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Field-Scale Variability of Soil Exchangeable Cations in a Chinese Ecological Research Network (CERN) Site

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Abstract: Geostatistics was applied to assess the spatial distribution of exchangeable calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and the sum of exchangeable bases (SEB) in the cultivated horizon in a Chinese Ecosystem Research Network (CERN) site in northeast China. A 42×30 m plot was divided into grids with 7×5 m spacing that included 49 sampling points. Soil samples were collected from depths of 0-10 cm and 10-20 cm. The results showed that most of the variables analyzed had normal distributions in the both horizon. Each of the variables presented a spatial structure and they were modeled quite well. Calcium, Na and SEB that showed smaller values of nugget effects in the both horizons indicated that the agricultural land use practice somehow favored close distance continuity for these variables. The spatial dependence range was 11.80-91.00 m, indicating that the grid spacing was adequate for the characterization of the spatial variability of the exchangeable cations. Both the variograms and the maps obtained with kriging showed that the spatial variability for the exchangeable cations and SEB was tended to be greater in the subsoil than in the topsoil, suggesting that the land use practices had led to more homogeneity in the top soil than in the subsoil. The maps obtained with kriging also showed that the spatial variability was stronger in the north part of the plot near a traffic passage than in the remainder area, indicating the effect of anthropogenic disturbance on soil exchangeable cations.

Key words: Soil exchangeable cation, geostatistics, special variability, Chinese Ecosystem Research Network

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 farmland, within a suburban house lot and even within a single soil individual (Benayas *et al*., 2004; Cambardella *et al*., 1994; Chien *et al*., 1997; Jiang *et al*., 2005; Paz-González *et al*., 2000; Liang *et al*., 2003). The small-scale variability may be difficult to measure and not apparent to the casual observe. In some cases the height or vigor of vegetation reflects the subsurface variability (Jiang *et al*., 2006). Analysis of small-scale variability has practical uses in managing soil fertility for a given field (Brady and Weil, 2002). Conventional farmers manage fields as if they were homogeneous, i.e., one sit of practices is applied to the entire field (Cahn *et al*., 1994; Bourennane *et al*., 2003). Traditionally, soil sampling protocol is generally based on finding a central tendency of soil properties for a field or an experimental plot and assess the status and changes of soil properties through analyzing the traditional statistical parameters, i.e., mean, standard deviation, coefficient of variation, median, minimum, maximum and data normality. When small-scale variability exists, the actual level of soil properties at most spots in a field or an experimental plot is likely to be either higher or lower than the average soil test value for the field or the experimental plot. The development of global positioning systems, geographic information systems and geostatistical techniques have renewed challenges to develop efficient sampling and mapping procedures that accurately define spatial variability and hence, the within-field scale spatial variability analysis of soil properties is expected to improve the experimental accuracy for long-term experiments (Legendre *et al*., 2002; Van Meirvenne, 2003).

When combined with other measures of soil fertility, cation exchange capacity CEC is a good indicator of soil quality and productivity (Brady and Weil, 2002). Soil exchangeable Ca, Mg, K and Na are traditional referred to as exchangeable bases. Long-term field experiments on soil exchangeable cations are of significant importance for investigating soil fertility and soil quality changes under

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specific crop systems and field management practices. The spatial variability of soil exchangeable cations has been largely reported at the field-scale (Cambardella *et al*., 1994; Chien *et al*., 1997; Paz-González *et al*., 2000; Cahn *et al*., 1994; Van Meirvenne, 2003). However, it is still limited at the field-scale related to long-term experiment of soil properties. Soil exchangeable Ca, Mg, K and Na are the dominant exchangeable cations in Northeast China (Jiang *et al*., 2003) 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.

The objectives of this study were to describe the field-scale variability of exchangeable Ca, Mg, K and Na and to map the spatial distributions of these bases at a long-term experimental field in the Shenyang Experimental Station of Ecology, Chinese Academy of Sciences. The results obtained may be useful for identifying the appropriate sampling density for these scales of soil surveys and fertilizer experiments.

