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Estimating of the Relationship between Chemical Water Quality Parameters and Flow Rate of Karun River in Wet and Dry Seasons

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ABSTRACT: Hydro-Chemical Studies using regression tests would be efficient operational to save the time and cost, If the regression tests confirmed the correctness of regression analysis. In this study, water quality parameters of Karun river that are varies during a year by flow rate of the river, has been separated in two categories, Wet and Dry Seasons. Water quality and flow rate data were analyzed by using SPSS 18.0 in six regression models from October 1971 to September 2012. The best regression model selected based on the p-value and the largest adjusted R-Square. Correctness of estimated values was evaluated by using the t-test, in this way residuals of the best model should be distributed normally around zero. The result of statistical analysis showed that obtained regression equation in the Dry Seasons estimates values that are close to reality values at 5% probability level and Inverse regression model is suitable for all parameters except pH and HCO_3. In the Wet Season, except the Mg, regressions equation had a good performance. Theory of residuals proved that in the Wet Seasons Inverse regression pattern for TDS, EC, SO_4, Cl, Na and SAR and Logarithmic regression pattern for estimating the HCO_3 values were appropriate but none of the regression models did not have satisfactory for pH and EC.

Keywords: Adjusted R Square, Hydro chemical, Karun River, Residual, Regression pattern, t-Test

INTRODUCTION

Has long been rivers for the exploitation of water for drinking, industry and agriculture are attention human, as human societies are usually organized around river. Community development and population growth over time and consequently increase the use of water resources and abnormal manipulation cause that river water quality reduced.

Measurement, analysis and interpretation of water quality data of streams that facilitates the possibility to adopt appropriate management methods and progressively reduce the pollution of rivers. Thus, water quality studies and reviews the trend of river for adopt management decisions in basin is essential. Groundwater (springs, wells and Qanats), water in the atmosphere (rain and snow), surface water (oceans, seas, lakes and rivers) are the most important resources on Earth. The ocean is about 1,320 cubic kilometres (97.2%), the glaciers by about 25 cubic kilometres (1.8%), approximately 13 million cubic kilometres of aquifers (0.9%) found in freshwater sea, lakes and rivers about 250 thousand cubic kilometres (0.02%) and approximately 13 thousand cubic kilometres of water vapor in the atmosphere to are allocated to (7). There are always some solutes, suspended solids and gases in this water. Some of these minerals are essential for human health. Also, excessive amounts of these substances are very harmful and can cause a lot of risks. Some of these minerals are essential for human health. Also, excessive amounts of these substances are very harmful and can cause a lot of risks.

Therefore, in order to understand the water quality parameters, will be explain.

Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) are solids in water that can pass through a filter. TDS is a measure of the amount of material dissolved in water. This material can include carbonate, bicarbonate, chloride, sulphate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. A certain level of these ions in water is necessary for aquatic life. Changes in TDS concentrations can be harmful because the density of the water determines the flow of water into and out of an organism's cells. TDS is used to estimate the quality of drinking water, because it represents the amount of ions in the water. Water with high TDS often has a bad taste and/or high water hardness, and could result in a laxative effect.

Electrical Conductivity

Electrical conductivity is a measure of how well a material accommodates the movement of an electric charge. It is the ratio of the current density to the electric field strength. Its SI derived unit is the Siemens per meter. Since the electrical conductivity is a measure to the capacity of water to conduct electrical current, it is directly related to the concentration of salts dissolved in water, and therefore to the Total Dissolved Solids (TDS). Salts dissolve into positively charged ions and negatively charged ions, which conduct electricity. Since it is difficult to measure TDS in the field, The electrical conductivity of the water is used as a criterion.

Sodium Adsorption Ratio

SAR is a mathematical relationship, set out in Equation 1, the concentration of sodium in relation to

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calcium and magnesium to known effects on soil dispersibility. SAR and the electrical conductivity of irrigation water can be assessed for the potential to cause dispersion in a soil. Sandy soils are not affected by the sodium (because of the low clay content), but the plants growing on them may be affected.

