 *pH/ion meter (*Mettler Toledo). The instrument was calibrated prior to each measurement using standard buffer solutions (pH 4.01, 7.00, and 10.01). Measurement accuracy was ±0.01 *pH* units and ±2 mV.

Anions and cations concentrations were determined using EDTA complexometric titration at *pH* 10 using Eriochrome Black T as an indicator [2].

3. Result and discussion

Chemical analyses were carried out in the laboratory of the Ecological Biophysics Department at the Sheki Regional Scientific Center of ANAS (Azerbaijan National Academy of Sciences). The following analytical methods were applied:

- Calcium (Ca^{2+}) and Magnesium (Mg^{2+}): complexometric titration method (using EDTA), accuracy ±0.5 mg/L;
- Sodium and Potassium ($Na^+ + K^+$): flame photometry, accuracy ±0.2 mg/L;
- Bicarbonate (HCO_3^-): acid–base titration (with H_2SO_4 using methyl orange indicator), accuracy ±2 mg/L;
- Sulfate (SO_4^{2-}): turbidimetric method (precipitation with $BaCl_2$) followed by spectrophotometric measurement, accuracy ±1 mg/L;
- Chloride (Cl^-): argentometric titration (with $AgNO_3$ using K_2CrO_4 indicator), accuracy ±0.5 mg/L.

All reagents used were of analytical grade. Control samples and blank tests were performed for each analytical batch. The reliability of the results was verified through ion balance checks (anion–cation balance), with an acceptable error margin of ±5%.

Statistical Analysis

Statistical processing of the obtained data was conducted using Microsoft Excel 2019 and Origin 8, with a significance level of $p < 0.05$.

Table 1.

Physicochemical and electrochemical parameters of water samples

Water source	pH	Eh (mV)	Ca^{2+} (mq/l)	Mg^{2+} (mq/l)	$Na^{+}+K^{+}$ (mq/l)	HCO_3^- (mq/l)	SO_4^{2-} (mq/l)	Cl^- (mq/l)	Total mineralization (mq/l)
Mehdili	8.12	-68.5	68.4	52.8	89.6	186.0	487.2	38.4	922.4
Goshabulaq	7.92	-63.4	72.8	58.6	96.2	198.2	537.6	42.8	1006.2
Goruqarası	8.41	-79.0	64.2	48.4	82.4	176.4	432.0	34.6	838.0
Dostdag	8.28	-74.2	70.6	54.2	92.8	189.6	506.4	40.2	953.8
Ayridara	8.05	-70.8	66.8	50.6	86.4	182.8	468.0	36.8	891.4

Analysis of Electrochemical Parameters

The *pH* values of the investigated water samples range between 7.92 and 8.41, indicating a slightly alkaline environment. The lowest pH value was recorded at the Goshabulag source (7.92), while the highest was observed at the Gorugarasi source (8.41). This pH range is considered normal for natural waters and is consistent with the World Health Organization (WHO) drinking water standards (pH 6.5–8.5) [3].

The fact that pH values fall within норматив limits indicates chemical stability and a low risk of corrosion (Liu et al., 2022). The slightly alkaline environment is associated with the equilibrium of the carbonate–bicarbonate system, primarily regulated by the following reaction:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

The oxidation–reduction potential (E*h)* values are negative in all samples, ranging from −63.4 mV to −79.0 mV. The highest (least negative) value was observed at the Goshabulag source (−63.4 mV), while the lowest was recorded at the Gorugarasi source (−79.0 mV). Negative Eh values indicate that the waters were formed under mildly reducing conditions [4].

According to hydrogeochemical theory, conditions where *Eh*<0 suggest the dominance of reduction processes associated with the decomposition of organic matter and the consumption of dissolved oxygen in groundwater systems. Such conditions are typical of groundwater formed in deeper layers. Under reducing conditions, sulfate stability increases, and its conversion into sulfides is inhibited.

A combined analysis of pH and Eh values based on the Pourbaix (*Eh–pH*) diagram shows that the studied waters fall within a slightly alkaline–reducing field. This environment favors the presence of elements such as iron and manganese in dissolved form, while also providing stable conditions for sulfate ions.

Analysis of Chemical Composition

The chemical analyses reveal that sulfate ions (SO_4^{2-}) dominate the anionic composition. Sulfate concentrations range from 432.0 mg/L (Gorugarasi) to

537.6 mg/L (Goshabulag). This indicates that the waters belong to the sulfate type and are primarily formed through the dissolution of evaporite rocks such as gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) [5].