MATERIALS AND METHODS

Study site: This study was conducted at the Shenyang Experimental Ecological Station (41°31′ N, 123°22′ E), Chinese Academy of Sciences, a Chinese Ecosystem Research Network (CERN) site established in 1990. The station is located in a continental temperate monsoon zone, with a dry-cold winter and a warm-wet summer. The annual temperature ranges between 7.0-8.0°C, annual precipitation ranges between 650-700 mm and annual non-frost period ranges 147-164 days. The study site (42×30 m) was chosen for its apparent homogeneity. It was marked with regular rectangle grids (7×5 m each) and included 49 sampling points. Before it was changed to be an upland field in 1990, the field had been used as a paddy field for dozens of years. A corn-soybean rotation system has been established for about 10 years at the study site. The crops relied on natural rainfall and the field was somewhat poorly drained in summer (Jiang *et al*., 2006). The previous crop was maize (*Zea mays* L.). Rotary plowing to a depth of 15 cm was performed every spring. The soil at the study site is classified as an aquic brown soil (silty loam Hapli-Udic Cambosols in Chinese Soil Taxonomy) (Cooperative Research Group, 2001), with 10.50 g kg^{-1} total C, 1.08 g kg^{-1} total N, 0.40 g kg^{-1} total P, 21.4% sand, 46.5% silt and 32.1% clay at the 0-20 cm depth. The soil pH varied from 5.5-6.5 across the field. The bulk density was about 1.25 g cm^{-3}. The field was fertilized with 225 kg N, 60 kg P and 112 kg K per hectare annually. NPK nutrients were applied as basal dressing before soybean sowing.

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. Some of the extracts were diluted to fit the absorption range when necessary. The Sum of Exchangeable Bases (SEB) was calculated by adding up the total amount of Ca, Mg, K and Na measured above (Page, 1982).

Statistical analysis: Classical statistical parameters, i.e., mean, standard deviation, coefficient of variation, median, minimum, maximum and data normality, were calculated using SPSS 11.0 software. Isotropic and anisotropic semivariances of data were calculated using GS^+ geostatistical software (Gamma Design Software, 2000). Semivariance γ(h) is defined in the following equation:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left[z(x_i) - z(x_i + h) \right]^2 \qquad (1)$$

where, N(h) is the number of sample pairs at each distance interval h and $z(x_i)$ and z (xi + h) are the values of variable at any 2 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 of spatial dependence a (Cambardella *et al*., 1994; Cahn *et al*., 1994).

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

RESULTS AND DISCUSSION

Descriptive statistics: Table 1 summarized the statistics of soil exchangeable Ca, Mg, K, Na and SEB. The coefficients of skewness and kurtosis indicated that most of the variables analyzed had normal distributions. The distributions of K in 0-10 cm horizon and Ca and SEB in 10-20 cm horizon were fairly symmetric, but Ca and SEB in 0-10 cm horizon and K in 10-20 cm horizon were dissymmetric with skewness coefficient exceeding 1.0. Even though the coefficients of skewness were not too high, the exchangeable Na in both horizons seemed to depart slightly from normal distribution, because it had slightly negative kurtosis (-1.023 and -1.197).

