

Evaluation of Spatial and Temporal Variation in River Water Quality

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ABSTRACT: Multivariate statistical techniques were applied for evaluation of temporal/ spatial variations and interpretation of a large complex water-quality data set of Shiroud River that discharges to southern part of Caspian Sea, Iran. Totally 16 parameters of water quality were monitored during 12 months at 8 sites in mountainous, flat and estuary areas. Factor analysis (FA) results showed that the first factor explained 25.76% of the total variance [comprise of electrical conductivity (EC), total dissolved solids (TDS), total hardness, calcium ion and water temperature levels]. The second factor called water quality indicator factor explained 13.99% [comprise of silicate, dissolved oxygen (DO) and pH levels], and the third factor called phosphate pollutant factor explained 10.72% (comprise of orthophosphate and total phosphorus (TP)). Additional factors were affected by part of nutrient, flow rate and general water quality, each of them recorded variance less than 10%. Discriminate analysis (DA) gave the best results for both spatial and temporal analysis. It has provided an important data reduction as it uses only four parameters (mean river depth, DO, NH₄⁺, and EC). Thus, DA allowed a reduction in the dimensionality of the large data set, explaining a few indicator parameters responsible for large variations in water quality. The present study shows the usefulness of multivariate statistical techniques for analysis and interpretation of complex data sets, and identifies probable source components in order to explain the pollution of Shiroud River.

Key words: Shiroud River, MANOVA, Discriminate analysis, Factor analysis, Water quality

INTRODUCTION

Surface waters are most exposable to pollution due to their easy accessibility for disposal of wastewaters (Samarghandi *et al.*, 2007). Both the Anthropogenic influences such as urban, industrial and agricultural activities increasing exploitation of water resources as well as natural processes, such as precipitation inputs, erosion, weathering of crustal materials, degrade surface waters and damage their use for drinking, industrial, agricultural, reaction or other purposes (Jarvie *et al.*, 1998, Simeonov *et al.*, 2003, Mahvi, *et al.*, 2005, Nouri *et al.*, 2008, Karbassi *et al.*, 2008). Rivers play a major role in assimilation or transporting the municipal and industrial wastewater discharge constitutes a constant

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polluting source, whereas surface run off is a seasonal phenomenon, largely affected by climate within the basin (Singh *et al.*, 2004, Karbassi *et al.*, 2007, Karbassi *et al.*, 2008). Seasonal variation in precipitation, surface run off, interflow, groundwater flow and pumped in and outflows have a strong effect on the river discharge and subsequently on the concentration of pollutants in the river water (Vega *et al.*, 1998, Monavari and Guieysse, 2007; Khadka and Khanal, 2008; Mtethiwa *et al.*, 2008). The application of different multivariate methods such as Cluster analysis (CA), principal analysis (PA), factor analysis (FA), multivariate analysis of variance (MANOVA), and discriminate analysis (DA) has been used widely in recent years for analyzing environmental data

and drawing meaningful information (Vega *et al.*, 1998; Lee *et al.*, 2001; Reghunath *et al.*, 2002; Simeonov *et al.*, 2004). In this study, a large data matrix was obtained during (July 2003 through June 2004) to investigate the influence of possible sources (natural and anthropogenic) on the water quality parameters in order to explain the pollution status of Shiroud River. The relationship between the sampling sites, identification of water quality variables responsible for spatial and temporal variations in water quality was investigated. The last objective of this research was to identify the relative contribution for all parameters responsible in discriminating the seasons and different sites.

MATERIAL & METHODS

Shiroud River is located in the southern part of Caspian Sea. The longitudes and latitudes of water sampling sites along the river were $50^{\circ}, 45'$ through $50^{\circ}, 52'$ E and $36^{\circ}, 52'$ through $35^{\circ}, 45'$ N, respectively (Fig. 1). The total length of the river from different branches and tributaries to the estuary is almost 32 km (from mountain site through estuary of the river). Eight sampling sites were chosen from different branches and tributaries of the river. Sampling sites are located as follows: Sites 1, 2 and 5 are located in the mountains area, site 3 is located on plain after intersection of two tributaries (sites 1 and 2) of the river, sites 4 and 6 are located on plain, site 7 is located on plain after intersection of the two main branches, and site 8 is located at the estuary. Majority of the sites are surrounded by orchards, tea farms and paddy fields. In addition to the paddy fields, there is an asphalt preparation factory near site 7 that can affect on ecosystem of the river bed.

