

Spatial distribution and geochemistry of heavy metals in soils: A case study from the NE area of Vaslui county, Romania



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ABSTRACT

This study reports the concentrations and sources of heavy metal pollution (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) in 193 soil samples from the northeast part of Vaslui county. Spatial distribution patterns, principal component analysis (PCA), and hierarchical clustering analysis (HCA) were used to assess the distribution of elements in the area and to identify the sources of elements and to classify them as geogenic or anthropogenic. PCA and HCA results suggest that As, Ni, and Co were consistently from natural sources; Pb, Zn, and Cu were consistently from anthropogenic sources; and Cr and Cd may be affected by both lithogenic and anthropogenic sources. A spatial interpolation allowed for the identification of agricultural activities as the main source of Cu pollution. Some places in the north of the area show high values of Zn and Pb, probably due to anthropogenic pollution caused by traffic or human activities. Maps of the heavy metal distribution were constructed for the whole area.

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1. Introduction

Soils have always been important to humans and their health, providing services such as food production, prevention of land degradation, water quality, and shelter (Abrahams, 2002; Ballabio et al., 2015). They also play a principal role in biochemical transformations, cycling of elements, supporting plants, infrastructure, and recreational activities (Luo et al., 2012). Urban soils differ very much from natural ones as they are strongly influenced by humans and typically contain higher loadings of contaminants than those in rural settings thanks to the higher density of anthropogenic activity (Davidson et al., 2006; Luo et al., 2012). Lately, because of the difference between urban soils and natural soils, numerous studies have been conducted on urban soil contamination with heavy metals (Apostoa and Iancu, 2009; De Miguel et al., 1998; Iancu and Buzgar, 2008; Lux, 1986; Madrid et al., 2004; Manta et al., 2002; Wilcke et al., 1998).

The ecological importance of heavy metals in soils has attracted great attention from governmental and regulatory bodies, leading to the development and establishment of legislation to control the risk associated with excessive heavy metals in the environment (Morton-Bermea et al., 2009). An evaluation of the environmental risk due to soil pollution is of particular importance for agricultural and non-agricultural areas because heavy metals persist in soils for a very long time (Grzebisz et al., 2002). Studies on heavy metal contamination in

urban soils assist in developing strategies to protect urban environments and human health against long-term accumulation (Guo et al., 2012). Metals are nondegradable pollutants that are usually harmful for humans, especially for young children who are more susceptible than adults with large area of health effects (Li et al., 2004; Maas et al., 2010).

Urban soils can receive large amounts of heavy metals from both natural and anthropogenic sources. Natural inputs include elements present in parent rocks or the atmospheric deposition of particles emitted from natural sources, such as forest fires, biogenic emissions, and volcanic activity (Cachada et al., 2013). Anthropogenic inputs include fossil fuel combustion, industrial and residential wastes, and uncontrolled factory emissions (Guo et al., 2012; Morton-Bermea et al., 2009; Cachada et al., 2013). Direct inputs from agricultural activities like sewage sludge or fertilizer use are other important sources of soil contamination (Maas et al., 2010; Alloway, 1995a; Romic and Romic, 2003). In the risk assessment of sites contaminated with heavy metals, it is important and necessary to consider metals from the geochemical background (Maas et al., 2010).

The quality of the environment and the maximum permitted level of some potentially toxic elements is a matter of increasing. Institutions responsible for environmental quality have thus set alerts and intervention limits regarding chemical element concentrations based on ecotoxicology criteria in various surface environments (air, water, soil, sediment, etc.). In some topsoils, there are chemicals that may exceed limits due to geogenic factors. Thus, action limits on ecotoxicology bases, space components, and scales of work should be to established (Salminen et al., 2005; Reimann and Garrett, 2005).

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The main purpose of this study is to develop a geochemical modeling approach for the soils from the northeastern county of Vaslui that can be used in the future for other areas. This requires a study of the levels and distributions of heavy metals in the soils from this area to identify potential pollution sources and compare the results with the maximum limits in Romanian legislation. The study of trace elements is important from the perspectives of both soil fertility and pollution, depending on the pedogenic influences on their mobility and availability to plants.

The main objectives of this study are therefore 1) the determination of minor elements such as As, Cd, Co, Cr, Cu, Ni, Pb, and Zn (units: mg/kg); 2) to establish possible sources of these elements, and 3) to compare the results with the maximum limits in legislation. The assessment of natural and anthropogenic contributions was made possible by the quantification of a large number of soil samples and multivariate statistical methods such as cluster analysis.

2. Description of the study area

2.1. Location

The studied area is located on the northeastern part of Vaslui county. It covers a surface of 1032 km² and has about 96,000 inhabitants, with the densest population in the Husi municipality (Fig. 1). The study area is characterized by a temperate continental climate specific to Eastern Europe, with an annual mean temperature of 9.5 °C and an average rainfall of 512.8 mm featuring higher rainfall in the north of the county and the lowest in the south (<http://www.isuvaslui.ro/>).

2.2. Geological setting of the study area

Geologically, the study area is a component of the Moldavian Platform, where we found Sarmatian (Basarabian and Chersonian), Meotian, and Quaternary deposits (Fig. 2) (Ionesi et al., 2005; Jeanrenaud and Saraiman, 1995). In the Sarmatian, there are four undergrowths according to fauna content: Buglovian, Volhinian, Basarabian, and Chersonian (Ionesi, 1988). These outcrops occur successively across the platform in order of age from north to south.

