Application of geostatistical methods for mapping groundwater phosphate concentration in Eyvan plain, Ilam, Iran

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Abstract
The purpose of this study was to evaluate the spatial changes of groundwater phosphate concentrations using geostatistical methods based on data from 10 groundwater wells. One of the conventional tools in decision making on the groundwater management is geostatistical method. To evaluate the spatial changes of phosphate concentrations in groundwater, the universal kriging method with cross-validation was used for mapping and estimating groundwater phosphate concentrations in Eyvan Plain, Iran. Phosphate concentration followed a log-normal distribution and demonstrated a moderate spatial dependence according to the nugget ratio (60%). The experimental variogram of groundwater phosphate concentration was best-fitted by a spherical model. Cross-validation errors were within an acceptable level. According to the spatial distribution map, phosphate pollution in the groundwater occurred mostly in the west of the plain because of the phosphate discharge from the industrial effluents.

KEYWORDS: Decision-Making, Groundwater, Phosphate, Spatial Analysis, Water, Iran

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Introduction
Water resources are poorly renewable for agriculture and other activities and it is crucial to conserve them worldwide. Among the parameters used for water quality definition, phosphate content is of primary importance. Phosphate is the most frequently introduced pollutant into groundwater systems. Ground water and surface waters contamination with phosphate usually originates from diffuse sources, such as intensive agriculture, and can pose risks to human health and the environment. Hence, agriculture stands as the most commonly correlated land use with phosphate contamination of groundwater. High rate of application of chemical and organic fertilizers are attributed to the severe phosphate contamination. Moreover, in addition to an abundant fertilization, the agricultural irrigated areas have considerable potential for contaminating groundwater because the crops are occasionally over-watered. As a response to this threat, the European Union (EU) has adopted the Phosphate Directive (91/976/EC), which imposed Member States to take measures to protect water against pollution caused by phosphate from agricultural sources, and to implement these measures within the identified phosphate vulnerable zones. As a consequence, where groundwater features may be altered permanently due to anthropic disturbance, it is essential to identify the

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areas with an inherent sensitivity to pollution. This allows a correct land planning, and a good agronomic intervention scheduling through the implementation of Best Agricultural Management Practices. The maximum allowable concentration conforming to WHO guideline is 50 mg/l. Since the criteria for the designation of phosphate vulnerable zones (that undergo limitations in agricultural practice) cannot be univocally established, testing rapid and cheap methodologies for decision support is crucial.

Geostatistics provides a set of statistical tools for analyzing spatial variability and spatial interpolation. This technique generates not only prediction surfaces but also error or uncertainty surfaces. A semivariogram is used to describe the structure of spatial variability. The semivariogram plays a central role in the analysis of geostatistical data using the kriging method. The spatial autocorrelation is considered in data to create mathematical models of spatial correlation structures commonly expressed by variograms. Kriging provides the best linear unbiased estimation for spatial interpolation.

Geostatistical methods are integrated with GIS environment, making spatial changes evaluated more easily and quickly. GIS is potentially powerful in gathering and investigating several variables to support decision making. Geostatistics is a technique for saving time, money, effort, and spatializing the characteristics of the area through using the relationships between the parameters in parallel with the advances in the computer technology. Today, geostatistics is increasingly combined with GIS software for modeling groundwater, soil mapping, and respective commercial domains.

Thus, the purposes of this paper were to analyze the spatial pattern and to map phosphate and phosphate concentration for the observation period; and to evaluate distribution of phosphate concentration with geostatistical methods in the Eyvan Plain, Iran.

Materials and Methods

Using quantitative measures of spatial correlation, i.e. variograms, is one of the merits of geostatistics. The semivariogram is a basic tool in geostatistics. The empirical semivariogram (γ (h)) is defined as half the average quadratic difference between two observations of a variable separated by a distance vector h. It is calculated according to equation 1:

\[ γ \ (h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (Z(x_i) - Z(x_i + h))^2 \]  

Where, γ (h) is the semivariogram value at the distance h; N (h) is the total number of the variable pairs that separated this distance, and Z (x) is the value of the variable.

A variogram is calculated for classes of distance between sample pairs before the geostatistical estimation. The main models used are spherical, exponential, Gaussian, and pure nugget effect. Cross-validation is a technique used for the validation and the sufficiency of the developed model variogram. Its estimation is obtained by leaving one sample out and using the remaining data. This test allows to assess the type of kriging used, the appropriateness of neighborhood, and the goodness of fitting of the variogram model. The interpolation values are compared with the real values and then the least square error models are selected for regional estimation.

Kriging method is used for linear optimum appropriate interpolation with a minimum mean square error. It is believed that one of the main gains of kriging is its capability in presenting the possibility of interpolation of estimation error of the regionalized variable (ReV), where there are no initial measurements. This feature offers a measure of the estimation precision and reliability of the spatial variable distribution. The general equation of the kriging method is as follows (Equation 2):

\[ Z^*(x_p) = \sum_{i=1}^{n} \lambda_i Z(x_i) \]
The model parameters (range and sill variance) describe the structure of spatial variation and are used for estimating at unsampled locations. A nugget variance parameter is common for a sample of continuous variable. Measurement error and stochastic variation in data contribute to the nugget; the largest source of variation is commonly due to spatially dependent variation that occurs over distances much smaller than the shortest sampling interval. When the difference between samples in space is at a maximum for the average separation distances, the sill variance is reached and the model is bounded. The lag distance at which the variogram reaches its sill is the range, which indicates the limit of spatial dependence.\(^{21}\)

In the present study, the groundwater phosphate concentrations were collected in April 2015 from 10 observation wells for geostatistical analysis. Sampling was carried out twice according to the method described by WHO.\(^{22}\) The mean value of measurements was used as input data. Calculation of experimental variograms and modeling of spatial variability of groundwater phosphate concentrations were performed using the Geostatistical Analyst integrated into ArcGIS (Version 10.1) software.

