

Assessment of spatial variability of cation exchange capacity with kriging and cokriging

S.A.R. Seyed Jalali^{a*}, F. Sarmadian^b, Z. Mohammad Esmaili^c, M. Navidi^a

^a Soil and Water Research Institute, Agricultural Research, Education and Extension Organization (AREEO), Karaj, Iran

^b Soil Science Dept., Faculty of Agriculture, University of Tehran, Karaj, Iran

^c Researcher of Soil and Water Research Institute, Karaj, Iran

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Abstract

Cation exchange capacity (CEC) is one of the most important soil attributes which control some basic properties of soil such as acidity, water and nutrient retaining capacity. However, the measurement of cation exchange capacity in large areas is time consuming and requires high expenses. One way to save time and expenses is to use simple soil covariates and geostatistical methods in mapping CEC. Therefore, the aim of the present research was to investigate the role of soil covariates in the improvement of spatial variability of CEC. The study area is located in southwest Iran on the Aghili plain, Gotvand, Khuzestan province. In this study, ordinary kriging and cokriging methods were used to predict CEC. 107 soil samples were gathered on a random grid of 200-700 m. 74 samples were used for training and 33 samples for testing the results. A principle component analysis was performed for covariate selection. Clay was selected as a covariate in cokriging due to high correlation between clay and CEC in the first principle component analysis. Based on the cross validation result of predicted dataset, RMSE and ME for cokriging were 2.16 and 0.03 cmol (+)/kg respectively, and 3.36 and 0.09 cmol (+)/kg for kriging, respectively. Based on these results, cokriging performed better than kriging for prediction of cation exchange capacity since it used a covariate such as clay, for the improvement of CEC spatial prediction.

Keywords: Geostatistics; Soil; Khuzestan; Gotvand

1. Introduction

An accurate knowledge on soil cation-exchange-capacity (CEC) is very important in land drainage and reclamation, groundwater pollution studies, and modelling chemical characteristics of soils (Shiri *et al.*, 2017). cation-exchange-capacity CEC is considered as one of the key factors in soil fertility and productivity management (Manrique *et al.*, 1991). Therefore, a detailed and accurate spatial information on soil CEC is necessary. Thus, an alternative way to cope with this problem is to numerically map CEC with a digital soil mapping (DSM) framework proposed by (McBratney *et al.*, 2003). In DSM, spatial

distribution of soil properties and classes are obtained using expensive field and laboratory observation methods. In order to save costs, auxiliary data can be used through quantitative relationships.

Geostatistical methods have been successfully applied to spatial interpolation of soil properties for nearly 30 years (Stein and Corsten 1991; Yanai *et al.*, 2003; Shi *et al.*, 2009). Kriging is a basic geostatistical technique that provides the best linear unbiased estimation (BLUE) for spatially dependent variables. Cokriging is another geostatistical method which based on the correlation of the primary variable, extends the kriging of a primary variable to secondary variables. Such variables are also said to be co-regionalized and are spatially dependent. It has been extensively demonstrated that cokriging is superior to kriging in minimizing the estimation

* Corresponding author. Tel.: +98 24 35824293
Fax: +98 24 35824293
E-mail address: ajalali@areeo.ac.ir

variance when auxiliary variables are in high correlation with primary variables (Istok *et al.*, 1993; Wu *et al.*, 2009). Auxiliary variables used in previous researches for cokriging of soil CEC were single soil properties such as content of organic matter (OM) (Paz-González *et al.*, 2000) and electrical conductivity (EC) (Jung *et al.*, 2006). It has long been known that soil CEC is mainly determined by the amount of clay and OM. In general, clay and OM have a positive impact on CEC. The best-fitting linear CEC function (R^2 , 68%) was attained with fine sand, clay, and OM with relative contributions of 26, 38, and 36%, respectively (Obalum *et al.*, 2013). Moreover, significant correlations between CEC and other soil properties, such as sand, silt, pH, bulk density, and EC, have also been observed (Horn *et al.*, 2005; Jung *et al.*, 2006; Igwe and Nkemakosi 2007). Therefore, in order to show a better spatial variability of soil CEC, numerous soil factors should be considered. A principal component analysis (PCA) is a method that reduces multidimensional data to a smaller number of orthogonal linear combinations, while preserving the most important information during the process (Wander and Bollero 1999; Mouser *et al.*, 2005). The main purpose of the current study was to compare soil CEC predictions by kriging and cokriging using the principal components.

