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Spatial variation of Pb, Cu and Zn content in the soils of the Botanical Garden in Iaşi, Romania

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Abstract

The content of heavy metals in urban soils is an indicator of the degree of environmental pollution. In order to determine the level of pollution with Pb, Zn and Cu we have collected 144 samples from the soils of the Botanical Garden and its adjacent areas. Background values and probability kriging were used to characterise the spatial structure of the distribution of Pb, Zn and Cu contents. By comparison with the normal values in soils, average contents and background values indicate higher values, namely Cu > Pb > Zn. The probability maps of Pb, Zn and Cu suggest a high pollution risk which, related to the studied area, increases in the order Zn > Cu > Pb. Although the sources of the heavy metals studied in the soils of the Botanical Garden are hard to identify precisely, due to developments occurring in time, we can estimate that high heavy metal contents are the result of the complex interaction between car traffic, agricultural chemicals and the use of the adjacent land plots.

Keywords: soil, heavy metals, background, semivariogram, kriging.

1. Introduction

The concept of green growth in cities (OECD, 2013) highlights the essential role played by the green infrastructure in urban agglomerations (EC, 2012) as well as the benefits offered to their inhabitants (Dunnett et al., 2002; Maas et al., 2006; Abkar et al., 2010; EEA, 2010). The more than 3,000 botanical gardens currently existing in the world play multiple roles in urban agglomerations, namely a leisure and cultural role, a hygiene and sanitary role, a didactic, scientific role, the role to preserve the genetic fund of indigenous plants (Forbes, 2008; BGCI, 2012; Tănase and Oprea, 2013) and an economic role (Sharpley, 2007). Although they are protected ecosystems theoretically, botanical gardens are subject to the anthropic stress that is a characteristic feature of urban agglomerations, which is mirrored by the abnormal heavy metal (HM) contents in soils and in some species of bio-

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accumulator plants (Samecka-Cymerman and Kempers, 1999; An et al., 2006; Meng et al., 2011; Abou El Saadat et al., 2011; Słomka et al., 2011; Scanferla et al., 2012).

2. Materials and methodologies

2.1 Research site

Founded more than a century and a half ago by the physician and naturalist Anastasie Fătu, the Botanical Garden (BG) of Iaşi currently owns an area of 83.18 hectares (Tănase and Oprea, 2013). On the soil of the Botanical Garden (BGS), which is of cambic chernozem type (Secu, 2008), one can find more than 6,000 vegetal taxons originating in various bio-geographic areas (Tănase and Oprea, 2013).

2.2 Sampling and analysis

The samples were collected between the 1st of April and the 15th of June 2014 so as to avoid the impact of the urban microclimate (extreme temperatures, heavy rain or snow-fall) upon the representativeness of the heavy metal contents in soils. A total of 144 soil samples were collected from the nodes of a virtual square network (Fig. 1). The size of the basic sampling cell was 100×100 m, the sampling interval was between 0.0 m and 0.30 m, while the mass of the samples ranged between 1.5 and 2.0 kg. The samples were collected manually, using a stainless steel spade shovel, and they were then put in plastic bags.

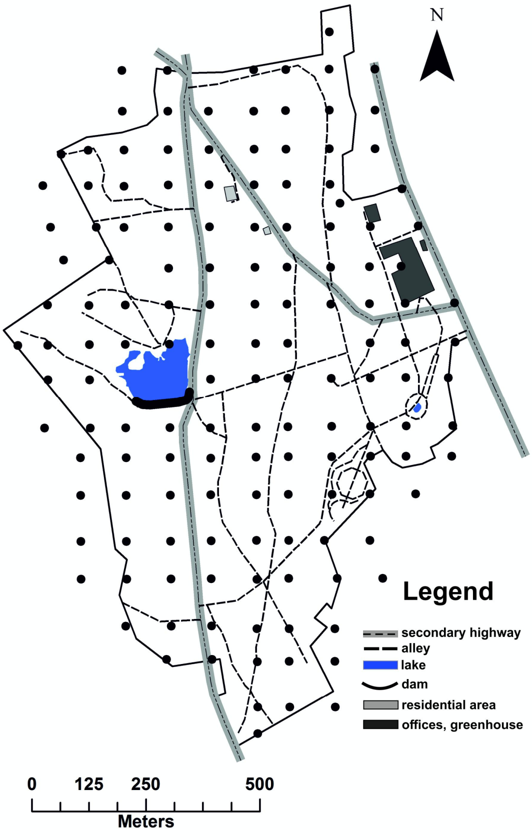

Fig. 1 Samples location of Botanical Garden soil.

