Original Research

Assessment of Spatial Variation of Water Quality Parameters in the Most Polluted Branch of the Anzali Wetland, Northern Iran

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Abstract

In four consecutive seasons along 9 stations, water parameters such as TDS, pH, temperature, DO, BOD, COD, TOC, TP, NH_4^+, TN and NO_3^- were determined on the Siahroud River southwest of the Caspian Sea in northern Iran. The results indicated higher TDS values in some parts of the river due to the agriculture and residential activities. The addition of ammonia fertilizers in the paddy fields is one of the major causes for the higher NH_4^+ in the downstream sites. Total phosphorous (TP) and total nitrogen (TN) levels in the river were mainly in the organic forms. Factor analysis showed that agriculture and urban activities were the major pollutant sources. Four zones were identified by cluster analysis, suggesting local pollution sources or the accumulation of pollution effects downstream.

Keywords: Anzali wetland, cluster analysis, factor analysis, Siahroud River, water quality parameters

Introduction

The ever-growing demands for water resources coupled with the rate at which much of the earth's fresh waters are being adversely affected by human activities, demonstrates a developing crisis in the not-too-distant future if environmental water resources are not appropriately managed [11]. Iran is not an exception to this future crisis. Indeed Iran, with an average rainfall of less than one third of the world average, is a country located in an area that suffers critically from a shortage of water resources. So the conservation of impoverished water resources is indispensable for the sustainability of our economic development. For this reason, in the past few decades more attention has been given to the water quality of river systems in the northern parts of Iran. This region has a high potential for agriculture and industrial development as a result of relatively high rainfall and rich water resources. Thus, both sanitation needs and industrial activities have led to total destruction of these aquatic and terrestrial ecosystems. This deterioration influx caused one of the endangered aquatic ecosystems on the list of the Ramsar Convention, namely the Anzali wetland (especially the eastern parts), to turn into a highly degraded water system.

The wetland is a precious water body which every year hosts more than 150 species of migrant birds. However, in recent years eutrophication coupled with the high burden of industrial effluents and domestic sewage threaten this ecosystem on the verge of complete extinction. According to published reports, the most important external pollutant source of Anzali wetland is the Siahroud River. The influx delivers relatively high amounts of industrial, agricultural and urban pollution to the wetland [15]. For example, measurements in 1997 indicated that the mean annual inputs of sediment, nitrogen, phosphorus and phosphate were 86,000, 931, 184 and 21.3 tons, respectively [12]. Moreover, this river passes the middle part of Rasht City, the most populated urban area in the northern part of Iran,

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releasing a high amount of untreated sewage to the river. Research has revealed that in 1998 Rasht City discharged 1.34 million m^3 of untreated sewage into the river, which is attributed to the mounting urban spread out of Rasht in recent years [15]. In addition, the presence of industrial sites in the middle reaches of the river is another major pollution source [17].

Therefore, a study of the sources of water quality degradation in the Siahroud watershed, especially phosphorus and nitrogen species due to their important role in eutrophication effects, was undertaken. The main objectives of this study were:

(1) to identify the processes governing the behaviour of water quality parameters in different parts of the river,
(2) to study the temporal and spatial variation of pollution levels in the river.

Materials and Methods

Sampling Procedures and Analysis

Land use, vegetation, and river network information was used to select stations for water sampling. The water samples were collected along the Siahroud River during four consecutive seasons. The selection of sampling stations was based on the vicinity of the main pollutant sources such as agriculture, industry, and residential land use (Fig. 1). The samples were taken from 10 to 15 cm below the water surface using acid-washed, wide-mouth polyethylene plastic bottles. Standard procedures were followed for the collection of water samples [7]. The samples were kept in a cool place over ice and transported to laboratories for analysis. Total organic carbon (TOC) was measured by oxidation, followed by IR gas measurements [1].

Total nitrogen (TN) was measured colorimetrically after oxidation with peroxodisulfate and reduction in a Cu-Cd column [1]. The NO_3-N was analyzed following reduction in a Cu-Cd column and colorimetry determination of azo-colour [1]. The NH_4^+-N was determined spectrophotometrically with hypochlorite and phenol [1]. Total phosphorus (TP) was determined by the molybdenum blue method after digestion with peroxodisulfade [1]. Total dissolved solids was measured by gravimetric analysis. The Winkler method was used for the analysis of dissolved oxygen (DO) and biological oxygen demand (BOD) while for chemical oxygen demand (COD) the dichromate reflux method was utilized [1]. The in-situ measurements of pH and temperature were taken with a Datasond 3 (Hydrolab, USA) and digital thermometer, respectively. The detection limits for TP, BOD, COD, DO, TOC, TN, NO_3^-, and NH_4^+ were 0.01 mg/l.

