Turk. J. Fish.& Aquat. Sci. 19(9), 727-737
http://doi.org/10.4194/1303-2712-v19_9_02

Turkish Journal of
FISHERIES and
AQUATIC SCIENCES

RESEARCH PAPER

Determination of Spatial and Temporal Changes in Water Quality at Asi River Using Multivariate Statistical Techniques

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Article History
Received 08 March 2018
Accepted 28 August 2018
Early View 31 August 2018

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Keywords
Orontes River
Environmental impact assessment
Cluster analysis
Discriminant analysis
Principal component analysis

Abstract

Water quality in surface waters is a critical issue since they are used in domestic, agricultural and industrial purposes. Therefore, proper water management strategies should be taken care of to protect water bodies. To accomplish this goal, ten years (2004-2014) seasonal water quality monitoring results consisting of 16 parameters (BOD_5, COD, DO, NO_2^-, NO_3^-, NH_4^+, PO_4^{2-}, SO_4^{2-}, EC, SS, TDS, T, Na^+, Mg^2, Ca^{2+}, Q) measured at 5 stations taken from State of Hydraulic Works of Turkey was examined using multivariate statistical techniques like cluster analysis (CA), discriminant analysis (DA) and principal component / factor analysis (PCA/FA). Hierarchical CA grouped 5 monitoring stations and 4 seasons into two clusters as polluted/less polluted area and wet/dry season, respectively. DA showed that parameters responsible for temporal change in Asi River are Na^+, Mg^{2+}, Ca^{2+}, Q, BOD, NH_4^+ and SS with 92.2% accuracy. Likewise, SO_4^{2-}, DO and T were found as parameters responsible for temporal change with 90% accuracy. PCA revealed that mineral pollution, nutrient pollution, and organic pollution are major latent factors which influence the water quality of Asi River. It also showed that erosion, agricultural activities, domestic and industrial discharges are fundamental causes of water pollution in the study area. To conclude, the study revealed that multivariate statistical methods are beneficial tools for the evaluation of complex datasets like water quality monitoring data.

Introduction

Surface waters are primary and limited water resources to meet agricultural, industrial and domestic water needs of human and living beings. They also play an important role in the transport and assimilation of domestic and industrial wastewater as well as agricultural runoff (Zhou, Liu, & Guo, 2007a). This situation makes surface water vulnerable to pollution. Surface water quality is depended on both anthropogenic activities like urban, agricultural, industrial activities which are spatial and have continuous impacts on the environment and natural processes like precipitation rate, weathering processes, soil erosion which are temporal and climate depended (Giri & Singh, 2014). Therefore, determination of water quality in surface waters is a problematic matter and require monitoring studies. However, monitoring studies often result in complex and huge datasets and interpretation of water quality from these results is difficult due to latent interrelationships between measured parameters (Zhou, Guo, Liu, & Jiang, 2007b; Ruždjak & Ruždjak, 2015).

Multivariate statistical techniques are widely applied tools in order to understand the relationships between variables and their relevance to the problem being studied. In these study four different multivariate statistical technique namely cluster analysis (CA), discriminant analysis (DA), principle component analysis (PCA) and factor analysis (FA) were employed

Published by Central Fisheries Research Institute (SUMAE) Trabzon, Turkey in cooperation with Japan International Cooperation Agency (JICA), Japan

to extract meaningful information from long-monitoring study results. CA helps a researcher to cluster (group) a set of variables in such a way that similar variables are perched in a same cluster. DA is widely applied to assess the adequacy of classification between clusters. Lastly, PCA/FA is a dimension-reduction tool that is used to reduce large set of variables into smaller ones that are still contain most of the meaningful information in the large set.

These multivariate statistical techniques are widely applied in environmental monitoring datasets because, (1) they reflect multivariate nature of the system more accurately, (2) provide a way to handle large data sets and (3) provide a means of detecting and quantifying multivariate patterns that arise out of the correlation structure of variable set (McGarigal, Cushman, & Stafford, 2000; Boyacioglu & Boyacioglu, 2008). Studies conducted in this field indicated that multivariate statistical analysis are widely accepted and effective tools in the identification of water quality status of ecological systems, in the evaluation of spatial and temporal variations in surface waters and in the identification of latent factors causing water pollution (Singh, Malik, & Sinha, 2005; Shrestha & Kazama, 2007; Zhou *et al.*, 2007a; Wang, Liu, Liao, & Lee, 2014; Azhar, Aris, Yusoff, Ramli, & Juahir, 2015; Ogwueleka, 2015; Muangthong & Shrestha, 2015; Jung *et al.*, 2016; Monica & Choi, 2016; Chow *et al.*, 2016; Zheng, Yu & Wang, 2016). However, there are very few studies conducted in Turkey's surface waters for the evaluation of spatial and temporal variations (Boyacioglu & Boyacioglu, 2008; Ödemis, Sarıgün & Evrendilek, 2010). Also, even though there are some studies in Asi River which aim to investigate water quality (Taşdemir & Göksu, 2001; Ağca, Ödemiş &Yalçın, 2009), they are not proper for the investigation of spatiotemporal changes in an integrated way.

