

*Original Article***Geostatistical Approach for Groundwater Quality Evaluation in Zarin Abad Plain, Iran**Abdollah Taheri Tizro^{1*} Mohamad Mohamadi²

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(Received: 26 Feb. 2019; Revised: 8 May 2019; Accepted: 30 Jun. 2019; Published: 18 Sep. 2019)

Abstract

Background and Purpose: This study was undertaken, first, to investigate the hydrogeological setting of the study area and geophysical data, second to examine the general nature of the groundwater quality. In this regard, ordinary Kriging, Co-Kriging, and Inverse Weighted Distance (IWD) strategies were applied to develop spatial variability maps, and study the fluctuations in groundwater quality parameters in Zarin Abad plain, Zanjan Province, Iran in 2017-2018.

Materials and methods: To inquire the groundwater quality parameters, samples were provided from 61 shallow and deeply drilled observed wells in Zarin Abad Goltapeh plain. The studies were carried out by using geostatistical methods to find out the most applicable method, which can be used to develop spatial variability maps in order to study the changes in groundwater quality parameters (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , Cl^- and EC). The local geophysical, geological, and hydrogeological surveys were precisely accomplished to specify the architecture of various subsurface geological horizons. In addition, a geophysical investigation with a Schlumberger configuration was performed in the study region for the purpose of field data generation.

Results: Based on key results, the values of electrical conductivity (EC) were recorded within the range of 480 and 6580 $\mu\text{S}/\text{cm}$. The order of major cations and anions were $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$, respectively. It is worthwhile mentioning that groundwater salinity was found to be dependent upon factors, such as water long residence time and minerals dissolution.

Conclusion: To assess the spatial distribution in groundwater parameters, the variable mode was used. The results obtained from Kriging, Co-Kriging, and IDW methods were then evaluated by the error indices of RMSE and MAE. Co-Kriging Model was the most optimal approach in studying the spatial variation of groundwater quality parameters.

Keywords: Geostatistical Analysis; Groundwater quality; Zarin Abad plain; Water quality

Citation: Taheri Tizro A*, Mohamadi M. Geostatistical Approach for Groundwater Quality Evaluation in Zarin Abad Plain, Iran Iran J Health Sci. 2019; 7 (3): 9-20. DOI: 10.18502/jhs.v7i3.1529

1. Introduction

Groundwater is the largest available resource of fresh water in the areas where surface water resources are confined or scarce (1). Quality of groundwater is a significant environmental factor, which requires to be analyzed and managed depending on its spatial distribution. Insufficient management of groundwater resources generates not only a quantity reduction but also deterioration in quality of groundwater (3-5). Excessive withdrawal from the groundwater resources is another reason which has caused major decay in the quality of groundwater resources. Therefore, controlling the qualitative parameters of groundwater resources in arid and semi-arid regions is of great importance (6,7). To establish the hydro chemical categorizes of groundwater in a survey, the application of beneficial strategies is highly demanded for the spatial, temporal, and graphical representation of the relevant data. Understanding the spatial and temporal variation of groundwater quality is an essential factor for implementing the optimal management of water resources. Although reliable data is highly required for evaluating and monitoring groundwater quality, in many cases, collecting data throughout the area is time-consuming, and it is not economically possible, so interpolation methods can save time and money significantly. In this context, the application of geostatistics-based approaches might be considered as robust and accurate tools for a real-time monitoring of these parameters variations (5-8). So far, numerous attempts have been carried out to use these methodologies for modeling groundwater qualitative/quantitative parameters (1-4, 7-12). Among others, Karami et al., 2018 utilized ordinary

kriging method to evaluate some main quality parameters of groundwater in Varamin plain, Iran (3). Maroufpoor et al., (2019) carried out an experiment by geostatistical-based Kriging and Co-Kriging approaches, and compared the results with data-driven artificial neural network (ANN) and ANFIS models for predicting spatial distribution of groundwater quality in Kerman Province, Iran (4). Geostatistical models and multivariate statistical techniques were then employed to assess the source spatial variability of groundwater pollutants at the Lakshimpur district of Bangladesh (5). Abdulrasoul et al., (2017) applying geostatistical methods (6), carried out the analyses of 180 groundwater samples of Al-Kharj, Saudi Arabia. Narany et al., (2015) assessed the suitability of groundwater for agricultural usage on the Amol–Babol Plain, Iran (7). Hamzah et al., 2019, on the other hand, emphasized the main hydro geochemical features of groundwater chemistry in Terengganu (Malaysia) and its spatial distribution (11). The quality of groundwater in rice cultivation areas was also investigated by Rezaei et al. in northern parts of Iran by Kriging and IWD methods to develop spatial variability maps of SAR, EC, and Na (12).

