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Assessment Hydro geochemical of Karst springs in Zagros Mountain, Iran

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ABSTRACT

Groundwater quality comprises the physical, chemical, and biological qualities of ground water. The pir-e-Qar spring, located in the Zagrus mountains Iran have been considered as an important water source for people in the area southwards. We used data samples water quality (SAR, Cation^{+}, Anion^{-}, EC, TDS, Cl, Mg, Na, CaSo4 and Hco3) and discharge at 1987-2013 period. The results M-k test show that Hco3,Cation^{+},Anion^{-},Cl,EC and TDS have upper ward but discharge has downward trend at period(1987-2013). Other results show that the calculated Z element Hco3, Cation^{+}, Anion^{-}, Cl, EC and TDS are $z \geq + 1.96$ that these amounts show elements have upper ward . There is enough evidence to determine that there is an upper ward trend. The calculated z discharge is -3 that it was $\geq - 1.96$. Discharge has down ward trend there is not enough evidence to determine that there is a downward trend at Pir-e-qar spring.

Key word: Karoon River, Discharge, Water Quality, PH, EC.

INTRODUCTION

Groundwater quality comprises the physical, chemical, and biological qualities of ground water. Temperature, turbidity, color, taste, and odor make up the list of physical water quality parameters. Since most ground water is colorless, odorless, and without specific taste, we are typically most concerned with its chemical and biological qualities[5]. Naturally, ground water contains mineral ions. These ions slowly dissolve from soil particles, sediments, and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer. Some dissolved sediment rocks may have originated in the precipitation water or river water that recharges the aquifer. In water, all of the dissolved sediment rocks are either positively charged ions (cations) or negatively charged ions (anions). The total negative charge of the anions always equals the total positive charge of the cations.

A karst spring is a spring that is part of a karst system. That includes the underground drainage of a much larger area, which means that karst springs often have a very large discharge. The properties of karst springs are suitable for the supply of drinking water. Water recharge to karst aquifers occurs directly, either through swallow holes and sinkholes, or indirectly through the pores in the soil overlying the limestone bedrock. Although the soil overlying a karst aquifer provides some filtration of contaminants from in-flowing water, almost none takes place between swallow holes and springs. The water also has little opportunity to be filtered or for the contaminants to become bound to the bedrock as the water flows rapidly through the karst conduits[21].

Water quality is assuming great importance with the rising pressure on industries and agriculture and rise in standard of living [15]. The quality of water is a subject of continuing concern and because of inextricably linked to water quantity, it is very important for the hydrologist to understand the significance of developing and modeling techniques that can accommodate both the features. The assessment of long-term water quality changes is also a challenging problem. Water quality has been rapidly declining worldwide particularly in developing countries due to natural and anthropogenic processes [26]. The study of stream geochemistry reveals the pattern and linkage between evaporation, chemical weathering, precipitation and anthropogenic impacts [21].

Changes in air temperature and rainfall could affect river flows and, hence, the mobility and strength of contaminants. With increased flows, there will be changes in stream power and, hence, sediment loads with the potential to alter the morphology of rivers and the transfer of sediments to lakes, thereby impacting freshwater habitats in both lake and stream systems [24].

The results of these studies compiled as reliable long-term water quality records and the examination of this data for long-term trends [6]. Quantifying the major ion composition of stream waters also has broad implications, i.e., water quality type, hydrogeology characteristics, weathering processes and rainfall chemistry [2, 3].They showed that drainage network, geology, lit logy and hydro-geochemical reason decreasing water quality this karst cave[12].

Karstified rocks scattered in all parts of the world. Karst is estimated to cover 20 to 25 % of the surface of all continents[2]. Karstic carbonate formations cover about 11% of Iran's land area (Figure 1). About 55.2% of these formations are located in the Zagros Mountain Ranges [12]. Most of the potable and irrigation waters of the inhabitants are supplied by the springs emerging from karstic formations. Protection of these water resources from pollution is necessary.

