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# ASSESSMENT OF NITRATES CONTAMINATION IN TOPSOILS OF BABAGORGOR WATERSHED, WESTERN IRAN

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**ABSTRACT**

The objectives of this study were to identify spatial variability and main sources of $NO_3^-$ in rural soils of Northern Ghorveh. Influences of topography, land use and soil properties on $NO_3^-$ concentrations were investigated. A total of 87 composite soil samples were collected in an area of about 1352 $km^2$. The average concentrations of the analyzed nitrates in topsoil were 8.373 mg /kg. In addition, the pH, organic matter (OM), cation exchange capacity (CEC), soil grain sizes and $CaCO_3$ were measured for each sample. The results indicated that land use had significant effect on $NO_3^-$ concentrations. The experimental variogram of $NO_3^-$ has been fitted with an exponential model. The mapping showed the highest contents of $NO_3^-$ found in northern and southern parts of the watershed which is along the main water channel or irrigated farming.

**Keywords:** nitrates, soil contamination, GIS, rural soils.

## 1. INTRODUCTION

Nitrogen is a vital nutrient to enhance plant growth. This fact has motivated the intensive use of nitrogen-based fertilizers to boost up the productivity of crops in many regions of the world (Laftouhi *et al*., 2003). Nitrate ($NO_3^-$) contamination of water resources is an increasing problem in many agricultural areas around the world. $NO_3^-$ is highly soluble in water and has low retention in soil due to its negative charge. It is believed that the major contribution of nitrate to groundwater is derived from the application of nitrogen fertilizer to agricultural lands. When the human body takes high quantities of nitrate via drinking water and food meals, it may cause health disorders such as intestinal cancer and methemoglobinemia.

Nitrate is also related to environmental problems including Eutrophication of fresh waters and depletion of the ozone layer. Elevated nitrate concentrations in surface water can cause qualitative changes in algal communities, for example, from diatoms to blue-green algae which is often toxic to humans (Koo and Connell, 2006).

Direct determination of nitrate in soil is required for improving N-application management and reducing environmental pollution (Roblin and Barrow, 2000; Robert, 2002). Identification of regions under the risk of $NO_3^-$ contamination is an important step in deciding on appropriate alternative management practices to protect aquifers (Masetti *et al*., 2008). Geostatistics is used to determine the hot spots where nitrate concentrations exceed the predetermined threshold value in groundwater. Kriging, an interpolating technique, can be used for this purpose. Kriging technique can provide a map of spatial distribution of a variable across a study area by taking spatial structure into account. This spatial structure, explained by a semivariogram, shows how the variability of a variable increases with the distance (Flipo *et al*., 2007).

This study was conducted in agricultural lands of northern Ghorveh to (1) assess the spatial distribution patterns of $NO_3^-$ in the study area, (2) evaluate the effects of different land uses on the concentration of $NO_3^-$ and (3) evaluate the effect of soil properties on the concentrations of $NO_3^-$ on a regional scale.

## 2. MATERIALS AND METHODS

### 2.1. Study area

#### 2.1.1. Location and land use

The study area is located between 47° 32´ and 48° 11´ E in longitude and between 35° 05´ and 35° 30´ N in latitude and situated 6 km from northern Ghorveh county in Kurdistan province, western Iran; the total area is 1352 $km^2$. This area is characterized by cold, snowy winters and a Mediterranean climate with an average annual rainfall of 480 mm (for the period 1993 to 2003 at Ghorveh Station), and the average annual temperature is about 6.13°C. The land is traditionally associated with agriculture and residential uses (of the total area: orchard: 2.15%; irrigated farming: 1.1%; dry farming: 83.1%; rangeland: 13.25%; and residential: 0.389%) see figure 1b. The agricultural lands north of Ghorveh are well known for wheat production. The study area map and sampling sites are shown in Figure-1(a).