This paper investigated the spatial distribution of the groundwater quality parameters of Zarin Abad plain (Zanjan Province, Iran). Geostatistical methods were applied to determine the most suitable approach to develop spatial variability maps and study the fluctuations in groundwater quality parameters. Firstly, the hydrogeological setting of the study region was investigated using drilling and geophysical data. Secondly, the general characteristics of groundwater quality data and the accuracy of different interpolation

methods (ordinary Kriging, Co-Kriging, IWD) were examined.

2. Material and Method

2.1. Study area

The study area lies between the geographical coordinates of 35°10' and

36°13' north latitude and 47°56' and 48°57' east longitude. The region is also posited in the western part of Iran and is known as a central tectonic zone (Fig. 1) (13).

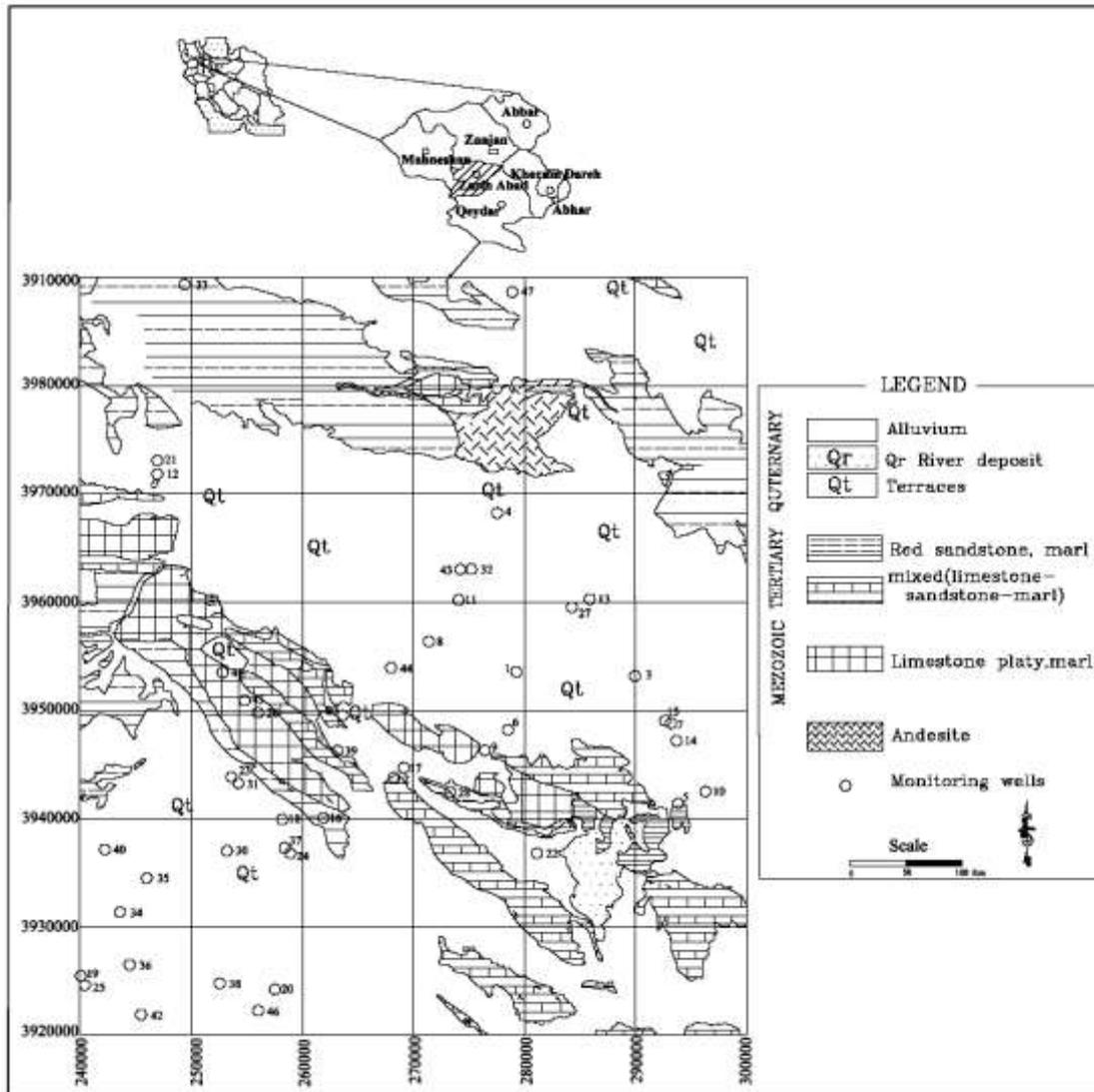


Figure 1. Geological plot of the study region, representing the sampling position (14).

