Time series analyses for predicting the water quality and river discharge at Al-Kufa river in Iraq

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Abstract. In this study, raw water samples collected from Al-Kufa River station in Al-Kufa city, Iraq were monitored and tested monthly from 2013 to 2017. Chemical and time series analyses were performed on 13 water quality parameters, the river discharge (Q), and water surface elevation (WSE). These water quality parameters were the magnesium (Mg), calcium (Ca), potassium (K), sodium (Na), chloride (Cl⁻), nitrate (NO₃⁻), phosphate ([PO₄]³⁻), dissolved oxygen (DO), electrical conductivity (EC), pH, water temperature (Temp), total dissolved solids (TDS), and total hardness (TH). Regression was used to examine the relationships between the concentrations of the assayed water quality parameters and river discharge. The theoretical models best-fitted with the assayed parameters were evaluated by two tests, the Kolmogorov-Smirnov (K-S) test and the chi-squared (χ²) test. The relation between the concentrations of the assayed parameters and river discharge was moderate (r-value is between 0.5-0.95) for the parameters EC, TDS, Ca, Cl, Na, and WSE while weaker correlation resul for the other parameters (r<0.5). Equations with second order provided a superior characterization for most of the parameters for which trends were detected, and the river discharge was the unique parameter showing an upward trend based on the nonparametric Spearman’s criterion. Together, the time series analyses and trend detection would help to forecast the safety of water at Al-Kufa station for human consumption.

1. Introduction

Although water is the fundamental need of all living organisms, the worldwide water sources are gradually degraded and polluted, due to various factors, such as a drastic increase in human population and economic activities, domestic and industrial wastes, climate changes, and the inability of raising environmental awareness among the general public [1]. Presently, the desperate need for clean water has become one of the most pressing global problems with more than 1.2 billion people worldwide not have availability to access clean drinking water while half the world's population, or three billion people, do not have adequate sanitation services. Meanwhile, an estimated five million people die each year from the consumption of contaminated water [2]. Therefore, before the water can be used for drinking and other purposes, it must be tested over a period of time using various physico-chemical parameters to evaluate the changes in water quality [3]. In this study, the water quality of Al-Kufa water treatment station at Al-Kufa River of Iraq was monitored and tested from 2013 to 2017 via chemical analyses using a time series approach. In hydrology, a time series analysis would allow us to model the stochastic mechanisms that affect water quality, thereby forecasting the stability of water quality in the near future. Taken together, the
repetitive water testing in this study would allow the detection of chemical contaminants that would likely present a hazard to human health. This paper objective to examining statistically: (1) the time series of monthly values of water quality parameters, water surface elevation and river discharge at Shatt Al-Kufa station, (2) the existence of trends and the evaluation of the best fitted trend models for each parameter, and (3) the relationships between concentration of the assayed parameters and the river discharge.

2. Materials and Methods

2.1. The study area

The raw water samples analysed in this paper were collected from Al-Kufa water treatment station (coordinates: E44.4075, N32.03941) located along Al-Kufa River of Najaf Governorate, Iraq (see figure 1). Al-Kufa River, about 75.2 km in length, is one of the two tributaries of the Euphrates River, which is an important water source for Iraq, especially for the city of Najaf. The depth of Al-Kufa River varies substantially, and its average discharge volume is about 100 cubic meter per second with the highest level occurring between the end of March and April each year while the lowest discharge happens in the summer. The average annual temperature of the study area is moderate, i.e., 24.4°C; the highest temperature occurring in July (monthly average 31.2°C) while January is the coolest month (monthly average 17.6°C). Meanwhile, the wet season of the study area occurs between October and May, with an average annual rainfall of 94.2 mm. The highest amount of rainfall occurs in December (16.2 mm), but there is usually no rain at all between June and September.

Figure 1. Location of Shatt Al-Kufa station.