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \qquad \text{Equation 1}$$

The relationship between chemical water quality parameters such as electrical conductivity, total dissolved solutes, sodium adsorption ratio and total hardness versus water flow of Haraz River using regression analysis in SPSS software was analyzed. The results of this study showed that in most cases, showing the relationship between water chemical and flow parameters by using a logarithmic regression model was statistically significant (Vafakhah et al. 2009).

The study of changes of the water quality parameters Influenced by flow changes of Gorganrood river, expressed that, by changing the river flow, the concentration of dissolved substances in water are has changes during periods of high water and low water, so the water quality parameters should be examined separately (Amin Karami Moghaddam, 2006). He collect the required parameters for the analysis of changes of anions and cations in GorganRoud River route from the stations of Qzaqly, Gonbad and Gorgan dam, then draw Collins and Schuler diagrams and the results obtained are as follows: there is a close relationship between increasing of flow rate and decreasing of EC in Gonbad station and increase flow rate leads to decrease Na and Cl in Qazaqly station and cause of decreasing of all of chemical elements especially Sulphates in Gorgan station.

For investigating the causes of salinity of Ajichay River and how to optimal utilization of water by using flow rate and water quality data from 30 recent years, calculated the mean of flow rate and mean of annual salinity of the Ajichay River. suggested for Optimal Utilization of Ajichay River, use water of Ajichay River for cultivation, storage and Injecting into underground water resources, in that Seasons river has wet regime (April and May) and has good quality (Gorji et al., 1994).

In a study entitled The Effects of water withdrawals on water quality of downstream of Mamlou dam by QUAL2E has been proved that before and after the construction of dams, the water quality changes before entering of Parchin complex wastewater was not tangible, but Assuming even that the Parchin complex wastewater refined to the extent of Surface Water Quality Standards, it makes the river water quality varies greatly. This is due to the flow rate of wastewater that enters to the river is more than flow rate of river in the entrance section. Also the construction of dams and withdrawal of water, enhance its effects (Torabiyan, 2004). In a study that took place to order to investigate the effects of upstream activities on water quality of Aravandrud and Karun River, stated the Aravandrud and Karun river water quality depends on flow rate and Due to a very noticeable reduction in flow in recent years, water quality was affected (Ghandehari, 2006).

Study Area

Karun River Watershed with an area equivalent to 45,221 square kilometers is one of the largest catchments in the Iran. This river originates from Zagros Mountains and after passing through the mountains near the Gotvand city enters to the Khuzestan plain (Figure 1). Karun River in the north of Ahvaz is divided to two branches that are connected to each other in South of Ahvaz. In this maze way, Karun river provides water needed for drinking, agriculture and industry, dozens of cities and villages, thousands of hectares of agriculture, hydroelectric power generation, fish farming and several design projects and provides industrial plants. In this study to evaluate the Water quality of Karun River, water quality parameters were taken from Khuzestan Water and Power Authority. Ahvaz Hydrometric Station with code 309-21 on the Karun River and geographical coordinates: 48° 41' 28" E and 31° 20' 25" N is located in Ahvaz.