A temperate climate and cold winters followed by moderate summers are remarkable characteristics of the study area. The average minimum and maximum temperature are recorded in January (-3.6°C) and July (21.8°C), respectively. Therefore, the climatic is classified in the semiarid regions regarding the De Martin assortment. Over a recent 20-year period (1985–2005), the range of yearly rainfall was recorded to be 272–373 mm (14).

According to the oldest geological series of rocks, Zarin Abad plain comprises of slate and schistose rocks, which are partly metamorphosed and belong to the Upper Triassic-Jurassic sequences. The crystallization of limestone is observed between these rocks. Rocks with low metamorphic formations in the area are Nayeen and Shemshak formations followed by outcrop in the northeast and southeast parts of the plain. Conglomerate and sandstone with a limestone base of Cretaceous rocks owed to the Albian along with andesite-basalt, Albian shales, and shales owed to the Upper Cretaceous are exposed in the southern parts, and they all have been metamorphosed. The Cretaceous exposures form slopes against Jurassic rocks (Fig. 1) (13, 14).

Quaternary sediments consisting of clay and sand with horizontal bedding are deposited in the central and western parts of the plain. The main aquifer systems of high transmissivity are developed within these sediments of the study region.

The major aquifer is developed within the alluvial deposits. The depth of the water table is extremely changeable; it is relatively shallow (6 m below ground surface) in the central part near Zarin Abad River, while the depth is 60 m below ground surface or more in the eastern regions. The water table has the highest level in May or April, and the lowest level belongs to

October or September. Groundwater flow originates from the recharge area of the upper hills of east and northeast and slopes toward the central part of the plain and ultimately discharges to Zarin Abad River. As concluded from the pumping test analysis, transmissivity is estimated to be $30 \text{ m}^2/\text{day}$ around the periphery, and up to $900 \text{ m}^2/\text{day}$ in the southern part of the basin (14).

2.2. Geophysical investigation

A geophysical investigation with a Schlumberger configuration was performed in the study region for the purpose of field data generation. The apparent resistivity data, generated for diverse values of $AB/2$, was processed and the results were then employed to provide a realistic image of the geological framework (15). Quantitative (direct and indirect) and geologic strategies were applied in the interpretation. Zohdy et al. (16) determined the comprehensive accounts of various techniques to the automatic interpretation of resistivity data. The automatic interpretation of sounding data, which is the cause of interpreted depths and resistivity, respectively, was utilized to obtain the true resistivity values and the corresponding layer thicknesses (17).

The field data were evaluated with the LithoLogs of boreholes, which were posited near the corresponding soundings. Resistivity for sandy horizons was within the range of 35 to $100 \Omega\cdot\text{m}$, while mainly silt and clay zones revealed lower resistivity range (2 to $7 \Omega\cdot\text{m}$). The rock formations also exhibited wider ranges of resistivity ($150\text{--}400 \Omega\cdot\text{m}$). A low resistivity value for these formations refers to a crispy and weathered nature. Fences diagram (Fig. 2), constructed from the resistivity data, and illustrates the stratigraphic framework of the basin in quasi-three-dimensional form.

