

DISTRIBUTION AND MINOR ELEMENTS CONTAMINATION IN URBAN AND PERI-UBAN SOILS AREA OF SLĂNIC MOLDOVA, ROMANIA

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Abstract: The main purpose of this study is to assess the minor elements contamination (Cr, Co, Ni, Cu, Zn, As, Cd and Pb) from urban and peri-urban soils of Slănic Moldova city by analyzing their possible pollution sources through Nemerow pollution index and cluster analysis. Evaluation results showed that the concentrations of minor elements in soil were found for the most elements in standard limits, exception in this case for As and Pb which showed moderate contamination. It is recommended that supplementary measures should be considered for controlling the current contamination in the studied area. As a preliminary observation, the concentrations from the studied soils come mostly from parental material (lithogenic context), but in some cases with an additional input from agricultural practices. The Cluster Analysis indicates that four main groups are correlated and are divided into anthropogenic and geogenic groups.

Keywords: minor elements, Slănic Moldova, XRF, soils, NPI, dendrogram

1. INTRODUCTION

Surface soil pollution by toxic elements is a growing concern for environment and for human health because these pollutants can reach the food crops, surface and groundwater by producing negative effects on ecosystems. Therefore, the assessment of specific reference values of the geochemical background for potentially toxic elements has become a major concern in many research studies (Fernandes et al., 2018, Maftei et al., 2014, Yotova et al., 2018).

Minor elements released in soil may result from different sources such as the parental rock of the soil (lithogenic source) or various anthropogenic activities, e.g. irrigation, chemical fertilizers, industrial and municipal wastes, traffic roads, or pesticides used in tree treatment (Beygi & Jalali, 2019, Huzum et al., 2012, Kurt, 2018, Prundeanu et al., 2013).

According to other studies, some trace elements can be categorized as essential and non-essential

elements based on their necessity for organisms. Essential elements are called micronutrients (e.g., Cu, Zn, Mn, Fe) and are required for organisms but are also potentially harmful and could be toxic to plants in high concentrations. Non-essential elements (e.g., Cd, Pb, Cr, Ni, As) are not required for organisms due to their toxicity and are considered contaminants (Liu et al., 2018, Radovanović et al., 2017, Simon, 2014, Sipos et al., 2018).

The study area is located in the eastern part of Nemira Mountains being one of the most important balneo-climatic resorts in terms of curative properties. It is situated at the latitude of 46°12'00" N and longitude 26°26'00" E (Fig. 1). Slănic Moldova is a very popular location in Romania due to the diversified mineral waters and their high therapeutic effect. The mineral springs were grouped based on chemical composition, into alkaline, oligomineral, iodate, brominated, sulfurous, carbonated, chlorosodic etc., waters (Fig. 1) (Saraiman et al., 1998).

Slănic Moldova area mainly crosses the external flysch in which two tectonic nappes were formed