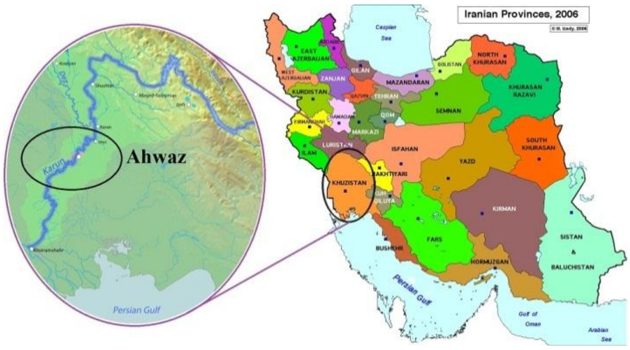

Figure 1. The Ahvaz and Karun River Location

MATERIAL AND METHODS

In a manner, The Water Quality data from October 1971 to September 2012, were classified in two separate tables, the first two Seasons and the second two Season of year. Graphs between each of the parameters of water quality (the dependent variable) and river discharge (independent variable) plotted and to determine the best regression model the six pattern Linear, Exponential, Logistic, Exponential, Logarithmic and Inverse is used. To judge and choose the best model, the ANOVA results are used. Finally the best regression line between the water quality parameters (such as TDS, EC, pH, HCO_3, Cl, SO_4, Ca, Mg and Na) and the flow rate were fitted by different patterns and using results of the software SPSS 18.0 (Analysis of Variance for Regression and values of Sig., and Adjusted R Square) judged on the appropriateness of the fitted models (To obtain regression equations should be ensured that correlation coefficient between two variables are statistically significant). The SPSS software using Sum of Squared Residuals as default and stop calculation when the difference between the two end-stage were 1E-8. If on ANOVA for regression Sig. was less than 0.05 the regression models was fitted properly. Also it should be noted that adjusted R Square of the Best model is more than other models. After obtaining the regression equation based on river flow, the independent variable (Q: Flow Rate) put into the equation and for each Q, a water quality parameter estimated.

To verify the ability of the regression equations to estimate reliable values the One-Sample t-test is used. One-Sample T-test between the amounts of residuals (the

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difference between the estimated values and actual values) and zero is done. This test is based on a uniform distribution of residues around zero, so that the algebraic sum of all negative values of residuals and sum of all positive values should be equal. If this test were statistically significant, obtained regression equation estimates the acceptable values (Helsel and Hirsch, 2002).

RESULTS AND DISCUSSION

The results of regression test and ANOVA for regression were divided to two categories, Dry and Wet Seasons. To determine the best fitting model of six patterns that include Linear, Logarithmic, Inverse, Power, Logistic, and Exponential were applied and for judging about superior pattern and choosing it the results of ANOVA were worked.

A transmittal diagram can present all the base aspects of existence or non-existence between two variables. It should be noticed, that straight judgment based on correlation coefficient between two variables will not be right judgment. As instance, the diagrams of EC and TDS against discharge were shown separately in Figure 2, and the earned results of ANOVA, correlation coefficients and determination coefficients in Dry Seasons were presented in Table 1.

The results of ANOVA test for all the presented in Table 1 showed p-values that were less than 0.05 and the regression test was statistically significant. It was avoided to present the result of ANOVA for HCO_3 and pH In table 1 because they were not statistically significant. The results of ANOVA, correlation coefficients and determination coefficients in Wet Seasons were presented in Table 2.

The result of ANOVA shows that obtaining regression equation for SO_4 and pH were not statistically significant because their p-values were more than 0.05. As instance in Wet Seasons, the diagrams of EC and TDS vs. discharge were shown separately in Figure 3.

In Table 2, only significant cases were reported. In figures 2 and 3 the superior regression pattern was presented by interrupted curve. The obtained regression relations for every parameter, separately in 2 categories- Wet and Dry Seasons- were presented in Table 3.

After obtaining regression equations for each parameter, the values of dependent variables (water chemical qualities parameters) were estimated by putting different values of independent variable (discharge) in obtained regression equations. According to base of regression, the estimated values are different with real values. In other words, in the scatter plot estimated values would not equal with the real values. This difference between them is known as Residual or Error.

These comparisons and tests that presented in Table 1, 2 and 3 don’t mention to accuracy of estimated values. In fact it doesn’t point to amount of Error of Estimating. To check the accuracy of the estimated regression equation, the Residuals values are plotted vs. estimated values. If the residuals values were uniformly distributed around zero, the estimated regression parameter would be successful. In other words, if the average of the residuals is not significantly different from zero, water quality parameters were predicted correctly with regression equations. If p-value be higher than 0.05, the regression equation that obtained from top models was successful and estimates acceptable values.