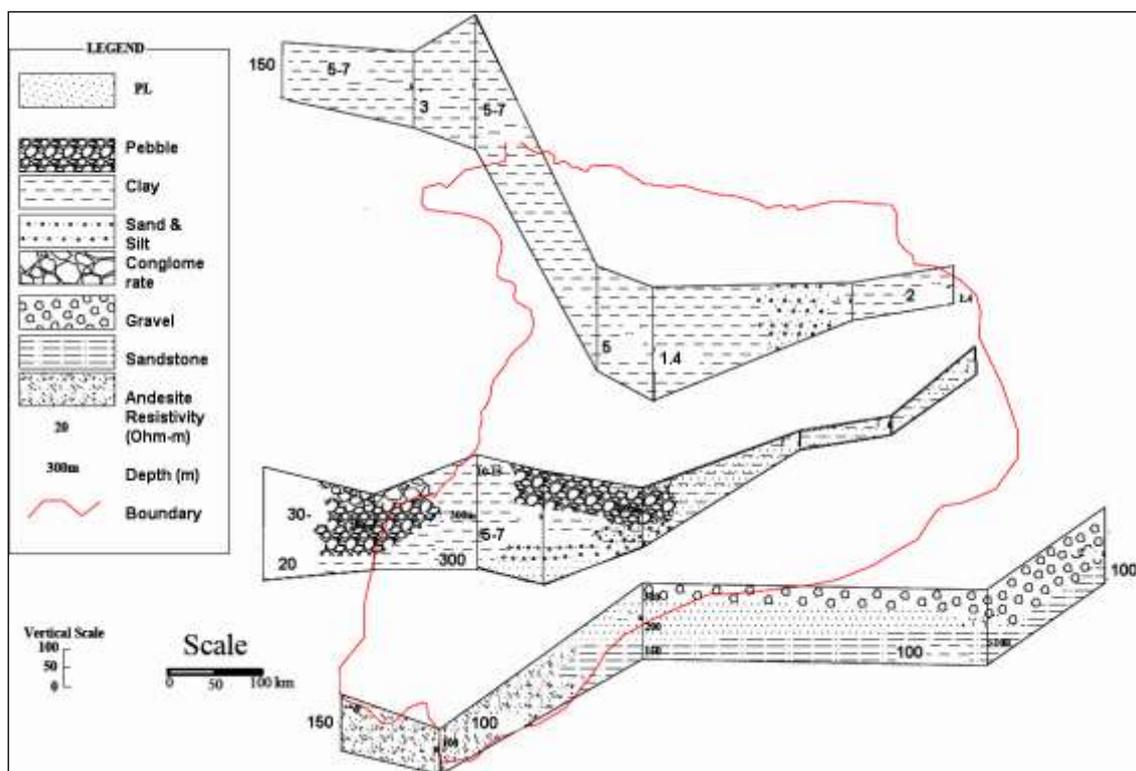


Figure 2. Fence diagram of the study area (14).

2.3. Water samples collection and chemical analysis

To evaluate the groundwater quality and the characteristics of the study area, a program of groundwater quality monitoring was developed. The program was employed to supply relevant parameters of water quality for the whole area with a network of optimally selected observation wells regarding the overall distributions of alluvium and consolidated geological formations. 62 groundwater samples were collected during field visit and analyzed with the procedures described by standard methods (18). The overall precision of the analyses was within $\pm 5\%$, as indicated from the ionic balance.

Considering the sampling protocol given by Claasen (19), 32 shallow and deep (refers to the depth of more than 60 m) wells followed by 21 springs and 8 Qantas were considered in the present research. The sampling positions are demonstrated in Figure 1. Majority of the wells were constructed by the stainless steel and some of them were made by the PVC. Shallow

and deep wells were sampled at the same time. The water temperature ($^{\circ}\text{C}$) at the head of the wells, Electrical Conductivity (EC), Total Dissolved Solids (TDS) concentration, and pH values of 62 samples were measured in situ, using a portable multimeter (MM-40, Crison). The samples were then analysed with the procedures described by standard methods (18) in the laboratory of the Zanzan Regional Water Centre (ZRWC) for major ions including Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , Cl^{-} , NO_3^{-} , SO_4^{2-} , HCO_3^{-} and Total Hardness (TH). Flame photometry and EDTA titrimetric methods were then applied to measure the Na^{+} , K^{+} cations, and Ca^{2+} and TH, respectively. Anions NO_3^{-} and SO_4^{2-} were determined using the Hatch spectrophotometer. After sample collection, HCO_3^{-} and Cl^{-} were immediately determined by 0.02 N H_2SO_4 and AgNO_3 , respectively, based on the titration approach. Finally, Total Hardness (TH) was applied to determine Mg^{2+} .

The selected models were utilized to analyse the spatial correlation of the research variables,

while the spatial distribution of the parameters was determined by Kriging, Co-Kriging, and Inverse Weighted Distance (IWD) techniques.

2.4. Geostatistical methods

In this study, 61 samples, taken from the observational wells were employed to estimate the spatial variation of some chemical parameters of groundwater in the Zarin Abad plain. To assess the spatial distribution in the groundwater parameters, the variable mode was used. The variable mode is generally calculated to anticipate the changes in variables considering temporal and spatial variations. In this regard, ordinary Kriging, Co-Kriging, and Inverse Weighted Distance (IWD) strategies were applied.