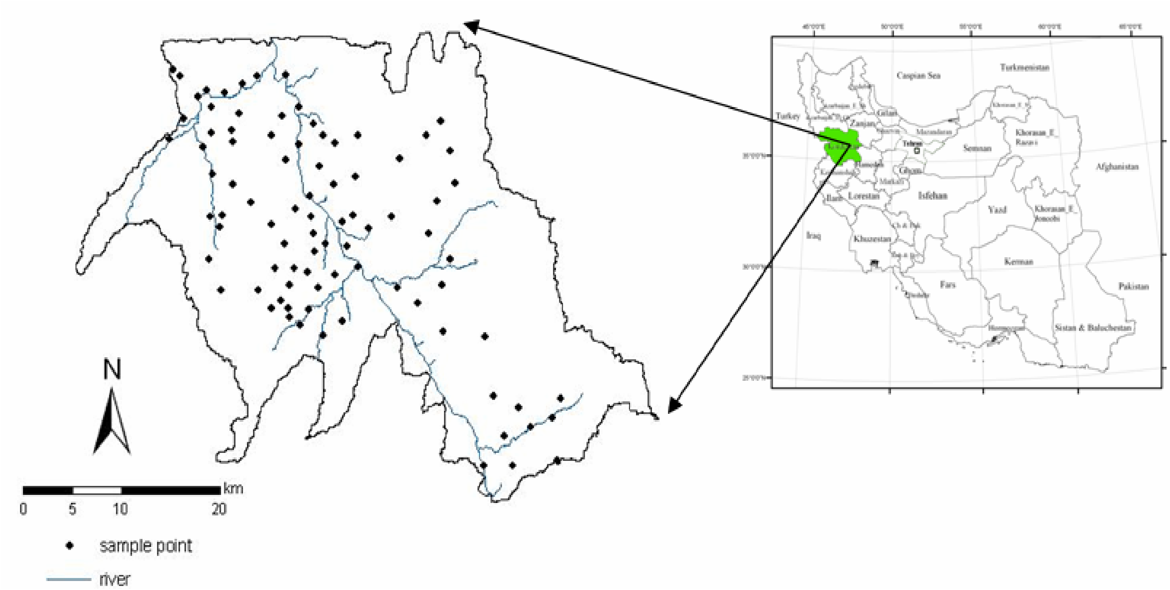


**Figure-1(a).** Soil sampling locations in northern Ghorveh, west of Iran.

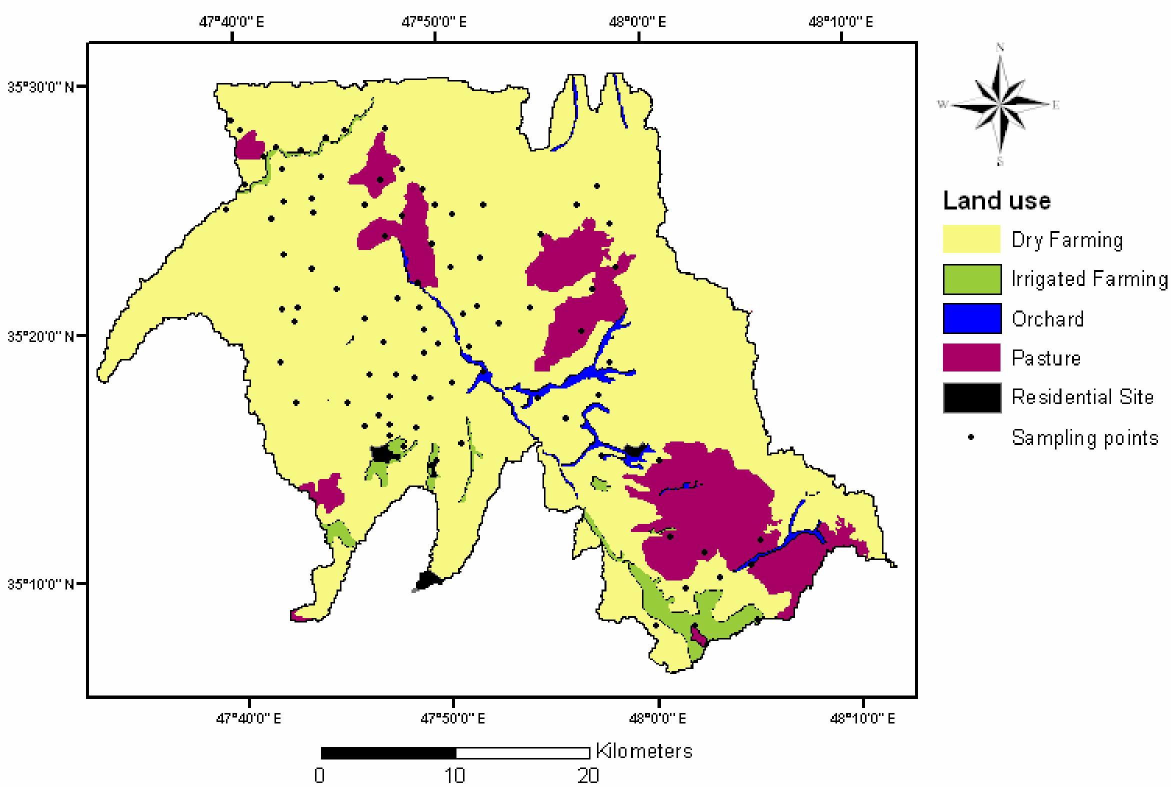


**Figure-1(b).** Land use map of the study area.

**2.2. Soil sampling and laboratory analysis**

Eighty-seven topsoil samples (0-20 cm in depth) were collected from the study area in September 2010 at intervals of 3 km. During the soil sampling, the planned regular sampling of 3 × 3 km was not possible to be followed accurately because of topographical problems and mountainous terrain of the study area, but care was taken to preserve a uniform distribution of sampling sites as possible. At each sampling point, five sub samples were taken from the four corners and the center of a rectangular block and mixed to achieve a composite soil sample. The sub samples were mixed into one composite sample for

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each soil and were analyzed in triplicate. A global positioning system (GPS) was used to precisely locate every sampling site (latitude and longitude). About 1.5 kg of each sample was stored in a polyethylene package and transported to the laboratory.

All of the samples were air-dried and grounded to pass through a 2 mm sieve. The soil samples were digested by aqua regia with a mixture of nitric and hydrochloric acids according to the 3050B method of the United States Environmental Protection Agency (USEPA, 1996). Nitrate was determined by the sulphanilamide method on autoanalyser following extraction of 100 g frozen soil crushed to 2 mm with 200 ml 1 M KCl for 2 h (Keeney and Nelson, 1982). The soil organic matter was determined by the Walkey-Black method (Schnitzer, 1982). The soil pH was determined by a pH meter with a soil/water ratio of 1:2.5. The cation exchange capacity (CEC) was measured using 1 mol/L ammonium acetate solution. Soil grain sizes (sand, silt and clay) were measured by hydrometric method.

### 2.3. Statistical and Geostatistical analysis

Some fundamental statistical parameters, which are generally accepted as indicators of the central trend and data spread, were analyzed, including the mean, standard deviation, variance and maximum and minimum values. The Kolmogrov-Smirnov (K-S) test, skewness and kurtosis were applied to assess normality of the data set.

Geostatistics uses the technique of variograms to measure the spatial variability of the recognized variable and to provide the input parameters for the spatial interpolation of kriging (Webster and Oliver, 2001). Kriging has been widely used as an important interpolation method at different scales, especially in soil pollution (Chen *et al*., 2008). The semivariogram $\gamma$ (h) measures the mean variability between the two points x and x + h, as a function of their distance h, for data located at discrete sampling locations. The semivariogram is an autocorrelation statistic defined as follows (Isaaks and Srivastava, 1989):

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

where Z(xi) represents the measured value of the soil property at location of xi, r(h) is the variogram for a lag distance h between observations Z(xi) and Z(xi + h), and N(h) is the number of data pairs separated by h. The variogram model is chosen from a set of mathematical functions that describe spatial relationships. The appropriate model is chosen by matching the shape of the curve of the experimental variogram to the shape of the curve of the mathematical function.

