

GEOSTATISTICAL ANALYSIS OF TOPSOIL FREE IRON OXIDES CONTENT USING COKRIGING

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ABSTRACT

Geostatistics provides descriptive tools to characterize the spatial distribution of soil attributes. Kriging techniques rely on the spatial dependence between observations to predict attribute values at un-sampled locations. Cokriging on the other hand, utilizes the spatial correlation between two variables to map the primary one, which is under-sampled, using information content of the secondary variable. The present study aimed at applying cokriging technique to map topsoil free iron oxides content (Fed) (primary variable) measured in 32 samples, using the information content of topsoil clay content (secondary variable) measured in 54 samples. Topsoil Fed ranged between 2.10 and 4.80%, whereas topsoil clay content varied from 24.0 to 69.0%. The correlation coefficient, r , between the two variables is 0.93, which satisfies the most important criteria for carrying out cokriging. The fitted semivariograms for both variables are Gaussian, and the cross-semivariogram between the two variables is also Gaussian. The cokriged spatial distribution of topsoil Fed was mapped and compared to kriged Fed. The cokriging results were cross-validated and the standard error of estimation was matched to that of kriging. The study showed the superiority of cokriging upon kriging as a spatial mapping method, especially if the primary variable is under-sampled.

Keywords: Terra Rossa, Geostatistical analysis, Cokriging, Kriging, Clay content, Free iron oxides, Cross-semivariogram, Semivariogram.

INTRODUCTION

The red color of many of the soils in the Mediterranean region was the main reason that in the past the broad term "Red Mediterranean soils", occasionally "terra rossa", became quite a common indication for all soils in the region (Yaalon, 1997). Bresson (1993) stated that Red Mediterranean soils resulted from a bisiallitic type of weathering with the release of high amounts of iron oxides closely bound to clay minerals.

Terra rossa is reddish clayey to silty-clayey soil especially widespread in the Mediterranean region, which covers limestone and dolomite in the form of a discontinuous layer ranging in thickness from a few centimeters to several meters. It is also found along more or less karstified cracks and between the bedding surfaces of limestones and dolomites. Thick accumulations of terra rossa-like material are situated in karst depressions in the form of pedo-sedimentary colluvial complexes (Durn et al., 1999).

In Soil Taxonomy (Soil Survey Staff, 1998) terra rossa is classified as Alfisols (Haploxeralfs or Rhodoxeralfs), Ultisols, Inceptisols (Xerochrepts) and Mollisols (Argixerolls or Haploxerolls). According to the FAO system (FAO, 1974) terra rossa is recognised as Luvisols (Chromic Luvisols), Phaeozems (Haplic Phaeozems or Luvic Phaeozems) and Cambisols.

Qualitative and quantitative analysis of soil Fed are of great pedological interest because Fed content and mineralogy reflect duration and intensity of pedo-genesis. In addition, Fed greatly affect the adsorption capacity of soils with respect to oxyanions. Therefore, the knowledge of their spatial variability is crucial, for example, for the risk assessment of selenate and or arsenate toxicity (Zhang and Sparks, 1990; Bowell, 1994) or for the site-adapted application of phosphate fertilizers (Torrent, 1987; Van der Zee et al., 1988; Scheinost and Schwertmann, 1995).

Based on analysis of 48 terra rossa samples from various locations around the world (Italy, Greece, Israel, Spain, Lebanon, France, Mexico, Germany and Australia) Boero and Schwertmann (1989) found that Fed, Fed/Fet, haematite/goethite ratios and Al substitution in haematite and goethite vary to a rather limited extent which may indicate the specific pedoenvironment under which terra rossa is formed. They suggested this pedoenvironment is characterised by an association of Mediterranean climate, high internal drainage due to the karstic nature of a hard lime-stone and neutral pH conditions.

The average of Fed in this 48 terra rossa samples is 3.5% (± 0.3). While, Al-Zafry (2001) found that mean of Fed at Jabal Al-Akhdar "Libya" is 5.15%. Whereas, Durn (2003) found in 40 samples from Istria "Croatia", Fed averaged 3.68% (± 0.28). This supports Boero and Schwertmann's (1989) conclusion, that the rather limited extent of variation of selected Fed characteristics may indicate a specific pedo-environment in which terra rossa is formed.

According to Durn et al. (1999) terra rossa clay content ranges from 32.1 to 77.2% and generally increases with depth in the profiles. The higher content of sand sized particles observed in a few samples is attributed to rhizoconcretions which formed in terra rossa as the result of palaeopedological processes which post-date terra rossa formation (recalcification of terra rossa following its burial) or to the recent colluvial additions of flysch.

