REGIONAL GEOCHEMICAL MAPPING OF TOPSOIL HEAVY METALS: A SCORPAN KRIGING APPROACH CONDITIONAL ON SOIL MAP DELINEATIONS AND LAND USE.

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INTRODUCTION

According to the Italian Legislative Decree 152/06 of April 3rd, 2006, concerning the consolidated law governing environmental issues ("Testo Unico recante le Norme in Materia Ambientale"), the Contamination Threshold Value is defined as follows (art. 240, comma 1, letter b): "*threshold values are the values of contamination of environmental matrix above which the characterization and specific risk analysis of the contaminated site, as described in the Appendix 5 at part four of the present law, becomes necessary. In the event the potentially polluted site is located in an area where geogenic or anthropogenic factors are responsible for exceeding the threshold values for some parameters, the background content of these parameters is assumed as threshold*."
In the last decades the increase of industrial activities and the massive use of pesticides in agriculture, enhanced the risk of soil contamination by pollutants. Among these, heavy metals, due to their persistence, accumulate in soils possibly reaching concentrations above regulatory contamination thresholds. An accurate knowledge of the "usual" background content of metals in soils is then necessary to assess their contamination state. Aim of this work is to map the concentration of topsoil heavy metals using a Scorpan Kriging approach. The approach combines the trend of metals concentrations, as derived from the 1:50,000 soil map, with geostatistical modeling of the stochastic, locally varying but spatially correlated component. The trend component is described in terms of varying local means, calculated accounting for soil pedo-geochemical affinity and dominant land use.

MATERIALS AND METHODS

In the frame of soil survey carried out in Emilia Romagna (North Eastern Italy) most of the alluvial plain (about 12000 km^2) was investigated at the scale 1:50,000. The area, main agricultural area, covers slightly more than half of the region (12002 km^2), stretches south of the Po River and is delimited by the Apennines range in the south and by the Adriatic Sea in the east. The climate is temperate sub- continental, with an average annual temperature between 12 and 14°C and a mean annual precipitation ranging from 600 to 800 mm. Elevation ranges between -3 and 150 m a.m.s.l.

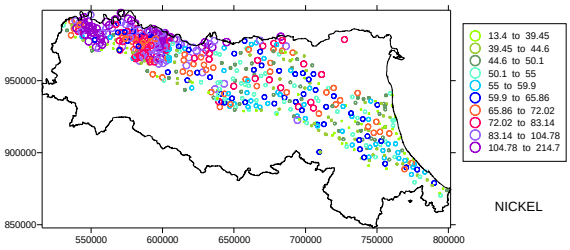

Figure 1 – Nickel sampling points and concentrations (the classes are the deciles of the observed distribution; values in mg kg^{-1}).

Metal	N	Mean	SD	Min	Median	90P	95P	Max
As	500	7.19	2.29	3.5	6.70	9.50	11.7	27.7
Cd	483	0.21	0.08	0.00	0.21	0.31	0.34	0.69
Cr	568	84.7	32.2	22.1	77.4	123.0	148.0	242.6
Cu	568	51.2	33.3	5.0	42.1	87.40	106.0	323.6
Ni	568	67.0	29.9	13.4	59.9	104.8	126.9	214.6
Pb	567	20.7	6.97	3.1	19.8	27.6	31.6	69.4
Sb	475	0.35	0.26	0.0	0.32	0.59	0.70	2.9
Sn	475	2.03	0.88	0.01	1.80	3.0	3.6	8.1
Zn	568	85.9	22.6	17.6	85.0	112.8	123.7	193.8

Table 1 – Heavy metals'descriptive statistics (mg Kg^{-1}).

