

Spatio-temporal changes of hydrochemical properties and factors controlling hydrochemistry of springs in the Seyfe Basin

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Introduction
Recently, the demand for water resources is continuously increasing. Reliability plays an important role in supplying these rising water demands in our country. Hydrogeological studies regarding the assessment of the potential of water resources need to be carried out on water. Hydrochemistry and statistical techniques are used within this context. The aim of this study is to determine the hydrochemical properties and hydrochemical evaluation of water resources in the Seyfe Basin and to understand processes involving water chemistry using statistical techniques such as principal component analysis (PCA) and cluster analysis.

Geological Setting and Hydrogeology
The oldest rock units outcropping in the study area are the Paleozoic age Kizilirmak Massif, which consists of metamorphic rocks. Kizilirmak Massif is composed of different formations according to their stratigraphic features. (Yildizoglu et al., 2016). Kizilirmak Massif metamorphic rocks are intruded by Late Cretaceous age igneous units (Bazarkaya granitoid, Buzlukun granitoid) (Figure 1). The Eocene units which consist of thermal sediments and Miocene-Pliocene age Tuzluk Formation which is widely outcropping in the study area, unconformably overlie Miocene units. Quaternary alluvium is the youngest unit which is found in the study area.

Spatio-temporal changes of hydrochemical properties
In order to characterize hydrogeological system accurately, water samples were collected from springs, wells and discharge channels during September and December 2019 field campaigns from the Seyfe Lake sediment basin. The temperature, pH, total dissolved solids (TDS) and specific electrical conductance (SEC) were measured at the field and spatio-temporal changes of major ions are evaluated. The pH values of water samples are an important parameter that shows the water is acidic, neutral or alkaline in nature. Hydrogions are found more in basic water whereas are hydrogen ions in acidic water. The water samples have neutral to slightly alkaline character in the basin. (Figure 2).

Multivariate Statistical Analysis
The SPSS (v23.0) software was used to analyze the water samples. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) have been used to explain the main hydrochemical processes controlling water chemistry in the basin. Principal component analysis is an effective statistical technique which is used to analyze water data with smaller quantities than correlated dependent variables (Gökçen et al., 2017). The aim of this analysis is to transform the data sets into a new orthogonal and uncorrelated set of factors called principal components and to reduce the number of variables from the data. (Jolliffe and Cadima, 2016). PCA analysis was applied to the measured EC_{eq} and pH values in the field and the concentrations of the major cations to identify the variables with the most descriptive power that control the chemical composition of the water chemistry. It is indicated that the PCA explains 80.80% of the total variance.

Conclusions
In this study, hydrochemical applications and statistical techniques were applied. The aim is to understand the hydrochemical evaluation and chemical processes affecting the chemistry of waters in the Seyfe Basin.
Generally, most of the water samples is dominated by calcium and bicarbonate (hard to the hard).
According to the Piper diagram, Ca^{++} and HCO_3^- were dominant ions in western and southern parts of the basin.
Water types are determined as $CaHCO_3$. No springs, $NaHCO_3$ for wells, $NaCl$ for discharge channel in the city center and $NaCl$ in the spring basin.
The Piper diagram indicates that the rock weathering processes control the water chemistry in the basin. Discharge channel samples are also influenced by evaporation process.

References
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Chemical Variables

Chemical Variables	Principal Components	1	2
EC _{eq}	0.938	0.861	
pH	0.893	-0.560	
Ca ⁺⁺	0.938	0.861	
HCO ₃ ⁻	0.938	0.861	
Na ⁺	0.938	0.861	
Cl ⁻	0.938	0.861	
SO ₄ ²⁻	0.938	0.861	
Mg ²⁺	0.938	0.861	
Fe ²⁺	0.938	0.861	
NO ₃ ⁻	0.938	0.861	
PO ₄ ³⁻	0.938	0.861	
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Al ³⁺	0.938	0.861	
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INTRODUCTION

Recently, the demand for water resources is continuously increasing. Wetlands play an important role in supplying these rising water demands, in our country.

Hydrogeological studies regarding the assessment of the potential of wetlands as water resources need to be carried out at basin scale. Hydrochemistry and statistical techniques are used within this context.

The aim of this study is to determine the hydrochemical properties and hydrochemical evaluation of water resources in the Seyfe Basin and to understand processes involving water chemistry using statistical techniques such as principal component analysis (PCA) and cluster analysis.

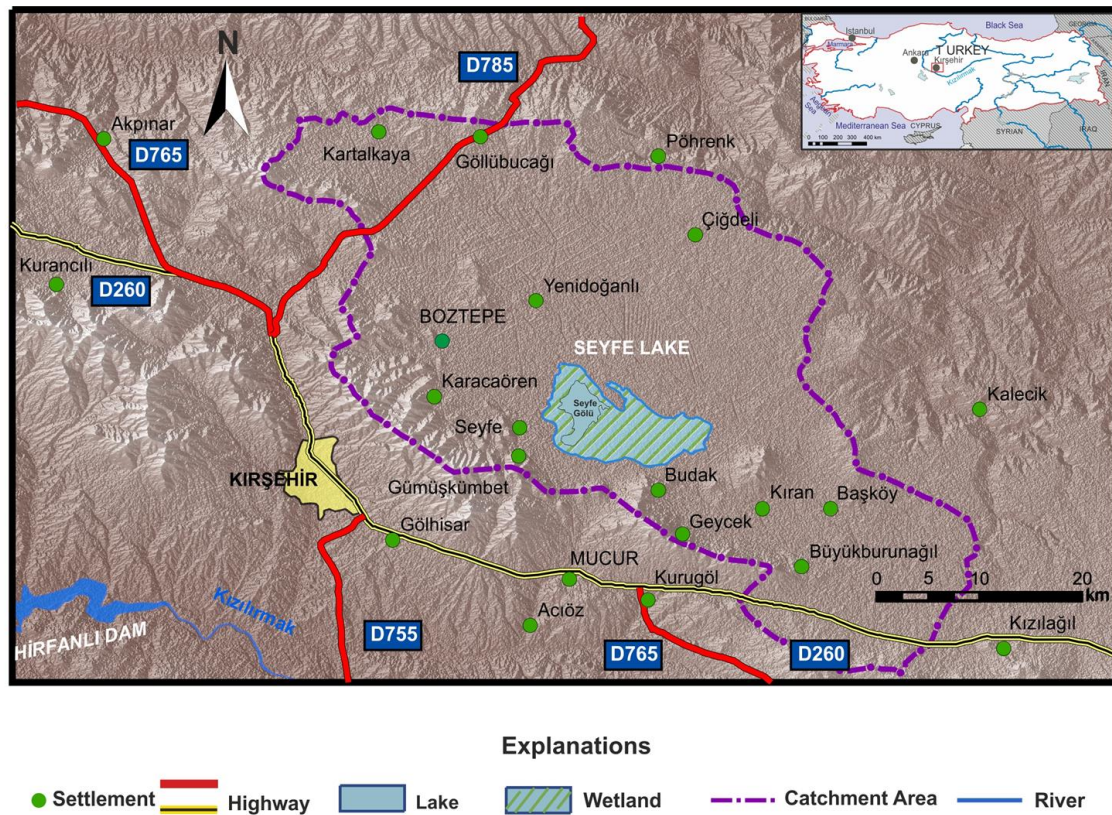


Figure 1. Location map of the basin.