Table 1: Descriptive statistics for data sets of soil exchangeable Ca, Mg, K, Na and SEB (cmol$_c$ kg^{-1})

Item	Mean	S.D.	C.V. (%)	Median	Minimum	Maximum	Skewness	Kurtosis
(a) In the topsoil horizon (49 observations)								
Ca	12.397	0.902	7.28	12.150	10.920	15.338	1.001	1.467
Mg	2.442	0.264	10.83	2.400	1.900	3.182	0.702	1.038
K	0.516	0.118	22.88	0.492	0.261	0.756	0.021	-0.552
Na	0.606	0.176	29.01	0.584	0.365	0.997	0.413	-1.023
SEB	15.961	1.136	7.12	15.685	14.324	19.923	1.242	2.230
(b) In the subsoil horizon (49 observations)								
Ca	12.976	1.024	7.89	12.963	10.455	15.177	0.038	-0.187
Mg	3.034	0.310	10.20	3.020	2.365	3.828	0.256	0.097
K	0.354	0.127	35.91	0.317	0.216	0.684	1.267	0.896
Na	0.532	0.126	23.73	0.491	0.340	0.750	0.337	-1.197
SEB	16.896	1.330	7.87	16.870	13.887	19.984	0.194	-0.163

Table 2: Parameters of the best-fitted semivariogram model for anisotropic variogram

				Effective range				
Item	Model	Nugget C_0	Sill C_0+C	A_1 (m)	A_2 (m)	C/(C_0+C) (%)	Model R^2	RSS
(a) In the topsoil horizon (49 observations)								
Ca	Spherical	0.279	1.973	131.2	87.4	85.9	0.620	1.8545
Mg	Exponential	0.027	0.173	169.6	81.4	81.8	0.510	7.911E-3
K	Linear	0.011	0.044	241.9	163.0	71.8	0.292	6.826E-4
Na	Linear	0.001	0.069	53.5	53.5	98.3	0.866	3.097E-3
SEB	Linear	0.441	3.292	95.6	59.6	86.6	0.616	4.8777
(b) In the subsoil horizon (49 observations)								
Ca	Linear	0.878	2.454	259.5	136.9	64.2	0.140	1.842
Mg	Linear	0.057	0.273	158.6	55.4	79.2	0.404	0.012
K	Linear	0.012	0.045	204.8	70.8	73.5	0.448	4.185E-4
Na	Linear	0.0006	0.035	53.7	53.7	98.3	0.638	8.537E-4
SEB	Linear	1.278	4.392	178.7	88.1	70.9	0.201	4.844

Mean Ca, Mg and SEB were slightly lower but mean K and Na higher in the 0-10 cm horizon than in the 10-20 cm horizon (Table 1). The comparatively lower contents of Ca and Mg in the topsoil might be caused by plant cycling and some abiotic process such as the preferential retention of leached Ca and Mg in the subsoil (Jiang *et al*., 2003; Shaw *et al*., 2001). Jobbáge and Jackson (2001) had compared more than 10000 soil profiles across a range of ecological conditions and found that among exchangeable base cations, K had the shallowest distribution and was the only base cation with a distribution shallower than CEC.

The coefficients of variation were lower for Ca, Mg and SEB than for K and Na in the both horizons. The higher variability of K and Na may be attributed to soil fertilization. The mean values were slightly higher than the median values for all the variables in the both horizons, but the differences were very little (Table 1), indicating that the test variables were not deeply influenced by extreme values at the studied scale (Chien *et al*., 1997; Paz-González *et al*., 2000; Jiang *et al*., 2006).

Variograms: The directional variograms were computed in 4 principle directions of east-west (0°), southeast-northwest (45°), south-north (90°) and northwest-southeast (135°) with a tolerance of 22.5 degrees. The model-fitted parameters were listed in Table 2. The best-fitted model for most of the variables was linear, but Ca and Mg in the 0-10 cm horizon showed spherical and exponential, respectively. The anisotropic semivariograms indicated that the spatial structures of Ca, Mg, K and SEB were geometrically nested with an anisotropic ratio of 1.50, 2.08, 1.48 and 1.60, respectively, in the 0-10 cm horizon, while those in the 10-20 cm horizon were 1.90, 2.86, 2.89 and 2.03, respectively. The anisotropic semivariograms for Ca, K and SEB in the 135°, direction and for Mg in the 0° direction of the 0-10 cm horizon exhibited the strongest anisotropies, as indicated by their maximal differences between the major and minor axis range parameters (A_1 and A_2) in their models (Fig. 1 and Table 2). In comparison with the other 4 variables, the directional varigrams of Na showed no differences of sill and range among the four directions in the both horizons. Furthermore, sodium in each of the 2 horizons showed the shortest range as compared with the other four variables. The anisotropic semivariograms showed that the structural component of sample variance for most of the variables was highly spatial dependence with the ratio of C/(C_0+C) >70%, Ca in the 10-20 cm horizon was the exception.