The water samples were collected from eight different sites along the river (Fig.1). The pathway of the river from its different branches and tributaries to the estuary is almost 32 km. A total of 96 samples were collected over a period of 12 months (July 2003 through June 2004). Before collecting the water samples, all sample bottles were washed with different types of chemicals and rinsed with distilled water. The freshwater samples were carried in one liter bottle and kept in a low temperature (stored in ice) until the samples were transferred to main laboratory for further analysis. The parameters such as dissolve oxygen (DO), pH, water temperature and flow rate of the river were measured in situ. The analysis of physico-chemical parameters namely water

temperature, pH, mean river depth, EC, DO, biochemical oxygen demand (BOD_5), calcium ion, alkalinity, TDS, nutrients such as ammonia ion, orthophosphate, nitrite, nitrate, total phosphorus and silicate were analyzed according to standard methods (APHA, 1999). For determination of nitrate using reduction column by Cadmium (APHA, 1999), total hardness and calcium ion by using EDTA [Ethylene-diamine-tetra-acetic acid], titri-metric method, the relative acidic or basic level of water body (pH) measured by pH meter model TOA-Japan, and silicate was determined by the method of molybdate-reactive silica (EPA, 1979; APHA, 1999). Multivariate analysis of variance was used where several dependent variables were measured for each sampling unit instead of one variable. The objective of MANOVA was to investigate whether the mean vectors of several groups were the same, and if not, which means the variables were differed significantly from group to group.

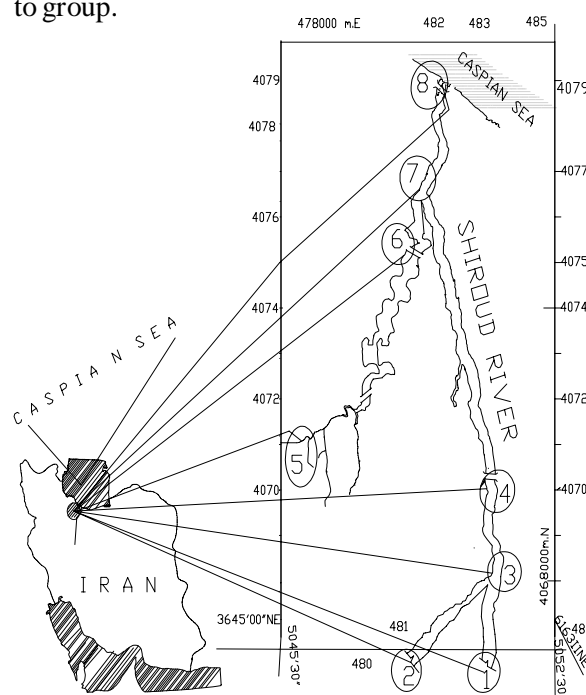


Fig. 1. Map of sample locations of Shiroud River in eight sites with scale of 1:400,000

Factor analysis (FA) is designed to transform the original variables into new uncorrelated variables called factors, which are linear combinations of the original variables. The FA is a data reduction technique and suggests how many varieties are important to explain the observed variances in the data. Principal components method (PCA) is used for extraction of different

factors. The axis defined by PCA is rotated to reduce the contribution of less significant variables (Johnson and Wichern, 2002). This treatment provides a small number of factors that usually account for approximately the same amount of information as the original set of observations. The FA can be expressed as:

$$F_i = a_1 x_{1j} + a_2 x_{2j} + \dots + a_m x_{mj} \quad (1)$$

Where F_i is the factor, a is the loading, x is the measured value of variable, j is the factor number, j is the sample number and m is the total number of variables. The factor scores can be expressed as:

$$Z_{ij} = a_1 f_{1j} + a_2 f_{2j} + \dots + a_m f_{mj} + e_{ij} \quad (2)$$

Where Z is the measured variable, a is the factor loading, f is the factor score, the residual term accounting for errors or other source of variation. Discriminate analysis is a multivariate technique used for two points, the first point is description of group separation in which linear functions of the several variables (discriminate function (DFs)) are used to describe or elucidate the differences between two or more groups and identifying the relative contribution of all variable to separation of the groups. Second aspect is prediction or allocation of observations to group

in which linear or quadratic functions of the variable (classification functions (CFs)) are used to assign an observation to one of the groups (Rencher, 2002; Johnson and Wichern, 2002).

RESULTS & DISCUSSION

Descriptive statistics including the maximum, minimum, mean and standard deviation are summarized in (Table 1). The maximum value was exhibited by total hardness of 387 mg/L, whilst ammonium ion exhibited the lowest value of 0.10 mg/l. The observed spread around the mean is substantially high and random; this could be due to seasonal changes and different anthropogenic activities surrounding the sites. The correlation matrix of water quality parameters obtained from Shiroud River was examined. The relevant data for water quality parameters (Table 2) show strong significant correlation between all of the parameters. This indicates that the entire parameters share a common origin source except BOD₅ did not show a significant correlation with all of the parameters. The data for water quality parameters were further analyzed to different multivariate statistical techniques to explore temporal and spatial variations. The results of multivariate analysis of variance (MANOVA) for water quality parameter are presented in (Table 3). According to obtained data, the eight sites are significantly different in terms of selected water quality parameters.