2. Materials and Methods

The study area was located in southwest Iran on the Aghili plain, Gotvand, Khuzestan province, 32° 07' and 32° 10' northern latitude and 48° 52' and 48° 56' eastern longitude, and with a surface area of about 3500 hectares. The climate type of the area is semi-arid with a maximum daily temperature of 46.6°C in July, a minimum temperature of 8.1°C in January, and a mean annual temperature of 26.1°C. The mean annual precipitation, from October to May, is 324 mm. The physiographic units of the study area consisted of undulating and plain landforms. The samples however, were taken from the Aghili plain in which irrigated wheat was a major cultivating crop. Soil samples were taken from 51 soil profiles and 59 soil augers of a depth of 0 to 150cm. 4 to 5 samples were taken in each location based on observed diagnosis horizons. These samplings were taken by a random sampling method with a varying distance between 200 to 700 meters (Figure 1). Soil texture was determined by the hydrometer method (Gee and Bauder, 1986), the soil pH and E_c were determined by the

saturated paste extract (Rhodes, 1996), calcium carbonate equivalent was measured by neutralization of the carbonate with acid and back titration of the excess acid (Loeppert and Suarez, 1996), The CEC of soil samples were measured using acetate sodium 1N (Chapman, H. D., 1965). Soil organic carbon was also measured based on the Walkley-Black chromic acid wet oxidation method (Nelson, D. W., and L. Sommers. 1982). According to the USDA Soil Taxonomy (2010), soils in this study area were classified as subgroups of Typic Haplustepts, Typic Haplusterts, and Typic Calcitusterts. Later, some physicochemical analysis was done on soil samples.

Due to the limited sample quantity, the database of soil samples were randomly subdivided into two datasets using the create subset tool in ArcGIS Geostatistical Analyst. The prediction dataset consisted of 74 soil samples that were used for soil CEC prediction and the test dataset consisted of 33 soil samples which were used to compare the performance of the two interpolation methods.

2.1. Multivariate Data Analysis

PCA is a multivariate statistical technique used to transform a set of interrelated variables into principal components. When variables are correlated, PCA is useful in reducing the multidimensional data into a smaller number of orthogonal linear combinations by summarizing the principal sources of variability in the data.

Only those principal components whose Eigen values are greater than 1 are retained during the PCA process because they preserve the data's variability information (Khattree and Naik 2000). Principal components with an Eigen value of less than 1 are excluded in accordance to this criterion. Theoretically, the first principal Component (PC1) explains most of the total variation in the original variables and each succeeding PCA accounts for the remaining variability as possible (Li *et al.* 2007). With the aim of using the physical-chemical properties of soil's PC1, as the auxiliary variable for cokriging of soil CEC, PCA was performed on the prediction dataset. First, it is necessary to check the probability distribution of each original variable because Pearson correlation coefficients used in the PCA input matrix are sensitive to non-normality (White *et al.*, 1991). In this study, among soil physical-chemical properties, only EC did not pass the Kolmogorov-Smirnov (K-S) test for normality ($P > 0.05$). Therefore, a natural

logarithmic transformation was applied to improve the normality of EC before statistical analysis.

2.2. Cokriging Technique

Cokriging is an important basic geostatistical method that extends kriging of a primary variable to secondary variables based on their correlation with the primary variable. Such variables are not only are spatially dependent but are also called co-regionalized. The cross semi-variogram functions used in cokriging describe the spatial variability of the attributes (Cahn et al., 1994). With the addition of one secondary variable, the traditional cross-semi-variogram is defined as:

$$\gamma_{12}(h) = \frac{\sum_{i=1}^n \{ [z_1(x_i + h) - z_1(x_i)] [z_2(x_i + h) - z_2(x_i)] \}}{2n} \quad (1)$$

(1), γ_{12} is the cross-semi-variogram, which is a function of separation distance h , and n is the number of pairs of $z_1(x_i)$ and $z_2(x_2)$ in given lagged distance intervals $(h+dh)$ (Yates and Warrick 1987). The formula of cokriging estimation of attribute Z_1 at location x_0 is given by:

$$z_1(x_0) = \sum_{i=1}^{n_1} \lambda_{1i} z_1(x_i) + \sum_{j=1}^{n_2} \lambda_{2j} z_2(x_j) \quad (2)$$