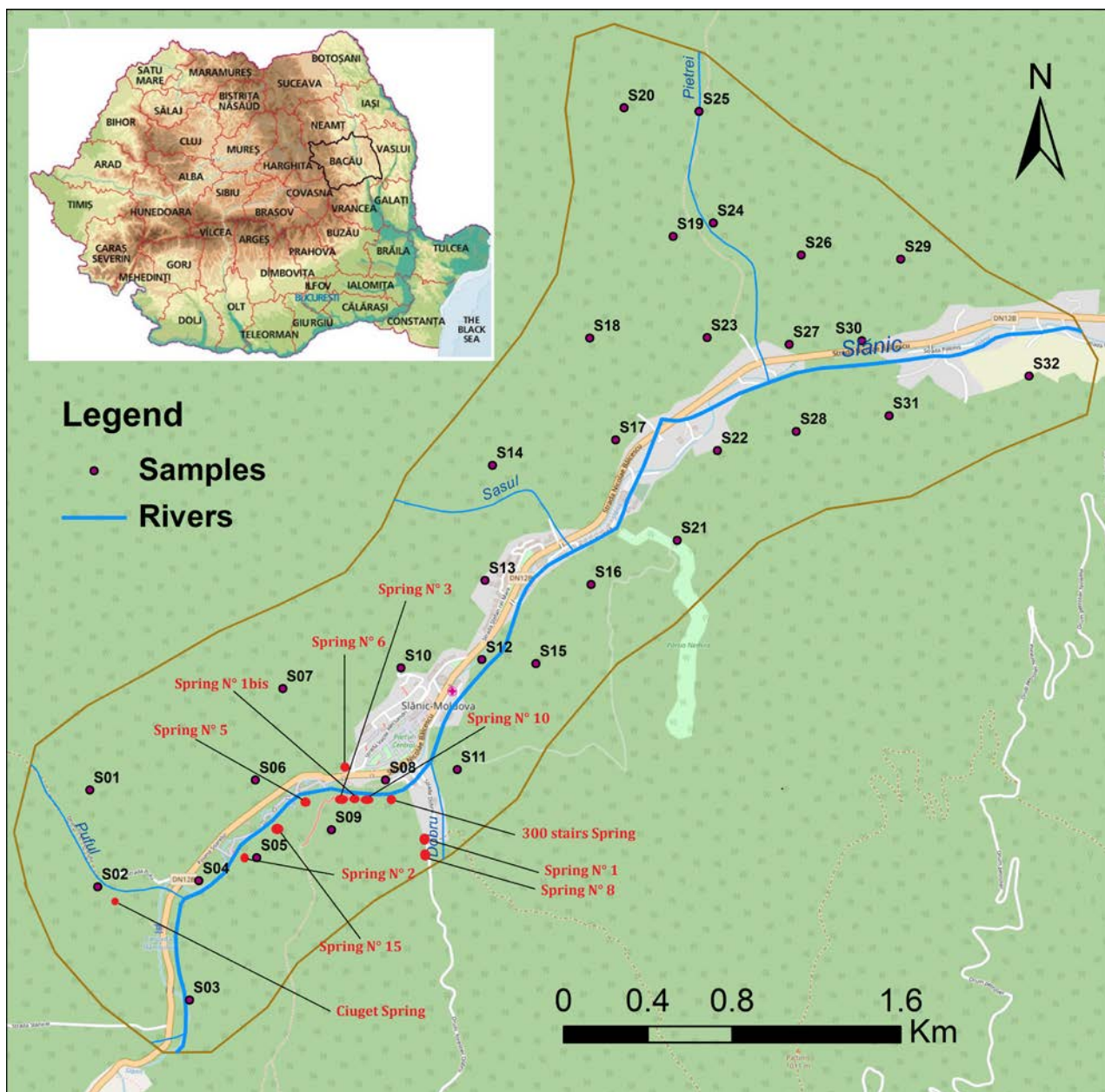


Figure 1. Sampling sites and mineral springs identification in Slănic Moldova area

during the Miocene, Tarcău and Vrancea Nappes. The deposits of these pericarpethian units include a various lithological profile composed in principal by sandstones, clays, bituminous marls, dysodile schists, menilites and Kliwa sandstones (Saraiman et al., 1998). From the pedological point of view, the most representative soil types in the area of Slănic Moldova and the surroundings are the Distric Cambisols and the Eutric Cambisols (Florea & Munteanu, 2003). As a general overview regarding the soils characterization in the studied area, the Distric Cambisols are formed on acidic rocks, as for example Tarcău and Kliwa sandstones, menilites, dysodiles or materials resulting from their alteration,

while Eutric Cambisols are generally formed on rocks rich in calcium or other basic elements, such as marls, clays, conglomerates, sandstones etc. (Șandru et al., 1989, Saraiman et al., 1998).

The aims of the present study are: i) identifying the spatial distribution of 8 chemical elements (Cr, Co, Ni, Cu, Zn, As, Cd and Pb) in relation to their geochemical background and reference values established by Order no. 756 of 3 November 1997 issued by the Minister of Water, Forests and Environmental Protection, Romania; ii) assessing the pollution degree of the studied elements; and iii) finding the contamination sources by multivariate statistical methods (cluster analysis).

