



## Soil exchangeable cations: A geostatistical study from Russia

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### Abstract

In present study, geostatistical techniques was applied to assess the spatial variability of exchangeable cations such as; calcium (Ex-Ca<sup>2+</sup>), magnesium (Ex-Mg<sup>2+</sup>), potassium (Ex-K<sup>+</sup>) and sodium (Ex-Na<sup>+</sup>) in the tillaged layer in a Perm State Agricultural Academy Farm site in Perm region, West Urals, Russia. A 250x100 m plot (approximately 2.35 ha) was divided into grids with 25x25 m spacing that included 51 sampling points from 0-0.2 m in depth. Soil reaction (pH) was the least variable property while the Ex-K was the most variable. The greatest range of influence (237.6 m) occurred for Ex-Ca and the least range (49.7 m) for Ex-Mg.

**Keywords:** exchangeable cations, spatial variability, site specific management

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### Introduction

Soil properties of terrestrial ecosystems are controlled by a variety of factors that operate at different spatial and temporal scales. Soil physical, chemical and biological properties are all likely to change markedly across small distances, within a few hectares of agricultural fields (Benayas et al., 2004; Cambardella et al., 1994; Chien et al., 1997). The small-scale variability may be difficult to measure and not apparent to the casual observer. Analysis of small-scale variability has practical uses in managing soil fertility for a chosen field (Brady and Weil, 2002). The five cations in soils are calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), potassium (K<sup>+</sup>), sodium (Na<sup>+</sup>) and, in strongly acid soils, aluminium (Al<sup>3+</sup>). Exchangeable Al only becomes significant at pH levels less than 5.5 in water or about 4.7 in CaCl<sub>2</sub>. The cations manganese (Mn<sup>2+</sup>), iron (Fe<sup>2+</sup>), copper (Cu<sup>2+</sup>) and zinc (Zn<sup>2+</sup>) are usually present in amounts that do not contribute significantly to the cation complement. Therefore, it is common practice to measure the concentrations of only the five most abundant cations. Cation exchange capacity (CEC) is the capacity of the soil to hold and exchange cations. It provides a buffering effect to changes in pH, available nutrients, calcium levels and soil structural changes. As such it is a major controlling agent of stability of soil structure, nutrient availability for plant growth, soil pH, and the soil's reaction to fertilizers and other ameliorants (Brady and Veil, 2002).

Soil properties can be evaluated as statistically due to application of geostatistical methods on soil science recently. Geostatistics, increasingly popular in soil science, are useful in predicting the spatial distribution of spatially dependent soil properties in the field with a number of samples (McBratney and Webster, 1983; Oliver, 1987; Kerry and Oliver, 2004, Aşkın and Kızılkaya, 2006; Aşkın, 2010). Semivariograms and autocorrelograms are typically used to study the spatial structure of soil properties. Soil exchangeable Ca,

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Mg, K and Na are the dominant exchangeable cations in soils and hence, to examine the spatial variability was expected to better understanding of the related soil chemical parameters for long-term observatory study within a field-scale (Jiang et al., 2008).

The objective of the present study was to assess the spatial variability of soil exchangeable cations in field-scale using geostatistical techniques.

## Material and Method

### Study site

The study area was located in a field on the Perm State Academy Farm in the Perm Region, West Urals, Russia in 2011. Perm is a city and the administrative center of Perm Krai, Russia, located on the banks of the Kama River, in the European part of Russia near the Ural Mountains. From 1940 to 1957 it was named Molotov (Figure 1). This area is characterized gently sloping with a well-drained medium textured soil.



Figure 1. Location map of the study area showing the sampling design. The coordinates are in meters in UTM datum.

Perm has a continental climate with warm summers and long, cold winters. The highest and the lowest the temperature was from  $-47.1\text{ }^{\circ}\text{C}$  to  $37.2\text{ }^{\circ}\text{C}$ . The annual mean temperature was  $7.1\text{ }^{\circ}\text{C}$  and the annual mean precipitation was 657 mm based on a 50 year period.

The study site (250x100 m) was chosen for its apparent homogeneity. It was marked with regular rectangle grids (25x25 m each) and included 51 sampling points.

### Soil analyses

Soil samples were air-dried and ground to pass a 2 mm sieve for related chemical analysis. Soil samples were extracted with 1.0 M ammonium acetate at pH 7.0 and the extracts were then analyzed for exchangeable Ca, Mg, K and Na by flaming emission at the wavelength of 422.7, 285.2, 766.5 and 589.0 nm, respectively, using an atomic spectrophotometer (Page, 1982). Selected soil physicochemical properties were determined by the following methods: organic carbon content by the modified Walkley-Black method (Nelson and Sommers, 1982), particle size distribution by the hydrometer method (Gee and Bauder, 1979), soil pH and electrical conductivity (EC) in 1:1 (w/v) soil-water ratio using pH-meter and EC-meter (Peech, 1965).