Table 1. The results of regression test and ANOVA in Dry Seasons (1971-2012)

	(Model)	(R)	(R Square)	(Adjusted R Square)	(Std. Error of the Estimate)
TDS	Inverse	0.772	0.596	0.595	238.615
EC	Inverse	0.866	0.749	0.748	288.179
Cl	Inverse	0.876	0.768	0.767	1.806
SO_4	Inverse	0.776	0.602	0.601	1.506
Ca	Inverse	0.710	0.504	0.502	0.988
Mg	Inverse	0.733	0.537	0.535	0.808
Na	Inverse	0.871	0.759	0.758	1.928

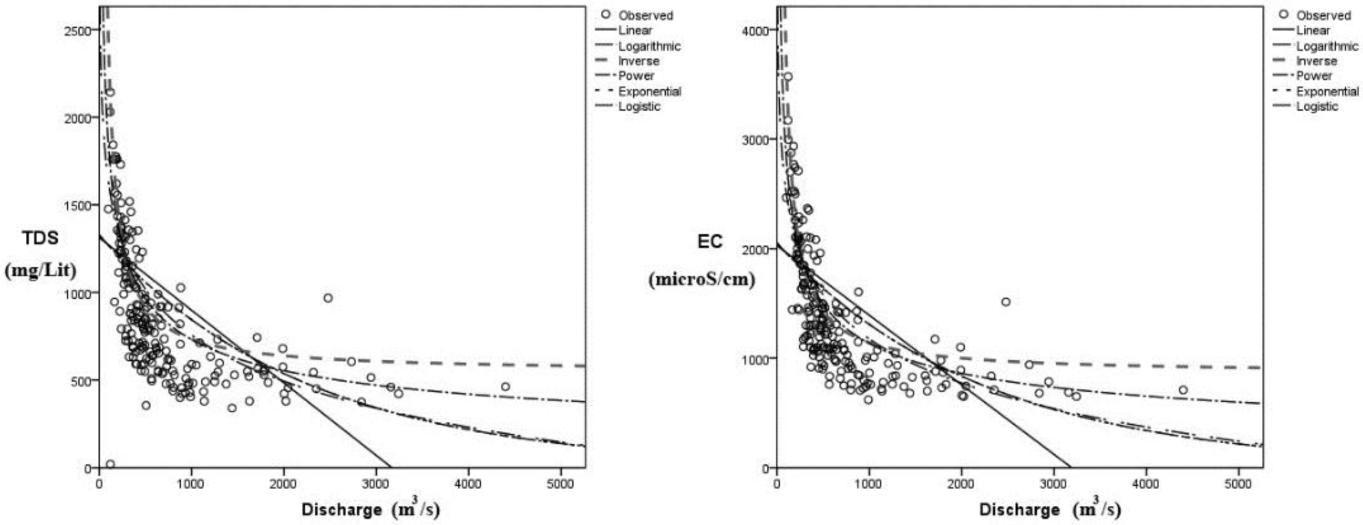

Figure 2. Transmittal diagram of EC and TDS against discharge river and regression patterns in Dry Seasons (1971-2012)

Table 2. The results of regression test and ANOVA in Wet Seasons (1971-2012)

	(Model)	(R)	(R Square)	(Adjusted R Square)	(Std. Error of the Estimate)
TDS	Inverse	0.555	0.308	0.305	273.675
EC	Inverse	0.646	0.417	0.415	376.887
HCO_3	Logarithmic	0.449	0.201	0.197	0.464
Cl	Inverse	0.703	0.494	0.492	2.398
SO_4	Inverse	0.379	0.144	0.140	1.952
Mg	Power	0.704	0.496	0.493	0.286
Na	Inverse	0.711	0.505	0.503	2.463