Table 1. Descriptive statistics of selected water quality parameters in Shiroud River

Parameter	Min.	Max.	Mean	Std. Deviation
Water Temperature	7.00	30.00	17.36	6.93
Mean River Depth	30.00	75.00	52.81	14.32
pH	7.23	8.64	8.02	0.23
DO	7.70	14.40	11.38	1.53
BOD ₅	0.20	7.20	1.57	1.13
Total Alkalinity	80.00	280.00	177.51	31.08
Ca ²⁺	8.00	75.00	41.15	11.88
Total Hardness	70.00	387.00	225.85	58.53
TDS	40.00	250.00	159.06	42.77
Orthophosphate	0.01	0.44	0.10	0.06
Total phosphorus	0.05	0.40	0.17	0.07
NO ₃ ⁻	0.45	3.90	1.95	0.85
NO ₂ ⁻	0.00	0.06	0.01	0.01
SiO ₂	0.85	2.83	1.59	0.46
NH ₄ ⁺	0.00	0.10	0.04	0.03
EC	100.00	500.00	323.23	82.21

Table 2. Correlation coefficient matrix for selected water quality parameters samples

Parameter	W.T	Depth	PH	DO	BOD ₅	T.Alkali.	Ca	T.Hard	TDS	PO ₄	T.Pho	NO ₃ ⁻	NO ₂ ⁻	SiO ₂	NH ₄ ⁺	
Water. Temp.	1															
Mean River Depth	-0.09	1														
pH	0.21 [*]	0.09	1													
DO	-0.52 ^{**}	0.01	-0.17	1												
BOD ₅	0.16	0.01	-0.01	0.26 [*]	1											
T. Alkalinity	0.12	0.13	-0.09	-0.04	0.09	1										
Ca ²⁺	0.35 ^{**}	0.22 [*]	-0.24 [*]	-0.10	0.13	0.27 ^{**}	1									
T. Hardness	0.63 ^{**}	0.14	-0.04	-0.32 ^{**}	0.09	0.29 ^{**}	0.76 ^{**}	1								
TDS	0.52 ^{**}	0.22 [*]	0.01	-0.20	-0.03	0.24 [*]	0.63 ^{**}	0.67 ^{**}	1							
Orthophosphate	-0.14	-0.1	-0.16	-0.07	-0.09	-0.05	-0.14	-0.23 [*]	-0.01	1						
T. Phosphorus	-0.22 [*]	0.07	-0.13	0.01	-0.11	-0.16	-0.27 ^{**}	-0.40 ^{**}	-0.14	0.58 ^{**}	1					
NO ₃ ⁻	-0.31 ^{**}	0.11	-0.14	0.20	-0.09	-0.10	-0.01	0.26 ^{**}	-0.11	0.20	0.29 ^{**}	1				
NO ₂ ⁻	0.02	-0.14	-0.01	-0.12	0.05	0.08	0.01	0.03	0.03	0.11	0.07	0.03	1			
SiO ₂	-0.20 [*]	-0.06	-0.50 ^{**}	0.31 ^{**}	0.18	0.18	0.22 [*]	0.03	-0.05	0.12	0.08	0.32 ^{**}	0.06	1		
NH ₄ ⁺	-0.15	0.01	-0.04	-0.01	-0.11	0.09	-0.23 [*]	-0.22 [*]	-0.24 [*]	0.03	0.21 [*]	-	0.09	-0.22 [*]	1	
EC	0.44 ^{**}	0.21 [*]	-0.09	-0.18	-0.01	0.32 ^{**}	0.69 ^{**}	0.70 ^{**}	0.93 ^{**}	-0.02	-0.16	-0.12	0.01	0.01	-0.22 [*]	1

Factor analysis was carried out to identify the sources of variation in the obtained data. The Score plot is shown in (Fig. 2). which includes the percentage variance explained by each component and gives an idea on how the different components were extracted. The Eigen-values for different factors percentage variance accounted, cumulative percentage variance and component loading are summarized in (Table 4). The amount of total initial Eigen-values, percentages of variance before rotation and total Eigen-values, variance percentages after rotation using Varimax with Kaiser Normalization are also shown in (Table 4).

Table 3. Multivariate test (MANOVA) for all sites of Shiroud River

Test	Value	F	Sig.
Pillai's Trace	2.10	2.11	0.00
Wilks' Lambda	0.02	3.73	0.00
Hotelling's Trace	14.44	9.19	0.00
Roy's Largest Root	12.65	62.45	0.00

In general, six factors were extracted, and 73.03 % of the total variation is explained as shown in Table 4. The extracted factors are shown in (Table 5). It is clear from this table that most of the parameters associated with each factor are well defined and contribute very little to other factors, that helps in the interpretation of factors. Factor 1, has a high positive loadings for EC, TDS, total hardness, calcium ion and water temperature. This factor can be labeled as a measurement for conductivity and hardness which explains 25.76% of the total variation belongs to EC and hardness factor. The contribution of this factor is the average of all parameters related to this factor.