Statistical Analysis

In pollution research, if the main aim is to search for underlying factors that are not directly observable in datasets, the technique of factor analysis is suitable [19]. The major objectives of factor analysis are to use the computed correlation matrix to identify the smallest number of common factors that best explain or account for the correlation among the indicators. To achieve a smaller factor structure that can be meaningfully interpreted by the researcher, factor rotation can be utilized to identify the most plausible factor solution [14]. Therefore, to find the main pollutant sources causing differences between the stations, factor analysis based on a varimax rotation technique was used [5, 16].

After identification of the major hidden pollutant sources in the watershed, the next step was to examine the similarity among considered stations for possible zonations according to the level of existing pollution. For this purpose, the cluster analysis was used to decide which of the sites are most similar to each other, considering all of the pollution properties simultaneously.

Results and Discussion

Spatial and Temporal Variations of the Parameters

Water temperature varied from 14.1°C in the winter of 2002 to 28.3°C in the summer of 2002, which was within the potable range of 20°C set by the US-EPA. The pH values were within the permissible level of 6.5 to 8.5 varing between 7.6 in the autumn to 8.0 in the winter of 2002 [4]. The higher pH in station 1 as compared with those of other stations revealed the existence of aerobic conditions that may stem from the fact that this river reach is a forested area and there are no anthropogenic sources.

Total dissolved solids of the water samples varied from 579 mg/l in the autumn of 2002 to 845 mg/l in the summer of 2002 during the sampling periods. At high flows, the TDS values tend to be diluted by surface runoff and for most rivers there are an inverse correlation between discharge rate and TDS [3]. This explains why in this river, the level of TDS values in winter and autumn is lesser than the values of spring and summer seasons (Table 1). Seven out of nine stations were higher than the standard level of 500 mg/l set by the EPA [4] to indicate the effects of anthropogenic sources along the river (Fig. 2d). Particularly in stations 7, 8 and 9, as a result of some improper agricultural activities such as over fertilization, the level of TDS is critically higher than the standard level.

Meanwhile, in station 4 the higher level of TDS is more likely due to the influence of industrial activities such as effluent addition to the river. The higher levels of TDS in stations 5 and 6 (industrial sites) and in station 3 (land clearance in the forested area) are attributable to their land use systems in the upper river reaches. The sedimentation surveys during past decades in the Anzali wetland showed significant increases, implying mounting erosion in the watershed, including the Siahroud basin as one of the major contributing subbasins to the sedimentation of the Anzali Wetland [8]. The present erosion is

Table 1. Average and standard deviation of water quality parameters in the Siahroud River during four subsequent seasons in 2002 across nine sampling stations.

Seasons	Value	TDS	TP	BOD	COD	DO	TOC	TN	NO_3^-	NH_4^+	Temp °C	pH
		(mg/l)										
Winter	Avg.	585.8	0.46	8.73	27.19	8.91	3.15	5.9	0.02	5.54	14.1	8.0
	Std.	257.7	0.63	7.79	27.46	2.17	1.06	2.34	0.02	2.42	1.62	0.33
Spring	Avg.	737.2	0.22	7.82	17.33	9.19	11.71	8.45	4.17	3.49	15.9	7.7
	Std.	317.4	0.20	3.73	8.17	2.56	4.46	3.42	2.53	1.65	1.19	0.29
Summer	Avg.	845.4	0.02	25.33	32.95	6.49	2.77	7.36	4.69	1.77	28.4	7.7
	Std.	316.9	0.03	16.34	17.86	2.21	2.14	3.44	2.82	0.91	1.57	0.34
Autumn	Avg.	578.9	0.36	6.60	10.98	5.61	4.82	7.79	4.80	1.95	15.7	7.6
	Std.	216.6	0.51	4.12	4.50	1.77	2.22	3.43	2.38	0.87	3.34	0.28