λ_{1i} is the weight associated with $z_1(x_i)$; and, λ_{2j} is the weight associated with $z_2(x_j)$, and n_1 and n_2 are neighbourhood of z_1 and z_2 used in the estimation, respectively (Wu et al., 2003). The following criteria should be met in order to provide the best linear unbiased estimation (BLUE) for spatially distributed data:

$$\sum_{i=1}^{n_1} \lambda_{1i} = 1 \quad (3)$$

$$\sum_{j=1}^{n_2} \lambda_{2j} = 0 \quad (4)$$

(1)

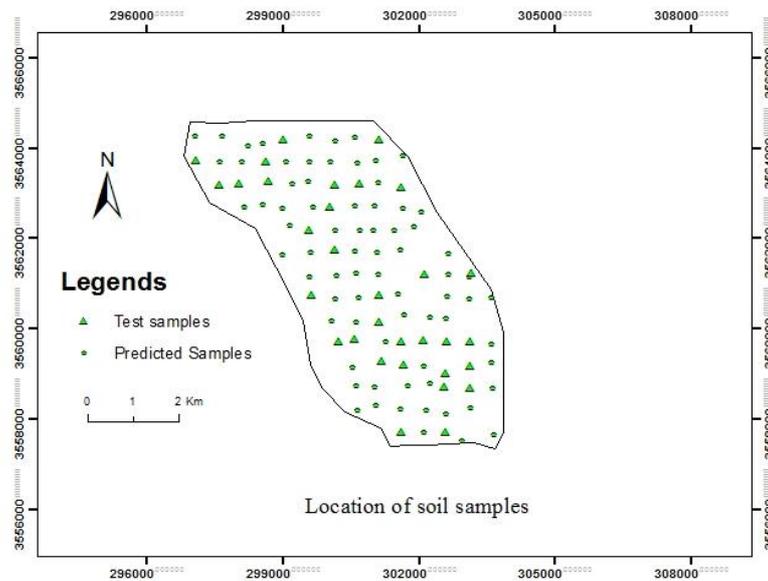


Fig. 1. The location of soil test and validation points

2.3. Evaluation criteria

For testing and the predictions, the performance of kriging and cokriging methods were evaluated using mean error (ME) and root mean square error (RMSE) between the measured soil CEC of 33 soil samples. ME is a measurement of estimation errors and RMSE provides a measurement of accuracy. They are defined as follows:

$$ME = \frac{\sum_{i=1}^n [z(u_i) - z^*(u_i)]}{n} \quad (5)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n [z(u_i) - z^*(u_i)]^2}{n}} \quad (6)$$

$z(u_i)$ is the measured value of z at location u_i , and $z^*(u_i)$ is the predicted value at the same location. Cross-validation is also used as

another way to assess the predictive capabilities of interpolators (Myers 1997).

All statistical calculations were performed using Microsoft Excel (2007) and SPSS 17.0 (SPSS Inc., USA). Geostatistical analyses and generation of prediction maps of soil CEC were carried out with ArcGIS 10.1 software (ESRI, Redlands, CA, USA).

3. Results

The soil samples collected in such a way that included a relatively wide range of soil

texture classes, and according to the results of coefficient of variation (CV%), for soil salinity LN(EC) was 42.7%, Organic Carbon(37.9%) and sand(35.6%) exhibited weak variation, these results are due to natural variation in the soil samples and also different landforms, while other variables such as CEC (25.2%), sand (35.6%), clay (27%) showed moderate variation due to low variability of these parameters of soils in the study areas. CV of silt (8.2%) showed lowest coefficient of variation because the variation of silt size in the study area is low due to silty soil textures (Table 1).

Table 1. Descriptive statistics of soil CEC and physico-chemical properties in Gotvand, Khuzestan, Iran

Variable	Min	Max	Mean	St.Dev.	CV (%)	Skew	Kurt
Number of samples for prediction (n=74)							
EC(ds.m ⁻¹)	1.48	30.60	3.80	3.70	97.40	5.50	37.7
ln(EC)	0.39	3.42	1.17	0.50	42.70	1.72	4.75
OC (%)	0.11	1.30	0.66	0.25	37.90	-0.14	-0.18
CEC (cmol.kg ⁻¹)	5.80	20.90	12.30	4.02	32.50	0.56	-0.69
Clay (%)	16.60	47.50	30.70	8.30	27.00	0.22	-1.14
Silt (%)	40.70	56.90	48.70	4.00	8.20	-0.03	-0.79
Sand (%)	6.60	39.90	21.60	7.70	35.60	0.40	-0.44
Test samples (n=33)							
CEC (cmol.kg ⁻¹)	7.00	18.90	12.06	3.04	25.20	0.49	2.65

CEC: cation exchange capacity; OC: Organic Carbon; EC: electrical conductivity; Ln (EC): Logarithm of Ec; SD: standard deviation; CV: coefficient of variation; Skew: skewness; Kurt: kurtosis.