After extracting gravel and coarse organic matter or plant root residues, soil samples were oven dried at a temperature of 50ºC for 72 hours and ground to pass through a 0.01-mm sieve.

Sample reduction was performed through the coning and quartering method (Pitard, 1993), finally retaining 25 sample grams.

In order to determine the Cu, Zn and Pb contents, an EDXRF spectrometer (Epsilon 5 PANalytical) was used. The 25 sample grams were mixed with a binder at a 5:1 ratio and homogenised for 20 minutes in an agate mortar, using a mechanical mill. Approximately 15 g of the mixture were pressed into 40 mm-diameter aluminium pellets, using a hydraulic press operating at a pressure of 20 tons. Standardisation was performed by using 23 Certified Reference Materials (SO1-4, RT, RTH, GSD and LKSD). The exposure time was 50 seconds. Result accuracy was tested via Certified Reference Materials.

2.3 Descriptive analysis and correlation coefficient

A descriptive data analysis, including minimum and maximum values, mean, standard deviation (SD), skewness, kurtosis and coefficient of variation (CV) was carried out. The coefficient of variation was used to reflect the degree of discrete distribution of different metal element concentrations and to indicate, indirectly, the activeness of the selected element in the examined environment. Skewness and kurtosis were also utilised to highlight different distributions of the metals. The Spearman correlation coefficients (SCC), very robust about outliers (Pan and Harris, 2000), were calculated to determine relations among different metals.

2.4 Geochemical background

Considered to represent either the absence of an anomaly (Matschullat et al., 2000) or the content of a chemical element resulting from natural processes that characterise one particular soil, including the diffuse source of anthropogenic inputs (Cave et al., 2012), the geochemical background (GBK) was calculated according to the method indicated by Chen et al. (2004; 2005) for urban soils.

2.5 Semivariogram

Utilised to quantify the spatial structure of regionalised variables, the semivariogram consists in the graphic representation of the mean square variability between two neighbouring points of distance *h*:

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

where: $\gamma(h)$ = the semivariogram; $N(h)$ = the number of observation pairs for x_i and $(x_i + h)$.

The experimental semivariogram is adjusted according to theoretical models, which leads to the determination of the nugget effect (C_o), the sill (C_0+C) and the range of influence (a_0). With the help of multi-directional semivariograms one can establish the presence of isotropy or anisotropy.

2.6 Probability kriging

Probability kriging (PK) is an improved variant of indicator kriging (Journel, 1983; Sullivan, 1984; Journel, 1988). Goovaerts (1997) defines PK as the cokriging (CK) of indicator data using the rank order transform as a secondary variable; indicator data are values of 0 or 1. The rank order transform is the standardized ranks, namely the rank-order of each datum of the primary variable divided by sample size. By replacing the values of the first variable in the CK system with indicator data, and by using the rank order transform as a secondary variable in CK, one obtains an estimator of PK. Murray and Baker (1992) consider that PK implies the following stages: exploratory data analysis; data preparation; semivariogram analysis; kriging plan; cross validation; determination and utilization of posterior cumulative distribution function models.

2.7 Assessing the Kriging Model's Accuracy

The kriging process outputs statistics for cross-validation is a means of assessing the model's accuracy. In cross-validation, one data point is removed and the whole model is run without that data point. A predicted value for that data point will then be compared to the actual, observed value removed from the model (ESRI, 2013). The mathematical expressions of the various types of errors are as follows (Li and Heap, 2008):

- mean error (ME):

$$ME = \frac{1}{n}\sum_{i=1}^{n} p_i - o_i \cong 0 \quad (2)$$

- root mean square error (RMSE):

$$RMSE = [\frac{1}{n}\sum_{i=1}^{n} (p_i - o_i)^2]^{1/2} \cong \text{minimum} \quad (3)$$

- mean standardised error (MSE):

$$MSE = \frac{1}{n}\sum_{i=1}^{n} (p_{si} - o_{si}) \cong 0 \quad (4)$$

- root mean square standardised error (RMSSE):

$$RMSSE = [\frac{1}{n}\sum_{i=1}^{n} (p_{si} - o_{si})^2]^{1/2} \cong 1 \quad (5)$$

where: n = number of observations or samples; o = observed values; p = predicted (estimated values); o_s = standardised observed value; p_s = standardised predicted value.

