An assessment of heavy metal variability in a one hectare plot under natural vegetation in a serpentine area

Evaluation de la variabilité de teneurs en métaux lourds sur une parcelle d’un hectare sous végétation naturelle et sur roche serpentine

VIEIRA R. Sisney¹, TABOADA Teresa², PAZ Antonio²

Introduction
The elemental composition of soils varies greatly depending on the nature of their parent materials. This is also true for trace and toxic metals from lithogenic origin, i.e. directly inherited from the lithosphere. Soil variability arises naturally from pedogenesis factors, through complex interactions between parent material, time, topography and living organisms. Thus, if we consider the average elemental concentration much variation between soil types and within a given soil series will be obscured. As a consequence, soils can show marked spatial variability at the macro- and micro-scale. The lack of soil spatial uniformity is thus emphasizing the need for thorough sampling, since spatially dependent behavior can lead to misinterpretation of a standard sampling scheme.

The development of geostatistics has been a prime force in allowing soil spatial variability to be better quantified, especially at finer scales. By means of variogram and kriging, the theory of regionalized variables allows one to compute an estimation variance. When the estimation variance is less than the dispersion variance an optimal sampling pattern can be established.

In the Spanish region of Galicia (NW Spain) soils developed over serpentines present distinctive infertility characteristics, mainly show by excess of Ni and Cr, high Mg : Ca ratios and shortage of available nutrients such as Ca, K and P (Guitián Ojea y López López, 1981; López López et al., 1985). These soils, like most soils over serpentine, are
also characterized by the sparse development of the vegetation, which determines an important contrast with the surrounding areas with different parent material. Most of the land has been and is now devoted to agroforestry, in spite of their characteristics of low fertility. Recently a study was undertaken to investigate average concentrations and its analytical and spatial variability in particle size components, routine soil analysis and heavy metal contents (Taboada et al., 1997) in a small plot located within a serpentinite area in La Sierra de La Capelada (La Coruña province). Results showed high statistical variability, both in general soil properties and heavy metal contents.

The spatial distribution of heavy metal contents in soil has been evaluated using geostatistical techniques at different scales (Wopereis et al., 1988; Boekhold and van der Zee, 1992, Webster et al., 1994). In the work reported here we analyze the spatial variability in topsoil heavy metal (Fe, Mn, Cr, Ni, Cu, Zn and Co) contents in a 1 hectare plot. The aims of this study were i) to analyze the spatial distributions and if possible to map then and ii) to investigate potential relationships between the distributions of heavy metals.

**Material and Methods.**
The studied plot is located at Sierra de La Capelada (La Coruña, Spain). Total heavy metal contents (Fe, Mn, Cr, Ni, Cu, Zn and Co), particle size components, and routine soil fertility analysis were determined in samples collected from the topsoil of a 1 ha forested plot in order to allow description of the spatial variability. The details of the sample design, chemical analysis and the statistical analysis are given in Taboada et al. (1977) and included a combination of grid and nesting sampling schemes. The spatial variability was assessed using analysis of scaled semivariograms of some variables, cross semivariograms between them, and examination of maps obtained with kriging estimation, according to Vieira et al. (1983). Analysis of the semivariograms was done by comparing the adjusted model equation and its parameters. The cross semivariograms were analyzed only for the pairs of variables which present significant correlation, and whose use and interpretation are useful. For the fitting of semivariogram models, jack-knifing was used to help in the decision between two or more models.

**Results and discussion**
The main statistical data for all heavy metals were analyzed by Taboada et al., (1998). The proximity of the skewness and kurtosis of 0 and 3, respectively, indicates that most of the metals studied have a frequency distribution close to normal. The exceptions are for EDTA cobalt and lead, and for zinc. Most of the coefficients of variation are between 20 and 50% which means medium to high variation. The mean values indicate that most metals exceed the toxic limit acceptable for agricultural purposes.

According to correlation matrix results (Taboada et al., 1998), the highest positive correlation found was between Fe and Co with Mn of about 0.8, and Ni with Cu and EDTA Ni of 0.768. It should be emphasized the highly significant negative correlation between Cr and Ni, and Cr and EDTA Ni.

