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Water quality assessment of the Cassaffousth Reservoir using multivariate statistical techniques

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Abstract. Lakes, rivers and reservoirs are the main water resources for multiple purposes, so it is important to have reliable information on the state and quality of the resource through the implementation of a monitoring plan. Due to spatial and temporal variations in water quality, these programs must include a large number of physicochemical and biological parameters taken at different sampling sites, which implies large financial inputs, generating a complex data matrix that is difficult to interpret. Thus, it is necessary to optimize these monitoring, without losing useful information through the application of different multivariate statistical techniques, which allow a better interpretation and understanding of extensive and complex databases. The objective of this work was to analyze the water quality variability of the Cassaffousth reservoir (Córdoba, Argentina), detecting the main sources of contamination. On a data matrix obtained during a monitoring program carried out in 2016, several statistical techniques were applied, finding differences and similarities between sampling sites and measured variables. By means of cluster analysis (CA), sites with similar characteristics were grouped. A principal component analysis (PCA) was performed to detect similarities between the measured variables. It was also observed that the greatest variation in water quality was explained by soluble salts, while the rest of the variation was related to nutrients, organic pollutants and physical parameters. Based on the results, it was possible to optimize the sampling strategy, reducing the number of sampling sites and measured variables, which would lead to a reduction of economic costs.

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Resumen. Los lagos, ríos y embalses constituyen los principales recursos hídricos para múltiples propósitos, por lo que es importante tener información confiable del estado y calidad del recurso mediante la implementación de un plan de monitoreo. Debido a las variaciones espaciales y temporales de la calidad del agua, estos programas deben incluir un gran número de parámetros fisicoquímicos y biológicos tomados en diferentes sitios de muestreo y en diferentes momentos del año lo que implica grandes insumos financieros, generando una matriz de datos de difícil interpretación. Así, surge la necesidad de optimizar estos monitoreos, sin perder información útil mediante la aplicación de diferentes técnicas estadísticas multivariadas, lo que permite una mejor interpretación y comprensión de las bases de datos. El objetivo de este trabajo fue analizar la variabilidad de la calidad del agua del embalse Cassaffousth (Córdoba, Argentina), detectando las principales fuentes de contaminación. Para ello, se realizaron muestreos bimestrales en siete sitios de muestreos seleccionados estratégicamente, con el fin de analizar la variabilidad espacial y temporal del recurso durante el año 2016. Se aplicaron diversas técnicas estadísticas multivariadas que permitieron encontrar diferencias y similitudes entre sitios de muestreo y variables medidas. El análisis de cluster agrupó los sitios de muestreo con características similares y el análisis de componentes principales detectó similitudes entre las variables medidas. Se observó que la mayor variación en la calidad del agua fue explicada por la cantidad de sales solubles, mientras que el resto de la variación se relacionó con nutrientes, contaminantes orgánicos y parámetros físicos. Estos resultados permitieron optimizar la estrategia de muestreo , reduciendo el número de sitios de muestreo y variables medidas, y de esta manera disminuir los costos económicos.

INTRODUCTION

Surface water quality is a matter of serious concern today. Anthropogenic influences (urban, industrial and agricultural activities, increasing exploitation of water resources) as well as natural processes (changes in precipitation, erosion, weathering of crustal materials) degrade surface water quality and impair their use for drinking, industrial, agricultural, recreation or other purposes (Varol et al. 2012; Damir et al. 2017).

Because lakes, reservoirs and rivers constitute the main inland water resources for different purposes, it is imperative to prevent and control water pollution and to have reliable information on water quality (Bonansea et al. 2015). Therefore, regular monitoring programs are required for representative and reliable estimates of surface water quality (Kazi et al. 2009; Xiaoyan et al. 2017).Due to spatial and temporal variations in water quality, such programs need to include a large number of physicochemical parameters taken at different times and from many sites involving huge financial inputs and resulting in a large and complex data matrix which is often difficult to interpret towards drawing meaningful conclusions. Thus, there is a need to optimize the monitoring networks, reducing the number of water quality parameters, sampling sites and monitoring periods to representative ones without losing useful information (Singh et al. 2004). Thus, the application of different multivariate statistical techniques for interpretation and better understanding of water quality is required when large and complex databases are used. These techniques also allow identification of the possible factors/sources that are responsible for the variations in the water quality and influence the water system and in apportionment of the sources, which, thus offers valuable tool for developing appropriate strategies for effective management of the water resources (Singh et al. 2005).