EXPERIMENTAL SECTION

Geographical area:
Saldaran Mountain is located in centeral of Zagros in Caharmahal-Bakhtiari province, Iran (Figure 2). Most of this mountain is composed of limestone-dolomite Asmari formation, which is cover, by im marl formation (or sand and marl Aghajari Formation) and underlain by shale and marly Pabdeh-Gurpi formation. Because of high elevation of the Pabdeh-Gurpi core, the hydrogeological relationship of two flanks is disconnected in most parts of the anticline (Figure 1).The highest elevation is up to 3563 m above sea level in the top of Saldaran Mountain, while the minimum absolute elevation is about 2050 m in the Pir-e-qar spring. Climate of the study area is of semiarid to Mediterranean type with a cool winter and a dry summer. The study area receives an average of about 630 mm of rainfall per year and discharge between 0.8 to 12m^3.

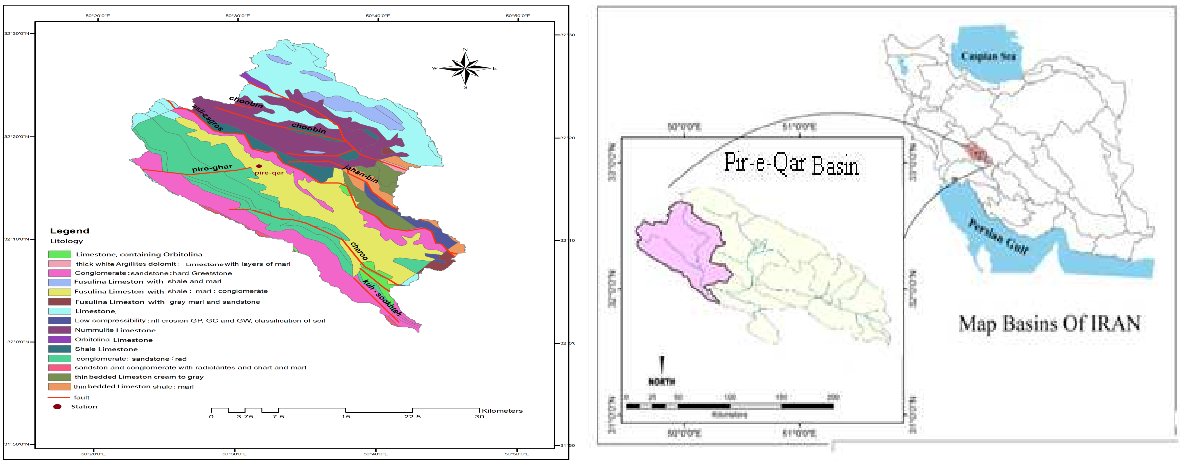


Fig.1. The location of North Karoon basin and Armand station

The samples are 221that they collected by Chaharmahal and Bakhtiari Regional Water (CBRW) (Table.1)from October 1987 to September 2013.The samples collected do analysis by CBRW. This data are monthly in the time series 1987 to 2013.Monthly measurements of the discharge and water quality variables were obtained, and monitored the Armand station (include bPit-e-qar spring) of the Pir-e-qar spring by CHRW (Table 1)[18, 30].

Table 1. Geography of Characteristics Pir-e-Qar station

Station	longitude°	latitude°	Rainfall mean(mm)	Elevation (m)
Pir-e-qar	50-33	32-13	560	2050

The following variables are measured by CBRW: above (Q) as m3/s, pH, electrical conductivity (EC) as µs/cm, Total dissolved solid (TDS), chlorides (Cl^-) (Anion$^-$), Cation$^+$ include elements: (sodium (Na^+), potassium (K^+), Magnesium ($Mg2^+$), calcium (Ca2+)) , Sodium Absorption Ratio (SAR), temporary hardness and total hardness as meq/lit at the above station (Table1). The monitoring data of these variables are available for the analysis as presented in this paper on monthly and yearly basis for the period of 1987-2013.

Methodology

Monthly average and yearly of the data time series have analyzed by statistical methods. Parametric and non-parametric statistical methods were use correlation (Pearson (Ш), Mann-Kendall (MK) [17, 19].The significance level in this study was $p < 0.05$.To evaluated the impact of discharge on water quality by correlation coefficient and trend analysis by Mann-Kenddal test. In this study are used correlation Man-Kendal Model for determined trend.

