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[Research]

Appraisal of the geostatistical methods to estimate Mazandaran coastal ground water quality

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ABSTRACT

The present study was carried out to evaluate three interpolation methods including weighted moving average (WMA) with the power of 2 and 3, Kriging and Cokriging methods. Data of 23 wells in Mazandaran province were collected in fall and spring 2006. Seven parameters including electrical conductivity (EC), pH, total dissolved solids (TDS), sodium adsorption ratio (SAR), total hardness (TH), chloride concentration (Cl^-) and sulphate concentration (SO_4^{2-}) have been chosen as groundwater quality indices in the study area. Variogram analysis and extracting the spatial distribution maps of groundwater quality parameters were done using Geostatistics extension program in GIS environment. All interpolation methods have been evaluated based on mean bias error (MBE) and mean absolute error (MAE) criteria. The spherical model for semi-variograms had the less value of RSS (residual sum of square) for Cl^-, EC, pH, SAR and SO_4^{2-} parameters. TDS and TH parameters followed a Gaussian model. All semi-variograms and cross variograms had high confident level due to little values of nugget effects (C_o) relative to sill. The covariance matrix demonstrated that magnesium concentration (Mg^{2+}), sodium concentration (Na^+), Total anions, Cl^-, EC and TDS parameters have been the best covariate for estimating TH, SO_4^{2-}, Cl^-, PH, TDS and EC parameters, respectively. Co-Kriging was the best method for estimating all parameters far apart TH for which Kriging method was the best. Spatial distribution maps of groundwater quality indices demonstrated that the groundwater in the study area is slightly basic and the values of EC exceeded the permeable limit in more than 40% of the study area. Also there was sodium hazard and high concentration of TDS in the north-east part. Therefore, further studies are needed to recognize the pollution sources in order to reclaim the polluted part in the study area.

Key Words: *Groundwater quality, Geostatistics, Kriging, Co-Kriging, Mazandaran, Spatial distribution.*

INTRODUCTION

Groundwater is a very important source of fresh water all over the world. It is used for domestic, industrial water supply and irrigation. However in the absence of appropriate waste management strategies, many human activities and their by-products have the potential to pollute this worthy water source. Industrial effluents, wastes from urban infrastructures, agriculture, horticulture, transport and discharges from horticulture, transport and discharges from abandoned mines and deliberate or accidental pollution, improper disposal due to rapid urbanization in developed countries stream pollutions, all eventually affect the groundwater quality. According to World Health Organization (WHO, 2003) 80% of diseases in human being are water borne. Therefore it is imperatives to regularly monitor the quality of groundwater and to take measures to prevent the pollution. A lot of researches are conducted on analyzing groundwater quality and its temporal changes due to various factors (Sayana et al, 2010; Satish et al, 2007; Sunitha et al, 2002). Udayalaxmi et al. (2010) examined the quality of groundwater using Wilcox plot and Piper triangular diagram in a 40 km squared of India. It was found that the samples in the study area fell under C3S1 class and are characterized by alkaline therefore the groundwater in the entire region was too hard for drinking. Obiefuna et al. (2010) evaluated the groundwater quality for drinking and irrigation use in Yola in northeastern Nigeria. Their results showed that linear regression equations could be applied in predicting groundwater quality in that area.

Temporal monitoring of groundwater quality would let having some observed data in some points (wells) in an area. However well understanding of polluted area needs to convert measured point data to continuous surface. As measuring the groundwater quality parameters is too costly, therefore choosing a proper interpolation method to estimate the favorite object would be economic and has a great effect on data management (Habashi, 2007).

Geostatistical methods are one of the best interpolation techniques (Akhavan et al., 2010) which their accuracy for spatially prediction of ground water quality has been useful in different studies. Kriging method has been recognized as the best method for estimating the values of TDS (Ahmed, 2002), heavy metals (Istock and Cooper, 1998) and nitrate concentration (Barcae and Passarella, 2008) in groundwater. Gaus et al. (2003) had a geostatistical analysis of arsenic concentration in groundwater in Bangladesh using disjunctive kriging method. Their results showed that 35 million people were exposed in high concentration of arsenic (50ppm) and 50 million people were exposed in 10ppm. Fetouani et al. (2008) have assessed groundwater quality in the irrigated plain of Triffa in north-east of Morocco using Kriging method. Amadi et al. (2012) assessed the ground water quality by geostatistical methods in Eastern Niger Delta. The usefulness of geostatistical methods in interpreting the hydro geochemical data as well as identifying and categorizing pollutants are being demonstrated in their study. Rizzo and Mouser (2000) supposed that Cokriging method was an appropriate method to interpolate water quality indices. Dagostino et al. (1998) studied spatial and temporal variability of groundwater nitrate concentration. They demonstrated that Cokriging method could increase the accuracy of estimating groundwater nitrate concentration. Nazari et al. (2006) used geostatistical method to study spatial variability of groundwater quality in Balarood plain. The result showed that the spherical model was the best model to estimate EC, chloride concentration Cl^- and SO_4^{2-} variables.

Although geostatistical methods are suitable for preparing spatial distribution of groundwater quality indices, an appropriate geostatistical method for estimating a variable depends on the selected variable and the study area (Safari, 2002). Thus, the present study was carried out to evaluate three interpolation methods including weighted moving average (WMA) with the power of 2 and 3 Kriging and Cokriging intended to estimate different groundwater quality variable including electrical conductivity (EC), pH, total dissolved solid (TDS), sodium adsorption ratio (SAR), total hardness (TH), chloride concentration (Cl^-) and sulphate concentration (SO_4^{2-}) in Mazandaran, Iran.

MATERIAL AND METHODS

Study Area and Research Method

The study area falls within longitudes of 645550m and 671700m; latitudes of 4030900m and 4067200m in Mazandaran, Iran. De-Martin method used in climate regime assessment revealed a humid climate, with an average annual rain fall of 700 mm.

Data of 23 wells obtained from Mazandaran Regional Water Organization were used. Fig. 1 shows the location of the selected wells in the study area. Data were collected twice in fall and spring 2006.

Seven parameters including electrical conductivity (EC), pH, total dissolved solid (TDS), sodium adsorption ratio (SAR), total hardness (TH), chloride concentration (Cl-) and sulphate concentration (SO_4^{2-}) were chosen as groundwater quality indices in the study area.

Initially to investigate interpolation methods, the histogram of all selected parameters was drawing. Then the normality hypothesis of all parameters was checked using SPSS software. Data which had high skewness, were normalized using logarithmic method. A suitable covariate among HCO_3^-, Na^+, Mg^{2+}, Ca^{2+} and K^+ was determined for each groundwater quality index using a covariance matrix. The normality of covariates was also checked.

