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A nine-year assessment of annual changes in chemical and physical parameters of Karun River's water

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Abstract

Rivers are of the major sources of surface waters. The quality of water of these resources depends on different factors, including hydrological, physical, chemical and biological factors. The aim of this project was to study the annual variations of physical and chemical parameters of the water in Karun River for a nine-year period since 2003 to 2011. It was found that in 2010, a large number of factors have had increased concentrations, which cause can be attributed to the drought occurred during this year. Also, among the studied factors, the COD factor has had the most changes during different years, so that from the concentration of 6.7 mg/l in 2003 has reached to 12.4 mg/l in 2011. Instead, the CO_3^{2-} factor has remained without changes and at about zero in all these years. Also, review of pH factor shows that the region water has had basic features in all years of the study. It was found in review of correlations between factors during various years that the EC factor has a significant negative correlation with pH at 5% level as well as a negative correlation with the BOD factor. The TDS factor is negatively correlated with factors of pH and RSC at 99% level. The TH factor has negative correlation with factors of pH, RSC and COD at 1% level. The factors, including HCO_3^- , Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} and Mg^{2+} are in a same situation. The BOD factor is also negatively correlated with factors of pH, SAR, SSP, RSC and COD.

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Introduction

In many parts of the world, the most common water resources used for various purposes and consumptions (drinking, industry, agriculture) are the rivers. Thus, when a dangerous chemical pollutant is entered into a river by industrial or agricultural plants, there would be adverse effects on the quality of its downstream water. Therefore, a comprehensive study on river and its pollutant sources is of special importance (EPA, 2004). Although we know that water is one of the most abundant compounds found in the nature and almost has occupied three-quarters of the land surface, the geographically uneven distribution of water resources has become the underlying cause of water shortages around different parts of the world. More than 97% of the total water resources are in the oceans and seas, and slightly more than 2% of the total water resources are placed in glaciers and polar resources, or as moisture in the soil and the earth atmosphere that the former, due to its high soluble salts and the latter due to the unavailability of using them in terms of economic feasibility are not justifiable (Salemi and Murray, 2005; Chapman, 1996). Hence, the human being can access only to 0.62% of the remaining water in lakes and rivers and groundwater for survival and in order to meet industrial, agricultural and drinking needs. On the other hand, the world population increasing growth has increased the various consumptions of water. This not only has reduced the quantity of available water and has caused more limitations, but also has been associated with pollution of water resources and reduced quality of water resources (Salemi and Murray, 2005; Chapman, 1996).

Low pH increases the solubility of minerals, including metals in the water and creating toxic effects for aquatics as well as leading to dissolution of calcium of the shells of crustaceans and mollusks and weakening them. High pH causes the production of ammonia, which is toxic to aquatic life in very low concentrations. The EPA has determined its range as 6.5-9 to protect the aquatic environment (Zarkami and Hassan-Nia, 2005). The water capacity to conduct electric current is called "specific

conductance", which is a function of the ionic strength of water. The specific conductance is measured using a conductivity meter device and expressed in terms of milli-siemens per centimeters (mS/cm) or micro-siemens per centimeters (μ S/cm). The electrical conductivity in fresh waters varies from 10 to 1000 mS/cm, but in contaminated waters and in waters receiving runoffs from agricultural lands will reach to more quantities (Chapman, 1996). The biochemical oxygen demand of a water sample determines the amount of oxygen used by organisms in the water, and its measurement can specifies the water quality. If it is low, the water is clean and free of organisms or the water microorganisms do not need to consume the oxygen within the water (Metcalf and Eddy, 2003; Bartram and Balance, 1996). The European Standards (EU) has determined the BOD value as 6 mg/l, while the Russian Standard has specified it as 3mg/l (Chapman, 1996). The chemical oxygen demand is a criterion of the total concentration of organic matter in the water and is equal to the amount of oxygen used for oxidation of oxidized organic material using a strong oxidizing agent (Salemi and Murray, 2005; Chapman, 1996; APHA, 2003). The presence of COD and BOD in water resources indicates the entry of oxygen-consuming organic materials to the water resources, which cause the decreased water dissolved oxygen in such resources. Total solids in water are found as two forms of suspended and dissolved solids; suspended solids in water include minerals such as sand, silt, and other soil and organic compounds including plant fibers, algae and bacteria (King *et al.*, 1994). The total dissolved solids (TDS) in drinking water contain mineral salts with a small concentration of organic matter that is the major ions forming dissolved solids of carbonate, bicarbonate, chloride, sulfate, nitrate, sodium, potassium, calcium and magnesium (Zuane, 2002). The water contains high values of soluble material (metal ions) is called "hard water". These ions mainly include Mg^{2+} and Ca^{2+} (Weiner and Matthews, 2003). To investigate the self-purification capability and potential of Karun River and its quality classification, eight stations