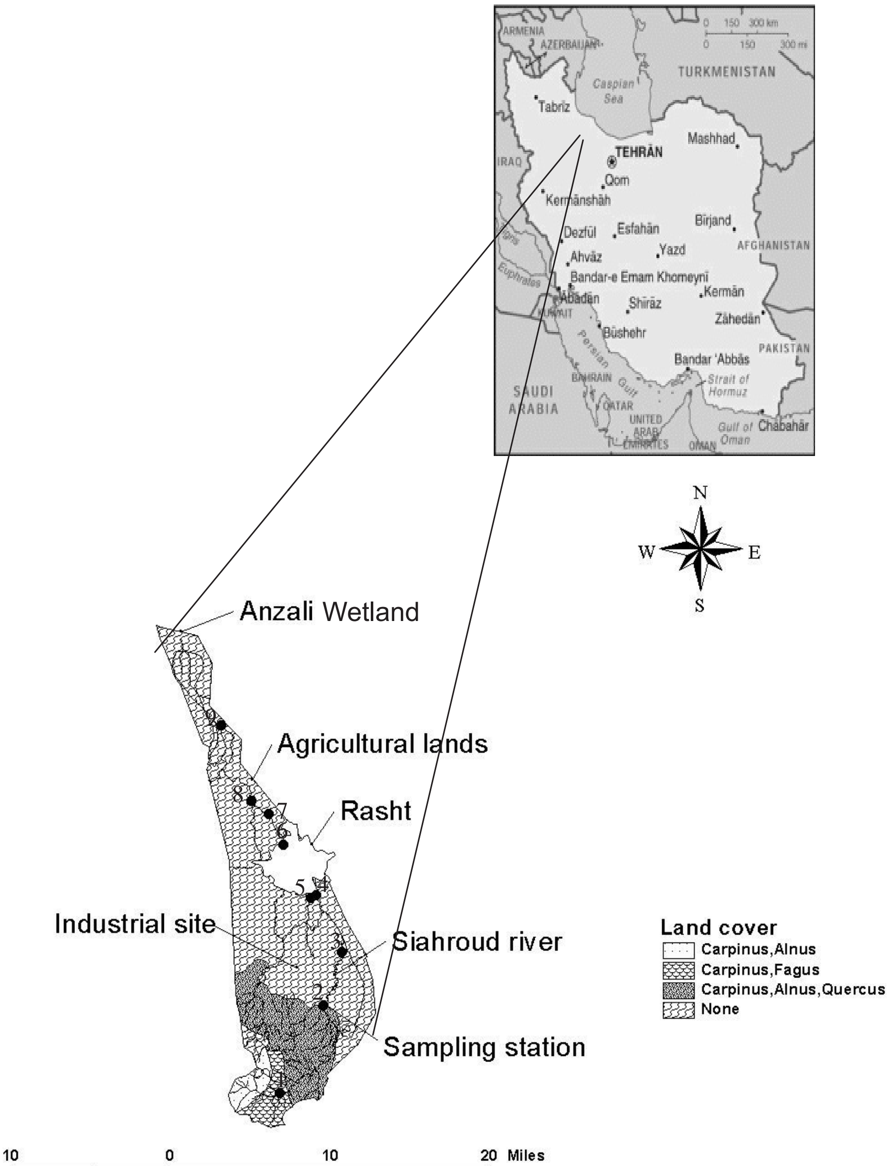

Fig. 1. Sketch map of the study area in the Siahroud watershed, Gilan province south of the Caspian Sea, showing the sampling sites and land cover and land uses.

partly responsible for the higher level of TDS in the clear-cut forested area (Fig. 1).

The average concentration of NO_3^- ranged from 0.02 mg/l in the winter of 2002 to 4.80 mg/l in the autumn 2002 among the sampling stations. These temporal changes might be due to the fact that the nitrate loading is usually highest in winter and spring. Therefore, soil-water recharge in autumn and winter causes N-mineralization to be increased when soil is drying, followed by a re-wetting period [11]. In addition, the risk of NO_3^- leaching is particularly high after the harvest, when plant uptake is low, but N-release as mineralization continues.

