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Impact of Urbanization and Land Use Changes on Water Geochemical Properties. A Case Study: Gharaso River in Golestan Province, North of Iran

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ABSTRACT

Rapid growth of urban populations and the expansion of urban areas in the north of Iran have led to changes in land use and subsequently changes in water quality of the Gharaso River in Golestan Province. Thus, the aim of this research was to investigate the role of urbanization and land use change on water quality in seven stations (Siahab, Angirabad, Shastkalateh, Yasaqi, Naharkhoran, Abgir and Poleordogah). In this paper, principal component analysis and hierarchical cluster analysis were used to investigate the water quality of the Gharaso River. Water samples collected every month over a ten-year period from 7 sampling stations, along a 50 km section of Caspian Sea that is under the influence of anthropogenic and natural changes were analyzed. The highest pollutions were equal with, electrical conductivity 1448.6 and 1127.5 (mmho/cm), total dissolved solids 911.16 and 722.3 (mg/l), bicarbonate 293.37 and 331.83 (meq/l), chloride 221.7 and 139.56 (meq/l), calcium 81.74 and 93.44, sodium 150.7 and 86.49 (meq/l), potassium 6.9 and 14.31 (meq/l), sodium adsorption ratio 2.83 and 1.9 (meq/l), temporary hardness 230.6 and 262.19 (mg/l), total hardness 404.59 and 370.6, in the Siahabad and Naharkhoran, respectively, sulfate 195.6 and 153.9 (meq/l), magnesium 52.8 and 40.34 (meq/l), in the Siahabad and Abgir, respectively. The highest pH was 7.8 in the Naharkhoran station. The results indicated that water quality in Siahab and Naharkhoran stations was in the poorest quality among other stations because of anthropogenic effects. The best water quality was in Shast Kalateh station because there were no changes in the land uses. The Gharaso River joins the Caspian Sea creating sediment problems and an increasing threat to human and marine health.

Keywords: cluster analysis, health ecosystem, land use change, principal component analysis, quality water, urbanization
Abbreviations: **Ca^{+2}**, calcium; **CA**, cluster analysis; **Cl^{-1}**, chloride; **EC**, electrical conductivity; **HCO_3**, bicarbonate; **K^{+1}**, potassium; **Mg^{+2}**, magnesium; **Na^{+1}**, sodium; **PCA**, principal component; **SAR**, sodium adsorption ratio; **SO_4**, sulfate; **TDS**, total dissolved solids; **Temp**, temperature; **T-Hard**, total hardness

INTRODUCTION

The growth rate of a population in urbanization is affected by changes in the population, wealth, social trends (for example household size and lifestyle choices) and transport costs (Reginster and Rounsevell 2006). In the north of Iran, rapid growth of the population requires additional farmland for producing crops. For this reason, one way to expand cropland is by clear-cutting forests and converting pastures to croplands. Land use has always changed in response to changing human needs, driven by gradual trends and abrupt changes in the economy, society, technology, governance structures, and environmental conditions such as the climate and soil degradation (Rounsevell *et al.* 2009). Conversion of forest and grasslands into agricultural land is one of the main concerns worldwide in the context of environmental degradation and global climate change (Wali *et al.* 1999). Conversion of natural land resources to crop production was considered as the largest source of anthropogenic carbon emissions after burning fossil fuel (Fitzsimmons *et al.* 2004). The quality of river and lake water is affected by both natural processes and human activities. Surface water quality is affected by chemical, physical and biological contaminants and is influenced by anthropogenic activities and is thus one of the greatest environmental challenges all over the world (May *et al.* 2006; Ouyang *et al.* 2006; Noori *et al.* 2010). Surface waters are controlled by both natural processes, i.e. precipitation inputs, erosion, weathering, and on the other hand, anthropogenic activities via point sources, such as industrial effluents and wastewater treatment facilities, or are diffuse, such as runoff from urban area and farming land (Lie *et al.* 2008). Recent studies demonstrated that surface water quality has deteriorated noticeably in many countries in the past decades due to poor management in land use practices (Liu *et al.* 2003), indicated by strong relationships between declining water quality and increasing agricultural development at a catchment scale (Buck *et al.* 2004). Therefore, researchers have focused on the effect of land use on water quality, by considering agricultural activities and its effect on nutrients and suspended particulate matter in water (Johnson *et al.* 1997). Increases in urbanized areas suggest that there is an increase in environmental pressure on rivers, particularly on urban rivers. The increment of water use consequently causes the reduction of river flows, lower dilution capacity and a minor departure capacity (Li *et al.* 2009). Thus, these anthropogenic activities are directly reflected on landscape characteristics, the morphological, geographical, and land-use attributes of catchments with the chemical characteristics or ecological status of aquatic systems. This discussion has long been a major research focus on watershed management (Donohue *et al.* 2006). Rivers play an important role in a watershed, for carrying off municipal and industrial wastewater and runoff of farmlands (Wang *et al.* 2007). The constant discharges of domestic and industrial wastewater and seasonal surface runoff all have a strong effect on the river discharge and its water quality. Rivers are the main water sources for domestic, industrial and agricultural irrigation purposes in