### Statistical analysis

Classical statistical parameters, i.e., mean, standard deviation, median, minimum, maximum and data normality, were calculated using SPSS 15.0 software. Isotropic semivariances of data were calculated using GS+ geostatistical software (GS+, 2006). Semivariance  $\gamma(h)$  is defined in the following equation:

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

where,  $N(h)$  is the number of sample pairs at each distance interval  $h$  and  $Z(X_i)$  and  $Z(X_i + h)$  are the

values of variable at any two places separated by distance  $h$ . The semivariogram is the plot of the semivariance against the distance. Its shape indicates whether the variable is spatially dependent. Experimental semivariograms were fitted by theoretical models that have well-known parameters nugget ( $C_0$ ), sill ( $C_0 + C$ ) and range ( $A_0$ ) of spatial dependence (Cambardella et al., 1994).

GS<sup>+</sup> has several models that can be fitted to estimate semivariograms, but in this study, we used the isotropic exponential, spherical and Gaussian models:

$$\begin{aligned} \gamma(h) &= C_0 + C \cdot \left[ 1,5 \cdot \left( \frac{h}{A_0} \right) - 0,5 \cdot \left( \frac{h}{A_0} \right)^3 \right] & h \leq A_0 & \text{Spherical model} \\ \gamma(h) &= C_0 + C & h > A_0 & \\ \gamma(h) &= C_0 + C \left[ 1 - \exp\left( \frac{-h^2}{A_0^2} \right) \right] & & \text{Gaussian model} \\ \gamma(h) &= C_0 + C \left[ 1 - \exp\left( \frac{-h}{A_0} \right) \right] & & \text{Exponential model} \end{aligned}$$

Where;  $C_0$  is the nugget variance  $\geq 0$ ,  $C$  is the structural variance  $\geq C_0$ ,  $(C_0 + C)$  is the sill variance, and  $A_0$  is the range of spatial correlation (GS<sup>+</sup>, 2006).

In this study, point kriging was used before constructing of contour maps to provide enough estimated data. The contour maps of exchangeable Ca, Mg, K and Na were constructed using ArcGis software.

## Results and Discussion

### Soil properties and exchangeable cations

The soils of study are has 33.6% sand, 39.7 silt and 26.7% clay fraction and soil textural class was named as loamy. Also descriptive statistics of soil properties are given in Table 1.

Table 1. Summary statistics on the soil properties and exchangeable cations ( $n = 51$ )

Soil Properties	Mean	$S_e$	Min.	Max.	$S_d$	Skw	Kur
pH (1:1 soil: water suspension)	7.07	0.028	6.67	7.67	0.203	0.785	1.177
Electrical conductivity ( $EC$ ), $dS\ m^{-1}$	0.15	0.007	0.05	0.29	0.053	0.797	-0.021
Organic carbon content ( $OCC$ ), %	1.15	0.060	0.45	2.75	0.430	1.560	3.420
Exchangeable sodium (Ex-Na), $cmol(+) kg^{-1}$	0.22	0.006	0.15	0.35	0.041	0.839	1.227
Exchangeable potassium (Ex-K), $cmol(+) kg^{-1}$	1.08	0.083	0.48	4.32	0.591	3.526	17.695
Exchangeable calcium (Ex-Ca), $cmol(+) kg^{-1}$	10.29	0.251	7.00	14.70	1.790	0.430	-0.524
Exchangeable magnesium (Ex-Mg), $cmol(+) kg^{-1}$	1.37	0.051	0.68	2.24	0.361	0.565	0.132

$S_d$ , standard deviation;  $S_e$ , standard error; Skw, skewness; Kur, kurtosis

The soils were mostly medium in texture, neutral in soil reaction, medium in organic matter content (average of 1,98%) and low in electrical conductivity ( $<0.98\ dS\ m^{-1}$ ) (Soil Survey Staff, 1993).

### Spatial variability of exchangeable cations

Distances between Ex-Na, Ex-K, Ex-Ca and Ex-Mg pairs and semivariance values were calculated using the GS<sup>+</sup> package program. The exponential, spherical and Gaussian models with the smallest reduced sums of squares (RSS) values and the biggest  $R^2$  values were selected for evaluating spatial variability of these exchangeable cations in the study area by the GS<sup>+</sup> package program (Table 2).