Therefore, monitoring data obtained from State Water Works (DSİ) of Turkey covering the year from 2004 to 2014 based on query pattern was analyzed using CA, DA and PCA/DA. The objective of the present study is (1) to evaluate current water quality status of Asi Basin, (2) to understand significant parameters responsible for temporal and spatial variation, (3) to identify similarities between monitoring periods and stations and to identify pollution sources in the study area.

Materials and Methods

Study Area

Asi River is a transboundary river and its water is shared among Lebanon, Syria, and Turkey. The river rises in the mountains of Lebanon and flows 40 km in Lebanon to continue into the Syrian for about 325 km before arriving in Turkey for its last reach of 88 km to the Mediterranean Sea (FAO, 2009). The Asi Basin is located in the Mediterranean climate zone where the summers are hot and arid, and the winters are warm and rainy. Watershed has an average annual precipitation of 816 mm, an average temperature of 16.8°C, an annual total flow of 1,17 km³ / year (TUBİTAK MAM, 2013). Main anthropogenic activities carried out in the Asi Basin are agriculture, animal husbandry, and agriculture-based industries. Therefore, the river is subjected to the various kinds of point and diffuse pollution sources. The figure representing the study area is given Figure 1.

Water Quality Data and Pretreatment

Water quality monitoring data covers 16 different parameters which are biological oxygen demand (BOD_5), chemical oxygen demand (COD), dissolved oxygen (DO), nitrite (NO_2^-), nitrate (NO_3^-), ammonia (NH_4), dissolved phosphate (PO_4), sulfate (SO_4^{2-}), electrical conductivity (EC), suspended solids (SS), total dissolved solids (TDS), water temperature (T), sodium ion (Na^+), magnesium ion (Mg^{2+}), calcium ion (Ca^{2+}), flowrate (Q) measured at 5 different stations analyzed using multivariate statistical methods for the determination of spatio-temporal variations in Asi River. Samandağ, Antakya, Eşrefiye and Demirköprü stations are located at the main stream of Asi River. Former two stations are near the urbanized areas; whereas, latter two are located inside agricultural areas. Different from other stations, Küçük Asi station is located at the tributary of Asi River. This tributary is important because it reflects the impact of Amik Plain on the river quality. Figure 1 represents monitorıng stations with CORINE 2012 land use map.

Measurement of water quality parameters was carried out at the accredited laboratory of State of Hydraulic Works of Turkey. BOD, COD, TDS measurement were done using standard methods (SM 5210, SM 5220 B, SM 2540C, respectively). DO measurement was carried out with electrochemical probe method (TS EN ISO 5814). NO_2^-, NO_3^-, PO_4 measurement were carried out by ion chromatography in accordance with TS EN ISO 10304-1 standards. NH_4, Na^+, Mg^{2+}, Ca^{2+} measurement were done with ion chromatography in accordance with TS EN ISO 14911 standards. SO_4^{2-}, EC, and SS analysis was done with iodometric method, electrode method and gravimetric method in accordance with SM 4500-S^2-F, TS 9748 EN 27888 and TS EN 872 standards, respectively.

BOD_5 is defined as the amount of oxygen required by aerobic microorganisms to dissolve organic matter in a water body. It reflects the biodegradable organic content of water (Kwok, Dong, Lo, & Wong, 2005; Simon, Penru, Guastalli, Llorens, & Baig, 2011). Different from BOD, COD includes whole organic matter including the non-biodegradable portion (Hur & Cho, 2012). DO is a measure of dissolved oxygen amount in water and indicates water body's ability to

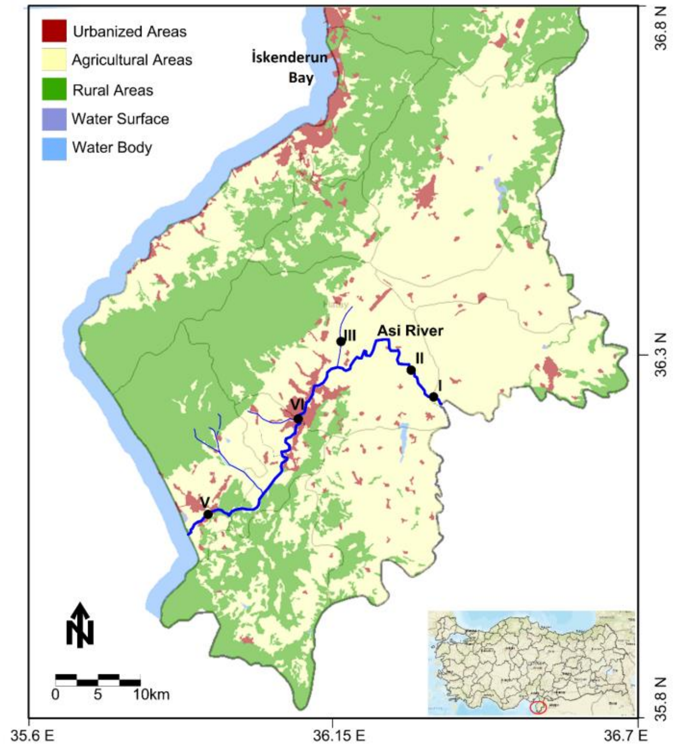

Figure 1. Monitoring Stations (I: Eşrefiye Station, II: Demirköprü Station, III: Küçük Asi Station; IV: Antakya Station; V: Samandağ Station).