The soils of the area, mainly on quaternary alluvial deposits, are characterized by a high degree of heterogeneity, ranging from coarse textured Arenosols to fine textured Vertisols, leached paleosols along the Apennine border, and soils characterized by the presence of organic horizons in the reclaimed areas of the Po delta. For a variable number (475-568) of representative sites (e.g. Nickel, Fig. 1), topsoil samples (20-30 cm) were analyzed for heavy metals. The pseudo-total contents of Cr, Pb, Zn, Cu, Ni, Sn, As, Sb and Cd were determined through acid extraction with aqua regia (UNI/EN 13346 method C) and detection by ICP (Inductive Coupled Plasma, EPA

6020). The upper limit of the “usual” background value defined for topsoil samples following the ISO international standards (ISO/DIS 19528). The descriptive statistics of the different metals are shown in Table 1. In order to take into account the non-stationarity of metal concentration, a simple kriging with varying local means (SKlm) approach was chosen (Goovaerts, 1997). This approach can be considered as one of the many spatialisation variants that have been termed as geostatistic-scorpan kriging by McBratney et al. (2003). The model is then partially deterministic and partially stochastic, and the locally varying mean can be estimated in various different ways. In this study, the locally varying means were calculated from the observations: these were divided into classes and mapped as categorical secondary information i.e. genetic functional soil unit - district combinations. The soil units were based upon: i) texture; ii) degree of weathering; iii) origin of parent material. This scheme led to 11 groups (Amorosi et al. 2011); these were further divided subgroups of using the nine agricultural districts of the plain a proxy of dominant land use. The geostatistical analysis followed the following steps:

- the available data in each of the nine districts were grouped in terms of soil units, and for each metal the local mean was computed and retained;
- the non-stationary local mean was subtracted from each observation to compute the residuals of each variable;
- a normal score transform was used to normalize the residuals assuming a Gaussian random function model;
- experimental variography of the transformed residuals was carried out computing the residual semivariograms;
- using the semivariogram models of the normalized residuals, these were simulated with simple kriging over a 1 km x 1 km regular grid and the corresponding local mean was added to the average (N = 1000) of the estimated residuals after being back-transformed;
- the final maps were prepared for each metal.

DISCUSSION AND CONCLUSIONS

The proposed methodology highlights for some metal the same trend described by the pedo-geochemical map of the natural background concentrations. In particular, topsoil Cr (Fig. 2) and Ni concentrations are due to the origin of soil parent materials and are higher in the province of Piacenza, Parma and Reggio Emilia where sediments are originated form catchments characterised by the presence of ophiolitic rocks. In this case land use does not affect metals distribution and their values are locally above the regulatory thresholds.

The distributions of Zn and Cu, on the other hand, are only in part explained in term of genetic-functional soil unit, with the coarser soils along the coastline showing the lower concentrations as compared to fine textured soils; nevertheless the higher contents which characterise the provinces of Reggio and Modena (and secondly Parma for Cu) are due to dominant land uses and management practices (vineyards, slurry applications); Cu values are always below the threshold, while Zn concentrations are locally above the threshold. Pb is uniformly distributed in agricultural soils regardless dominant land use and soil unit; it values is well below the regulatory threshold.

As, Cd and Sb have unclear distribution patterns, with extremely low concentrations; Sn, on the other hand, is systematically above the regulatory threshold in all the area, with higher concentrations in the provinces of Bologna (only in fine textured soils), Ravenna, Forlì-Cesena, Rimini and Ferrara, as far as the surveyed part is concerned. Sn is widely present is acaricides used in orchards and vineyards and in fungicides widely used in sugar beet and rice fields so that its abundance is likely to be due to dominant land use and management; further investigations are needed to confirm this evidence.

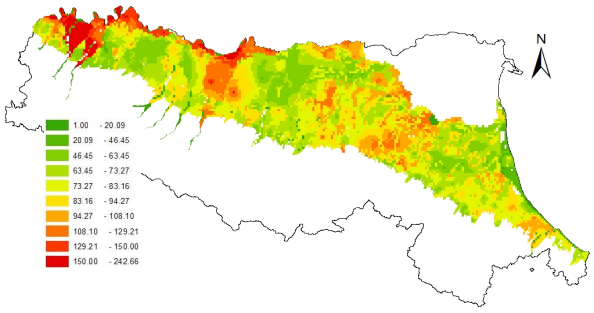

Figure 2 - Estimated Cr toposoil concentration (mg kg^{-1}).

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