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Water quality trend analysis for the Karoon River in Iran

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Abstract The Karoon River basin, with a basin area of 67,000 km^2, is located in the southern part of Iran. Monthly measurements of the discharge and the water quality variables have been monitored at the Gatvand and Khorramshahr stations of the Karoon River on a monthly basis for the period 1967–2005 and 1969–2005 for Gatvand and Khorramshahr stations, respectively. In this paper the time series of monthly values of water quality parameters and the discharge were analyzed using statistical methods and the existence of trends and the evaluation of the best fitted models were performed. The Kolmogorov–Smirnov test was used to select the theoretical distribution which best fitted the data. Simple regression was used to examine the concentration-time relationships. The concentration-time relationships showed better correlation in Khorramshahr station than that of Gatvand station. The exponential model expresses better concentration – time relationships in Khorramshahr station, but in Gatvand station the logarithmic model is more fitted. The correlation coefficients are positive for all of the variables in Khorramshahr station also in Gatvand station all of the variables are positive except magnesium (Mg^{2+}), bicarbonates (HCO_3^-) and temporary hardness which shows a decreasing relationship. The logarithmic and the exponential models describe better the concentration-time relationships for two stations.

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Introduction

The water quality of water resources is a subject of ongoing concern. The assessment of long-term water quality changes is also a challenging problem. During the last decades, there has been an increasing demand for monitoring water quality of many rivers by regular measurements of various water quality variables. The result has been the gradual accumulation of reliable long-term water quality records and the examination of these data for long-term trends (Hirsch et al. 1991). According to Antonopoulos et al. (2001), some of the necessities of water quality monitoring are the following: (1) to provide a system-wide synopsis of water quality, (2) to monitor long-range trends in selected water quality parameters, (3) to detect actual or potential water quality problems; if such problems exist (3a) to determine specific causes and (3b) to assess the effect of any convective action and (4) to enforce standards. Computer systems now offer the possibility of handling and manipulating very large databases in ways which were not previously a practical option. Littlewood et al. (1998) have used such databases for the estimation of UK river mass loads of pollutants. Miller and Hirst (1998) used the hydrochemical databases from an upland catchment in Scotland for a period of five years to assess the annual variation in amounts and concentration of solutes and to examine the variation in stream water quality due to changes in flow, season and long time trend. Ferrier et al. (2001) analyzed in detail databases for Scotland and identified temporal changes in water quality over the last 20 years.

The Karoon River basin, with a basin area of 67,000 km^2, is located in southern part of Iran. The Karoon River water pollution due to increasing water withdrawals from and wastewater discharges into this river has endangered the aquatic life of the river. Furthermore, the drinking and in-stream water quality standards have been violated in many instances. Water pollution of the Karoon River system can significantly affect the development of Khuzestan Province as one of the strategic provinces of the country with a high potential for agricultural and industrial development. A good part of used agricultural water is returned to the rivers by drainage and return flows. The return flows have a high concentration of fertilizers, heavy metals, suspended and dissolved solids and pesticides, which violate the national effluent standard. Agricultural and agro-industrial return flows, domestic wastewater of the cities and villages and industrial effluents are the main pollution point sources of the Karoon River. The Karoon river system supplies the water demands of 16 cities, several villages, thousands of hectares of agricultural lands, and several hydropower plants. Increasing water demands at the development stage including agricultural networks, fish hatchery projects, and inter-basin water transfers, could result in a gloomy future for water quality of the Karoon River (Karamouz et al. 2004).

This paper examines statistically, the time series of monthly values of water quality parameters and the discharge at Gatvand and khorramshahr stations, the existence of trends and the evaluation of the best fitted trend models, and also the evaluation of water quality deterioration between these stations.

Methodology for the analysis of water quality parameters

In planning control and management programme of streams, the statistical and trend analysis are important steps for the understanding of the behavior and the variation of water quality parameters and stream flows. This variation is affected by many factors. These factors may be formed by different substances in the surface water due to activities in the catchments and may be further obscured by random events. Furthermore, the stream flow data exhibit hydrological persistence and seasonal variance (Antonopoulos et al. 2001).