Litologically, during the Sarmatian, the main deposits are represented by clay, silt, marl, sand, and subordinate sandstones. Oolitic limestones, biosparitic limestones, and greso-limestones have been accumulated. The thickness of accumulated deposits varies from 800 m in the East to 2600 m in the West (Ionesi, 1988).

The lithology in the lower Basarabian continues with pelitic sedimentary through the accumulation of “clays with *Cryptomactra*” (350 m), over which there are clay and sands with thickness of 60–80 m (Ionesi, 1988). Sedimentation in the western part has the same look as in the Volhinian, with clays, sand, and some layers of sandstone and limestone (Ionesi, 1988). The upper Basarabian is regressive and reassures uniformity of sedimentation. It is represented by Repedea oolitic limestone, followed by a sequence of sands, clays, and calcaro-sandstones in packages with a very rich fauna. In terms of lithology, Chersonian deposits are represented mostly by sands with some intercalations of clay and limestone (<150 m) (Ionesi, 1988). A Meotian outcrop has approximately the same surface area as Chersonian. According to Jeanrenaud (1971), the Meotian starts with Nutasca-Ruseni andesitic cinerite (10–80 m), followed by sands and clays with alternate sandstone and conglomerate stabs and a thickness of 80 m.

The Meotian is geological period that is close to the sedimentation on the Moldavian Platform. Quaternary terrace deposits are represented by accompanying arteries that cross the platform basin and were made in a relatively short time. These were separated by 7 to 8 levels of terraces, the highest being at 190 to 200 m (Moldova River), 160 to 170 m (Bistrita River), and 180 m (Suceava River). The age of terraces high above 100 m is not strictly specified but is within the upper Pliocene or Lower Pliocene (Ionesi, 1988).

2.3. Soil description

Six soil classes from the study area (Anthrosols, Cernisols, Hidrisols, Luvisols, Salsodisols, and Protisols) were divided into 10 soil types (OJSPA Vaslui) (Fig. 3). According to the study conducted by OJSPA Vaslui, the Cernisols class has the largest expansion in the study area. Together with these soil types, there were also soil complexes represented by associations of soils developed on small surfaces, which

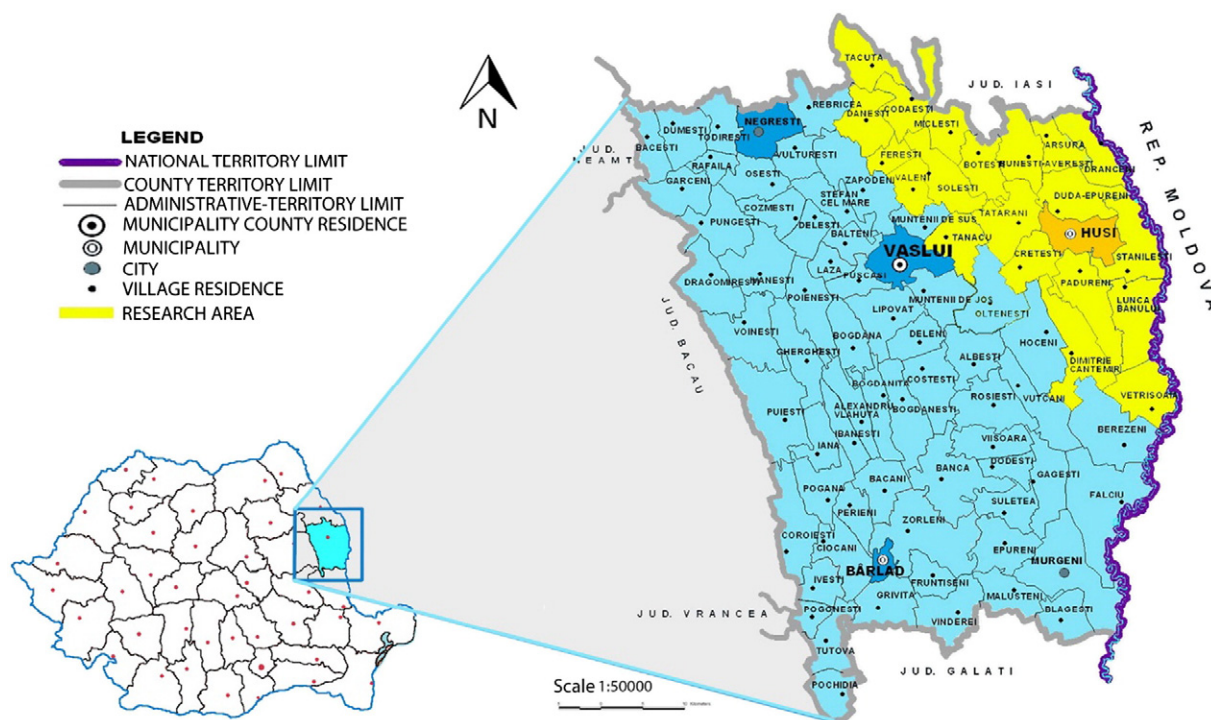


Fig. 1. Location map of the study area (modified from <http://www.isuvaslui.ro/>).