2. MATERIALS AND METHODS

2.1. Sampling and minor elements determination

A total of 32 soil samples were collected from topsoils in urban and peri-urban area of the Slănic Moldova city (Fig. 1). The samples were collected from an equidistance approximately of 500 m, at the depth of 20 cm. In laboratory, the soil samples were air-dried at room temperature and each sample was sieved at 1 mm granulometry. Total concentration of 8 minor elements (Cr, Co, Ni, Cu, Zn, As, Cd and Pb) were analyzed through energy-dispersive X-ray fluorescence spectroscopy (ED-XRF) at Department of Geology, “Alexandru Ioan Cuza” University of Iași, using ED-XRF Epsilon 5 Spectrometer. The exposure time was 60 s, with the exception of As and Cd for which the exposure time was 90 s. The detection limits for analyzed elements are the following: Cr = 7.03 mg·kg⁻¹, Co = 1.14 mg·kg⁻¹, Ni = 10.65 mg·kg⁻¹, Zn = 2.27 mg·kg⁻¹, As = 1.13 mg·kg⁻¹, Cd = 0.05 mg·kg⁻¹. The calibration was performed by using 23 certified reference materials (JA1-3, JB1-3, JLk1, JSd1-3, JR1-2, JMs1-2, SO1-4, STSD1-4, RGM-1). Quality control and quality assurance were assessed using the SO-4 certified reference material by measuring the standard after each 10 samples measurements.

2.2. Pollution degree assessment of minor elements in topsoils

Nemerow pollution index (NPI) is applied to assess the soil quality and degree of contamination (Keshavarzi et al., 2019, Kowalska et al., 2016). NPI was calculated by the following equations:

$$NPI = \sqrt{\frac{\left(\frac{1}{m} \sum_{i=1}^m PI\right)^2 + PI_{max}^2}{m}} \quad (1)$$

And the equation for PI is:

$$PI = \frac{C_s}{B_s} \quad (2)$$

where *PI* is single pollution index of particular elements, *m* – number of studied elements (*M* = 8), *PI_{max}* – maximum value of single pollution index of all studied elements, *C_s* – concentration of elements in soils collected, *B_s* – is the geochemical background calculated after the method suggest by Reimann et al. (2005):

$$B_s = \text{Median} \pm 2\text{MAD} \quad (3)$$

where MAD is median absolute deviation.

Nemerow pollution index (NPI) is classified in five levels of quality: ≤ 0.1: clean, 0.7 - 1: warning limit, 1 - 2 slightly pollution, 2 - 3: moderate pollution and ≥ 3: heavy pollution (Gasiorek et al., 2017, Kowalska et al., 2016).

2.3. Statistical analysis

The data were statistically analyzed by using the software OriginPro 2016 and Microsoft Excel 2016. Descriptive statistics, Pearson’s correlation, as well as hierarchical cluster analysis (HCA) were performed to identify the source of minor elements in Slănic Moldova city soils. Cluster analysis on this study was performed on standardized data and the results are shown in a dendrogram based on Pearson distance and sum of squared distance.

Table 1. Statistical parameters of Slănic Moldova soils (N = 32)

Element / Variable	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
	mg·kg ⁻¹							
Mean	78.5	14.0	20.8	24.0	67.3	11.6	0.06	30.3
Median	74.5	14.0	14.5	22.5	55.5	11.0	0.06	25.0
St. Dev.	28.2	8.07	15.6	8.76	50.6	5.51	0.04	22.9
Variance	795	65.2	244	76.7	2561	30.3	0.002	527
Kurtosis	-1.19	-0.97	-0.89	2.98	12.3	20.7	1.09	26.7
Skewness	-0.06	-0.01	0.71	1.63	3.07	4.18	1.07	4.97
Minimum	25.0	0.21	3.60	14.0	28.0	6.90	0.01	17.0
Maximum	124	28.0	57.0	51.0	292	39.0	0.19	151
Background mean	78.5	13.1	11.4	21.0	50.8	10.4	0.05	25.1
Geochemical threshold	127	27.3	31.1	31.5	97.5	14.2	0.13	35.0
RSQS (target value)*	30.0	15.0	20.0	20.0	100	5	1	20.0
RSQS (intervention value)*	300	50.0	150	200	600	25.0	5	100

*RSQS – Romanian soil quality standard (Romania Guidelines, 1997)