The objective of this study was to analyse the water quality variability of Cassaffousth reservoir (Argentina), detecting the main sources of contamination. In the present study, a data matrix obtained during a one-year monitoring program was subjected to different multivariate statistical techniques to evaluate data and draw conclusions about the similarities and dissimilarities existing between sampling sites and measured variables, as well as to identify variables responsible variations in water quality. The influence of pollution sources on reservoirs water quality was ascertained. Thus, we illustrated the usefulness of the multivariate statistical analysis to improve the understanding of the surface water system.

METHODOLOGY

Study area

Cassaffousth reservoir (32° 10´ S, 64° 23´ W) (Figure 1), located in the western region of Córdoba province, has an area of 86 ha, a volume of 10.5 hm^3 and a maximum and mean depths of 28.7 and 11.9 m, respectively (Dippolito 1988). This reservoir is the fourth of a system of six chained reservoirs, which were built between 1930 and 1950 for multiple purposes such as water supply, power generation, flood control, irrigation, tourism and recreational activities (Boltovskoy et al. 1999; Bonansea et al. 2016). Cassaffousth reservoir receives water from Río Tercero reservoir, which is the largest artificial lake in the province of Córdoba, and has a unique effluent called Tercero river.

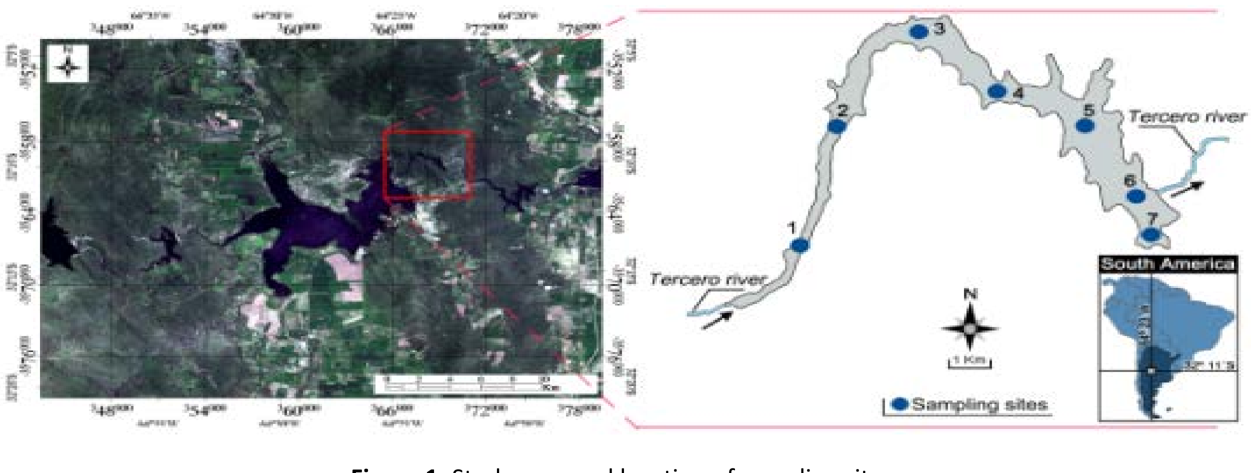

Figure 1: Study area and location of sampling sites.

Sampling and analytical procedures

Water samples were collected bimonthly during 2016. Seven sampling sites, distributed uniformly across the reservoir, were evaluated (Figure 1). The methodology of sampling, preservation and transportation of the water samples to the laboratory were performed according to standardized methods (APHA-AWWA-WEF 2000). Water samples were taken at 20 cm depth. A total of 19 parameters were analyzed. *In situ*, water temperature (WT), pH, dissolved oxygen (DO), electrical conductivity (EC) and Secchi disk transparency (SDT) were evaluated. In laboratory, we have evaluated total dissolved solid (TDS), bicarbonates (HCO_3^-), nitrate (NO_3), sulphate (SO_4), chloride (Cl), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), fluoride (F), total hardness (T-Hard), total alkalinity (T-Alk), RAS and chlorophyll-a concentration (Chl-a)

Statistical analysis

Collected samples were analysed using InfoStat statistical software (Di Rienzo et al. 2016). One way multivariate analysis of variance (MANOVA) and one way analysis of variance (ANOVA) were performed as a first approach to compare the significant spatial and temporal differences of water quality variables ($p < 0.05$; least significance difference, LSD).