(three stations at upstream, three stations in Ahvaz city limits) were selected and the factors of temperature, electrical conductivity, pH associated with Benthos, planktons, BOD, COD, NH_3 , DO were determined. The researchers showed that while there is self-purification in the rivers, due to entry, accumulation and transfer of contaminants to downstream of rivers, the rivers' downstream has less self-purification than the upstream (Eskandari, 2009). The Kor river water quality status in Fars province was investigated by Karimi Jashni and coworkers in 2009. They studied the qualitative parameters, such as electrical conductivity, dissolved oxygen, pH, COD, BOD, chloride amount, and the amount of dissolved materials over the years of 1991 - 2005. Their review showed that prior to 2002, the contamination rate of river has been rising, but in recent years due to control and treatment of industrial wastewater in the region, the contamination rate of the river has lost its increasing trend. In another study on chemical quality of Bandar Abbas water, the amounts of fluoride, sulfate, chloride, TDS, EC, sodium, and the total hardness in the groundwater resources has been more than the desirable level, but the quality of surface water resources was satisfactory (Dindarloo, 2005). Because this River provides water, the city of Ahwaz in Khuzestan province, and also used in sugarcane agro-industry, is one of the most important river in Iran. Research objectives are: 1- Study on Karun River water quality at scope Cultivated Sugarcane industry Amir Kabir 2-The study of annual changes in river water quality 3- Predict river water quality status in the coming years.

Material and methods

Studied region

This research project was performed during nine years in the period of 2003_2011 in a regional scale in Khuzestan Province, with the longitude of 47 degrees and 42 minutes to 50 degrees and 39 minutes, and the latitude of 29 degrees and 58

minutes to 32 degrees and 58 minutes north. The research was done on water quality of the Amir Kabir cane growing and industry region. The sugarcane agro-industrial units of Amir Kabir and Mirza Kochak Khan collectively include over 29,000 hectares of lands located in the west of Karun River and in the south of city of Ahwaz. The lands of the region are low and their height above sea level is between 2 to 16 meters.

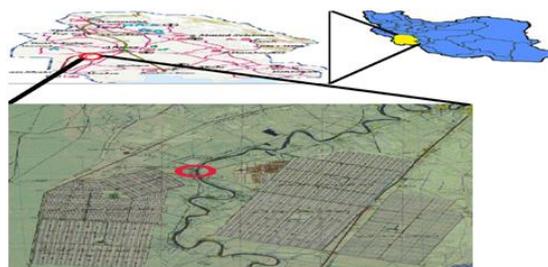


Fig. 1. Geographical situation of the studies region.