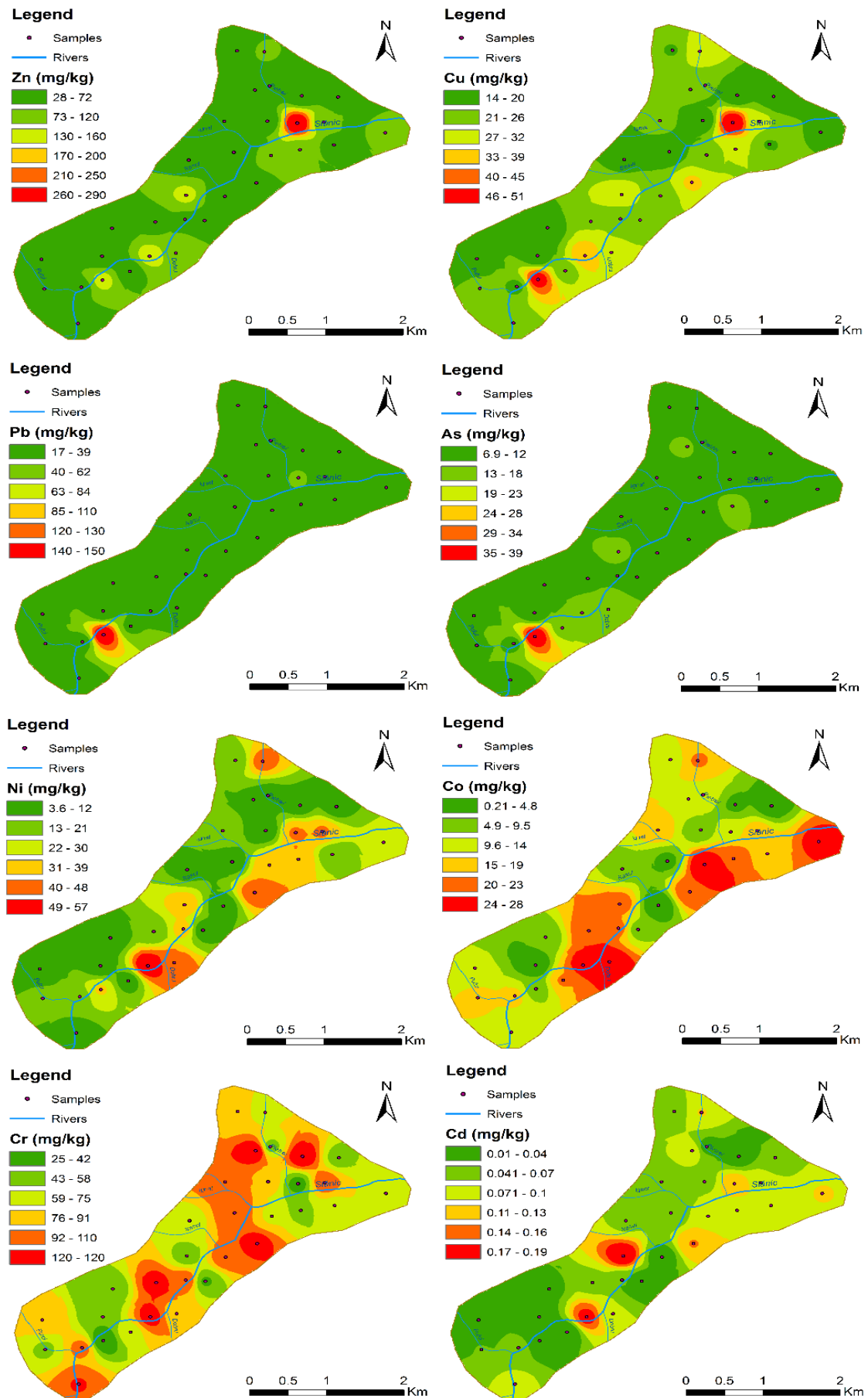


Figure 2. The spatial distribution maps of minor elements analyzed in Slănic Moldova soils

3. RESULTS AND DISCUSSION

The descriptive statistics of minor elements from topsoil of Slănic Moldova area are presented in Table 1. The elements suggest through Skewness coefficient a relatively normal distribution and the Kurtosis coefficient shows for elements Zn, As and Pb a positive peakedness associated with a slightly positive asymmetry. The variance indicates a high degree of dispersion for Zn, while the rest of analyzed elements shows a high variability for the entire data set.