2.2. Water quality parameters and testing

In the present study, chemical analysis was conducted to monitor 13 water quality parameters monthly from January 2013 to December 2017. The parameters being tested were: calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), chloride (Cl-), nitrate (NO3-), phosphate ([PO4]3-), dissolved oxygen (DO), electrical conductivity (EC), pH, water temperature (Temp), total dissolved solids (TDS), and total hardness (TH). This monitoring encompassed the testing of elements (Ca, Mg, K, and Na), ions (Cl-, NO3-, and [PO4]3-), and physical attributes (DO, EC, pH, Temp, TDS, and TH). The river discharge (Q) and water surface elevation (WSE) were also monitored.

Following the US, EU, EPA, Canadian, and FAO standard methods for water quality testing (citation for the standard), where applicable, the testing generally involved the methods of titration, atomic
absorption spectrometry, and colourimetry. For example, the Cl- ion was measured with Mohr titration, the content of Mg and TH were quantified with ethylenediaminetetraacetic acid (EDTA) titration, the DO was determined with Winkler titration, the contents of Ca, Na, and K were assayed using atomic absorption spectrometry, and the ions of NO3- and [PO4]3- were quantified with colourimetry. Meanwhile, TS was examined using the Gravimetric method upon drying the filtrate.

2.3. Statistical, concentration-discharge, and trend analyses
Probability plots were used to fit the assayed water quality parameters with a theoretical distribution based on the comparison of histograms of the assayed values to the probability density curves of a theoretical distributions. A comparison was performed with eight theoretical probability functions, i.e., the exponential (Ex), gamma (G), logistic (L), log-normal (LN), normal (N), beta (B), uniform (U), and Weibull (W) distribution. The goodness-of-fit between the observed and expected values was evaluated with the tests of Chi-square (χ2) and the nonparametric Kolmogorov-Smirnov (K-S) at the significant level of α = 0.05 [4]. Meanwhile, water solutes concentrations in rivers vary over time, due mainly to the stream discharge [5]. Therefore, the relationship between the load (flux) of water solutes and the product of discharge (solute concentration) is crucial in determining the chemical constituents of the water, especially the upstream of reservoirs, lakes, and estuaries, where the water has an extended residence time. As a water source for human consumption, as well as a living medium for aquatic organisms, the safety of this water is an issue of main concern [6]. As a result, various models were implemented to characterize the relationships between the concentrations of water quality parameters and river discharge and between the load of water solutes and river discharge [4]. For parameters of water quality that are dependent on streamflow in a high degree such as Cl-, Ca, and NO3-, the embarrassing effects of variation in river discharge must be removed. Therefore, in the present study, the residuals from the relationship of the river-discharge and the concentration (C) of each parameter (Q-C) relationship, rather than the raw data, were used for trend analyses. In this study, the linear (Cij = C1 + C2Qij), power (Cij = C1QijC2), exponential (Cij = C1 exp(C2Qij)), and logarithmic (Cij = C1 + C2 log(Qij)) models were used for trend analysis. The method of least squares for the pairs of monthly measured values of each water quality parameter and its discharge was used to determine the constants of these models [7].

On the other hand, the trend analysis describes whether the measured value of a water quality parameter would increase or decrease over time, i.e., whether the measured probability distribution would change over time. The quantity or the changing rate is often expressed in terms of deviations in some middle values of the model distribution, such as the median or mean. In this study, the criterion of nonparametric named Spearman’s (correlation coefficient) was used to identify the trends in the time series for each one of assayed parameters. Also, different trend models were fitted to the parameters time series of the river flow and the water quality with several models, namely the linear type, quadratic type, exponential type, and mixed type models. Finally, the superior fitted distribution model of the time series trend for each water quality parameter was elected by using of the following statistical criteria, namely the mean square error (MSE), mean absolute percent error (MAPE), mean error (ME), and mean absolute error (MAE) [8]. The distribution of the water quality parameters was summarised with the boxplots to compare their medians, variation (boxplot height), skewness, and outliers.