Research methodology

To determine water quality, water samples was taken from Karun water in place of pumping station Amir Kabir and the water drains in place out of the Agro-industry from the specified location in Figure 1, and after transferring to the the laboratory were analyzed regarding physical and chemical parameters. Among the measured parameters, the amount of sodium was measured by the flame photometer Systronics k1/mk-III at a wavelength of 589 nm. Calcium, magnesium, bicarbonate and chloride were measured by titration method (Li *et al.*, 2011). The BOD values were measured by the standard method, meaning at 20 ° C, dark conditions and in 5 days. For measuring COD, an acidic environment with strong oxidizing agents such as potassium dichromate and permanganate were used. Statistical analyses were performed using the statistical software like Excel and SPSS. Thus, the factors measured at average every week were converted into monthly means and at the end to annual means, and in general, 15 different factors were examined. Also, the factors, including SAR, SSP and RSC were obtained using the following mathematical formulas, but other factors were directly measured in the laboratory.

$$SAR = \frac{Na^{+2}}{\sqrt{\frac{Ca^{+2} + Mg^{+2}}{2}}} \quad (1)$$

$$RSC = (CO_3 + HCO_3) - (Ca^{2+} + Mg^{2+}) \quad (3)$$

$$SSP = \frac{\text{Soluble } Na^{+2} \text{ Concentration}}{\text{Total Cations Concentration}} \times 100 \quad (2)$$

Table 1. Results of the correlation among the measured factors.

	EC	pH	TDS	TH	SAR	SSP	RSC	HCO ₃	CL ⁻	So ₄ ²⁻	Na ⁺	Mg ²⁺	Ca ²⁺	BOD
pH	-.816**		-.879**	-.905**	-.684*	-.099	.885**	-.805**	-.883**	-.844**	-.766*	-.811**	-.931**	-.273
TDS	.840**	-.879**		.906**	.769*	.170	-.876**	.770*	.862**	.906**	.825**	.795*	.924**	.226
TH	.950**	-.905**	.906**		.871**	.336	-.992**	.859**	.991**	.929**	.937**	.957**	.987**	.185
SAR	.941**	-.684*	.769*	.871**		.723*	-.869**	.672*	.902**	.877**	.985**	.805**	.883**	-.053
SSP	.505	-.099	.170	.336	.723*		-.358	.120	.406	.396	.611	.326	.342	-.459
RSC	-.956**	.885**	-.876**	-.992**	-.869**	-.358		-.815**	-.987**	-.942**	-.937**	-.976**	-.973**	-.150
HCO ₃	.804**	-.805**	.770*	.859**	.672*	.120	-.815**		.856**	.715*	.749*	.813**	.839**	.465
CL ⁻	.972**	-.883**	.862**	.991**	.902**	.406	-.987**	.856**		.924**	.960**	.950**	.984**	.187
So ₄ ²⁻	.957**	-.844**	.906**	.929**	.877**	.396	-.942**	.715*	.924**		.920**	.890**	.936**	.206
Na ⁺	.977**	-.766*	.825**	.937**	.985**	.611	-.937**	.749*	.960**	.920**		.885**	.940**	.034
Mg ²⁺	.918**	-.811**	.795*	.957**	.805**	.326	-.976**	.813**	.950**	.890**	.885**		.906**	.169
Ca ²⁺	.951**	-.931**	.924**	.987**	.883**	.342	-.973**	.839**	.984**	.936**	.940**	.906**		.185
BOD	.192	-.273	.226	.185	-.053	-.459	-.150	.465	.187	.206	.034	.169	.185	
COD	-.563	.411	-.565	-.561	-.515	-.170	.567	-.328	-.553	-.643	-.555	-.535	-.544	-.406

* Correlation is significant at the 0.05 level (1-tail)

