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Zoning of Groundwater Contaminated by Nitrate Using Geostatistics Methods (Case Study: Bahabad Plain, Yazd, Iran)

Z. Kherad Pisheh^a, S.A. Almodaresi^b, Y. Khaksar^c, L. Rafati^{a*}

^a School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran ^b GIS & RS Department, Islamic Azad University, Yazd Branch, Yazd, Iran ^c Faculty of Dentistry, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

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Abstract

Groundwater quality management is one of the most important issues in many arid and semi-arid regions, including Iran. Nitrate (NO_3) is one of the most common anions contaminating groundwater. This study aimed to range nitrate concentrations in water resources in Bahabad plain in Yazd province. To evaluate the nitrate data in this descriptive study, 260 nitrate samples from 13 wells in Bahabad were assessed from 2003 to 2013. The two interpolation techniques of kriging and inverse distance weighting (IDW) were used to obtain the spatial distribution of groundwater quality parameters by means of Arcview GIS 10 software. The results of this study showed that the kriging method is more accurate than IDW for groundwater quality mapping, based on the lower root mean square error (RMSE) of kriging. Nitrate levels in samples from regional wells were lower than standard levels for Iran and the world. However, nitrate contamination tended to increase from 2003 to 2013. Furthermore, the greatest nitrate contamination was found in the southern part of Bahabad. In conclusion, kriging seems to be an appropriate method for estimating nitrate levels in groundwater nitrate action be taken in order to stop the increasing trend of groundwater nitrate contamination in this area.

Keywords: Groundwater; Nitrate; Kriging; IDW; Bahabad plain

1. Introduction

Groundwater contamination caused by industrial and agricultural development is a great concern in all societies. At present, most arid and semi-arid regions, such as Iran, are facing high nitrate concentrations in drinking water, the most important reason for which is the introduction of agricultural runoff and urban and industrial sewage to groundwater resources (Firat, Ersoy *et al.*, 2007). The Environmental Protection Agency (EPA) of the United States of America has set the standard limit of nitrate at 10 mg-N/L or 45 mg-NO₃/L (EPA, 2003). Iran's Institute of Standards

Fax: +98 351 6238555.

and Industrial Research (Standard 1053) has determined the maximum concentration level (MCL) of nitrate in drinking water to be 50 mg-NO₃/l (ISIRI, 2009). Consumption of nitratecontaminated water and high-nitrate-containing food stuffs can lead to the accumulation of high amounts of nitrate to the human body. It has long been established that high amounts of nitrate in water can result in diseases such as methemoglobinemia and specific cancers (Greer and Shannon, 2005; Bernaadt *et al.*, 1997; Gilli *et al.*, 1984).

One suitable way to prevent the contamination of groundwater is to identify the water table's vulnerable sites and manage water resources and land use. Despite the great importance of spatial variations in groundwater resource quality, this

Corresponding author. Tel.: +98 918 3334018,

E-mail address: l.rafati@yahoo.com

subject has not been given adequate attention. One of the most significant reasons for this shortcoming is the inability of traditional methods used in classic statistics to provide the required information about the spatial situation and local variation of groundwater resources. Recent advances in introducing and developing nonclassical methods such as geostatistics and definite methods have helped with this issue. Definite methods are based on determining levels from sample points and similarities (such as inverse distance weighting (IDW)) to the leveling degree (radial basis functions). The IDW method predicts the unknown quantity by weighting the data surrounding the prediction point and then interpolating it. It is assumed that points that are close to each other are likely to be more similar than those far from each other; therefore, the closer points have greater weights. The theoretical basis of geostatistics, including kriging, is that, contrary to definite statistical methods, data and observations are not random, but have a spatial correlation (Yamamoto, 2000; Mousavifazl et al., 2013; Burrough and McDonell, 1988).