An aspect of technical analysis that tries to predict the future movement of a stock based on past data. Trend analysis based on the idea that what has happened in the past gives traders an idea of what will happen in the future. A trend can be creating as the general movement over time of a statistically detectable change [9].The MK test, usually used to assess the trend of a time-series. The purpose of the Mann-Kendall (MK) test [17,19,10] is statistically assess if there is a monotonic upward or downward trend of the variable of interest over time. A monotonic upward (downward) trend means that the variable consistently increases (decreases) through time, but the trend may or may not be linear. The MK test is using to in place of a parametric linear regression analysis, which is used to test if the slope of the estimated linear regression line is different from zero [11, 5, and 7]. A trend can be creating as the general movement over time of a statistically detectable change [9]. If the calculated $z \geq +1.96$ there is an upward and or $z \leq -1.96$ there is downward trend at alpha ≥ 0.05.The regression analysis requires that the residuals from the fitted regression line be normally distributed; an assumption not required by the MK test, that is, the MK test is a non-parametric (distribution-free) test (Equation 2, 3, and 4).

(2) $$Z_c = \begin{cases} \frac{S-1}{\sqrt{\mathrm{var}\,(s)}}, & S > 0 \\ 0, & S = 0 \\ \frac{S+1}{\mathrm{var}\,(s)}, & S < 0 \end{cases}$$ Where: (3) $$S = \sum_{i=k}^{n-1} \sum_{k=i+1}^{n} sgn(x_k - x_i),$$

(3) $$sgn(x_k - x_i) = \begin{cases} 1, & x_k > x_i \\ 0, & x_k = x_i \\ -1, & x_k < x_i \end{cases}$$

In which the x_k, xi are the sequential data values, n is the length of the data set, t is the extent of any given tie, and $\sum$ denotes the summation over all ties.

RESULTS AND DISCUSSION

Pir-e-Qar spring has an important role in drinking water supply for Farsan Township. Geology formations, precipitation, temperature and dissolution of limestone have the main role in decreasing water quality in this spring. The formation of this basin is sedimentary. Lithologies of the rocks are limestone, marl, sandstone, dolomite and gypsum. In terms of tectonic, Pir-e-qar spring affected by Zagrous and Pir-e-Qar faults. This fault is parallel to main Zagros fault direction.

Quality analyses:

Table 2 shows that statistical profile of the Pir-e-Qar spring. SAR values vary from 0.06 to 0.79. $Cation^+$ values vary from 1.37 to 6.03. The pH values and anions concentration changed from 7.0 to 8.9 .Na^+ values between 0.04 to 1.06mlg/lit, Cl^- fluctuation is between 0.1to 1.4 mlg/lit and Hco3 is from 1 to 4.2melg/lit. Also, Ec have change from146 t0581 μohm. The concentration of these elements in water is different at summer and winter. In the summer season concentration have increasing trend and in the winter, spring and autumn seasons have decreasing trend in Pir-e-qar spring. In addition, the data show that the spring water is in good class water quality for drink.

Table2. Descriptive Statistics of water quality characteristics of Pir-e-qar station

Variable	Mean	StDev	Coef Var	Minimum	Maximum	Skewness	Kurtosis
SAR	0.30	0.14	48.13	0.03	0.79	0.55	0.41
$Cation^+$(milg/lit)	4.40	0.93	21.04	1.37	6.03	-0.61	-0.28
Na^{++}(milg/lit)	0.42	0.22	50.95	0.04	1.06	0.34	-0.32
$Ca2^{++}$(milg/lit)	2.90	0.61	21.05	0.80	4.20	-0.52	0.41
$Anion^{-+}$(milg/lit)	4.36	0.92	21.11	1.37	6.00	-0.61	-0.33
$So4^+$(milg/lit)	0.64	0.35	54.66	0.02	1.70	0.37	-0.17
Cl^{-+}(milg/lit)	0.75	0.35	46.71	0.10	1.40	-0.15	-1.14
$Hco3^+$(milg/lit)	2.96	0.49	16.71	1.00	4.20	-0.86	1.73
PH^+(milg/lit)	7.92	0.29	3.68	7.00	8.90	0.32	2.04
Ec^+(milg/lit)	439.34	90.28	20.55	146.00	581.00	-0.69	-0.34
TDS^+(milg/lit)	285.45	58.68	20.56	95.00	377.00	-0.69	-0.35
Debi(m^3)	2.17	2.43	112.30	0.8	12.43	2.13	4.11