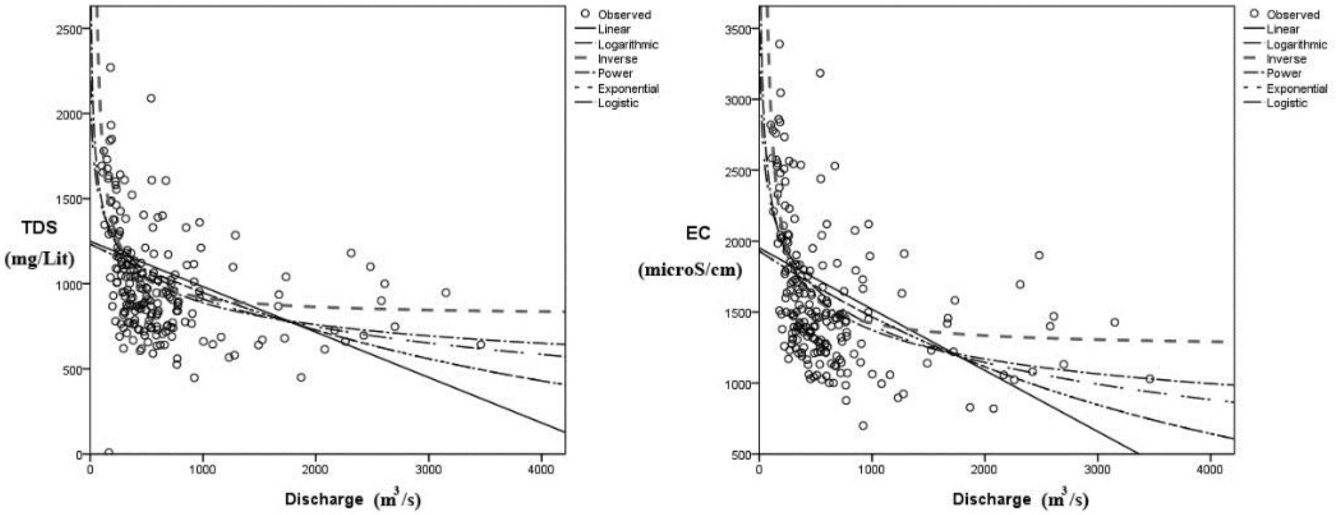

Figure 3. Transmittal diagram of EC and TDS vs. discharge river and regression patterns in Wet Seasons (1971-2012)

Table 3. The superior regression relations in Dry and Wet Seasons

Parameter	Regression relation of Wet Seasons	Proportional pattern`	Parameter	Regression relation of Dry Seasons	Proportional pattern
TDS	$729.2+\frac{108917.52}{Q}$	Inverse	TDS	$441.141+\frac{172617}{Q}$	Inverse
EC	$1104.731+\frac{190171.3}{Q}$	Inverse	EC	$665.62+\frac{296391}{Q}$	Inverse
pH	-	-	pH	-	-
CO_3	-	-	CO3	-	-
HCO_3	$5.012-0.335Log(Q)$	Logarithmic	HCO_3	-	-
Cl	$4.715+\frac{1412.98}{Q}$	Inverse	Cl	$2.151+\frac{1954.95}{Q}$	Inverse
SO_4	$3.518+\frac{477.4}{Q}$	Inverse	SO_4	$1.461+\frac{1103.07}{Q}$	Inverse
Ca	-	-	Ca	$2.782+\frac{592.64}{Q}$	Inverse
Mg	$30.726\times Q^{-0.408}$	Power	Mg	$1.329+\frac{518.141}{Q}$	Inverse
Na	$4.589+\frac{1482.56}{Q}$	Inverse	Na	$2.07+\frac{2036.14}{Q}$	Inverse

Q = discharge (m^3/s)

To test the distribution of Residuals of parameters of Dry Seasons around zero One-Sample t-test is used. In Table 4 the results are presented. Referring to Table 4, Residual of all parameters of Dry Seasons, are statistically significant.