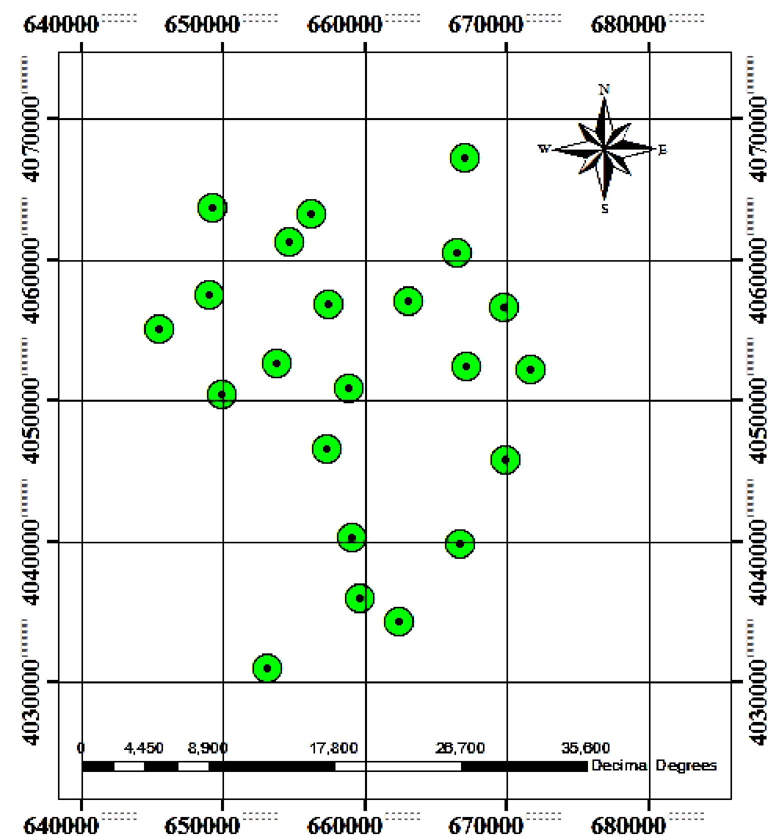

Fig.1. Position of wells in the study area used in analyzing ground water quality

After data normalization and choosing a suitable covariate, Variograms analysis were performed using Geostatistical extension program in Geographic Information System (GIS). The experimental semi-variogram was calculated, and then the best model was fitted with experimental variograms. The best model was selected based on less Residual Sum of Square (RSS) value. Then, the confidence level of all variograms was evaluated using the ratio of nugget variance to sill which is regarded as a criterion for classifying the spatial dependence of ground water quality parameters. If this ratio is less than 25%, then the variable has strong spatial dependence; if the ratio is between 25 and 75%, the variable has moderate spatial dependence and the ratio greater than 75%, represents weak spatial dependence (Taghizadeh *et al*, 2008).

After variograms analysis, the accuracy of ordinary kriging, Cokriging and weighting moving average (WMA) with power of 2 and 3 in interpolating groundwater quality indices was evaluated using cross validation technique. Evaluation criteria included mean bias error (MAE) and mean absolute error (MBE). Finally, spatial distribution maps of selected water quality indices have been prepared in Geographic Information System (GIS). After all, a physicochemical analysis of the groundwater quality in the study area was carried out based on prepared maps.

Interpolation Methods

Interpolation methods can be broadly classified into two major categories: exact and approximate. The interpolated surface goes through observed point data in exact methods while it may deviate from point data in approximate methods. For instance, Theissen polygon and WMA are exact while kriging and thin plate smoothing spline "TPSS" are approximate. Interpolation methods vary based on how they estimate the weight parameter of the following general equation:

$$Z^*(x) = \sum_{i=1}^{n} \lambda_i Z(x_i) \quad (1)$$

Where $Z^*(x)$ is the estimated value of location x; $Z(x_i)$ is the value of observation point x_i; n is the number of points; and λ is the weight. For example, the weight in WMA method, also known as Inverse Distance Method (IDW), is determined based on the distance between the data points as follows:

$$\lambda_i = \frac{D_i^{-\alpha}}{\sum_{i=1}^{n} D_i^{-\alpha}} \quad (2)$$

Where D_i is the distance between the observed and target points; α is the power; and n is the number of data points. Spatial correlation and smoothing function are used for estimating the weights in kriging and TPSS methods, respectively (Issaks and Srivastava 1989; Hutchinson 1994; Tabios and Salas 1985). In ordinary kriging, λ can be obtained by the solution of the following matrix of linear equations (Issaks and Srivastava, 1989):

$$[C].[\lambda] = [D] \quad (3)$$

Where [c] is the matrix of covariance between observed data points; and [D] is the matrix of covariance between pairs of observed and target points. For solving Eq.3, a semivariogram model must be used.

Cokriging is a derivative method from Kriging which uses a covariate, such as elevation, in the estimation process. The cross variogram between the main variable to be estimated and the covariate used in the determination of weights. Cokriging has been extensively described by Goovaerts in 1997, 2000 and Issaks and Srivastava in 1989. Due to the known influence of elevation on rainfall in the region of study, the elevation was used as the covariate.

In the TPSS method, the following relationship must be minimized (Hutchinson1994):

$$\sum_{i=1}^{n} \left[\frac{Z_i - F(x_i, y_i)}{n\sigma^2} \right]^2 + \rho.J_m(F) \quad (4)$$

Where Z is the observed value; F(x, y) is the splines function at the location (x, y); n is the number of data points; σ^2 is the variance of observed data; $J_m(F)$ is the integral of MTh order derivatives of F(x, y); and ρ is the smoothing parameter. The order (power) of derivative and ρ must be optimized by the cross validation technique.

Overall, ordinary kriging, Cokriging and WMA with power of 2 to 4 were compared in this study.

Variogram Analysis And Estimation Variance

In classic statistical analysis, samples are treated as if they were stripped of spatial dimension. In geostatistics, however, the location of a data point is considered in conjunction to its value. Semivariogram is a variable. The experimental semi Variogram(γ) is calculated as follows (Borgaand Vizzaccaro, 1997; Issaks and Srivastava, 1989):

$$\gamma(h) = \frac{1}{2.n(h)} \sum_{i=1}^{n(h)} \left[Z(x_i + h) - Z(x_i) \right]^2 \quad (5)$$

Where n (h) is the number of sample pairs separated by distance h; $Z(x_i)$ is the measured value at location x_i; and $Z(x_i + h)$ is the measured value at distance h from x_i .Range (R) is the distance where γ reaches a constant value. The value of semivariogram at R is defined as sill. In theory, sill value is equal to the sample variance under the assumption of second-order stationary. The value of γ at h=0 in the semivariogram is called the nugget effect(C_0). γ is used in kriging methods for estimating the weight parameters [Eq.3] and deriving the spatial distribution of estimation variance. One of the characteristics of geostatistical methods is their ability to determine the estimation variance (Hohn 1999), usually shown as E_δ^2, as an indicator of the error between the actual and estimated values.

The estimation variance is calculated as follows:

$$E_{\delta^2} = 2\sum_{i=1}^{n} \lambda i.\gamma_{0i} - \gamma_0 - \sum_{i=1}^{n}\sum_{j=1}^{n} \lambda_i.\gamma_{ij} \quad (6)$$

Where n is the number of data points; λ_i is the weight at location i; γ_0 is the nugget effect; γ_{0i} is the semi- variance between data points i and j.