Table 4. Extracted values of various factors analysis parameters for Shiroud River

Component	Total variance explained before rotation Extraction sums of squared loadings			Total variance explained after rotation Rotation sums of squared loadings		
	Initial Eigen-value			Eigen-value		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.12	25.76	25.76	3.94	24.61	24.61
2	2.24	13.99	39.75	2.03	12.67	37.28
3	1.72	10.74	50.49	1.82	11.35	48.63
4	1.38	8.60	59.09	1.36	8.52	57.14
5	1.23	7.72	66.81	1.34	8.37	65.51
6	1.00	6.22	73.03	1.20	7.52	73.03

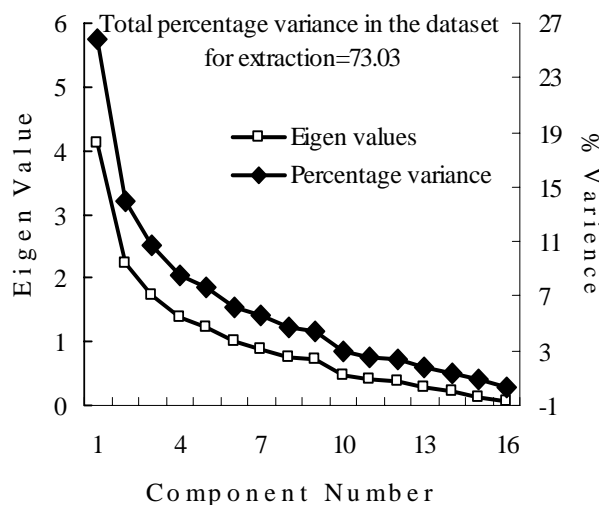


fig. 2. Score plot of Eigen-value vs. components along with % variance components in Shiroud River

Factor 2, has a high positive loadings for silicate, DO and a high negative loading for pH. This factor can be labeled as water quality indicator, which explains 13.99% of the total variation. The contribution of this factor represents the difference between pH and other two parameters (silicate and DO). Factor 3, has a high positive loading for total phosphorus and orthophosphate. This factor can be labeled as a phosphate pollutant. The amount of variation that explained by this factor is 10.72 % of the total variation. The average of phosphorus and orthophosphate represents the contribution of factor 3. Factor 4, has a high positive loading for ammonium ion, total alkalinity and a high negative loading for nitrate. This factor can be labeled as a nutrient and buffering indicator of water quality, which explains 8.6% of total variation. This factor represents the difference between ammonium,

Table 5. Results of the factor analysis for water quality parameters of Shiroud Rive during one year (July 2003 to June 2004)

Parameters	Components					
	1	2	3	4	5	6
EC	0.92	0.03	0.03	0.01	0.11	-0.04
TDS	0.90	-0.07	0.05	-0.05	0.11	-0.05
Total Hardness	0.86	-0.02	-0.29	0.05	-0.09	0.03
Calcium ion	0.81	0.28	-0.16	-0.03	0.09	0.05
Water Temperature	0.66	-0.45	-0.10	-0.03	-0.35	0.13
SiO ₂	0.04	0.80	0.06	-0.17	-0.08	0.19
pH	-0.08	-0.79	-0.10	-0.13	0.17	0.12
DO	-0.36	0.47	-0.12	-0.15	0.34	0.40
T. Phosphorus	-0.20	0.03	0.87	0.04	0.10	0.05
Orthophosphate	-0.03	0.08	0.83	-0.05	-0.17	-0.04
NH ₄ ⁺	-0.29	-0.09	0.12	0.81	0.00	-0.15
NO ₃ ⁻	-0.13	0.37	0.36	-0.54	0.24	-0.08
T. Alkalinity	0.36	0.27	-0.08	0.51	0.11	0.15
River Depth	0.23	-0.06	0.10	0.14	0.82	0.05
NO ₂	0.07	0.13	0.24	0.23	-0.49	0.11
BOD ₅	0.05	0.03	-0.06	0.01	0.06	0.95

Rotation Method: Varimax with Kaiser Normalization

alkalinity and nitrate. Factor 5, has a high positive loading for mean river depth and a high negative loading for nitrite. This factor can be labeled as a flow rate effecting on water quality. This factor explains 7.72 % of total variation. This factor represents the difference of depth and nitrite.

