Spatial variability of Cu, Zn and Mn contents in Non-anthropized soils in the Santa Catarina state

Variabilidade espacial dos teores de Cu, Zn e Mn em Solos não antropizados no estado de Santa Catarina

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ABSTRACT
The aim of this study was to evaluate the spatial variability of Cu, Zn and Mn in non-anthropic soils in the Santa Catarina state, using ordinary kriging and ordinary cokriging models. The Cu, Mn and Zn contents were taken from the database of the Department of Soils and Natural Resources of the State University of Santa Catarina. The geostatistical methods of ordinary kriging and ordinary cokriging were applied to fit the theoretical models to the experimental semivariograms. The model choice with the best fit was based on the parameters of Average Square Root, Average Standard Error, Akaike Criterion and Spatial Dependency Index. For ordinary kriging the Gaussian model (R² 0.998) explains the spatial variability of Cu, while the circular model describes the variations of Mn (R² 0.894) and Zn (R² 0.991). For ordinary cokriging, the exponential model describes the behavior of trace elements versus land elevation. Geostatistical methods are effective in the spatializing of Cu, Mn and Zn contents in non-anthropic soils in the Santa Catarina state. Finally, land elevation does not show a linear relationship with the trace elements levels, which are concentrated in the western region, correlating with the source material.

Keywords: trace elements, spatial variability, ordinary kriging, ordinary cokriging.

RESUMO
O objetivo deste estudo foi avaliar a variabilidade espacial de Cu, Zn e Mn em solos não antropizados do Estado de Santa Catarina com uso de modelos de krigagem ordinária e cokrigagem ordinária. Os teores de Cu, Mn e Zn foram retirados do banco de dados do Departamento de Solos e Recursos Naturais da Universidade do Estado de Santa Catarina. Os métodos geoestatísticos de krigagem ordinária e cokrigagem ordinária foram aplicados para o ajuste dos modelos teóricos aos semivariogramas experimentais. A escolha do modelo com melhor ajuste fundamentou-se nos parâmetros de Raiz Quadrada Média, Erro Padrão Médio, Critério de Akaike e Índice de Dependência Espacial. Para krigagem ordinária o modelo gaussiano (R² 0.999) explica a variabilidade espacial de Cu, e o modelo circular descreve as variações de Mn (R² 0.999) e Zn (R² 0.999). Para cokrigagem ordinária, o modelo exponencial descreve o comportamento dos elementos-traço versus elevação do terreno. Os métodos geoestatísticos são eficazes na espacialização dos teores de Cu, Mn e Zn em solos não antropizados do estado de Santa Catarina. Por fim, a elevação do terreno não demonstra relação linear com os teores de elementos-traço, os quais concentram-se na região oeste, correlacionando-se, com o material de origem.

Palavras-chave: elementos-traço, variabilidade espacial, krigagem ordinária, cokrigagem ordinária.

1 INTRODUCTION
Trace elements occur naturally in environments such as soil. They consist of chemical elements arranged, commonly, in low concentrations, i.e., levels below 100 µg L⁻¹ (Martín-Consuegra et al., 2015; Antoniadis et al., 2019). In nature, they are distributed between non-essential elements such as, for example, As, Cd, Cr, Hg and Pb, and biologically essential
elements, such as Cu, Fe, Mn, Mg and Zn (Campos et al., 2017; Bonanno et al., 2018; Idrissi et al., 2022).

Still, trace elements are characterized as potentially dangerous to ecosystems and, therefore, to all living organisms (Tchounwou et al., 2012), due to their toxicity, non-biodegradability and prolonged half-life (Milićević et al., 2017; Balerini et al., 2018; Gupta et al., 2019).

The natural levels and distribution of trace elements in soils are mainly controlled by the constitution and mineralogy of the source material (Bini et al., 2011; Souza et al., 2015; Toth et al., 2016). Moreover, the accumulation of these elements in the environment is accentuated by anthropogenic sources, especially agricultural and industrial activities (Suppi et al., 2018).

Therefore, the concentration and translocation of trace elements are related directly and specifically to the spatial variation of soil properties, such as the geographic location of the lithogenic material (Tripathi et al., 2015; Santos et al., 2016). Thus, the analysis and characterization of the spatial variability of trace elements in the soil can be performed using geostatistical models (Liang et al., 2017; Ayele et al., 2020; Monego et al., 2020).