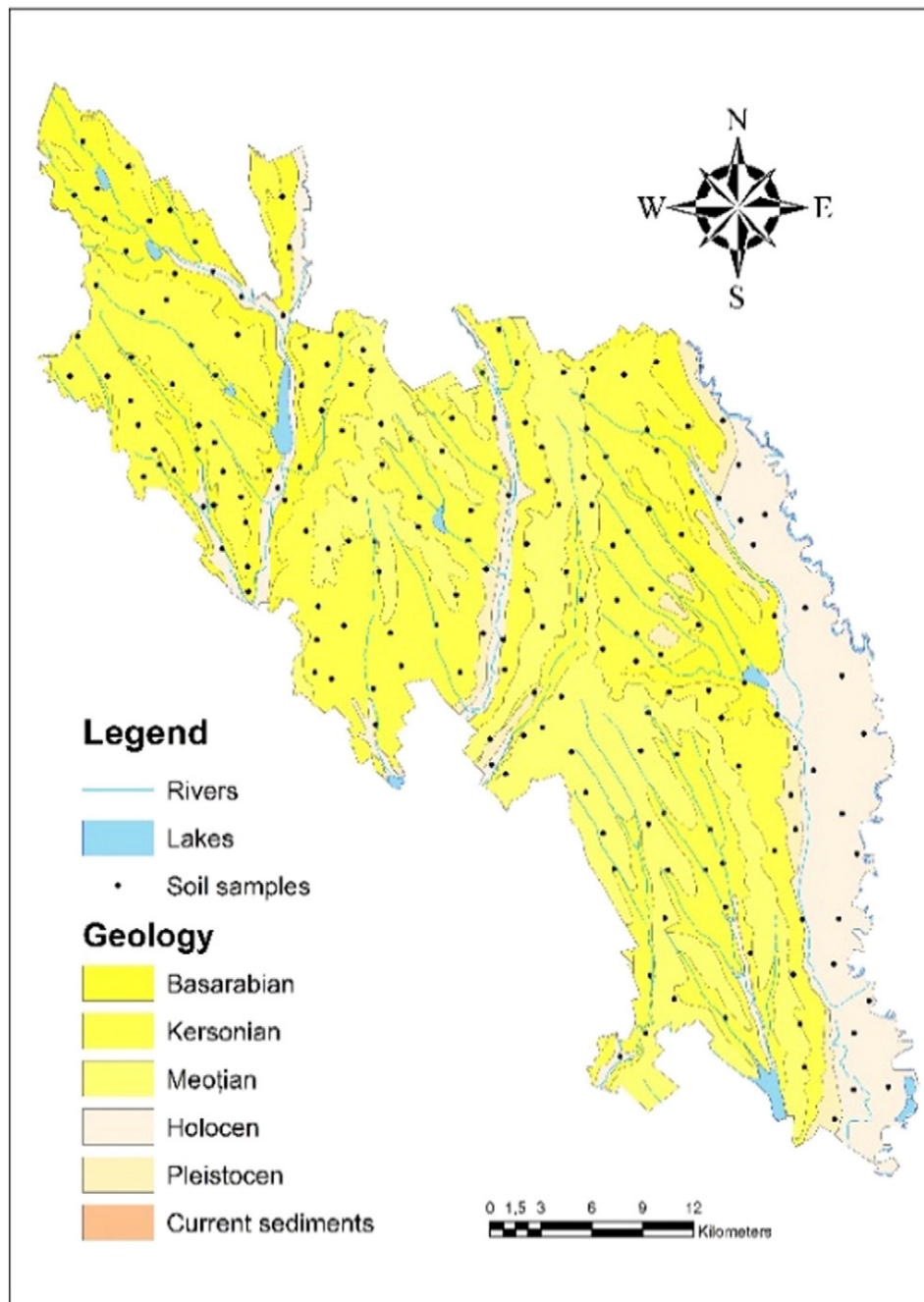


Fig. 2. Geological map of the study area (modified from Romanian geological map, scale 1:200,000).

repeated frequently in intervals of meters or hundreds of meters, depending on the micro relief. According to [Order no. 756 of 3 November 1997 from Romania](#), the soil samples collected in the study area belong to a soils class with sensible usage for residential and recreational areas, farming purposes, protected areas, or sanitary areas with special restrictions.

3. Materials and methods

3.1. Sampling methodology

Between the years 2013 and 2014, a total of 193 soil samples were collected from 20 communes and the Husi municipality in the county of Vaslui after an irregular network sampling. In order to cover the area of study fully and to obtain conclusive data for interpreting the

results, 88 soil samples were collected from residential areas and 105 soil samples were collected from areas relatively unaffected by humans (28 soil samples from forests or protected areas and 77 soil samples from pastures and meadows). All 193 samples were collected from a depth of 0 to 25 cm (topsoil). Samples were taken with specific weights between 1.5 and 2.0 kg based on the need to meet the specific characteristics of a geochemical sample and on grain size. The sampling was performed with stainless-steel materials to avoid contamination of the samples. The samples were also stored in tightly sealed plastic bags and properly numbered.