Figure 2 shows the scaled experimental semivariances and the adjusted semivariogram models for all the variables in both horizons and the corresponding model-fitted parameters are listed in Table 3. All the

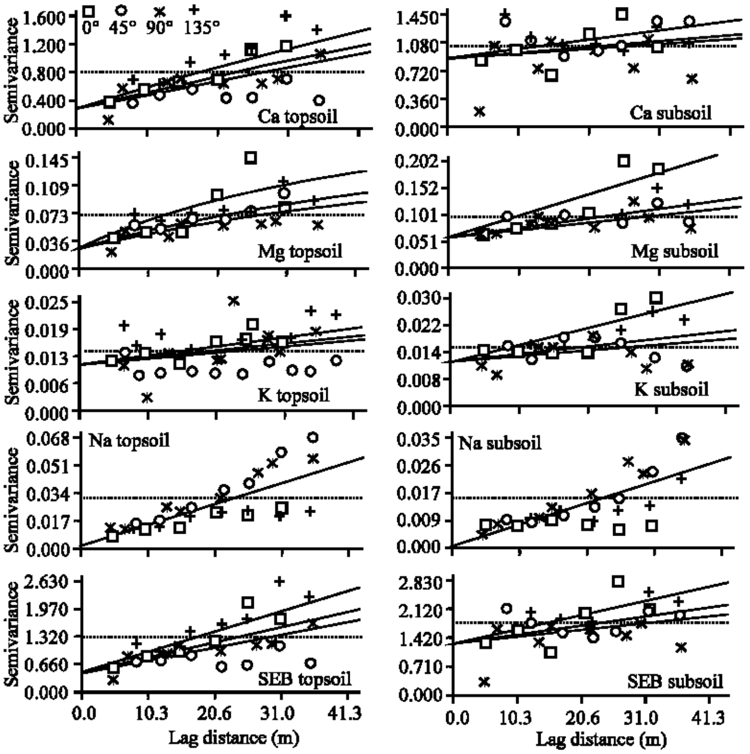


Fig. 1: Anisotropic semivariograms for soil exchangeable Ca, Mg, K, Na and SEB

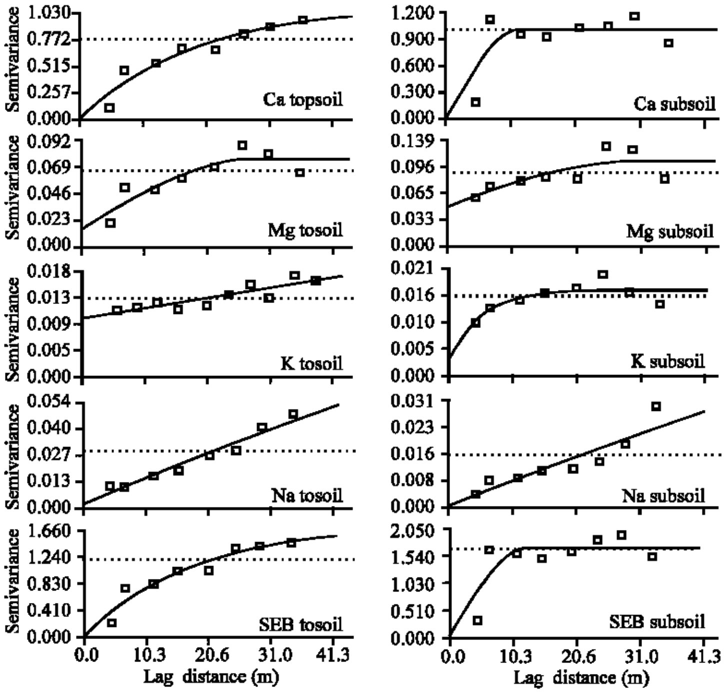


Fig. 2: Isotropic semivariograms for soil exchangeable Ca, Mg, K, Na and SEB

Table 3: Parameters of the best-fitted semivariogram model for isotropic variogram

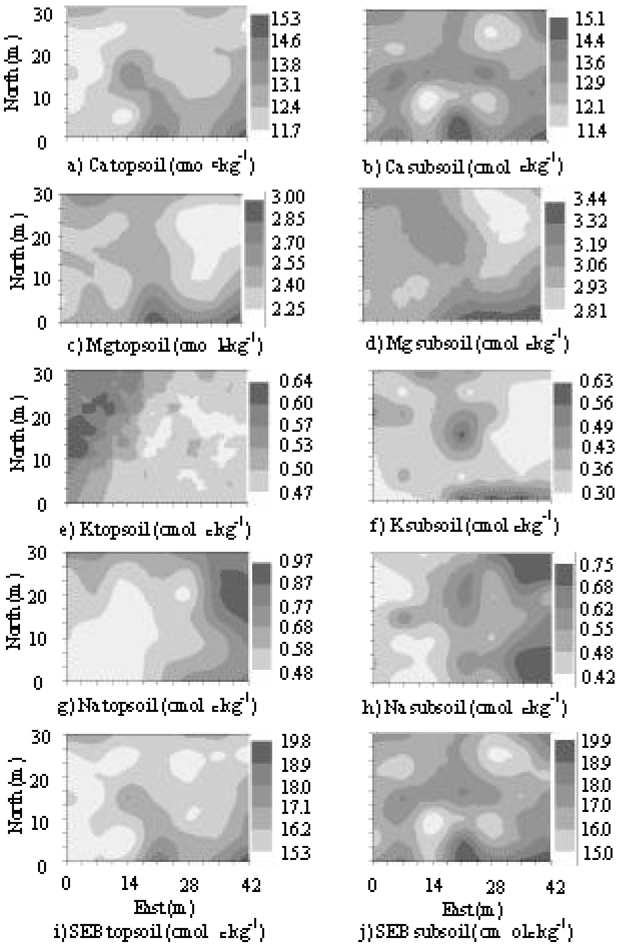
Item	Model	Nugget C_0	Sill C_0+C	C/(C_0+C) (%)	Range A, (m)	Model R^2	RSS
(a) In the topsoil horizon (49 observations)							
Ca	Exponential	0.001	1.149	99.9	54.66	0.911	0.052
Mg	Spherical	0.015	0.080	81.3	27.50	0.800	6.658E-4
K	Spherical	0.010	0.021	51.2	87.91	0.756	1.092E-5
Na	Spherical	0.002	0.083	97.7	91.00	0.953	6.824E-5
SEB	Exponential	0.001	1.859	99.9	55.59	0.916	0.118
(b) In the subsoil horizon (49 observations)							
Ca	Spherical	0.001	1.043	99.9	11.80	0.600	0.333
Mg	Spherical	0.051	0.111	53.6	30.59	0.585	1.546E-3
K	Exponential	0.003	0.018	84.8	16.32	0.659	2.069E-5
Na	Spherical	0.0002	0.044	99.5	91.00	0.822	8.745E-5
SEB	Spherical	0.001	1.786	99.9	13.44	0.659	0.736