The fitted model provides information about the spatial structure as well as the input parameters such as nugget, sill and range for kriging interpolation. By fitting the appropriate variogram model, the distance-dependent coefficients can be estimated and graphically interpreted. In this study, to make distribution maps, several spatial interpolation techniques, such as kriging, global/local polynomial interpolation (G/LPI), inverse distance weighting (IDW) and radial basis functions (RBF), were evaluated for the best results. We used kriging (ordinary kriging) as a spatial interpolation technique to make distribution maps because it is very flexible and allows users to investigate graphs of spatial autocorrelation. It also allows for prediction, prediction standard error, and probability maps, and at the same time, it minimizes the error of predicted values.

The statistics of the differences between the measured and predicted values at the sampled points is often used as an indicator of the performance of an inexact method (Burrough and McDonnell, 1998). For the evaluation of the simulation quality and the model-experiment comparison of the different model approaches, cross validation indicators and additional model parameters can be used. In this paper, to compare these models, cross validation was performed using the statistical parameters of mean error (ME), root mean square error (RMSE), average standard error (ASE), mean standard error (MSE), and root mean squared standardized error (RMSSE) (Robinson and Metternicht, 2006).

The statistical analysis was performed using Microsoft Excel (Version 2003) and SPSS (V.15) software package (SPSS Inc., Chicago USA) for Windows. Geostatistical analysis and spatial distribution using ordinary kriging were performed with GIS software ArcGIS V.9.3 (ESRI Co, Redlands USA).

## 3. RESULTS AND DISCUSSIONS

### 3.1. Descriptive statistics

The main soil properties and $NO_3^-$ in the soil are summarized in Table-1. The average values for the seven soil properties were 22.197%, 0.928%, 8.379, 46.172%, 42.152%, 11.68% and 11.084 cmol +/kg for CaCO3%, OM%, pH, sand%, silt%, clay% and CEC, respectively. The mean value for $NO_3^-$ was 8.373 mg/kg.

Table-1 presents the summary statistics of the datasets for soil and terrain properties, including the NO3- concentrations. The analysis showed that $CaCO_3$, OM, pH, sand and CEC passed the Kolmogorov-Smirnov normality test (K-S $p< 0.05$), but $NO_3^-$, silt and clay did not pass. Because further geostatistic analysis would need data to follow a normal distribution, data transformation was carried out on the $NO_3^-$ prior to the next analysis. In our study, the log transformation was used to make the data more normal and less skewed (Webster and Oliver, 2001).

**Table-1.** Statistical summary of $NO_3^-$ concentration (mg/kg), soil and terrain properties.

| | $NO_3^-$ | $CaCO_3$ % | OM% | pH | Sand % | Silt % | Clay % | CEC[C] | Elevation | Slope % |
|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 8.373 | 22.196 | 0.92760 | 8.3795 | 46.172 | 42.152 | 11.68 | 11.084 | 1806 | 4.4597 |
| Std. Deviation | 7.291 | 11.041 | 0.41616 | 0.1698 | 13.910 | 10.346 | 7.071 | 2.6514 | 82 | 3.6989 |
| Minimum | 0.67 | 0.625 | 0.033 | 7.80 | 11.4 | 13.4 | 2 | 3.880 | 1689 | 0.353 |
| Maximum | 34.24 | 48.375 | 2.129 | 8.98 | 82.0 | 65.6 | 45 | 15.758 | 2039 | 25.598 |
| Skewness | 2.034 | -0.036 | 0.175 | -0.148 | 0.346 | -0.362 | 1.770 | -0.340 | 1.095 | 2.882 |
| Kurtosis | 3.758 | -0.194 | -0.039 | 3.385 | -0.112 | 0.206 | 4.862 | -0.233 | 0.917 | 12.443 |
| K-Sp a | 0.004 | 0.958 | 0.930 | 0.214 | 0.827 | 0.045 | 0.042 | 0.851 | - | - |
| K-Sp Log[b] | 0.056 | - | - | - | - | - | - | - | - | - |
| CV (%) | 87.1 | 49.74 | 44.86 | 2.02 | 30.13 | 24.54 | 60.54 | 23.92 | 4.54 | 82.94 |