For each soil sample, the general characteristics of a geochemical sample were recorded: location, homogeneity, and the quantity collected that is sufficient for the proposed analyses. One or two photos were taken, and any information that can help further interpretations of the final results were noted. Sampling was carried out where plants with

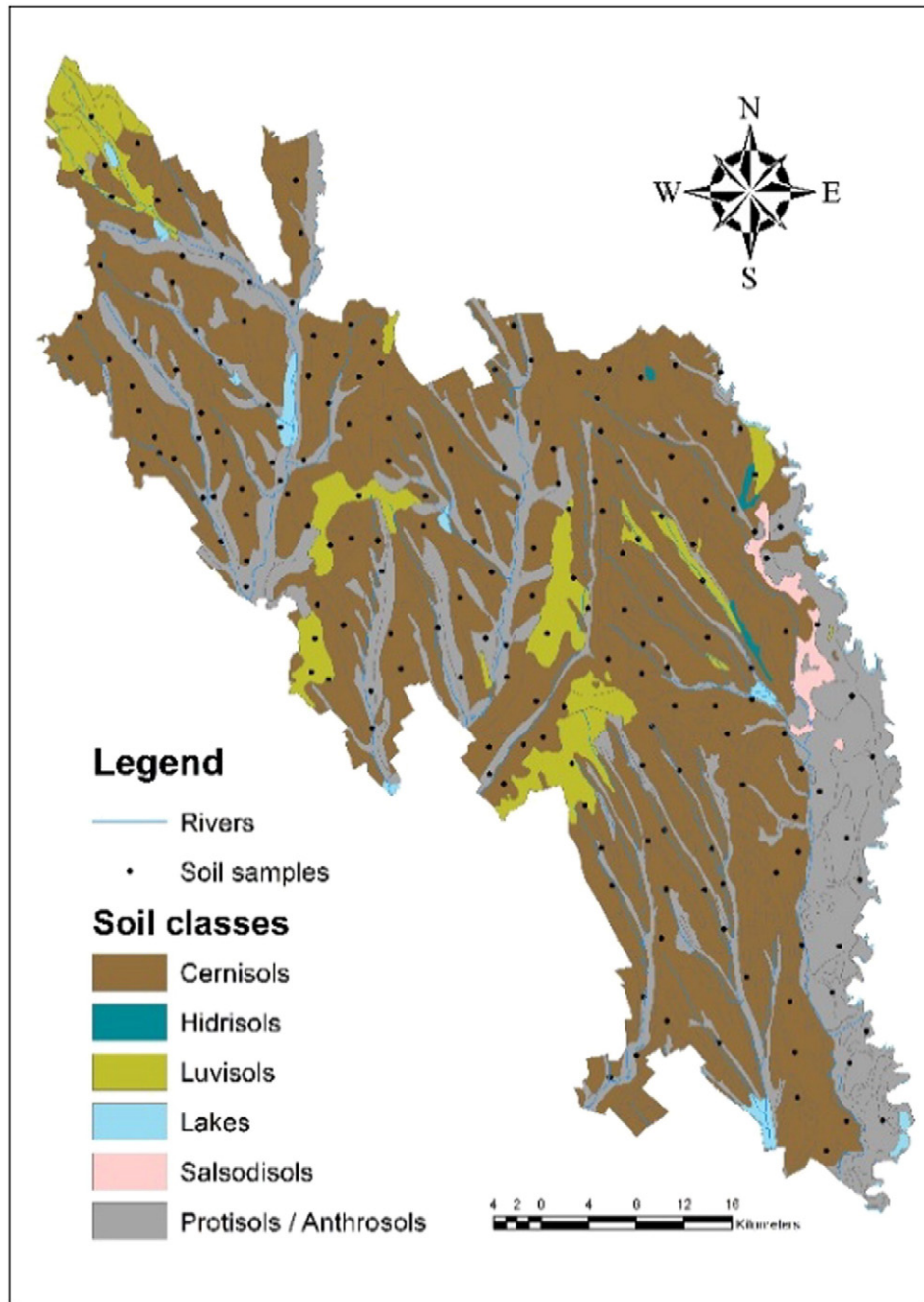


Fig. 3. Soil map of the study area (modified from soil map RSR, scale of 1: 200,000).

superficial roots were not present, and locations were identified using a Global Positioning System (GPS). Sampling location maps were produced with ArcGis Software (version 10.2).

3.2. Analytical procedure

All soil samples were air-dried, gently milled, and sieved to 2-mm fractions to remove stones, coarse materials, and other debris (the samples that still required drying were dried for 12 h in an oven at 40 °C). After the homogenization with an agate mortar, the total amount of each sample has been separated in four equal parts (quartation). Three parts were stored as a blank, and one part was used for determining the following analysis: ED-XRF and pH-Eh. All tools were thoroughly cleaned between the samples to avoid cross contamination. Control

samples were labeled, packaged, and properly stored in the Department of Geology, University Alexandru Ioan Cuza de Iași.

3.2.1. Determination of pH and Eh

For each sample, pH was measured using a standard pH meter using the potentiometric method in an aqueous solution using a soil:water ratio of 1:2.5 (STAS 7184/13-88). For this study a Hach Lange GmbH pH meter was used, model HQ40D, made in Colorado, USA. For each analysis, 20 g of each sample and 50 ml of distilled water were used. The results were determined after 2 h after the preparation of the suspension, and the mixture was intermittently stirred with a glass rod for homogenization. Calibration of the pH meter was carried out with buffer solutions of pH 4, 7, and 10 at the beginning of each set of analysis.

3.2.2. X-ray fluorescence analysis

After milling, homogenization, and sieving the soil samples to 2-mm fraction, about 15 g of each sample was mixed with Hoechst® wax (sample:binding-agent ratio of 5:1). The mixture was stirred for 15 min at 180 revolutions/min using an agate mill (Frisch Pulverisette Planetary Mill 5/2, Germany). After homogenization, 9 g of the mixture was placed in aluminum caps and pressed into pellets at 20 t/cm² for 30 s using a hydraulic press (Fluxana PR-25A Press, Germania). ED-XRF analyses were performed using an ED-XRF spectrometer (Epsilon 5, Panalytical N.V., Holland) in the XRF spectrometry laboratory of the Department of Geology, University Alexandru Ioan Cuza Iași. ED-XRF analysis determined the following minor elements: Cr, Co, Cu, Zn, Ni, Cd, Pb, and As (units: mg/kg).