support balanced aquatic environment (Synder, 2007). Nitrogen compounds are the indicators of diffuse pollution since they are usually found in effluents of agricultural drainage waters (Ogwueleka, 2015). In addition, they decrease primary production in a water body and may cause eutrophication problem (Aksoy, Bulut, & Yenilmez, 2006). Dissolved phosphate amount in water is important since it is essential for photosynthesis (Froelich, 1988). Therefore, excess amount of it will support the algal development and may lead to eutrophication. SO_4^{2-} accelerates the dissolution of nutrients found in sediments into surface waters (Orem, 2011). EC shows electric conductivity of water and as the amount of dissolved ion increases, its value increases (Anonymous, 2016). SS may comprise both organic and inorganic matter like plankton, silt, clay (Ell, 2008). TDS is a measure of total dissolved solids found in water. Na^+, Mg^{2+}, Ca^{2+} are the most common alkali metals found in surface waters (Grochowska & Tandyrak, 2009). They usually reach water bodies due to dissolution of rocks found in watershed structure (Gałczyńska, Gamrat, Burczyk, Horak, & Kot, 2013).

Before applying any multivariate statistics to the dataset, it was visualized using scatter graphs to exclude extreme values. Thereafter, all missing data were replaced with yearly average values. Since multivariate statistical tools require confirmation of normal distribution, the normality of each variable was checked by using Kolmogrov-Smirrow (K-S) z test (Muangthong & Shrestha, 2015). Then, for DO and T square transformation, for Na^+ square root transformation and for other parameters logarithmic transformation was applied to satisfy normal distribution assumption. To analyze whether or not the dataset is suitable for PCA/FA, Kaiser-Mayer-Olkin (KMO) and Barlett's test were performed. KMO is a measure of sampling adequacy that indicates the proportion variance (Ogwueleka, 2015). KMO results greater than 0.5 obtained in this research shows that data set is suitable for PCA/FA. Barlett's test of sphericity indicates whether correlation matrix is an identity matrix or not. Lastly, DA was applied to normalized data, whereas CA and PCA were applied to normalized data that was standardized through z-scale transformation to avoid misclassifications arising from the different orders of magnitude of both numerical values and variance of the parameters analyzed (Lei, 2013).

Cluster Analysis

CA is a beneficial tool which helps explication of large and multidimensional datasets like environmental data (Cieszynska, Wesolowski, Bartoszewicz, Michalska, & Nowacki, 2012). Cluster analysis help researcher to group water samples resulting in high interval (within clusters) homogeneity and high external (between clusters) heterogeneity (Shrestha & Kazama, 2007). Hierarchical agglomerative clustering is the widely used approach to analyze similarity between sample and entire dataset (McKenna, 2003). The Euclidean distance is widely used distance coefficient, which measures the similarity between two samples and a distance that can be represented by the difference between analytical values from both the samples (Otto, 1998). Result of cluster analysis is usually given with a tree like diagram called dendrogram, which visualizes the summary of clustering process with a considerable reduction in dimensionality of the original data (Shrestha & Kazama, 2007). In this study, hierarchical agglomerative CA was performed on the normalized data set by means of Ward's method, using Euclidean distances as a measure of similarity.

Discriminant Analysis

DA is a method of analyzing dependence that is a special case of canonical correlation, and one of its objectives is to determine the significance of different variables, which can allow the separation of two or more naturally occurring groups (Zhou *et al.*, 2007b). The DA constructs a discriminant function for each group (Johnson & Wichern, 1992; Wunderlin, Wesolowski, Bartoszewicz, Michalska & Nowacki, 2001) as in the equation below:

$$f(G_i) = k_i + \sum_{j=1}^{n} w_{ij} p_{ij} \quad (1)$$

where *i* is the number of groups (*G*), *ki* is the constant inherent to each group, *n* is the number of parameters used to classify a set of data into a given group, *wj* is the weight coefficient, assigned by DA to a given selected parameter (*pj*).

DA was used on normalized data matrix using standard modes for the construction of discriminant functions to evaluate spatiotemporal variations in Asi River (Wang *et al.*, 2014). Monitoring stations and seasons were the grouping variables, all the measured parameters were the independent variables.

Principal Component Analysis

The main goal of factor analysis is to explain the covariance relationships among a large number of variables with the help of the least number of random variables (Johnson & Wichern, 1992). The most widely used method of obtaining factors is principal component analysis (Kalaycı, 2016).

PCA is designed to transform the original variables into new, uncorrelated variables (axes), called the principal components (PCs), which are linear combinations of the original variables (Shrestha & Kazama, 2007). PC provides information on the most significant parameters which describes the whole dataset without losing any information (Helena *et al.*, 2000). Therefore, it allows the identification of latent factors depending on pollution sources and its origins like anthropogenic sources (industrial and domestic discharges etc.) or natural sources (climate, erosion etc.) (Kowalkowskia, Zbytniewskia, Szpejnab & Buszewki, 2006). Equation which describes principal components mathematically is given below:

$$z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + \cdots + a_{im}x_{mj} \quad (2)$$

Where z is the component score, a is the component loading, x the measured value of a variable, i is the component number, j the sample number and m the total number of variables.