In topsoils from urban and peri-urban area of Slănic Moldova city was observed a very significant positive correlation ($p = 0.05$) between As and Pb ($r = 0.933$), a strong relationship between the pairs Cu – Zn ($r = 0.854$, $p = 0.05$), Co – Ni ($r = 0.722$, $p = 0.05$) and a good positive correlation between Co – Cd ($r = 0.603$, $p = 0.05$). The maximum concentration of minor elements in soil samples follows the descending order of: Zn ($292 \text{ mg}\cdot\text{kg}^{-1}$) > Pb ($151 \text{ mg}\cdot\text{kg}^{-1}$) > Cr ($124 \text{ mg}\cdot\text{kg}^{-1}$) > Ni ($57 \text{ mg}\cdot\text{kg}^{-1}$) > Cu ($51 \text{ mg}\cdot\text{kg}^{-1}$) > As ($39 \text{ mg}\cdot\text{kg}^{-1}$) > Co ($28 \text{ mg}\cdot\text{kg}^{-1}$) > Cd ($0.19 \text{ mg}\cdot\text{kg}^{-1}$).

The average value of the monitored contents does not exceed the intervention value stated by Romanian soils quality standards (Romania Guidelines, 1997). However, in one sampling point - S05, the elements As and Pb exceed the value of $25 \text{ mg}\cdot\text{kg}^{-1}$, respectively $100 \text{ mg}\cdot\text{kg}^{-1}$ stated by national legislative.

By evaluating the geochemical background, it can be observed that the most elements show slightly higher values than the geochemical threshold in 12 sampling points, more exactly 37.5% from the total of samples exceed the calculated geochemical threshold. The geochemical threshold is slightly exceeded by Co in 2 sampling points. In case of As, Cd and Pb the limit was overtaken by 3 sampling points (e.g. As and Cd) and respectively 4 points in case of Pb. In five samples the concentrations are higher than the threshold value for Cu and Zn but remain in a good agreement with Romanian Soil Guidelines. Regarding the concentration of Ni, 10 samples exceed the geochemical threshold but without major consequences. The spatial distribution maps of the minor elements in Slănic Moldova city soils were characterized by an increment concentration trend from the central part to the external ones (Fig 2).

In Slănic Moldova soils, the contents of Zn and Cu vary between $28 \text{ mg}\cdot\text{kg}^{-1}$ and $292 \text{ mg}\cdot\text{kg}^{-1}$, respectively $14 \text{ mg}\cdot\text{kg}^{-1}$ and $51 \text{ mg}\cdot\text{kg}^{-1}$ with the maximum concentration recorded in S27 sampling point. As shown in Fig. 2, the elevated concentration identified in the sampling point S27 could be due to chemical fertilizers used in soil treatment. Other

authors confirm that the anthropogenic sources of Cu and Zn are related with the agricultural practice by using pesticides, sewage sludges, manures and mineral fertilizers (Hong et al., 2019, Kabata-Pendias, 2011, Simon, 2014, Oorts, 2013). However, the maximum concentration of Cu recorded in this study does not have a negative impact on the environment, because it becomes toxic when the concentration in soil exceeds $60\text{--}125 \text{ mg}\cdot\text{kg}^{-1}$ (Napoli et al., 2018).

The measured contents of As and Pb in Slănic Moldova soils range between $6.90 \text{ mg}\cdot\text{kg}^{-1}$ - $39 \text{ mg}\cdot\text{kg}^{-1}$ in case of As and $17 \text{ mg}\cdot\text{kg}^{-1}$ - $151 \text{ mg}\cdot\text{kg}^{-1}$ for Pb, with the maximum values recorded in S05 sampling point (Fig. 2). For both elements the general reference values provided by the Romanian legislation were exceeded in this sampling point. The overall concentrations of As and Pb in the studied area are slightly higher than typical soils composition, due to their association with mineral waters. By analyzing the position of S05 sample, the high contents of As and Pb can be caused by the presence of mineral springs, located near this position. But, if we are talking about a geological context, then the As and Pb contents should not be higher than the background values. Despite this, the results for As and Pb in this sample show even greater values than the Romanian threshold guidelines. The significant correlation between As and Pb ($r = 0.933$, $p = 0.05$) could explain the same natural source for these two elements (i.e. mineral springs), but nevertheless, an anthropogenic input in sample S05 can also be considered, since it shows a punctual behavior. Lead arsenate (PbHAsO_4) is extensively used in agricultural activities to control tree pests (Prundeanu et al., 2012, Schooley et al., 2008, Simon, 2014).

By evaluating the Ni concentration in Slănic Moldova city soils, a wide range of values was observed among the sampling points. For instance, the maximum concentration of Ni recorded in the S08 sample ($57 \text{ mg}\cdot\text{kg}^{-1}$) is much higher than the rest of the sites.