Seyfe Lake closed basin is located west of Kırşehir (Turkey) in the Central Anatolia. Seyfe Lake has a 1447 km² catchment area (Figure 1).

Considering the importance of the Seyfe Lake Basin for its water resources potential and due to its fragile ecosystem, a detailed hydrogeological characterization of the basin has been carried out during this study.

GEOLOGICAL SETTING AND HYDROGEOLOGY

The oldest rock units outcropping in the study area are the Paleozoic aged Kirsehir Massif, which consist of metamorphic rocks. Kirsehir Massif is composed of different formations according to their lithostratigraphic features. (Hinsbergen et al; 2016).

Kirsehir Massif metamorphic rocks are intruded by Late Cretaceous aged intrusive units (Baranadag granitoid, Buzlukdağ syenitoid) (Figure 2).

The Eocene units which consists of terrestrial sediments and Miocene-Pliocene aged Kizilirmak Formation which is widely outcropping in the study area, unconformably overlie Mesozoic units.

Quaternary alluvium is the youngest unit which is found near streams and around the lake area in the basin. It consists of alluvial deposits (gravel, coarse and fine sand, silt, sandy clay and clay).

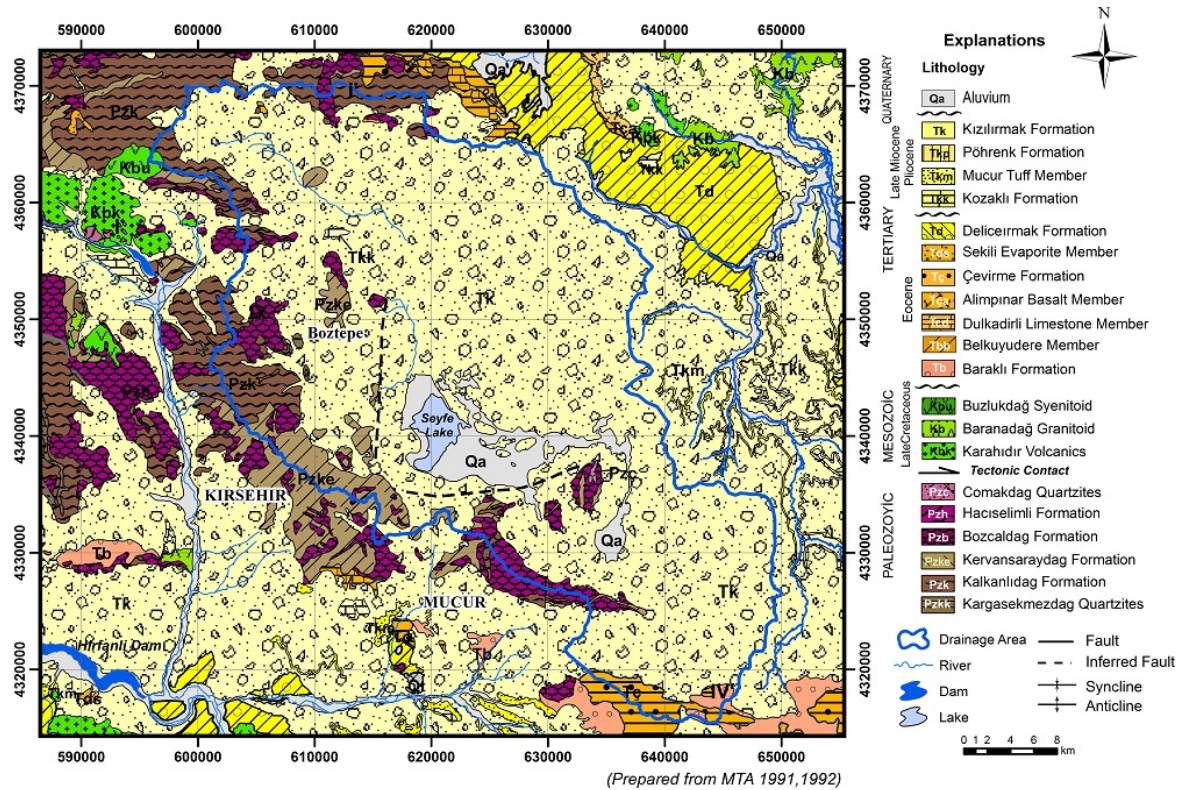


Figure 2. Geological map of the study area.

Metamorphic basement and volcanic rocks which crop out generally at the highlands of the basin and they are characterised by no primary porosity.

The hydrogeological behaviour of the formations are controlled by secondary porosity which has a result of weathering and fracturing of the rocks.

The fractured and faulted zones of the marble and limestone levels representing the Bozcaldag Formation of the Paleozoic Kirsehir Massif show aquifer characteristics in the basin (Figure 3).