Geostatistics encompasses methods such as, for instance, ordinary kriging and ordinary cokriging, being effective for analyzing the spatial variability of trace elements in the soil, as they possess sufficient statistical tools to integrate the information into a mapping using spatial interpolation (Pham et al., 2019; Belkhiri et al., 2020). Ordinary kriging is a simple and common method, used for the optimal unbiased interpolation of regionalized variables (Qin et al., 2019). In turn, ordinary cokriging provides multivariate spatial interpolation (Giraldo et al., 2020), providing an optimal estimation of the correlation between different regionalized variables (Mirzaee et al., 2016; Golden et al., 2020).

Then, the aim of this study was to evaluate the spatial variability of Cu, Zn and Mn in non-anthropic soils in the Santa Catarina state, using ordinary kriging and ordinary cokriging models.
2 MATERIAL AND METHODS

For the study, the Department of Soils and Natural Resources of the State University of Santa Catarina database was used as the original source. The information integrates, in particular, the Cu, Mn and Zn contents observed in the A horizon of 42 soil profiles sampled in the territorial extension of Santa Catarina (Figure 1).

The determination of Cu, Mn and Zn contents was performed in duplicate. For this purpose, samples of air-dried fine soil (ADFS) were crushed, homogenized in an agate mortar and sieved in 145 mm sieves.

To quantify Mn, the USEPA 3050B method in a digester block was used, determining the levels by optical emission spectrometry with inductively coupled plasma source (ICP OES) (Suppi, 2017). While for the Cu and Zn contents determination, 0.75 g of samples were kept in contact, in a digester block, with 0.5 mL of H₂O and 7.0 mL of aqua regia solution (sample opening) under 90 ± 5°C for 120 min. Subsequently, 10 mL of distilled H₂O was added to the cooled samples, followed by filtration. Aliquots were subjected to high-resolution atomic absorption spectrophotometry with flame atomization (HR-F-AAS) and continuous source (Hugen, 2011).

Figure 1. Location of soil profiles sampled in the Santa Catarina state.

Source: Adapted from IBGE.
The Cu, Mn and Zn contents were submitted to descriptive exploratory analysis, obtaining the values of arithmetic mean, median, maximum and minimum values, standard deviation, coefficient of variation, asymmetry and kurtosis.

To estimate the spatial variability of Cu, Mn and Zn, the lag size was previously established with the application of an empirical rule. The lag size corresponds to a distance vector, which must be equal to half of the largest interval between the sampled points (Ramos and Blanco, 2019; Khayli et al., 2021).

The geostatistical methods of ordinary kriging (Equation 1) and ordinary cokriging (Equation 2) were applied to fit the theoretical models to the experimental semivariograms, being prepared using the ArcGIS Desktop® software, version 10.1 (Esri, 2013).

\[
z^*(x_0) = \sum_{i=1}^{n} \lambda_i^* z(x_i) \quad (1)
\]

Whereas:

\[z^*(x_0)\] is the forecast location; \(n\) is the number of evaluated values; \(z(x_i)\) is the value evaluated at the i-th location and \(\lambda_i\) is an unknown weight for the value at the i-th location.

\[
z_{p_0}^*(x_0) = \sum_{p=1}^{N} \sum_{i=1}^{n_p} \lambda_i^p z_p(x_i) \quad (2)
\]

Whereas:

\(p_0\) and \(p\) are specific variables of a set of \(N\) variables.

For Cu, Mn and Zn, six theoretical models were selected among all the fitted models, summarized in the Circular, Spherical, Stable, Exponential, Gaussian, Hole Effect, J-Bessel, Pentaspherical, Rational Quadratic and Tetraspherical models. Finally, the model choice with the best fit was based on the parameters of Average Square Root (ASR) (Equation 3), Average
Standard Error (ASE) (Equation 4), Akaike Criterion (AIC) (Equation 5) and Spatial Dependence Index (SDI) (Equation 6).

\[
\text{ASR} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Y_i - X_i)^2}
\]  

Whereas:

\(N\) is the number of samples; \(Y_i\) is the value estimated by interpolation and \(X_i\) is the measured value of the variable.

\[
\text{ASE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \sigma^2 (X_i)}
\]  

Whereas:

\(\sigma^2\) is the variance of the sample.

\[
\text{AIC} = N \times \ln(\text{SQ}_{\text{res}}) - N \times \ln(N) + 2
\]  

Whereas:

\(\text{SQ}_{\text{res}}\) is the residual sum of squares and \(p\) is the number of model parameters.

\[
\text{SDI} = \left( \frac{C}{C_0 + C} \right) \times 100
\]  

Whereas:

\(C\) the contribution of the semivariance and \(C_0 + C\) the threshold.
3 RESULTS AND DISCUSSION

Depending on the results observed in the descriptive statistics analysis (Table 1), the Cu content ranged from 0.28 to 344.23 mg kg\(^{-1}\), Mn from 9.62 to 5060.00 mg kg\(^{-1}\) and Zn from 9.62 to 126.35 mg kg\(^{-1}\). The discrepancy between the contents of Cu, Mn and Zn explains the high values of standard deviation (SD) and coefficient of variation (CV), explaining, consequently, the high degree of dispersion of the contents of trace elements.

Additionally, the asymmetry and kurtosis information vary, in due order, from 0.46 to 1.47 mg kg\(^{-1}\) and 1.97 to 4.26 mg kg\(^{-1}\). It indicates that the Cu, Mn and Zn contents behave as asymmetric and have non-normal distribution.

Table 1. Descriptive statistical parameters for Copper, Manganese and Zinc contents in soils in the Santa Catarina state.

<table>
<thead>
<tr>
<th>Element</th>
<th>Average</th>
<th>Median</th>
<th>Maximum</th>
<th>Minimum</th>
<th>SD</th>
<th>CV (%)</th>
<th>Asymmetry</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>90.64</td>
<td>76.62</td>
<td>344.23</td>
<td>0.28</td>
<td>99.10</td>
<td>109.34</td>
<td>1.13</td>
<td>3.45</td>
</tr>
<tr>
<td>Mn</td>
<td>1046.10</td>
<td>301.96</td>
<td>5060.00</td>
<td>9.62</td>
<td>1332.20</td>
<td>127.35</td>
<td>1.47</td>
<td>4.26</td>
</tr>
<tr>
<td>Zn</td>
<td>56.93</td>
<td>48.60</td>
<td>126.35</td>
<td>9.62</td>
<td>35.60</td>
<td>62.54</td>
<td>0.46</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Source: Elaborated by the authors.

The normality absence makes the structure and properties of semivariograms vulnerable (Vasu et al., 2020). Therefore, data transformation is an efficient alternative to minimize the effect of extreme values, allowing the production of kriging and cokriging mappings (Ramzan and Wani, 2018).

For the Cu, Mn and Zn contents, the logarithmic transformation was applied, being enough to improve the data distribution, in agreement with the results of the descriptive statistics (Table 2).

Table 2. Descriptive statistical parameters, with logarithmic transformation, for Copper, Manganese and Zinc contents in soils in the Santa Catarina state.

<table>
<thead>
<tr>
<th>Element</th>
<th>Average</th>
<th>Median</th>
<th>Maximum</th>
<th>Minimum</th>
<th>SD</th>
<th>CV (%)</th>
<th>Asymmetry</th>
<th>Kurtosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3.41</td>
<td>4.34</td>
<td>5.84</td>
<td>-1.27</td>
<td>1.90</td>
<td>55.67</td>
<td>-0.55</td>
<td>2.10</td>
</tr>
<tr>
<td>Mn</td>
<td>5.97</td>
<td>5.71</td>
<td>8.53</td>
<td>3.08</td>
<td>1.58</td>
<td>26.54</td>
<td>-0.13</td>
<td>2.01</td>
</tr>
<tr>
<td>Zn</td>
<td>3.81</td>
<td>3.88</td>
<td>4.84</td>
<td>2.26</td>
<td>0.74</td>
<td>19.29</td>
<td>-0.38</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Source: Elaborated by the authors.

The transformed Cu, Mn and Zn contents exhibit normality, thus sustaining the consistency of the data for use in geostatistical models (Kostopoulou, 2020). The results of the
central tendency measure are similar, denoting a symmetrical distribution, also validated by the asymmetry and kurtosis values close to zero and two, respectively (Wani et al., 2012).