Trend analysis:

Trend analysis is based on the idea that what has happened in the past gives traders an idea of what will happen in the future [5, 7]. The results M-k test show that Hco3, Cation$^+$, Anion$^-$, Cl, EC and TDS have upper ward but discharge has downward trend at period(1987-2013). Other results show that the calculated Z element Hco3(graph.3), Cation$^+$(graph.4), Anion$^-$(graph.5), Cl(graph.2), EC and TDS(graph.6) are $z \geq + 1.96$ that these amounts show elements have upper ward(Table.4). There is enough evidence to determine that there is an upper ward trend. The calculated z discharge is -3 that it was $\geq - 1.96$. Discharge has down ward trend (graph.7) there is not enough evidence to determine that there is a downward trend. The results show that elements chemistry have upward trend but discharge has downward trend at Pir-e-qar spring station Table 4.

Table4. Mann-Kendall Trend Test by Normal Approximation in Pir-e-qar station

Mann-Kendall	Hco3	Cation	Anion	Cl	EC	TDS	Discharge
The calculated z	2.7	2.95	2.26	2.3	1.97	1.99	-3
P-value	.003	0.04	0.01	0.01	0.02	0.02	0.001

The calculated z > + 1.96 and -1.96, For Ha: Upper and Down ward trend, at alpha = 0.05, there is enough evidence to determine that there is an upward trend.

