

Application of Multivariate Statistical Analysis in Mine Water Hydrogeochemical Studies of the Outcropped Upper Carboniferous, Ruhr Area, Germany

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Abstract

This study aimed to identify the processes controlling the geochemical characteristics of adit mine waters using correlation analysis and multivariate statistical techniques. The Hierarchical cluster analysis (HCA) classified water samples into 5 geochemically distinct clusters of similar characteristics. HCO_3^- and Ca^{2+} were the dominant ions in the mine water (clusters C1, C2, C3, and C4), indicating the processes of carbonate dissolution, while Na^+ was the most abundant of the cations in cluster C5, suggesting processes of rock weathering. Samples of C2, C4, and C5 were of Ca-Na- HCO_3 - SO_4 , Ca-Mg-Na- HCO_3 - SO_4 -Cl, and Na-Ca- HCO_3 - SO_4 types, respectively, while those from C1 and C3 were of Ca-Mg- HCO_3 - SO_4 type. A total of three principal component analysis (PCA) components accounted for 82.95% of the total variance. PCA 1 accounted for a variance of 58.18%, characterized by high positive loadings for HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , TDS, and EC, suggesting carbonate dissolution, rock weathering, and water salinity. The other components may be related to more local and geological effects. This study demonstrated the usefulness of multivariate statistical analysis in hydrogeochemistry.

Keywords: multivariate statistics, cluster analysis, principal component analysis, mine water

Introduction

The last remaining German active hard coal mine was closed in December 2018. However, after mining, the mine water quality is still one of the concern issues nowadays. The study area is a part of the Ruhr coalfield, where the coal-bearing Upper Carboniferous strata crop out directly on the surface of the Ruhr river valley or underneath very thin overlying sediments of Quaternary age (Frankenhoff et al. 2017; Zieger et al. 2018), with about 50 km in East-West length and 15 km North-South width (Drozdowski et al. 2008). It covers an area of about 754 km² (Fig. 1), spreading over the cities Hattingen, Sprockhövel, Witten, Wetter and Schwerte, and including parts of the cities Essen, Bochum, Dortmund, Holzwickede and Herdecke. The topography of the study area is generally shallow hills and undulating terrain, the elevation ranges

between 20 and 333 m above sea level. The highest elevations are in Sprockhövel (about 330 m in Holthausen). The annual average precipitation in the area is 891 mm (DWD 2019). The geology is characterized by Upper Carboniferous cyclothems: sandstone, silt-, mud-, and claystone layers, interspersed with hard coal seams. The layers contain clay minerals and mica (kaolinite, chlorite, biotite), feldspar (albite, anorthite), siderite, dolomite, calcite, quartz, and pyrite (Strehlau 1990; Wisotzky 2017).

It is not easy to identify the processes controlling the geochemical characteristics of mine water, especially in abandoned coal mines, through complex hydrogeochemical data. To protect water resources, it is important to understand processes controlling geochemical variability in such post-mining systems.

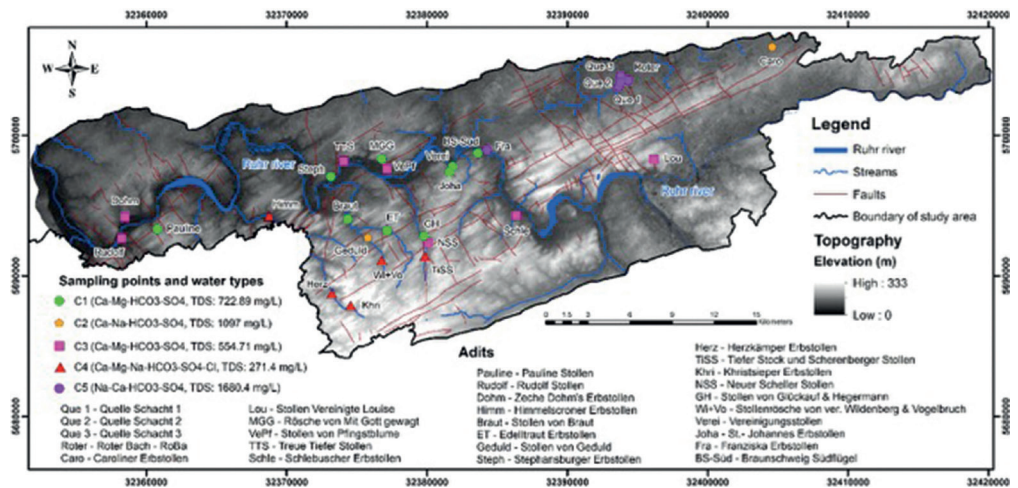


Figure 1 Map of the study area, including sampling points and spatial distribution of the mine water types.