3.1 ORDINARY KRIGING

The Gaussian model provides a better fit to explain the spatial variability of Cu, while the circular model adequately describes the variations of Mn and Zn (Table 3). The choice of models was based on the conditions of approximate and lowest possible values of Average Square Root (ASR), Average Standard Error (ASE) and Akaike Criterion (AIC) (Mello and Oliveira, 2016; Barbosa et al., 2019).

Table 3. Parameters of semivariogram models adjusted using the ordinary kriging method for Copper, Manganese and Zinc contents in soils in the Santa Catarina state.

<table>
<thead>
<tr>
<th>Model</th>
<th>Range (Km)</th>
<th>Baseline (Km)</th>
<th>SDI</th>
<th>R²</th>
<th>ASR</th>
<th>ASE</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Gaussian</td>
<td>38.47</td>
<td>5868.26</td>
<td>100</td>
<td>0.998</td>
<td>72.81</td>
<td>55.95</td>
</tr>
<tr>
<td>Mn</td>
<td>Circular</td>
<td>38.47</td>
<td>1891987.60</td>
<td>100</td>
<td>0.894</td>
<td>1071.78</td>
<td>1075.99</td>
</tr>
<tr>
<td>Zn</td>
<td>Circular</td>
<td>38.47</td>
<td>856.98</td>
<td>100</td>
<td>0.991</td>
<td>22.57</td>
<td>22.90</td>
</tr>
</tbody>
</table>

Source: Elaborated by the authors.

The trace elements contain equal range, corresponding to 38.47 km. The reach refers to the parameter that expresses the maximum distance with spatial correlation (Moratto et al., 2021). Hence, sampling points with a distance greater than the range defined for Cu, Mn and Zn exhibit random behavior and spatial discontinuity (Behera and Shukla, 2014; Laekemariam et al., 2018).

The threshold comprises the moment when the spatial variance stabilizes (Machado et al., 2022), with Zn presenting the lowest value (856.98) followed by the values of Cu and Mn, which refer to 5868.26 and 1891987.60, respectively.

The SDI totals 100% for both independent variables, indicating weak spatial dependence even over large distances (Belkhiri et al., 2020; Fei et al., 2021). This behavior for Cu, Mn and Zn is explained by intrinsic variations in the soil, such as texture, mineralogy and material of origin (Costa et al., 2012; Ramzan and Wani, 2018).

The models applied to the trace elements levels, using ordinary kriging, support accurate predictions of spatial variability, due to correlation coefficient values (R²) approximate to 1. However, the applicability and accuracy of the ordinary kriging method are supported by statistical error evaluations, such as ASR and ASE. The contents of Cu, Zn, but in particular Mn,
present high values of ASR, ASE and AIC, indicating that the contents of the elements were not accurately predicted, being overestimated or underestimated. Thus, it signals a sparse and heterogeneous distribution, contributing to the obstacle in establishing a sufficiently defined spatial relationship (Kostopoulou, 2020).

The maps predicting the concentration of the trace elements in the soils of the state of Santa Catarina (Figure 2) show that the Cu, Mn and Zn contents have similar distribution patterns. The content of these elements was high for most of the territory, with hotspots in the western region. On the other hand, the lowest levels are in the east zone, i.e., on the state coast.

Figure 2. Maps of spatial variability of Copper (a), Manganese (b) and Zinc (c) in the soils of the state of Santa Catarina.

The higher concentrations of Cu, Mn and Zn predominating in the western region of Santa Catarina territory are justified by the preponderance of igneous rocks, such as basalt. These rocks are characterized as basic, intermediate and with a prominent amount of trace elements. Therefore, the parent material consolidates itself as the determining factor for the distribution of
Cu, Mn and Zn in the soils of the state of Santa Catarina (Shukla et al., 2016; Oliveira et al., 2018; Oliveira, 2019; Madeira et al., 2021; Suppi et al., 2021).

3.2 Ordinary Cokriging

In accordance with the parameters of the adjusted semivariograms (Table 4), it is recognized that for the geostatistical method of ordinary cokriging, the exponential model is satisfactory to elucidate the behavior of trace elements versus terrain elevation. It corroborates with the minimum possible values of ASR, ASE, AIC and maximum $R^2$ value, providing an exact measure of how well the model fitted the semivariogram data (Fei et al., 2021).