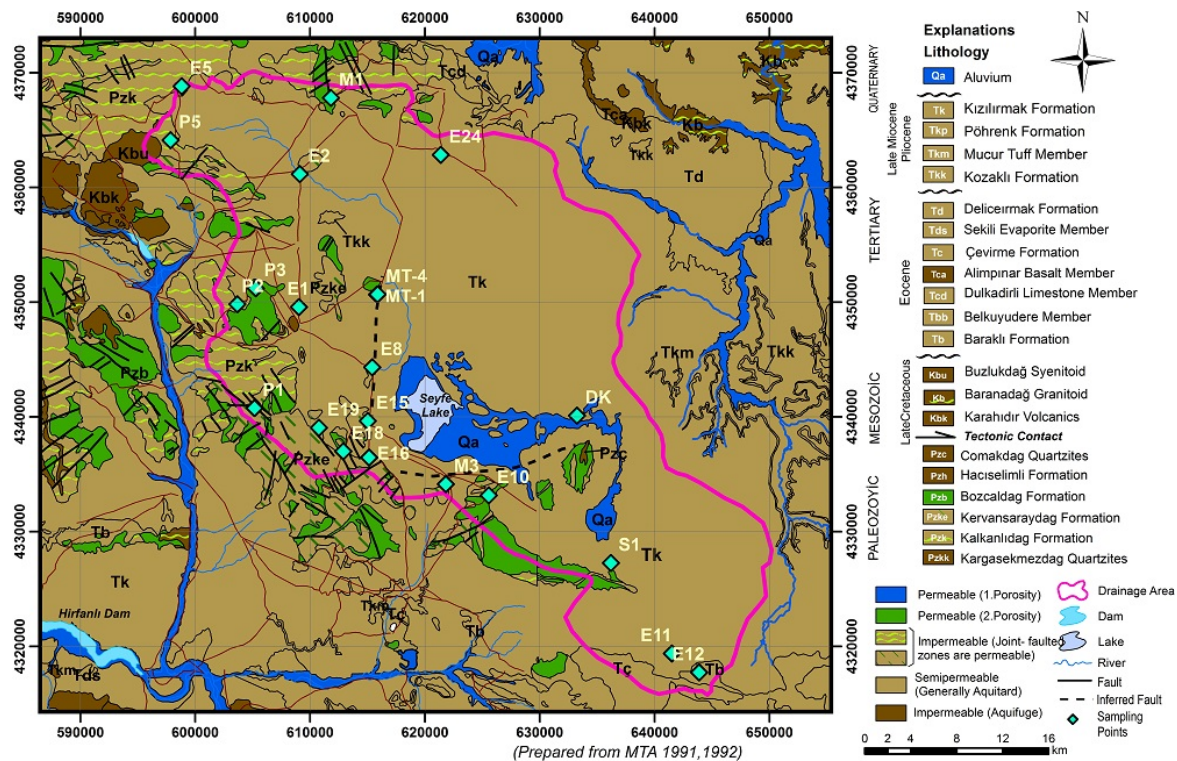


Figure 3. Hydrogeological map of the study area.

Eocene and Pliocene aged units are considered to be generally semipermeable.

Also sandstone, conglomerate and limestone levels of the Eocene and Pliocene aged units show local aquifer characteristics.

Quaternary alluvium show permeable character where the unit thickness is relatively high in the basin.

In order to understand the groundwater flow direction, water level data from 54 wells (DSİ, 2004) were evaluated and hydraulic heads of each well point were calculated from these datas.

Piezometric levels were then drawn based on the hydraulic head, which varied from 1111.6 to 1252 m in the basin.

The highest elevation is observed in the northern part of the study area, near to the Kartalköy and Göllü settlements. The lowest elevation is seen in the central of the basin especially around the lake area.

According to the groundwater level map; groundwater flow direction is towards to the Seyfe Lake area in the basin (Figure 4).

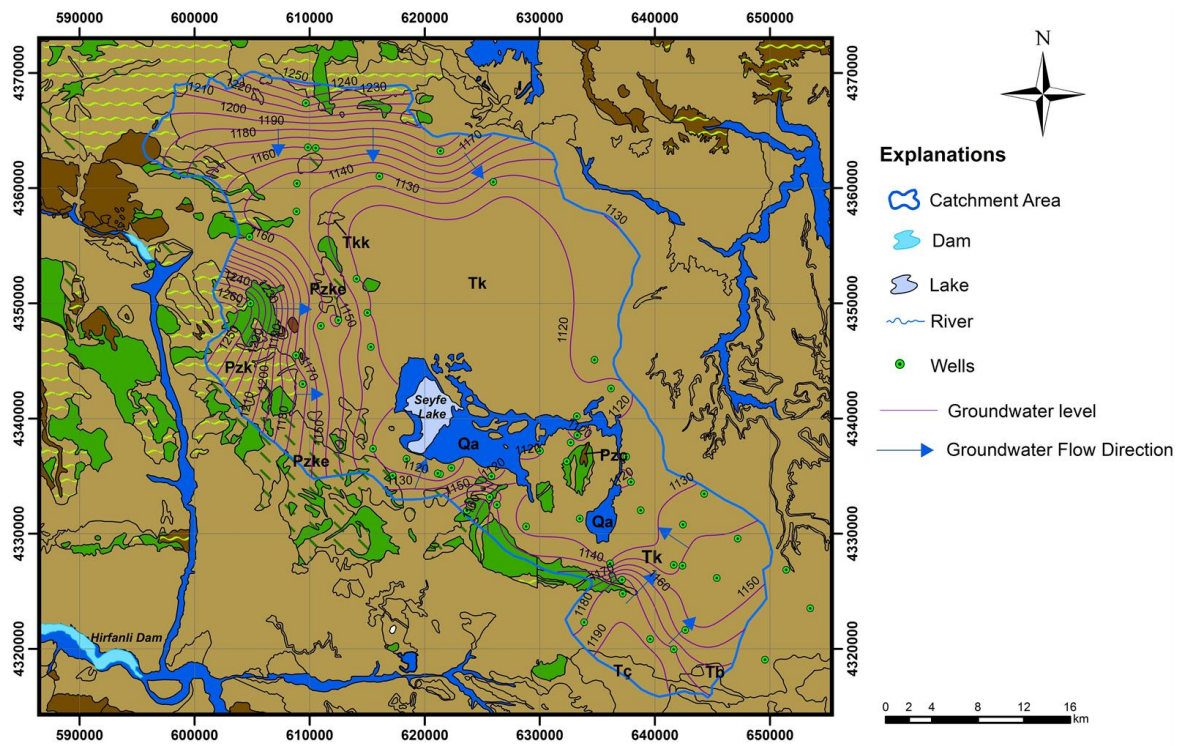


Figure 4. Groundwater level map of the basin.

SPATIO-TEMPORAL CHANGES OF HYDROCHEMICAL PROPERTIES

In order to characterize hydrogeological system accurately, water samples were collected from springs, wells and drainage channels during September and December 2019 field campaigns from the Seyfe Lake wetland basin.

The temperature, pH, total dissolved solids (TDS) and specific electrical conductance ($EC_{25}^{\circ}C$) were measured at the field and spatio-temporal changes of major ions are evaluated.

The pH value of water samples are an important parameter that show the water is acidic, neutral or alkaline in nature.

Hydroxyl ions are found more in basic water whereas are hydrogen ions in acidic water. The water samples have neutral to slightly alkaline character in the basin. (Figure 5).