Pearson´s correlation analysis was made to obtain a measure of the magnitude and direction of association between variables. Multivariate statistical analysis for classification modeling and interpretation of large datasets from environmental monitoring programs allow the reduction of the dimensionality of the data and the extraction of information that will be useful for water quality assessment (Simeonov et al. 2003). Multivariate analysis of the reservoir water quality data set was performed through principal component analysis (PCA), cluster analysis (CA) and source apportionment by multiple regression analysis on principal components. The data set was previously standardized using z-scale transformation in order to avoid misclassifications arising from the different orders of magnitude of both numerical value and variance of the parameters analyzed (Wunderlin et al. 2001; Singh et al. 2004).

CA technique

CA was applied to detect similarity clusters or groups between sampling sites. The resulting clusters should then exhibit high internal (within-cluster) homogeneity and high external (between clusters) heterogeneity (Shrestha et al. 2007). Hierarchical clustering is the most common approach in which clusters are formed sequentially, by starting with the most similar pair of objects and forming higher clusters step-by-step. Result can be displayed as a dendrogram, which presents a picture of the groups and their proximity to one another, with a dramatic reduction in the dimensionality of the original data (Zhao et al. 2012). Hierarchical CA was performed using the Ward's method and the Euclidean distances as a measure of similarity. The Ward's method uses an analysis of variance approach to evaluate the distances between clusters, attempting to minimize the sum of squares of any two clusters that can be formed at each step (Wunderlin et al. 2001). The Euclidean distance usually gives the similarity between two samples and a distance can be represented by the difference between analytical values from the samples (Otto 1998). In this study, hierarchical agglomerative CA was performed on the normalized data set by means of the Ward´s method using squared Euclidean distances as a measured of similarity. The Ward´s method uses an analysis of variance approach to evaluate the distances between clusters in an attempt to minimize the sum of squares (SS) of any two clusters that can be formed at each step. The linkage distance is reported as Dlink/Dmax, which represents the quotient of the linkage distances for a particular case divided by the maximal distance, multiplied by 100, as a way to standardise the linkage distance represented on the y-axis (Varol et al. 2012).

PCA technique

The PCA technique starts with the covariance matrix describing the dispersion of the original variables, and extracting the eigenvalues and eigenvectors. An eigenvector is a list of coefficients by which we multiply the original correlated variables to obtain new uncorrelated (orthogonal) variables called principal components (PC), which are weighted linear combinations of the original variables. A PC is the product of the original data and an eigenvector; the result of projecting the data on to a new axis is a new variable. There are as many PC as original variables. However the first PC loading explains the most variance and each subsequent component explains progressively less. As a result, a small number of factors usually account for approximately the same amount of information as the much larger set of the original observations do (Chen et al. 2007). Thus, PC provides information on the most meaningful parameters, which describe the whole data set affording data reduction with minimal loss of information. The PC loadings can be examined to provide further insight into the processes that are responsible for the similarities in the trace element concentrations in the water samples (Helena et al. 2000; Wunderlin et al. 2001; Singh et al. 2004).

Source apportionment

The source apportionment is an important environmetric approach aiming to the estimation of contribution of identified sources to the concentration of each parameter (Simeonov et al. 2003). After the determination of the number and identity of possible sources affecting surface waters by using PCA technique, source contribution was calculated using multiple regression of sample mass concentration on the absolute PC scores. A detailed description of the modelling approach can be found in Thurston and Spengler (1985). Source apportionment technique makes it possible to apportion the component mass among various source components obtained by PCA. The PCA assumes the total concentration of each element is made up of the sum of elemental concentrations from each identified component. The approach calculates the weight of source in the total sum using multiple regressions.