To evaluate the field data and select the most optimal strategy of interpolation coefficient, the coefficient of determination of (R^2), Root Mean Square Error (RMSE), and Mean Absolute Error (MAE) were calculated. Statistical Package for the Social Sciences (SPSS, version 18) was then utilized to verify the normal distribution of data. Parameters,

such as pH, HCO_3^- , and TDS, had normal distribution; however, other parameters did not follow a normal distribution. Therefore, normalization of the logarithm was used.

3. Results

Major ion concentrations in groundwater were Ca^{2+} (1.47-28.4 meq/L), Mg^{2+} (1.01-16.48 meq/L), Na^+ (0.41-23.34 meq/L), HCO_3^- (12.08-9.77 meq/L), and SO_4^{2-} (0.37-34 meq/L). The Cl^- concentration ranged from 0.16 meq/L to 1465 meq/L, and the mean value was found to be 4.67 meq/L. In addition, pH fluctuated in the range of 6.85 to 7.78.

The variation range of Electrical Conductivity (EC) was also 480 and 6580 $\mu\text{S}/\text{cm}$. Based on the mean values (Table 1), the orders of the major cations and anions were $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$, respectively. The increase of salinity (TDS) recorded along the direction of the groundwater flow (down-gradient part of the plain) was caused by the long water residence time and the minerals dissolution.

Table 1. Statistical summary of the chemical parameters in groundwater samples

Groundwater quality Parameters	Unit	Max	Min	Mean	St. Dev.*
pH	-	7.78	6.85	7.23	0.195
HCO_3^-	meq/L	9.77	2.08	4.5	1.82
TDS	meq/L	4040	244	1024	817
SAR	-	13.63	0.266	3.035	2.86
EC	$\mu\text{cm}/\text{S}$	6580	410	1695	1335
Na^+	meq/L	23.34	0.41	6.09	5.77
K^+	meq/L	0.831	0.007	0.123	0.18
Mg^{2+}	meq/L	16.48	1.01	4.35	3.53
Ca^{2+}	meq/L	28.42	1.47	5.96	5.24
SO_4^{2-}	meq/L	34.08	0.37	6.97	7.9
Cl^-	meq/L	27.1	0.165	4.67	6.57
TH	meq/L	2090	130	511.97	450.45
Sum Anions	meq/L	63.93	3.5	16.14	13.1
Sum Cations	meq/L	3.8	65.34	16.51	13.3

*St. Dev.=Standard Deviation

Based on the physicochemical analyses, the following results were concluded in the present research. The pH values were obtained within the range of 6.85-7.78 with a mean value of 7.23 revealing the characteristics of Alkali of the groundwater in Zarin Abad plain. The variation range of EC was 480 and 6580 $\mu\text{S}/\text{cm}$ (Table 1) and the highest values belonged to the western parts of the plain. The reason can be attributed to the lithological formations, composed of marl and evaporates (halite and gypsum). An abnormal increase in the EC may also be due to the presence of sodium chloride in the sediments of the lower red formations. The higher values of total dissolved solids (TDS) in groundwater were associated with high concentrations of all major ions.

A wide range of values for the major ions of Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- and SO_4^{2-} was found in the groundwater. The Cl^- concentration was obtained between 0.16 meq/L to 1465 meq/L with the mean value of 4.67 meq/L. High Cl^- content in the groundwater samples could also be caused by the upcoming or lateral flow of the outdated saline groundwater. Dissolution of minerals and long residence time of water together with irrigation and rainfall evaporation returns were documented as the main causes of the groundwater salinity (21). Salts are usually precipitated after short rainfalls and irrigation times, in which the water is removed by

evapotranspiration, while these salts are dissolved and leached into the subsurface during the large rain events or irrigation (2).

The high Sulphate (SO_4^{2-}) concentrations in groundwater could be associated with the dissolution of the mineral pyrite (FeS_2). It should be pointed out that Sulphur is widely distributed in both sedimentary rocks and igneous, as metallic Sulphides (22).

Table 2 renders the correlation coefficients between the major ions in the groundwater. High positive correlation (>0.70) with significance p-level of 0.05 was obtained to be between: Na^+ - Cl^- (0.90), Na^+ - SO_4^{2-} (0.95), Na^+ - Mg^{2+} (0.86), Na^+ - HCO_3^- (0.85), Mg^{2+} - Cl^- (0.70), and Mg^{2+} - SO_4^{2-} (0.83). Based on the statistical analyses, a strong correlation was found between ions of some charge with different valence number. At the same time, a relatively strong chemical correlation was observed between ions of some type of charge and different valence number (20). The coherence between ions could be utilized to determine the common (or no common) origin of the ions in the groundwater. It should also be said that the simultaneous changes (increase or decrease) in the groundwater ions was a sign of minerals dissolution. EC was extremely dependent upon the concentration of major ions including Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- .