To reduce the contribution of less significant parameters on data structure obtained after PCA, FA was conducted by rotating the axis defined by PCA, according to well established rules. At the end of the FA, new variables called varifactors (VF) were obtained. The main difference between PC and VF is that while PC is a linear combination of observable water quality variables, VF can include unobservable, hypothetical, latent variables (Vega, Zbytniewskia, Szpejnab & Buszewki, 1998, Helena *et al.*, 2000). The equation representing the factor analysis is given below:

$$z_{fi} = a_{f1}f_{1i} + a_{f2}f_{2i} + a_{f3}f_{3i} + \cdots + a_{fm}f_{mi} + e_{fi} \quad (3)$$

Where z is the measured variable, a is the factor loading, f is the factor score, e is the residual term accounting for errors or another source of variation, i is the sample number and m is the total number of factors.

Results and Discussion

Preliminary Assessment of Water Quality

Descriptive statistic tools and two-way ANOVA test was used for the preliminary assessment of water quality in Asi River. Table 1 indicates the basic statistic of water quality dataset.

Descriptive statistics indicate that most of the parameters have high standard deviation and high change interval. Therefore, it can be said that water quality in Asi River is time and space depended because of the natural and anthropogenic processes carried out in the watershed (Gonzalez, Almeida, Calderón, Mallea, & González, 2014).

When average values of water quality parameters compared with Water Pollution Control Regulation of Turkey, it is found that Asi River is suffered from oPO_4^{3-}, NH_4^+ and NO_2^- pollution. This indicates that Asi River has high organic pollution since nitrogen compounds in surface waters usually related to organic pollution (Yang, Shen, Zhang, & Wang, 2007). Also, severe oPO_4^{3-} pollution indicates the impact of agricultural diffuse water and domestic discharges (Wu, 2005).

Two way ANOVA test was performed to determine the existence of spatial and temporal variation in the dataset. It showed that TDS, SO_4^{2-}, Ca^{2+}, Q parameters were changing both temporally and spatially ($P<0.05$). BOD_5, COD, NH_4, NO_2, oPO_4, SS, EC, Mg^{2+}, and Na^+ were changing spatially, whereas NO_3

Table 1. Descriptive Statistics of Water Quality Data

Parameter (Unit)		Station				
		Eşrefiye	Demirköprü	Küçük Asi	Antakya	Samandağ
BOD_5	Min-Max	2.00-8.00	1.00-8.00	1.00-15.00	1.70-22.00	2.00-24.00
ng/L)	Mean±Std	4.14±1.49	3.45±1.48	4.12±2.90	7.05±5.04	7.92±5.39
COD	Min-Max	3.00-12.00	4.00-80.00	4.00-125.00	3.00-45.00	8.00-73.00
(mg/L)	Mean±Std	7.83±2.90	16.02±16.80	26.02±30.65	18.99±12.22	23.50±15.70
DO	Min-Max	2.10-10.30	2.10-10.00	2.30-10.40	2.20-9.80	3.40-10.60
(mg O_2/L)	Mean±Std	7.00±2.34	7.51±1.51	7.22±1.71	6.95±1.78	7.85±1.45
NH_4^+	Min-Max	0.10-1.09	0.10-3.60	0.12-5.00	0.19-10.00	0.10-2.80
(mg/L)	Mean±Std	0.46±0.27	1.05±0.92	1.36±1.19	2.69±2.35	1.01±0.71
NO_2^-	Min-Max	0.01-0.14	0.01-0.33	0.01-0.60	0.00-0.31	0.01-0.63
(mg/L)	Mean±Std	0.06±0.03	0.06±0.06	0.11±0.13	0.10±0.08	0.15±0.14
NO_3^-	Min-Max	0.30-7.00	0.60-6.70	1.00-4.20	0.90-7.50	0.47-6.90
(mg/L)	Mean±Std	2.38±1.69	2.77±1.60	2.46±0.80	3.00±1.52	2.32±1.46
oPO4	Min-Max	0.64-2.54	0.11-3.13	0.07-0.64	0.07-5.00	0.08-4.05
(mg/L)	Mean±Std	1.41±0.67	0.63±0.64	0.30±0.16	1.09±1.17	0.65±0.70
SO_4^{-2}	Min-Max	82.60-198.0	67.20-339.30	63.80-315.90	18.24-286.50	60.3-301.92
(mg/L)	Mean±Std	136.03±42.17	160.74±72.26	169.53±62.56	135.82±74.95	135.82±58.28
SS	Min-Max	36.00-213.00	12.00-148.00	31.00-241.00	15.00-186.00	8.00-193.67
(mg/L)	Mean±Std	118.33±67.80	55.20±35.66	101.46±49.37	89.70±42.34	86.45±50.29
TDS	Min-Max	506-979	486-1530	487-1364	458-1102	314-862
(mg/L)	Mean±Std	687.92±154.55	732.70±207.46	782.05±204.33	668.26±151.37	587.80±126.81
EC	Min-Max	862-1497	760-2040	391-2130	691-1630	564-1320
(µS/cm)	Mean±Std	1045.50±198.58	1135.00±279.89	1198.35±310.23	1048.35±216.94	936.97±175.20
T	Min-Max	12.00-29.00	8.00-31.00	4.00-28.00	6.00-32.00	6.00-34.00
(^{0}C)	Mean±Std	21.50±5.77	20.51±6.27	18.66±6.90	20.60±6.91	20.89±7.40
Na^+	Min-Max	12.88-72.92	9.20-95.45	13.11-126.96	11.73-89.73	7.82-97.33
(mg/L)	Mean±Std	42.04±14.50	42.76±17.23	51.07±23.55	44.63±17.29	40.12±17.51
Mg^{+2}	Min-Max	33.40-73.10	31.20-98.50	20.90-109.40	32.83-105.79	34.10-72.96
(mg/L)	Mean±Std	47.35±11.96	53.68±14.88	75.45±18.42	57.46±16.65	54.52±10.60
Ca^{+2} (mg/L)	Min-Max	64.25-148.30	36.10-132.30	29.17-108.00	42.10-112.00	35.20-110.00
	Mean±Std	104.39±22.89	90.07±18.70	66.86±17.81	73.39±14.32	72.69±14.13
Q	Min-Max	0.86-135.20	0.34-155.07	0.75-53.00	0.27-486.40	0.34-798.45
(m^3/s)	Mean±Std	69.94±52.01	19.77±28.42	13.45±11.56	56.37±107.45	235.10±221.83