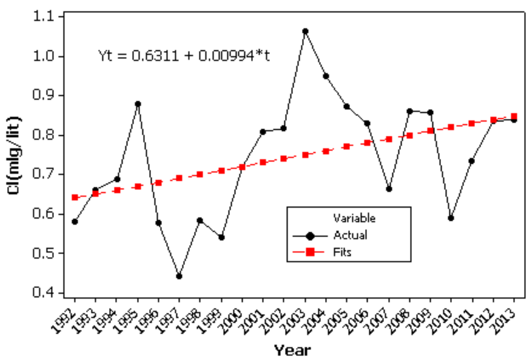


Fig2.Time series and trend line Cl

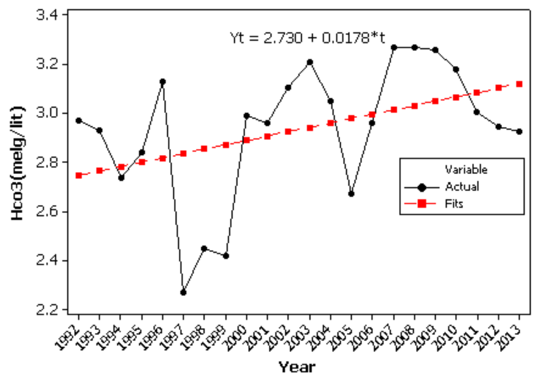


Fig3.Time series and trend line Hco3

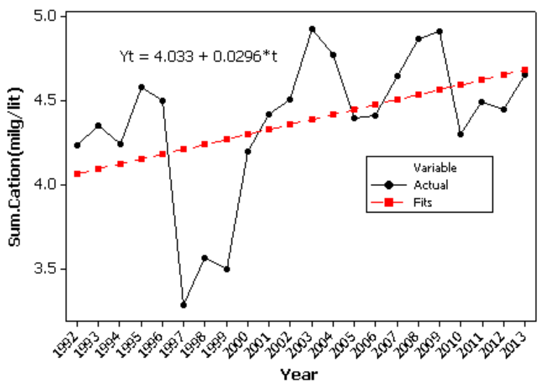


Fig4.Time series and trend line Cation$^-$

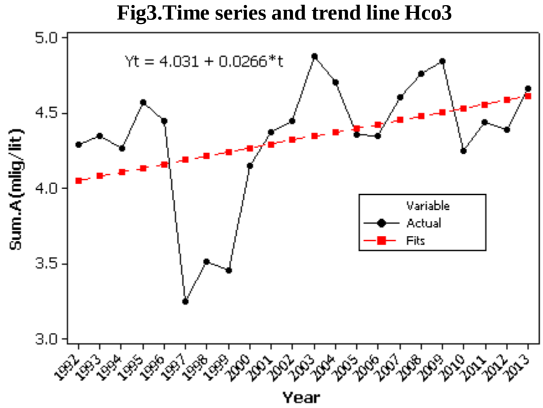


Fig5. Time series and trend line Anion$^-$

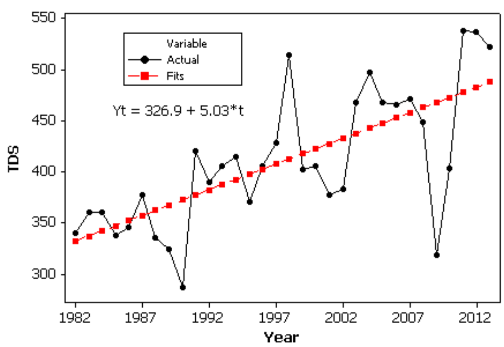


Fig6.Time series and trend line TDS

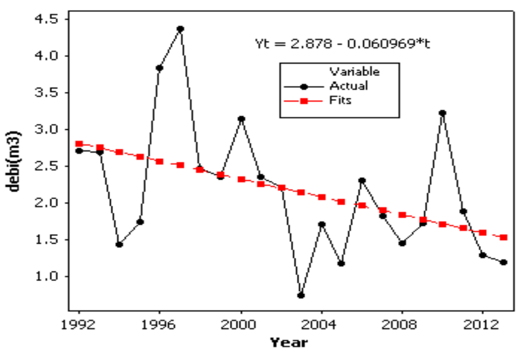


Fig7. Time series and trend line Discharge

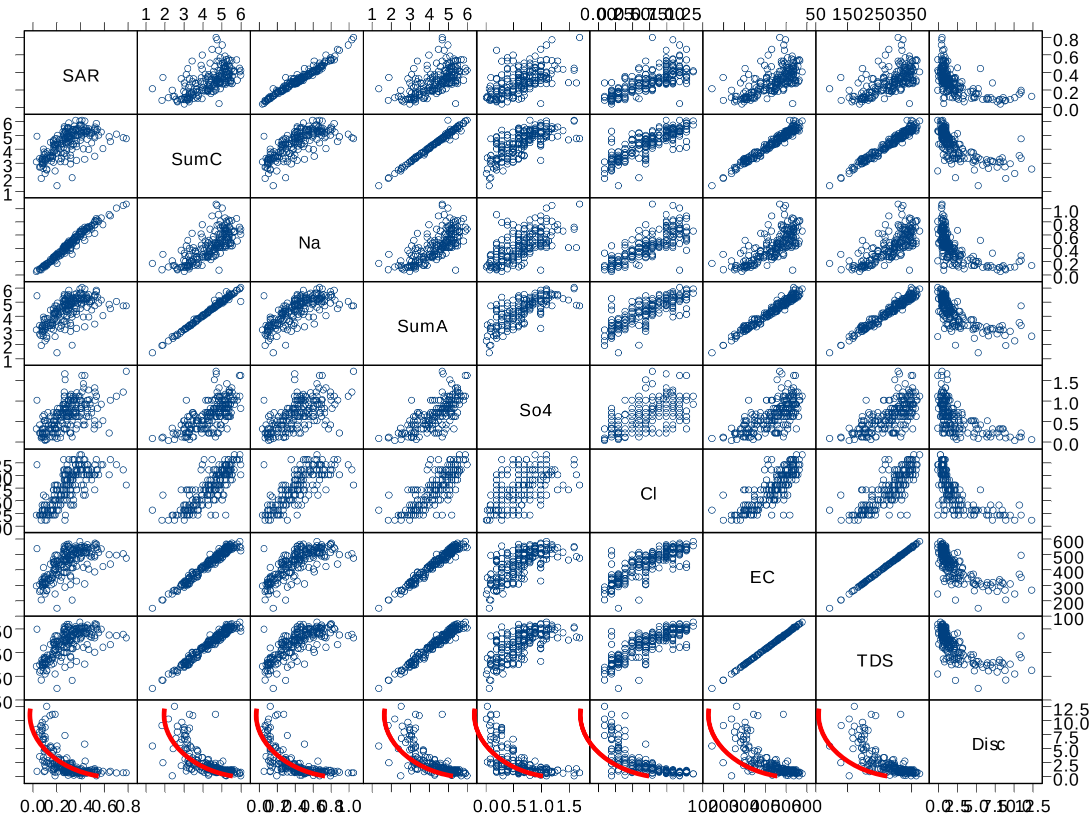
The results showed that the discharge rate change was effective on the water quality in Pir-e-qar spring. Therefore, droughts among water basins increase the concentration of Cations$^+$, Anion$^-$, SAR, PH, EC and TDS.