Evaluation Criteria

All interpolation methods must be evaluated for their accuracy and/ or proper parameters election. In the cross-validation technique, a given point is removed in the interpolation process and estimated by the remaining observations. The difference between the estimated and observed values measure of spatial correlation of a given represents the error. This procedure is repeated for all points and the cumulative error is determined for each interpolation method. Following Willmott (1982), mean absolute error MAE and mean bias error MBE were used for the selection of the most accurate interpolation method.

$$MAE = \frac{1}{n} \sum_{i=1}^{n} \left| Z^*(x_i) - Z(x_i) \right| \quad (7)$$

$$MBE = \frac{1}{n} \sum_{i=1}^{n} \left(Z^*(x_i) - Z(x_i) \right) \quad (8)$$

Where $Z^*(x_i)$ is the estimated value, $Z(x_i)$ is the observed value. MAE indicates the average error of interpolation and MBE represents the deviation between the average of estimated data and the average of observed data.

RESULTS AND DISCUSSIONS

Variogram Analysis

Table 1, summarized the evaluated statistical parameters namely minimum (Min), maximum (Max), mean, standard deviation (S.D), Skewness and kurtosis values for each of the measured constituent of the groundwater samples from study area. Table 1 shows that the majority of studied parameters had high skewness, due to insufficient number of samples and unsuitable distribution. However, all data were normalized using logarithmic method apart from pH and calcium concentration (Ca^{2+}). Table 2 shows the residual sum of square (RSS) of different variograms models for all selected parameters. Results showed that spherical model had the less value of RSS for Cl^-, EC, PH, SAR and SO_4^{2-} parameter. However TDS and TH parameter followed a Gaussian model in the study area. The results are in agreement with Nazari *et al.* (2006) who used geostatistical methods to study spatial variability of Groundwater quality in Balarood plain. Their results showed that the spherical model was the best model for estimating EC, Cl^- and SO_4^{2-} concentration.

Semi-variograms of selected parameter in the study area were illustrated in Fig. 2. Table 3 also summarized the parameters of semi-variograms in the study area. The ratio of nugget variance to sill showed that there was a moderate spatial dependence among the values of TH, TDS, pH and SO_4^{2-} parameters.

However three parameters including SAR, EC and Cl^- had weak spatial structure separately. Taghizadeh *et al.* (2008) demonstrated that there was a weak spatial structure among the values of Cl^- parameter in Yazd-Ardakan plain.

Table 3 showed that the range of influence ranged between 16.37 and 34 kilometer. The maximum and minimum value of the range of influence belonged to EC and TDS respectively. However this value in SO_4^{2-} (32 Kilometer) is near to the maximum value of the range of influence (34 Kilometers). Little value of C_o relative sill in all parameters (apart from TH) showed that deterministic variance is low. In the other words, variograms had high confidence level. Among all parameters apart from TH (3300) C_o value ranged between 0.01-0.07.

Table 1: Statistics of groundwater quality analysis. Parameters include electrical conductivity (EC), sodium adsorption ratio (SAR), total dissolved solid (TDS), total hardness (TH), pH, chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), bicarbonate concentration (HCO_3^-), sodium concentration (Na^+), potassium concentration (K^+), magnesium concentration (Mg^{2+}), and calcium concentration (Ca^{2+}).

Parameter	Min	Max	Mean	S.D	Skewness	kurtosis
µS	804	4035	1480	700	2.42	6.48
µS	6.96	8.30	7.23	0.37	1.00	1.59
SAR	1.28	12.14	3.26	3.26	2.30	5.30
SAR**	0.25	2.50	1.00	0.58	0.89	0.27
TDS (mg/lit)	539	2577	949	437	2.49	6.72
TDS (mg/lit)**	6.30	7.86	6.79	0.36	1.17	1.91
TH (mg/lit)	270	560	389	72.07	0.52	-0.17
TH (mg/lit)**	5.60	6.33	5.95	0.18	0.10	-0.42
PH	7.50	8.00	7.76	0.14	-0.22	-0.76
Cl^- (mg/lit)	0.90	24.85	5.04	5.23	2.54	7.06
Cl^- (mg/lit)**	-0.11	3.21	1.26	0.84	0.39	-0.44
SO_4^{2-}**	0.85	4.65	2.40	0.86	0.63	0.41
SO_4^{2-}(mg/lit)**	-0.16	1.54	0.81	0.38	-0.50	0.51
HCO_3^- (mg/lit)	5.10	10.20	7.01	1.47	0.80	-0.21
HCO_3^-(mg/lit)**	1.63	2.32	1.93	0.20	0.46	-0.64
Na^+(mg/lit)	2.25	28.55	6.66	5.82	2.60	6.99
Na^+(mg/lit)**	0.81	3.35	1.67	0.64	0.82	0.37
K^+(mg/lit)	0.05	0.18	0.07	0.03	1.98	4.25
K^+(mg/lit)**	-3.00	-1.71	-2.62	0.33	0.89	0.92
Mg^{2+}(mg/lit)	1.85	6.15	3.33	0.94	1.14	1.81
Mg^{2+}(mg/lit)**	0.62	1.82	1.17	0.27	0.20	0.37
Ca^{2+}(mg/lit)	2.95	5.95	4.46	0.84	-0.22	-0.81

** Using logarithm to normalize data

Table 2. RSS values (residual sum of square) of different experimental methods for different groundwater quality indexes. Parameters include total hardness (TH), sodium adsorption ratio (SAR), chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), PH, total dissolved solid (TDS) and electrical conductivity (EC).

Parameter	TH	SAR	$SO4^{2-}$	Cl^-	pH	TDS	EC
Spherical	2.20E+08	5.11E-02	1.90E-02	2.35E-01	2.85E-04	9.00E-03	9.20E-03
Exponential	2.37E+08	6.25E-02	2.51E-02	2.43E-01	3.03E-04	1.30E-02	9.40E-03
Gaussian	2.37E+08	5.31E-02	3.55E-02	2.54E-01	3.60E-04	8.00E-03	8.80E-03