Table 2. The correlation coefficients between the major ions in the groundwater.

	TH	SAR	Sum Cation	K ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	Sum Anion	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻	pH	TDS
TH	1												
SAR	.30*	1											
Sum Cations	.97**	.39**	1										
K⁺	.42**	0.11	.43**	1									
Na⁺	.84**	.49**	.94**	.38**	1								
Mg²⁺	.88**	.33*	.91**	.58**	.86**	1							
Ca²⁺	.95**	0.24	.88**	0.25	.70**	.68**	1						
Sum Anions	.97**	.39**	1**	.44**	.95**	.91**	.88**	1					
SO₄²⁻	.94**	.35**	.91**	.31*	.78**	.83**	.89**	.90**	1				
Cl⁻	.74**	.39**	.84**	.33*	.90**	.70**	.66**	.85**	.56**	1			
HCO₃⁻	0.21	-0.05	0.21	.62**	0.15	.43**	0.05	0.21	0.10	0.01	1		
pH	-	-0.14	-.35**	-0.2	-.32*	-0.25	-	-.37**	-0.24	-	-0.12	1	
TDS	.37**	.97**	.40**	.99**	.43**	.94**	.91**	.88**	.99**	.92**	.83**	0.20	-
EC	.95**	.41**	.99**	.43**	.94**	.90**	.86**	.99**	.91**	.83**	0.45**	-.32*	.35**
													1
													.99**

*Correlation is significant at the 0.05 level (2-tailed)
 **Correlation is significant at the 0.01 level (2-tailed).

To anticipate the spatial variation of the groundwater quality variables, the geostatistical method of the Arc GIS Software (Version 9.3) was applied. Diverse geostatistical approaches of Kriging, Co-Kriging, and IDW with powers of 1, 2, 3, and 4 were chosen to anticipate the spatial hydro-chemical parameters. According to the evaluation criteria, the Kriging strategy was found the best strategy to estimate the TDS parameters. Other parameters were determined by Co-Kriging Method. The spatial maps were also illustrated in the GIS environment.

Figure 3 demonstrates the spatial distribution of EC in the alluvial aquifer with an increase in the EC values towards the central and western parts (Fig. 3). This increase may be due to the presence of sodium chloride in the sediments of the lower red formations and the lithological formations composed of marls and evaporates (halite and gypsum), respectively. As expected, the total dissolved solid (TDS) followed a similar pattern. Figure 4 shows the spatial variation of Na⁺ (meq/L) using the Co-Kriging Method.