variables were spatially dependent and they were modeled quite well, with high model R^2 (0.585-0.916) and small model reduced sum of squares (RSS). Calcium was modeled with exponential and spherical semivariograms in the topsoil and subsoil, respectively, with little nugget effects, while SEB with spherical and exponential semivariograms in the topsoil and subsoil, respectively, with little nugget effects as well. Magnesium was modeled with a spherical semivariogram and exhibited nugget effects in both horizons, while Na with a spherical semivariogram also but showed little nugget effects. Potassium was modeled with spherical and exponential semivariograms in the 2 horizons respectively, but the nugget effect was higher in the topsoil than in the subsoil. The nugget effect could be viewed as an indicator of continuity at close distances, as a semivariogram was basically a plot of sample dissimilarity between sample distances (Paz-González *et al*., 2000). Calcium, Na and SEB, having small values of nugget effects in the cultivated horizon (in both the topsoil and subsoil horizons), indicated that the agricultural land use practice somehow favored close distance continuity for these variables.

The nugget effect was similar for Ca, Na and SEB in both horizons, but it was different for both Mg and K. The nugget effect for Ca, Na and SEB was small in both horizons, which might be induced by homogenous soil use that improved the continuity at close distances of CEC (Paz-González *et al*., 2000). The small nugget effect was in line with the results of Delcourt *et al*. (1996) who examined the variability of soil fertility in a field-scale of 5 ha in Belgium and observed that the exchangeable Ca and Na had no nugget effect but K and Mg had a nugget variance of 0.006 and 2.7 cmol_c^2 kg^{-2}, respectively. It should be mentioned here that in some previous studies, when soil exchangeable acidity is small enough to be neglected, the SEB could be named as the Effective Cation Exchange Capacity (ECEC) depending on the differences of determination methods for exchangeable cations (Brady and Weil, 2002) and hence, SEB was comparable to CEC or ECEC. Castrignanò *et al*. (2000) also reported that the nugget effect for CEC was smaller than any of the other test soil physico-chemical properties at a field-scale. However, the nugget effect of CEC could be greater than either exchangeable Ca or Mg in a field-scale, e.g., Mueller *et al.* (2001) had conducted a field study of 20.4 ha area in Clinton country, Michigan, USA and observed that the ratio of nugget to sill was 25% for CEC, but it was only 11 and 9% for exchangeable Ca and Mg, respectively.

It should be taken into account that the underlying processes causing modifications in the geostatistical parameters were to some extent outlined, nor are they well known or easily determined from collected data set. The nugget effect differences may also be due to errors in sample location determination, laboratory measurements, interpolation and local random occurrence (Cambardella *et al*., 1994; Chien *et al*., 1997; Paz-González *et al*., 2000; Jiang *et al*., 2006). Since, semivariograms and kriging estimate and describe, but do not explain spatial variation, it should also be taken into account that measured variability and sample distance are dependent on each other (Chien *et al*., 1997; Paz-González *et al*., 2000). The sampling design used in this work seemed adequate for quantifying spatial variability within the field-scale, but the cause of the nugget effect differences of a same variable in both horizons could not be clearly explained yet.

The range of spatial dependence was 11.80-91.00 m, indicating that the grid spacing was adequate for the characterization of the spatial variability of the exchangeable cations. The parameter values and semivariograms were similar for SEB to those for Ca in both horizons (Table 3 and Fig. 3), this might be due to the dominant contribution of exchangeable Ca to SEB. In this study, SEB was not a directly determined index through laboratory experiment so that it would be certainly affected by the most influential individual variables. Chien *et al*. (1997) analyzed the spatial variability of soil extractable P, Ca, Mg, Fe, SEB and the



a) Ca topsoil (cmol ckg^{-1})
b) Ca subsoil (cmol ckg^{-1})
c) Mg topsoil (cmol ckg^{-1})
d) Mg subsoil (cmol ckg^{-1})
e) K topsoil (cmol ckg^{-1})
f) K subsoil (cmol ckg^{-1})
g) Na topsoil (cmol ckg^{-1})
h) Na subsoil (cmol ckg^{-1})
i) SEB topsoil (cmol ckg^{-1})
j) SEB subsoil (cmol ckg^{-1})