Fed/clay ratios are relatively uniform in terra rossa from Istria and clearly indicate a predominance of co-illuviation of clay and Fe-oxides, i.e. a connection between Fe-oxides and the clay fraction (Durn et al., 2001). According to Fedoroff (1997) rubification occurs in the upper horizons, then rubified soil material is translocated with the clays at depth. So, the translocation of clay particles is responsible for the distribution of the red colour throughout the whole profile. However, since they have been exposed to various climatic fluctuations terra rossa soils can be affected by eluviation, yellowing and secondary hydromorphy.

Geostatistics has been applied by many researchers to describe the spatial variability using the semivariogram and predict the values of soil attributes at un-sampled locations by different kriging (named after D.J. Krige) techniques (Trangmar et al., 1985; Warrick et al., 1986; Burrough, 1989; Webster and Oliver, 1989; Webster, 1991; Goovaerts, 1992, 1998 and 1999; Bahnassy et al. 1995; and Bahnassy and Morsy, 1996), ecological properties (Banerjee and Gelfand, 2002), and categorical variables (Bogaert, 2002).

The term cokriging is used for spatial linear regression that uses data defined by different attributes. The data set will contain the primary variable of interest in addition to one or more secondary variables, which are spatially cross-correlated with the primary variable. Thus, the dataset will contain useful information about the primary variable. The cross-correlation between variables is utilized to improve these estimates, and to reduce the variance of the estimation error. The usefulness of the secondary variable is often enhanced by the fact that the primary variable of interest is under-sampled (Issacks and Srivastava, 1989). The spatial relationship between the values of the attribute is governed by the regionalized variable theory, which states that observations close to each other are more correlated than observations taken at a further distance (Journel and Huijbregts, 1978). This means that points spatially close to the estimation points should be given higher weights than those further away (Cressie, 1993). The coregionalized variable theory deals with the same situation as the regionalized variable theory, but the variables under consideration are correlated, and behave the same (McBratney and Webster, 1983 and 1986). Consequently, the cross-semivariogram can be modeled as a joint function between the two variables (Issacks and Srivastava, 1989). The linear coregionalization model allows for different ranges of spatial correlations for each variable (Wackernagel, 1994 and 1995).

Due to computation and notation difficulties related to cokriging system (Journel and Huijbregts, 1978; Myers, 1982; and Deutsch and Journel, 1998), a limited number of researches have been carried out utilizing cokriging as a best linear unbiased estimator (B.L.U.E.). Danielsson et al, (1998) applied cokriging to estimate the total amounts and the spatial distribution for organic carbon, nitrogen and phosphorus in the Gulf of Riga surficial sediments, using loss on ignition as a covariable. Goovaerts (1998) used different methods of kriging and cokriging to model the spatial distribution of pH and electrical conductivity in two transects in forest and pasture soils. Rivoirard (2001) indicated that the cokriging could be collocated or multi-collocated depending on the configuration of data and the location at which the value will be estimated. Bannassy (2002) applied collocated cokriging to study the spatial distribution of topsoil sodicity using the information content of soil salinity. Morsy (2004) estimated the SAR and EC contents in the surface and subsurface layers.

The current study aimed at applying cokriging to predict the values of the primary variable (free iron oxides), which is sparsely sampled and hard to measure, using the information content of topsoil Clay content, which is densely sampled and easy to measure, taking into consideration the fact that these two variable are correlated. The cokriged free iron oxides is compared to the kriged free iron oxides and the standard error of estimation for both methods was matched.

MATERIALS AND METHODS

The Study Site

The studied site is located about 2 km. to the southwest of Al-Beida city and named as Bil Ghara area (figure 1). The area is characterized by the presence of short Wadies and some of them are branched from wadi al-Kuf. The studied site is part of one of these short wadies coarse. This site is belong Omar Al-Mukhtar University as research farm for faculty of Agriculture. Soils in the studied site are mainly Terra Rossa (Red Mediterranean soil) which includes Typic Haploxerafals and Typic Rhodoxerafals.

One of the most unique features characterizing Jabal Al-Akhdar region, which is located in the north east part of Libya, is the diverse soils it has. Six Soil order (out of 12 worldwide) are represented in this relatively small area. The richness of soils in numerous sites was a result of environmental and biotic factors. The most obvious of all is the annual rainfall, characterized by wide range extending from 800 mm/ year.

The favorable environmental conditions such as moderate average temperature throughout the months of the year has supported the development of diverse vegetative cover , including big trees like Juniper, cedar, and Mastic in the South . Also, these environmental differences have supported a wide range of aromatic as well as medical herbs.