3. Results and Discussion

3.1. Statistical analyses and river discharge
Figure 2 display the time series of monthly observed values for Ca, Mg, K, Na, Cl-, NO3-, [PO4]3-, DO, EC, pH, Temp, TDS, TH, Q, and WSE at Al-Kufa station. Meanwhile, table 1 gives the statistical results of the hydraulic and water quality parameters through time at Al-Kufa station. Seasonal
variation was striking in several water quality parameters, such as the concentrations of each assayed parameter, river discharge, and water surface elevation. In particular, the [PO4]3- ions showed the greatest seasonal fluctuation with the highest ratio of concentration to water discharge (C/Q; 13.7) and then followed by total calcium (7.4), discharge (4.6), NO3-(4.2), Na (4.1) and Mg (3.5). In comparison, this ratio (C/Q) was low for DO (2.6), K (2.6), Cl- (2.6), Temp (2.2), EC (1.9), TDS (1.9), TH (1.9), WSE (1.2), and pH (1.1). By contrast, seasonal variation was relatively uniform for water temperature during the study period.

Meanwhile, the concentration of NO3- ions appeared to be affected by anthropogenic activities with an assayed value of 4.46 mg/l in the present study. However, because it was twelve times less than the critical value of the World Health Organisation (WHO) Guidelines, namely 50 mg/l [9], therefore, the NO3- ions in the water would unlikely pose a safety hazard for human consumption.

Figure 2. Time series data of river discharge, water surface elevation, and parameters of water quality at Al-Kufa station.
Tables 1 shows the regression between each of the water quality parameter’s concentration and its discharge at Al-Kufa station while the best-fitted regression models are shown in figure 5. In general, most of the parameters showed a weak concentration-discharge relationship in linear regression with their absolute correlation coefficient substantially smaller than 0.5, except for water surface elevation and Ca, which showed an increasing relationship each with their $r = 0.54$ and $r = 0.94$, respectively. In contrast, the two models logarithmic and the power are explained the data better in the
concentration-discharge relationship for most of the parameters. Specifically, the parameter Na showed a highest r value (r = -0.70) in the concentration-discharge relationship, and followed by Cl- (r = -0.54), EC (r = -0.54), TDS (r = -0.52), TH (r = -0.49), and Mg (r = -0.48) while the DO, total [PO4]3-, K, Temp, pH, and NO3- showed a weak correlation each with r values less than 0.5. Meanwhile, the river discharge showed a strong seasonal variation with high values during the summer and autumn as a result of increasing releases by Al-Kufa barrage for rice planting at the Najaf

Figure 3. The boxplots of assayed values for the water quality parameters and river discharge at Al-Kufa station.
region. The seasonal variation in river discharge and the reverse relationships with the solutes of Mg and Ca were attributable to the presence of groundwater sources while Na and K were predominantly derived from point sources, thereby yielding the inversely proportional patterns for these solutes. In contrast, the parameter of NO3- showed no well-defined seasonal patterns with the river water discharge, and this indicating the existence of many several potential sources and the possibility of sources for transportation within the river system.

Table 2. Parameters of the best fitted distribution models and the goodness-of-fit tests.

| NO | Variable | Distribution | Values of Parameters | K-S test | \( \chi^2 \) test |
|----|----------|--------------|----------------------|---------|------------------|
|    |          |              | \( \mu \), \( \sigma \) | D       | \( \chi^2 \) | d.f. |
| 1  | PH-value | Log-Normal   | 2.014031, 0.03859424 | 0.091   | 4.1596          | 5    |
| 2  | PO4, Mg/l| Log-Normal   | -2.588143, 0.5384369 | 0.135   | 3.564           | 5    |
| 3  | NO3, Mg/l| Log-Normal   | 1.404882, 0.3542261  | 0.099   | 5.4218          | 5    |
| 4  | TH, Mg/l | Gamma        | 31.929, 13.186       | 0.129   | 5.3169          | 3    |
| 5  | EC, US/cm| Gamma        | 31.491, 44.178       | 0.0875  | 0.35175         | 3    |
| 6  | DO, Mg/l | Weibull      | 4.663903, 7.9229     | 0.094   | 3.187           | 3    |
| 7  | TDS, ppm | Gamma        | 32.241, 27.849       | 0.084   | 0.89885         | 3    |
| 8  | Mg, Mg/l | Normal       | 30.592, 0.0767       | 0.083   | 3.6045          | 4    |
| 9  | Ca, Mg/l | Log-Normal   | 4.8632, 0.42357      | 0.215   | 2.1722          | 3    |
| 10 | CL, Mg/l | Log-Normal   | 4.968715, 0.212894   | 0.149   | 7.6136          | 5    |
| 11 | Na, Mg/l | Log-Normal   | 4.262736, 0.3256247  | 0.075   | 0.52486         | 4    |
| 12 | K, Mg/l  | Normal       | 5.247222, 1.276276   | 0.077   | 0.37897         | 4    |
| 13 | Temp, C' | Normal       | 23.81597, 5.23810610 | 0.094   | 1.3105          | 4    |
| 14 | Q, m3/s  | Weibull      | 2.8715, 111.33       | 0.089   | 4.208           | 5    |
| 15 | WSE, m   | Logistic     | 20.33062, 0.3404217  | 0.068   | 2.4443          | 5    |