**Correlation is significant at the 0.01 level (2-tail)

Results and discussion

As can be seen in the following figures, the rates of changes for various factors are different so that factors such as total dissolved solids (TDS) and sodium absorption ratio (SAR) have slight variations during the period of 2003-2011, and only have slightly increased at the beginning of 2009 up to the end of 2010. Factors such as total hardness (TH), chloride (Cl⁻), soluble sodium percentage (SSP), sulfate (SO₄²⁻), calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), electrical conductivity (EC) as well as factors of BOD (biochemical oxygen demand) and COD (chemical oxygen demand) have had many changes; so that all the above factors except for BOD and COD factors have had an increasing trend at the beginning of 2008 that has continued up to the

beginning of 2010. The pH factor has also had a decrease in 2010, but after 2010, it found an increasing trend; however, its value has never become less than 7.6, which is due to the alkaline feature of rivers water. The COD factor has also continued its decline trend and seems to be continued in such a trend in the future, but the BOD factor has started its decline at the end of 2007, but has returned to its previous status at the beginning of 2010. The RSC factor has also begun a reduction trend so. That it has reached from -5 in 2003 to -11 in 2010, and has started its increasing trend from this year onwards.

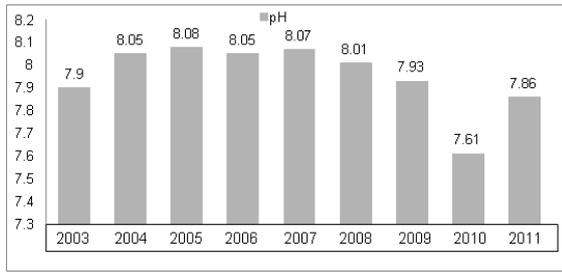


Fig. 1. PH changes during the years of 2003-2011.

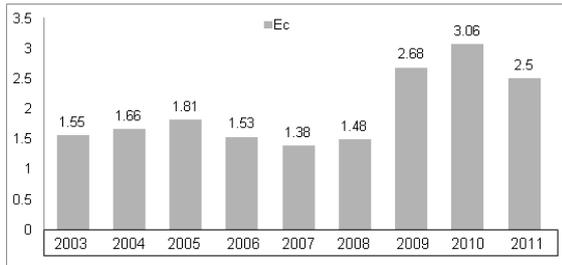


Fig. 2. EC (ds/m) changes during the years of 2003-2011.

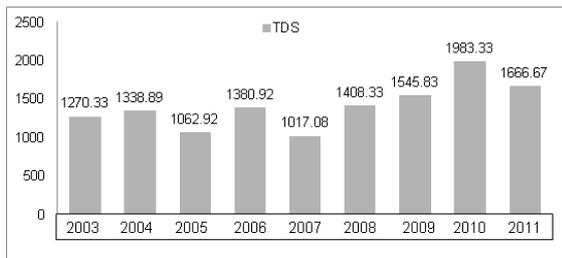


Fig. 3. TDS (mg/l) changes during the years of 2003-2011.

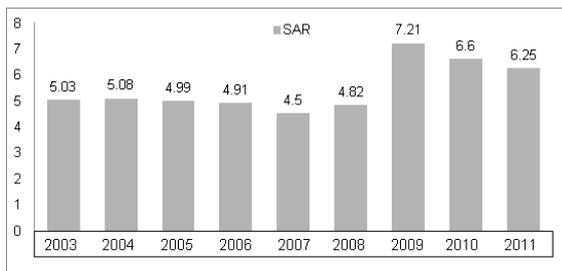


Fig. 4. SAR changes during the years of 2003-2011.

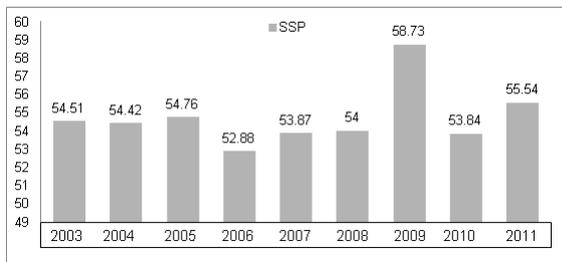


Fig. 5. SSP (%) changes during the years of 2003-2011.