3.1. Principal Component Analysis

Loading plots for the first and second components are shown in Figure 2. In this loading plot, CEC, clay, and OC had large positive loadings on component 1, which means that this component primarily measures CEC

stability. EC and silt had large negative loadings on component 2.

Positive loading indicates that the contribution of the variables increase with increased dimensional loading, and negative loading indicates a decreased dimensional loading (Kumar *et al.*, 2009). For PC1, the strongest positive loading was clay, followed by CEC and organic carbon. The strongest negative loading for clay was sand, followed by sand and EC. PC2 was mainly dominated by silt and EC with high negative loadings values. The remaining variables had both small positive and negative loadings on PC2 (Table 2).

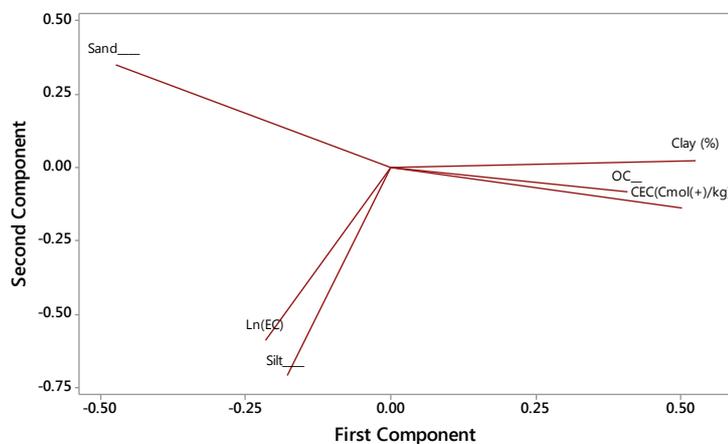


Fig. 2. Loading plots for the first and second components

Table 2. PC loadings for each variable

Components	PC1	PC2	PC3	PC4	PC5
log EC(ds.m ⁻¹)	-0.22	-0.59	-0.70	0.34	-0.02
OC (%)	0.40	-0.082	-0.44	-0.80	-0.019
CEC (cmol.kg ⁻¹)	0.50	-0.14	0.05	0.23	0.82
Clay (%)	0.53	0.03	-0.03	0.30	-0.40
Sand (%)	-0.48	0.35	-0.23	-0.16	0.40
Silt (%)	-0.18	-0.71	0.51	-0.30	0.04

As it is observed (Table 3), Loading values of PC1 and PC2 had Eigen values greater than 1, which means the percent of variance explained in PC1 and PC2 were relatively high

(PC1=56% and PC2=77%). This indicates that more than 78% of the information is contained within PC1 and PC2.

Table 3. Results of principal component analysis for soil physical- chemical properties in Gotvand, Khuzestan, Iran

Table 2: Loading values of The PCA					
Component	PC1	PC2	PC3	PC4	PC5
Eigenvalue	3.3	1.25	0.77	0.49	0.15
Proportion	0.56	0.21	0.13	0.08	0.025
Accumulated	0.56	0.77	0.89	0.98	1.00

Pearson correlation analysis indicated that there was a strong positive correlation between CEC and clay ($r=0.85$, $P<0.01$), CEC and organic carbon ($r=0.62$, $P<0.01$), a strong negative correlation between CEC and sand ($r=-0.88$, $P<0.01$), and no significant correlation between CEC and other variables.

3.2. Geostatistical Analysis

The regression graph between CEC and clay (%) showed *R square* (adj) equal to 75 % (Figure 3). This showed that clay had a strong correlation with CEC and therefore could be used as an auxiliary variable in improving the accuracy of soil CEC predictions. The regression graph between CEC and OC (%) showed *R-sq* (adj) equal 35 % (Figure 4). This

showed that organic carbon had a moderate correlation with CEC and could be used as second auxiliary variable in cokriging to improve the accuracy of soil CEC predictions.