RESULTS AND DISCUSSION

Physical, chemical and biological analysis

The basic statistics of the 19 water quality variables measured in Cassaffousth reservoir are summarised in Table 1. These results were compared with the maximum limits recommended by the World Health Organization (WHO 2006), revealing that the concentrations of all analysed parameters were below the prescribed maximum limits by WHO guidelines for drinking water.

MANOVA indicated significant temporal and spatial variations ($p < 0.05$). Significant spatial variations ($p < 0.05$) were observed in almost all water quality variables except for pH, DO, Chl-a and F.

Table 2 shows the Pearson correlation matrix of the 19analysed variables. Only those correlation values higher than 0.50 were considered and highlighted. High and positive correlations were observed between EC, TDS, HCO_3^-, Cl, Na, K, Ca, F, T-Hard, T-Alk, and RAS (r = 0.61 to 0.97; $p < 0.50$). Most of these associations are responsible for water mineralization, being directly related to hydrochemical characteristics of the region. EC is always determined by the presence of dissolved substances that are dissociated in anions and cations (Kazi et al. 2009). This affirmation explains the relation between EC with TDS, T-Alk, T-Hard, Ca, Cl, K, and Na, among others. The positive correlation between NO_3 and Chl-a (r = 0.76) indicates the relationship between nutrients and phytoplankton growth. As expected, DO is negatively correlated with WT (r = -0.71) because the solubility of oxygen in water decreases with increasing temperature (Vega et al. 1998; Helena et al. 2000; Varol et al. 2012).

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Table 1: Mean, range and standard deviation (Sd) values of water quality parameters measured in the studied reservoir.

Parameters	WHO limits	Mean±Sd	Range
WT (°C)	-	17.11±6.39	11.70-29.40
Ph	6.5-8.5	7.44±0.58	6.88-8.90
DO (mg/L)	-	8.09±1.89	4.80-12.80
EC (µS/cm)	1500.00	0.18±0.03	0.15-0.22
SDT (m)	-	3.37±1.69	1.00-7.00
Cl-a (µg/L)	-	16.23±12.39	1.76-40.44
TDS (mg/L)	1000.0	183.25±29.16	149-223
HCO_3^- (mg/L)	-	103.13±16.89	82.50-125.00
NO_3 (µg/L)	-	0.51±0.74	0.00-1.80
SO_4 (mg/L)	250.0	29.21±4.36	21.20-35.40
Cl (mg/L)	250.0	4.65±1.24	2.90-5.70
Na (mg/L)	200.0	16.00±5.05	11.00-22.20
K (mg/L)	12.0	2.54±0.44	2.10-3.10
Ca (mg/L)	100.0	20.40±2.77	19.20-27.20
Mg (mg/L)	50.0	6.49±2.02	4.40-9.80
F (mg/L)	1.5	0.20±0.08	0.10-0.30
T-Hard (mg/L)	500.0	1.55±0.20	1.30-1.80
T-Alk (mg/L)	200.0	1.65±0.27	1.30-2.00
RAS	-	0.78±0.23	0.50-1.20

Table 2: Pearson correlation matrix of the 19 variables determined.