In other words, at the level of 5% the average of residuals were equal to zero and obtained Equations estimate acceptable values.

Also to test the distribution of Residuals of parameters of Wet Seasons around zero One-Sample t-test is used and results are presented in Table 5. Referring to Table 4, Residual of all parameters except HCO_3 and Mg of Dry Seasons, are statistically significant. In other words, for HCO_3 and Mg at the level of 5% the average of residuals were not equal to zero. So obtained Equations for HCO_3 and Mg in table 3 does not work correctly.

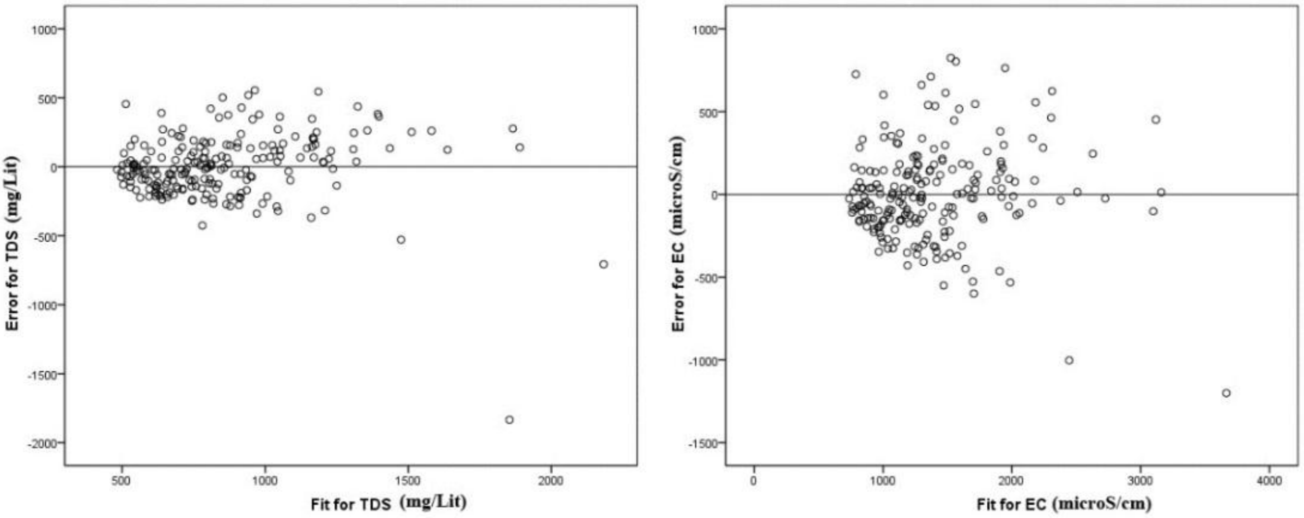

Figure 3. The scatter plot of the residuals vs. estimated values of Dry Seasons

Table 4. The results of one sample t-test for Dry Seasons

	Test Value=0.0					
					95% Confidence Interval of the Difference	
Parameter	**t**	**df**	**Sig. (2-tailed)**	**Mean Difference**	**Lower**	**Upper**
TDS	0.000	209	1.000	0.004	-32.378	32.388
EC	0.000	209	1.000	-0.002	-36.112	39.107
Cl	0.002	209	0.998	0.000	-0.245	0.245
SO_4	-0.003	209	0.998	-0.002	-0.205	0.204
Ca	0.003	209	0.997	0.000	-0.134	0.134
Mg	-0.002	209	0.998	0.002	-0.110	0.110
Na	-0.023	209	0.982	-0.003	-0.265	0.26

Significant: $P< 0.05$.