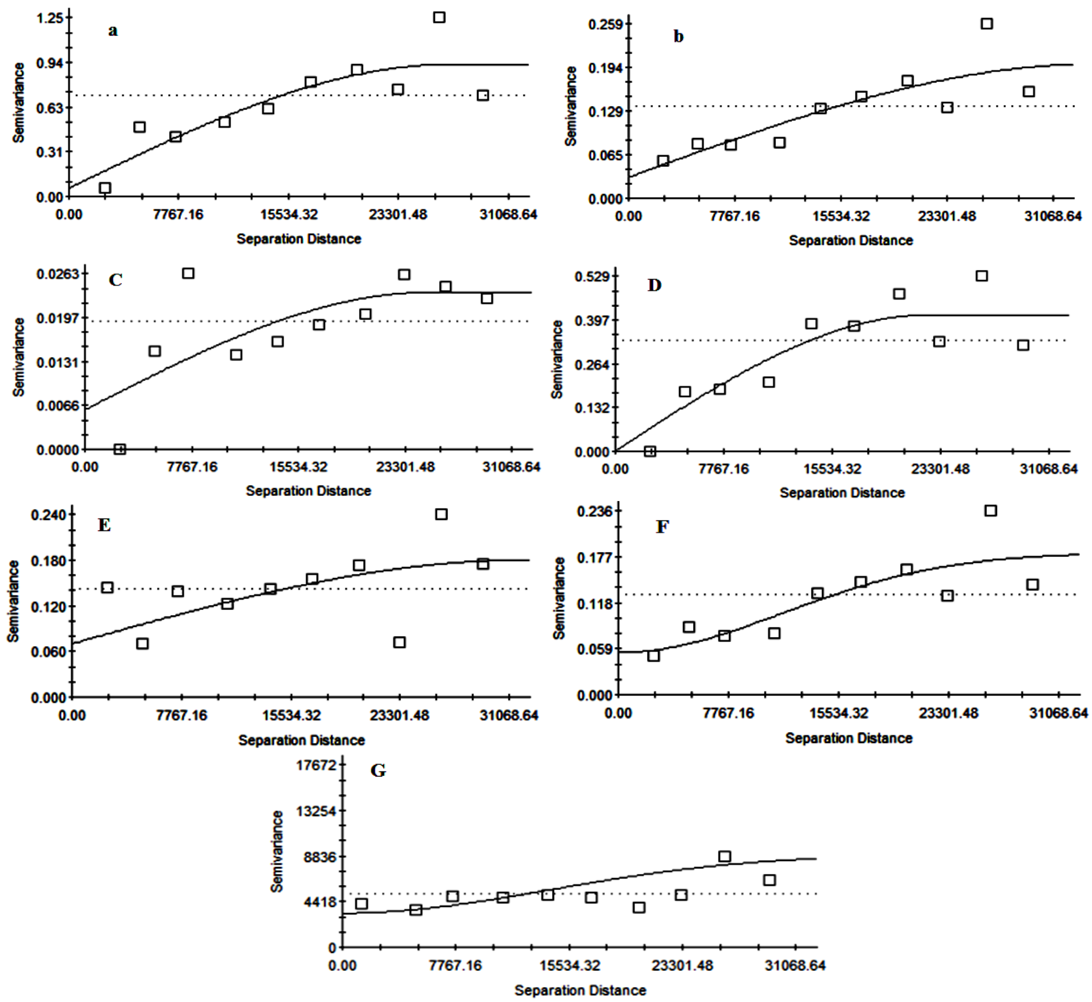

Fig. 2: Experimental variograms of a) chloride concentration (Cl^-), b) electrical conductivity (EC), c) pH, d) Sodium adsorption ratio (SAR), e) sulphate concentration (SO_4^{2-}), f) total dissolved solid (TDS) and g) total hardness (TH)

Table 3: Parameters of experimental variogram for different groundwater quality index. C_0 is nugget effect and C_0+C is the variogram sill. Parameters include total hardness (TH), sodium adsorption ratio (SAR), chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), PH, total dissolved solid (TDS) and electrical conductivity (EC).

Parameter	Model	C_o	C_o+C	Range (m)	C/(C_0+C)
TH	Gaussian	3300	9000	20000	0.61
SAR	Spherical	0.001	0.420	22510	0.99
SO_4^{2-}	Spherical	0.070	0.180	32000	0.61
Cl^-	Spherical	0.057	0.926	27000	0.93
pH	Spherical	0.005	0.023	25000	0.75
TDS	Gaussian	0.054	0.182	16370	0.70
EC	Spherical	0.031	0.199	34100	0.84

In order to determine the covariate parameter in Co-kriging method, the covariance matrix was extracted using SPSS software and the parameter which had the highest correlation coefficient was selected as the auxiliary parameter in Co-Kriging method (Table 4). Mg^{2+} (Magnesium concentration), Na^+ (Sodium concentration), Total anions, Cl^-, EC and TDS parameter had the best covariate for estimating TH, SO_4^{2-}, Cl^-, pH, TDS and EC parameter using Co-Kriging method, respectively, and the correlation coefficient was 84%, 99%, 66%, 66% 37%, 99% and 99% respectively. Analyzing different models for cross variograms showed that Spherical model had the lowest RSS value (Table 5).

Cross Variogram of Cl^-, EC, TDS, pH, SAR, SO_4^{2-} and TH parameters and the characteristics of mentioned cross-variograms are illustrated in Fig. 3 and Table 6, respectively. Table 6 shows that the ratio of nugget variance to sill is more than 75% for all parameters and therefore all parameters had weak spatial structure in the study area. The range of influence is ranged between 10 and 35 kilometers among different cross variogram. The maximum values of the range of influence belong to pH and TDS and EC and the minimum value belongs to TH parameter. The lowest value of C_0 belongs to TH and SO_4^{2-}. However the C_0 value of all parameters is close to each other. It is within the range of 0 to 0.042. Therefore all cross variograms have high confidence level.

Table 4: Correlation coefficient among different groundwater quality indices. Parameters include electrical conductivity (EC), sodium adsorption ratio (SAR), total dissolved solid (TDS), total hardness (TH), pH, chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), bicarbonate concentration (HCO_3^-), sodium concentration (Na^+), potassium concentration (K^+), magnesium concentration (Mg^{2+}), and calcium concentration (Ca^{2+}).

	TH	SAR	K^+	Na^+	Mg^{2+}	Ca^{2+}	Total	SO_4^{2-}	Cl^-	HCO_3^-	pH	TDS	EC
TH	1												
SAR	0.38	1											
K^+	0.55	0.52	1										
Na^+	0.44	0.99	0.57	1									
Mg^{2+}	0.84	0.43	0.61	0.47	1								
Ca^{2+}	0.79	0.17	0.20	0.22	0.39	1							
Total	0.63	0.92	0.62	0.95	0.59	0.43	1						
SO_4^{2-}	0.53	0.66	0.48	0.66	0.64	0.16	0.62	1					
Cl^-	0.51	0.92	0.53	0.94	0.47	0.34	0.96	0.54	1				
HCO_3^-	0.76	0.33	0.48	0.34	0.67	0.62	0.47	0.27	0.37	1			
pH	0.19	0.30	0.30	0.32	0.03	0.37	0.30	-0.03	0.37	0.29	1		
TDS	0.63	0.91	0.63	0.93	0.59	0.43	1.00	0.63	0.95	0.47	0.29	1	
EC	0.66	0.91	0.65	0.94	0.61	0.46	0.99	0.61	0.94	0.52	0.32	0.99	1

Table 5. RSS values of different experimental methods for different groundwater quality indices including total hardness (TH), sodium adsorption ratio (SAR), chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), pH, total dissolved solid (TDS) and electrical conductivity (EC).

Parameter	TH	SAR	SO_4^{2-}	Cl^-	pH	TDS	EC
Spherical	1997	0.060	0.021	0.044	0.003	0.010	0.010
Exponential	1997	0.069	0.024	0.048	0.002	0.011	0.011
Gaussian	1997	0.061	0.022	0.045	0.002	0.011	0.011