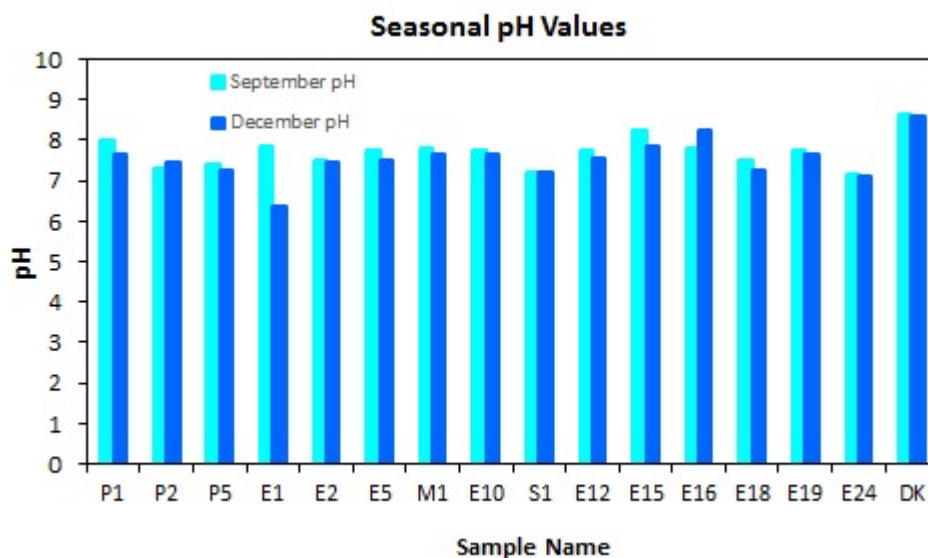


Figure 5. Seasonal change of pH values.

The spatial distribution of the different parameters were drawn by using interpolation (IDW) technique over the basin. As an example, pH distribution in the basin is given in Figure 6.

In the study area, the pH of water samples range from 7.15 to 8.65. Water samples with pH values change within 7.1 to 8.2 is shown by light blue colour in the study area. The area with pH values above 8.2 is shown by dark blue colour.

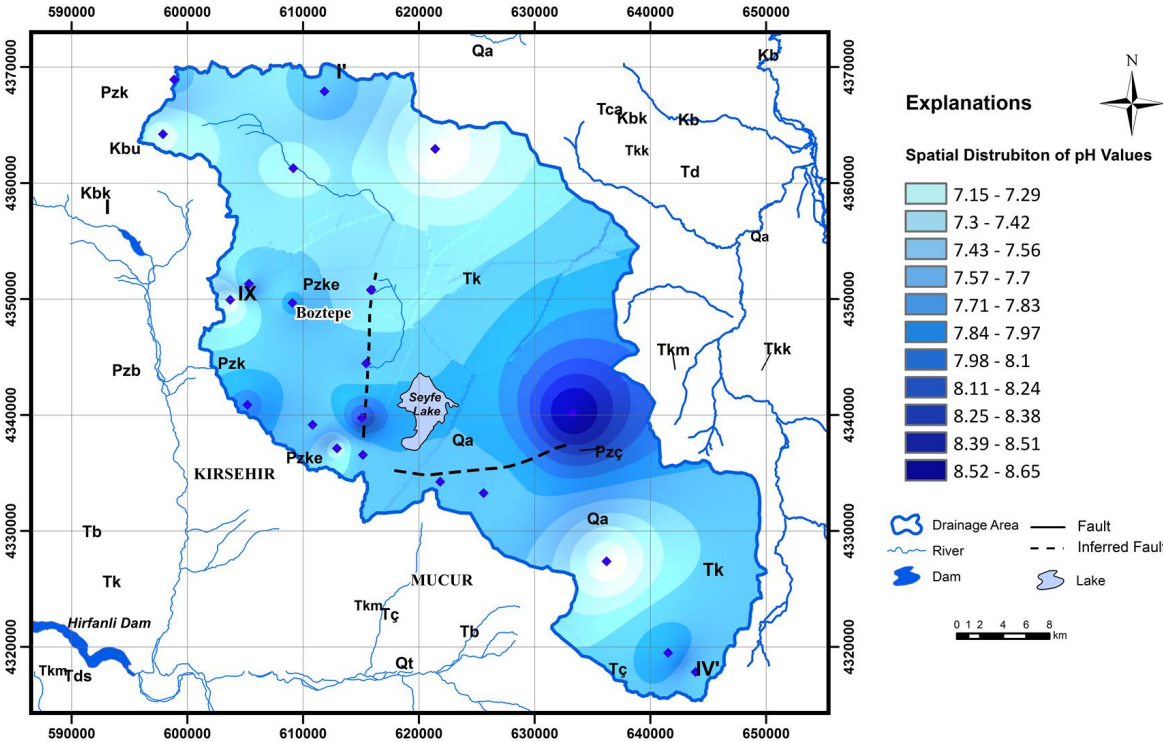


Figure 6.Spatial Distribution of pH Values.

According to the Gibbs plots; rock weathering-which is the dominant factor controlling the groundwater chemistry (Figure 7).