Factor 6, has a high positive loading for biochemical oxygen demand (BOD₅). This factor can be labeled as a biochemical pollutant indicator. This factor explains 6.22 % of total variation. Only one parameter (biochemical oxygen demand) represents this factor. An attempt was made to study the relationship between sites based on the factors that extracted from the data; this relationship can be done by studying the factor scores for all stations. (Fig. 3). represents factor scores for factor 1; it is clear that all sites have low EC and hardness during the month of March, whereas the EC and hardness were high in the months of June through November. Low score of this factor were noticed from December through May. Low EC and hardness could be due to the cold season and related changes of some parameters such as flow rate of the river, the amount of rainfall and water temperature. The highest EC and hardness was noticed in the month of August in site 7, while the lowest EC and hardness was observed in the month of March in

site 5. Second factor represents water quality indicator. Scores for this factor is represented in (Fig. 4). It can be seen that low contribution of this factor was in May through July, this may be due to the amount of diatoms biomass which have an effect of using silicate and dissolved oxygen and as a result pH is high (more than 8). On the other hand, majority of sites had high contribution in other months, which means the diatoms biomass was low when the dissolved oxygen and silicate were high. The highest contribution was seen in site 4 in the month of April, and the lowest contribution was in site 8 in month of July.

The concentrations of phosphate pollutant in majority of sites were low for factor 3. This may be due to the high flow rate and as a result of more water dilution was occurred. (Fig. 5). shows, the scores of this factor and the highest concentration of this factor noticed in April at site 4 whereas, the lowest concentration was at site 2 in September. High concentration could be due to the agricultural activity since farmers use phosphate as a fertilizer. The last three factors such as factors 4, 5, and 6 are less contribution in explaining the total variation since the amount of variation explained by each factor less than 10%. It can be interpreted in the same manner.

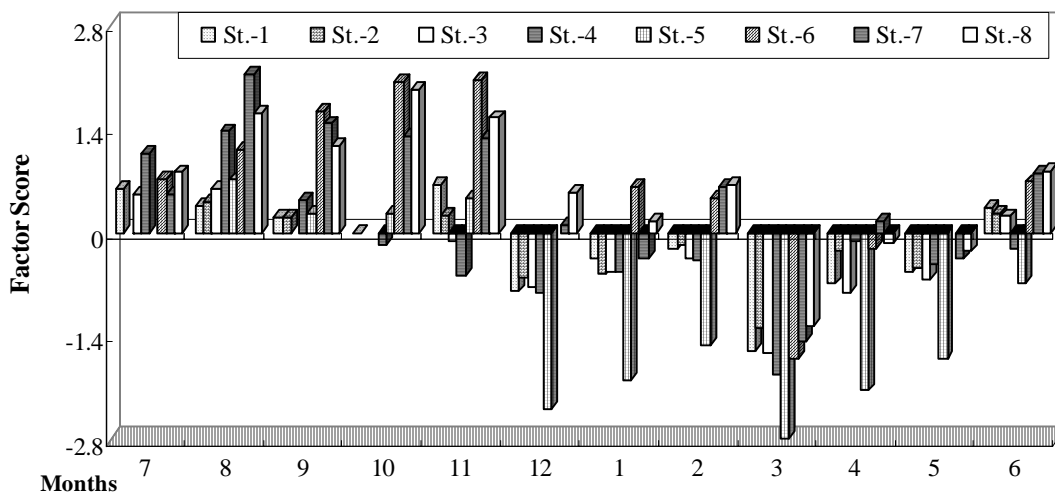


Fig. 3. Factor score for factor 1 (conductivity and hardness group) in Shiroud River

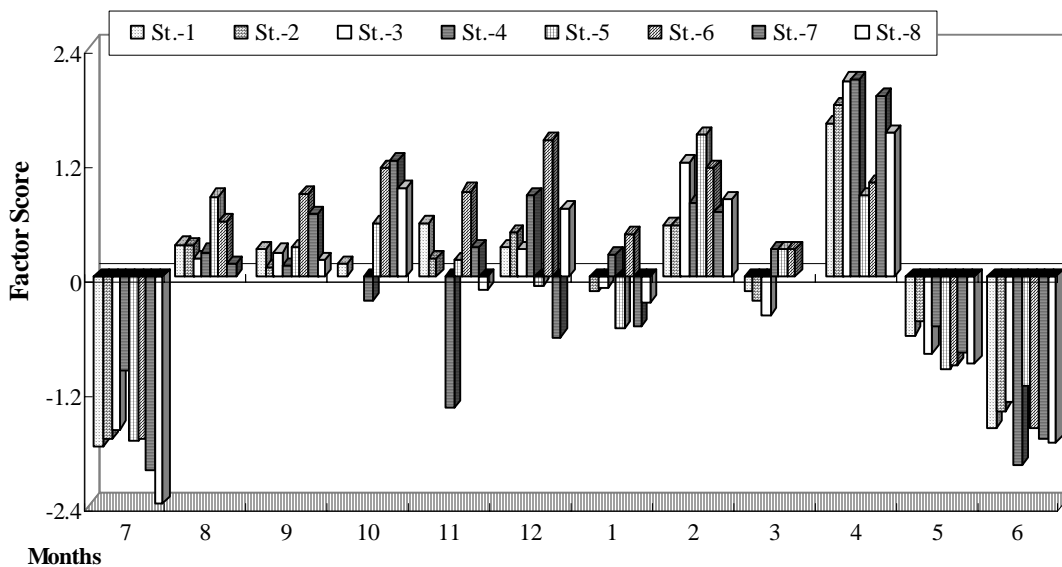


Fig. 4. Factor score for factor 2 (water quality indicator group) in Shiroud River