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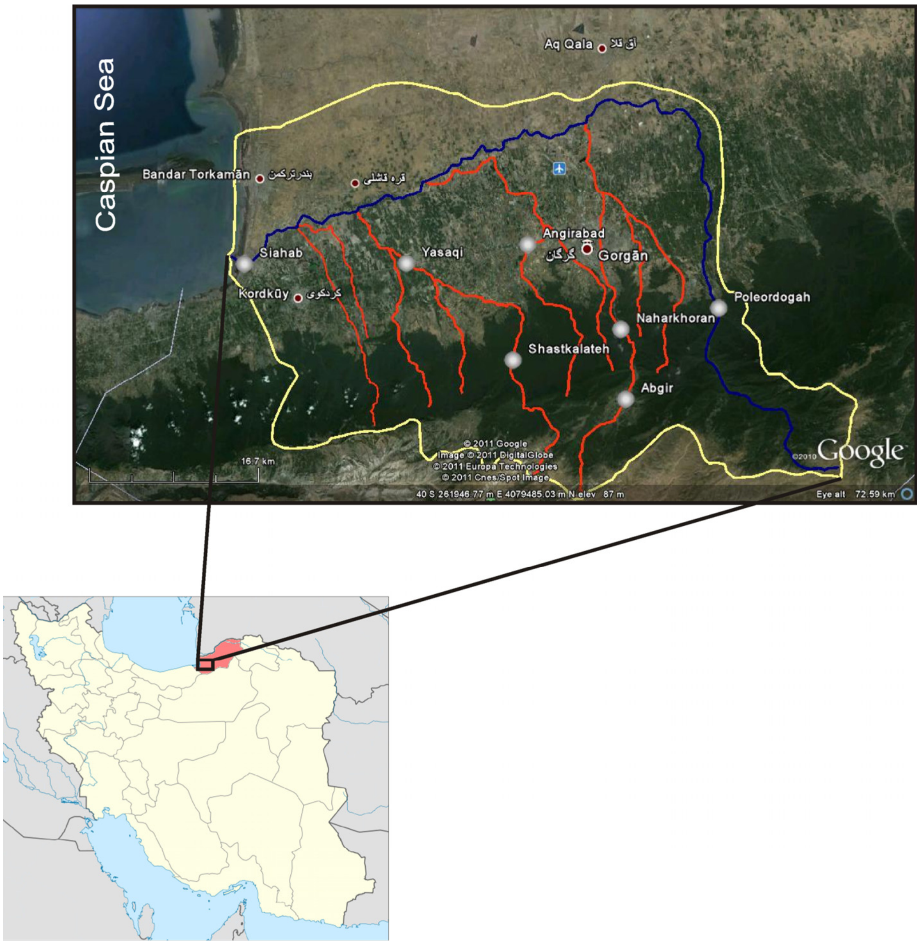


Fig. 1 Location map and the stations of the sampled areas.

every region (Yu *et al.* 2003). So, river water quality is one important factor which directly affects the health of humans and other living beings (Kazi *et al.* 2009). Therefore, it is imperative and important to have reliable information on the characteristics of water quality for effective pollution control and water resource management. Rivers are the most important land water resources for human consumption, agricultural needs, and industrial and recreational purposes. For these reasons, there is a great need to evaluate river water quality (Fan *et al.* 2010). It is important to have reliable information on trends of water quality for effective water management. This is especially more important in tourist regions such as the north of Iran, which experiences water pollution, is a densely populated region and has seen rapid population growth due to the large influx of people seeking employment (Razmkhah *et al.* 2010). The purpose of a water quality monitoring system in a river or a watershed is to provide a system that would generate sufficient and timely information. It must be able to help managers to make informed management decisions regarding the exposure health risk of the populations who are utilizing this resource. Component analysis (CA) and principal component analysis (PCA), among all available methods, are frequently used as they are capable of detecting similarities among samples and/or variables (Wenning and Erickson 1994; Battegazzore and Renoldi 1995; Wang *et al.* 2006; Mendiguchia *et al.* 2007; Fan *et al.* 2010; Tran *et al.* 2010; Ruggieri *et al.* 2011).