Probability distribution of water quality and quantity parameters

Water quality data do not usually follow convenient probability distributions such as the well-known normal and lognormal distributions on which many classical statistical methods are based (Lettenmaier et al. 1991).

The K–S test is a non-parametric test (Antonopoulos et al. 2001) of the fitting of data to a theoretical distribution using the maximum absolute deviation (D) between the two functions of cumulative distribution. It is calculated by

$$D = \max F_{\mathrm{n}}(x) - F_{\mathrm{o}}(x) \tag{1}$$

Where $F_{\mathrm{n}}(x)$ is the cumulative density function based on n measurements, $F_{\mathrm{o}}(x)$ is the specified theoretical cumulative distribution function under the null hypothesis H_0 The values of $D(n,\alpha)$ are given in tables (Antonopoulos et al. 2001). If $D \geq D(n, \alpha)$, the H_0 hypothesis is rejected and if $D < D(n, \alpha)$, H_0 is accepted, for the chosen level of significance (α=0.05).

Trend analysis

Testing water quality data for trend over a period of time has received considerable attention recently. The interest in methods of water quality trend arises for two reasons. The first is the intrinsic interest in the question of changing water quality arising out of the environmental concern and activity.

The second reason is that only recently has there been a substantial amount of data that is amenable to such an analysis.

Trend analysis determines whether the measured values of a water quality variable increase or decrease during a time period. In statistical terms, has the probability distribution from which they arise changed over time? It would be useful to describe the amount or rate of that change, in terms of changes in some central value of the distribution such as mean or median (Dave 2006).

Different models were proposed to describe the relationship between concentration-time (Pinol et al. 1992). These relationships give information on the variation of quality parameters due time.

Materials and methods

Description of study site

The Karoon River basin, with a basin area of 67,000 km^2, is located in southern part of Iran between longitudes 48°15′ and 52°30′ east, latitude 30°17′and 33°49′ north. The origin of the Karoon River is 75 km far from the south of Esfahan city in the Zagros Mountain ranges and divided in two branches, Gargar and Shatit, in the north of Shooshtar city, in Bandeghir the two branches and the Dez river join each other and form a great river called the Karoon. Monthly measurements of the discharge and water quality variables were established, and those variables have been monitored at the Gatvand and Khorramshahr stations of the Karoon River by Khuzestan Water and Power Authority.

The Gatvand station is an upstream station between Gatvand dam and Shooshtar city, located at longitudes 48°49, latitude 32°15′ and altitude of 100 m. Figure 1 shows the location of the monitoring stations (Gatvand and Khorramshahr) and main agricultural, industrial and domestic pollution sources in the study area.

Also Khorramshahr station is a downstream station that is located near Khorramshahr city, located at longitudes 48°10′, latitude 30°26′ and altitude of 3 m.

Figure 1 shows the location of the monitoring station and main agricultural, industrial and domestic pollution sources in the study area.

Among the variables measured by Khuzestan Water and Power Authority at the Gatvand and Khorramshahr stations are discharge (*Q*) as m^3/s, water temperature (*T*) as Celsius, Turbidity as NTU, pH, conductivity (EC) as µs/cm, TDS, bicarbonates (HCO_3^-), sulphates (SO_4^{2-}), chlorides (Cl^-), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}),Sodium absorption ratio (SAR), temporary hardness and total hardness as meq/l. The monitoring data for these variables available for the analysis as presented in this paper are on a monthly basis for the period 1967–2005 and 1969–2005 for Gatvand and khorramshahr stations, respectively.

To select the distribution which provided the best fit, 14 theoretical probability distribution functions were examined:

Inverse Gaussian, Birnbaum – Saunders, Lognormal, Largest extreme value, Loglogistic, Gamma, Weibull, Logistic, Laplace, Normal, Smallest extreme value, Exponential, Uniform and Pareto. To select the distribution which fitted the data best, the Kolmogorov–Smirnov test (K–S) were used.