The detection limits for each analyzed element are as follows: As = 1.13 mg·kg⁻¹, Cd = 0.05 mg·kg⁻¹, Co = 1.14 mg·kg⁻¹, Cr = 7.03 mg·kg⁻¹, Ni = 10.65 mg·kg⁻¹, Pb = 2.92 mg·kg⁻¹, Zn = 2.27 mg·kg⁻¹. The exposure time was 60 s except for As and Cd, for which the exposure time was 90 s. Calibration of the detection device was assured by the use of 23 standards: 14 standards produced by the Geological Survey of Japan (JA-1-3: andesite powder; JB-1-3: basalt powder; JLK-1: lake sediment powder; JSd-1-3: stream sediment powder; JR-1-2: rhyolite powder; JMS-1-2: marine sediment powder), 8 standards produced by the CCRMP-CANMET-MMSL of Natural Resources Canada (SO-1-4: regosolic clay soil, podzolic B horizon soil, calcareous C horizon soil and chermozemic A horizon soil; STSD-1-4: stream sediment powder), and a standard produced by the United States Geological Survey (RGM-1: rhyolite powder).

Quality control and quality assurance were assessed using the SO-4 certified reference material, measuring the standard after each 10 sample measurements. Twenty analytical duplicates were randomly included and yielded relative per cent differences of <10%. The results for As, Co, Cu, Cr, Ni, Pb and Zn indicated an analytical precision <6% measured as relative standard deviation (RSD) with an accuracy below 5%. Accuracy for Cd was slightly higher (28%) due to the low concentrations of this element in CRM (0.34 mg/kg) very close to the detection limit of the instrument (0.05 mg/kg).

3.3. Statistical analysis and geochemical mapping

The first step in statistical analysis was the calculation of the main descriptive parameters for each element (minimum, maximum, mean, standard deviation, skewness, and kurtosis). The multivariate statistical analysis and descriptive statistics used for this study were performed using XLSTAT 12 and NCSS 2007 software. The Pearson correlation matrix, principal component analysis (PCA), and hierarchical clusters analysis (HCA) were used to evaluate the relationships among data quantitatively. PCA and HCA were used to distinguish the different groups of heavy metals as tracers of natural or anthropic sources and to assist in identification of pollutant sources (Guo et al., 2012; Manta et al., 2002).

The PCA varimax rotation method was applied to extract key components responsible for variation in elemental concentrations. The resulting components were interpreted to identify the origin (geogenic or anthropogenic) or geochemical behavior of the relevant elements (Argyaki and Kelepertzis, 2014). Pearson's product-moment correlation coefficient was used to determine the correlation between the studied elements (Romic and Romic, 2003). Following spatial analysis, we integrated all available and generated information in a geographical information system (GIS) using ArcMap v.10.2 (ArcGIS).

4. Results and discussions

4.1. Leaching tests

According to investigations conducted by various authors (e.g., Adriano, 2001; Cachada et al., 2013), the pH has an important role in

the availability or immobilization of heavy metals. Consequently, there is a direct proportion between the soil's capacity retention of heavy metals and pH (reaching the maximum near neutral pH), and there is an inverse correlation between pH and the accessibility of elements Cu, Mn, and Zn (their availability for plants decreases as the pH increases in the range of 5 to 8).

The pH analyses performed on the samples show pH from 5.12 (strongly acid) to 9.55 (extremely alkaline). According to the classifications provided by the USDA (1998), soil samples from the study area can mostly be classified as moderately alkaline soils (44.0%). These are followed distantly by slightly alkaline (20.2%), strongly alkaline (10.9%), neutral (10.9%), moderately acidic (7.3%), and slightly acidic soils (3.6%). Only a very small proportion of the samples were strongly acidic (1.6%) and extreme alkaline soils (1.6%).

pH does not correlate with heavy metal concentrations. Most of the pH samples fit into the moderately alkaline soil class (7.9–8.4). Due to the neutral subalkaline environment, this parameter has limited importance for the heavy metal distribution, substantially limiting their mobility (Manta et al., 2002).

4.2. Heavy metal concentrations in the study area soils

In order to identify possible contamination and/or soil pollution, minor element values obtained from ED-XRF analyses were compared with normal values in soils, as well as alert and intervention thresholds from Order no. 756 of 3 November 1997 issued by the Minister of Water, Forests, and Environmental Protection, Romania.

The descriptive statistics of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn in the soils of the study area are listed in Table 1, together with median values, standard deviations, and variability ranges, as well as normal values in soils and alert and intervention thresholds from legislation. Additionally, for comparison, Table 1 reports ranges of variability of the same metals estimated by Salminen et al. (2005) and by Adriano (2001). The concentration ranges of Cr, Co, Ni, Cu, Zn, Cd, Pb, and As were 27–93, 2.5–18.4, 24–73, 14–300, 31–192, 0.02–0.8, 16–84, and 6.7–16.3 mg/kg, with mean values of 62.05, 10.83, 47.36, 29.83, 68.22, 0.32, 25.27, and 10.14 mg/kg, respectively. The mean concentrations of the heavy metals decreased in the order of Zn > Cr > Ni > Cu > Pb > Co > As > Cd.