In this research, PCA and hierarchical CA methods have been used to investigate the water quality of the Gharaso River and the relative magnitude of anthropogenic and "natural" influences on the quality of river water.

MATERIALS AND METHODS

Sampling stations

Gharaso River is located in the Gharaso watershed (**Fig. 1**). This watershed is located at 54.00–54.39 longitude and 36.36–37.47 latitude, covering an area of 1762 km^2. Mean elevation is 624 m with the highest and the lowest points being 3200 and -26 m above sea level, respectively. Average annual temperature and precipitation are 7.5°C and 575 mm. Precipitation is maximum in April and minimum in August. This river joins the Caspian Sea after traversing a 50-km route. The area surrounding the river has seen an increase in cities, land-use change and urbanization.

Fig. 1 shows the location of the 7 sampling stations designed by Golestan Regional Water Co. in order to monitor water quality. Selected stations were sampled every month for 10 years on a rotational schedule. Some stations located in densely populated areas were sampled more often. Fourteen parameters including water temperature (Temp), pH, electrical conductivity (EC), total dissolved solids (TDS), bicarbonate (HCO_3), sulfate (SO_4), chloride (Cl^{-1}), temporal hardness, total hardness (T-Hard), calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^{+1}), sodium (Na^{+1}), sodium percent, and sodium adsorption ratio (SAR) were analyzed over a 10-year period as physicochemical variables.

Analytical procedures

Standard analytical methods for monitoring parameters were APHA *et al.* (2005) and AOAC (1990). Measured parameters included: calcium (3500-Ca B); chloride (4500-Cl B); sulfates (4500-SO_4 2 D); temperature (2550 B, field measured); pH (4500-Hþ B, field measured); total and temporary hardness (2340 C); potassium (3500-K B); sodium (3500-Na B); total dissolved solids (2540 C); magnesium (3500-Mg B); and conductivity (2510 B). All the analyses were run in duplicate and devices used were Jenway 430, Jenway Flame Photometer PFP7, Jenway Spectrophotometer 6715 and Hach 2100p.

Table 1 Statistical descriptive for the sample analyzed at all stations in the Gharaso River.

Stations	TDS (mg/l)	EC (mmho/cm)	pH	Hco3 (meq/l)	Cl (meq/l)	So (meq/l)	Ca (meq/l)
Siahabad	911.17 ± 302.16	1448.67 ± 460.2	7.67 ± 0.17	293.37 ± 30.33	221.72 ± 119.07	195.62 ± 68.93	81.74 ± 15.3
Yasaghi	327.07 ± 36	502.13 ± 42	7.64 ± 0.34	252.02 ± 36.24	20.2 ± 4.41	34.77 ± 5.73	51.05 ± 10.06
Shastkalate	282.1 ± 34.08	433.27 ± 52.44	7.62 ± 0.33	223.19 ± 13.56	13.86 ± 1.84	32.4 ± 9.96	46.28 ± 4.58
Anjirabad	253.29 ± 34.32	392.88 ± 50.47	7.52 ± 0.37	202.5 ± 16.38	12.41 ± 2.41	30.89 ± 5.85	53.86 ± 10.36
Abgir	496.1 ± 30.15	786.61 ± 39.71	7.61 ± 0.11	225.49 ± 12.54	46.6 ± 2.59	153.9 ± 15.73	69.7 ± 7.37
Poleordogah	396.32 ± 37.6	611.83 ± 46.2	7.67 ± 0.16	211.35 ± 9.27	30.56 ± 3	111.82 ± 14.77	62.66 ± 5.23
Naharkhoran	722.3 ± 49.63	1127.58 ± 80.73	7.8 ± 0.18	331.83 ± 21.91	139.56 ± 27.2	120.71 ± 11.56	93.44 ± 8.59
Stations	**Mg (meq/l)**	**Na (meq/l)**	**K (meq/l)**	**SAR**	**Total H (mg/l)**	**Temporal H (mg/l)**	
Siahabad	52.87 ± 14.5	150.7 ± 76.8	6.99 ± 2.57	2.83 ± 1	230 ± 24	404.6 ± 64	
Yasaghi	27.29 ± 1.7	15.04 ± 3.53	2.5 ± 1.09	0.41 ± .087	210.87 ± 26.85	238.62 ± 28.81	
Shastkalate	24.62 ± 2.73	8.62 ± 2.18	1.12 ± 0.56	0.25 ± 0.05	184.76 ± 10.3	215.89 ± 16.23	
Anjirabad	15.78 ± 3.23	7.55 ± 3.37	1.51 ± 0.8	0.23 ± 0.1	169.26 ± 19.26	198.68 ± 19.22	
Abgir	40.34 ± 2.72	31.48 ± 2.62	2.7 ± 0.61	0.74 ± 0.06	184.18 ± 10.27	338.18 ± 17.41	
Poleordogah	31.89 ± 2.91	20.44 ± 2.45	1.91 ± 1.06	0.52 ± 0.05	165.144 ± 27.72	270.03 ± 45.44	
Naharkhoran	722.3 ± 49.63	1127.58 ± 80.73	7.8 ± 0.18	331.83 ± 21.91	139.56 ± 27.2	120.71 ± 11.56	