For trend analysis, the linear $(Cij = a + bQj)$, the power (Cij=aQj b), the exponential (Cij=a exp (bQj)), and the logarithmic $(Cij = a + b \ln(Qj))$ models were used. The method of least squares for the pairs of monthly measured values of each variable and the time was used to determine the constants of these models. All the statistical procedures were established by Statgraphics Centurion XV.I version 1995.

Results

Statistical analysis of water quality parameters

The statistical measures of time series of water quality variables at the Gatvand and khorramshahr stations, used in the following analysis, are given in Tables 1 and 2 .

Trend analysis of water quality and quantity

The time series of 15 water quality parameters and the discharge of the Karoon River at the Gatvand and Khorramshahr stations were tested for existence of trend, by using the non-parametric Spearman's criterion and analyzed by fitting different trend models.

The results of simple regression applied between each water quality variable's concentration (dependent variable) and the time (independent variable) monitored at the Gatvand and Khorramshahr stations of the Karoon River are given in Tables 3 and 4. In these tables the equations of linear $(Cij = a + bQj)$, power (Cij=aQj b), exponential (Cij=a exp (bQj)) and logarithmic $(Cij = a + b \ln(Qj))$ models as well as the correlation coefficients are given.

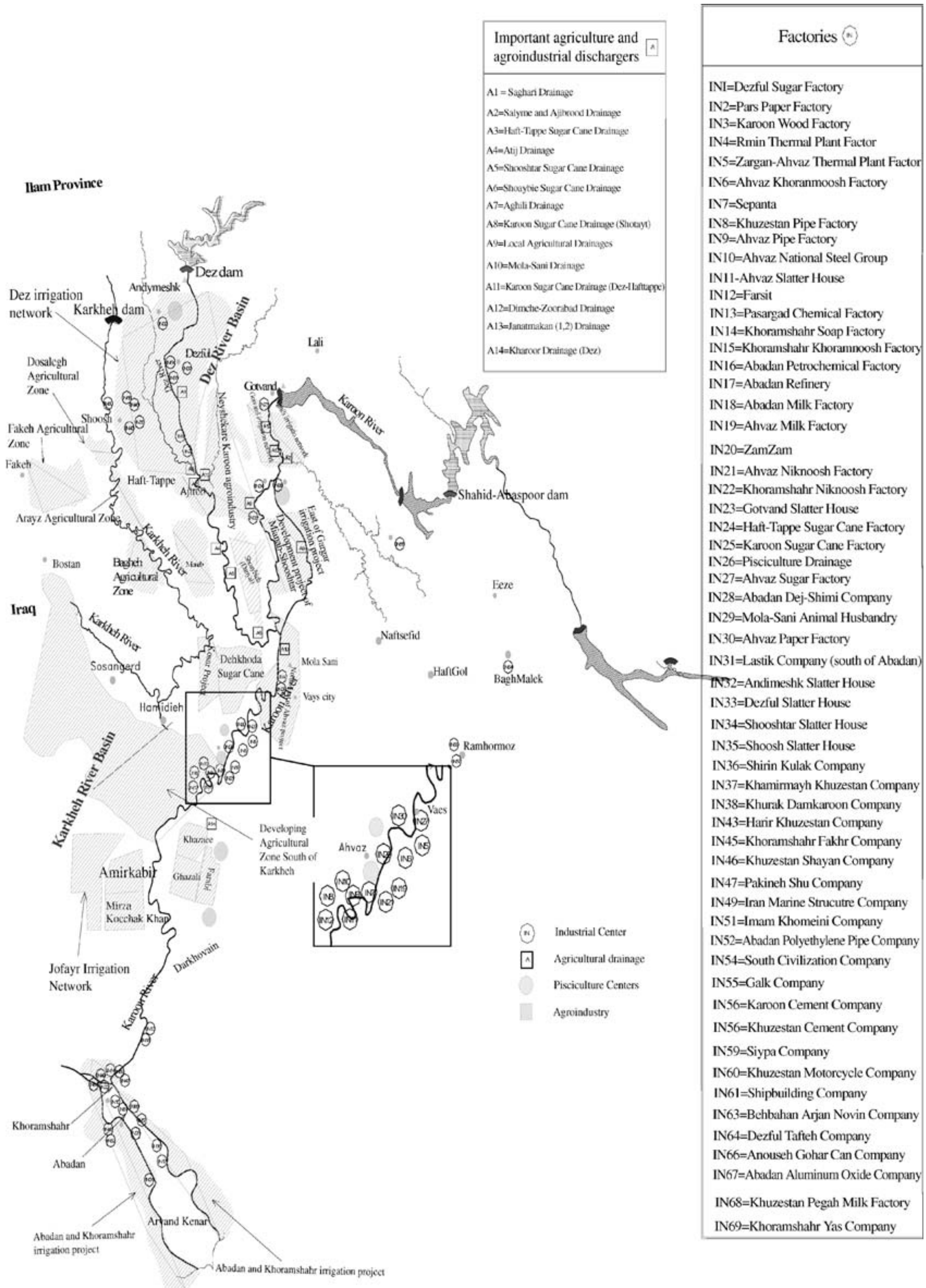

Fig. 1 The location of the monitoring stations and main pollution sources in the study area

Table 1 Statistical parameters of the time series of monthly levels of water quality parameters and discharge of the Karoon River at Gatvand station