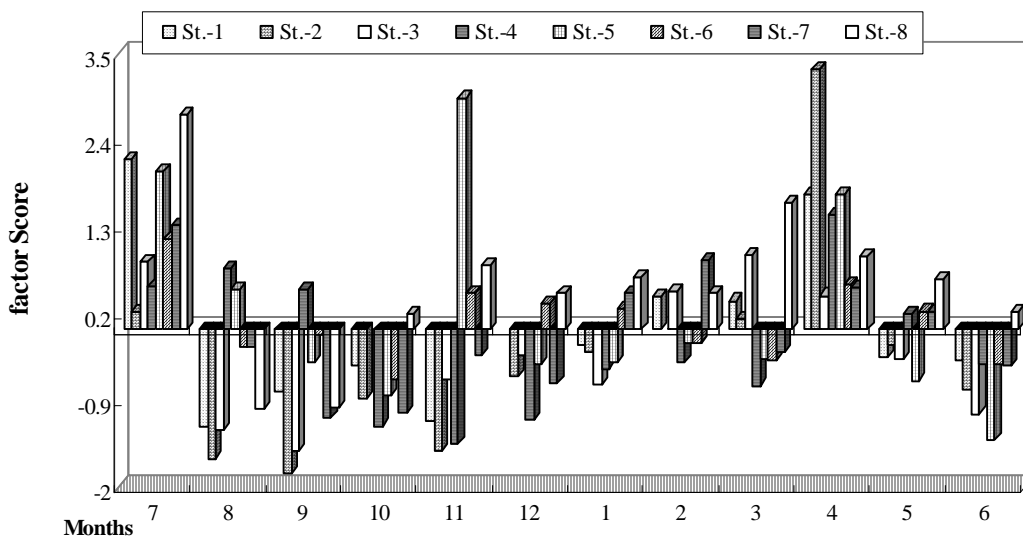


Fig. 5. Factor score for factor 3 (phosphate pollutant group) in Shiroud River

Spatial variations in water quality were evaluated through discriminate analysis (DA). DA was applied on raw data. Seven discriminate functions (DFs) were found to discriminate the eight sites as shown in (Table 6). Wilk's Lambda test showed that only the first two functions are statistically significant (Table 7). Furthermore, 93.7% of the total variance between the eight sites explained by the first two DFs. The first DFs explained 87.6% of the total spatial variance, and the second DFs explained 6.1%. The relative contribution of each parameter is given in (Table 8). Mean river depth exhibited strong contribution in discriminating the eight sites and account for most of the expected spatial variations in the river, while less contribution exhibited from other parameters. Second group of parameters that contribute in explaining the spatial variations are DO, EC, and NH_4^+ as shown in function 2. The classification matrix showed that 92.7 % of the cases are correctly classified to their respective groups, as shown in (Table 9). The result of classification shows that there are significant differences between these eight sites, which are expressed by in terms of two discriminate functions.

Table 6. Eigen-values for seven discriminant function for eight sites

Function	Eigen-value	% variance	Cumulative %
1	12.65	87.60	87.60
2	0.87	6.10	93.70
3	0.46	3.20	96.90
4	0.24	1.70	98.60
5	0.10	0.70	99.20
6	0.07	0.50	99.70
7	0.04	0.30	100.00

Table 7. Wilks' Lambda test of DFs for spatial variation of Shiroud River

Test of Function(s)	Wilks' Lambda	Chi-square	Sig.
1 through 7	0.02	335.36	0.00
2 through 7	0.24	118.43	0.02
3 through 7	0.45	66.32	0.60
4 through 7	0.66	34.68	0.97
5 through 7	0.82	16.66	1.00
6 through 7	0.90	8.88	0.99
7	0.96	3.37	0.97

Table 8. Discriminant function coefficients of spatial variation of Shiroud River

Parameter	Function	
	1	2
Water Temperature	0.02	0.46
M. River Depth	1.16	-0.10
pH	-0.12	-0.09
DO	-0.21	0.76
BOD ₅	-0.03	0.36
Total Alkalinity	0.15	-0.07
Ca ²⁺	-0.34	-0.01
Total Hardness	0.22	0.36
TDS	0.01	-0.03
Orthophosphate	-0.23	-0.01
Total phosphorus	0.15	0.29
NO ₃ ⁻	-0.16	0.48
NO ₂ ⁻	-0.12	0.27
SiO ₂	0.39	-0.43
NH ₄ ⁺	0.06	0.56
EC	0.40	0.68