**Study area**
The Eyvan Plain is geographically situated between 41.31º North latitudes. It is located in the north west of Ilam (Figure 1). The average area is about 453 km\(^2\).

**Results and Discussion**
The interpolation method was used to generate a surface giving the best results if the data is normally distributed. To determine whether the groundwater phosphate concentrations followed a normal distribution, the related testing methods were used.

![Figure 1. Location map of the study area and sampling stations](http://jaehr.muk.ac.ir)
Table 1 summarizes basic statistics of the groundwater phosphate concentrations. The skewness values in the first line were obtained without making any transformation on the phosphate concentrations values. If these values are close to zero, this means it has normal distribution. In table 1, skewness values in the first line are not close to 1. In order to adjust the phosphate concentrations values to the normal distribution, log-transformation was made and the histogram was formed again. Skewness values for the obtained histogram are listed in the second line in table 1. Thus, it was concluded that the data matches the normal distribution using log-transformation.

A Q–Q plot is a plot of the quantiles of two distributions against each other, or a plot based on estimates of the quantiles. The pattern of points in the plot is used to compare the two distributions. In this study, as shown in figure 2, there was a considerable deviation from the straight line in the untransformed data plots. The linearity of the points suggests that the data are normally distributed.

The trend analysis can help to identify global trends in the input datasets and provides a three-dimensional perspective of the data. The points projected onto the perpendicular planes were east and south. The east and south concentration of this parameter was reduced; this reduction was significantly linear. That is, it was observed that the data exhibited a trend using the ArcGIS Trend Analysis tool (Figure 3). Hence, universal kriging was used because universal kriging is only used for those exhibiting a trend.

The performance of five models (circular, spherical, tetra-spherical, exponential, and Gaussian) were compared. According to the cross-validation parameters, generally all five models performed fairly well. As root mean square standardized (RMSS) prediction error of spherical isotropic model is close to 1, this model was best fitted model among other models (Table 2). The model fitted to experimental variogram was spherical as the cross-validation indicated. Nugget-sill rate can be used in the classification of the spatial dependency. If the nugget-sill rate of a variable is less than 0.25, it can be said that it has a strong spatial dependency and if the rate is between 0.25 and 0.75, it can be said that the variable has moderate dependency.

Table 1: Basic statistics of the raw phosphate data and the log-transformed data

<table>
<thead>
<tr>
<th>Variable</th>
<th>Count</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>SD</th>
<th>Skewness</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw phosphate data</td>
<td>10</td>
<td>0.1</td>
<td>1.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.69</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Figure 2. Probability-probability plots of groundwater phosphate concentrations
Otherwise, it can be concluded that the variable has a weak dependency. In this study, the calculated nugget-sill ratio was 0, indicating moderate dependency. The semivariogram model and some geostatistical parameters are shown in figure 4 and table 3, respectively.

Table 2. Prediction errors of the groundwater phosphate concentrations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Prediction error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.26</td>
</tr>
<tr>
<td>RMSS</td>
<td>0.54</td>
</tr>
<tr>
<td>ASE</td>
<td>2.77</td>
</tr>
</tbody>
</table>

RMSS: Root mean square standardized; ASE: Asymptotic Standard Error

As it was mentioned above, universal kriging method is used in such studies for the estimation of the groundwater phosphate concentrations. Figure 5 shows the spatial distribution map of the values of kriged groundwater phosphate concentrations.

Mapping groundwater phosphate concentration provides strategically important information in the struggle to control the spread of chemical contaminants. From the spatial distribution map of groundwater phosphate concentration, it can be noticed that the highest groundwater phosphate concentrations occur in the west of the plain. The lower values of groundwater phosphate concentrations were located at the center and east of the plain. As figure 5 presents, the values in the study area were below the limit values revealing no health risk in this regard. The field observation indicated that agricultural activities are important factors for increasing of phosphate in the area. However, the acceptable and accurate data linking phosphate concentration to the geological and soil characteristics are not available for the study area, which is one of the gaps and limitations in this study. Moreover, the water samples were taken twice because of the financial limitation otherwise a more reliable and accurate data could be achieved.

As it was mentioned above, universal
Table 3. Semivariance parameters for the groundwater phosphate concentrations

<table>
<thead>
<tr>
<th>Model</th>
<th>Nugget</th>
<th>Sill</th>
<th>Range</th>
<th>Nugget/Sill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>0</td>
<td>0.774</td>
<td>15557 m</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 5. Spatial distribution map of groundwater phosphate concentrations

Conclusion

This study attempted to predict the spatial distribution and uncertainty of groundwater phosphate concentration in the Eyvan Plain, Ilam, Iran. Universal kriging, a type of geostatistical techniques, was applied to the groundwater phosphate concentrations data for a distribution map. Groundwater phosphate concentrations were log normally distributed. The spherical model was found to be the best model representing the spatial variability of groundwater phosphate concentrations. The average value of the variograms for the spatial analysis was approximately 15.557 km in the spherical model. Phosphate pollution in the groundwater occurred most in the west of the plain because of the phosphate excess from industrial effluents. As a solution, the groundwater quality can be saved from phosphate pollution by treating the industrial wastewater. The modeling results indicated that the kriged groundwater phosphate concentrations were satisfactorily matched the observed groundwater phosphate concentrations.

Conflict of Interests

Authors have no conflict of interests.

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