A normality test was done to insure that Kriging's data was normal. The results showed that clay content of soil samples followed a normal distribution with a mean of 30.7% and a standard deviation of 8.3 (skewness=0.22, kurtosis=1.1). Soil CEC also followed a normal distribution, with a mean of 12.3 cmol. Kg⁻¹ and a standard deviation of 4.02 cmol. Kg⁻¹ (skewness=0.56 kurtosis = -0.69) (Table 1). In our study, both CEC and clay passed the Kolmogorov-Smirnov (K-S) normality test ($P>0.05$).

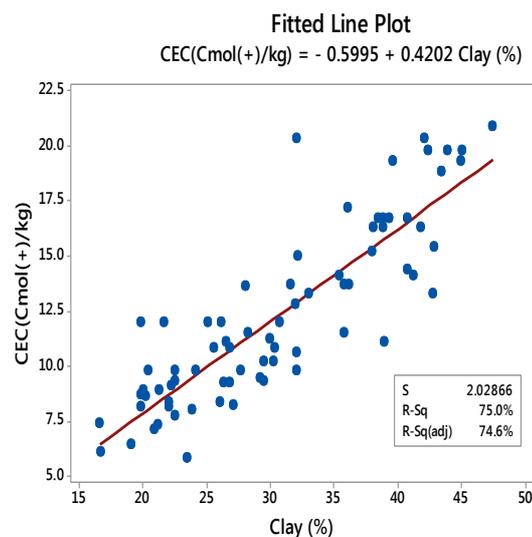


Fig. 3. The relationship between CEC and Clay percentage

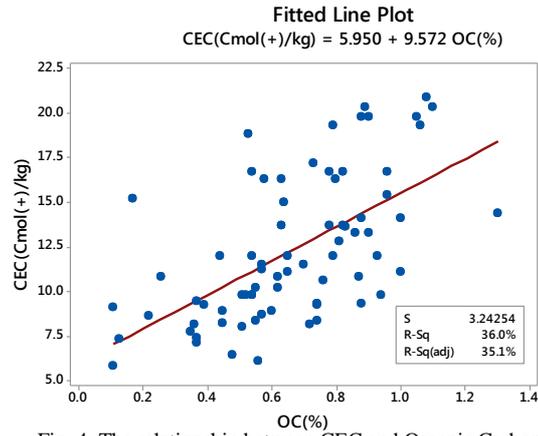


Fig. 4. The relationship between CEC and Organic Carbon percentage

The semi-variogram of soil CEC provides a description of its spatial dependency and some insight into possible processes affecting its spatial distribution. As depicted in Figure 5a, the best fitted semi-variogram model for CEC was an exponential model with a coefficient of determination ($R^2=0.32$), nugget/ sill ratio $[C/(C+C)]$ of 0.24, and an effective range of 1.2 km. The best fitted semi-variogram model on clay data was a Gaussian model (Figure 5b),

with a coefficient of determination ($R^2= 0.46$), nugget/ sill ratio $[C/(C+C)]$ of 0.30, and an effective range of 1.2 km. However, in comparison to the other models, the exponential model which was the best fitted cross-semi-variogram model had a high coefficient of determination ($R^2=0.74$), low nugget/sill ratio $[C/(C+C)]$ of 0.17, and an effective range of 2.6 km (Figure 5c).