Kriging, a generic name adopted by geostatisticians, refers to a family of minimumerror- variance estimation techniques (Yamamoto, 2000). This method provides unbiased, linear interpolation of a regionalized variable with a minimum mean interpolation error and correct reestimation. The first step in determining water quality with this method is to choose a suitable model to interpolate and range the data. The kriging estimation variances are only related to the spatial arrangement of the sample data and to the model variogram. Kriging is more flexible than other interpolation methods such as inverse distance weighing (IDW) and spline. In cases of normally distributed data, essentially no observation network is needed. Only neighboring points of estimation data are considered (Mousavifazl et al., 2013; Webster and Oliver, 2001; Oliver and Webster, 1990).

Numerous studies have explored spatial analyses, interpolation, and zoning methods all over the world (Gaus *et al.*, 2003; Barca and Passarella, 2008; Dayani *et al.*, 2010; Motaghian and Mohammadi, 2012; Jafari *et al.*, 2011). In recent years, various studies have been carried out in Iran to study the spatial change of quality and quantity properties of groundwater (Badeenezhad *et al.*, 2012; Abdolahimansorkhani *et al.*, 2012; FathiHafshejani *et al.*, 2013; Ostovari *et al.*, 2012; Mousavifazl *et al.*, 2013; Taghizadeh *et al.*, 2009).

While both kriging and IDW have shown themselves to be suitable, precise methods in terms of spatial interpolation (Mousavifazl *et al.*, 2013; Abdolahimansorkhani *et al.*, 2012; Ostovari *et al.*, 2012; Taghizadeh *et al.*, 2009), in most studies that compared kriging and IDW, kriging was found to be more accurate (Mousavifazl *et al.*, 2013; Abdolahimansorkhani *et al.*, 2012; Taghizadeh *et al.*, 2009). In only a few did IDW show more precision (Ostovari *et al.*, 2012).

As there is no study which investigates nitrate concentrations in the groundwater of the Bahabad plain in Yazd, this research aimed to range the contamination of groundwater resources with nitrate using kriging and IDW methods.

2. Materials and methods

2.1. Study area

The Bahabad plain is located in Yazd province in Iran's Central Plateau river basin. The geographical location of this plain is 56°20' to 56°56' east longitude and 31°40' to32°16' north latitude (Fig. 1). Its center is Bahabad city, located 85 km northeast of Bafq city. This city covers 8 km^2 and has an altitude of 1398 m above sea level. The annual long-term precipitation rate of the region is 55.1 mm; average temperatures are maximum 26°C and minimum 10°C. Bahabad plain has remarkable ground tables which are used for agricultural development, animal breeding, and drinking water. Due to the paucity of precipitation and overuse of water in the region, the withdrawal of groundwater is 25 cm annually, which creates an annual regional underground water deficit of 8-12 million m³ (WRS, 2014).

2.2. Data collection and analysis

This research is a descriptive study in which 260 nitrate samples from 13 wells in the Bahabad plain were assessed from 2003 to 2013. Kriging and IDW methods were used in Arcview GIS 10 software.

This research was carried out in two stages: providing initial data and entering data to geographical information bank. First, geological, hydrological, and hydrogeological data was collected, namely a topography map, satellite images, geological map, precipitation information, evaporation, well stratigraphic column, static level depth, land use map, table hydrodynamic coefficient, bedrock depth map, sampling results, and determination of nitrate ion concentrations of wells in the Bahabad plain. Having collected the

data from the respective organizations, we organized and entered it into Arcview GIS10.



Fig. 1. Location of study region (Bahabad case study)

Kriging is known as the best linear unbiased estimator. In order for the kriging method to be used, the Z variable must have a normal distribution; otherwise, the nonlinear kriging method must be used or the variable distribution will be normalized. The general relationship of kriging is as follows:

$$Z * (xt) = \sum_{t=1}^{n} \lambda t Z(xt) \tag{1}$$

where Z is the estimate value of the variable in position λi , xi is the weight related to ith sample, Z is the observed value of its variable, and n is the number of observations.

The IDW method predicts the unknown quantity by weighting the data surrounding the prediction point and interpolating it. It is assumed that points that are closer to each other are likely to be more similar than those that are farther away. Therefore, the closer points have greater weights.