Table 9. Classification results for discriminant analysis of eight sites

Site	%correct <i>a</i>	Predicted Group membership							
		1	2	3	4	5	6	7	8
1.00	66.7	8	2	0	0	0	0	2	0
2.00	100	0	12	0	0	0	0	0	0
3.00	100	0	0	12	0	0	0	0	0
4.00	100	0	0	0	12	0	0	0	0
5.00	100	0	0	0	0	12	0	0	0
6.00	91.7	0	0	0	0	0	11	1	0
7.00	83.3	0	0	0	0	0	2	10	0
8.00	100	0	0	0	0	0	0	0	12

a 92.7% of original grouped cases correctly classified

In summary, the spatial DA results suggest that mean river depth, DO, EC, and ammonium ion are the most significant parameters to discriminate between the eight different sites. Most of the parameters showed different pattern of spatial variations due to the obvious reasons of different types of weathering processes in the near basin area. Temporal variations in water quality were evaluated through discriminate analysis (DA). DA was carried out with the same raw data after dividing the whole data into four seasonal groups; the spring season was given as group 1, summer group 2, fall group 3 and winter group 4. Three discriminate functions (DFs) were found as shown in (Table 10). Wilk's Lambda test showed that the all functions are significant in discriminating the four seasons (Table 11). Furthermore, only 100% of the total variance between seasons is explained by the three DFs. First function explained 63.7% of the total variance between seasons; second function explained 23.2%, while the third DFs explained only 13.1 of the total variance between the seasons. The relative contribution of each parameter is reported in (Table 12). A new pattern of the water quality relationship exhibited to discriminate the four seasons, since the highest contribution was correlated with silicate, water temperature in DFs-1 as shown in (Table 12). While Ca²⁺, DO, TDS and nitrate exhibited less contribution compared to silicate and water temperature in general and these parameters correlated with more than one DFs. Total hardness correlated with second and third DFs than first discriminate functions. The classification matrix showed that 100 % of the cases are correctly classified to their respective groups, as shown in (Table 13). The result of classification shows that there are significant differences between seasons. In summary, the temporal DA results suggest that Ca²⁺, TDS, silicate, water temperature, total hardness and BOD₅ are the most significant parameters to discriminate between the four different seasons. This suggests that the anthropogenic pollution, which is the major river pollution problem, mainly due to discharge of wastewater into river dose not discriminate between seasons and it is regular source through the year. DA provides additional information over descriptive statistics in evaluation of spatial and temporal differences between sites as expressed by the corresponding classification matrix.

Table 10. Eigen-values for seven discriminant function for four seasons

Function	Eigen-value	% variance	Cumulative %
1	4.00	63.70	63.70
2	1.46	23.20	86.90
3	0.82	13.10	100.00

Table 11. Wilks' Lambda test of DFs for temporal variation of Shiroud River

Test of Function(s)	Wilks' Lambda	Chi-square	Sig.
1 through 3	0.05	264.21	0.00
2 through 3	0.22	127.48	0.00
3	0.55	51.09	0.00

Table 12. Discriminant function coefficients of temporal variation of Shiroud River

Parameter	Function		
	1	2	3
Water Temperature	0.95	0.97	0.08
Mean River Depth	0.02	0.22	-0.38
pH	0.25	0.10	0.37
DO	-0.68	0.25	0.56
BOD ₅	0.28	-0.23	-0.52
Total Alkalinity	-0.18	0.28	0.41
Ca ²⁺	-0.78	2.18	-0.10
Total Hardness	-0.22	-1.57	0.62
TDS	0.68	-0.74	0.35
Orthophosphate	-0.14	0.13	-0.07
Total phosphorus	0.27	-0.10	-0.37
NO ₃ ⁻	-0.62	-0.02	0.62
NO ₂ ⁻	0.16	0.11	0.21
SiO ₂	1.35	-0.34	-0.01
NH ₄ ⁺	-0.21	0.02	0.32
EC	-0.10	-0.39	0.04

Table 13. Classification results for discriminant analysis of four seasons

Seasons	% correct	Predicted Group			
		Membership			
	<i>a</i>	1	2	3	4
Spring	91.7	22	1	1	0
Summer	100	0	24	0	0
Fall	83.3	2	0	20	2
Winter	100	0	0	0	24

a 93.8% of original grouped cases correctly classified

CONCLUSION

In this study, multivariate statistical techniques were used to evaluate spatial and temporal variations in water quality of Shiroud River basin. Discriminate analysis gave the best result both spatially and temporally. DA spatial identified only four parameters to discriminate between eight sites (mean river depth, DO, NH_4^+ , and EC) with 92.7% correct assignments, and only seven parameters to discriminate between four seasons to explain the temporal variation (mean river depth, water temperature, Ca^{2+} , TDS, silicate, Total hardness, and BOD_5) with 93.8% correct assignments. Therefore, discriminate analysis helped to identify and understanding the source of spatial and temporal variations. Thus, the application of multivariate statistical techniques has been proved to be an effective tool for analyzing a huge and complex environmental data matrix.