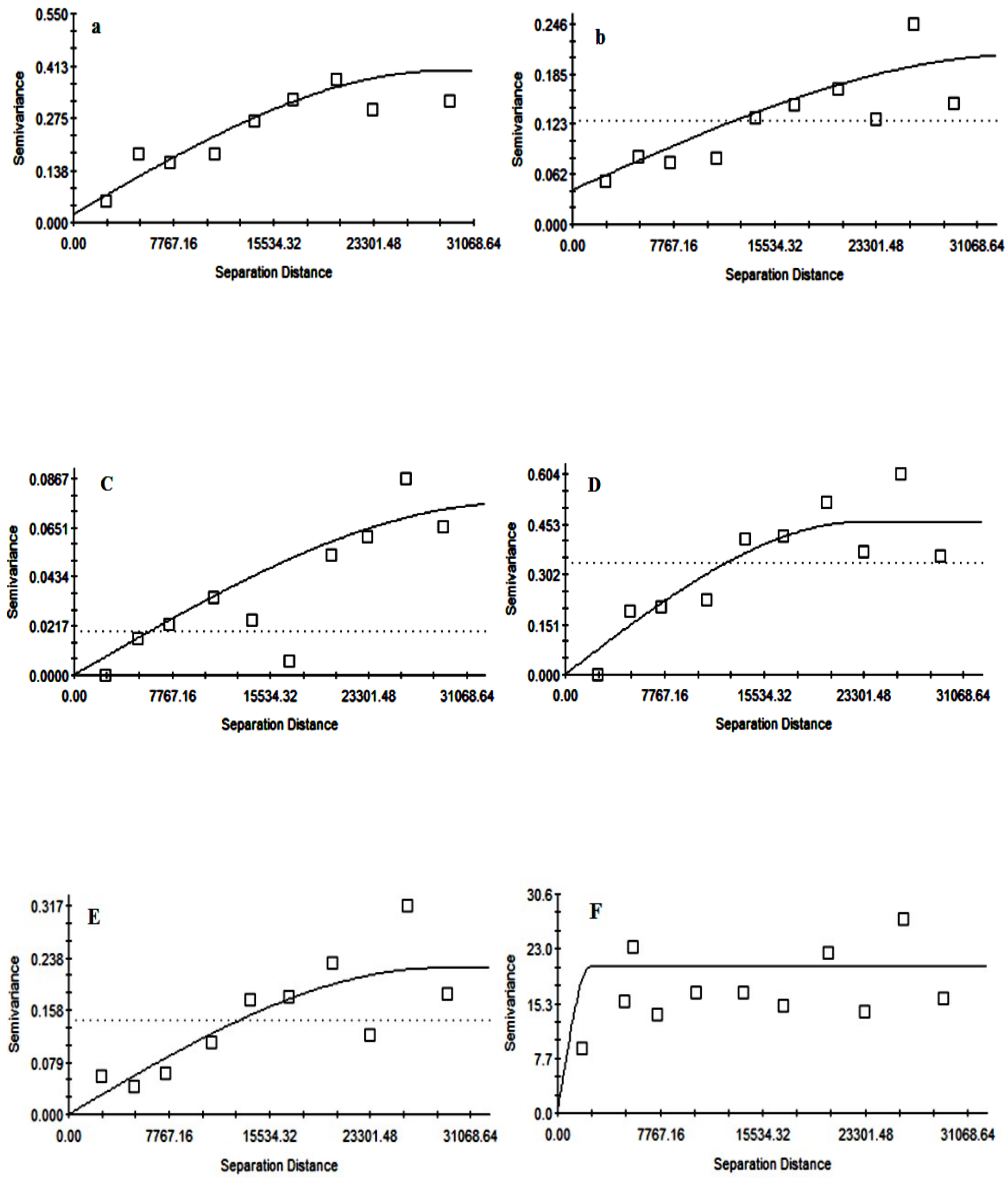

Fig. 3. Experimental cross variograms of a)chloride concentration (Cl^-), b) electrical conductivity (EC), c) pH, d) Sodium adsorption ratio (SAR), e) sulphate concentration ($SO4^{2-}$), f) total dissolved solid (TDS) and g) total hardness (TH).

Table 6. Parameter of cross variogram for different groundwater quality index. C_0 is nugget effect and C_0+C is the variogram sill. Parameters include electrical conductivity (EC), sodium adsorption ratio (SAR), total dissolved solid (TDS), total hardness (TH), pH, chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), sodium concentration (Na^+), magnesium concentration (Mg^{2+}), calcium concentration (Ca^{2+}) and total anions concentration.

Parameter	Covariate	Model	C_o	Sill	Range	$C/(C_0+C)$
TH	mg^{2+}	Spherical	0	20	10000	1.00
SAR	Na^+	Spherical	0.001	0.461	23320	1.00
SO_4^{2-}	Na^+	Spherical	0.000	0.222	28650	0.99
Cl^-	total anions	Spherical	0.022	0.400	28830	0.95
pH	Ca^{2+}	Spherical	0.000	0.076	35000	0.99
TDS	EC	Spherical	0.042	0.209	35000	0.80
EC	TDS	Spherical	0.042	0.209	35000	0.80

Evaluating Interpolation Method

Evaluating the different interpolation methods was done first based on MBE and later by MAE (if the decission was under doubt). The WMA method was executed using different number of neighbourhood points. Results showed that 9 neighbourhood points performed the best precision. The mentioned method was accomplished with power of 2 to 3 and it was proved that WMA with the power of 3 performed better and gave higher accuracy than the other power (Table 7).

Comparison of the values of MBE among different methods showed that difference between observed data and estimated data of all parameters were low among different interpolation method (Table 7).

Table 7: Results of comparison different interpolation methods in estimating water quality indexes based on evaluation criteria (mean bias error (MBE) and mean absolute error (MAE)). WMA-2 and WMA-3 is weighting moving average with power of 2 and 3 respectively. Parameters include total hardness (TH), sodium adsorption ratio (SAR), chloride concentration (Cl^-), sulphate concentration (SO_4^{2-}), pH, total dissolved solid (TDS) and electrical conductivity (EC).

Method	Kriging		CO-Kriging		WMA-2		WMA-3	
Parameter	MBE	MAE	MBE	MAE	MBE	MAE	MBE	MAE
TH	-0.281	67.31	2.126	77.01	-3.219	62.23	-2.176	66.57
SAR	-0.223	1.400	-0.217	1.443	-0.384	1.420	-0.294	1.237
SO4	-0.108	0.610	-0.075	0.674	-0.113	0.608	-0.103	0.619
PH	0.002	0.128	0.000	0.133	0.008	0.120	0.005	0.124
TDS	-39.69	270.1	-19.07	325.1	-43.93	246.6	-32.00	278.8
EC	-56.76	420.3	-31.49	493.5	-71.97	370.5	-53.38	418.8
Cl	-0.767	3.333	-0.663	3.516	-1.081	2.988	-0.895	3.083

Therefore, all methods have enough accuracy to interpolate the selected data of groundwater. This result demonstrated that Geostatistical methods were strong enough to estimate the values of groundwater parameters in the study area. This is in agreement with the finding of Safari (2002), Nazarizade et al. (2006), Ahmed (2002) and Taghizadeh *et al.* (2008), who stated that Geostatistics is superior to IDW in interpolating the parameter of groundwater quality parameters. However Co-Kriging is the best method to estimate SAR, SO_4^{2-}, PH, TDS, EC and Cl^- which have the lowest MBE criteria. For TH, Kriging has the lowest value of MBE and therefore is the best method for interpolating the mentioned parameter in the study area. This result is in agreement with the findings of Rizzo and Mouser (2000). They considered Cokriging as a suitable method for mapping the quality indicators such as: Na^+, Cl^-, SO_4^{2-}, Ca^{2+} and EC. Taghizadeh *et al.* (2008) have also included that the Co-Kriging methods as the most accurate geostatistical methods in estimating SAR, TDS, EC, TH, Cl^- and SO_4^{2-}. Also, the ability of Co-Kriging method for interpolating the values of nitrate concentration in groundwater has been proven by Dagostino *et al.* (1998).