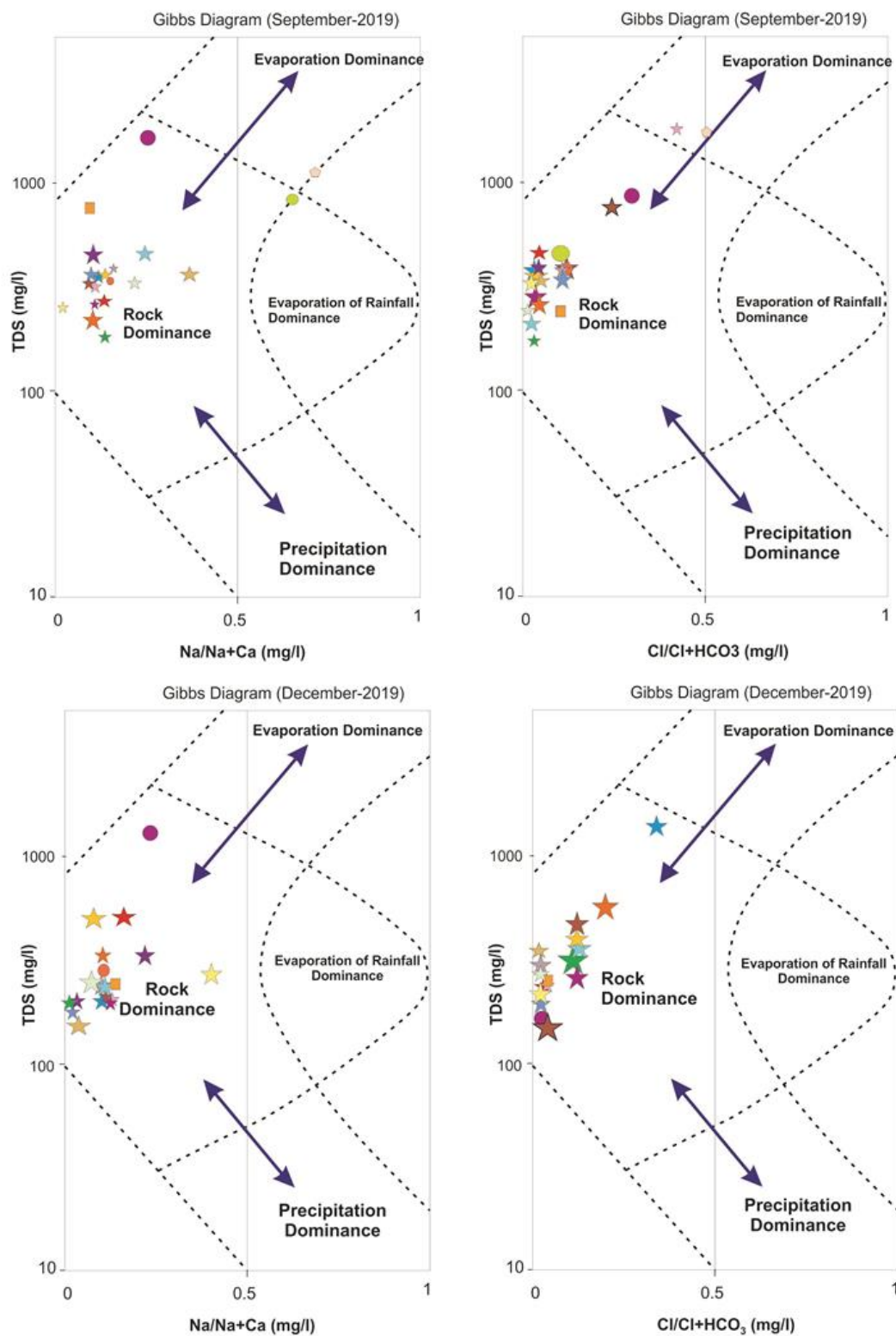


Figure 7. Gibbs Plots (September-December 2019).

Water facies identified with the Piper diagram, supports this view. Water types are determined as Ca-HCO₃ for springs; Na-HCO₃ for wells; Na-SO₄ for drainage channel in the dry season and Na-Cl in the rainy season (Figure 8).

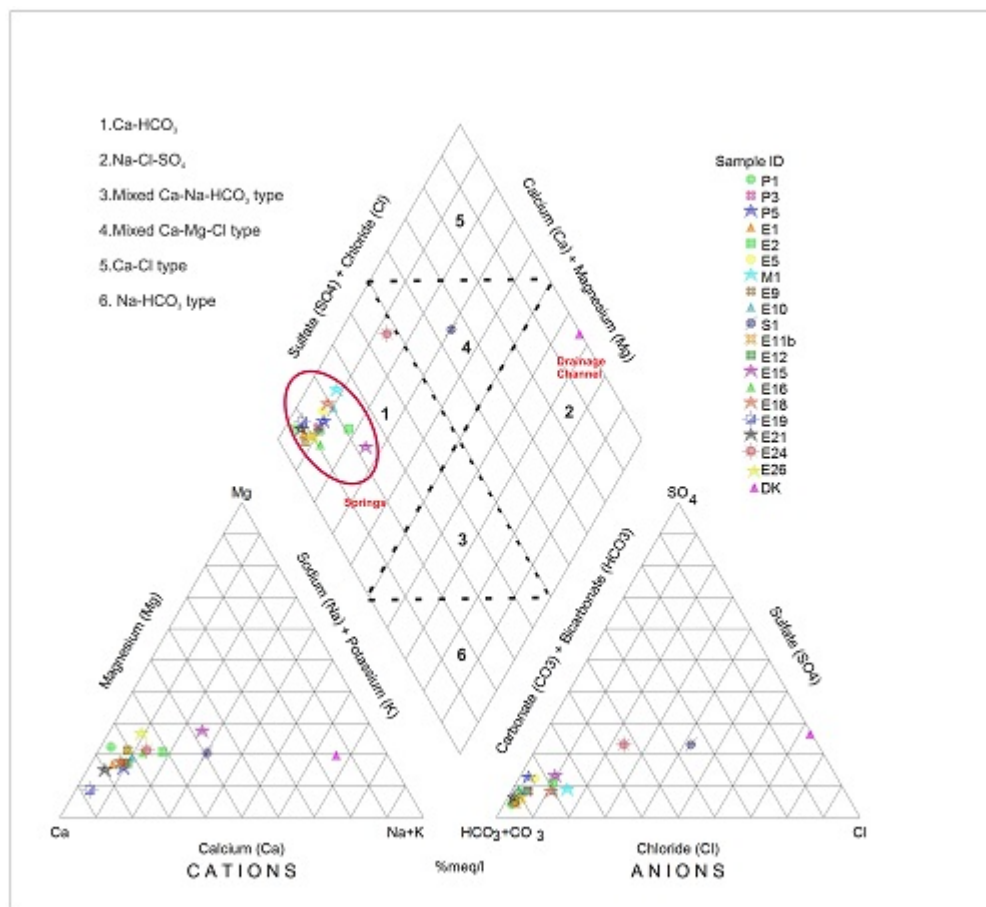


Figure 8. Hydrochemical facies of water samples on the Piper Diagram (December-2019).

$\text{Ca}^{+2}/\text{Mg}^{+2}$ molar ratio of the water samples greater than 2 in the study area. And also $\text{Ca}^{+2} + \text{Mg}^{+2}/\text{HCO}_3$ molar ratio of the water samples less than 1 in the study area. This values may indicate that the dissolution of the silicate minerals in the study area (Figure 9).

Na concentrations of the samples are higher than Cl concentrations in the basin. This might be the result of cation exchange reactions (Sethy et al., 2016).

The molar ratio of Na/Cl for water samples generally ranges from 0.7-4.2. Most of the samples Na/Cl molar ratio is greater than 1 in the basin. This indicate excess sodium, which may come from silicate weathering.

If silicate weathering is a probable source of sodium, the groundwater samples would have HCO_3^- as the most dominant abundant anion (Rogers, 1989). This is because the reaction of feldspar minerals with carbonic acid in the presence of water releases HCO_3 (Elango et al, 2003).