3. Results and discussions

3.1 Heavy metal concentrations and correlation coefficient

Descriptive statistics of heavy metal concentrations in the soil of the Botanical Garden as well as background values of Romanian soils (Law 756/1997), which are considered to be reference values (NVS), are presented in Table 1 and Figure 2. Table 1 shows that the relations between NVS and the mean values of the chemical elements studied are supra-unitary and they increase in the order Cu > Pb > Zn (3.673 > 1.690 > 1.130), which suggests the presence of an anthropic contribution that varies from high values (Cu) to low values (Zn). Although CV values (Tab. 1) suggest the presence of a low anthropic contribution (Cu and Zn) up to an average contribution (Pb) (Yongming et al., 2006), the absence of the normal distribution mirrored both by skewness and/or kurtosis values (Tab. 1) and by the distribution of sample contents, in relation to 25 and 75 percentiles (Fig. 1) indicates the presence of certain non-homogeneous populations.

SCC values (Tab. 2) indicate significant associations between Pb-Zn and Zn-Cu which, corroborated with the lack of a significant correlation between Pb and Cu, suggests multiple sources of provenience for Zn.

3.2 Geochemical background

After the elimination of the exceptional samples and the application of different transformations (lognormal if coefficient of skewness is greater than 1, square root if coefficient of skewness is between 0.5 and 1 – Webster and Oliver, 2007) followed by the verification of normal distribution with the Shapiro-Wilk test, GBK was calculated for the studied chemical elements (Tab. 1). In terms of Zn, we can notice the value close to 1 of the formula $GBK_{Zn} \cdot (NVS_{Zn})^{-1}$ (1.062), while in the case of Pb and Cu, the value of the formula $GBK_{HM} \cdot (NVS_{HM})^{-1}$ is supra-unitary (1.623, respectively 3.780). These aspects suggest that if in the case of Zn, the anthropic contribution was reduced, the contents of Pb and Cu were strongly influenced by anthropic factors.

3.3 Semivariogram

Theoretical models and the corresponding parameters of the semivariograms studied for several directions are presented in Table 3 and Figure 3. The study of semivariograms indicates a geometric anisotropy in the case of the studied chemical elements. One can notice the quasi-common orientation of the ellipses of the Pb and Zn anisotropy while Cu presents a slightly different orientation. The $[C_0/(C_0+C)]$ ratio, which quantifies the spatial dependence of variables (Cambardella et al., 1994), indicate a strong spatial dependency in the case of Pb and Zn, which decreases strongly in the case of Cu.

Tab. 1 Heavy metal concentrations of BGS (mg/kg)

	Min / Max	Mean	Skewness	Kurtosis	SD	CV	GBK / NVS*
Pb	22 / 234	33.809	8.867	90.164	19.508	0.577	32.456 / 20
Cu	39 / 137	73.471	0.760	-3.527	22.927	0.312	75.615 / 20
Zn	73 / 236	113.062	2.206	5.902	31.583	0.279	106.208 / 100