Han et al. (2006) reported that coefficients of variations (CV) of heavy metals dominated by natural sources are relatively low, while those of heavy metals affected by anthropogenic sources are quite high. Thus, based on the CVs, these heavy metals can be divided into two groups. The CV values of As, Cd, Co, Cr, Ni, Pb and Zn are below 0.40, while Cu has a CV value higher than 0.40. Therefore, As, Cd, Co, Cr, Ni, Pb and Zn seem to be associated with natural sources, while Cu seem to be influenced by anthropogenic activities.

The coefficients of skewness of Cu, Zn, and Pb are much higher than zero, indicating high values in the samples. On the other hand, the coefficients of skewness of Cr, Co, Ni, Cd, and As are closer to zero, revealing that they follow normal distributions (Chen et al., 2010). High values for Cu, Zn, and Pb and normal distribution of Cr, Co, Ni, Cd, and As can also be observed with the help of histograms and boxplots (Fig. 4).

As shown in Table 1, the concentrations of the metals in the soils from the study area showed similar or higher values for all the elements in comparison with the Geochemical Atlas of Europe (Salminen et al., 2005). Values reported by Adriano (2001) show comparable or lower values for almost all the elements except for Co and As.

Rudnick and Gao (2003) estimated the abundance of arsenic in the Earth's crust to be 2.5 mg/kg, with values of 4.8 mg/kg in the upper crust and 0.2 mg/kg in the lower crust. The average content in soils is 6.83 mg/kg (Kabata-Pendias, 2011). The anthropogenic sources for arsenic may be fossil fuel and waste combustion, the metallurgical industry, fertilizers, and volcanic emissions (Argyaki and Kelepertzis, 2014; Cachada et al., 2013; Chen et al., 2010). The As concentrations of the samples analyzed range between 6.7 and 16.3 mg/kg with a mean

Table 1

Main statistical parameters (SD = standard deviation, NVS = normal values in soils) of 193 soil samples and environmental legislation for the measured heavy metals (mg/kg) and pH.

	Element	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	pH	
Statistics	Mean	10.14	0.32	10.83	62.05	29.83	47.36	25.27	68.22	7.74	
	Median	10.2	0.31	10.9	61	27	47	24	63	7.98	
	Minimum	6.7	0.02	2.5	27	14	24	16	31	5.12	
	Maximum	16.3	0.8	18.4	93	300	73	84	192	9.55	
	SD	1.48	0.13	2.33	9.90	22.19	8.00	6.53	23.04	0.86	
	Variance	2.19	0.02	5.42	97.96	492.22	64.04	42.58	530.64	0.73	
	Skewness (Pearson)	0.44	0.43	0.11	0.19	10.10	0.31	4.72	2.32	1.09	
	Kurtosis (Pearson)	1.99	0.74	1.04	0.90	114.75	0.75	34.57	8.08	0.76	
	Variation coefficient	0.15	0.40	0.22	0.16	0.74	0.17	0.26	0.34	0.11	
	Low Quartile	9.3	0.23	9.6	56	24	42	22	55	7.45	
	Upper Quartile	11	0.41	12.1	67	30	52	26	75	8.3	
	Order no. 756 of 3 November 1997	NVS*	5	1	15	30	20	20	20	100	–
		Alert threshold	15	3	30	100	100	75	50	300	–
Intervention threshold		25	5	50	50	200	150	100	600	–	
Salminen et al., 2005	Europe soils	7.03	0.145	7.78	60.00	13.00	18.00	22.60	52.00	–	
	Adriano, 2001	World soils	6.00	0.35	8.00	70.00	30.00	50.00	35.00	90.00	–

value of 10.2 mg/kg. In the samples analyzed for the present study, all the As contents exceeded normal values in soil, but only two samples had higher levels than alert thresholds.

Across the globe, the limits within which Cd is found in the upper horizon of different types of soil are between 0.01 and 2.70 mg/kg (Lăcătușu, 2008). In Romania, Lăcătușu et al. (1997) assessed a content of 1.11 mg/kg using a geometric mean for cadmium in horizon A of soils in 1112 samples. In heavily industrialized areas, the total cadmium can reach values of up to 10–20 mg/kg, and the concentration of mobile cadmium may increase to 5–8 mg/kg. Production factors of Cd in soils may have different sources, such as agricultural amendments, phosphate fertilizers, atmospheric deposition from industry, or sewage sludge (Alloway, 1995b; Maas et al., 2010). According to Kabata-Pendias (2001), the concentration of Cd for most of the soils worldwide does not exceed 1.0–1.1 mg/kg, while concentrations of Cd in the analyzed samples were under 1.0 mg/kg with a range of 0.02–0.80 mg/kg and median value of 0.31 mg/kg. In comparison with normal values in soils (1.0 mg/kg) and alert and intervention thresholds (3 mg/kg and 5 mg/kg) in Romanian legislation, there is no soil pollution due to this element.

In worldwide soils, the limits of Co found in the upper horizon are between 0.1 and 116 mg/kg with a mean value of 9.6 mg/kg (Lăcătușu, 2008). According to Fiedler and Rösler (1988), the average content of cobalt in the worldwide soils is 5.0 mg/kg. The content of Co in soils may be affected by anthropogenic sources, which include coal combustion, special steels, fertilizers, and iron and silver mining and processing (Salminen et al., 2005). For the soils from the investigation area, contents of Co range between 2.50 and 18.4 mg/kg with an average content of 10.827 mg/kg. From the total number of the samples analyzed, only six of them slightly exceeded the normal values in soils, but none of them were higher than the alert or intervention thresholds of the legislation. In this case, we can assert that Co is not a pollutant element for the soils analyzed in the study area.