For decades, besides hydrogeochemical and isotopic methods, multivariate analysis techniques have also been used widely in mine water studies (e.g. Li et al. 2018). These methods are performed as useful tools to reduce and organize a large hydrogeochemical data set into a small number of factors, grouping samples with similar characteristics (Reghunath et al. 2002). Multivariate techniques also were used to study the environmental impacts of medieval mining (Horák and Hejzman 2016) or have been extensively applied to groundwater quality data (Khelif and Boudoukha 2018). Moreover, multivariate analysis has been applied to hydrogeochemical data by many researchers to analyze hydrogeochemical parameters to classify groundwater of varied geochemical features and to identify primary processes controlling groundwater chemical components (e.g. Qian et al. 2016).

The purpose of this study was to characterize the chemistry of mine water and to develop hypotheses about processes controlling mine water composition and the origin of the chemical constituents present in mine water of abandoned coal mines in the outcropped Upper Carboniferous of the Ruhr area, Germany. The present study also contributed and demonstrated the usefulness of multivariate statistical analysis in mine water assessment and established a better understanding of hydrogeochemical characteristics of mine water in the study area.

Sample collection and methods

Sampling and analysis

Water samples were collected from the 28 different drainage sites of abandoned coal mines in the study area from January to March 2018. The sampling locations are given in Fig. 1. Physicochemical parameters of water (pH, EC) were measured in situ using portable meters (WTW, Weilheim, Germany). These probes were calibrated using standard solutions, and bottles were washed and rinsed thoroughly with sample water. Samples for cation analysis were acidified using concentrated HNO₃. Samples were stored in the refrigerator at 4 °C until completed analyses. HCO₃⁻ concentrations were measured using HCl titration. Major anions (SO₄²⁻, Cl⁻, NO₃⁻, F⁻) were measured using the DIONEX Ion Chromatography System model ICS-1000, with an AD20 Absorbance Detector system. Major cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) were analyzed by CD25 Conductivity Detector, IP 20 Isocratic Pump DIONEX.

Multivariate statistical techniques

The correlation matrix, Hierarchical cluster analysis (HCA), and Principal component analysis (PCA) methods were used to evaluate the physicochemical parameters of water samples. Spearman correlation was used to evaluate correlations between different variables, using the statistical software SPSS

23, combined with the XL-Stat software to check and compare results. These methods were applied to a subgroup of the dataset to evaluate their usefulness for classifying water samples and identifying relevant geochemical processes. The dataset consisted of 28 hydrogeochemical analyses.

The Q-mode HCA technique was performed on the water chemistry data to classify samples into distinct hydrogeochemical groups using values for 12 physicochemical parameters (HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , F^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , pH, EC, and TDS). The Ward's linkage method with Euclidean distance was used for the measurement of similarity between the water quality variables. The results were represented in a dendrogram. PCA was used to identify major factors governing mine water geochemistry. The varimax rotated factor analyses were carried out for 12 parameters and factor loading was calculated using eigenvalue greater than 1 and sorted by the results having values greater than 0.3. Most mine water physicochemical parameters in this study are non-normally distributed, the Spearman method and Kaiser-Meyer-

Olkin (KMO) test were used to indicate the proportion of common variance

Results and discussion

General hydrogeochemical characteristics

The pH values ranged from 6.39 to 7.65, indicating circum-neutral mine water conditions. EC values were in the range of 202 to 1713 $\mu\text{S cm}^{-1}$ and TDS values ranged between 157 and 1806 mg L^{-1} , which indicates that mine water of several adits is highly mineralized, implying fresh and brackish waters. A Durov diagram (Durov 1948) was plotted for 28 water samples to examine the hydrogeochemical types of mine waters (Fig. 2).