Root mean square error (RMSE) (Eq. 2) was also used to compare the accuracy of kriging and IDW interpolation methods.

$$RMSE = \frac{1}{n} \sqrt{\sum_{t=1}^{n} (z^{*}(xt) - z(xt))^{2}}$$
(2)

3. Results

The results of sampling regional wells showed that the nitrate levels were lower than the world standard and equal to Iran's standard (EPA, 2003; WHO, 2008; ISIRI, 2009); however, the trend of nitrate contamination tended to increase during 2003-2013 (Table 1).

Table 1. The average of nitrate content (mg/l) in different locations and years (Water and Wastewater Company of Yazd province)

					Year						
zone	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Zakoye	2.4	2.8	5.2	8.4	9.8	9.5	10	10.4	11.4	12.4	12.8
Ahmadabad	2.6	4.4	5.6	5.2	10.4	10.5	10	11.2	11.6	12.4	12.6
Darbhamzeh	1.4	5.6	6.2	9.6	9.6	10.8	10.5	11	12	13	13.6
Karimabad	-	4	4.2	9.6	9.6	10.4	10.4	10	11.4	12.4	13.4
Sherkatemeka	1.4	2.4	4	9.5	9.6	9.8	9.5	9.6	10	12.4	12.5
Azimabad	1.4	4	5.6	7.6	9.6	9.5	9.4	10.6	11	12.5	12.6
Rajaei	2.4	2.8	5.6	7.2	9.5	9.4	10.2	10.6	11.6	12	13.2
Jalili	1.4	4	6.4	7.5	8.6	9.5	10	10.4	11.6	12.6	13
Niestan	4	4.4	5.2	9.6	9.8	10	11	11.5	12.6	13.2	14.6
Pirboshkan	2.4	2.8	5.2	9.5	12.8	12.8	11	14.6	15.4	6.4	15.4
Beheshtabad	1.4	4	7.6	8.4	9.9	10.2	10.5	10.8	11.2	12.4	14
Hoseinabad	2.4	4.4	4	5.6	9.6	10	11.5	11.8	12	12.5	14
MortezaaliAsfij	4	4.4	5.2	5.8	6.6	8.2	9.6	10	11.5	12.5	13.2
Ave	2.26	3.84	5.38	7.96	9.64	10.04	10.27	10.96	11.79	12.05	13.45
Max	4	5.6	7.6	9.6	12.8	12.8	11.5	14.6	15.4	13.2	15.4
Min	1.4	2.4	4	5.2	6.6	8.2	9.4	9.6	10	6.4	12.5

As seen in Figure 2, the greatest nitrate contamination was found in the south part of the Bahabad plain. The Bahabad contour, and the wells and nitrate zonation of the Bahabad plain obtained by means of kriging are shown in Figures 2 and 3, respectively.

Figures 4 and 5 show the zoning of nitrate contamination in groundwater of the Bahabad plain by kriging and IDW methods, respectively.

Root mean square error (RMSE) was used to compare interpolation methods and select the best estimation method. Both kriging (RMSE= 0.009) and IDW (RMSE=0.02) methods estimated the amount of nitrate with good accuracy, but the kriging method was more accurate.

4. Discussion

As mentioned, all samples from the Bahabad plain had nitrate levels lower than the world standard maximum concentration and equal to Iran's standard (EPA, 2003; WHO, 2008; ISIRI, 2009); however, the nitrate contamination in the region tended to increase during 2003-2013. This annual increase might be due to the grade effect of concentration in well domains. The highest nitrate concentrations were always seen in the south part of the Bahabad plain in the Beheshtabad, Niestan, and Pirboshkan wells. The rate of nitrate in groundwater may be influenced by sewage and the physical characteristics of regional soil such as soil type, bedrock type, well depth, well structure and its domain. Lack of quality control for the water, flow gradient from up sites to wells, and inappropriate location of wells in the plain can also be influential factors of increasing nitrate concentration in wells (Firat, Ersoy *et al.*, 2007). Accordingly, the higher nitrate concentrations found in the south of this plain might be due to the presence of the newly-built town, the intensive farming in that region, and the flow gradient to the south of the Bahabad plain. The results of our study showed that kriging has a lower RMSE and as a result is more accurate.