	WT	pH	DO	EC	SDT	Cl-a	TDS	HCO_3	NO_3	SO_4	Cl	Na	K	Ca	Mg	F	T-Hard	T-Alk	RAS
WT	1																		
Ph	-0.39[b]	1																	
DO	**-0.71**[a]	-0.26	1																
EC	**0.63**[a]	**-0.58**[a]	-0.47	1															
SDT	**-0.80**[a]	0.24	0.47	**-0.52**[a]	1														
Cl-a	-0.34	**-0.50**[a]	0.34	0.29	0.44	1													
TDS	0.60	-0.54	-0.43	**0.97**[a]	-0.51	0.37	1												
HCO_3	0.48	-0.49	-0.36	**0.96**[a]	-0.36	0.45	**0.98**[a]	1											
NO_3	0.37	-0.33	-0.3	**0.86**[a]	-0.36	**0.76**[b]	0.81	**0.83**[a]	1										
SO_4	0.38	-0.51	-0.16	0.66	-0.51	0.29	**0.78**[b]	0.68	0.53	1									
Cl	**0.77**[b]	**-0.80**[b]	-0.31	**0.91**[a]	-0.65	0.36	**0.88**[a]	**0.82**[a]	0.67	0.63	1								
Na	**0.91**[a]	-0.49	-0.62	**0.85**[a]	**-0.83**[a]	-0.02	**0.84**[a]	0.75	0.66	0.60	**0.87**[a]	1							
K	**0.88**[a]	-0.44	-0.53	**0.80**[b]	**-0.81**[b]	0.02	**0.76**[b]	**0.71**[b]	**0.72**[b]	0.44	**0.81**[b]	**0.95**[a]	1						
Ca	0.06	-0.10	-0.46	0.61	-0.02	0.39	0.63	0.60	0.54	0.62	0.42	0.37	0.16	1					
Mg	0.43	-0.47	-0.14	0.45	-0.36	0.04	0.50	0.53	0.16	0.20	0.49	0.44	0.49	-0.20	1				
F	0.33	0.08	**-0.77**[b]	**0.73**[b]	-0.34	0.16	**0.70**[b]	**0.70**[b]	**0.79**[b]	0.39	0.43	-0.64	0.64	0.60	0.19	1			
T-Hard	0.37	-0.39	-0.48	**0.76**[b]	-0.26	0.23	**0.81**[b]	**0.82**[a]	0.43	0.53	0.64	0.59	0.47	0.52	**0.73**[a]	0.57	1		
T-Alk	0.44	-0.46	-0.34	**0.94**[a]	-0.33	0.45	**0.97**[a]	**0.97**[a]	**0.82**[a]	**0.70**[b]	**0.78**[b]	**0.72**[b]	0.68	0.60	0.53	**0.71**[b]	**0.83**[a]	1	
RAS	**0.94**[a]	-0.43	-0.64	**0.77**[b]	**-0.85**[a]	0.10	**0.74**[b]	0.63	0.61	0.50	**0.82**[a]	**0.82**[a]	**0.94**[a]	0.31	0.32	0.59	0.44	0.59	1

[a] Correlation is significant at the 0.01 level (2-tailed); [b] Correlation is significant at the 0.05 level (2-tailed); bold indicates correlation values higher than 0.50.

Spatial similarities

CA was applied on reservoirs water quality data, to detect similarity for grouping of sampling sites. This technique rendered a dendrogram (Figure 2) where all seven sampling sites were grouped into three statistically significant clusters.

The clustering procedure generated groups in a very convincing way. The elements of each as the elements in these groups had similar characteristic features and natural background source types. Besides, each cluster represented geographical location of sampling sites into the reservoir. Cluster 1 corresponded to sites 1 and 2, which were located in the beginning of the reservoir, receiving waters from Rio Tercero river. Cluster 2 included sites 3 to 6, which were located in the central region of the reservoir. This cluster was surrounded by natural vegetation, being related with few anthropogenic activities, so it was classified as a relatively low polluted region. Cluster 3 was generated by site 7 and was situated in the west region of the reservoir. The results obtained with the spatial CA suggested that for rapid assessment of water quality, only one site in each cluster may serve as a good spatial assessment of the water quality of the whole system.

According to Singh et al. (2004) and Kazi et al. (2009), the CA technique is useful in offering reliable classification of surface waters in the whole region and will make possible to design a future sampling strategy in an optimal manner. Thus, sampling frequency, number of sites and cost in the monitoring network will be reduced without missing much information.

Data structure determination

PCA was applied to the normalized data to compare the compositional patterns between the analysed water samples and to identify the factors that influence each one. Results of PCA are summarized in Table 3. There are several criteria to identify the number of PCs to be retained in order to understand the underlying data structure (Chen et al. 2007). In the present study, all the PCs with eigenvalues equal to or greater than 1.0 were used. Thus, four PCs with eigenvalues > 1 were retained, explaining the 93 % of the total variance in the water quality data set.

The first PC (PC1) accounting for 59.65 % of the total variance, had positive loadings for WT, EC, TDS, HCO_3, SO_4, Cl, Na, K, Ca, Mg, F, T-Hard, T-Alk, and RAS. This PC can be related to natural sources of the ionic groups of salts in the basin of the reservoir from inflows, soil weathering and runoff, so this PC was defined as the "mineral" component.