Table 3. The relationship between concentration-discharge.

| NO | Variable | Equation Type | Model Coefficients | r    |
|----|----------|--------------|--------------------|------|
|    |          |              | \( C_1 \)         | \( C_2 \) |      |
| 1  | PH       | Logarithmic  | -0.18          | 8.3146 | -0.249 |
| 2  | PO4, mg/l| Logarithmic  | -0.021         | 0.1846 | -0.127 |
| 3  | NO3, mg/l| Power        | 15.717         | -0.298 | -0.276 |
| 4  | TH, mg/l | Power        | 1145.4         | -0.22  | -0.493 |
| 5  | EC, US/cm| Logarithmic  | -326.9         | 2902.6 | -0.538 |
| 6  | DO, mg/l | Linear       | -0.0152        | 8.9849 | -0.317 |
| 7  | TDS, ppm | Power        | 2502.4         | -0.225 | -0.520 |
| 8  | Mg, mg/l | Logarithmic  | -10.7          | 80.074 | -0.481 |
| 9  | Ca, mg/l | Linear       | 0.2846         | 116.35 | 0.94  |
| 10 | Cl, mg/l | Power        | 578.51         | -0.307 | -0.543 |
| 11 | Na, mg/l | Logarithmic  | -40.11         | 260.12 | -0.695 |
| 12 | K, mg/l  | Logarithmic  | -1.261         | 11.078 | -0.400 |
| 13 | Temp, C' | Linear       | 0.036          | 19.881 | 0.259 |
| 14 | WSE, m   | Exponential  | 19.43          | 0.0004 | 0.549 |
Figure 4. Frequency histograms of monthly observed values for the river discharge, water surface elevation and parameters of water quality and the best fitted theoretical distribution.
Figure 5. The relationships of concentration of water surface elevation and water quality parameters versus the river discharge with the best fitted model.

3.3. Trend analyses
Table 4 shows Spearman’s rank correlation for the time series of the river flow, water surface elevation, and 13 water quality parameters. In general, the observation values of the given series for pH, Cl-, Q, TH, EC, TDS, Mg, Ca, Na, and K changed over time. Meanwhile, the best-fitted models for each of the measured parameters in the time series are shown in figure 6. In general, the se-
second-order equation explained the time series data better for most of the parameters except for Q and Ca. Meanwhile, the parameter Q showed an upward trend while the EC, pH, and the concentration of Mg, Na, TDS, TH, Ca, Cl-, and K each showed a downward trend. In contrast, the WSE, Temp, and

Figure 6. The monthly observation values of river discharge, water surface and parameters of water quality, and their best fitted trend models.
the concentrations of NO₃⁻, [PO₄]³⁻, and DO showed no trends. The upward trend of river discharge appeared to be inversely related to the trend for Na, Cl⁻, EC, TDS, TH, K, and Mg, i.e., an increase in discharge caused a decrease in these parameters. In contrast, the discharge was weakly related to pH, DO, NO₃⁻, [PO₄]³⁻, Ca, Temp, and WSE with no influence on the trends of these parameters.