and DO vary only seasonally (P<0.05). As a result, both descriptive statistics and two way ANOVA test confirmed the existence of the spatiotemporal change in water quality of Asi River. However, since these methods are insufficient to explain correlations between parameters in complex datasets (Vega *et al.*, 1998), multivariate statistics were used to analyze water quality changes in detail.

Temporal/Spatial Similarities and Grouping

Temporal CA generated a dendrogram, grouping 4 seasons into 2 clusters. Cluster 1 comprised winter and spring indicating wet season, high flow, whereas; cluster 2 comprised summer and fall season indicating dry season, low flow (Figure 2). Therefore, water quality in Asi River is influenced by the local climate and similar results can be found on literature (Ogwueleka, 2015; Zhang, Guo, Meng, & Wang, 2009).

Spatial CA generated a dendrogram, grouping 5 stations into 2 clusters. Cluster 1 comprised Eşrefiye and Demirköprü stations, whereas; cluster 2 comprised Küçük Asi, Antakya and Samandağ stations (Figure 3). While Demirköprü and Eşrefiye stations are located near the agricultural land; Küçük Asi, Antakya ve Samandağ stations are locations where urbanizations begin in addition to agricultural activities. Therefore, it can be said that first cluster is suffered from agricultural diffuse pollution more severely than second one. So, like Boyacioglu and Boyacioglu (2008) study, it is concluded that water quality similarities are highly depended on land use in Asi watershed.

As it can be seen from Figure 3, linking distance between Küçük Asi station with Antakya and Samandağ stations is the greatest distance in the dendrogram. Küçük Asi station is located at the downstream of Amik plain. As a result of agricultural activities taking care of at the plain, inorganic pollution is a great concern in the surface waters in addition to organic pollution. On the other hand, Antakya and Samandağ stations are located near the urbanized land and suffered from domestic discharges, industrial discharges as well as agricultural pollution. As a result, it can be said that even though Küçük Asi, Antakya and Samandağ stations are similar in the aspect of water quality, main pollution sources are different from each other. Results indicate that cluster analysis is applicable to large water quality datasets for the examination of similarities in the monitoring area (Zhou *et al.*, 2007, Muangthong & Shresta, 2015, Zheng *et al.*, 2016).

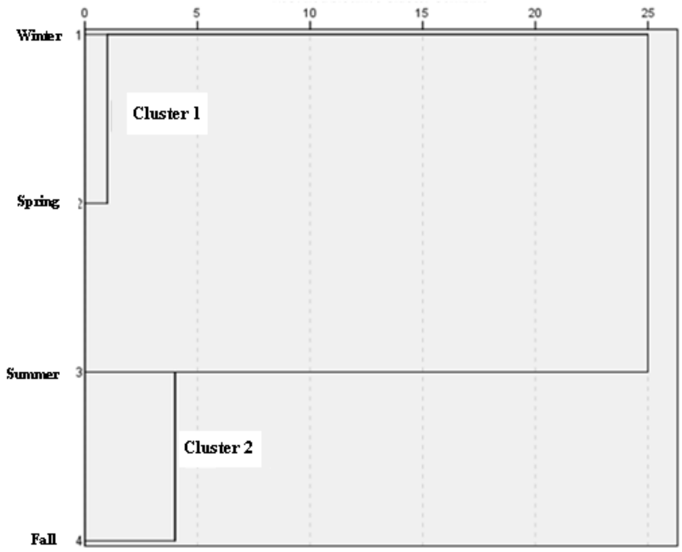

Figure 2. Dendrogram generated as a result of Temporal CA.