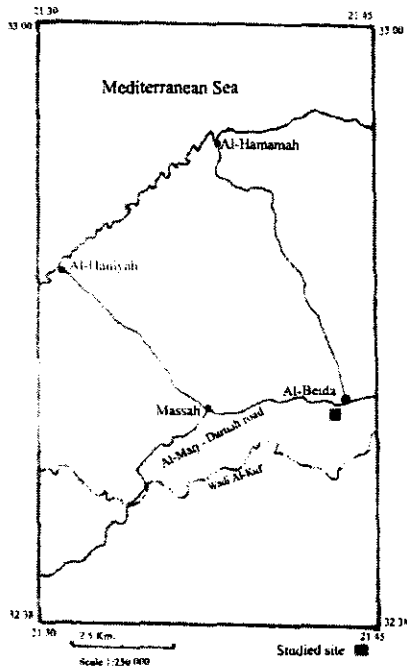


Fig. 1: Location of the study area.

Sampling Scheme and Soil Analysis

Fifty-four soil observations were collected over the study area. The topsoil was analyzed for Clay%. These soil observations were used as a secondary data for interpolating the Free Iron Oxides. Thirty-two soil observations were taken randomly as a subset of the original data and analyzed for Free Iron Oxides, which is considered as the primary variable. The samples locations were georeferenced to the UTM coordinate system. The spatial configuration of the soil observations used for Clay and Free iron Oxides is shown in figure 2. Free iron oxides extractable with Na dithionite-citrate bicarbonate (Fed)-extracts practically all secondary Fe oxides- were obtained after the method of Mehra and Jackson (1960) and measured with AAS (Pye-Unicam SP9).

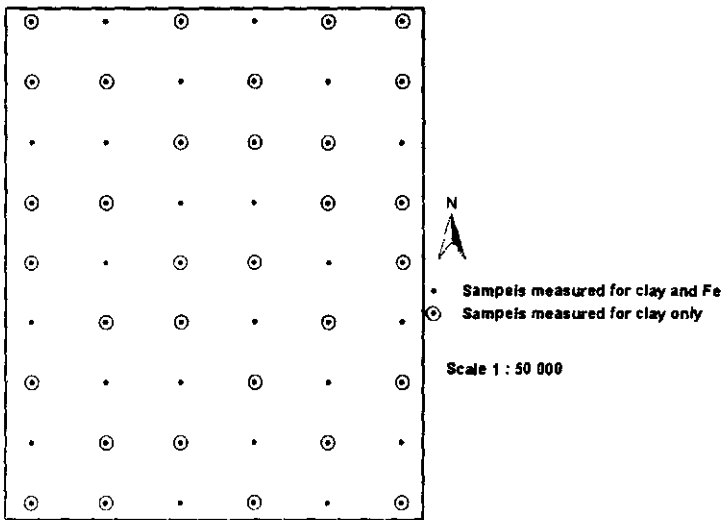


Fig. 2: Location of soil observations

Descriptive Statistical Analysis

The data for Clay% and Free Iron Oxides were analyzed for basic statistics including mean, variance, standard deviation, minimum, maximum, skewness, and kurtosis. The histogram for both variables was obtained, and the correlation between the two variables was calculated.

Semivariogram and Cross-semivariogram Analysis

The semivariogram is defined as half of the average squared difference between two attribute values separated by vector **h**, for one variable (Burrough and McDonnell, 1998):

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

where $N(h)$ is the number of pairs at lag h , $Z(x_i)$ is the value of the attribute at location (x_i) and $Z(x_i + h)$ is the value of the attribute at location $(x_i + h)$ separated by distance h . The separation vector h is specified with some direction and distance (lag) tolerance. This semivariogram is used to model both clay % and Fed %, and then fitting them to one of the known semivariogram functions (Gaussian, Exponential, and Spherical). In case of using two variables (cokriging) the cross-semivariogram is calculated as follows:

$$\gamma_{uv}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \{Z_U(x_i) - Z_U(x_i + h)\} \{Z_V(x_i) - Z_V(x_i + h)\}$$

where Z_U (Fed %) and Z_V (salinity %) are the two variables. This equation is used to model Fed using the information content of Clay, then fitting the obtained model to one of the known cross-semivariograms represented by Gaussian, Spherical, and Exponential functions.

Cokriging

A co-kriged estimate is a weighted average in which the value of U at location x_0 is estimated as a linear weighted sum of co-variables V_k . If there are k variables $k = 1, 2, 3, \dots, V$, and each variable is measured at n_v places, $x_{ik} = 1, 2, 3, \dots, N_k$, then the value of one variable U at x_0 is predicted by (Burrough and McDonnell, 1998):

$$Z_U(x_0) = \sum_{k=1}^V \sum_{i=1}^{n_v} \lambda_{ik} Z(x_{ik}) \quad \text{for all } V_k$$

where λ_{ik} is the weight assigned to variable k and $Z(x_{ik})$ is the value of the variable at location i .