Limits within which Cr is found in the upper horizon of different types of soils worldwide are between 1.4 and 500 mg/kg with a mean value of 63 mg/kg (Lăcătușu, 2008). If soils are formed on basic rocks, the chromium content in soils may be up to 1000 mg/kg higher (Lăcătușu, 2008). Dill et al. (2012) indicates average Cr contents in the Basarabian siliciclastic rocks from Eastern Carpathians Foreland Basin of 34 mg/kg for sands, 77 mg/kg for silts and 90 mg/kg for clays. Sources of Cr in the soils may be phosphate fertilizers or metallurgical industries (Maas et al., 2010). According to Irwin et al. (1997), chromium is considered one of the most harmful heavy metals for human health, with sources of pollution including chemical industries and combustion of natural gas, coal, oil, and wastes. Cr concentrations in soils can also be associated with weathering processes, and its values in soil normally do not reach contamination levels (Argyaki and Kelepertzis, 2014;

Lee et al., 2006; Manta et al., 2002). The concentration of Cr in the analyzed samples varies from 2.28 to 93 mg/kg with an average content of 55.44 mg/kg. Comparing average content of Cr obtained in this study (55.44 mg/kg) with results obtained by Dill et al. (2012) in Basarabian rocks, we can observe lower contents in case of sands (34 mg/kg), and higher contents in case of silts (77 mg/kg) and clays (90 mg/kg). We can see that concentrations of Cr do not surpass the alert or intervention thresholds in legislation, and only one of them is within the limits of normal values in soils. Therefore, high values of Cr may be influenced by both geogenic sources or phosphate fertilizers used frequently in agriculture.

Fiedler and Rösler (1988) found the average copper content in soil to be 30 mg/kg, while Rudnick and Gao (2003) estimated the abundance of copper in the Earth's crust as 27 mg/kg. Cu contamination of soil generally originates from agricultural chemicals (fungicides like Bordeaux mixture) or atmospheric deposition derived from industrial activities (Baker and Senft, 1995; Kabata-Pendias, 2001; Maas et al., 2010). The Cu content in soils from the study area varies between 14.0 and 300 mg/kg, with an average content of 29.83 mg/kg. Most of the samples exceed the normal values in soils, and two of them also surpass the alert thresholds. The two samples surpassing the alert thresholds are collected from areas planted with vines. Therefore, the source of high Cu concentration can be represented by the use of fertilizers or fungicides in vineyards.

Ni concentrations in soils may be influenced by either parent rock materials or by atmospheric deposition of vehicle emissions (Argyaki and Kelepertzis, 2014; Cannon and Horton, 2009; Chen et al., 2005). According to some authors (Luo et al., 2009; Molina et al., 2009), anthropogenic sources of Ni in soils include also various fertilizers used in agriculture. Luo et al. (2009) indicates a content of Ni in different fertilizers ranging from 9.6 to 11.4 mg/kg; while Molina et al. (2009) range the content of Ni in fertilizers from 1.8 to 17.9 mg/kg. In worldwide soils, the limits of Ni found in the upper horizon are between 1 and 450 mg/kg, with a mean value of 23 mg/kg (Lăcătușu, 2008). After investigating Basarabian siliciclastic rocks from Eastern Carpathians Foreland Basin, Dill et al. (2012) shows an average Ni contents of 14 mg/kg for sands, 42 mg/kg for silts and 37 mg/kg for clays. For the soils from the investigated area, concentrations of Ni vary between 24 and 73 mg/kg, with a mean value of 47 mg/kg. Ni content does not exceed the alert threshold, but all the concentrations are higher than normal values in soils. To conclude, we can say that high values of Ni are predominantly influenced by parent rock materials, and also easily influenced by fertilizers.

After analyzing 1112 samples, Lăcătușu et al. (1997) assessed the abundance of lead in horizon A of soils of Romania as being 31 mg/kg. The average lead content in soils given by Fiedler and Rösler (1988) is 15 mg/kg, while Rudnick and Gao (2003) estimate the abundance of