Multivariate statistical analysis

Exploratory data analysis was performed by linear display methods (PCA) and unsupervised pattern recognition techniques (CA) on experimental data. Since methods of classification used here are non-parametric, no assumptions about underlying statistical distribution of the data was made, therefore no evaluation of normal (Gaussian) distribution was necessary (Sharaf *et al.* 1986).

1. Cluster analysis

CA encompasses a wide range of techniques for exploratory data analysis. The main aim of CA is grouping objects (cases) into classes (clusters) so that objects placed within a class are similar to each other but different from those in other classes. In CA, the objects are grouped by linking inter-sample similarities and the outcome illustrates the overall similarity of variables in the data set (Massart and Kaufman 1983). Many applications of CA for water quality assessments have been reported (Singh *et al.* 2005; Mahbub *et al.* 2008). CA allows the grouping of river water samples on the basis of their similarity in chemical composition. Unlike PCA, which normally uses only two or three principal components (PCs) for display purposes, CA uses all the variance or information contained in the original data set. Hierarchical agglomerative CA was carried out on the normalized data by means of Ward's method, an extremely powerful grouping mechanism, which yields a larger proportion of correct classified observations (Willet 1987), using squared Euclidean distances as a measure of similarity (Massart and Kaufman 1983).

2. Principal component analysis

PCA, as a technique for variable reduction, dispense with nonhomogeneity in sampling data, missing value and periodic trends in data and identifies temporal variation in water quality and effective factor on it. It also extracts the most important parameter in polluted station (Dillon and Goldstein 1984). In this way diagonal of the correlation matrix transforms the original p correlated variables into p uncorrelated (orthogonal) variables called PCs, which are weighed as linear combinations of the original variables (Wenning and Erickson 1994). The characteristic root (eigen values) of the PCs is a measure of associated variances and the sum of the eigen values coincides with the total number of variables. Correlation of PCs and original variables is given by loadings, and individual transformed observations are called scores (Wunderlin *et al.* 2001). Other scientists (Zhou *et al.* 2007; Wu and Wang 2007; Andrade *et al.* 2008) also applied PCA in order to assessment water quality. In this research, SPSS v. 16 was used for PCA and CA.