To avoid bias, i.e. to ensure that

$$E[z_u(x_0) - z'_u(x_0)] = 0 \text{ and}$$

the sum of weights $\lambda_{ik} = 1$ for $U = V$ and

the sum of weights $\lambda_{ik} = 0$ for $V_k \neq U$

The first condition (sum of weights $\lambda_{ik} = 1$) implies that there must be at least one observation of U for cokriging to be possible. The interpolation weights are chosen to minimize the variance:

$$\sigma^2_u(x_0) = E[\{z_u(x_0) - z'_u(x_0)\}^2]$$

There is one equation for each combination of sampling site and attribute, so for estimating the value of variable j at site x_0 , the equation for the g -th observation site of the k -th variable is:

$$\sum_{j=1}^V \sum_{i=1}^{N_v} \lambda_{ij} \gamma_{ij}(x_{ij}, x_{gk}) + \Phi_k = \gamma_{uv}(x_u, x_{gk})$$

for all $g=1$ to n_v , and all $k=1$ to V , where Φ_k is the Lagrange's multiplier. These equations together make-up the cokriging system.

Cross Validation

Cross validation is a technique, which is used to compare estimated and true values using the information available in the data set. In cross validation, the estimation method is tested at the locations of existing samples. The sample value at a particular location is temporarily discarded from the sample data set; the value at the same location is then estimated using the remaining samples. Once the estimate is calculated, it is compared to the true sample value that was initially removed from the sample data set. This procedure is repeated for all samples. This could be expressed as (Issaks and Srivastava, 1989):

$$Error = r = v' - v$$

Where v' is the estimated value and v is the true value. Mean square error (MSE) is calculated from the formula:

$$MSE = \frac{1}{n} \sum_{i=1}^n r^2$$

Linking Geostatistics to Geographic Information Systems (GIS)

The estimates from cokriging and kriging, and the associated error (Gamma Design, 2001) were exported to Arc View GIS software (ESRI, 1997) for better visualization, mapping and printout.

RESULTS AND DISCUSSIONS

Description of Spatial Patterns

The analysis of spatial data starts with posting the data values. Fig (3) shows the spatial distribution of Free Iron Oxides sampled at 32 locations. The spatial distribution of the variable is not random, but follows the regionalized theory, i.e., observations close to each other on the ground tend to be more alike than those further apart (Journel and Huijbregts, 1978). The presence of such spatial structure is prerequisite to the application of Geostatistics, and represents the first step towards spatial prediction (Burrough and McDonnell, 1998).

The main pedogenic process which characterises terra rossa in mediterranean region and Jabal Al-Akhdar is the accumulation of clay and is manifested through: (1) clay illuviation in the form of coatings and/or (2) microaggregates incorporated in the groundmass due to argilloturbation and soil stress (Al-Zafry, 2001, Durn et al, 2001 and Durn 2003). According to Fedoroff (1997) rubification occurs in upper horizons, then rubified soil material is translocated with clays to depth.

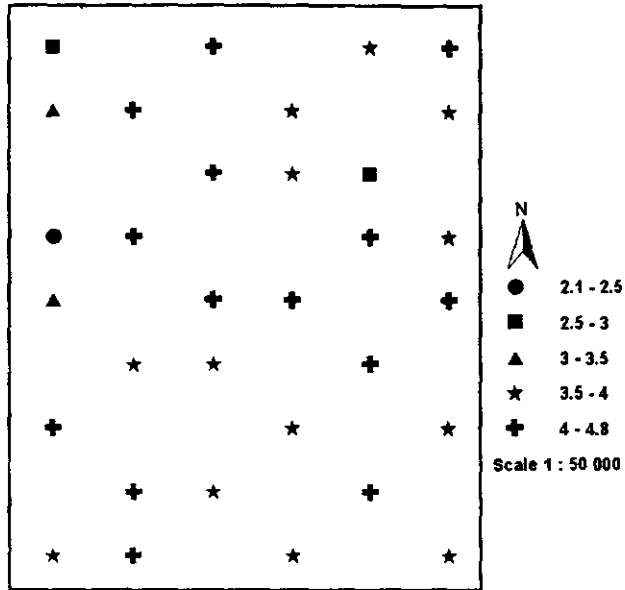
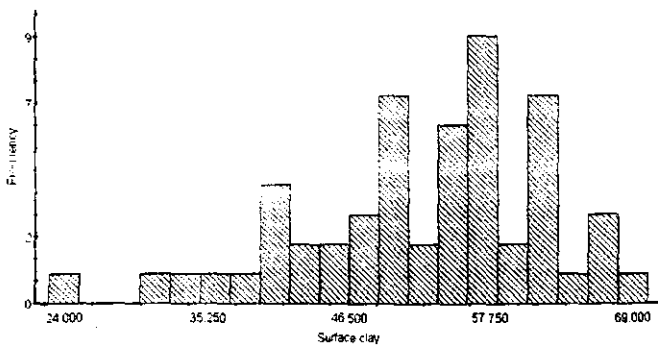