The second PC (PC2) explained 15.23 % of the total variance, and had positive loadings of NO_3 and Chl-a and negative loadings of WT and SDT. This PC was named as the "nutrient" source of the variability. The strong positive loading of NO_3 represented the contribution of point (municipal effluents) and non-point source pollution (agricultural runoff). In the studied region, farmers use nitrogenous fertilizers, which undergo nitrification processes, and the rivers receive nitrate nitrogen via groundwater leaching (Shrestha et al. 2007). The inverse relationship between WT and NO_3 reflected the biochemical re-

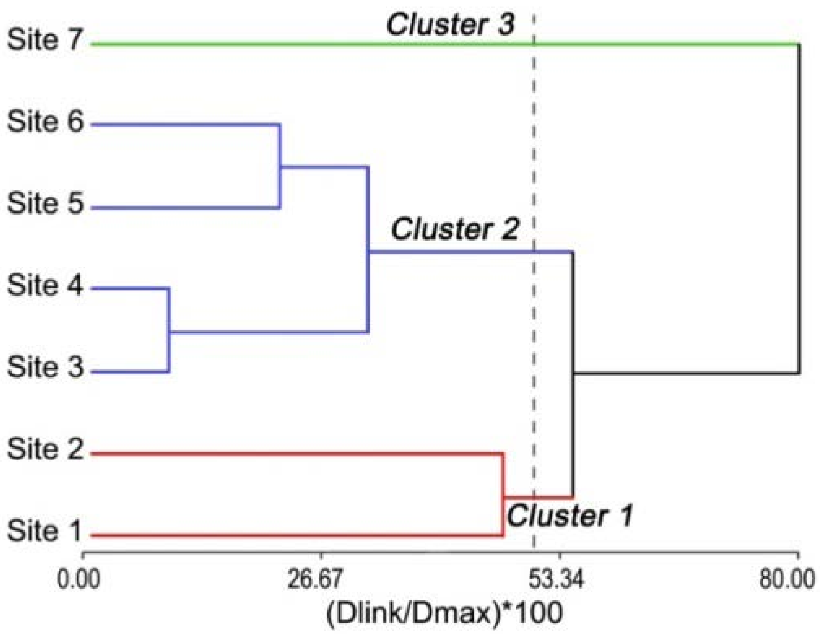

Figure 2: Dendrogram showing hierarchical clustering of sampling sites.

action and self-purification of the stream, as NO_3 decreases with higher temperature (Wang et al. 2013). Besides, the contribution of NO_3 could be related with the growth and development of algal blooms, increasing the primary productivity and eutrophication processes of the whole system. The negative loading of SDT in this PC, could be related with Chl-a which produces a decrease of SDT (Bonansea *et al*. 2015).

The third component (PC3) showed 11.07 % of the total variance, and had positive loadings on pH and DO, representing the "physicochemical" source of the variability. The last PC (PC4) explained 7.05 % of the variance, and as did not define any particular relationship between variables, was called as the "undefined" source of variability.

Results suggested that most of the variation in water quality was explained by a set of soluble salt (natural), while the rest of the variation was related with nutrients (point sources such as municipal effluents and non-point such as erosion and agricultural runoff), organic pollutants (anthropogenic), physical parameters and undefined sources. In this study, the PCA did not lead to significant data reduction as we still needed 19 parameters to explain 93 % of the data variance. However, PCA served as a means to identify those parameters that had the greatest contribution to variation in reservoir water quality and suggested possible sets of pollution sources in the watershed (Varol et al. 2012).

Table 3: Loadings of experimental variables (19) on the first four PCs for the data set.