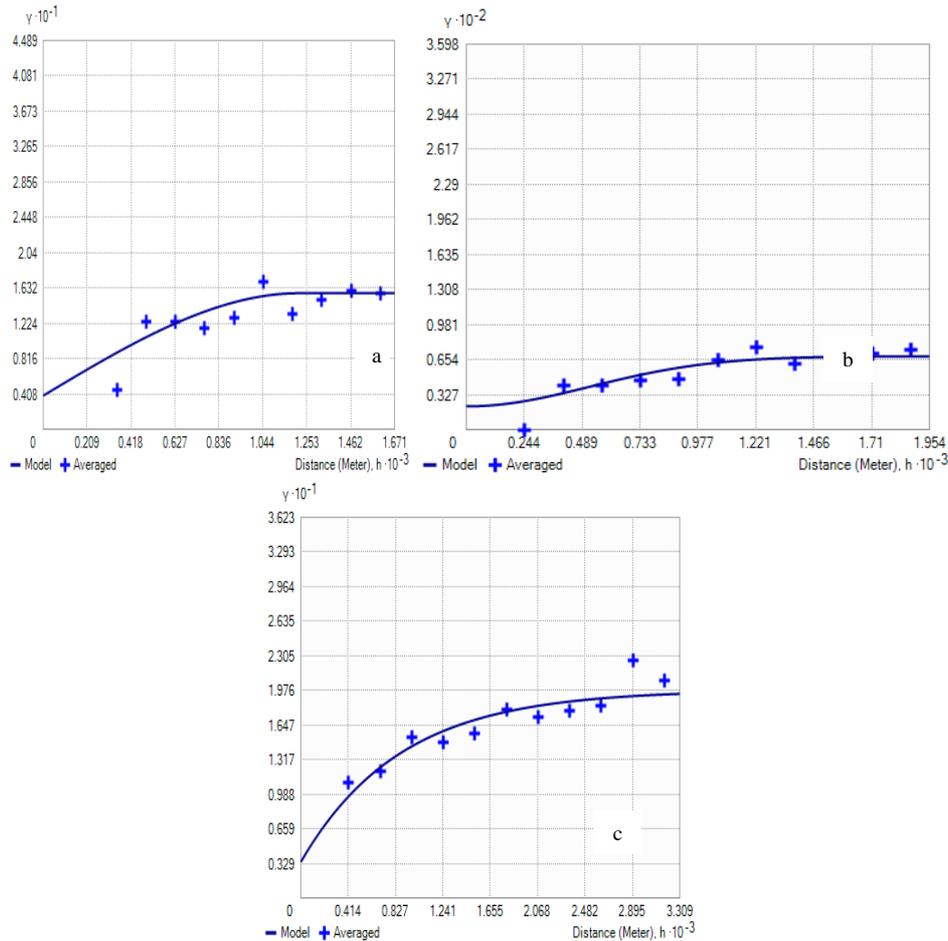


Fig. 5. a- exponential model of experimental variogram for CEC. b- Gaussian model of experimental variogram for Clay., c- exponential model of experimental variogram for cross validation of CEC and clay

The prediction map of soil CEC by cokriging and kriging methods is shown in Figure 6. The values of CEC were relatively higher in the central, southwest, and northeast regions due to higher clay and organic matter in these areas and relatively lower in the southeast and northwest regions of the study area because of lighter soil textures.

Comparison of Interpolation Performance

Summary statistics for soil CEC estimated by kriging and cokriging for the test dataset containing 33 soil samples and predicted dataset containing 74 soil samples are shown in Table 3.

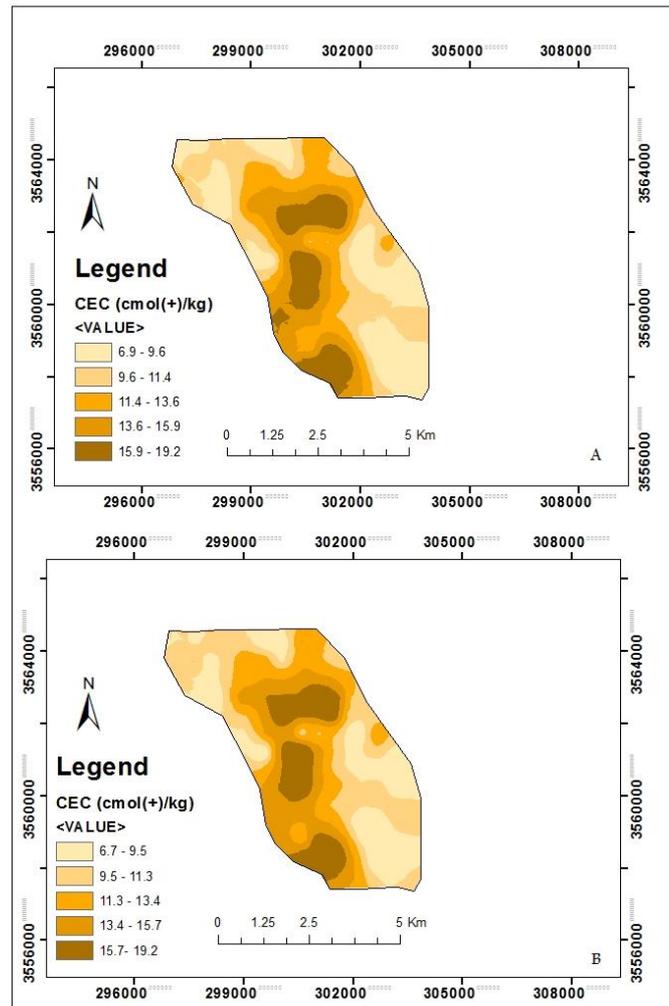


Fig. 6. Predicted soil CEC (coml. kg-1) by kriging (A) and cokriging (B) with PCI derived from soil physical-chemical properties in Gotvand, Khuzestan, Iran