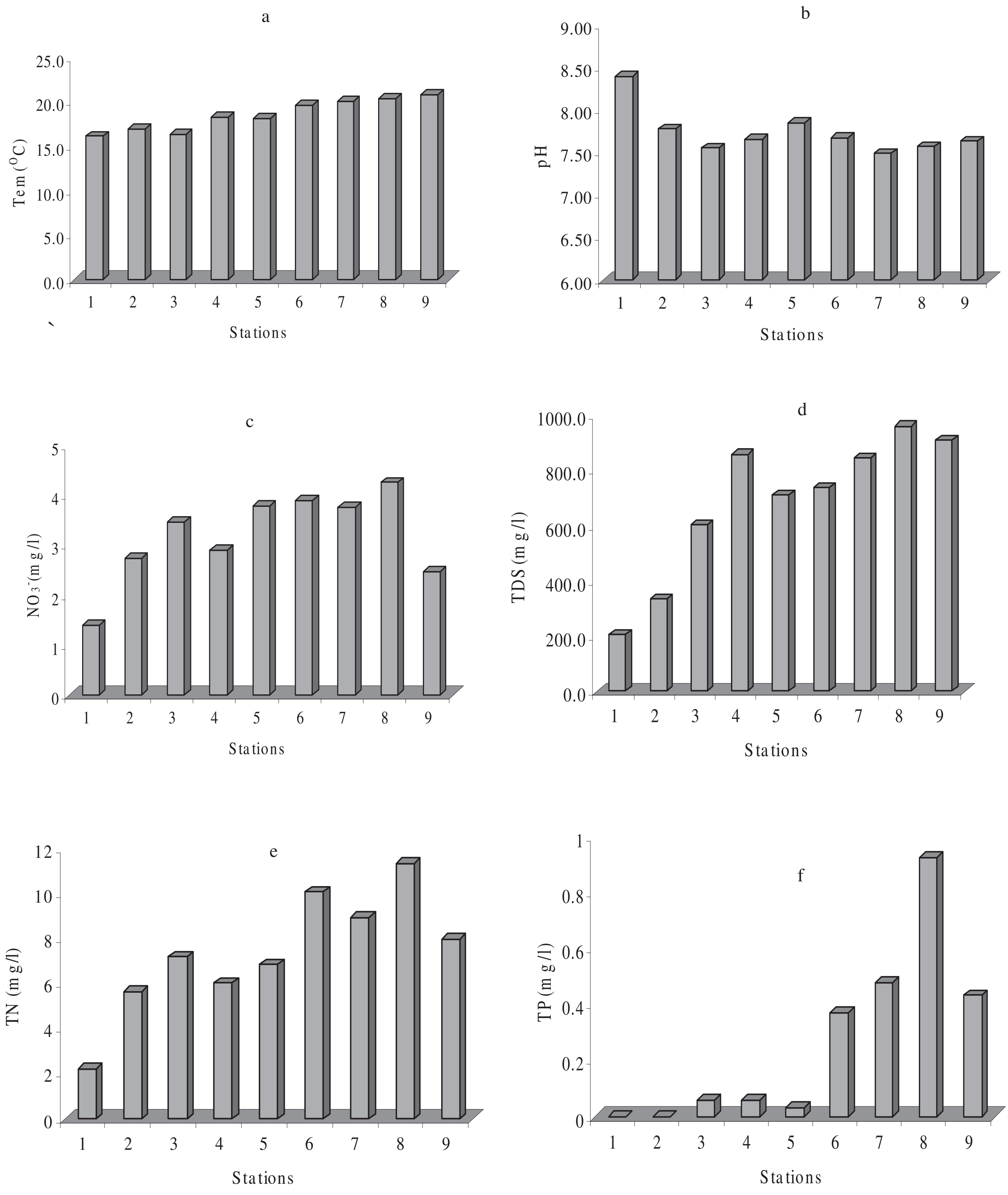

Fig. 2 (a-f). Spatial variation of water quality parameters averaged over four seasons of 2002 in sampling stations along the Siahroud River. Permisible levels for temperture, pH, and TDS are 20°C, 6.5-8.5, and 500 ppm, respectively.

Moreover, denitrification and leaching cause most N loss from a catchment. For example, aerobic conditions created by ploughing enables ammonification and subsequent nitrification that results in NO_3^- release from organic compounds in soils. However, in forest soils inorganic N concentrations are generally low and most N is in organic complexes associated with biological materials [13]. The extended and limited levels of NO_3^- in turn, in stations 8 and 1 derived from the aforsaid facts (Fig. 2c).