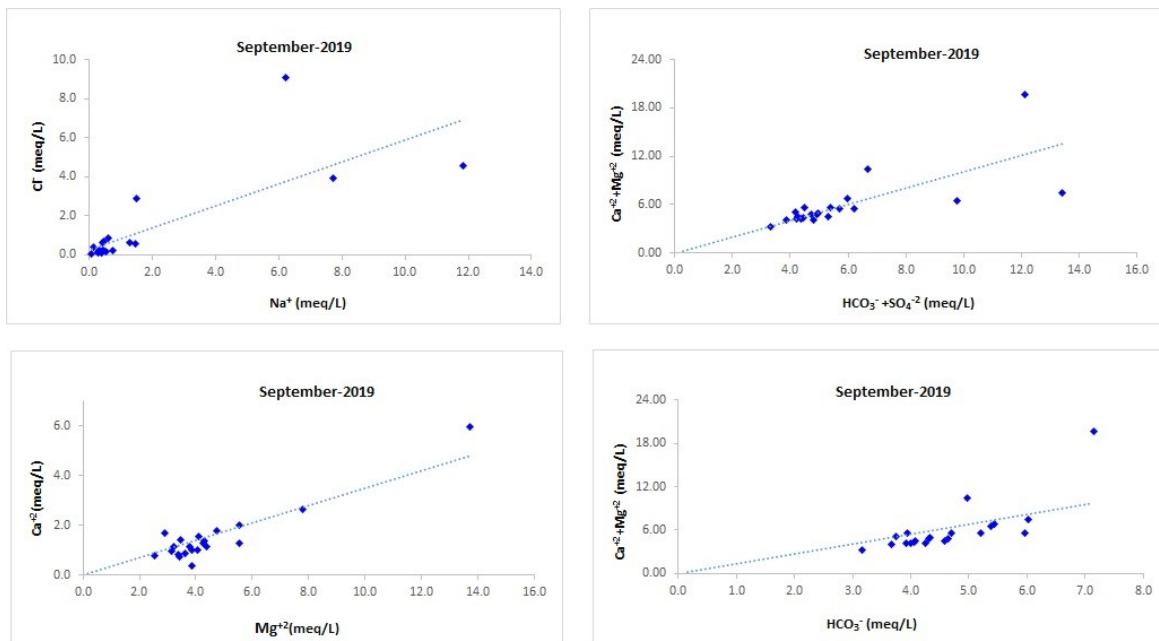


Figure 9. Different major ion correlations graphs.

Piper diagram also shows that HCO_3^- is the dominant anion for the springs in the basin. For this reason; silicate weathering was thought to be the main process responsible for the release of Na^+ into the groundwater. In the basin some samples Na/Cl ratio is less than 1.

However, samples with a Na/Cl ratio around and less than 1 indicate that the possibility of ion exchange (Elango et al., 2003).

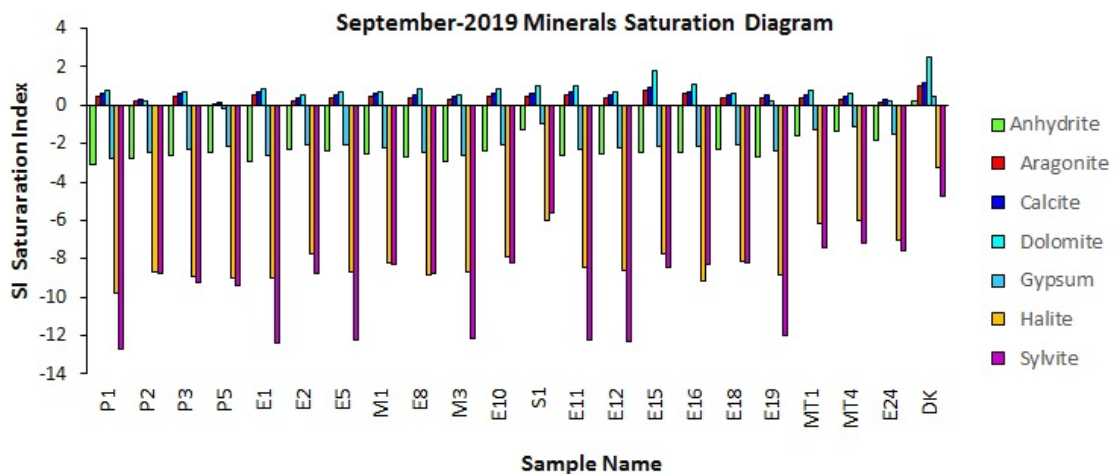


Figure 10. Mineral Saturation Diagram.

According to the mineral saturation diagram; water samples were saturated with calcite, dolomite and aragonite minerals and were undersaturated with sylvite, gypsum, halite and anhydrite (Figure 10, Figure 11 and Figure 12).

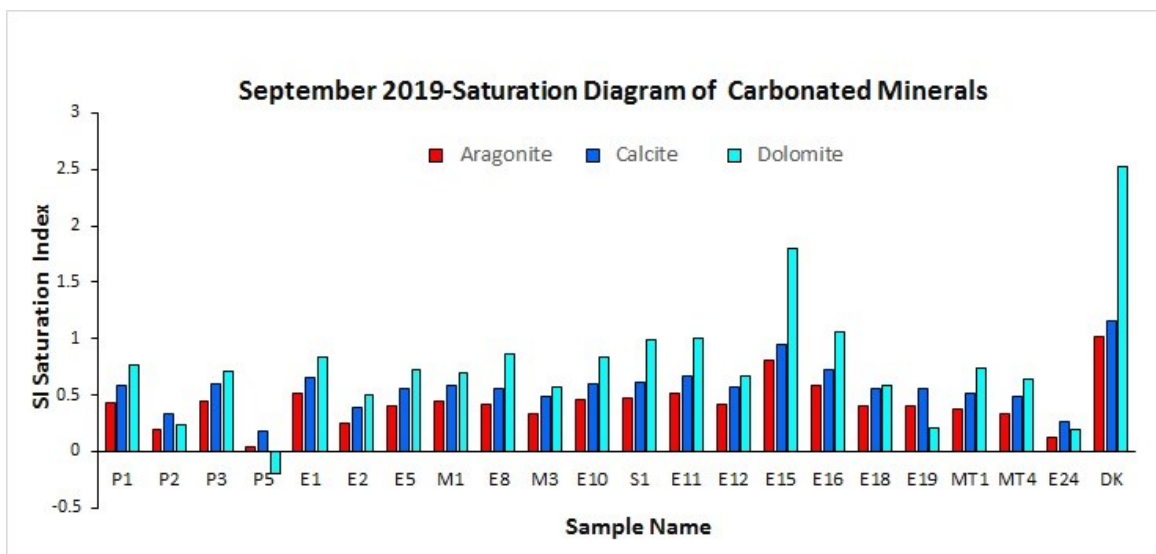


Figure 11. Saturation diagram of carbonated minerals in the basin.