The nugget effect, representing the undetectable experimental error and field variation within the minimum sampling space, was quite large relative to the sill, which represents total spatial variation. The ratio of nugget variance to sill expressed in percentages can be regarded as a criterion for classifying the spatial

dependence of soil properties. If this ratio is less than 25%, then the variable has strong spatial dependence; if the ratio is between 25 and 75%, the variable has moderate spatial dependence; otherwise, the variable has weak spatial dependence (Chien et al., 1997). Jiang et al (2008) interpreted strong and moderate spatial variability as interactions among field-scale variability of soil exchangeable cations physical, chemical, and biological soil components.

Table 2. Isotropic models fitted to variograms of exchangeable cations

Exchangeable cations	Nugget Co	Sill Co+C	Range (Ao), m	C/Co+C %	Co/Co+C %	R <sup>2</sup>	Model	SD
Ex-Na	0.000262	0.001844	62.4	85.8	14.2	0.522	Exp	S
Ex-K	0.127	0.468	58.2	72.9	27.1	0.715	Gaus	M
Ex-Ca	1.857	4.171	237.6	55.5	44.5	0.847	Exp	M
Ex-Mg	0.0033	0.1246	49.7	97.4	2.6	0.995	Sph	S

Exp, exponential; Gaus, Gaussian; Sph, spherical; SD, spatial dependence; M, moderate; S, strong

The influence zones for Ex-Na, Ex-K, Ex-Ca and Ex-Mg were 62.4 m, 58.2 m, 237.6 m and 49.7m, respectively. The highest nugget effect occurred for Ex-Ca and the lowest for Ex-Mg. The isotropic models showed the best fitting value for the computed semivariance values for exchangeable cations. The isotropic exponential model for Ex-Na and Ex-Ca; the isotropic spherical model for Ex-Mg and the isotropic Gaussian model showed the best fitting value for the computed semivariance values for Ex-K. The model parameters and the experimental variograms for Ex-Na, Ex-K, Ex-Ca and Ex-Mg are illustrated in Figure 2a,b,c, and 2d, respectively.

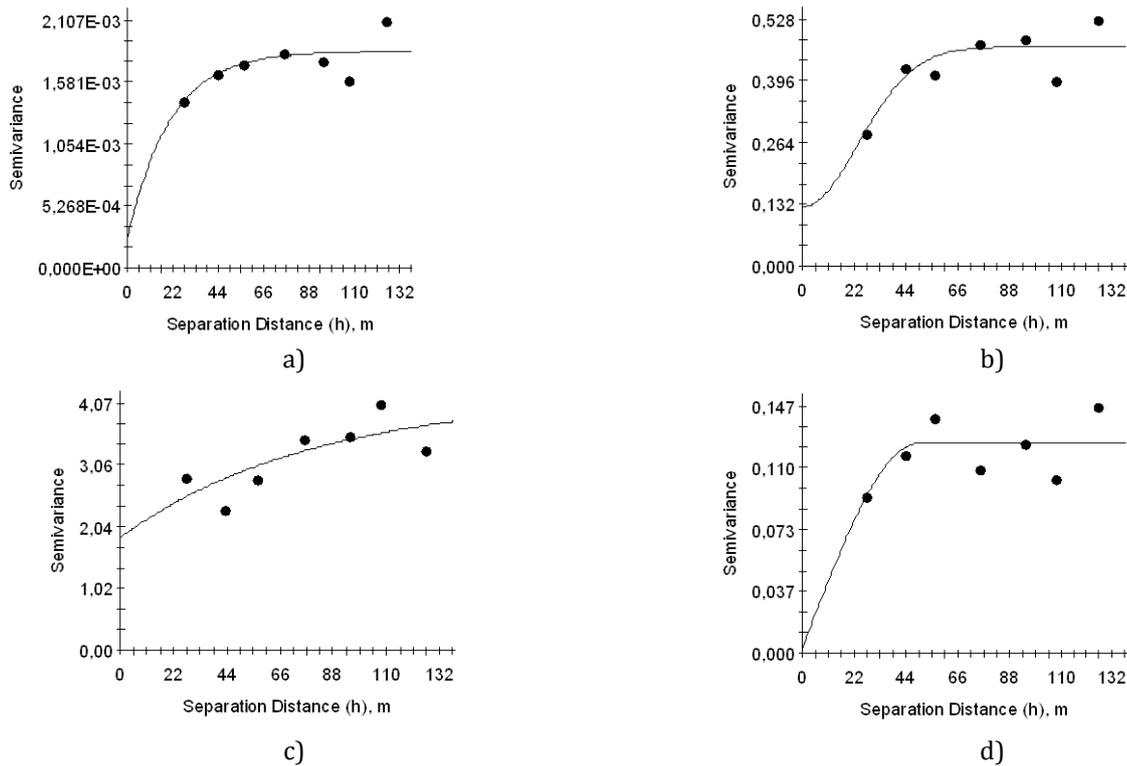


Figure 2. Isotropic semivarograms for a) Na, b)K, c)Ca d)Mg

Ex-Na, Ex-K, Ex-Ca and Ex-Mg were point-kriged based on the isotropic models by 7875 points using the ten nearest neighboring points. The descriptive statistics are presented in Table 4 for observed and point-kriged Ex-Na, Ex-K, Ex-Ca and Ex-Mg values.