Fig. 3: Maps obtained with block kriging showing the spatial distribution of soil exchangeable Ca, Mg, K, Na and SEB

particle-size distribution in mid-west Taiwan and reported that the parameters for best-fitted semivariogram models of soil exchangeable Ca and SEB were also quite similar at a large-scale of area up to 10 km^2. Overall, the spatial variability for the exchangeable cations and SEB tended to be greater in the subsoil than in the topsoil.

Spatial distribution via kriging: Figure 3a and b showed the contour maps obtained with kriging for Ca in the topsoil and subsoil horizons, respectively. The pattern of slightly greater spatial variability in the second one could be seen from the maps, as Fig. 3b exhibited much more variability in different directions.

The spatial variability of Mg was greater in the subsoil than in the topsoil, even though the coefficient of variance for samples was slightly smaller in the subsoil (10.2%) than in the topsoil (10.8%). The maps showed significant differences of Mg contents in both horizons. The map obtained with kriging showed that Mg was 2.25-3.00 cmol$_c$ kg^{-1} in the topsoil horizon, but it was 2.81-3.44 cmol$_c$ kg^{-1} in the subsoil horizon (Fig. 3c and d).

The directional variability of K mainly occurred in the 135 and 0° directions, while Na in the 45 and 90° directions in the topsoil (Fig. 3e and f). In the subsoil, the variability of K mainly occurred in the 0° direction, while Na in the 90 and 45° directions (Fig. 3g and h). Contrary to Mg, the topsoil contained more K and Na than the subsoil.

Maps for SEB (Fig. 3i and j) showed a similarity to those for Ca. As discussed above, SEB had the similar spatial variability to Ca and the pairs of maps in each horizon exhibited clearly the comparison between the 2 variables. The micro-regions of high SEB were well coincided with those of the high Ca, while fewer dissimilarities from the maps of the two variables might be affected by the secondary contributory cation of exchangeable Mg to SEB, as it accounted for 15.3 and 17.96% of SEB in the topsoil and subsoil horizon, respectively. As the total contributions of K and Na to

SEB were less than 7.03% in both horizons, their effects on the spatial distribution of SEB could be neglected.

For soil exchangeable cations that behaved as random variables, the estimation of main values could be achieved with any spatial distribution of sample sites. The sample size required for a reliable estimation of the mean value increases as the diversity increases. However, for the attributes exhibiting spatial structure, samples collected at close distances could not be regarded as independent experiments (Jobbáge and Jackson, 2001). Since spatial dependence could lead to misinterpretation of the results obtained by a standard sampling scheme, the lack of soil spatial uniformity is thus emphasizing the need for thorough sampling.

As one of the Chinese Ecosystem Research Network (CERN) sites for soil properties, the test field was designed and expected to sustain for at least 100 years, the spatial analysis of soil exchangeable base cations and the sum of exchangeable bases at the field-scale is looking forward to improving the accuracy and easier comparison of related observatory soil properties. Furthermore, it is beneficial to setting up a more precise, standard and sustainable long-term sampling scheme in comparison with the old, traditional method. This information also could be used as a reference for identifying the appropriate sampling density for these scales of field experiments and long-term experiment for soil fertility evolution.

CONCLUSION

The results of this study demonstrated that within a field-scale, spatial variability might vary among different exchangeable cations and between different soil horizons. Generally, Ca, Mg and SEB were slightly higher but K and Na were lower in the subsoil than in the topsoil. All the variables were spatially dependent and they were modeled quite well. Both the variograms and the maps obtained with kriging showed that the spatial variability for the exchangeable cations and SEB tended to be greater in the subsoil than in the topsoil, suggesting that the land use practices had led to more homogeneity in the topsoil than in the subsoil.

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