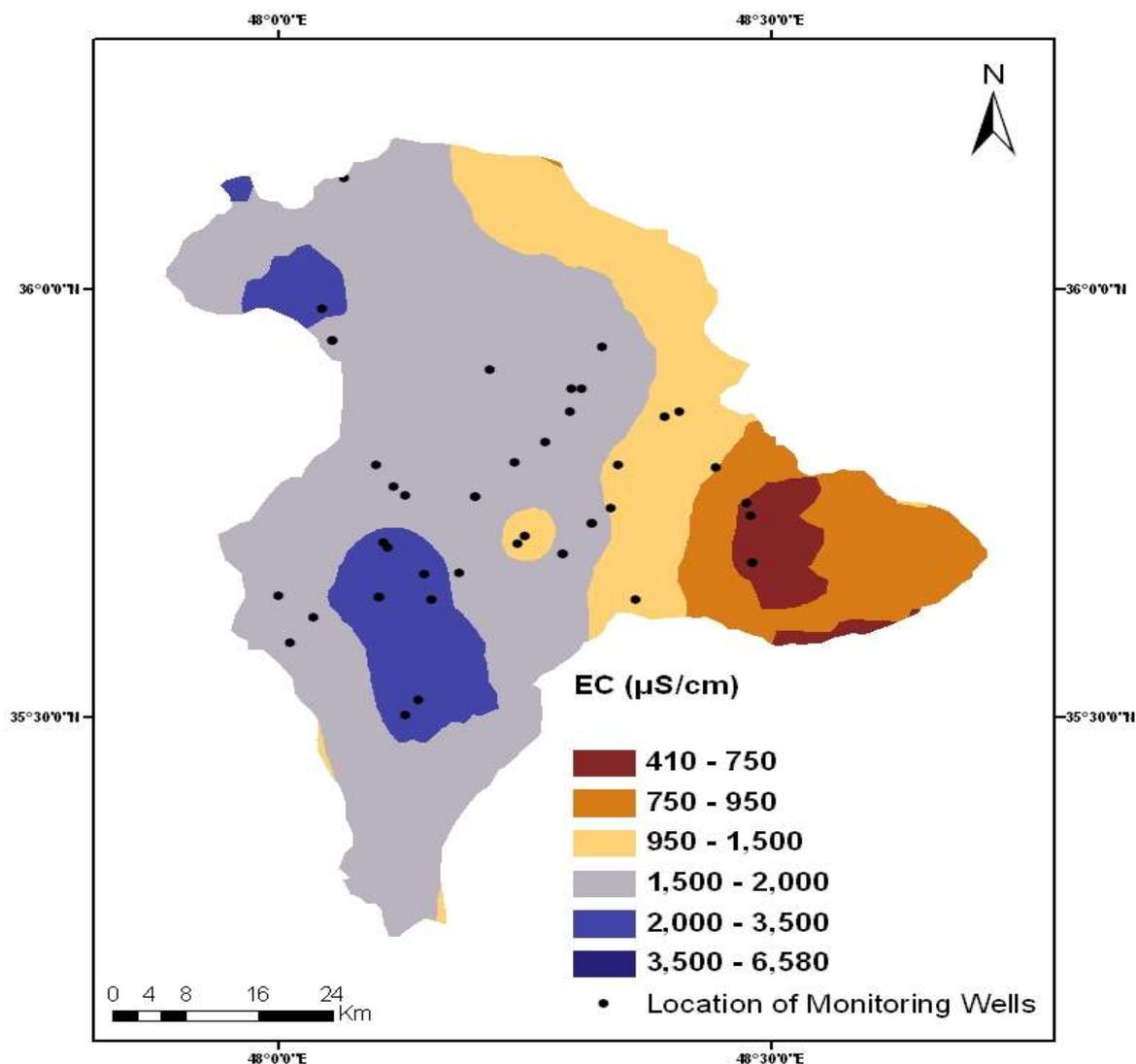


Figure 3. The spatial variation of EC ($\mu\text{S/cm}$) using Co-Kriging Method.

Figure 4 shows the spatial variation of Na^+ (meq/L) using the Co-Kriging Method. It was concluded that high sodium values were recorded in the eastern section of the basin, increasing along the groundwater flow. Regarding the sodium content (%Na) and SAR values, salinity took responsibility for the poor groundwater quality for irrigation application. Nevertheless, the majority of groundwater samples was relatively suitable for irrigation use with sodium content $\% \text{Na} < 35$ (21).

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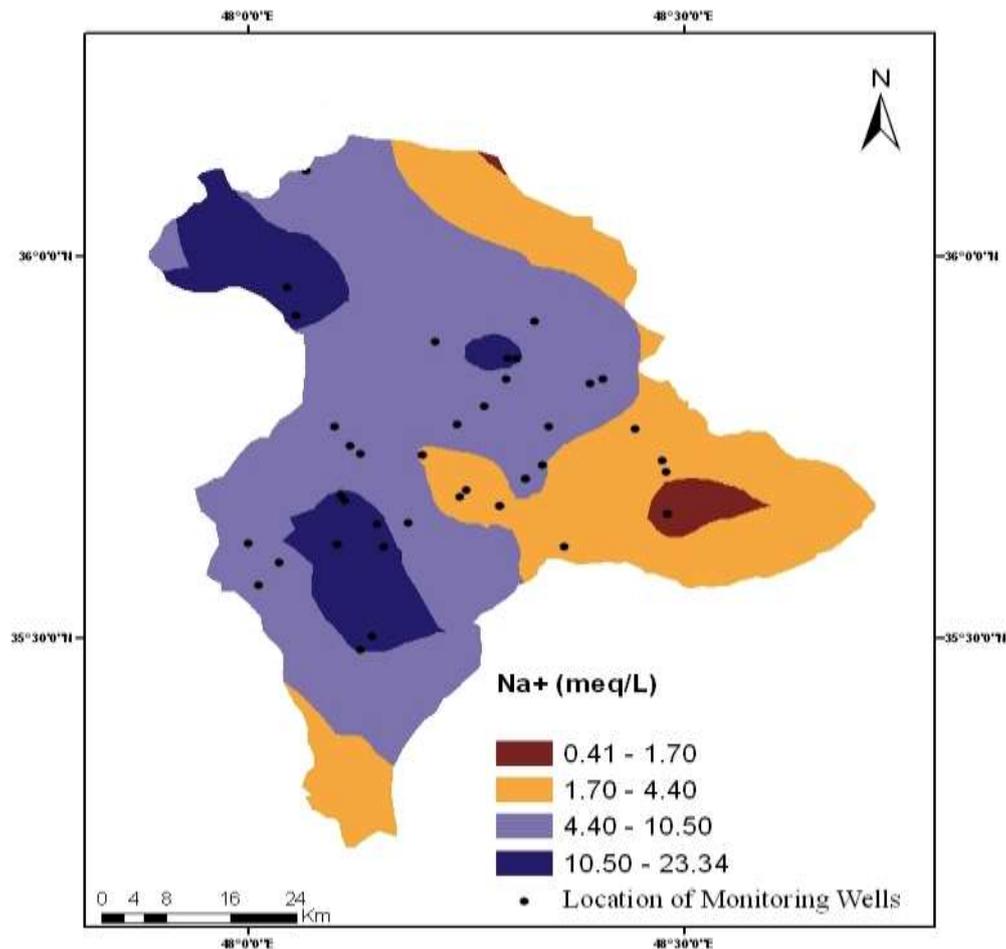