As seen from Table 3, the mean reduced error was near zero and the squared differences between the predicted and the original values, the variance of the reduced error, was lowest for the fitted models. This means that the kriging estimates are accurate, and the spatial relationships derived from the studied part of the research site may be applicable to other areas with similar characteristics in this area (Trangmar et al., 1985; Öztaş, 1996; Ardahanlıoğlu et al., 2003; Başkan 2004; Aşkın, 2010; Aşkın et al., 2011).

Table 3. Descriptive statistics on the observed and kriged values of exchangeable cations

Descriptive statistics	Ex-Na cmol(+) kg <sup>-1</sup>		Ex-K cmol(+) kg <sup>-1</sup>		Ex-Ca cmol(+) kg <sup>-1</sup>		Ex-Mg cmol(+) kg <sup>-1</sup>	
	Obs.*	Predict.**	Obs.	Predict.	Obs.	Predict.	Obs.	Predict.
Number of samples (n)	51	7875	51	7875	51	7875	51	7875
Minimum	0.15	0.16	0.48	0.51	7.00	7.54	0.68	0.72
Maximum	0.35	0.34	4.32	3.85	14.70	13.85	2.24	2.18
Mean	0.22	0.22	1.08	1.07	10.29	10.28	1.37	1.39
Standard deviation	0.041	0.0005	0.591	0.154	0.361	0.061	0.361	0.076
Prediction Errors								
Mean	0.00085		0.01987		0.04989		0.00575	
RMS	0.04093		0.5816		1.773		0.3331	
Mean Standardized	0.01508		0.02502		0.02029		0.0124	
RMS Standardized	0.973		1.095		0.9664		1.083	

\*Obs., observed; \*\*Predict., predicted; RMS, Root-Mean-Square

The range of point-kriged Ex-Na values (0.16-0.34 cmol(+) kg<sup>-1</sup> with a mean of 0.22 cmol(+) kg<sup>-1</sup>) was somewhat narrower than the range of the measured Ex-Na (0.15–0.35 cmol(+) kg<sup>-1</sup> with a mean of 0.22 cmol(+) kg<sup>-1</sup>). The standard deviation of the kriged Ex-Na values was lower than on the measured selected model. Figure 3a shows a point-kriged map of Ex-Na illustrated using the same 7875 points used to kriging Ex-Na.