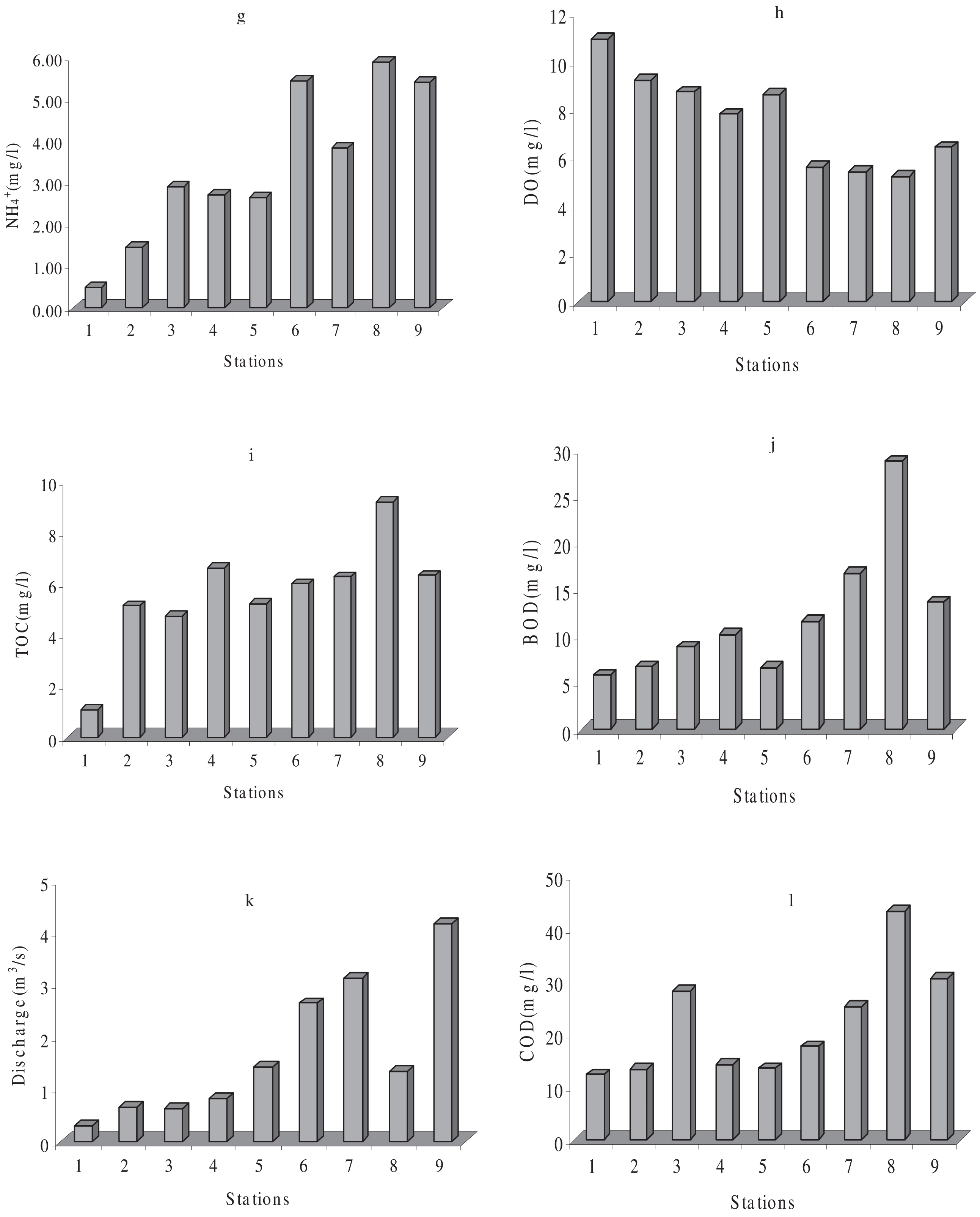

Fig. 2 (g-l). Spatial variation of water quality parameters averaged over four seasons of 2002 in sampling stations along the Siahroud River. Permisible levels for DO, BOD, and COD are 5, 7, and 20 (mg/l), respectively.

Table 2. Pearson correlation coeficients of water quality parameters in the surface water of the Siahroud River across nine sampling stations in 2002.