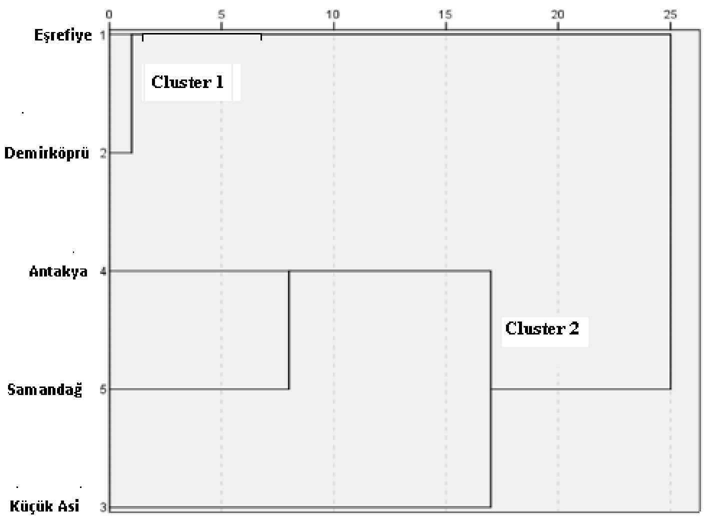

Figure 3. Dendrogram generated as a result of Spatial.

Temporal and Spatial Variations in Water Quality

Temporal DA was applied to the normalized dataset after dividing the dataset into two clusters (dry and wet season) resulted in CA. Discriminant functions are obtained using forward stepwise method in which variables are included step by step beginning with the more significant until no significant changes are obtained. Temporal DA results indicated that dissolved oxygen, SO_4^{2-} and T are the most significant parameters to discriminate between wet and dry seasons (Table 2). Main source of sulfate in the surface waters is mineral containing soils. Therefore, during periods when precipitation was abundant, sulfate was dissolved from the soil and reached the Asi River with surface runoff. Since the solubility of oxygen in water is inversely proportional to temperature (Shrestha & Kazama, 2007), decrease in dissolved oxygen content during the dry season (high temperature) is expected.

Spatial DA results indicated that Na^+, Mg^{2+}, Ca^{2+}, Q, BOD, NH_4^+ and SS parameters are the most significant parameters to discriminate between polluted and less polluted areas (Table 3). In other words, these 7 parameters are responsible for most of the expected the variation through Asi River. Box and whisker plots belonging to these parameters are given below Figure 4.

As it can be seen from Table 2 most significant parameters according to discriminant function coefficients are Mg^{2+}, Ca^{2+} and SS. Mg^{2+} concentration is greater in the second cluster (polluted zone) due to the surface flow which has a high salt content (Ağca *et al.*, 2009) coming from Amik Plain. SS concentration variation is in a similar trend with Mg^{2+}. This indicated the effect of erosion. Contrary to Mg^{2+} concentration, Ca^+ concentration is greater at the first cluster (less polluted zone). Soil content of Asi watershed especially at the Syrian and Lebanon part contains many karstic zones (Zwahlen, Gonzalez, & Asaad, 2014). Therefore, the lime found in the soil structure dissolves during rainy weathers and reaches the Asi River with surface flow.

Data Structure Determination and Source Identification

PCA is applied on standardized normalized dataset separated as polluted and less polluted area based on cluster analysis results to identify main pollution factors that influenced each identified regions (Zhang *et al.*, 2009; Monica & Choi, 2016). In order to understand the applicability of PCA on the dataset, Barlett and KMO tests were applied. KMO and Barlett sphericity test results of the less polluted region consisting of Eşrefiye and Demirköprü stations were found as 0.599 and 0.00, respectively. Similarly, KMO and Barlett sphericity test results of the polluted region consisting of Küçük Asi, Antakya and Demirköprü stations were found as 0.595 and 0.00, respectively. Results indicated that PCA could achieve a significant reduction of dimensionality of the original dataset.

Factor analysis of two datasets belonging to polluted and less polluted regions resulted in 6 variance factors (VFs) with eigenvalues greater than 1 and explained 77% and 73% of total variance, respectively. An eigenvalue gives a measure of the significance of the factor and eigenvalues greater than 1 are considered as significant (Kim & Mueller, 1987; Muangthong & Shrestha 2015). Corresponding VFs, variable loadings and explained variance are given at Table 4. Liu, Lin, & Kuo (2003), classified loadings greater than 0.75 as strong, loadings between 0.75-0.50 moderate and loadings smaller than 0.5-0.3 as weak.