Affect Discharge on Chemical concentration

Chemical concentration in this region shows that it depends on the amount of discharge fluctuations. Pearson's correlation results show that the relationship is logarithmic relationship with a discharge ion concentration. So to investigate changes in ion concentration in the water, check the changes. Results showed that discharge is upward trend. Discharge was calculated to estimate the dependence of the precipitation based on the results of the annual discharge of springs was a logarithmic relationship the best model to estimate the condition (t -1).Among the test stations, the max concentration was determined in Armand station (r=-0.40). Anions (So4-2, Cl, HCO3-, CO3-2) concentration increased in discharge in the station (r=0.48). Therefore, the concentrations the Cation and Anion increased in these samples. SAR showed decrease during increased discharge. EC (r=-0.3), pH (r=-0.01) and TDS (r=-0.3) were increased during increased discharge (Table 3, Annual Discharge). In addition, there is an inverse relationship between the discharge and the concentration of chemical factors(Table 3).SAR(-0.59),Cation(-0.70),Anion(-0.70), Hco3(-0.40),EC(-0.70),TDS(-0.70),Cl(-0.71),So4(-0.59) and Na(-0.63) were decrease chemical during increased discharge(Table3,Graph1).

Table 3. The correlation between discharge and chemical elements in Armand station

	sar	Sum.K	na	Ca	Sum.A	So4	Cl	Hco3	PH	Ec	TDS
debi	-0.59	-0.70	-0.63	-0.50	-0.70	-0.59	-0.71	-0.40	0.17	-0.70	-0.70



Graph1.Matrix correlation between chemical elements and discharge in Armand station

CONCLUSION

Groundwater quality comprises the physical, chemical, and biological qualities of ground water. The pir-e-Qar spring, located in the Zagrus mountains Iran have been considered as an important water source for people in the area southwards. We used data samples water quality (SAR, Cation+, Anion-, EC, TDS, Cl, Mg, Na, $CaSO_4$ and HCo_3) and discharge at 1987-2013 period. The results M-k test show that Hco3, Cation+, Anion-, Cl, EC and TDS have upper ward but discharge has downward trend at period(1987-2013). Other results show that the calculated Z element HCo_3, Cation+, Anion-, Cl, EC and TDS are $z \geq +1.96$ that these amounts show elements have upper ward. There is enough evidence to determine that there is an upper ward trend. The calculated z discharge is -3 that it was