RESULTS AND DISCUSSION

Spatial variation of water quality

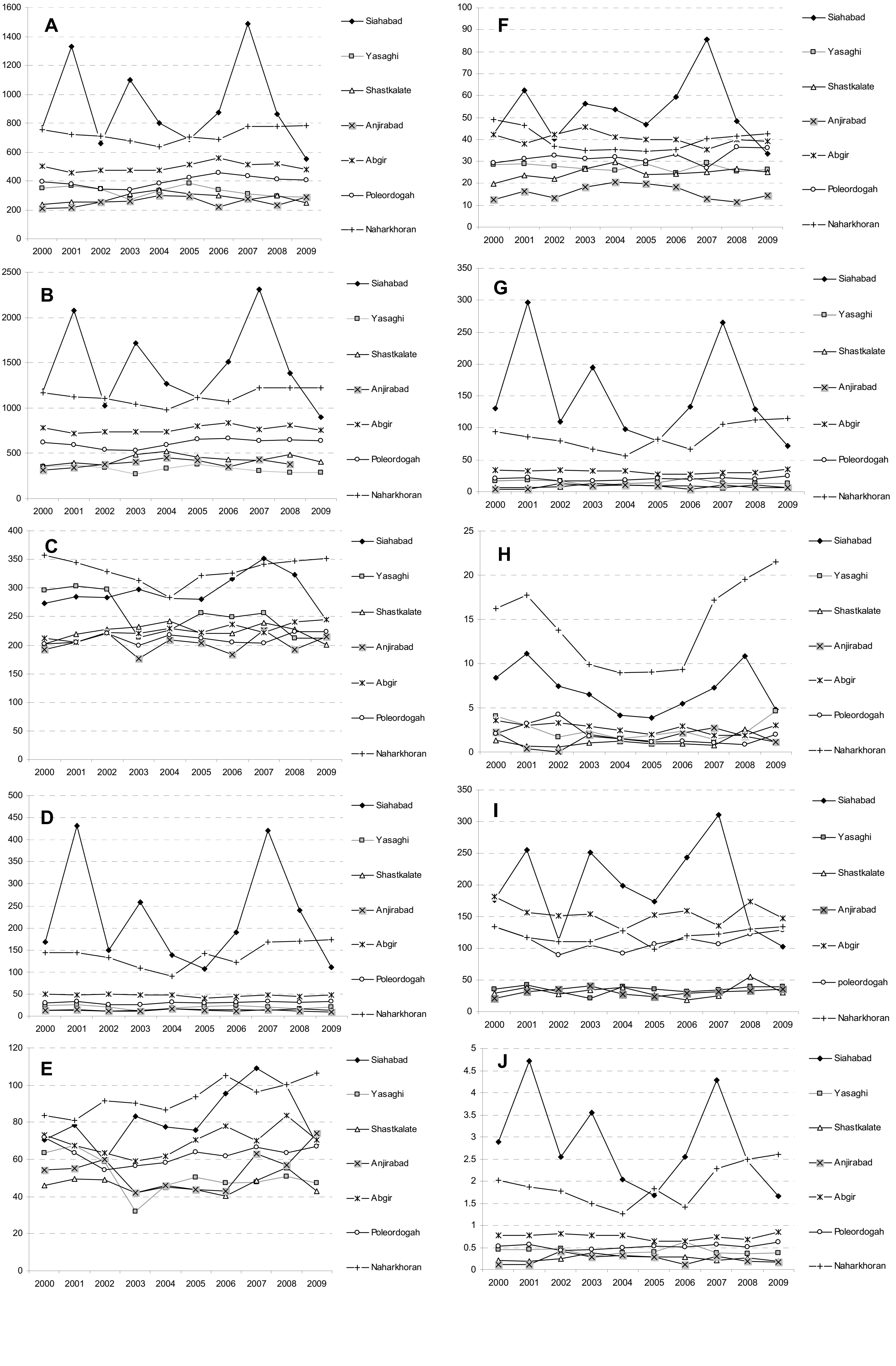
Table 1 provides a summary of the mean value, standard deviation of 13 measured variables in the river water samples at 7 stations. The TDS, Cl^{-1}, EC, Na^{+1} and SAR had more concentration than other parameters in the Siahab and Naharkhoran stations but there were not considerable differences among other parameters. There were no spatial and temporal changes at the Anjirabad and Shastkalate stations. This can be attributed to absent land use change and intact nature. However, there were some peaks during the years of 2001, 2003 and 2007. This may have been due to increased precipitation resulting in more runoff, soil degradation and finally extensive changes in water quality (**Fig. 2**; Mendiguchia *et al.* 2007). The highest amount of SO_4 was detected in Siahab followed by Naharkhoran, Abgir, Poleordogah stations and finally in Anjirabad, Yasaghi and Shastkalate stations. This result was probably a consequence of the morphology of soils irrigated by the river, which are formed mainly by limestone, marl and gypsum (Vega *et al.* 1998).

Increases in HCO_3 and Ca^{+2} were observed in Siahab and Naharkhoran. This may be due to the kind of morphology of soils irrigated by the river which are formed primarily by limestone. In the other stations, there were no significant differences.

Water hardness, containing dissolved metals such as Mg^{+2}, originated from industrial, agricultural and domestic sewage and showed high levels in Siahab, Naharkhoran and Abgir, possibly due to soil weathering, erosion (seasonal effect), urbanization and anthropogenic sources of pollution. The SO_4 content was highest in the Siahab and Naharkhoran stations, an indication of weathering and erosion in this area. The highest content of K^{+1} was observed in the Naharkhoran station. This is probably due to the consumption of manure in cultivated areas, building villas, agricultural and domestic sewage. There were no considerable changes in temporary hardness and pH, also shown by Ruggieri *et al.* (2011).

Principal component analysis

To maintain consistency and to avoid any biased approach, the number of PCs to be retained in order to comprehend the underlying data structure (Jackson 1991) was determined by the built-in criteria of the software throughout the analysis. Scree plots showed a pronounced change of slope after the first eigen value. Even though Cattell and Jaspers (1967) suggested the use of all PCs up to and including the first one after the brake, again default software criteria of eigen values greater than unity was used to determine the number of PCs to be retained. The scree plot (**Fig. 3**) was used to identify the number of PCs among parameters. This figure shows a pronounced change in slope after the TDS eigen value which explained 6.77% of the total variance by the 4th component, but the three components that were retained had eigen values greater than unity and explained 90% of the variance or information contained in the original data set. Projection of the original variables on the sub-