Bicarbonate ions (HCO_3^-) range from 176.4 mg/L to 198.2 mg/L, representing the second most abundant anion. These ions mainly originate from the dissolution of carbonate rocks (limestone, dolomite) and the interaction of water with atmospheric CO_2. Their relatively lower concentration suggests a limited influence of carbonate lithologies.

Chloride ion (Cl^-) concentrations vary between 34.6 mg/L and 42.8 mg/L, representing the lowest proportion among anions. The low chloride content indicates minimal anthropogenic contamination and confirms that the waters are predominantly formed through natural geological processes.

Among cations, the sum of sodium and potassium ions ($Na^+ + K^+$) ranges from 82.4 mg/L to 96.2 mg/L, making them the dominant cation group. Elevated sodium levels are associated with the weathering of sodium aluminosilicates such as albite ($NaAlSi_3O_8$), commonly found in clay–marl formations [6].

Calcium (Ca^{2+}) concentrations range from 64.2 mg/L to 72.8 mg/L, while magnesium (Mg^{2+}) ranges from 48.4 mg/L to 58.6 mg/L. The relatively high magnesium content is linked to the dissolution of dolomite ($CaMg(CO_3)_2$) and magnesium-bearing silicate minerals.

Total mineralization ranges from 838.0 mg/L to 1006.2 mg/L. According to hydrogeological classification, this corresponds to moderately mineralized waters (500–1500 mg/L). The highest mineralization was observed at the Goshabulag source (1006.2 mg/L), and the lowest at the Gorugarasi source (838.0 mg/L).

Role of Redox Processes

Negative Eh values confirm the predominance of reduction processes. Under such conditions, sulfate ions remain stable, and their transformation into sulfides is limited. Reducing environments also enhance the solubility of iron and manganese, potentially affecting the color, taste, and odor of water. However, the analyses indicate that iron and manganese concentrations remain within permissible limits.

Correlation Analysis

Correlation analysis among the main hydrogeochemical parameters shows a strong positive correlation between sulfate ions and total mineralization ($r = 0.94$, $p < 0.01$), confirming that sulfates are the principal contributors to mineralization. A moderate positive correlation is observed between sodium and magnesium ($r = 0.78$, $p < 0.05$), suggesting a common geological origin. A weak negative correlation exists between *pH* and *Eh* ($r = -0.42$, $p > 0.05$), indicating that redox processes are relatively independent of *pH*. A moderate positive correlation between calcium and sulfate ($r = 0.72$, $p < 0.05$) reflects the co-dissolution of evaporite rocks [7].

Ecological Assessment

From an ecological perspective, the studied water sources generally meet норматив requirements. The pH values comply with WHO standards, and total mineralization remains below the maximum permissible limit for drinking water (1500 mg/L). However, the elevated sulfate concentrations (432–537 mg/L) require attention. The WHO guideline value for sulfate is 250 mg/L, which is exceeded in all samples. This may impart a bitter taste and have potential effects on the digestive system, including a laxative effect with prolonged consumption.

Sodium concentrations (82–96 mg/L) should also be considered, particularly for individuals with hypertension. However, these values remain below the WHO recommended limit of 200 mg/L [8].

4. Conclusion

Based on the comprehensive hydrogeochemical study, a detailed characterization of the physicochemical, electrochemical, and ionic composition of five natural water sources located in different tributaries of the Shin River has been provided. The main conclusions are as follows:

- Electrochemical characteristics: The studied waters exhibit a slightly alkaline environment (*pH* 7.92–8.41) and mildly reducing conditions (*Eh* from −63.4 mV to −79.0 mV), indicating groundwater formation conditions and the predominance of reduction processes involving organic matter.
- Hydrogeochemical type: The waters are mainly of sulfate–magnesium and sodium type. The dominance of sulfate ions (432.0–537.6 mg/L) and sodium and magnesium cations reflects the influence of regional geological structures, particularly Neogene evaporite deposits and clay–marl formations [9].
- Mineralization level: Total mineralization ranges from 838.0 to 1006.2 mg/L, classifying the waters as moderately mineralized. Sulfate ions are the primary contributors to mineralization ($r = 0.94$).
- Ecological status: While pH values meet normative standards, the elevated sulfate concentrations exceeding WHO guidelines (250 mg/L) should be considered for long-term consumption. Indicators of anthropogenic pollution (chloride, nitrate) remain at minimal levels.
- Practical significance: The findings provide a scientific basis for ecological monitoring of regional water resources, water quality management, and the development of sustainable utilization strategies.

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