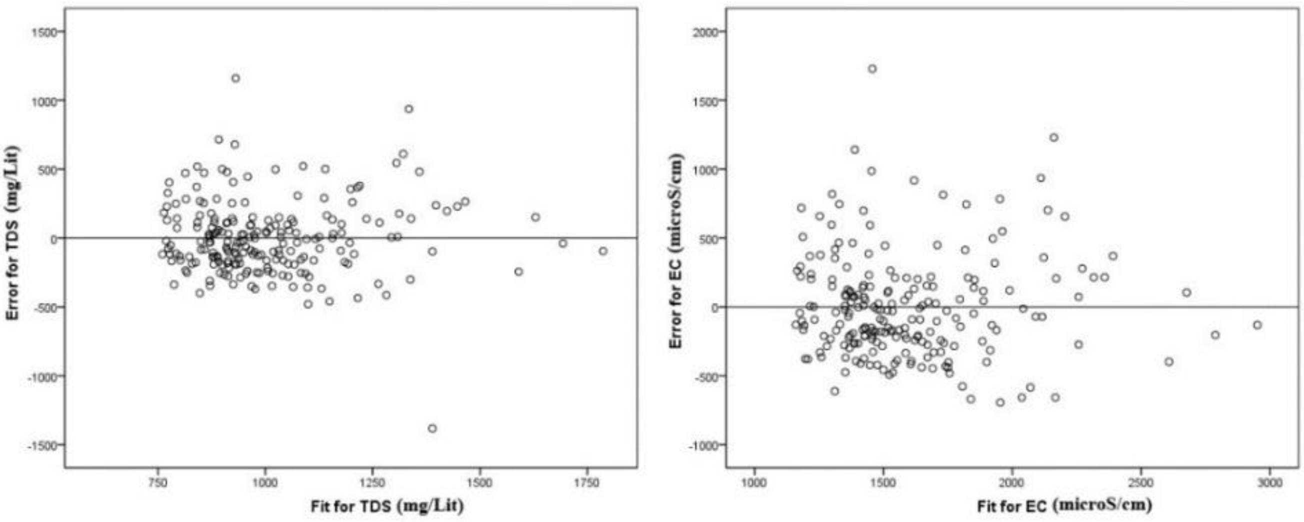

Figure 4. The scatter plot of the residuals vs. estimated values of Wet Seasons

Table 5. The results of one sample t-test for Wet Seasons

	Test Value=0.0					
					95% Confidence Interval of the Difference	
Parameter	**t**	**df**	**Sig. (2-tailed)**	**Mean Difference**	**Lower**	**Upper**
TDS	0.000	208	1.000	0.002	-37.230	37.233
EC	0.000	208	1.000	0.000	-51.270	51.270
HCO_3	-35.496	208	0.000	-1.181	-1.247	-1.116
Cl	-0.001	208	0.999	0.000	-0.326	0.326
SO_4	-0.002	208	0.999	0.000	-0.266	0.265
Mg	2.141	208	0.033	0.118	-0.009	0.227
Na	0.002	208	0.999	0.000	-0.335	0.335

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CONCLUSIONS

The presented Table 3 shows that the Inverse pattern is suitable to express the relationship between the Karun River discharge and water quality parameters including TDS, EC, Cl, SO4 and Na in wet Seasons of the year, and for HCO_3 the Logarithmic pattern, and for Mg the Power regression model are more appropriate. After testing the residuals with zero, the fitted regression equations for the HCO_3 and Mg were refused statistically and other obtained regression equations confirmed (Figure 4 and Table 5). Statistically, there weren't any significant correlation between Karun River discharge and pH and Ca in wet Seasons of the year, so adjusted R square was very little and at 5% probability level all regression models were unsatisfactory for them. According to the presented diagrams in Figure (3) and Tables 4 for dry Seasons, the Inverse pattern was suitable model with acceptable adjusted R square for the TDS, EC, Cl, SO4, Ca, Mg and Na. In these seasons, pH and HCO_3 have not any regression relationship with Karun river discharge. All of these earned equations were confirmed by residuals test and could predict acceptable values.

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