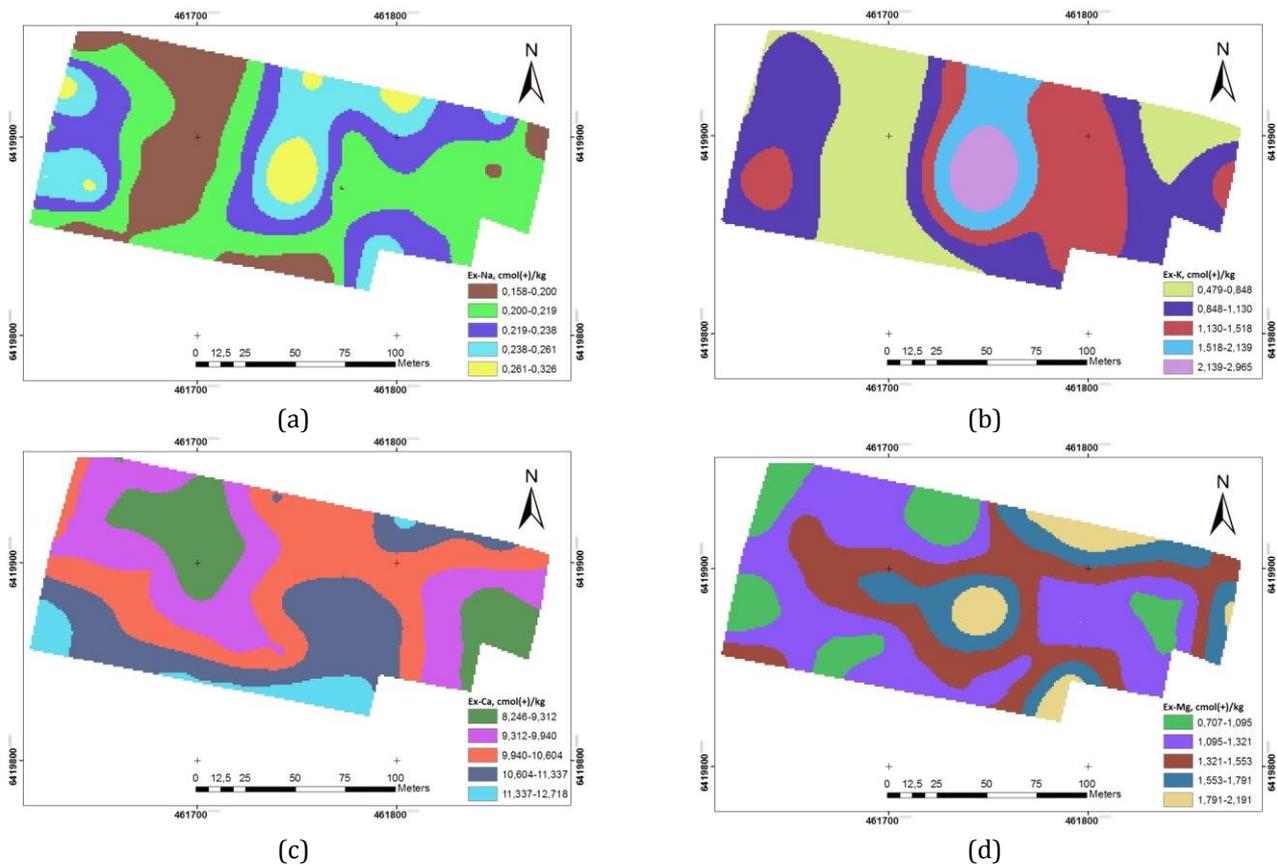


Figure 3. Point-kriged maps for a) Ex-Na; b) Ex-K; c) Ex-Ca; and d) Ex-Mg

The range of point-kriged Ex-K values (0.51-3.85 cmol(+) kg<sup>-1</sup> with a mean of 1.07 cmol(+) kg<sup>-1</sup>) was somewhat narrower than the range of the measured Ex-K (0.48–4.32 cmol(+) kg<sup>-1</sup> with a mean of 1.08 cmol(+) kg<sup>-1</sup>). The standard deviation of the kriged Ex-K values was lower than on the measured selected model. Figure 3b shows a point-kriged map of Ex-K illustrated using the same 7875 points used to kriging Ex-K. The point-kriged Ex-Ca values ranging from 7.54 to 13.85 cmol(+) kg<sup>-1</sup> with a mean of 10.28 cmol(+) kg<sup>-1</sup>

that was somewhat narrower than the range of the measured Ex-Ca (7.00–14.70 cmol(+) kg<sup>-1</sup> with a mean of 10.29 cmol(+) kg<sup>-1</sup>). The standard deviation of the kriged Ex-Ca values was lower than on the measured selected model. Figure 3c shows a point-kriged map of Ex-Ca illustrated using the same 7875 points used to kriged Ex-Ca. The point-kriged Ex-Mg values ranging from 0.72 to 2.18 cmol(+) kg<sup>-1</sup> with a mean of 1.39 cmol(+) kg<sup>-1</sup> that was somewhat narrower than the range of the measured Ex-Ca (0.68–2.24 cmol(+) kg<sup>-1</sup> with a mean of 1.37 cmol(+) kg<sup>-1</sup>). The standard deviation of the kriged Ex-Mg values was lower than on the measured selected model. Figure 3d shows a point-kriged map of Ex-Mg illustrated using the same 7875 points used to kriged Ex-Mg.

The range of spatial dependence ranged from 49.7 to 237.6 m, indicating that the grid scale was adequate for assessing of the spatial variability of the exchangeable cations. In this area or a similar field, in soil productivity and fertility research studies to be done about sampling interval can be chosen. Exponential isotropic models were the best semivariogram models for Ex-Na and Ex-Ca, Gaussian model was the best model for Ex-K and also spherical model was the best for Ex-Mg. The information obtained from geostatistical techniques can be used to gain a better understanding of the spatial distribution of soil exchangeable cations in field topsoil. This approach enabled maps to be drawn of soil exchangeable cations in the field-scale. The results suggested that the use of kriging should decrease the required sampling density in the field-scale. Spatial analysis of soil exchangeable cations could be useful for assessing soil fertility and soil quality status, as well as developing appropriate sampling strategies.

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