Table 7 shows that Kriging is the best method for estimating the values of TH. The ability of Kriging method in estimating the values of groundwater quality parameters such as TDS (Ahmed, 2002),heavy metals (Istock and Cooper, 1998),nitrate concentration (Barace and Passarella, 2008), arsenic concentration (Gaus *et al*, 2003) and all other groundwater quality parameters (Fetouani *et al*, 2008) have been proven.

Physiochemical Analysis of Groundwater Quality Based on Prepared Maps in GIS

Spatial distribution of selected groundwater quality parameters based on Cokriging method for Cl-, EC, PH, SAR, SO42- and TDS and based on Kriging method for TH are illustrated in Figs. 4- 10, respectively. A physicochemical analysis of groundwater quality has been done based on these maps.

Chloride concentration of the groundwater samples ranged from 0.9 to 24.85 mg/ lit (Fig. 4). The WHO limit of chloride in the groundwater is less than 250 mg/ lit (WHO, 1984). Fig. 4 shows that the values of Cl^- in the study area is less than permissible limit. Sulphates in groundwater in excess of the WHO limit of 150 mg/ lit have not been seen in any part of the study area (WHO, 1984).

EC values range from 1017 to 3981 µs/ cm (Fig. 5). The maximum permissible value of EC in groundwater is 1500µs/ cm (BIS, 1983). Fig 5 shows that the value of EC in more than 40% of the study area exceed the permissible value of EC.

The pH in the study area (Fig. 6) varies from 7.5 to 8 against permissible limits of 6.5 to 8.5 (BIS, 1983). The measure of pH is on a scale of 0-14 wherein pH less than 7 is acidic and greater than 7 is alkaline (basic) and exact 7 is neutral. Thus the groundwater samples are slightly basic and are in the permissible limit.

The value of SAR in groundwater shows the sodium hazard in groundwater and values upper than 5 could be an alarm of sodium hazard. The SAR values were found to vary from 2 to 11.9 (Fig. 7). Apart from the northeast of the study area, all other parts have the values of SAR which is less than 3.

TDS (Fig. 9) gives the general nature of groundwater quality and extent of contamination (Annon, 1946; Robinnove, 1958; Davis and de Wiest, 1966; AWWA, 1971). The permissible limit (BIS, 1983) for TDS is about 500 mg/ l. In general, TDS values of <1000 mg/ l are considered as fresh water and values >1000 mg/ l are considered brackish. Based on Fig. 9, The TDS values vary between 675 to 3981 mg/ l with mean value of 1044 mg/ l. the spatial distribution of TDS shows that mostly the northeast part of the study area has high concentration of TDS. Total hardness, as an important property indicating the quality of groundwater, is mainly caused by magnesium and calcium cations and is defined as the sum of their concentrations expressed in mg/ lit. Basically it is the soap consuming property of water. The desirable limit of TH is 300-600 mg/ lit and the entire study are has the value of TH in acceptable limit (Fig. 10).

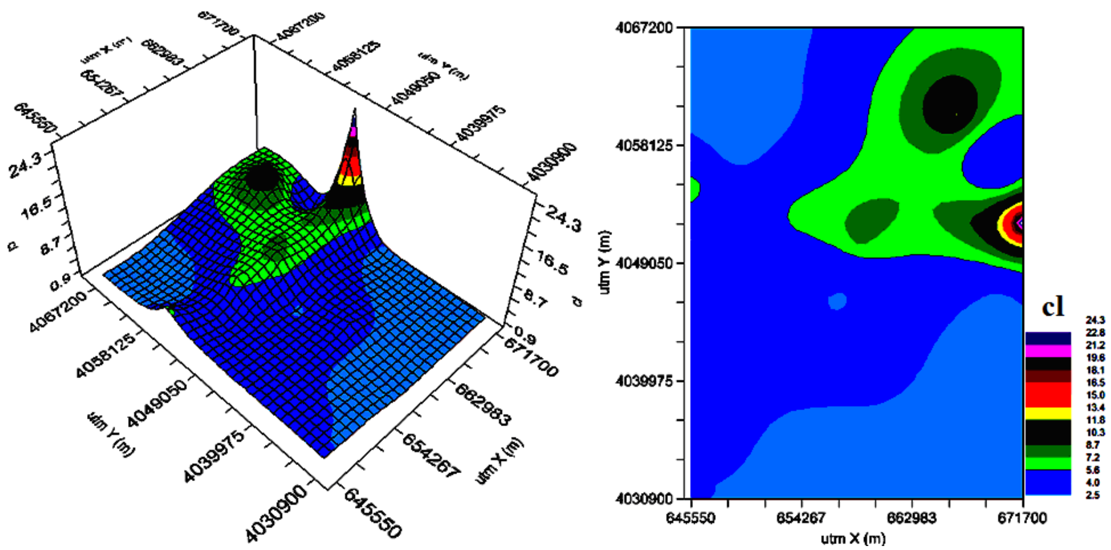

Fig. 4. Interpolated groundwater quality maps of electrical conductivity (Cl^-) based on Co-Kriging Method

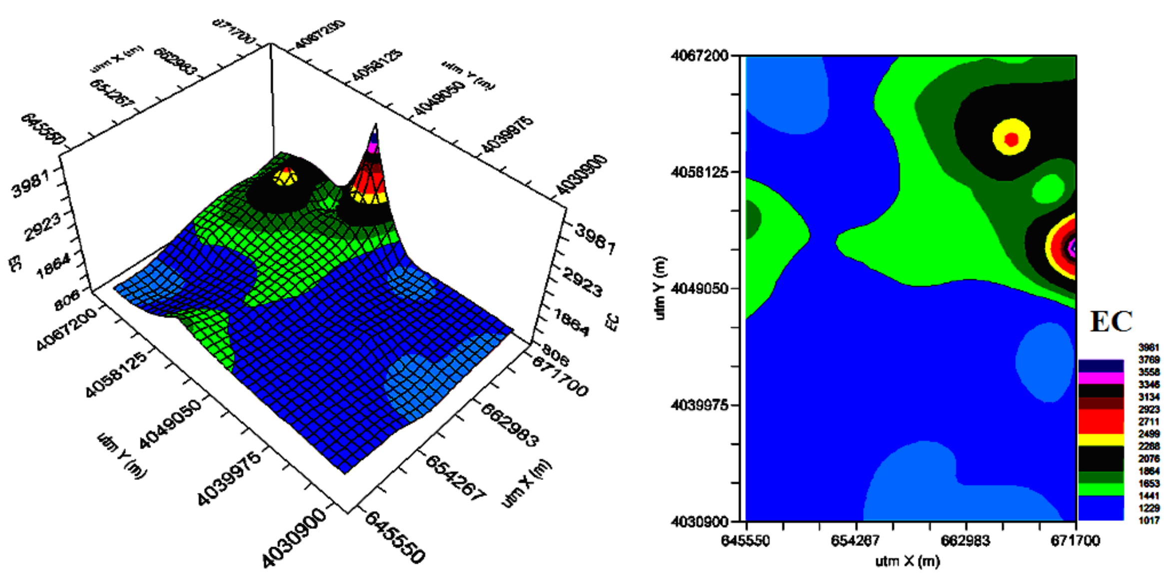

Fig. 5: Interpolated groundwater quality maps of electrical conductivity (EC) based on Co-Kriging Method