This diagram shows the chemical composition of water in the study area that was formed by the main types: Ca-Mg- HCO_3 - SO_4 , followed by Na-Ca- HCO_3 - SO_4 , Ca-Mg-Na- HCO_3 - SO_4 , and Na-Ca-Mg- HCO_3 - SO_4 water types. The average ion concentrations followed the order: $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$ and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ (% meq L^{-1}). The mine water samples showed the dominance of weak acids (HCO_3^-) over strong acids ($\text{SO}_4^{2-} + \text{Cl}^-$), and

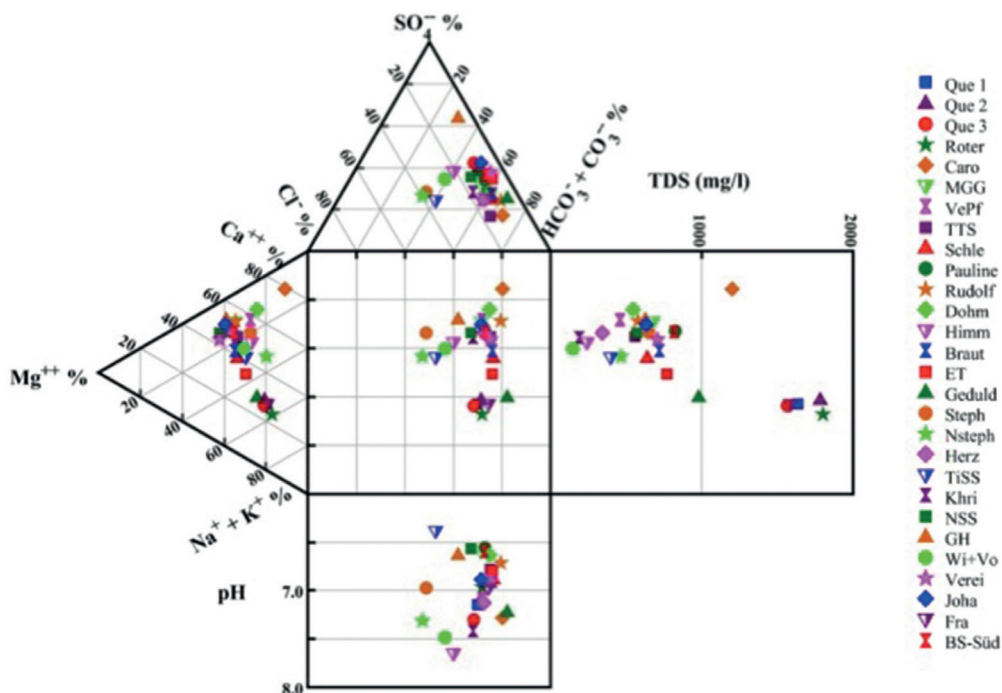


Figure 2 Durov diagram of mine water hydrogeochemistry in the study area.

alkaline earths ($\text{Ca}^{2+} + \text{Mg}^{2+}$) over the alkalis ($\text{Na}^+ + \text{K}^+$).

Multivariate Statistical Analysis

Correlation matrix

The Spearman correlation coefficients were calculated, the results of the correlation matrix for 12 variables are given in Table 1. The interpretation of the correlation matrix showed that the pH values are not correlated with ions.

TDS values are strongly correlated ($r > 0.8$) with most of the ions in the water samples, such as TDS - HCO_3^- ($r = 0.936$) and TDS - SO_4^{2-} ($r = 0.847$), mostly statistically significant at the 0.01 level ($p < 0.01$), while TDS values show a weaker correlation with Cl^- ($r = 0.44$), significant at the 0.05 level ($p < 0.05$).

Na^+ and K^+ in water samples are correlated positively with Cl^- ($r = 0.659$, $p < 0.01$) and ($r = 0.476$, $p < 0.05$), respectively. This may indicate halite/sylvine dissolution influencing mine water chemistry. Ca^{2+} and Mg^{2+} concentrations are correlated with HCO_3^- with $r = 0.738$ ($p < 0.01$). This suggests calcite and dolomite dissolution. Ca^{2+} is also correlated significantly with SO_4^{2-} ($r = 0.796$, ($p < 0.01$)), suggesting possible gypsum dissolution.