Variable	Sample size	Mean	Max	Min	Max–Min	S.d	C.V %	Stnd. skewness	Stnd kurtosis
Q (m^3/s)	418	500.31	4,487	1.83	4,485.17	487.63	97.47	26.74	63.63
T(°C)	287	19.02	50	6	44	4.62	24.3	7.11	20.55
Turbidity (NTU)	112	330.81	8,040	2	8,038	1,142.13	345.25	21.66	58.29
TDS (mg/l)	432	575.95	1,575	240	1,335	191.43	33.24	11.41	12.97
EC (μs/cm)	432	921.99	2,416	428	1,988	295.58	32.06	11.45	13.13
pH	432	8.01	9.6	7.3	2.3	0.25	3.08	5.17	14.31
HCO_3^- (meq/l)	432	2.56	4.58	0.66	3.92	0.44	17.07	−3.1	11.21
Cl^- (meq/l)	432	4.62	15.55	0.65	14.9	2.11	45.62	11.48	13.62
SO_4 (meq/l)	432	1.85	9.16	0.1	9.06	1.17	63.54	21.99	40.22
Ca (meq/l)	432	3.19	9.9	1	8.9	1.1	34.65	20.63	38.85
Mg (meq/l)	432	1.32	4.42	0.4	4.02	0.45	33.93	16.74	33.31
Na (meq/l)	432	4.48	14.8	0.65	14.15	2.1	46.96	12.56	15.57
K (meq/l)	394	0.04	0.7	0.01	0.69	0.04	84.35	115.25	1,002
SAR (meq/l)	432	2.95	8.8	0.56	8.25	1.17	39.75	9.35	10.05
Temporary hardness (meq/l) as $CaCO_3$	432	1.29	2.29	0.33	1.96	0.22	16.75	−3.07	11.86
Total hardness (meq/l) as $CaCO_3$	432	2.26	7.06	1.25	5.81	0.61	27.03	21.47	51.3

Discussion

Statistical analysis of water quality parameters

The ratio of highest to lowest concentration and water discharge in Gatvand station is very large for turbidity (4,020:1) followed by SO_4^{2-} (91.6:1), K^+ (70:1), Cl^- (23.9:1), Na^+ (22.77), SAR (15.71:1), Mg^{2+} (11.05:1) Ca^{2+} (9.9:1) and temperature (8.33:1). There is low ratio for temporary hardness (6.94:1), HCO_3^- (6.94:1), TDS (6.56:1), total hardness (5.65:1), EC (5.64:1), pH (1.31:1). Also in Khorramshahr station