### Table 4. The detection of trend in Al-Kufa river discharge and water quality parameters.

| Variable | Sum of D² | R²p  | tᵣ | Is There Trend? |
|----------|-----------|------|-----|-----------------|
| pH       | 45192     | -0.256 | -2.014 | Yes             |
| [PO₄]³⁻  | 28480.5   | 0.209  | 1.6245 | No              |
| NO₃⁻     | 38804     | -0.079 | -0.597 | No              |
| Cl⁻      | 47218     | -0.312 | -2.501 | Yes             |
| Q        | 17308     | 0.519  | 4.625  | Yes             |
| WSE      | 27674.5   | 0.231  | 1.809  | No              |
| TH       | 13652     | -0.757 | -6.756 | Yes             |
| EC       | 13765.5   | -0.772 | -7.073 | Yes             |
| DO       | 8258      | -0.063 | -0.367 | No              |
| TDS      | 13817     | -0.778 | -7.227 | Yes             |
| Mg       | 10420     | -0.341 | -2.116 | Yes             |
| Ca       | 13346     | -0.718 | -6.009 | Yes             |
| Na       | 13308     | -0.713 | -5.925 | Yes             |
| K        | 10574.5   | -0.361 | -2.257 | Yes             |
| Temp     | 6922      | 0.109  | 0.640  | No              |

### Table 5. Trend models equations which describe better trends of the Kufa River water quality variables and the values of the statistical tests for the goodness-of-fit.

| Variable | Trend model equation | ME  | MSE  | MAE  | MAPE  |
|----------|----------------------|-----|------|------|-------|
| PH       | 0.00002×T² - 0.0057×T + 7.6474 | 0.00 | 0.08 | 0.21 | 2.77  |
| PO4      | -0.0001×T² + 0.0062×T + 0.0204 | 0.00 | 0.00 | 0.04 | 44.02 |
| NO3      | -0.0004×T² + 0.0208×T + 4.2314 | -0.02 | 2.91 | 1.32 | 31.69 |
| Cl       | -0.0501×T² + 2.5722×T + 130.48 | -0.04 | 855.10 | 23.31 | 16.08 |
| Q        | 1.15×T + 65.225 | 0.00 | 967.91 | 25.99 | 32.05 |
| WSE      | 0.0004×T² - 0.0159×T + 20.326 | 0.00 | 0.35 | 0.46 | 2.26  |
| TH       | 0.0505×T² - 7.3558×T + 534.39 | -0.01 | 2122.86 | 36.38 | 8.75  |
| EC       | 0.1064×T² - 21.907×T + 1748.6 | 0.01 | 24798.41 | 121.70 | 8.89  |
| DO       | 0.0048×T² - 0.1852×T + 8.5755 | 0.01 | 2.98 | 1.49 | 22.32 |
| TDS      | 0.0465×T² - 12.987×T + 1117.2 | 0.02 | 10591.56 | 79.45 | 8.97  |
| Mg       | 0.0252×T² - 1.2186×T + 41.795 | 0.00 | 65.34 | 6.75 | 25.84 |
| Ca       | -2.3346×T + 190.66 | 0.00 | 12057.19 | 50.29 | 26.91 |
| Na       | 0.0275×T² - 2.614×T + 110.69 | -0.01 | 257.81 | 13.13 | 19.57 |
| K        | 0.002×T² - 0.1114×T + 6.4185 | -0.01 | 1.43 | 0.92 | 19.15 |
| Temp     | -0.0057×T² + 0.2565×T + 21.646 | -0.01 | 26.15 | 4.27 | 20.58 |
4. Conclusions

Among the water quality parameters assayed, the river discharge and DO assumed a Weibull distribution each while the pH value, NO3-, [PO4]3-, Ca, Cl-, and Na followed the log-normal distribution. In contrast, the K, Mg, and Temp obeyed the normal distribution while the TH, EC, and TDS followed the gamma distribution. On the other hand, the water surface elevation assumed the logistic distribution. Meanwhile, seasonal variation in the parameters EC, TDS, Ca, Cl, Na, and WSE of river water flow was moderately related to the discharge variation. However, the concentration of [PO4]3-, NO3-, TH, DO, TDS, Mg, K, and the pH value and water temperature were weakly correlated to the discharge. Also, Spearman’s test detected significant changes in the trends of Q, pH, Cl-, EC, TH, Mg, TDS, K, Na, and Ca. Taken together, the second-order equation provided a better description for most of the parameters for which trends were detected, and discharge was the only parameter showing an upward trend.

5. References

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