A
B
C
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E
F
G
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Siahabad
Yasaghi
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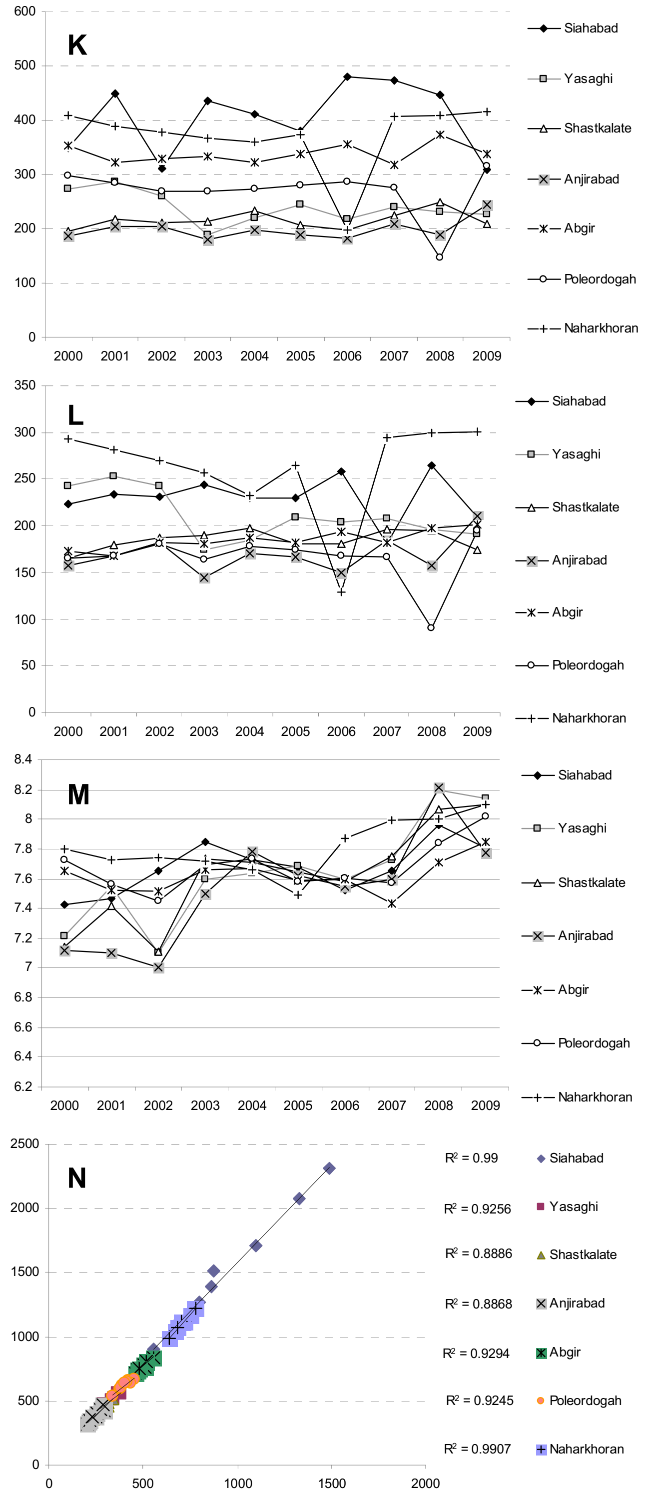

Fig. 2 TDS (**A**), EC (**B**), HCO_3 (**C**), Cl (**D**), Ca (**E**), Mg (**F**), Na (**G**), K (**H**), SO_4 (**I**), SAR (**J**), TH (**K**), Temporal H (**L**), pH (**M**) relationship between TDS (X-axis) and EC (Y-axis) (**N**).

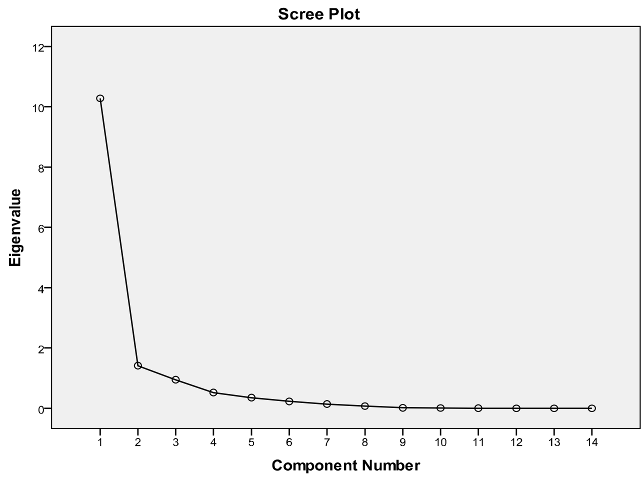

Fig. 3 Scree plot of eigenvalues.