Less Polluted Region

Among six VFs obtained for the less polluted region, VF1 explained 20.8% of total variance and had strong positive loading on TDS, EC and moderate positive loading on Mg^{2+} and SO_4^{2-}.TDS and EC indicate soil erosion occurring depending on seasonal storms (Kowalkowskia *et al.*, 2006). Similarly, SO_4^{2-} reaches to the surface water due to the dissolution of lime found in soil (Vega *et al.*, 1998). Also, Mg^{2+} is commonly found in agricultural drainage water (Boyacioglu, 2006). Therefore, this factor represents mineral pollution caused by seasonal storms. VF2 explained 12.3% of total variance and had moderate positive loading on Ca^{2+}, NO_3^-, oPO_4^{2-}. While NO_3^- and oPO_4^{2-} indicates diffused pollution resulted from agricultural activities (Ogwueleka, 2015), Ca^{2+} found in surface waters could be mainly due to natural processes like ion exchange between soil and water interface and dissolution from soil. (Guo & Wang, 2004). So, VF2 showed that nutrient pollution resulted from both anthropogenic and natural processes. VF3 explained 12.2% of total variance and had positive strong NH_4^-, COD, and positive moderate NO_2^-, NO_3^- loadings. Since fertilizers used in agricultural activities are the main sources of nitrogenous compounds in surface waters (Ogwueleka, 2015), VF3 represents diffuse agricultural pollution. Additionally, VF4 had positive strong BOD_5 and positive negative T loading and explained 12% of total variance. BOD_5 is an index indicating organic pollution resulted from domestic and industrial discharges (Kazi *et al.*, 2009; Juahir *et al.*, 2011). VF5 explained 10.5% of total variance and contained positive strong Q and negative moderate T loading. The inverse relationship between Q and T is a result of weather condition of the studied area. As temperature increases during dry season, evaporation increases, as a result; surface flow decreases. So, this factor represents the impact of seasonal change on surface water. Lastly, VF6 explained 9.1% of total variance and had positive strong SS loading. This factor represents diffuse pollution due to soil erosion (Muangthong & Shresta 2015, Chow *et al.*, 2016).

Polluted Region

VF1 explained 21.8% of total variance and has positively strong Mg^{2+}, TDS, EC and positively moderate Na^+ and SO_4^{2-} loadings. So, this factor points out the dissolution of minerals from soil. VF2 explained 10.5% of total variance and had positive moderate Q, DO and negative moderate T loading. As mentioned before, there is a negative correlation between T and Q as a result of evaporation. Additionally, as temperature of the water increases, dissolution of oxygen in water decreases (Wang *et al.*, 2013). As a result, VF2 is related to seasonal change and had natural causes. VF3, on the other hand; explained 10.5% of total variance and had positive strong NO_2^-, positive moderate oPO_4 and negative moderate NH_4^+. Therefore, this factor indicated nutrient pollution from agricultural runoff (Sing *et al.*, 2005). VF4 contained positive strong BOD_5 and COD loadings and explained 10.1% of total variance. BOD_5 and COD are indicators of organic pollution from industrial and domestic discharges (Kazi *et al.*, 2009). VF5 had positive moderate oPO_4 and negative strong SS loading and explained 9% of total variance. The inverse relationship between $oPO_4$and SS indicates that pollution at the studied area is a result of anthropogenic activities. Finally, VF6 explained 9% of total variance and had positive strong NO_3^- loading. The presence of nitrate was due to fertilizers used in crop cultivation which was carried by surface runoff.

To conclude, latent factors causing pollution in the first region (less polluted area) were determined as mineral pollution, nutrient pollution, agricultural runoff and erosion. Similarly, mineral pollution, agricultural runoff, and organic pollution were identified as latent factors indicating pollution sources in the second region (polluted area). Even though PCA did not

Table 2. Classification function coefficients for temporal discriminant analysis

Parameter	Wet Season	Dry Season
DO	0.088	0.015
SO_4^{-2}	61.527	58.068
T	0.021	0.031
(Constant)	-74.804	-67.971

Table 3. Classification function coefficients for spatial discriminant analysis

Parameter	Less Polluted Zone	Polluted Zone
Na^+	-2.651	-1.891
Mg^{2+}	78.413	89.618
Ca^{2+}	187.997	163.354
Q	-4.683	-2.772
BOD	14.062	17.854
NH^{4+}	-3.344	.166
SS	45.251	50.401
(Constant)	-286.694	-276.921

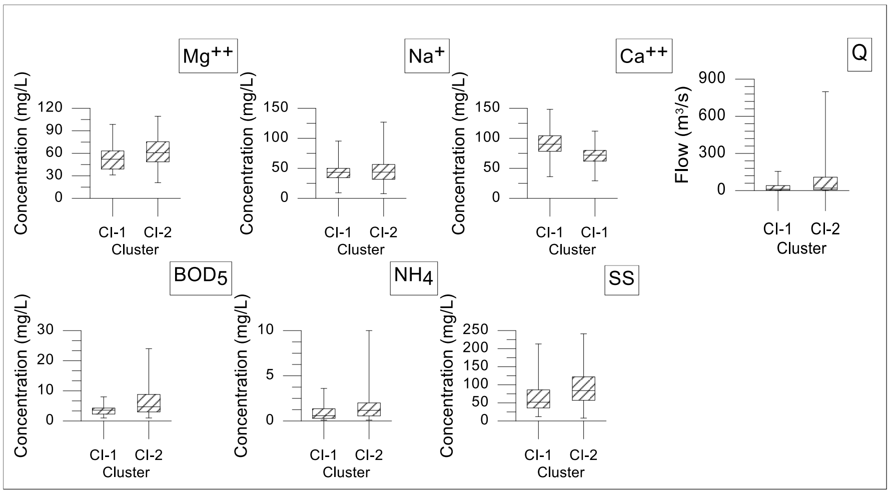

Figure 4. Box and whisker plots of water quality parameters responsible for spatial change.

provide significant data reduction, it helped to identify pollution sources specific to Asi River. Same situation is true in Sing *et al.* (2005) and Nie, Li, Jiang, Diao, & Li (2015) studies.