<table>
<thead>
<tr>
<th>Model</th>
<th>Range (Km)</th>
<th>Baseline</th>
<th>SDI (%)</th>
<th>$R^2$</th>
<th>ASR</th>
<th>ASE</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Exponential</td>
<td>144.00</td>
<td>-</td>
<td>100</td>
<td>0.999</td>
<td>54.06</td>
<td>49.94</td>
</tr>
<tr>
<td>Mn</td>
<td>Exponential</td>
<td>59115.62</td>
<td>22630.74</td>
<td>100</td>
<td>0.893</td>
<td>1039.05</td>
<td>977.05</td>
</tr>
<tr>
<td>Zn</td>
<td>Exponential</td>
<td>234.00</td>
<td>4420.28</td>
<td>100</td>
<td>0.962</td>
<td>21.22</td>
<td>16.31</td>
</tr>
</tbody>
</table>

Source: Elaborated by the authors.

The cross semivariance analysis is essential for the applicability of the ordinary cokriging method. Hence, auxiliary variables are used to understand the behavior of the primary variables, when their sampling is characterized as financially unrealizable or hard to be measured (Farzaneh et al., 2022).

The optimal parameters of the exponential model indicate an extensive range, reaching 114.00, 234.00 and 59115.62 Km for Cu, Zn and Mn, respectively, along with terrain elevation correlation. The value identified for Mn is emphasized, which has a range 100 times greater than the extent of the studied area. Therefore, any sampling points located in an area with a radius smaller than or equal to the range values exhibit similar behavior of trace elements, being estimated with greater precision due to the existing spatial correlation (Cunha et al., 2013; Pelissari et al., 2014).

The spatial variance remains constant when reaching levels of 9439.73 for Cu, 22630.74 for Mn and 4420.28 for Zn in correlation with the terrain elevation. That is, the moment when the spatial variability of the trace elements reaches its maximum, represented by the tangent of the curve (Marko et al., 2013).
The SDI for Cu, Mn and Zn corresponds to 100%, i.e., the spatial dependence is characterized as weak (> 75%) for distances below the range (Khashei-Siuki and Sarbazi, 2013; Lundgren et al., 2017). This condition is associated with high estimation errors, observed by the ASR and ASE values (Barreto, 2015), which should be always close to zero (Golden et al., 2020).

Through geostatistical modeling, using ordinary cokriging, inference maps were generated, enabling a visual analysis of the spatial behavior of Cu, Mn and Zn in the soils of the state of Santa Catarina (Figure 3).

Figure 3. Map of spatial variability of Copper (a), Manganese (b) and Zinc (c) in soils in the Santa Catarina state, interpolated by ordinary cokriging with terrain elevation.

The inference maps generated by the ordinary cokriging method exhibit smooth spatial prediction intervals for Cu, Mn and Zn, providing a continuous surface. It also mitigates the appearance of bull's eyes, i.e., circular regions around the location of the known points, differing from the general smoothing of the independent variables and not representing the predicted pattern (Mello et al., 2015; Ohmer et al., 2017).
The spatial distribution maps of Cu, Mn and Zn show a similar pattern, with the levels of trace elements being present in the soils of the western and eastern regions of the state. However, they are mainly concentrated in western Santa Catarina. This behavior is linked to the predominance of basalt in the region, which has trace elements in its chemical composition (Basso et al., 2012; Korchagin, 2018).

Regarding the secondary variable, the presence of a theoretical model adjustment to the semivariograms confirms the possibility of using the terrain elevation to estimate the values of Cu, Mn and Zn in the soils of the state of Santa Catarina (Figure 4).

Figure 4. Terrain elevation map of the Santa Catarina state.

According to the map, it appears that the levels of trace elements in the east and central regions have a positive correlation with the elevation of the terrain. However, the western region is characterized by medium elevation values, while Cu, Mn and Zn concentrations are classified as medium and high, not being linearly correlated with altitude.

4 CONCLUSION

The analysis of the maps proves that the geostatistical methods of ordinary kriging and ordinary cokriging are effective in the spatialization of Cu, Mn and Zn contents in non-anthropized soils in the Santa Catarina state.
Land elevation, as a secondary variable, does not show a linear relationship with Cu, Mn and Zn contents.

Finally, with the applicability of geostatistical analyses, it appears that the trace elements are concentrated in the western region, directly correlating with the source material.

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