	NO_3	TP	NH_4	BOD	DO	TDS	Tem	TN	TOC	pH
TP	0.546									
NH_4	0.645	0.844[b]								
BOD	0.564	0.968[b]	0.756[a]							
DO	-0.715[a]	-0.849[b]	-0.922[b]	-0.786[a]						
TDS	0.654	0.688[a]	0.839[b]	0.689[a]	-0.854[b]					
Temp.	0.488	0.821[b]	0.881[b]	0.728[a]	-0.916[b]	0.846[b]				
TN	0.867[b]	0.827[b]	0.923[b]	0.783[a]	-0.935[b]	0.798[a]	0.788[a]			
TOC	0.755[a]	0.749[a]	0.795[a]	0.794[a]	-0.837[b]	0.860[b]	0.762[a]	0.869[b]		
pH	– 0.747[a]	– 0.510	– 0.687[a]	– 0.538	0.773[a]	– 0.776[a]	– 0.591	– 0.802[b]	– 0.824[b]	
COD	0.468	0.856[b]	0.736[a]	0.877[b]	– 0.645	0.619	0.581	0.713	0.667[a]	0.577

Significant levels: [a] $p < 0.05$, [b] $p < 0.01$.

Table 3. The varimax rotated factor loadings for water quality parameters in the surface water of the Siahroud River across nine sampling stations in 2002.

water quality parameter	Factor1	Factor2	Factor3	Communality
$NO3^-$	0.289	0.236	0.924	0.997
TP	0.550	0.793	0.223	0.996
$NH4^+$	0.743	0.478	0.335	0.914
BOD	0.423	0.841	0.268	0.960
DO	-0.786	-0.409	-0.433	0.973
TDS	0.749	0.303	0.372	0.965
Tem	0.913	0.359	0.145	0.983
COD	0.252	0.902	0.179	0.982
Variance	3.19	2.82	1.47	7.48
% Var	39.9	35.3	18.3	
% Cumulative var	39.9	75.2	93.5	

In this study, all of the NO_3^- samples were well below the maximum permissible level [4] as shown in Fig. 2c. In a relatively acidic environment, nitrogen will predominate as NO_3^- and thus this anion is susceptible to leaching [11]. The high negative correlation between pH and NO_3^- supports this statment (Table 3).

The average concentrations of NH_4^+ in the study ranged from 1.77 mg/l in the winter of 2002 to 5.54.mg/l in the autumn of 2002 (Table 1). Naturally in unpolluted rivers, the concentration of NH_4^+ is generally higher during winters because the nitrification process in the river is more effective at higher summer temperatures [5]. Consequentely, we expected the ammonium levels to show an annual concentration pattern inverse to that of water temperature of the river (Fig. 2a). The seasonal variations of NH_4^+ concentrations also confirmed this finding (Table 1).

Moreover, the downsteam was characterized by the higher concentrations of NH_4^+ (Fig. 2g). In the downstream, where the higher levels were observed, the prevalent land-use is agriculture with paddy fields as the most common cultivation practice in which redox potential is suitable for NH_4^+ formation. In paddy soils, NO_3^--containing fertilizers are ineffective because of N lost by denitrification process. Some NO_3^- is always present, however, since a portion of NH_4^+ in an aerobic zone of plant-soil-water system is converted to NO_3^-, when NO_3^- diffuses into anaerobic subsoil, where it is rapidly and completely denitrified [18]. But NH_4^+ is usually bound to soil particles through cation exchange, which reduces the risk of leaching loss [11]. However, some NH_4^+ could discharge into the river via soil erosion by fine soil particles in agricultural lands. Furthermore, waterlogging of soil results in rapid denitrification by impeding diffusion of O_2 to sites of microbiological activities in these soils [18].

The average concentrations of TN varied between 5.90 mg/l in the winter 2002 to 8.45 mg/l in the spring of 2002 in this river (Table 1). In this study, two out of nine stations (stations 6 and 8) were higher than the permissible level of the EPA [4] for TN as shown in Fig. 2e. Moreover, a strong positive correlation between TN and TOC (Table 2) indicated that the loss of organic phosphorus is associated with leaching of humic substances [9]. The strong positive correlation between TN and temperature demonstrated the temporal changes of this parameter (Table 2). This may lead to the fact that during the growing seasons of summer and spring discharges of nitrogen species are higher than other seasons. Strong positive correlations between TDS and TN might indicate that the predominant fraction of nitrogen species are present in dissolved form instead of particulate N (Table 2).