Fig. 3: Data posting for Iron

Descriptive Statistical Analysis

The statistical analysis of the free iron oxides is clay% and shown in table (1). It is clear that clay% has more variability than Fed as the CV% is almost 18.57%. This is attributed to the greater number of soil samples (54) used in the analysis compared to the number of samples (32) used for free iron oxides analysis. Moreover, there is a greater number of soil samples with low Fed values (fig 3), which lowered the mean compared to the standard deviation. The histogram for both Clay% and Free Iron Oxides is shown in fig (4). On the other hand, variance indicates that Free Iron Oxides has spread on a wide range contrary to Clay%, which is distributed around a high number of samples with low values (Fig 4).



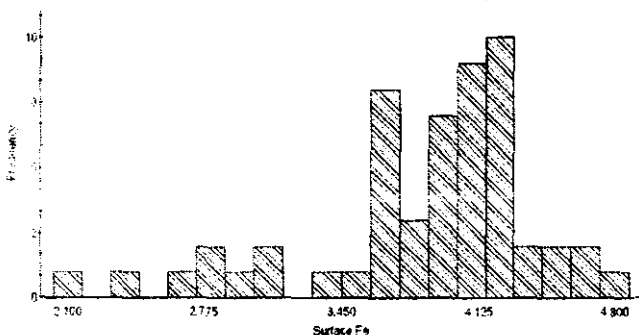


Fig. 4: The semivariograms for Clay% (above) and Fed (below)

Table 1: Descriptive statistical analysis for Clay % and Fed.

Statistical Parameter	Clay %	Fed
Mean	52.33	3.86
Standard Deviation	9.72	0.57
CV% (coefficient of variation)	18.57	14.77
Variance	94.45	0.33
Minimum	24.00	2.10
Maximum	69.00	4.80
N (number of samples)	54	32

Regression analysis of both clay% and free iron oxides indicated a positively highly correlated two variables, which satisfies the need to carry out cokriging analysis of Fed % using the information content of clay %. The correlation coefficient for this analysis is 0.93. Yates and Warrick (1987) showed that if the correlation coefficient between a primary variable and the covariable exceeds 0.5, then the inclusion of the covariable is favorable, and cokriging performs better than kriging.

Clay % and Free Iron Oxides (fed) Semivariograms

The semivariograms for both clay and Fed were fitted to the Gaussian model as shown in the following equation:

$$\gamma(h) = C_0 + C_1 \{1 - \exp(-\frac{3h^2}{a^2})\}$$

Where C_0 is the nugget, C_1 is the sill, h is the separation distance (lag) in meters, and a is the range.

The parameters for the fitted semivariograms for both clay and fed are shown in table (2), and the semivariograms are shown in figure (5). The formulated equations for these two variables are as follows:

$$\gamma_{Iron(h)} = 0.001 + 0.261 \{1 - \exp(-\frac{3h^2}{(600)^2})\}$$

$$\gamma_{Clay\%_0(h)} = 0.1 + 106.2 \{1 - \exp(-\frac{3h^2}{(600)^2})\}$$

Table 2: Semivariogram types and parameters for clay and Fed

Variable	Model	Nugget (Co)	Sill (Co+C1)	Range (a)	R ²
Clay%	Gaussian	0.1	106.2	600	0.95
Fed	Gaussian	0.001	0.361	600	0.937

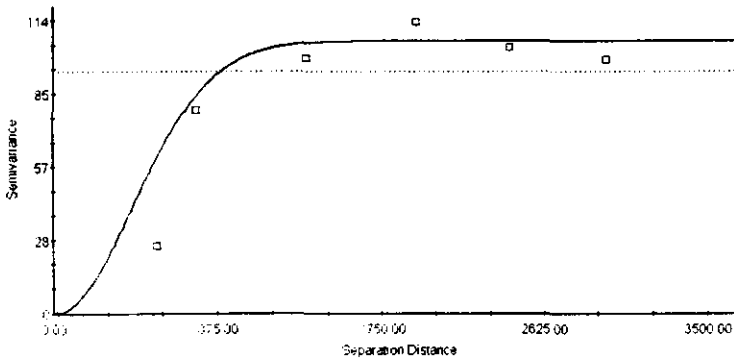
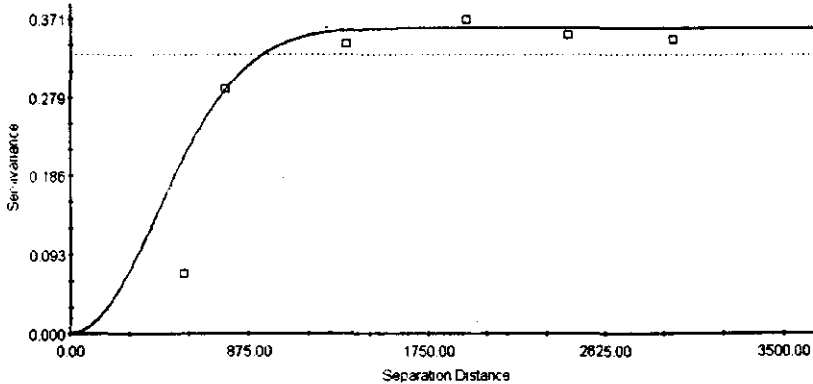