Table 4. Results of validation and cross-validation of kriging and cokriging methods for soil cation exchange capacity in Gotvand, Khuzestan, Iran

Variable	Min	Max	Mean	Std. dev.	CV (%)	ME	RMSE
Validation of test dataset (n=33)							
Measured	7.0	18.9	12.1	3.0	25.2		
Krigging	8.8	16.3	11.9	1.8	15.2	-0.13	2.76
Co-Krigging	7.9	16.4	12.0	1.9	15.8	-0.06	2.32
Validation of prediction dataset (n=74)							
Measured	4.8	20.9	12.1	4.1	33.8		
Krigging	8.0	19.1	12.2	2.6	21.4	0.09	3.36
Co-Krigging	7.2	18.3	12.2	2.9	24.1	0.03	2.16

This table shows the results of cross-validation by both interpolators. The predicted soil CEC for the data test-set by kriging ranged

from 8.8 to 16.3 cmol⁺/kg⁻¹, with a mean of 11.9 cmol/kg⁻¹, and a standard deviation of 1.8 cmol/kg⁻¹. The predicted soil CEC for the

data test-set by cokriging ranged from 7.9 to 16.4 cmol/kg^{-1} , with a mean of 12.0 cmol/kg^{-1} , and a standard deviation of 1.9 cmol/kg^{-1} . The measured soil CEC for the data test -set however, ranged from 7.0 to 18.9 cmol/kg^{-1} , with a mean of 12.1 cmol/kg^{-1} , and a standard deviation of 3.0 cmol/kg^{-1} . The ME and RMSE of kriging for the data test -set were -0.13 and 2.76 $\text{Cmol}^+/\text{kg}^{-1}$. ME and RMSE of cokriging for the data test-set were -0.06 and 2.32 cmol/kg^{-1} , respectively.

The predicted soil CEC for the prediction dataset of kriging ranged from 10.05 to 21.06 cmol/kg^{-1} , and the predicted soil CEC for the

prediction dataset by cokriging ranged from 7.2 to 18.3 cmol/kg^{-1} . The measured soil CEC of the prediction dataset, however, ranged from 4.8 to 20.95 cmol/kg^{-1} . The coefficients of variation of the two predictions were similar but significantly less than that of the observations. The coefficient of determination (R^2) for the prediction dataset was 0.32 for kriging cross-validation and 0.73 for cokriging cross-validation. In Figure 7, we can clearly see that the scattered points of performed kriging were more scattered than those of performed cokriging.