≥ - 1.96. Discharge has down ward trend there is not enough evidence to determine that there is a downward trend at Pir-e-qar spring. the results of the annual discharge of springs was a logarithmic relationship the best model to estimate the condition (t -1). Among the test stations, the max concentration was determined in Armand station (r=-0.40). Anions (So4-2, Cl, HCO3-, CO3-2) concentration increased in discharge in the station (r=0.48). Therefore, the concentrations the Cation and Anion increased in these samples. SAR showed decrease during increased discharge. EC (r=-0.3), pH (r=-0.01) and TDS (r=-0.3) were increased during increased discharge (Table 3, Annual Discharge). In addition, there is an inverse relationship between the discharge and the concentration of chemical factors (Table 3). SAR(-0.59), Cation(-0.70),Anion(-0.70), Hco3(-0.40), EC(-0.70), TDS(-0.70), Cl(-0.71), So4(-0.59) and Na(-0.63) were decrease chemical during increased discharge. In fact, the discharge fluctuation of the river under increasing condition, which increases the Karst formation erosion, leads to the intensity in the water basin lime formations that increase the chemical substance concentrations.

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REFERENCES

[1] Brennan S.K., & Lowenstein, T.K., (**2002**). *Journal of Geochim. Cosmochim. Acta* 66: 2683–2700.
[2] Bonacci, O. (**1990**). “Specific hydrological characteristics of the karst system”, Proc. Of the 3rd int. Iranian congress of civil Eng., Vol.2, P 175-196.
[3] Cruz J.v, and Amaral C.S., (**2004**). *Journal of Appl. Geochem*. 19: 445–459.
[3] Dongxian Konga, ,Chiyuan Miaoa, b,Alistair G.L. Borthwickc, Qingyun Duana, Hao Liud,Qiaohong Suna, Aizhong Yea, Zhenhua Dia,Wei Gonga,(**2015**), *Journal of Hydrology,* Volume 520, 2015, Pages 157–167.
[4] Esterby, S.R.(**1998**), Review of methods for the detection and estimation of trends with emphasis on water quality applications , Hydrological Processes 10:127-149.
[5]Harter.Th,(**2008**), Groundwater Quality and Groundwater Pollution, University of California, Davis, and Kearney Agricultural Center.
[6] Hirsch, R.M., J.R. Slack, and R.A. Smith. (**1982**), *Water Resources Research* 18(1):107-121.
[7] Hirsch, R. M., Alexander, R. B., & Smith, R. A.,(**1991**), *Journal of Water Resources Research*, 27: 803–813.
[8] Gary Benattar_ and Philippe Trebuchet,(**2011**), Trend Analysis in Polls, Topics, Opinions and Answers, HAL Id: hal-00601261.
[9] Gilbert, R.O. (**1987**), Statistical Methods for Environmental Pollution Monitoring, Wiley, NY.
[10] Gibbons, J.D, and S.Chakraborti,(**2003**),Nonparametric Statistical Inference, Marcel Dekker,NY.
[11] R. K. Isaac · T. K. Khura · J. R. Wurmbrand ,(**2009**), *Environ Monit Assess* (**2009**) 159:465–473.
[12] Raeisi, E. (**2002**). “Carbonate karst caves in Iran”, Evolution of karst: From prekarst to Cessation, 339-344, Ljubljana- Postojna.
[13] Kendall, M.G. **1975**. Rank Correlation Methods, 4th edition, Charles Griffin, London.
[14] Mann, H.B. (**1945**), *Econometrica* 13:163-171.
[15] Meteorology organization (Chaharmahal&Bakhtiari province), annual calendars of stations.
[16] Meybeck, M.,(**1987**),. *Am. J. Sci*. 287, 401–428.
[17] N. C. C., (**1984**), Topography maps, s. 1/50000
[18] P. G. Whitedhead, R. L. Wilby, R. W. Battarbee, M. Kernan&A. J. Wade, (**2009**), A review of the potential impacts of climate change on surface water quality, Hydrological Sciences–Journal–des Sciences Hydrologiques, 54(1) 2009.
[19] Siyue Li., Quanfa Zhang., (**2008**), *Journal of Applied Geochemistry* 23: 3535–3544.
[20]Water Resources of Chaharmahal&Bakhtiari Company, (**2008**), the appearance of water resources of province, studies and planning sector.
[21]. Whittow, John (**1984**). Dictionary of Physical Geography. London: Penguin, **1984**, p. 291. ISBN 0-14-051094-X