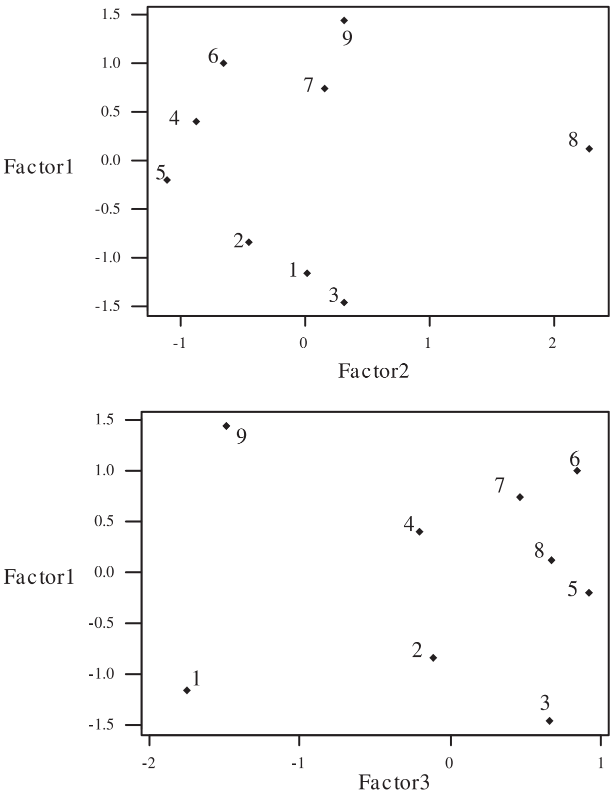

Fig. 3. Factor score plots of the sampling stations along the Siahroud River.

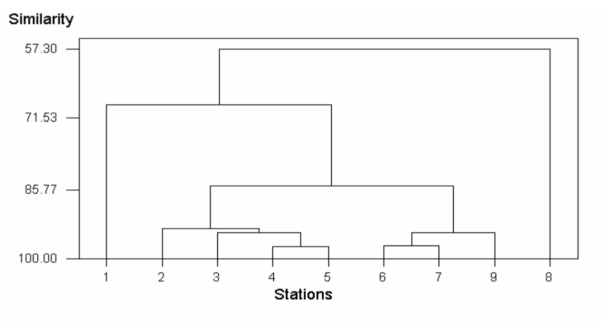

Fig. 4. Dendrogram of cluster analysis for the sampling stations along the Siahroud River for 9 selected stations.

The average concentrations of TP varied between 0.02 mg/l in the summer of 2002 to 0.46 mg/l in the winter of 2002 at the sampling stations (Table 1). The higher concentration of TP in the four last stations (Fig. 2f) is related to the increasing inputs of concentrated inorganic phosphorus from fertilizer sources and dissolved P from domestic sewage, which are the most important anthropogenic sources of phosphorus in aquatic ecosystems [20]. In autumn and winter seasons due to decreasing levels of biological activities, the amount of phosphate and therefore TP would rise while this phenomenon is reversed in the other seasons. In this study, the higher levels of TP were observed in the autumn and the winter (Table 1). High positive correlation (r = 0.75, Table 2) between TOC and TP mirrored the role of organic substances in the leaching of phosphorus to the river. Additionally it indicated that the prevailing phosphorus species in the study area forms organic P. Like TN, the predominant fraction of TP is in the form of dissolved species indicated by strong correlation between TDS and TP (r = 0.69, Table 2).

The average dissolved oxygen concentrations (DO) during the sampling periods ranged from 5.61 mg/l in the autumn of 2002 to 9.19 mg/l in the spring of 2002. Stations 6, 7 and 8 were below the permissible level of 6 mg/l set by the EPA [4] as shown in Table 1 and Fig. 2h. The BOD ranged from 6.6 mg/l in the autumn of 2002 to 25.33 mg/l in the summer of 2002 suggesting generally high values which may be caused by low discharge of the river leading into high BOD in the summer of 2002 (Table 1 and Fig. 2j). The same results were obtained for the COD values (Fig. 2l). The lowest concentrations were found in the autumn of 2002, while the highest were obtained in the summer of 2002 (Table 1). The average concentrations of TOC varies between 2.77 mg/l in the summer of 2002 to 11.71 mg/l in the spring of 2002 during the sampling periods. The present values do not seem to follow any distinctive trend (Table 1 and Fig. 2i).