Fig. 5: The semivariograms for clay% (above) and Fed (below)

It is clear that the coefficient of determination R² for both models exceeds 0.90, which indicates the goodness of the estimation. Moreover, The fitted Gaussian semivariogram indicates a smoothly varying pattern for both variables (Burrough and McDonnell, 1998).

The Cross-semivariogram (Collocated semivariogram)

The cross-semivariogram of Fed and clay is of the collocated type, which means that the estimation was performed using variables measured at the same location. Table (3) and figure (6) indicate the parameters of the fitted Gaussian cross-semivariogram between sodicity and salinity. The Gaussian joint semi-semivariogram is as follows:

$$\gamma_{Fed - Clay}(h) = 0.01 + 5.779 \left(1 - \exp\left(-\frac{3h^2}{(600)^2}\right) \right)$$

Table 3: Cross-semivariogram parameters between Fed and Clay%.

Variables	Model	Nugget (Co)	Sill (Co+C1)	Range (a)	R ²
Fed and Clay	Gaussian	0.01	5.779	600	0.949

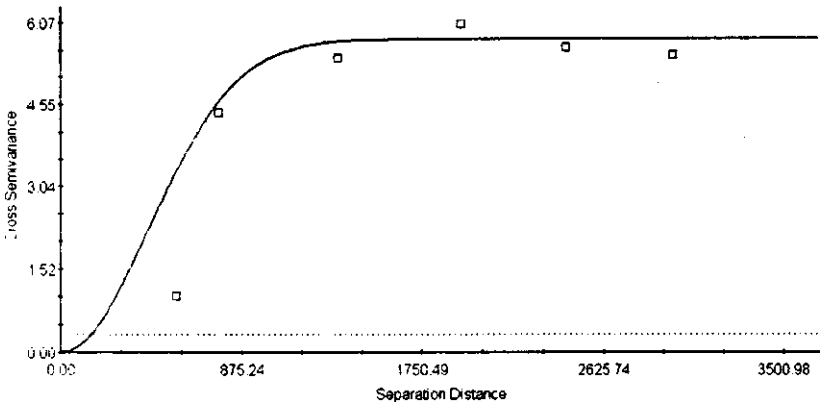


Fig. 6: The cross-semivariogram between Fed and Clay %

The most important parameter in this estimation is the high R² (0.95) obtained from the fitting process. This high estimation regression coefficient comes very close to that of the simple linear regression (0.98) between Fed and clay content. The advantage of cokriging over linear regression is that it takes into consideration the spatial variability of the surrounding points, rather than performing blindly the linear regression, which lacks this improvement.

Cokriging compared to Kriging

The output from cokriging process is a map of the spatial distribution of Fed % based on the information content and the high correlation with clay %. Fig (7) shows the cokriged Fed % for the study area.

It is clear that the cokriged fed % is smoothed out, because estimated values are less variable than actual values. This is expressed by an overestimation of small values while large values are underestimated; however the smoothing depends on the local data configuration (Goovaerts, 1999).

Topsoil free iron oxides (Fed) was kriged in order to compare both the cokriging results, and the standard error. Fig (8) indicates the results of kriging Fed % and the associated error (standard deviation, SD). It is clear that kriging aggregated the high Fed values in one contiguous group due to the lack of information in the area between the topsoil Fed samples. On the other hand, cokriging utilized the information content of soil clay content to predict the values of topsoil Fed at un-sampled locations. Moreover, the kriging standard deviation (standard error) shown in fig (8) have much higher values especially at the boundary of the study area, and behaved very erratically due to the lack of surrounding points. For these reasons, cokriging is much preferred over kriging, especially if the primary variable is under-sampled