These differences between samples could indicate that the element concentrations decrease with the distance from punctual source due to water transport and soil erosion. The mean concentrations of Ni, Cd and Co in soil were higher than their local background which might be attributed to the factors that control soil properties (e.g. pH, organic matter, clay content and cation exchange capacity) (Hernandez et al., 2003). On the other hand, according to Romania guidelines, the elements (except As and Pb) are still in safe limits, without negative impact.

As in the case of previously discussed elements, the highest concentration of Cr identified in

the soil samples does not affect the soil quality.

In this research study, the soil contamination was evaluated through Nemerow pollution index calculated based on single pollution index and geochemical background. It can be observed in Fig. 3 that the values of NPI of the selected elements show a moderate contamination in the sampling points S05 and S27. In addition, Nemerow pollution index indicated that the soils were moderate polluted with As, Pb, Zn and Cu.

As already discussed, the most likely explanation for this contamination could be due to chemical fertilizers and pesticides used to treat soils or the geological parent material known as an important contributable with a major role in variation of minor element contents in forest, agricultural and rural soils.

The similarity between elements and anthropogenic sources in Slănic Moldova soils were analyzed by means of Hierarchical Cluster Analysis (HCA). The HCA biplot graph is illustrated in Fig. 4 and it indicates four clusters. Cr was clustered independently of other elements, while the rest of the elements appear grouped as mainly three clusters: Co-Ni-Cd forms one cluster, Cu-Zn and As-Pb forms another two clusters.

The cluster shows significant positive correlation between elements indicating a similar source. The result of cluster analysis confirms that the

elements in soils (except Cr) may also originate from anthropogenic sources, besides their main geogenic source. The distribution of Cr in the studied soils indicates that it was not influenced by human contribution and could be derived from the parent materials in soil, therefore this element sources could be considered as geogenic or pedogenic sources.

4. CONCLUSIONS

This study provides data concerning the characteristics of minor elements distribution in surface soils of Slănic Moldova city, involving spatial distribution and major sources of contamination. Only As and Pb exceed the national guidelines values showing a moderate contamination degree in the sampling point S05. As a general conclusion, it was observed that the principal source of soil contaminants is controlled by lithogenic context, with additional agricultural input due to the fact that many sampling sites are located near of agricultural fields.

A significant positive correlation between elements explains a common and similar origin, which is locally influenced by anthropogenic impact. The statistical analysis and cluster analysis prove the elements could be grouped based on their geochemical affinity and sources. The variability of minor elements could be influenced by geogenic impact caused by e.g. mineral springs and anthropo-