* Law 756/1997

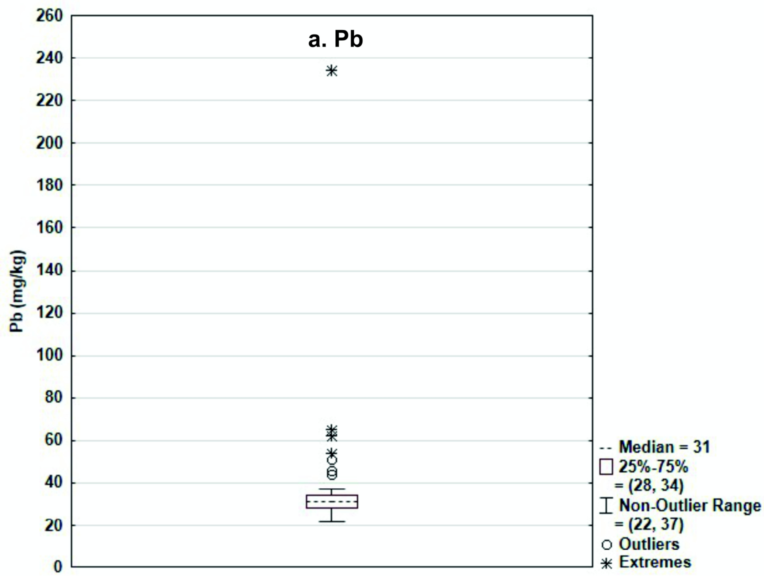

Fig. 2a Boxplot of Pb concentration.

3.4 Probability kriging

The maps drawn based on semi-variogram parameters (section 3.3) in relation with GBK (section 3.2) highlight increased probabilities of surpassing GBK (>80%) which, expressed in percentages in relation with the total studied surface, increase in the order Zn > Cu > Pb (18.0% > 12.6% > 12.2%) (Fig. 4).

For all the studied metals, the error statistics such as ME, RMSE, MSE, and RMSSE were estimated and presented in Table 4. We can notice that ME and MSE have values close to zero, while RMSE values are close for all the studied chemical elements. RMSSE values indicate slight overestimations of the variability of the studied chemical elements.

3.5 BGS and potential anthropic sources of Pb, Cu and Zn

In our opinion, the potential anthropic sources generating heavy metals with an impact on BGS can be classified into the following categories: *1*. General sources: car traffic on BG adjacent/internal streets, to which the use of

BG specific equipment is added; 2. Specific sources: maintenance treatments for plant species with various agricultural chemicals (fertilisers, pesticides, fungicides, insecticides) (Forman, 2008; Fuge, 2013), which contain trace amounts of heavy metals (Zovko and Romić, 2011) applied both inside BG and in its adjacent areas.

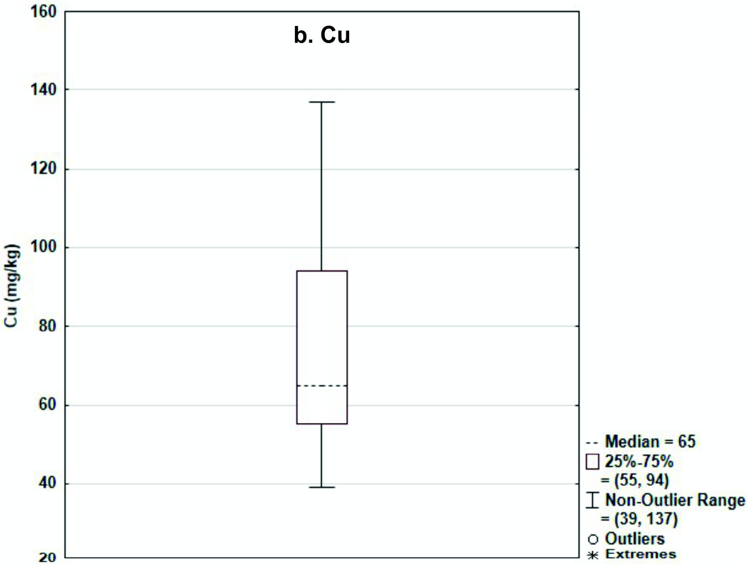

Fig. 2b Boxplot of Cu concentration.