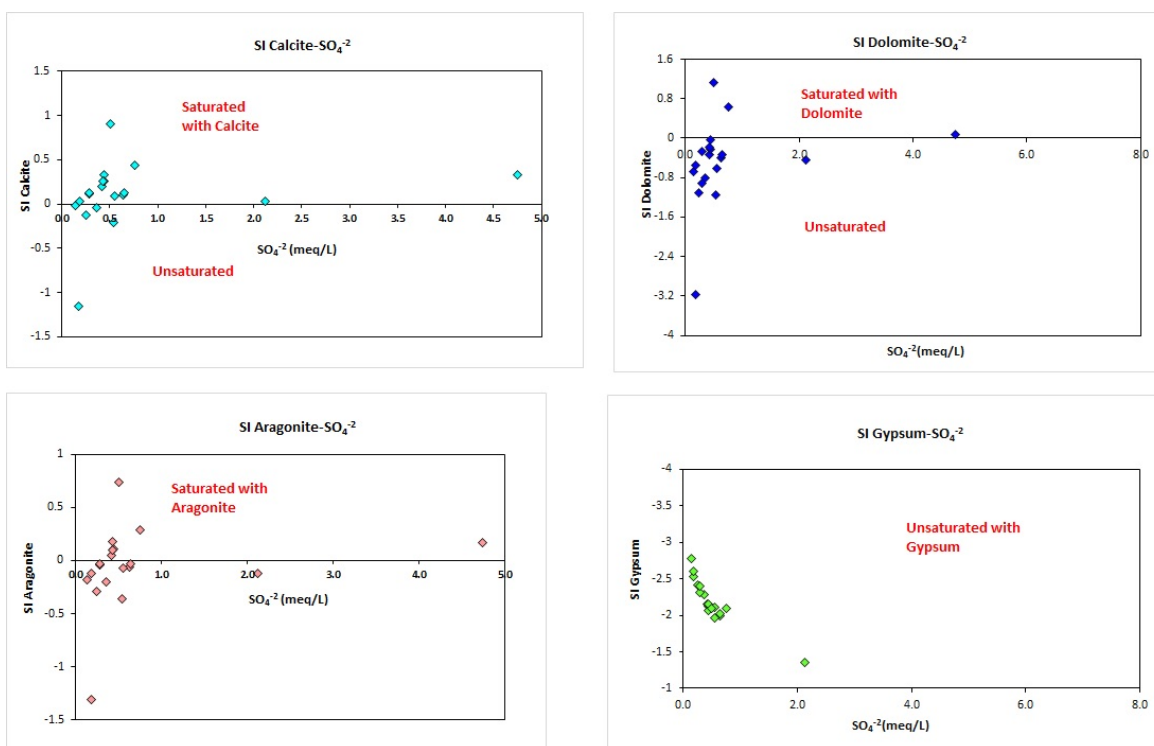


Figure 12. Saturation indices plots.

MULTIVARIATE STATISTICAL ANALYSIS

The IBM SPSS (v.23) software was used to analyse the water samples. Principal component analysis (PCA) and Hierarchical cluster analysis (HCA) have been used to explain the main hydrochemical processes controlling water chemistry in the basin.

Principal component analysis is the effective statistical technique which is used to analyse water data sets involve quantitative inter-correlated dependent variables (Zakhem et al., 2017).

The aim of this analysis is to transform the data sets into a new orthogonal and uncorrelated set of factors called principal components and to extract important knowledge from the data (Abdi and Williams, 2010).

PCA analysis was applied to the measured EC₂₅ and pH values in the field and the concentrations of the major ions to identify the variables with the most descriptive power that control the chemical composition of the water chemistry.

It is indicated that two PCs explain 89.88% of the total variance.

Chemical Variables	Principal Components	
	1	2
T	0.374	0.707
pH	0.643	-0.564
EC 25	0.991	0.044
K ⁺	0.584	0.704
Na ⁺	0.993	-0.027
Ca ⁺²	0.986	0.115
Mg ⁺²	0.995	0.008
Cl ⁻	0.994	0.003
SO ₄ ⁻²	0.993	-0.028
HCO ₃ ⁻	-0.615	0.692
Eigenvalues	7.18	1.81
% of Variance	71.79	18.08
Cumulative % of variance	71.79	89.88

Figure 13. Principal component analysis of water samples in the basin.

The first component (PC1) accounts for 71.79% of the variance. The second component (PC2) explains 18.08% of the total variance.

PC1 shows strong correlation between EC₂₅, Mg⁺², Na⁺, Ca⁺², Cl⁻, SO₄⁻², K⁺ and pH while correlating negatively with HCO₃ (Figure 13). This component indicates a high mineralization and EC₂₅ values correlated with low temperature and HCO₃ concentration. The correlations of these hydrochemical variables indicate carbonate and silicate weathering control the water chemistry in the basin.

The PCA generates a correlation matrix involve the correlation coefficient between all variables.

A high and positive correlation is measured between Ca and Na (r= 0.98); Ca and Mg (r=0.99); Ca and Cl (r=0.99); Ca and SO₄ (r=0.98).

According to the correlation matrix; major ions have a significant correlation (>0.50) with EC₂₅ is expected and normal (Figure 14).

Negative correlation coefficients are measured between HCO₃⁻ and Na⁺, Ca⁺², Cl⁻, Mg⁺², SO₄⁻² and pH.

Correlation matrix

Variable	T	pH	EC ₂₅	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
T	1.000	-0.002	0.346	0.617	0.314	0.389	0.342	0.333	0.316	0.126
pH	-0.002	1.000	0.568	0.046	0.610	0.515	0.596	0.595	0.612	-0.791
EC ₂₅	0.346	0.568	1.000	0.594	0.997	0.995	0.998	0.999	0.996	-0.549
K ⁺	0.617	0.046	0.594	1.000	0.534	0.649	0.568	0.563	0.534	0.116
Na ⁺	0.314	0.610	0.997	0.534	1.000	0.986	0.998	0.999	1.000	-0.602
Ca ²⁺	0.389	0.515	0.995	0.649	0.986	1.000	0.992	0.992	0.987	-0.508
Mg ²⁺	0.342	0.596	0.998	0.568	0.998	0.992	1.000	1.000	0.999	-0.588
Cl ⁻	0.333	0.595	0.999	0.563	0.999	0.992	1.000	1.000	0.999	-0.588
SO ₄ ²⁻	0.316	0.612	0.996	0.534	1.000	0.987	0.999	0.999	1.000	-0.608
HCO ₃ ⁻	0.126	-0.791	-0.549	0.116	-0.602	-0.508	-0.588	-0.588	-0.608	1.000

Figure 14. Correlation matrix for the different hydrochemical parameters.