Figure 4. The spatial variation of Na^+ (meq/L) estimated Co-Kriging Method.

4. Discussion

Zarin Abad plain with semiarid climate conditions is posited in the western part of Iran, and its main aquifer is developed within the alluvial deposits. Unmanaged groundwater extraction, minimal annual rainfall, rapid evaporation, and transpiration have caused a serious water imbalance problem in the plain. Current research, therefore, was undertaken to clarify the groundwater quality conditions in the study area. The comprehensive assessment of the ever-deteriorating groundwater quality in this arid area, confirmed by geostatistics-based appropriate strategies for sustainable management of water resources in similar regions. The results indicated a complex

hydro-chemical evolution of groundwater, with wide ranges of concentration. The values of EC varied within the range of 480 and 6580 $\mu\text{S}/\text{cm}$. Higher EC values were recorded in the western parts of the plain and associated with the dissolution of minerals (halite and gypsum), and water long residence time.

The groundwater in study area was enriched by salinity, caused by longer residence time and entrapment due to the low permeable aquifer, which received low recharge (23). Additionally, an essential and significant reason for developing salinization of the groundwater was observed to be the lack of proper management of the irrigation amount and drainage systems, which leads to

infiltration of these waters from the salinized soils, induces evaporation and consequently accelerates degradation of the land resource via intense salt accumulation associated with the increase of clay content that may increase the crusting potential of soils. The spatial distribution of EC in the alluvial aquifer showed an increase in EC values towards the central parts (Fig.4). As expected, the total dissolved solid (TDS) followed a similar pattern. It was low in the recharge area and progressively increased towards the downward gradient part of the basin. Abnormal increase in electrical conductivity was a result of sodium chloride presence in the sediments of the Lower Red formations. Further, an increase in the value of EC in the eastern parts of the Basin can be attributed to the lithological formations composed of marl and evaporates (halite and gypsum). High content of fine sediments and dissolved materials led to the sudden changes in the salinity of some parts in the plains.

The pH fluctuation was recorded to be between 6.85 and 7.78, representing that groundwater is slightly changing from acid to alkaline state. The order of major cations and anions were $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$, respectively. High concentrations of all major ions appeared to be responsible for the increase in the total dissolved solids (TDS) in the groundwater. An increase of TDS was also recorded along the direction of groundwater flow (down-gradient part of the plain) due to the dissolution of minerals and long-lasting residence time of water. Based on sodium content (%Na) and SAR values, poor groundwater quality for irrigation use was caused by salinity. The eastern part of the plain (recharge zone) were also found to have better quality (low EC, TDS, SAR and Na^+ values). The results obtained from

Kriging, Co-Kriging, and IDW methods were evaluated by the error indices of RMSE and MAE. It appeared that the Co-Kriging Model was the most optimal approach in studying the spatial variation of groundwater quality parameters. The quality maps should be taken into account by local authorities and policy makers in order to drill new boreholes in suitable sites and design protection zones of groundwater quality. The results of this study was in good agreement with research in which Co-Kriging Method was found the best in evaluating the spatial variation of groundwater quality (4,6,12).

Acknowledgments

The authors would like to thank Bu-Ali Sina University for providing support for the present project (the approval code: 2437368). Authors would also thank the editor and reviewers for their valuable feedback.

Conflict of interest

The Authors have no conflict of interest.

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