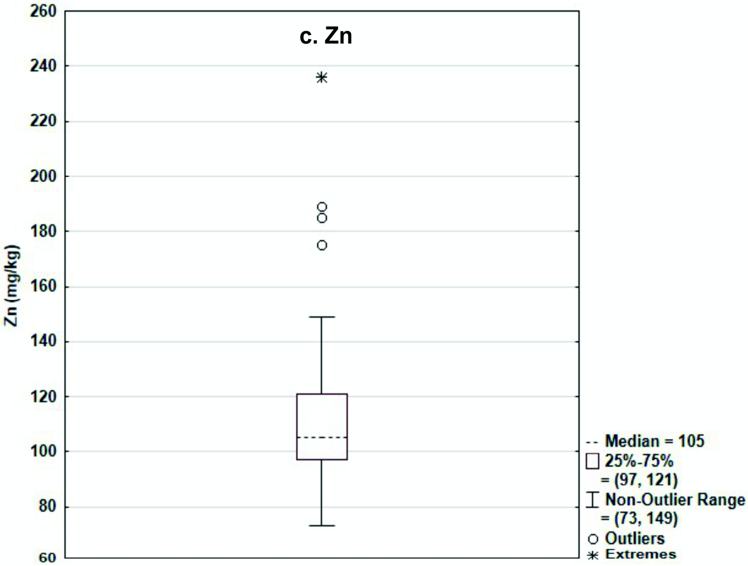

Fig. 2c Boxplot of Zn concentration.

Tab. 2 Spearman correlation coefficients of Pb, Cu and Zn

	Zn	Pb	Cu
Zn	1		
Pb	0.355**	1	
Cu	0.291**	0.110	1

** correlation is significant at the 0.01 level (2-tailed)

Tab. 3 Semivariogram parameters of the fitted theoretical models

	Model	Nugget (C_0)	Sill (C_o+C)	Major range (m) / Degrees azimuth	Minor range (m)	$[C_0/(C_0+C)]*100$ (%)
Pb	Exp	0.0005	0.0243	639.103 / 161.718	289.145	2.057
Cu	Sph	0.0798	0,2387	371.587 / 140.800	220.619	33.446
Zn	Exp	0,0006	0.2783	442.678 / 159.433	295.000	0.215

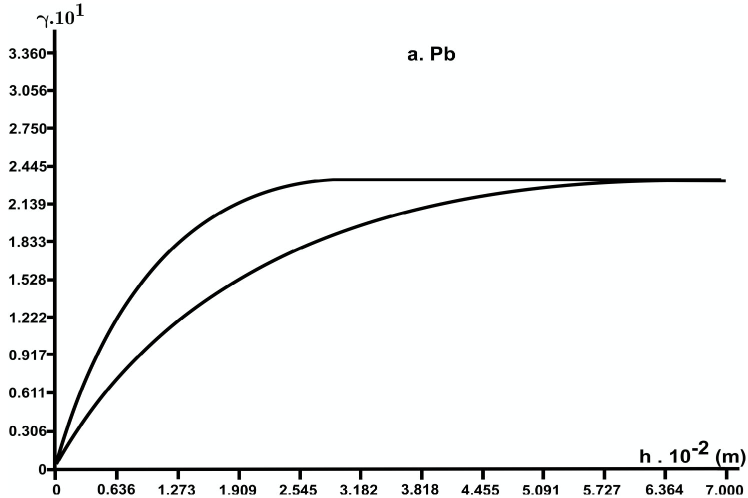

Fig. 3a Best fitted semivariogram for Pb concentration in BGS

Zn contents reflect, in most cases, BGS natural geochemical background, which is confirmed by the values of the ratios $\overline{Zn}\cdot(NVS_{Zn})^{-1}$ and $GBK_{Zn}\cdot(NVS_{Zn})^{-1}$. Nevertheless, the extended anomaly identified with the help of the probability map of Zn, as well as the Zn-Cu and Zn-Pb associations indicate that part of the Zn contents can be due both to the use of fertilisers and pesticides (Oertli, 2008) and to car traffic (Roldan et al., 2005; Mirsal, 2008).