Conclusion

In this study, multivariate statistical techniques were used to identify spatial and temporal changes in water quality at Asi River. Cluster analysis grouped both the sampling stations and seasons into two clusters as polluted / less polluted areas and wet / dry seasons. DA was used to determine most significant parameters among groups separated by CA. DA showed that parameters responsible for temporal change in Asi River are Na^+, Mg^{2+}, Ca^{2+}, Q, BOD, NH_4^+ and SS with 92.2% accuracy. Likewise, SO_4^{2-}, DO and T were found as parameters responsible for temporal change with 90% accuracy. PCA/FA helped to identify latent pollution factors/ sources; but, it did not provide considerable data reduction. Pollution indicating parameters for less polluted and polluted region were TDS, EC, SO_4^{2-}, COD, BOD_5, SS and TDS, EC, Mg^{2+}, NO_2^-, NO_3^-, respectively. Also, pollution sources were identified as erosion, agricultural activities, domestic and industrial discharges and dissolution of minerals. Among all these pollution sources, diffuse pollution is dominant in the area as a result of natural processes especially dissolution and transport of minerals and solid particles with surface runoff and agricultural activities. High positive NO_2^-, NO_3^- and PO_4^{2-} loadings observed in both clusters were directly related with fertilizer usage. Furthermore, it should be noted that as the urbanization begins, pollution load of Asi River increases because of the domestic and industrial wastewater discharges. Additionally, urbanization alters the natural habitat, land use and soil structure near the river catchment. This situation affects the water characteristic of surface runoff and results in more polluted water input to the river. To sum up, this study helped to identify seasonal and temporal changes as well as major pollution sources specific to

Table 4. Loadings of water quality parameters on significant principle components

Parameter	Less Polluted Area (Cluster 1)						Polluted Area (Cluster 2)					
	VF1	VF2	VF3	VF4	VF5	VF6	VF1	VF2	VF3	VF4	VF5	VF6
Na^+	0.392	0.432	-0.034	0.077	-0.459	-0.273	**0.669**	-0.361	0.146	0.011	0.170	0.271
Mg^{2+}	**0.672**	-0.279	0.127	-0.169	-0.043	0.022	***0.856***	0.091	0.000	-0.044	-0.173	-0.135
Ca^{2+}	0.369	**0.675**	-0.109	-0.041	0.427	0.029	0.341	0.324	-0.060	-0.023	0.391	0.404
Q	0.010	0.065	-0.016	-0.038	***0.825***	-0.114	0.022	**0.690**	0.425	-0.111	0.042	-0.007
BOD_5	0.104	0.158	0.069	***0.861***	-0.008	-0.058	-0.136	-0.184	-0.018	**0.775**	0.315	0.059
COD	-0.137	-0.061	***0.851***	0.214	-0.008	-0.241	-0.036	0.015	0.110	**0.892**	-0.114	0.114
DO	0.316	0.025	-0.030	-0.678	0.311	0.004	0.038	**0.733**	-0.277	0.075	0.164	-0.256
NH_4^+	0.190	-0.131	***0.779***	-0.153	0.080	0.396	0.041	-0.119	**-0.582**	-0.333	0.081	0.412
NO_2^-	-0.062	0.445	**0.553**	0.154	-0.122	-0.402	-0.027	0.002	***0.828***	0.041	0.075	0.229
NO_3^-	-0.166	**0.608**	**0.496**	-0.334	-0.141	0.025	0.016	0.018	0.096	0.189	-0.013	**0.814**
o-PO_4^{2-}	-0.330	***0.753***	-0.115	0.304	0.083	0.099	-0.249	-0.163	**0.510**	-0.100	**0.577**	-0.089
SO_4^{2-}	**0.712**	0.226	0.008	-0.332	0.194	-0.261	**0.706**	0.474	0.171	-0.053	0.007	-0.032
SS	-0.027	0.072	-0.045	-0.024	-0.071	***0.947***	-0.001	-0.092	-0.002	-0.122	***-0.829***	-0.030
TDS	***0.935***	0.019	-0.135	0.044	0.033	0.075	***0.860***	0.079	-0.192	-0.061	-0.086	0.050
EC	***0.942***	-0.035	-0.039	0.074	0.002	0.032	***0.930***	0.008	-0.141	-0.082	0.081	0.104
T	-0.115	-0.091	-0.008	**0.512**	**-0.648**	-0.062	-0.095	**-0.787**	-0.005	0.120	0.087	-0.325
Eigenvalue	3.664	2.302	2.149	1.843	1.311	1.041	3.840	2.114	1.994	1.374	1.290	1.120
% total variance	20.81	12.32	12.21	11.97	10.53	9.08	21.84	13.69	10.47	10.10	8.79	8.43
Cumulative % variance	20.81	33.13	45.34	57.32	67.85	76.93	21.84	35.53	45.99	56.10	64.89	73.33

*VFs had a strong loadings shown with dark and italic bold; whereas. moderate loadings shown only with dark bold.

Asi River. Also, it showed that multivariate statistical techniques are effective in the investigation of water quality datasets.

Acknowledgements

This study is conducted with the support of Mustafa Kemal University, coordination of scientific research projects in the framework of project number 14781.

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