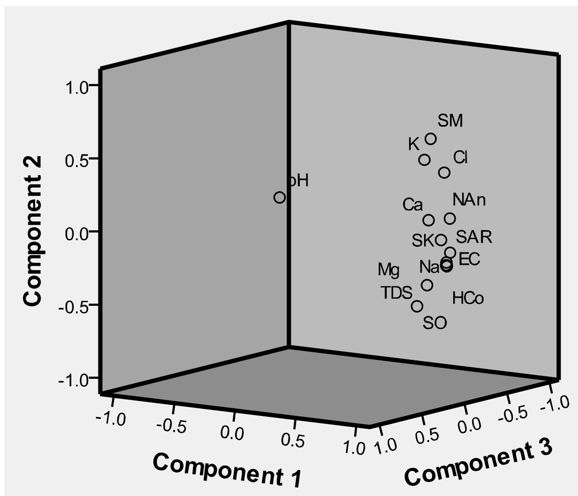

Fig. 4 The component plot of loading of 14 experimental variables on three significant principal components.

Table 2 Loadings of 14 experimental variables on three significant principal components for river water samples.

Component Matrix[a]	Component		
	1	2	3
TDS	.975	-.181	.012
EC	.978	-.177	.024
pH	.224	.337	.906
Cl	.828	.413	-.168
HCo3	.939	-.171	-.035
SO3	.824	-.455	.146
Ca	.846	.120	.042
Mg	.884	-.309	.114
Na	.935	-.198	-.046
K	.776	.518	-.009
SAR	.962	-.103	-.047
Na%	.932	.122	-.085
Temporal hardness	.678	.621	-.222
Total hardness	.920	-.014	.001

space of the PCs is called loading and coincides with the correlation coefficients between PCs and variables (Vega *et al.* 1998). Loading of three retained PCs are presented in **Table 2**. PC1 explains 73% of the variance and it is highly contributed to by most variables: EC, TDS, HCO_3, Na^{+1}, SAR, total hardness, Na%. PC2 explains 10% of the variance and it includes K^{+1}, Cl^{-1} and temporary hardness. PC3 (6.77% of variance) is positively contributed to by pH. These results are similar to those of Wang *et al.* (2006) and Fan *et al.* (2010). The component plot of loading of variables is shown in **Fig. 4** for three significant PCs.

As shown in **Table 2**, PC1 was highly contributed to by mineral compounds, but PC2 and PC3 were contributed to by anthropogenic and mineral pollution, therefore these components could not be explained only in terms of organic or mineral pollution.

A rotation of PCs (Upper Loads for each components are in bold) can achieve a simpler and more meaningful representation of the underlying factors by decreasing the contributions to PCs by variables with minor significance and increasing the more significant ones. Rotation produces

Table 3 Loadings of 14 experimental variables on the varimax rotated PCs on three significant varifactors for river water samples.

Rotated Component Matrix[a]	Component		
	1	2	3
TDS	.903	.407	.054
K	.342	.841	.213
EC	.904	.409	.068
SAR	.843	.477	.019
Na	.875	.388	-.009
Cl	.864	.408	.009
Mg	.910	.227	.106
So4	.945	.071	.090
%NA	.688	.645	.044
Ca	.629	.558	.156
Temporal hardness	.185	.927	.030
Total hardness	.762	.508	.086
HCO	.430	.836	.038
pH	.070	.127	.982

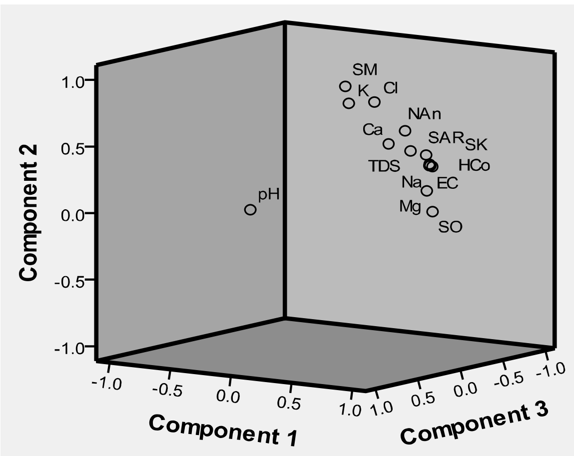

Fig. 5 The component plot of 14 experimental variables on the varimax rotated PCs on three significant varifactors.