Pollution sourcing

The results of the factor analysis using a varimax rotation technique are illustrated in Table 3. As indicated in this table, three factors encompased 93.5 percent of the total variance. The first factor accounted for 39.9 percent of the total variance, which was loaded with temp., TDS, NH_4^+, TP (postive loadings), in opposition to DO (negetive loadings). Anaerobic environments create a condition that favours the denitrification process; therefore, NH_4^+ trends are usually reversed compared with that of dissolved oxygen.

TDS and temperature are other variables affecting the depletion of the dissolved oxygen in water. Station 9 had a high positive score on the first factor, implying that this station is highly polluted with Factor 1 parameters (Fig. 3). The prevalent land-use in this station is agriculture, hence agricultural runoff is atributable to the extended level of these factors in this section of the river. Furthermore, both stations 3 and 1 indicated high negative scores in the first factor as well. This result demonstrated that water quality in these sections had not been influenced by any involved pollutants. These stations are located in the forested areas where the amount of erosion and leaching is considerably less than that of other stations. Thus, the level of TDS is minute and the river has a high potential to replenish its oxygen budget through the atmosphere. In addition, no detected anthropogenic sources were found in these river reaches; thereofore, they do not also suffer from thermal pollution. All of these conditions lead to the least level of NH_4^+ because there is a high level of dissolved oxygen in these stations.

The association of COD, BOD and TP variables marked the second factor (positive loadings). Here, BOD is a measure of organic carbon loading in the water system that exerts a high level of biological oxygen demand to the system [6]. Moreover, phosphorus compounds, which result from domestic sewage and agricultural runoff, are factors that raise the level of BOD and COD in water. Station 8 had a high positive score in the second factor, suggesting the amended level of TP, BOD and COD parameters in this station. This section of the river is a highly agricultural region and, due to improper fertilizer use along with high erosion, it discharges high levels of organic and phosphorus compounds [10]. In contrast, station 5 (located before Rasht City) was not affected by any of the cosidered parameters. Consequently, it showed a high negative score in this factor. NO_3^- showed a high positive loading in the third rotated factor with 0.924, whereas that of the other parameters' loadings on this factor were negligible. Both stations 1 and 9 showed high negative scores, indicating the lowest amount of NO_3^- in these sections of the river (Fig. 2b).

Zoning of the River System

Cluster analysis [2] was performed on the mean values of the parameters for each of the stations. Standardization of the data using euclidean distance coefficients with the average linkage method of clustering was used (Fig. 4) to segregate the stations according to the conccentration values of water parameters. The results separated four different clusters along the Siahroud River consisting all the measured values. The first cluster was comprised of station 1, which could be regarded as the least polluted zone in the river. This part of the river is a forested terrain where the level of erosion and leaching is also negligible. As mentioned earlier, no major anthropogenic sources can be detected in this zone. The second cluster was made up of stations 2, 3, 4 and 5 where the level of pollution was moderate. In this cluster station 4 is representative of an industrial site which indicated that the influence of industrial activities on physicochemical parameters of this river was negligible.

The third cluster included stations 6, 7 and 9, where the impacts of pollutant sources were higher than the abovementioned groups. This cluster contains Rasht City and the agricultural lands. Finally, the last cluster included station 8, where it is the most polluted part of the investigated area. This zone is identified by extensive arable lands, especially paddy fields, where relatively high levels of fertilizer and pesticides are used [10]. Therefore, the amount of these inputs as a result of soil erosion and leaching would be increased. Despite the fact that the predominant land-use in stations 7 and 9 is agriculture, the high level of discharge created more dilution in these stations (Fig. 2k).

Conclusion

This study showed that the level of pollution generally increases from upstream to downstream of the Siahroud River. Considering the results of the measured physiochemical water parameters and the results of factor and cluster analyses, the agriculture and urban land use were the most contributing factors to the pollution of the river. Therefore, industrial activities are not the main source of organic pollution in this river. We suggest that the remediation activities should be focused on the main factors such as nutrients from agricultural activities. However, the industrial activities should also be closely monitored to reduce their possible effects on the level of heavy metal pollution.

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