Ca^{2+} and Na^+ ions have an average correlation ($r = 0.536$, $p < 0.01$), indicating that Ca/Na ion exchange also increases the Ca^{2+} concentration in the mine water. EC showed strong to moderate positive and negative correlations with HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- and NO_3^- . It reflects the

participation of these elements in the brackish mine water environment in the study area.

Hierarchical Cluster Analysis (HCA)

The main result of the HCA performed on the 28 mine water samples is the Dendrogram (Fig. 3). The Q-mode factor analysis, sampling sites with larger similarities are first grouped. Next, groups of samples are joined with a linkage rule and the steps are repeated until all observations have been classified. Based on the desired level of resolution for interpretation and the potential of the data considered, the number of groups is chosen (Ribeiro and Macedo 1995). Ward's method was more successful to form clusters, with the phenomena line of 2.5. Results showed that the HCA classified mine water samples into 5 geochemically distinct clusters (C1-C5) of similar characteristics, represented in Dendrogram to categorize different levels, which the Stiff diagrams show for each group (Fig. 3).

Samples of C2, C4, and C5 are of $\text{Ca-Na-HCO}_3\text{-SO}_4$, $\text{Ca-Mg-Na-HCO}_3\text{-SO}_4\text{-Cl}$, and $\text{Na-Ca-HCO}_3\text{-SO}_4$ types, respectively, while those from C1 and C3 are of $\text{Ca-Mg-HCO}_3\text{-SO}_4$ type. The C4 cluster accounts for 17.9% of the total samples, including 5 samples, with the average EC and TDS values of $301.6 \mu\text{S cm}^{-1}$ and 271.4 mg L^{-1} , respectively, mostly distributed in the southern part (the highest elevation). C3 consists of 7 samples located at a lower elevation, accounts for 25% of the total samples (average EC: $579.71 \mu\text{S cm}^{-1}$ and mean TDS: 554.71 mg L^{-1}). The common feature of these water types is low

Table 1 Spearman correlation matrix of major physicochemical parameters.

	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	F	Ca^{2+}	Mg^{2+}	Na^+	K^+	pH	EC	TDS
HCO_3^-	1.000	0.758	<u>0.436</u>	-0.728	0.210	0.738	0.738	0.751	0.827	-0.036	0.877	0.936
SO_4^{2-}		1.000	<u>0.433</u>	-0.595	0.319	0.796	0.928	0.675	0.759	-0.140	0.898	0.847
Cl^-			1.000	-0.172	0.114	0.639	<u>0.417</u>	0.659	<u>0.476</u>	0.014	0.573	<u>0.440</u>
NO_3^-				1.000	-0.332	<u>-0.376</u>	-0.668	-0.557	-0.677	0.170	-0.537	-0.602
F					1.000	-0.014	0.231	<u>0.477</u>	<u>0.380</u>	0.185	0.268	0.299
Ca^{2+}						1.000	0.718	0.536	0.646	-0.063	0.865	0.767
Mg^{2+}							1.000	0.630	0.733	-0.268	0.794	0.773
Na^+								1.000	0.837	0.099	0.804	0.773
K^+									1.000	0.029	0.870	0.851
pH										1.000	0.038	-0.075
EC											1.000	0.933
TDS												1.000

Bold indicates correlation is significant at the 0.01 level (2-tailed),

Underlined indicates correlation is significant at the 0.05 level (2-tailed).