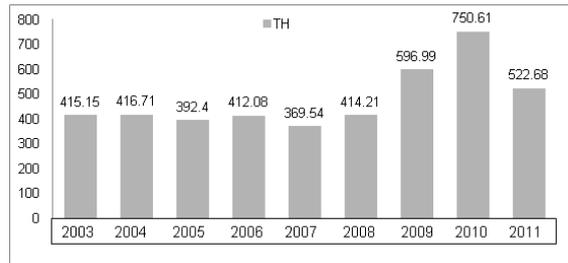


Fig. 6. TH (mg/l) changes during the years of 2003-2011.

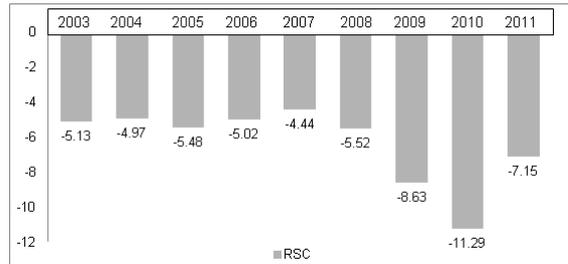


Fig. 7. RSC (meq/l) changes during the years of 2003-2011.

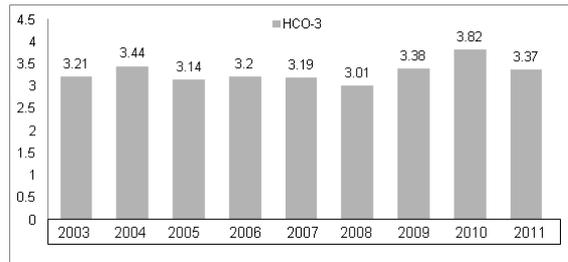


Fig. 8. HCO₃⁻ (meq/l) changes during the years of 2003-2011.

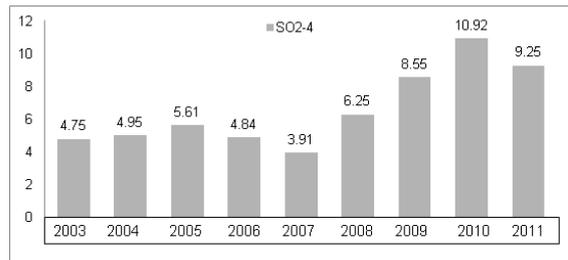


Fig. 9. SO₄²⁻ (meq/l) changes during the years of 2003-2011.

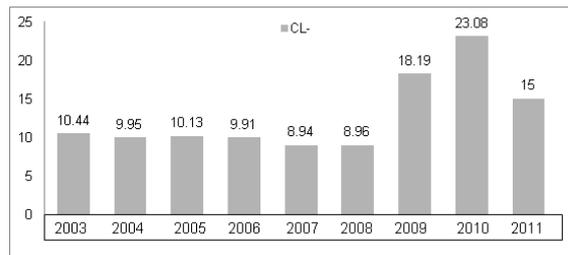


Fig. 10. CL⁻ (meq/l) changes during the years of 2003-2011.

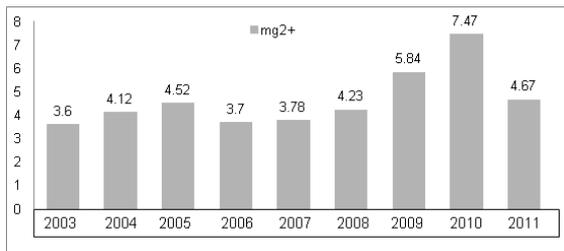


Fig. 11. Mg²⁺ (meq/l) changes during the years of 2003-2011.

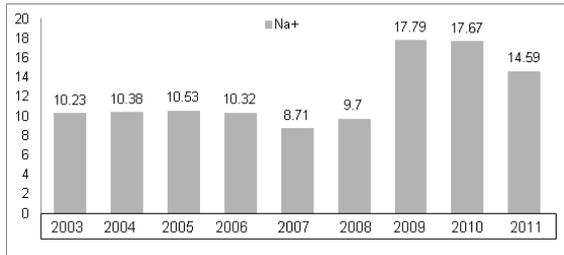


Fig. 12. Na⁺ (meq/l) changes during the years of 2003-2011.