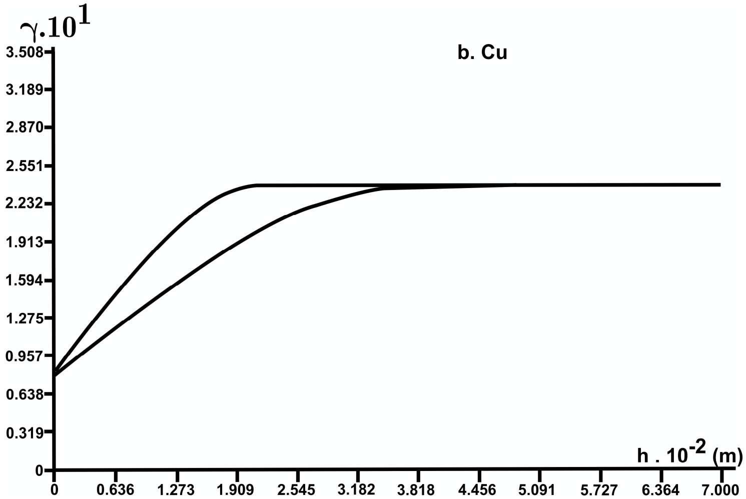

Fig. 3b Best fitted semivariogram for Cu concentration in BGS

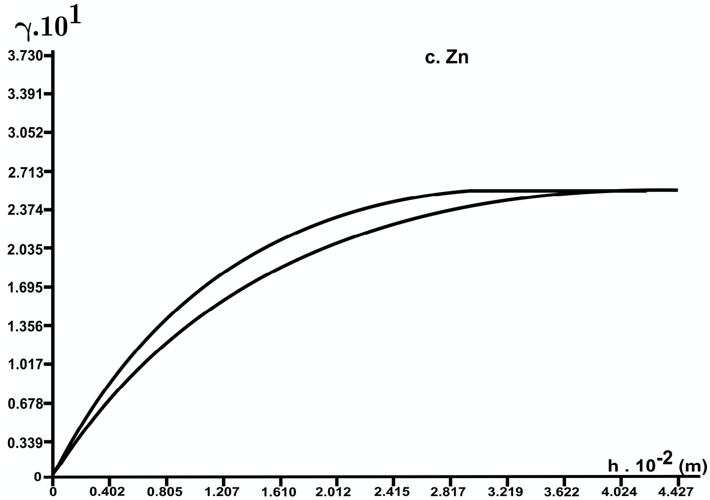

Fig. 3c Best fitted semivariogram for Zn concentration in BGS

Supra-unitary values of the ratios $\overline{Pb} \cdot (NVS_{Pb})^{-1}$ and $GBK_{Pb} \cdot (NVS_{Pb})^{-1}$, as well as the localisation of the maximal probability to exceed GBK lead to the idea that Pb contents can be correlated with the presence of the road infrastructure inside the BG/adjacent to the BG areas, more precisely a secondary highway (Laidlaw and Filippelli, 2008; Chen et al., 2010).

Tab. 4 Cross-validation results for probability kriging

	ME	RMSE	MSE	RMSSE
Pb	0.004401	0.322338	0.008333	1.041208
Cu	0.004578	0.397095	0.009069	1.020984
Zn	0.001882	0.387838	0.001746	1.088306

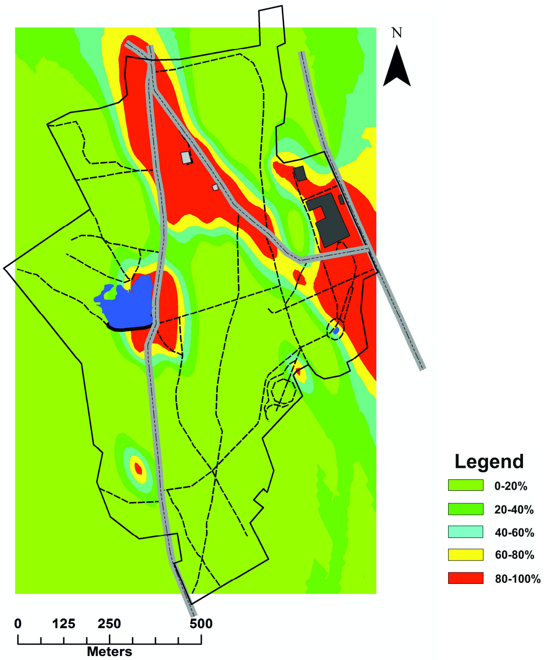

Fig. 4a Probability map of Pb concentration in BGS based on probability kriging.