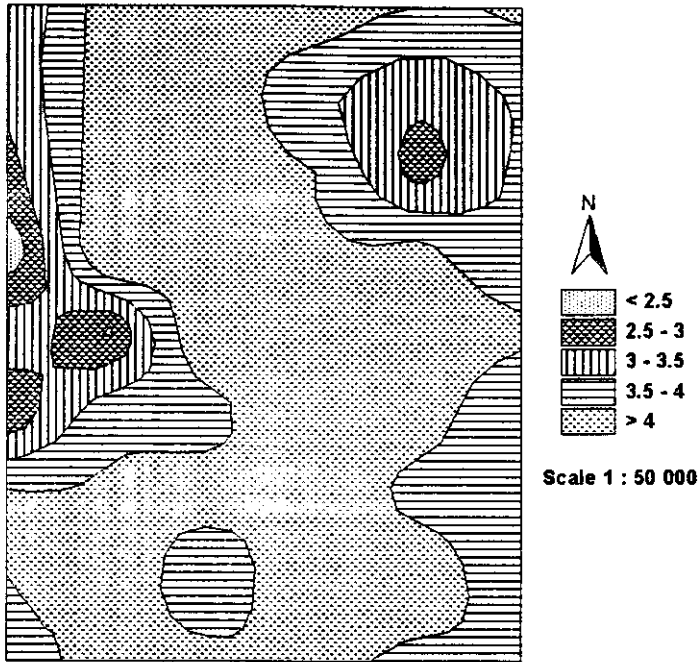


Fig. 7: Cokriged Fed %.

Cross Validation of Cokriging and Kriging

The process of cross validation between the estimated and the true value permits the evaluation of cokriging performance. Fig (9) shows the linear regression between the cokriged and actual values of free iron oxides (Fed). The standard error (SE) of prediction is low (0.01) due to the above-mentioned reasons related to smoothing effect of cokriging, and the configuration of the data.

For comparison sake, kriged Fed was cross validated to see how the standard error (SE) of prediction behaves and check the results with cokriging estimates. The standard error of kriging prediction is much higher (0.177) than that of cokriging (0.01). The kriging correlation coefficient is very poor (0.161), as compared to the cokriging one (0.71).

For these reasons, cokriging is much preferred over kriging, especially in the case of under-sampling the variable of interest. Moreover, there must be an intensely sampled covariable, which is correlated with the variable of interest.

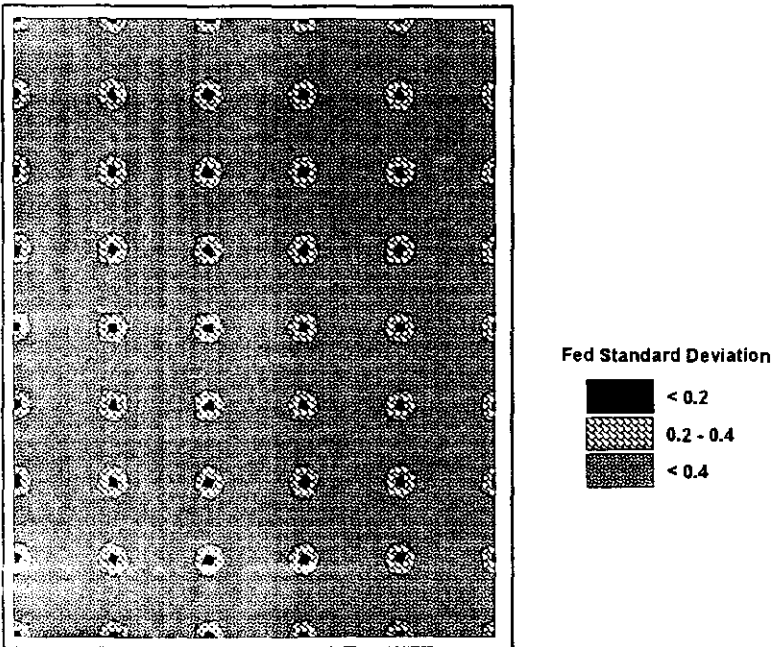
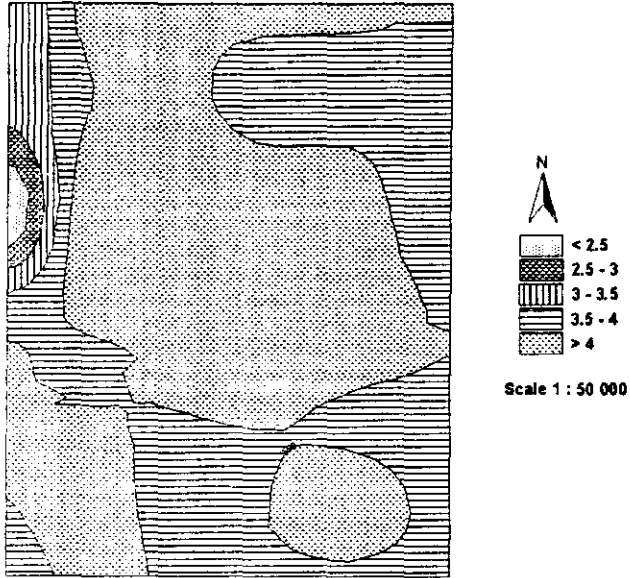
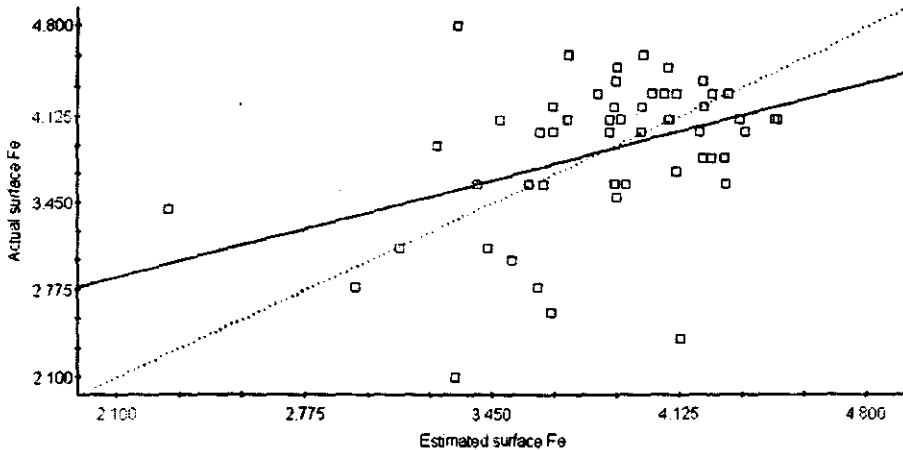