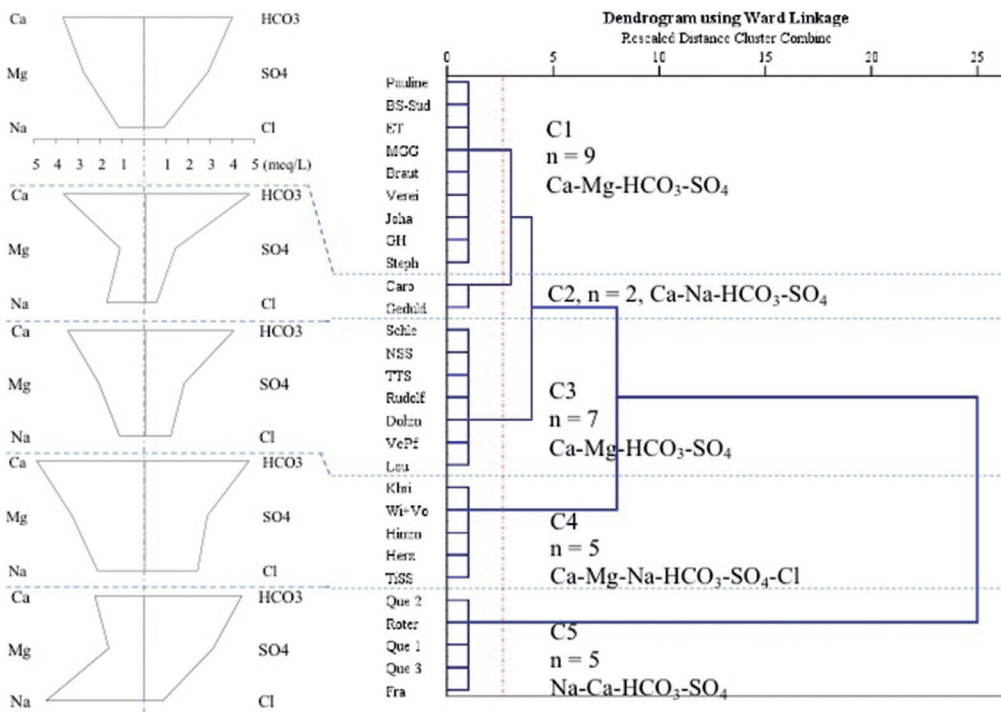


Figure 3 Dendrogram of the major ions in mine water and corresponding Stiff diagrams.

salinity. C1 is composed of 9 samples and represents 32.1% of the total samples. This water type is relatively fresh, with an average EC of $746.89 \mu\text{S cm}^{-1}$ (mean TDS = 722.89 mg L^{-1}), mostly distributed in the central study area (Fig. 1). C2 included by two water samples (mean EC and TDS values of $897.5 \mu\text{S cm}^{-1}$ and 1097 mg L^{-1} , respectively), characteristic for mixed water. C5 is represented by 5 samples, with an average EC of $1609.8 \mu\text{S cm}^{-1}$ (mean TDS = 1680.4 mg L^{-1}), interpreting the character of blended water and characterized by high salinity, mostly distributed in the east-northern part (Fig. 1). HCO_3^- and Ca^{2+} were the dominant ions in the mine water of the study area (clusters C1, C2, C3, and C4), while Na^+ was the most abundant of the cations (cluster C5). The Que 2, Roter, Que 1, Que 3 and Fra water samples presented the highest average values of HCO_3^- , Ca^{2+} , SO_4^{2-} and Na^+ ions.

Principal Component Analysis (PCA)

The PCA was used to identify major factors governing groundwater geochemistry by many researchers (e.g. Qian et al. 2016). The value of the KMO test is $0.752 > 0.5$, indicating

the total number of significant factors. The loadings of different elements, including the total eigenvalues of different factors, the percentage of variances, and the percentage of cumulative variances are summarized in Table 2. A system of orthogonal axes is created, which helped to visualize the projections of the data matrix elements in a plan diagram (Fig. 4).

From the hydrogeochemical data, a total of three PCAs were extracted with total eigenvalues higher than 1 which account for 82.95% of the total variance (Table 2). Three components reflect the major effective factors controlling the mine water chemistry.

The PCA 1 contributed 58.18% of the total variance and is characterized by high positive loadings on HCO_3^- , SO_4^{2-} , Ca^{2+} , and Mg^{2+} (Table 2, Fig. 4). High scores of this component indicate high mineralization of mine water. This suggested that PCA 1 represented the dissolution or precipitation processes of carbonate, such as calcite and dolomite and sulfate minerals (Qian et al. 2016). However, PCA 1 had also high positive loadings for Na^+ , K^+ , TDS, EC, and Cl^- (Table 2, Fig. 4), suggested that it represented rock weathering

Table 2 Loadings of different parameters for the three PCAs following varimax rotation.