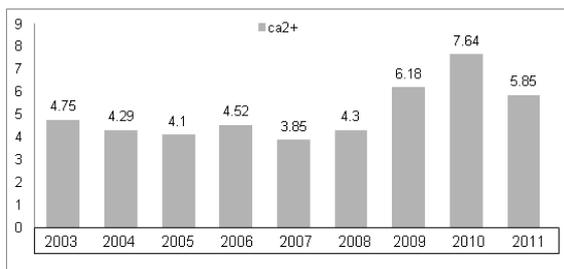


Fig. 13. Ca²⁺ (meq/l) changes during the years of 2003-2011.

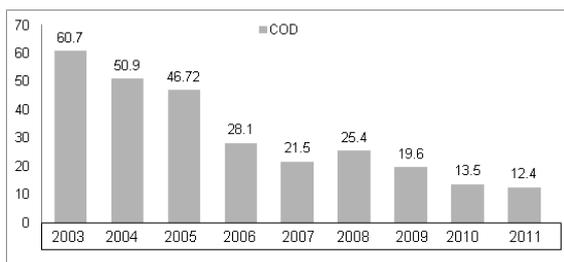


Fig. 14. COD (mg/l) changes during the years of 2003-2011.

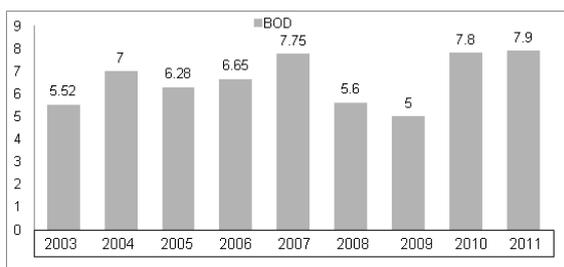


Fig. 15. BOD (mg/l) changes during the years of 2003-2011.

It was found in review of correlations between factors that the EC factor has a significant negative correlation with pH at 5% level as well as a negative correlation with the BOD factor. Thus as seen in figures 1 and 2, by increased EC in 2010, the pH value has dramatically reduced. The TDS factor is negatively correlated with factors of pH and RSC at 99% level. The TH factor has negative correlation with factors of pH, RSC and COD at 1% level. The factors, including HCO₃⁻, Cl⁻, SO₄⁻², Na⁺, Ca²⁺ and Mg²⁺ are in a same situation. The BOD factor is also negatively correlated with factors of pH, SAR, SSP, RSC and COD; so that by increased BOD, the biodegradation increases and chemical analysis (COD) decreases.

Conclusion

After a nine-year assessment, as seen in the obtained figures and correlation table, the factors have relatively large variations. Also, among the studied factors, the COD factor has had the most changes during different years, so that from the concentration of 6.7 mg/l in 2003 has reached to 12.4 mg/l in 2011. Instead, the CO₃ factor has remained constant and without changes and at about zero in all these years. One reason for the zero value of CO₃ in these all years can be attributed to the structural characteristics of CO₃, since this ion only appears at pH higher than 10.3, while in none of the studied years, the water pH has reached over the 10.3. Instead, the HCO₃⁻ factor due to being the dominant ion in pH range of 6.3- 10.3 has been present in the regional water in all these years. Also, review of the pH factor shows that in all the studied years, the region water has an alkaline feature. It also appears that the year of 2010 has been the most important year among the studied years, since the concentrations of many factors have somehow increased due to the occurred drought in this year. Also, study the overall process of factors during these nine years indicates that the studied have variations around there average values in different years and it seems such a trend will continue in the future. The COD factor is the only one with a decline trend than

to its mean. Study the correlation between the factors shows that most of the factors have correlation at 95% or 99%, which represents a very high impact of factors on each other that should be considered important in future studies and predictions.

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