Parameters	PC1	PC2	PC3	PC4
WT	**0.22**	**-0.38**	-0.09	-0.08
Ph	-0.17	-0.06	**0.53**	0.14
DO	-0.16	0.21	**0.47**	-0.14
EC	**0.29**	0.12	0.30	-0.02
SDT	-0.20	**-0.36**	0.11	0.21
Cl-a	0.08	**0.48**	-0.21	-0.19
TDS	**0.29**	0.12	-0.05	0.04
HCO_3^-	**0.28**	0.19	-0.02	0.13
NO_3	0.12	**0.33**	0.12	**-0.21**
SO_4	**0.21**	0.14	-0.06	**-0.21**
Cl	**0.27**	-0.01	-0.21	-0.10
Na	**0.28**	-0.20	0.02	-0.08
K	**0.26**	-0.22	-0.02	-0.05
Ca	**0t.26**	0.18	0.33	-0.19
Mg	**0.25**	-0.08	-0.30	0.34
F	**0.21**	0.06	0.42	0.07
T-Hard	**0.23**	0.13	0.01	**0.50**
T-Alk	**0.27**	0.21	0.01	0.15
RAS	**0.26**	-0.27	0.05	-0.17
Eigenvalue	11.24	2.17	2.09	1.27
% Total variance	59.65	15.23	11.07	7.05
Cumulative % variance	59.32	74.12	85.54	92.41

Source apportionment

The source apportionment is an important environmental approach aiming to the estimation of contribution of identified sources to the concentration of each parameter. The approach calculates the weight of source in the total sum using multiple regressions (Simeonov et al. 2003). The contribution of the possible source in each source type is presented in Table 4. As evident from the higher determination coefficients (R^2) the multiple regression analysis exhibited good adequacy between the measured and predicted values for most parameters. Therefore, PC assumes that the total concentration of each element is composed of the sum of the elemental concentrations of each pollutant component or identified natural source (Singh et al. 2005). Results showed that natural sources of the ionic groups of salt from inflows, soil weathering and runoff were the main contribution to the mineral factor. Point (municipal effluents) and non-point sources (agricultural runoff, erosion, and atmospheric deposition) were the main contributors to the nutrient parameters, whereas the physicochemical factors are mainly caused by anthropogenic pollution sources. According to Simeonov et al. (2003), this analysis could be used by local authorities for the pollution control/ management of a surface water.

Table 4: Source contribution to surface water in Cassaffousth.

Variables	Intercept	1- Mineral	2- Nutrient	3- Physicochemical	4- Undefined	R^2
WT	18.28	1.59	-2.74	-	-	0.94
Ph	7.49	-0.12	-	0.37	-	0.90
DO	7.85	-0.43	0.57	-1.27	-	0.87
EC	0.18	0.01	0.003	-	-	0.98
SDT	3.31	-0.30	0.55	-	-	0.82
Cl-a	13.91	-	5.12	-	-	0.66
TDS	183.25	8.45	3.41	-	-	0.98
HCO_3^-	103.13	4.66	3.15	-	2.22	0.97
NO_3	0.51	0.18	-	-	-	0.64
SO_4	29.21	0.92	-	-	-	0.50
Cl	4.65	0.34	-	-0.26	-	0.93
Na	16.00	1.41	-1.02	-	-0.41	0.98
K	2.54	0.12	-0.10	-	-	0.91
Ca	2.25	0.2	-	-	-	0.90
Mg	6.49	0.31	-	-0.60	1.29	0.96
F	0.20	0.02	-	0.03	-	0.89
T-Hard	1.55	0.05	-	-	0.10	0.88
T-Alk	1.65	0.07	0.06	-	0.04	0.97
RAS	0.78	0.06	-0.06	-	-0.04	0.98

CONCLUSIONS

The quality of the water of the planet is one of the main problematic, to this is added the amount available for human use. Therefore the use of this resource should be careful. In this study, different multivariate statistical techniques were used to evaluate the spatial variations in the surface water quality of the Cassaffousth reservoir.

Hierarchical cluster analysis grouped seven sampling sites into three clusters of similar water quality characteristics. With these results we can design an optimal future sampling strategy, reducing the number of sampling stations and thus the costs. Although the PCA did not results in a significant data reduction, it helped extract and identify the factors or sources responsible for variations in reservoir water quality. Four PCs indicated that the parameters responsible for water quality variation were mainly related to soluble salt (natural), organic pollution and nutrients (point and non-point), physicochemical parameters and undefined. Sources contributions were calculated using multiple regressions.

1. This study illustrates the usefulness of multivariate statistical techniques for analysis and interpretation of complex data sets, and in water quality assessments, identification of pollution sources and understanding variations in water quality for effective reservoir water quality management.

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