Table 2 Statistical parameters of the time series of monthly levels of water quality parameters and discharge of the Karoon River at Khorramshahr station

Variable	Sample size	Mean	Max	Min	Max–Min	S.d	C.V %	Stnd. skewness	Stnd kurtosis
Q (m^3/s)	2	644.06	1,073.51	214.61	858.9	607.33	94.3	–	–
T(°C)	132	21.89	33	9	24	6	27.4	−0.82	−2.34
Turbidity (NTU)	93	27.12	303	6	297	36.78	135.63	25.94	88.2
TDS (mg/l)	265	1,030.42	2,930	153	2,777	467.69	45.39	10.21	8.67
EC (μs/cm)	265	1,634.34	4,582	660	3,922	719.64	44.03	11.07	9.97
pH	265	7.98	9.2	7.2	2	0.26	3.22	1.99	4.64
HCO_3^- (meq/l)	265	2.83	6.22	1.1	5.12	0.51	18.01	5.81	26.73
Cl^- (meq/l)	265	8.88	32.72	2.25	30.47	5.41	60.93	13.48	14.65
SO_4 (meq/l)	265	4.62	14.1	1.07	13.03	2.4	51.9	8	4.52
Ca (meq/l)	265	4.66	10.8	2.5	8.3	1.46	31.42	8.11	5.3
Mg (meq/l)	265	2.77	7.77	0.55	7.22	1.36	49.16	9.22	5.64
Na (meq/l)	265	8.79	31	2.05	28.95	5.32	60.50	12.96	13.36
K (meq/l)	261	0.07	0.33	0.01	0.32	0.04	51.64	23.87	69.98
SAR (meq/l)	265	4.39	12.57	1.39	11.18	1.92	43.75	10.67	9.63
Temporary hardness (meq/l) as $CaCO_3$	265	1.42	3.11	0.55	2.56	0.24	17.17	8.05	29.69
Total hardness (meq/l) as $CaCO_3$	265	3.72	7.34	1.98	5.36	1.19	32.14	6.95	2.12

Table 3 The best fitted distribution parameters and concentration-time relationships of water quality parameters and discharge for the Karoon River at Gatvand station

Variable	Distribution	K–S test	Model	*R*	Equation
Q (m^3/s)	Loglogistic	0.044	–	–	–
T(°C)	Gamma	0.068	–	–	–
Turbidity (NTU)	Inverse Gaussian	0.185	Power	0.1930	$-518.549+0.00777708\ t^2$
TDS (mg/l)	Largest extreme value	0.036	Logarithmic	0.1991	377.131+39.1561 Ln t
EC (µs/cm)	Largest extreme value	0.045	Logarithmic	0.1580	678.427+47.9686 Ln t
pH	Loglogistic	0.095	Logarithmic	0.3694	7.53863+0.093719 Ln t
HCO_3^- (meq/l)	Loglogistic	0.044	Exponential	−0.1399	Exp (0.970867−0.000218591 t)
Cl^- (meq/l)	Lognormal	0.059	Logarithmic	0.1381	3.10346+0.299075 Ln t
SO_4 (meq/l)	Loglogistic	0.044	Logarithmic	0.1987	0.631727+0.240192 Ln t
Ca (meq/l)	Loglogistic	0.059	Logarithmic	0.2296	1.86623+0.260727 Ln t
Mg (meq/l)	Loglogistic	0.041	Exponential	−0.0970	Exp (0.280933−0.000241327 t)
Na (meq/l)	Lognormal	0.054	Logarithmic	0.1561	2.76795+0.337388 Ln t
K (meq/l)	–	–	Power	0.0515	$0.0417639+3.47988\ *10^{-8}\ t^2$
SAR (meq/l)	Largest extreme value	0.056	Linear	0.1274	2.69644+0.00119846 t
Temporary hardness(meq/l)as $CaCO_3$	Logistic	0.049	Exponential	−0.1127	Exp (0.275624−0.000172873 t)
Total hardness (meq/l) as $CaCO_3$	Largest extreme value	0.07	Logarithmic	0.1904	1.65093+0.119361 Ln t