a Kolmogrov-Smirnov test
b Kolmogrov-Smirnov test of Lognormal transformed data
c CEC: Cation Exchange Capacity(cmol+/kg)

Trend analysis was apply to diagnostic anisotropic parameters of Nitrates and their characteristic trends, which is helpful for removing a trend from the dataset before using kriging. The result of trend analysis is illustrated in Figure-2. In general, the spatial variation of $NO_3^-$ in soils demonstrates a U-shape curve.

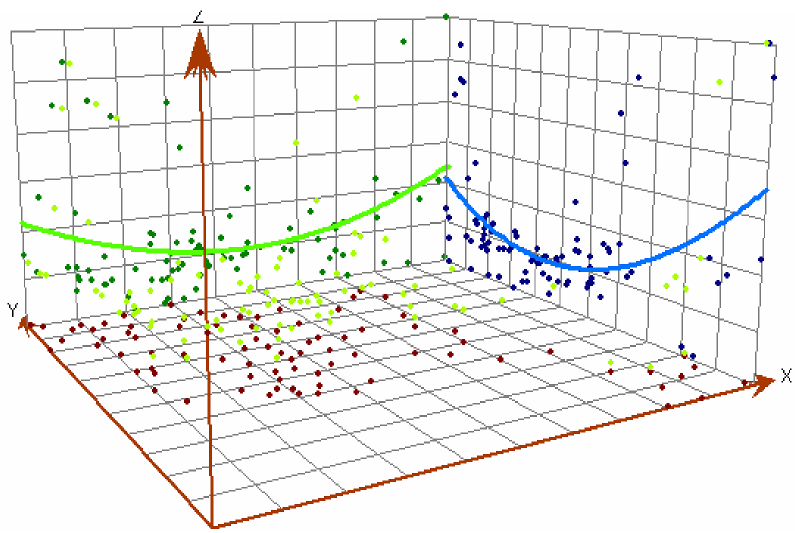


**Figure-2.** The spatial variation pattern of $NO_3^-$ . X axes represent east-west direction; Y axes represent south north direction; Z axes represent $NO_3^-$ content.

Distribution of $NO_3$-N contents in our study was skewed positively, which indicated the existence of some high $NO_3$-N concentration localities (hot spots) in the study area. However, this may not be a general case. High kurtosis, calculated for soil samples (Table-1), indicated that $NO_3$-N in soil had a high variability in our study area. Similar results were reported by others (Korsakov *et al*., 2004; Hu *et al*., 2005; Lamsal *et al*., 2009). The values for CV indicated that well water $NO_3$-N concentration was far more variable than soil NO3-N concentration (Table-1).

### 3.2. Geostatistical analysis

The attributes of the semivariograms for each heavy metal in the soil are summarized in Table-2. The experimental semivariogram depicts the variance of the sample values at various distances of separation. Nugget variance represents the experimental error and field variation within the minimum sampling spacing. The ratio of nugget to sill (nugget/sill) can be used to express the extent of spatial autocorrelations of environmental factors: if the ratio is less than 25%, the variable has strong spatial dependence; between 25% and 75%, the variable has moderate spatial dependence; and greater than 75%, the variable shows only weak spatial dependence. The spatial variability of the soil properties may be affected by intrinsic (soil formation factors, such as soil parent materials) and extrinsic factors (soil management practices, such as fertilization). Usually, strong spatial dependence of soil properties can be attributed to intrinsic factors, and weak spatial dependence can be attributed to extrinsic factors (Cambardella *et al*., 1994). The semivariogram showed that the soil $NO_3^-$ was fitted an Exponential model. The nugget/sill ratio of $NO_3^-$ was 51.6%; it has moderate spatial dependence on the large scale of the study area, indicating that intrinsic and extrinsic factors such as parent material, agricultural practice and topography changed its spatial correlation.