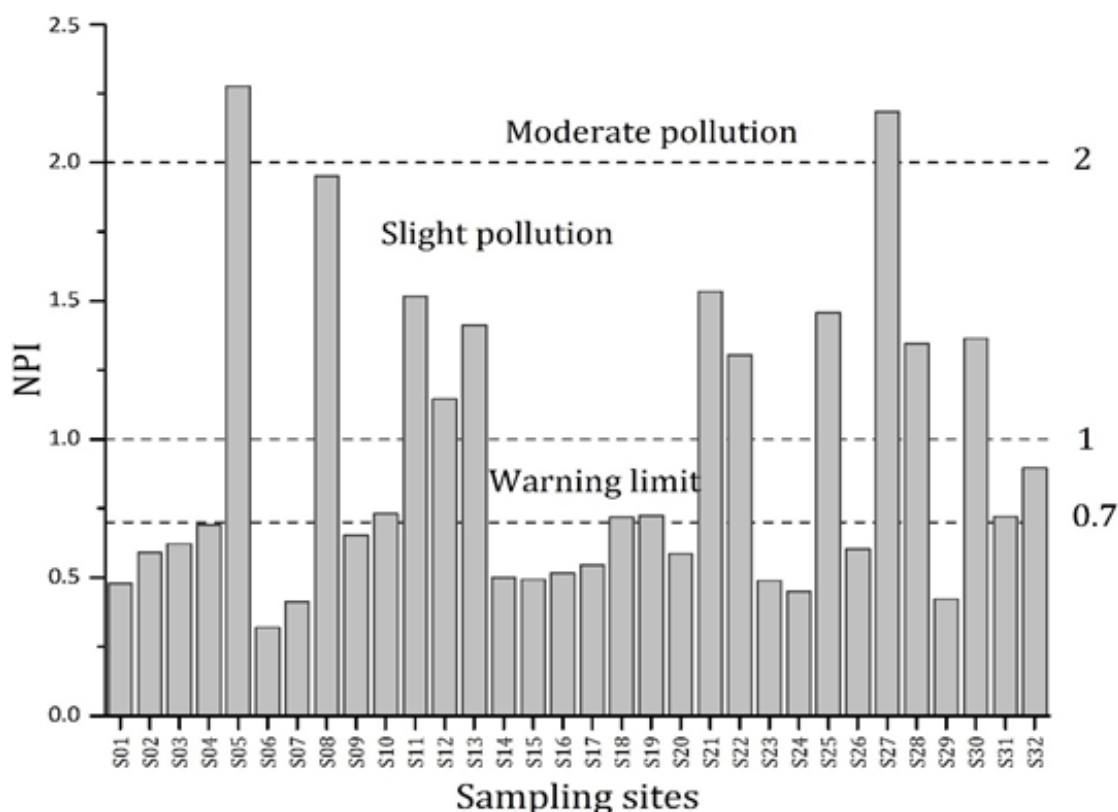


Figure 3. Estimated Nemerow Pollution Index (NPI) in Slănic Moldova city soils

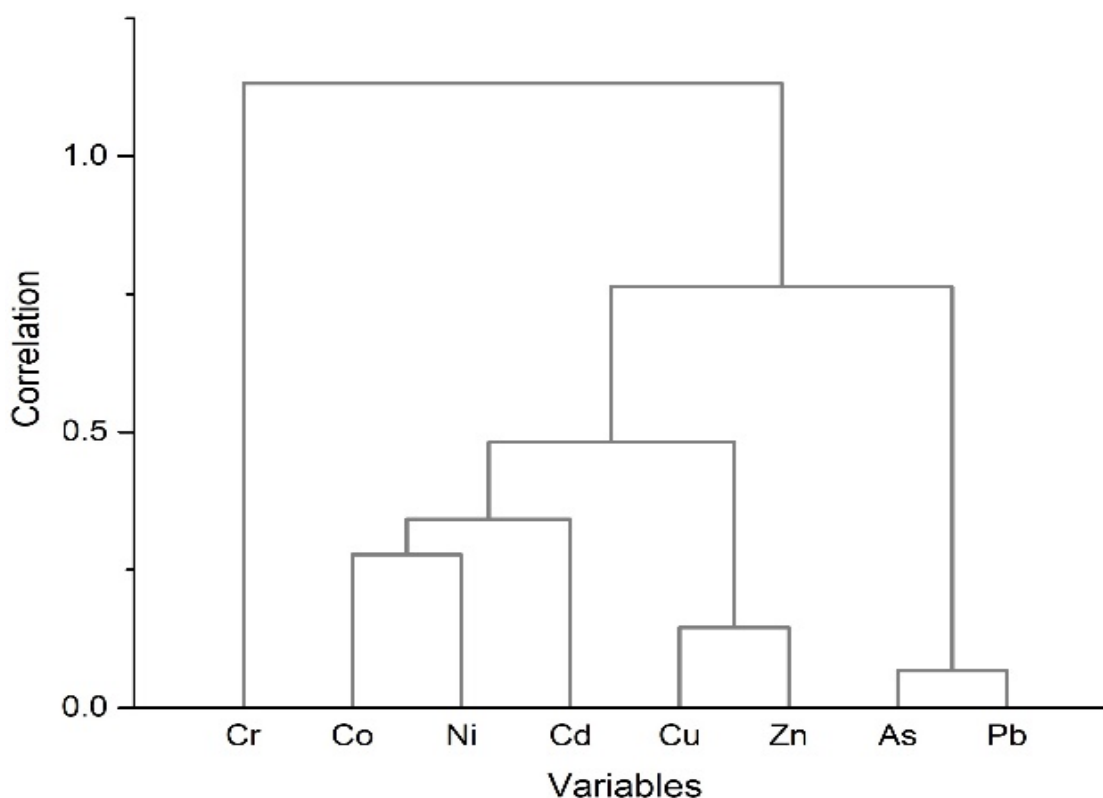


Figure 4. Dendrogram representation of hierarchical clustering results

genic contaminants which have been derived from agriculture, waste dump discharge, human activities or vehicles fuel combustion.

Nevertheless, further investigations and remediation measures are required in order to reduce the contamination with As and Pb in the studied area.

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