Figure 1 shows the semivariograms for some of the metals studied, with the adjusted models. The semivariograms were scaled by the variance values according to the procedure described in Vieira et al. (1997). Most of the semivariograms in figure 1
could be adjusted quite well to the spherical model. The best fit for Mn was a gaussian model. For Fe, Cr and Co, one single exponential model could be fitted reflecting the high correlation coefficient for these metals. For Ni, there was a dispute between a spherical and a gaussian model and jack-knifing was used to help the choice. The weakest variance structure is for Pb EDTA, as it can be seen by the high nugget effect value.

The cross semivariograms for all pairs of heavy metals analyzed are show in figure 2a. Figure 2b shows the cross semivariograms between the metals which presented the highest correlation. One single exponential model with zero nugget effect could be fitted to all of them.

Figure 3 shows the results of the jack-knifing for Ni with the spherical and the gaussian models show in figure 1. The jack-knifing parameters used in the judgement were the angular and the correlation coefficient between measured and estimated values, the mean reduced error and the variance of the reduced errors. According to Vieira et al. (1983), the best model should present jack-knifing results so that the above parameters are 1, 1, 0 and 1, respectively. Using this criteria, it can be seen that the gaussian model describes better the spatial variability of Ni, since it presented values closer to these criteria.

Using the spatial dependence for the metals analyzed, kriging was done on a 1 meter grid to produce the maps presented in figures 4 to 10, in which the variability of the heavy metals can be examined. Figure 10 shows the map of Co content obtained with kriging estimation. Figure 11 shows the map for Co content obtained with cokriging with Fe as the secondary variable. It can be seen that both maps, basically present the same results, with a little more detail on the cokriged map. Figures 12 and 13 show the maps for estimation variances for kriged and cokriged maps.

![Fig. 1.- Semivariograms for some of the metals studied, with models adjusted.](image-url)
Fig. 2.- Cross semivariograms for some heavy metals studied, with model adjusted.

Fig. 3.- Jack knifing for Niquel with spherical and gaussian models.
Figure 4. Chromium content (ppm) on serpentine soil, Galicia, Spain.

Figure 5. Copper content (ppm) on serpentine soil, Galicia, Spain.

Figure 6. Manganese content (ppm) in serpentine soil, Galicia, Spain.

Figure 8. Iron content (%) on serpentine soil, Galicia, Spain.

Figure 9. Nickel content (ppm) in serpentine soil, Galicia, Spain.

Figure 10. Cobalt content (ppm) in serpentine soil, Galicia, Spain.

Figure 11. Cobalt content (ppm) interpolated with cokriging.

Figure 12. Estimation variance for cokriging of Cobalt.

Figure 13. Estimation variance for kriging of Cobalt.
This study was undertaken to analyze the spatial variability of different heavy metals (Fe, Mn, Cr, Ni, Cu, Zn and Co) on a soil developed over serpentines used for wood production and occasionally as an extensive pasture. At the sampled site general soil properties such as pH, organic matter content, cation exchange capacity and texture fractions presented a distinctive ordered spatial distribution, revealing that the spatial variability of these properties at a one hectare scale could be mapped by kriging into micro-regions. It was difficult to discern common patterns and to seek common causes for the kriged maps. However, there seemed to be similarities and the general properties seemed to be corregrionalized to some degree. There is a still a need to investigate further the reasons for some of these relations.

Conclusions
It could be concluded that:
1.- There is a structure in the variance of heavy metals and average values may not represent them over space. The map obtained with kriging for manganese and for organic matter are very similar in appearance, except that were manganese values are high the organic matter contents are low.
2.- There is a still a need to investigate further the reasons for some of these relations.
3.- The variability of these heavy metal is so high that there is a need to use appropriate statistical tools such the semivariogram in order to reveal hidden information on the available data.

References

Key words : semivariogram, cross semivariogram, krigage, cokrigage
Mots clés : semi variogramme, semi variogramme croisé, krigage, cokrigage