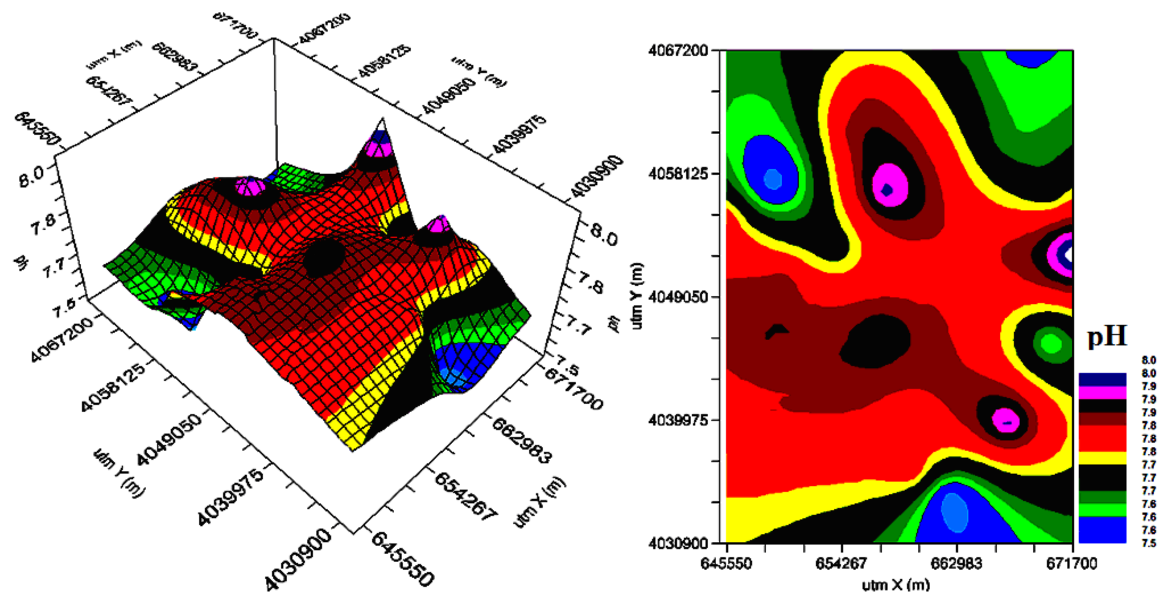

Fig. 6. Interpolated groundwater quality maps of pH based on Co-Kriging Method

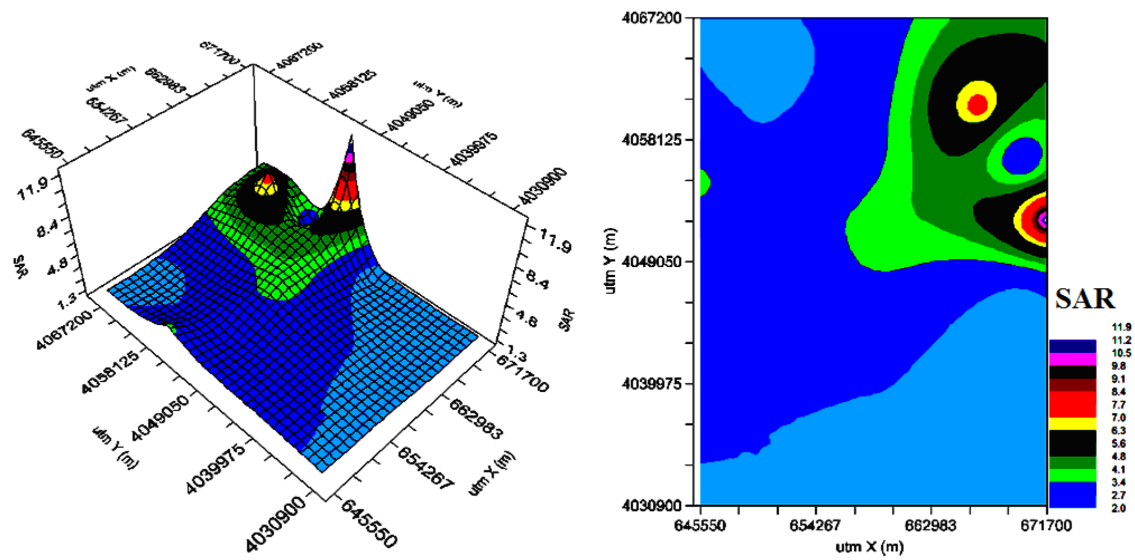

Fig. 7. Interpolated groundwater quality maps of sodium adsorption ratio (SAR) based on Co-Kriging Method

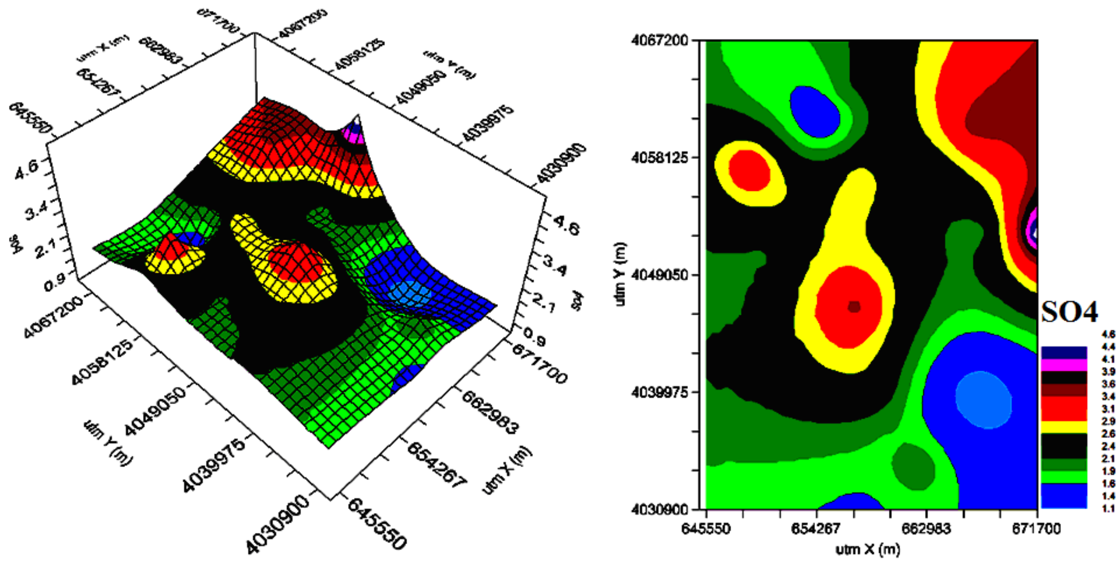

Fig. 8. Interpolated groundwater quality maps of sulphate concentration (SO_4^{2-}) based on Co-Kriging Method