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REFERENCES

- APHA (1999). *Standard Methods for the Examination of Water and Wastewater*. 20th edition, APHA, AWWA, Washington D.C.
- EPA. (1979). *Methods for chemical analysis of waters*, method 353.3, US. EPA, Washington D.C.
- Jarvie H.P., Whitton B.A., and Neal C., (1998). Nitrogen and phosphorus in east coast British rivers; speciation, sources and biological significance. *Sci. Total Environ.*, 210-211, 79-109.
- Johnson, R. A. and Wichern, D. W. (2002). *Applied multivariate statistical analysis*, Prentice Hall, 2002.
- Karbassi, A. R., Nouri, J., Mehrdadi, N. and Ayaz, G. O. (2008). Flocculation of heavy metals during mixing of freshwater with Caspian Sea water. *Environ., Geo.*, **53**(8), 1811-1816.
- Karbassi, A. R., Nouri, J. and Ayaz, G. O. (2007) Flocculation of Cu, Zn, Pb, Ni and Mn during mixing of Talar River Water with Caspian Seawater. *Int. J. Environ. Res.*, **1**(1), 66-73.
- Karbassi, A. R., Monavari, S. M., Nabi Bidhendi G. R., Nouri, J., Nematpour K., (2008). Metals pollution assessment of sediment and water in the Shur river. *Environ. Monitor. Assess.*, 1-10, Elsevier.
- Khadka, R. B. & Khanal, A. B. (2008) Environmental Management Plan (EMP) for Melamchi Water Supply Project, Nepal. *Int. J. Environ. Res.*, **2**(1), 87-96
- Lee, J.Y., Cheon, J.Y., Lee, K.K., Lee, S.Y., and Lee, M.H., (2001). Statistical evaluation of geochemical parameter distribution in a ground water system contaminated with petroleum hydrocarbons. *J. Environ. Qual.* **30**, 1548-1563.
- Mahvi A. H., Nouri J., Babaei A. A. and Nabizadeh R., (2005). Agricultural activities impact on groundwater nitrate pollution. *Int. J. Environ. Sci. Tech.*, **2**(1), 41-47.
- Monavari, S. & Guieysse, B. (2007) Development of Water Quality Test Kit Based on Substrate Utilization and Toxicity Resistance in River Microbial Communities. *Int. J. Environ. Res.*, **1**(2), 139-142.
- Mtethiwa, A. H.; Munyenembe, A.; Jere, W. & Nyali, E. (2008) Efficiency of oxidation ponds in wastewater treatment. *Int. J. Environ. Res.*, **2**(2), 149-152.
- Nouri, J., Karbassi, A. R., Mirkia S., (2008). Environmental management of coastal regions in the Caspian Sea. *Int. J. Environ. Sci. Tech.*, **5**(1), 43-52.
- Reghunath, R., Murthy, T.R.S., and Raghavan, B.R., (2002). The utility of Multivariate statistical techniques in hydrogeo-chemical studies: an example from Karnataka, India. *Water Res.*, **36**, 2437-2442.
- Rencher, A. C. (2002). *Methods of Multivariate Analysis*, Second Edition, John Wiley & Sons, INC, publication.
- Samarghandi M., Nouri J., Mesdaghinia, A. R., Mahvi A. H., Nasserli, S., Vaezi, F., (2007). Efficiency removal of phenol, lead and cadmium by means of UV/TiO₂/H₂O₂ processes. *Int. J. Environ. Sci. Tech.*, **4**(1), 19-25.
- Simeonov, V., Stratis J. A., Samara, C., Zahariadis, G., Voutsas D., Anthemidis A. Sofoniou M. and Kouimtzi T. (2003). Assessment of the surface water quality in Northern Greece. *Water Res.*, **37**, 4119-4124.
- Simeonov, V Simeonova, P., and Tisitouridou. R., (2004). Chemometric quality assessment of surface waters: two case studies. *Chem. Eng. Eco.* **11**(6), 449- 469.
- Singh. K.P., Malik, A., Mohan, D., and Sinha, S., (2004). Multivariate statistical technique for the evaluation of spatial temporal variation in water quality of Gomti River (India): a case study. *Water Research* **38**, 3980-3992.
- Vega, M., Pardo, R., Barrado, E., and Deban, L. (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Res.*, **32**, 3581-3592.