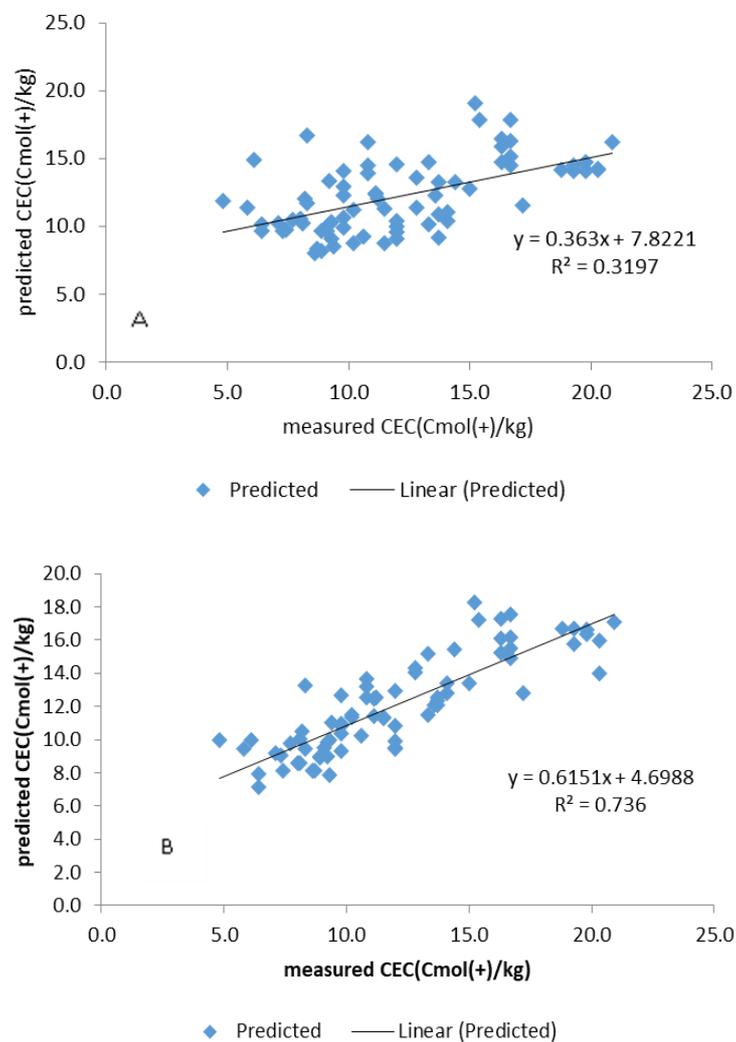


Fig. 7. Measured soil CEC (cmol. kg^{-1}) and predicted soil CEC from cross-validation by kriging (A) and cokriging (B), respectively, in Gotvand, Khuzestan, Iran

4. Discussion

As it was expected, CEC is highly correlated with soil clay and organic carbon content. The

regression graph between CEC and clay showed $R\text{-sq (adj)}$ equal to 75 %. This showed that clay had a strong correlation with CEC and can be used as an auxiliary variable in cokriging to

improve the accuracy of soil CEC prediction, meanwhile the eigenvalue in PC1 is 3.3 which is higher than 1 and in PC1 clay, organic carbon and CEC are grouped together and this is another reason for choosing clay as a covariate in cokriging. Is higher than 1. The regression graph between CEC and OC (%) showed R^2 (adj) equal to 35%. This showed that organic carbon had a moderate correlation with CEC and can be used as a second auxiliary variable in cokriging to improve the accuracy of soil CEC prediction.

In this study, most of the variance in soil physical-chemical properties was explained by PC1 and PC2. Soil CEC was highly correlated with PC1, whereas no significant correlation was between CEC and PC2. Compared to the OM and EC used by Paz-González *et al.* (2000) and Jung *et al.* (2006), PC1 had a better correlation with CEC. Therefore, PC1 was selected as an auxiliary variable for improving the prediction of soil CEC.

The nugget/sill ratio was used to divide the spatial dependence of the environmental variables. According to Cambardella *et al.* (1994), “a variable has strong spatial dependence when the ratio is less than 25%, a moderate spatial dependence when the ratio is between 25 and 75%, and a weak spatial dependence when the ratio is more than 75%”. The nugget/sill ratio of the exponential model for soil CEC by kriging was at 24%, which indicated that soil CEC had a strong spatial dependence on the study area. The spatial variability of soil CEC was affected by intrinsic factors of soil formation factors, such as soil parent materials (Cambardella *et al.* 1994), and this is consistent to the fact that soil CEC is related to the amount of clay and OM, the higher CEC is due to higher soil clay and organic matter in the study areas. The effective range could be reflected by some information about the spatial dependency of environmental variables (Journal and Huijbregts, 1978). The semivariogram of soil CEC had nearly a 1.2 km effective range, which indicated that soil CEC had a strong spatial dependence.

The predicted soil CEC for the data test-set based on kriging and cokriging methods had some differences in the measured values. Because of the smoothing effect, the maximum prediction values of kriging and cokriging were significantly lower than that of the observations, while the minimum prediction values of kriging and cokriging were significantly higher. The predicted soil CEC of cokriging had a more similar summary statistic

to the observations than that of kriging, which indicated that cokriging can better describe the spatial variability of soil CEC. Having negative ME values in their data test-sets, both kriging and cokriging showed an overall tendency of systematic overestimation of soil CEC. The ME and RMSE for kriging for the data test-set were -0.13 and $2.76 \text{ cmol}^+/\text{kg}^{-1}$, and ME and RMSE of cokriging for the test dataset were -0.06 and $2.32 \text{ cmol}/\text{kg}^{-1}$, respectively.

The absolute ME and RMSE of cokriging were relatively lower than those of kriging, which indicated that cokriging with clay can improve prediction accuracy of soil CEC.

5. Conclusion

Soil CEC was highly correlated with clay derived from soil physical-chemical properties ($r=0.85$, $P<0.01$). The clay was used as an auxiliary variable in cokriging for soil CEC prediction. The application of cokriging gave more precise results than kriging, which is shown in the lower ME and RMSE. This study demonstrates that the usage of clay derived from soil physical-chemical properties as an auxiliary data for cokriging of soil CEC was efficient in the improvement of prediction accuracy.

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