In their study, Badeenezhad et al. (2012) evaluated nitrate concentrations in groundwater from Shiraz (Iran) by means of ArcView GIS 9.3. This study included 220 groundwater samples from a total of 55 Shiraz plain wells taken in the dry and wet seasons. Results of this study showed that nitrate concentrations in 60% of the samples were higher than the threshold value of 20 mg/L as nitrate. They also demonstrated that as well depth increased, nitrate concentrations decreased. Furthermore, the nitrate concentration tended to increase from west to east of the city of Shiraz. The similarities in average nitrate concentrations in wet and low precipitating seasons might be due to the fact that the external surface soil of the impenetrable; plain was therefore. the precipitation rate could not show a remarkable effect on feeding the plain, depleting the nitrate concentration and annual variations.

Ostovari *et al.* (2012) assessed the spatial variability of nitrate in 32 wells of the Lordegan aquifer during 2010. Their results showed that seasonal nitrate concentrations were always below

the WHO limit. The IDW method had lower RMSE and higher R^2 in this aquifer compared with kriging. Therefore IDW was utilized for zoning the aquifer. According to IDW mapping, the southwestern part of the aquifer always had the least concentration of nitrate (4 mg/ml).



Fig. 2. Location of wells in Kavire Lot subbasin (Bahabad case study)



Fig. 3. Plot of contour lines and well positions of the Bahabad plain



Fig. 4. Zoning of nitrate contamination of groundwater by kriging in the Bahabad plain



Fig. 5. Zoning of nitrate contamination of groundwater by IDW in the Bahabad plain

The highest nitrate concentrations (19 mg/l) were always seen in the northern part of the aquifer (near Khardan village), which can with high probability be related to the leaching of nitrate from agricultural soils and the presence of

shale and marl formations which contain either nitrate or ammonium.

Mousavifazl *et al.* (2013) evaluated geostatistical methods for estimating spatial variables, including nitrate and sodium, in the groundwater of 276 wells in Mashhad (Iran).

According to their results, both kriging and IDW methods had good precision in estimating the amount of nitrates; however, the kriging method was more accurate and had less estimation error. Their results also indicated that kriging could be more appropriate based on its root mean square error (RMSE) in comparison to non-geostatistical methods (inverse distance weight and normal distance weight). Furthermore, sodium and nitrate concentrations were shown to be higher than the limit (even greater than 50 mg per liter) in a certain part of the scope of this study according to the sodium and nitrate maps drawn based on the kriging method.

Abdolahimansorkhani *et al.* (2012) employed spatial interpolation methods including kriging, co-kriging, inverse distance weighting, and radial basis functions to evaluate the spatial distribution of nitrate in 56 wells in Shahrekord, Iran. According to their results, kriging was the most accurate method for modeling nitrate spatial distribution because of its minimum RMSE. The map of nitrate spatial distribution in groundwater was prepared by means of ordinary kriging.

In a study by Taghizadeh *et al.*, (2009) the spatial variation of water quality characteristics using kriging, co-kriging and IDW interpolation methods in Rafsanjan, Iran were evaluated. According to the results of this study, kriging and co-kriging methods were more suitable than the IDW method.

FathiHafshejani et al. (2013) evaluated the spatial variability and mapping of nitrate and phosphate in 100 agricultural wells of Shahrekord (Iran) groundwater from 2006 to 2011. According to the results of their study, the mean concentration changes over this period were 18 to 27 mg/L and 0.05 to 0.15 mg/L for nitrate and phosphate, respectively. The higher concentrations of nitrate and phosphate in the south part of the aquifer in this study might be caused by the presence of the municipality treatment plant, intensive cattle farming. shallower water-table, and the inward flow gradient in this area.

Mixing water that has a low nitrogen concentration with regional water resources and installing a suitable purification system for drinking water can help in reducing the nitrate concentration in the Bahabad plain.

5. Conclusion

According to the results of the current study, kriging seems to be more appropriate than IDW for estimating the nitrate content in the groundwater of the Bahabad plain. The increasing trend of groundwater nitrate, although still lower than the standard level, may become a great concern if nothing is done to reduce it.

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