Fig. 8: Kriged Fed % (above) and the standard deviation (below).



**Fig. 9: Cross validation between cokriged and actual values of Fe.
(The solid line is the regression line, the dot-dash line is for $r = 1$)**

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تحليل جيواحصائي لمحتوى الحديد الحر في الطبقة السطحية باستخدام طريقة
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تقدم الإحصاء الجيولوجية أدوات وصفية لتمييز التوزيع الفراغى لخواص الأرض. تعتمد طرق kriging على الارتباط الفراغى بين العينات للتنبؤ بقيم الخاصية تحت الدراسة فى مواقع لم يؤخذ منها عينات. من جانب آخر، فإن cokriging يستفيد من الارتباط الفراغى بين خاصيتين لرسم خريطة توزيع الصفة الأساسية تحت الدراسة (والتي يؤخذ منها عينات قليلة) باستخدام المحتوى المعلوماتى للمتغير الثانوى (والذى يؤخذ منه عينات كثيرة). تهدف الدراسة الحالية إلى استخدام طريقة cokriging لرسم خريطة توزيع محتوى الحديد الحر (المتغير الأساسى) للطبقة السطحية و المقاسة فى ٣٢ عينة باستخدام معلومات محتوى الطين فى الطبقة السطحية (المتغير الثانوى) و المقاسة فى ٥٤ عينة. وقد تراوحت قيم Fed فى الطبقة السطحية بين ٢,١ و ٤,٨ % ، فى حين اختلفت قيم محتوى الطين فى الطبقة السطحية بين ٢٤ و ٦٩ % . وقد كان معامل الارتباط ٢ بين محتوى الطين و Fed ٠,٩٣ مما يوفى أهم شرط لاستخدام cokriging وهو وجود معامل ارتباط عالى بين المتغيرين. وقد تم عمل fitting لشكل توزيع الاختلافات semivariogram لكل من الخاصيتين (نسبة الطين و Fed) وقد كان يتبع نموذج Gaussain. وكذلك التصاحب بين الخاصيتين cross-semivariogram كان يتبع نموذج Gaussain. وقد تم رسم خريطة توزيع محتوى الحديد الحر (Fed) باستخدام cokriging و مقارنتها بخريطة توزيع Fed باستخدام kriging. بالإضافة إلى أن القيم المقدرة بكل من الطريقتين قد تم عمل cross-validation لها ورسم خريطة توزيع الخطأ القياسى لمقارنته بالقيم المحسوبة. وقد أوضح هذا البحث أفضلية استخدام الـ cokriging عن استخدام kriging كأحد طرق رسم الخرائط، خاصة إذا تم تجميع عينات قليلة للمتغير تحت الدراسة، مع وجود متغير آخر له علاقة ارتباط قوية مع المتغير الأساسى .