Parameters	Principal Components		
	PCA 1	PCA 2	PCA 3
HCO ₃ ⁻	0.913	-0.163	0.184
SO ₄ ²⁻	0.873	-0.192	0.249
Cl ⁻	0.650	0.354	-0.230
NO ₃ ⁻	-0.275	0.839	-0.277
F ⁻	0.206	0.014	0.843
Ca ²⁺	0.802	-0.018	-0.397
Mg ²⁺	0.738	-0.559	0.097
Na ⁺	0.852	0.035	0.419
K ⁺	0.785	-0.240	0.197
pH	0.059	0.801	0.360
EC	0.974	-0.082	0.184
TDS	0.944	-0.118	0.193
Total eigenvalue	6.981	1.702	1.271
% of variance	58.18	14.18	10.59
% of cumulative variance	58.18	72.36	82.95

High loading values are highlighted in **bold**

and water salinity. It is addressed as the highly mineralized factor, because of exhibited high loadings on TDS (0.944), EC (0.974), SO₄²⁻ (0.873), Cl⁻ (0.65) and Na⁺ (0.852). Therefore, mine water is not only contributed by Ca²⁺ and Mg²⁺ but also contributed by Na⁺. It implied that it might be represented the ion exchange. The PCA 2 was 14.18% of the total variance in mine water dataset, with mainly consisted of NO₃⁻ and pH (Table 2, Fig. 4), implied that it might be the consequence of agricultural activities in the study area. The PCA 3 explained 10.59% of the total variation of the matrix data and mainly consisted of F⁻ (Table 2, Fig. 4), suggested that it was contributed from the primary geological environment (Teng et al. 2018). Moreover, in Table 2, the PCA 3 had also a low positive loading on Na⁺ (0.419) and a negative one for Ca²⁺ (-0.397), implied that ion exchange processes may occur in the mine water environment, as mentioned above.

Conclusions

Multivariate statistical methods were used to characterize the origin of the chemical constituents present in mine water of abandoned coal mines in the study area. The correlation of ions in mine water was assessed. The dissolution of carbonate, sulfate, silicate, and chloride minerals are the primary processes controlling mine water chemical composition. The HCA in

Q-mode showed 5 statistical groups based on the major distinguishing factors of EC and TDS values. The PCA identified three principal components, which explained 82.95% of the total variance. The first PCA accounted for 58.18% of the total variance and is related to rock weathering, such as dissolution or precipitation of carbonate and sulfate minerals, ion exchange processes, and water salinity, while the other components are controlled primarily by agricultural activities and local geological environment (14.18% and 10.59%, respectively). The results of this study illustrated the usefulness of multivariate statistical analysis in hydrogeochemical studies.

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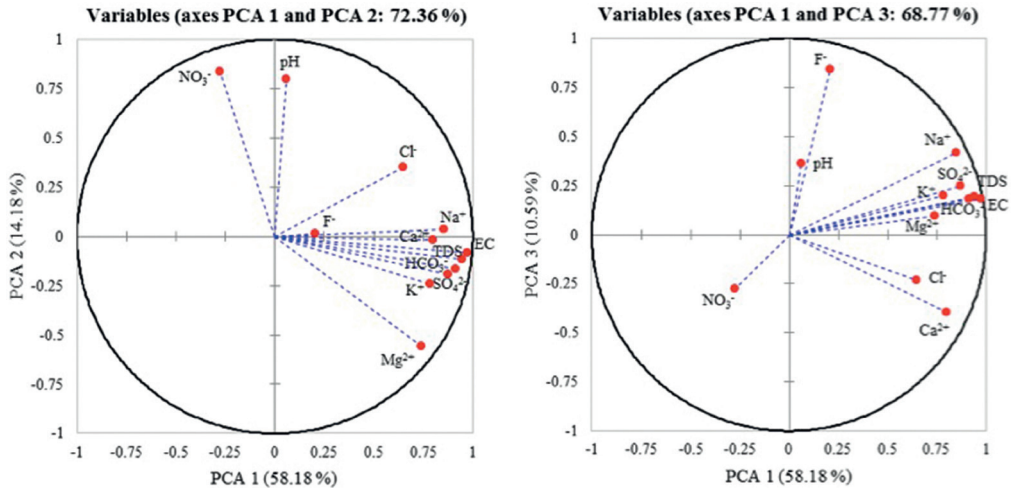


Figure 4 Representation of the parameters in the factorial plan PCA 1-PCA 2 and PCA 1-PCA 3.

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