The distribution of Cu contents whose $\overline{Cu} \cdot (NVS_{Cu})^{-1}$ and $GBK_{Cu} \cdot (NVS_{Cu})^{-1}$ ratios are strongly supra-unitary indicates the certain existence of a major anthropic contribution. By correlating the localisation of the maximal probability to exceed GBK with the presence of vineyards neighbouring the Botanical Garden, one can estimate that the natural geochemical background was influenced by the accumulations of copper sulphate, used frequently as a fungicide (Darriet et al., 2001; Van der Perk et al., 2004; Van-Zwieten et al., 2004) in Romania. The local energy of the relief and Cu high capacity of migration (Ginzburg, 1960), corroborated with the length of existence of vineyards, have facilitated the heightened modification of BGS natural geochemical background. An interesting aspect is the absence of significant positive correlation between Cu and Pb (Kelly et al., 1996), which, may indicate absent/reduced Cu inputs generated by car traffic.

4. Conclusion

Anthropic factors have led to the modification of the Pb, Zn and Cu natural geochemical background in BGS in Iaşi.

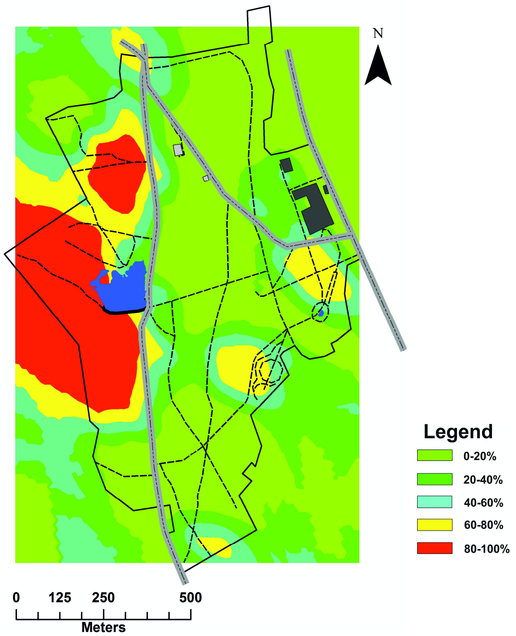

Fig. 4b Probability map of Cu concentration in BGS based on probability kriging.

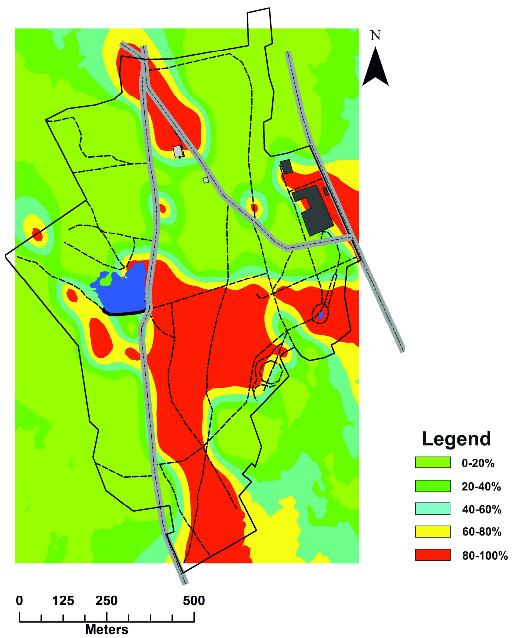

Fig. 4c Probability map of Zn concentration in BGS based on probability kriging.

The influence of anthropic factors is reflected both in the intensity of the accumulation of HM estimated with the help of the ratios $\overline{HM} \cdot (NVS_{HM})^{-1}$ and $GBK_{HM} \cdot (NVS_{Hm})^{-1}$, which are supra-unitary both in the preferential localisation of geochemical anomalies estimated with the help of thematic maps generated using the probability kriging.

The main dominant sources of heavy metals differ or are partially common for the studied chemical elements. Thus, if Zn contents were mainly dominated by natural sources to which are added traffic exhaust and agricultural chemicals from green spaces and high Pb contents can be strictly correlated with vehicle exhaust, abnormal Cu contents can be associated with agricultural chemicals used in the vineyards adjacent to BG.

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