the ratio of highest to lowest concentration of water quality parameters is lower than that of the Gatvand station and for turbidity (50.5:1) followed by K^+ (33:1), TDS (19.15:1), Cl^- (16.53:1), Na^+ (15.12), Mg^{2+} (14.13:1), SO_4^{2-} (13.18:1), SAR (9.04:1), EC (6.94:1), HCO_3^- (5.65:1), Temporary hardness (5.65:1),Ca^{2+} (4.32:1) and total hardness (3.71:1) and temperature (3.67:1) while there is low ratio for pH (1.28:1) (Table 2).

The dominant anion and cation in the water of the Karoon river at Gatvand and Khorramshahr stations was $Cl^-$and Na^+, respectively.

The procedure used to fit a theoretical continuous distribution function to the data time series provides the parameter estimates for the chosen distribution function and runs a Kolmogorov–Smirnov one-sample test for goodness of – fit with its maximum absolute deviation (D) (Statgraphics 2005). It has been

Table 4 The best fitted distribution parameters and concentration-time relationships of water quality parameters and discharge for the Karoon River at Khorramshahr station

Variable	Distribution	K–S test	Model	*R*	Equation
Q (m^3/s)	Uniform	0.5	Logarithmic	0.1375	14.9991+1.37248 Ln t
T(°C)	Uniform	0.125	Power	0.3280	$10.813+0.000629028\ t^2$
Turbidity (NTU)	Loglogistic	0.121	Exponential	0.4794	Exp (6.50383+0.00259902 t)
TDS (mg/l)	Loglogistic	0.033	Exponential	0.4939	Exp (6.98911+0.00248634 t)
EC (µs/cm)	Loglogistic	0.040	Logarithmic	0.2081	7.72494+0.0556467 Ln t
pH	Loglogistic	0.098	–	–	–
HCO_3^- (meq/l)	Laplace	0.073	Exponential	0.4495	Exp (1.64717+0.00298425 t)
Cl^- (meq/l)	Loglogistic	0.043	Exponential	0.5370	Exp (0.940779+0.00350053 t)
SO_4 (meq/l)	Birnbaum–saunders	0.050	Exponential	0.4798	Exp (1.25373+0.00181303 t)
Ca (meq/l)	Largest extreme value	0.060	Exponential	0.4659	Exp (0.553684+0.00272463 t)
Mg (meq/l)	Inverse Gaussian	0.072	Exponential	0.4820	Exp (1.60237+0.00323683 t)
Na (meq/l)	Loglogistic	0.037	Exponential	0.3690	Exp (−3.03054+0.00210102 t)
K (meq/l)	Loglogistic	0.124	Linear	0.2692	0.487122+0.000251744 t
SAR (meq/l)	Loglogistic	0.037	Power	0.2394	$1.35728+0.0000277812\ t^2$
Temporary hardness (meq/l) as $CaCO_3$	Loglogistic	0.041	Exponential	0.5557	Exp (0.97651+0.00217927 t)
Total hardness (meq/l) as $CaCO_3$	Largest extreme value	0.059	Exponential	0.5150	Exp (2.3564+0.00266022 t)

accepted that the best fitted theoretical distribution to each data time series is the one which satisfies K–S tests. After a thorough examination of the statistical tests parameter values the following conclusions about the distribution of each variable were reached: the Gatvand discharge, pH, HCO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} followed the Loglogistic distribution, Cl^- and Na^+ followed the Lognormal and turbidity fitted Inverse Gaussian distribution, also the water temperature followed the Gamma distribution. Temporary hardness fitted to the logistic distribution while TDS, EC, SAR and total hardness followed the largest extreme value distribution (Table 3).