a new set of factors, each involving primarily a subset of original variables with as little overlap as possible, so that the original variables are divided into groups somewhat independent of each other (Sharaf *et al.* 1986; Massart *et al.* 1998). Although rotation does not affect the goodness of fit of PCs solution, the variance explained by each factor is modified. A varimax rotation of PCs redounded to rotated PCs (called henceforth varifactors) is presented in **Table 3**. Therefore three varifactors (VF) were extracted, explaining 90% of the variance. Rotation resulted in an increase in the number of factors necessary to explain the same amount of variance in the original data set. VF1 with high and positive scores for TDS, EC, Mg^{+2} and SO_4 explains 52.5% of the total variance. This variable cluster points to a common origin for these minerals such as dissolution of gypsum in water. The gypsum factor can be due to urbanization and extensive building of villas around Naharkhoran and Abgir stations. VF2, containing 30% of the total variance, includes HCO_3 and temporary hardness. This VF can be explained by taking into account the hydrolysis of limestone compounds. VF3 (7.5% of variance) has a high and positive load of pH, indices of hydrolysis, dissolution and degradation of surrounding river soils. Therefore, in cold seasons, precipitation may cause dissolution of such minerals. PCA indicated that land-use and water quality variables were associated with non-point source contaminants (e.g. nutrients and specific conductance) (Tran *et al.* 2010). The component plot of variables on the varimax-rotated PCs are shown **Fig. 5**.

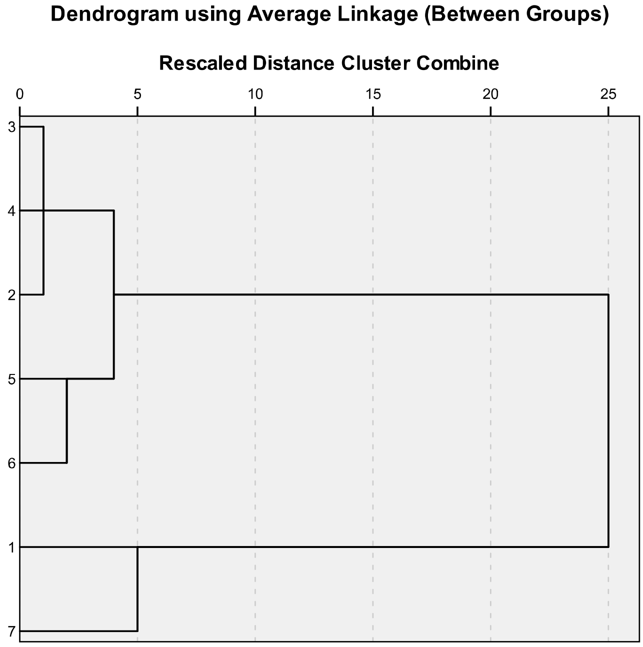

Fig. 6 Dendrogram based on agglomerative hierarchical clustering (Ward's method) for river stations.

Cluster analysis

The dendrogram of stations obtained by Ward's method in among different stations shown in **Fig. 6**. Two well differentiated clusters can be seen. The first group from the top is formed by two subgroups, with water quality decreasing from top to bottom. Siahab and Naharkhoran stations are in the same group and with least similarity to another group. This indicates the largest decrease in water quality by this group relative to all other stations. Another subgroup is composed of Angirabad, Shastkalateh, Iasaghi, Abgir and Poleordogah stations together with a group with lower pollution, then Siahab and Naharkhoran in PCA. This group had better water quality than the first subgroup, as seen by the PCA score plot.

CONCLUSIONS

Water quality is extremely important, particularly in tourist areas, which tends to be more easily polluted than other areas. The aim of this study was to analyze water quality changes in the Gharaso watershed caused by rapid growth of land use change and urbanization. Environmental analytical chemistry generates multidimensional data that requires multivariate statistics to analyze and interpret underlying information. PCA determined that a reduced number of 3 VFs that explained a high percentage of the experimental data set variance. PCA spatial variations were defined approximate. Explaining 90% of spatial variations with 3 VFs, PCA in combination with CA allowed nearly complete identification and assessment of spatial sources of variation affecting the quality and hydrochemistry of river water. CA was not able to define details but provided a guide through classification. Performing PCA for each cluster formed by CA could help identify pollution sources of stations in each cluster. The worst water quality was in Siahab and Naharkhoran stations relative to other stations. The Siahab station is the last station located before the Gharaso River joins the Caspian Sea, so it received the most pollution and therefore represented the greatest threat to aquaculture health. After Siahab, Naharkhoran station had the most polluted water relative to other stations. Important factors such as intensive urbanization and land use change are causes of the decrease in water quality in the Gharaso River. Soil degradation and land use change factors lead to increase solute concentration in the surface runoff. If these changes continue, there will be a serious threat to the entire ecosystem's health.

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