**Table-2.** The best fitted semivariogram model and its parameters for soil $NO_3^-$.

| $NO_3^-$ | Semivariogram Model | Nugget ($C_0$) | Sill ($C+C_0$) | $C_0/C+C_0$ | Range | RMSE | Anisotropy Angle |
|---|---|---|---|---|---|---|---|
| $NO_3^-$ | Exponential | 0.3075 | 0.59593 | 0.516 | 37770 | 1.106 | 33.8 |

### 3.3. Spatial variation of nitrates and land use

In order to apply agricultural practices precisely and appropriately, it is important to investigate the spatial distribution of $NO_3^-$ across large areas such as an entire watershed as in our case. The parameters derived from the exponential model were used for kriging which we produced a spatial distribution map of $NO_3^-$ concentrations in the study area. A search region of 15 nearest-neighbors was applied. The final result of this spatial interpolation process was shown as Figuire-3.

From the spatial distribution map of $NO_3^-$ contents (Figure-3), we can see that the highest $NO_3^-$ concentrations occur in northern and southern part of the watershed, which is along the main water channel or tributaries, while the lower values of NO3- content are located at the edge of the watershed. Comparison between spatial distribution map of $NO_3^-$ and land use map (Figure-3) of the study area can give us the information that the spatial distribution of nitrates is generally affected by different land use types. The highest amounts of $NO_3^-$ were found in irrigated soils followed by orchards (Table-3).

**Table-3.** ANOVA statistical results of the $NO_3^-$ concentration under the four land uses.

| Land use (sample numbers) | | Irrigated farming (6) | Rangeland (11) | Dry farming (67) | Orchard (3) | F | Sig |
|---|---|---|---|---|---|---|---|
| $NO_3^-$(mg/kg) | Mean | 32.013a | 1.26b | 8.199b | 7.83b | 23.179 | 0.000 |
| | CV | 0.061 | 0.33 | 0.699 | 1.103 | | |

Means with the same letter are not significantly different at $p<0.05$

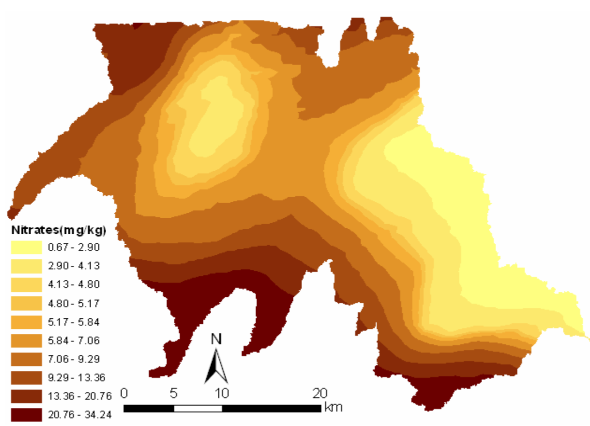


**Figure-3.** Filled contour maps of soil $NO_3^-$.

## CONCLUSIONS

This study evaluated the effects of land use and soil properties on soil $NO_3^-$ concentrations, using correlation and ANOVA analysis. The analyses showed that land use had significant effects on $NO_3^-$ concentrations. Studied nitrates ($NO_3^-$) contents are higher than guideline values, the highest amounts of $NO_3^-$ were found in irrigated soils followed by orchards. Thus these elements can threaten food safety and human health. The results can be helpful for improving agricultural and natural ecosystem in the region.

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