Also in Khorramshahr station turbidity, TDS, EC, pH, Cl^-, Na^+, K^+, SAR and temporary hardness fitted to Loglogistic distribution, HCO_3^- followed Laplace distribution, and also Ca^{2+} and total hardness came from Largest extreme value, while discharge and water temperature flowed the Uniform distribution (Table 4). Antonopoulos et al. (2001) showed that in the Strymon river in Greece discharge, EC, Na^+ and Ca^{2+} fitted to Weibull distribution while Mg^{2+} and SO_4^{2-} followed Logistic, Normal and Gamma distribution, respectively.

Trend analysis of water quality and quantity

It is clear that in Gatvand station discharge and temperature did not fit to any models also in Khorramshahr station pH had the same situation, for Gatvand and khorramshahr station no one of the applied models described well the concentration-time relationships or these relationships were very weak, the correlation coefficients were positive for all of the variables in Khorramshahr station also in Gatvand station all of the variable were positive except magnesium (Mg^{2+}), bicarbonates (HCO_3^-) and temporary hardness, which showed a decreasing relationship. The logarithmic and the exponential models describe better the concentration-time relationships for two stations, and in Khorramshahr station the relationship between total hardness and time, had the better correlation coefficient value (r=0.556), following by sulfate (r=0.537) and then by the other parameters EC (r=0.494), Na^+(r=0.480), Ca^{2+} (r= 0.480), TDS (0.479), Mg^{2+} (r=0.470), Cl^- (r=0.45) and SAR (r=0.42) while potassium (K^+), turbidity, temporary hardness, pH,bicarbonates (HCO_3^-) and temperature showed weaker relations.

Also in Gatvand station the relationship between pH and time, showed the better correlation coefficient value (r=0.369), following by Ca (r=0.230) and then by the other parameters EC (r=0.494), Ca^{2+} (r= 0.480), Na^+(r=0.480), TDS (r=0.479), Mg^{2+} (r= 0.470) while temperature (T), Turbidity, pH, bicarbonates (HCO_3^-), sulphates (SO_4^{2-}), chlorides (Cl^-), potassium (K^+), Sodium absorption ratio (SAR) and total hardness showed weaker relations.

The concentration-time relationships showed better correlation in Khorramshahr station than that of Gatvand station. The exponential model expressed better the concentration-time relationships in Khorramshahr station but in Gatvand station the logarithmic model was more fitted.

Also Antonopoulos et al. (2001) showed that the second order equation described the trend of the data time series better and the value of given series of observation of EC, DO, SO_4^{2-}, NO_3^-, Na^+, K^+ changed over time in a certain rate. Trend of the water quality parameters (EC, DO, SO_4^{2-}, NO_3^-, Na^+, K^+) were upward while Ca^{2+}, Mg^{2+} and TP had no trends.

Location trend analysis of water quality

Comparison between the mean data of Table 1 and that of Table 2 indicated that there was a significant difference between water quality variables in the Gatvand and Khorramshahr stations and TDS, EC, HCO_3^-, Cl^-, SO_4^{2-}, Ca^{+2}, Na^{+1}, K^{+1}, temporary hardness and total hardness values at Khorramshahr station (downstream station) were higher than those of at Gatvand (upstream station) station.

Also Jafarzadeh et al. (2005) showed an upward location trend in term of BOD, NH_3, NO_3 and EC along 500 km of the Karoon river.

This is due to rapid agricultural and industrial development during last decades in the basin of the Karoon River between these stations, the main reason of drastic increase in cations and anions in Khorramshahr station was agricultural drainage of Haft Tapeh and Karoon agricultural complex.

The Comparison between Cl^- value added between Gatvand and Khorramshahr stations and values contributed in municipal wastewater (4–8 g/cap.day) showed the pollution load entry to the Karoon River in term of Cl^- was equivalent to 1.7×10^9 persons.

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