According to the the Hierarchical cluster analyse approach has been applied in the basin.

The aim of the analyse is to group similar water samples in hydrogeochemical studies (Pacheco Castro et al., 2017).

According to the cluster analysis; similar water samples was grouped into their major ion concentrations.

The Q mode clustering resulted in three major water groups and six subgroups which were seen from the dendrogram (Figure 15).

The three major groups are distunquished by their EC and TDS values.

Cluster 1 waters have TDS value 14.925 ppm. Cluster 2 waters have TDS value 1366 ppm. TDS values changes between 145-525 ppm in Cluster 3 waters. HCA result is consistent with the Piper plot results.

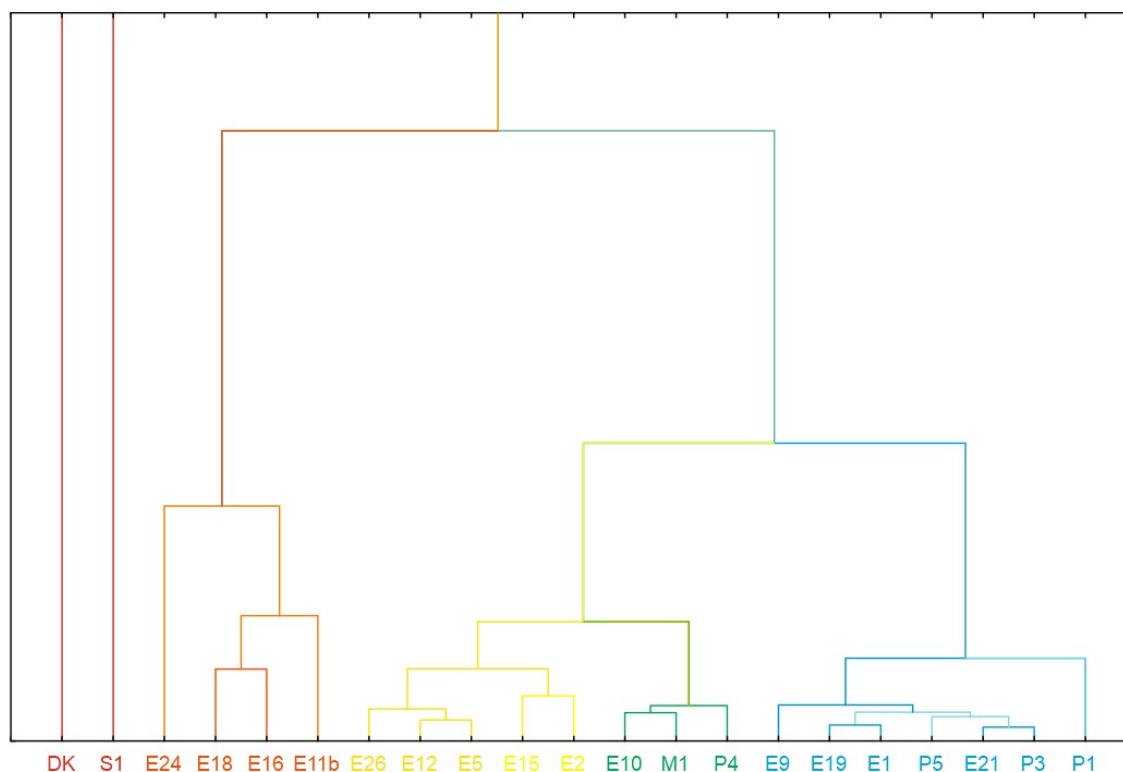


Figure 15. Dendrogram of Hierarchical Cluster Analysis for 21 samples.

CONCLUSIONS

- In this study; hydrochemical applications and statistical techniques were applied. The aim is to understand the hydrochemical evaluation and chemical processes affecting the chemistry of waters in the Seyfe Basin.
- Generally, most of the water samples is dominated by calcium and bicarbonate ions in the basin.
- According to the the Piper diagram; Ca^{+2} and HCO_3^- were dominant ions in western and southern parts of the basin.
- Water types are determined as Ca-HCO_3 for springs; Na-HCO_3 for wells; Na-SO_4 for drainage channel in the dry season and Na-Cl in the rainy season.
- The Gibbs plots indicate that the rock weathering process control the water chemistry in the basin. Drainage channel samples are also influenced by evaporation process.
- According to the hydrochemical assessments; the basin is influenced by rock-water interaction, dissolution of carbonate minerals, weathering of silicate minerals which is supported by Ca/Mg , Na/Cl and Ca+Mg/HCO_3 molar ratios, Gibbs plots, and saturation index values.
- Weathering of silicate minerals control by major ions such as sodium, calcium, magnesium and potassium in the basin.
- The water samples were saturated with respect to calcite, aragonite, dolomite minerals. and were undersaturated with respect to anhydrite, gypsum, sylvite and halite minerals.
- Three major cluster groups were identified using HCA in the basin, which is in accordance with the water types in the Piper plot. Cluster 1 and 2 groups hydrochemical facies of Na-Cl , mixed Ca-Mg-Cl respectively. Cluster 3 exhibits Ca-HCO_3 facies.

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ABSTRACT

The aim of this study is to determine the hydrochemical properties of water resources in the Seyfe Basin and to understand processes involving water chemistry using statistical techniques such as principal component analysis (PCA) and cluster analysis. Seyfe Lake closed basin is located west of Kirsehir (Turkey) in the Central Anatolia. Considering the importance of the Seyfe Lake Basin for its water resources potential and due to its fragile ecosystem, a detailed hydrogeological characterization of the basin has been undertaken. In order to characterize hydrogeological system accurately, water samples were collected from springs, wells and drainage channels during September and December 2019 field campaigns from the Seyfe Lake wetland basin. The temperature, pH, total dissolved solids (TDS) and specific electrical conductance ($EC_{25^{\circ}C}$) were measured at the field and spatio-temporal changes of major ions are evaluated. The waters have neutral to slightly alkaline character, and most of the water samples are saturated with calcite, dolomite and aragonite minerals. According to the results obtained from Gibbs, Piper plot, and PCA, the water-rock interaction takes place without any remarkable ion exchange reactions. Water facies identified with the Piper diagram, supports this view. Water types are determined as $Ca-HCO_3$ for springs: $Na-HCO_3$ for wells: $Na-SO_4$ for drainage channel in the dry season and $Na-Cl$ in the rainy season. In the study area: ionic compositions of the springs are not affected by seasonal changes. The high sulfate concentration is probably related to the weathering of evaporitic rocks in the basin. The waters are grouped according to the results, and the difference observed within the groups are related to the lithology of aquifers and flow path of the waters.

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