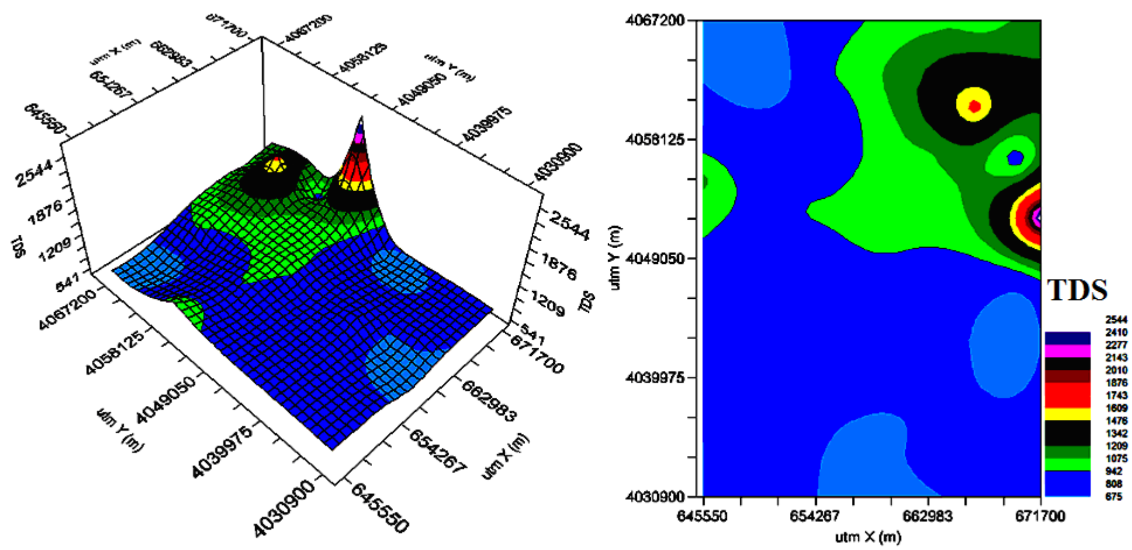

Fig. 9. Interpolated groundwater quality maps of total dissolved solid (TDS) based on Co-Kriging Method

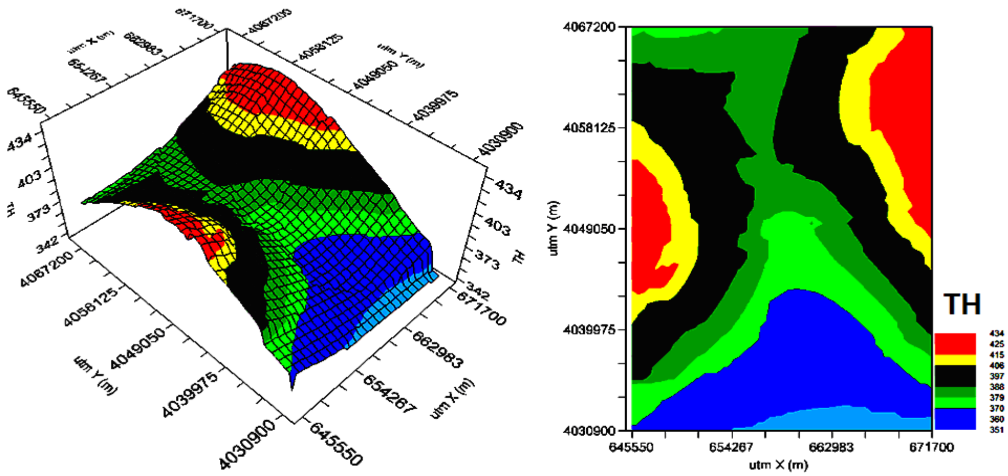

Fig. 10: Interpolated groundwater quality maps of total hardness (TH) based on Kriging Method

CONCLUSION

The present study was carried out to evaluate three interpolation methods including weighted moving average WMA with the power of 2 and 3, Kriging and Cokriging.for estimating seven groundwater quality parameters including EC, pH, TDS, SAR, TH, Cl^- and SO_4^{2-} in Mazandaran, Iran. Analyzing different geostatistical interpolation methods showed that Co-Kriging is the best method for estimating SAR, SO_4^{2-}, pH, TDS, EC and Cl^- which had the lowest MBE criteria. For TH, Kriging had the lowest value of MBE and therefore is the best method for interpolating thisparameter in the study area. Spatial distribution of PH showed that the groundwater in the study area was slightly basic and the values of PH were in the permissible limit, also the value of EC in more than 40% of the study area exceeded the permissible limit. Spatial distribution of TDS showed that mostly the north-eastern part of the study area had high concentration of TDS. There was no hazard with the excessive value of chloride, sulphate and total hardness (TH) in entire study area. Results demonstrated that there was sodium hazard in the north-east of the study area based on SAR values. Therefore, further studies are needed to recognize the pollution sources in order to reclaim the polluted part in the study area.

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ارزیابی روش‌های زمین‌آمار در تخمین کیفیت آب زیرزمینی ساحلی مازندران

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چکیده

این مطالعه، با هدف ارزیابی سه روش زمین‌آمار میانگین متحرک وزنی (WMA) با توان‌های ۲ و ۳، کریجینگ و کوکریجینگ در تخمین کیفیت آب زیرزمینی انجام شد. بدین منظور، داده‌های ۲۳ چاه مشاهده‌ای در فصل‌های پاییز و بهار ۱۳۸۵ جمع‌آوری شد. هفت پارامتر هدایت الکتریکی (EC)، اسیدیته (pH)، کل نمک‌های محلول (TDS)، نسبت جذبی سدیم (SAR)، سختی کل (TH)، غلظت کلر (Cl^-) و غلظت سولفات (SO_4^{2-}) به عنوان معیارهای کیفیت آب زیرزمینی در منطقه مطالعاتی انتخاب شدند. آنالیز واریوگرام و استخراج نقشه‌های توزیع مکانی پارامترهای کیفی آب زیرزمینی با استفاده از برنامه جانبی Geostatistics در محیط GIS انجام شد. ارزیابی روش‌های درون‌یابی بر اساس معیارهای میانگین خطای نسبی (MBE) و میانگین خطای مطلق (MAE) انجام شد. مدل نیم‌تغییرنمای کروی کمترین میزان مجموع خطای باقیمانده (RSS) را برای پارامترهای Cl^-، EC، pH، SAR و SO_4^{2-} داشت. نیم‌تغییرنمای پارامترهای TDS و TH از مدل گوسین پیروی می‌کند. تمام واریوگرام‌ها به دلیل داشتن مقادیر ناچیز اثر قطعه‌ای (C_0) در مقایسه با حد آستانه (Sill) از سطح اعتماد بالایی برخوردار بودند. ماتریس کوواریانس نشان داد که مقادیر غلظت منیزیم (Mg^{2+})، سدیم (NA^+)، آنیون کل، Cl^-، EC و TDS به ترتیب بهترین متغیرهای کمکی برای تخمین TH، SO_4^{2-}، Cl^-، pH، TDS و EC بودند. روش کوکریجینگ بهترین روش تخمین برای تمام متغیرها به جز TH بود. اما روش کریجینگ بهترین روش برای تخمین TH بود. نقشه‌های توزیع مکانی پارامترهای کیفی آب زیرزمینی نشان داد که آب زیرزمینی در منطقه مطالعاتی نسبتا بازی بوده و مقادیر EC در بیشتر از ۴۰٪ از سطح منطقهبیشتر از حد مجاز می‌باشد. همچنین خطر حضور سدیم و مقادیر بالای TDS در مناطق شمالی به چشم می‌خورد. بنابراین، مطالعات بعدی در راستای شناسایی منابع آلودگی جهت اصلاح بخش‌های آلوده در منطقه مطالعاتی لازم می‌باشد.

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