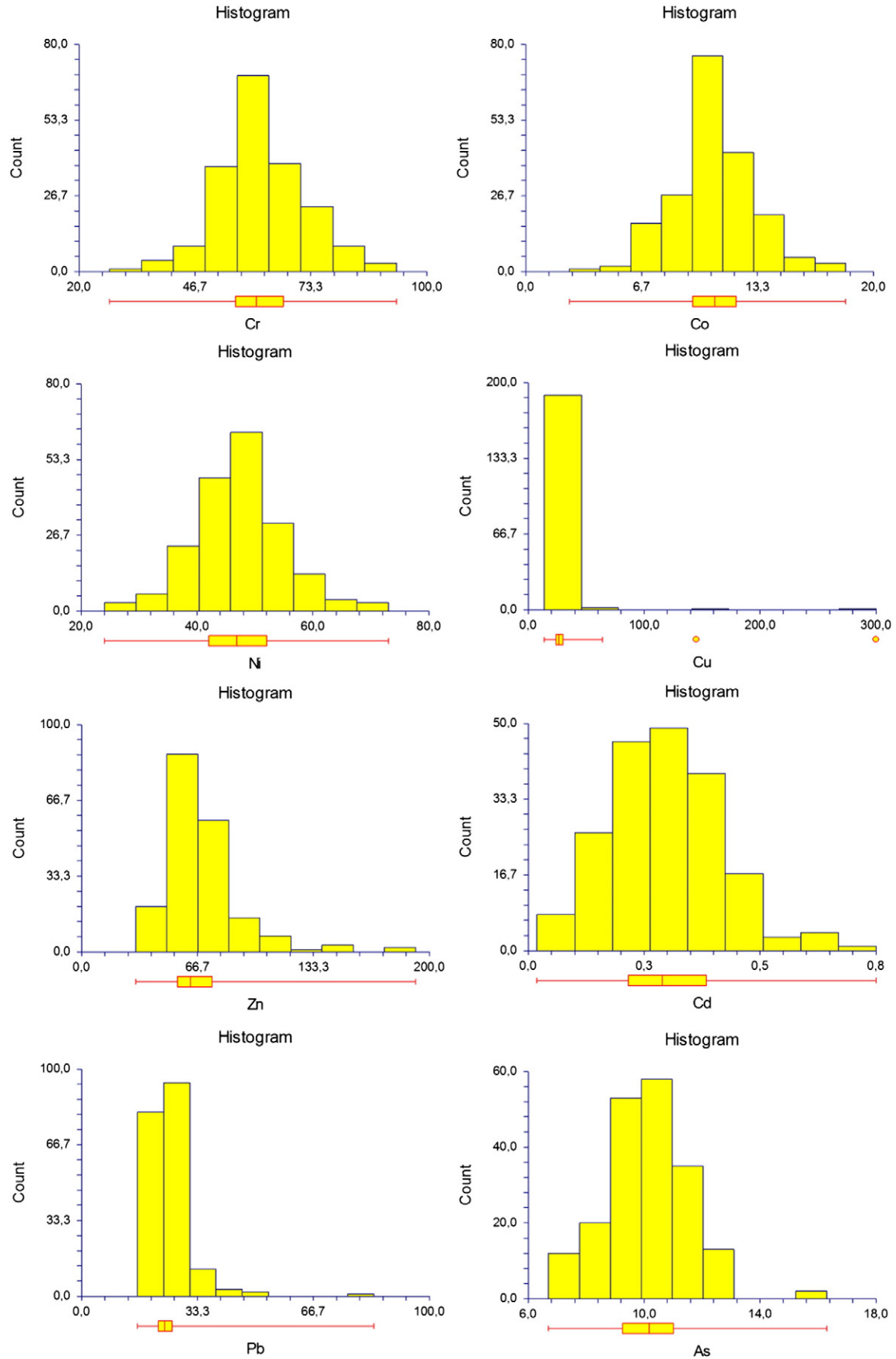


Fig. 4. Distribution plots (frequency histogram, boxplot) of the measured elements.

lead in the Earth's crust to be 11 mg/kg, with values of 17 mg/kg in the upper crust and 4 mg/kg in the lower crust. The natural Pb content in soil is related to the composition of the parent rock and is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides, and organic matter (Salminen et al., 2005). Anthropogenic sources of Pb include traffic, metalliferous mining, batteries, old lead-based paints, and sewage sludge (Salminen et al., 2005). Concentrations of Pb in the analyzed samples vary between 16 and 84 mg/kg with a mean value of 24 mg/kg. Almost all the samples exceeded normal values in soils, but only three of them were higher than the alert threshold. These contaminated soils are located near a road with high traffic (compared with the rest of the area) and near a village with a high population.

Across the globe, limits within which zinc is found in the upper horizon of different soil types are between 5 and 570 mg/kg, with a mean of 66 mg/kg (Lăcătușu, 2008). Rudnick and Gao (2003) estimate the abundance in the Earth's crust for zinc at 72 mg/kg, with values greater in the upper crust than in the lower one. The content of Zn in soil is closely related to the nature of parent rocks, texture, organic matter, and pH (Salminen et al., 2005). Anthropogenic sources of zinc are represented by industrial activities such as mining, coal and waste combustion, and steel processing (Salminen et al., 2005). The Zn concentration for the investigated area ranges between 31 and 192 mg/kg with a mean value of 63 mg/kg. Of all Zn values, fourteen of them exceed normal values in soils, but none of them surpass the alert thresholds. The highest concentrations were at the same sample points as the highest values for Pb. Given the fact that none of the samples exceed the alert thresholds, we can say that the studied area does not exhibit significant Zn contamination.

The average values of the elements within each soil type were analyzed and plotted in Fig. 5. Generally, the content of analyzed elements shows a constant tendency of concentration (average values do not vary in wide ranges) regardless of the type of soil in which they are found. The only differences of content that appear in the different soil types (e.g. Pb in Arenosol and Zn in Regosol) for a specific element are due to abnormalities caused by anthropogenic influences mentioned in the paper.

Out of the total of 10 soil types found in the researched area, four have very low expansion areas, and consequently no soil samples were collected from two of the types of soil, while other 2 types are represented by two, respectively one sample. Apart from two soil types that do not contain any samples, we consider that soil types with two, respectively one samples should also be excluded from comparisons

because the number of samples are not representative compared to the other types.

After the evaluation of the methods for determination of the geochemical background, the threshold, and abnormal values, Reimann et al. (2005) recommend the use of the boxplot method ($Me \pm 2MAD$). The boxplot diagram proposed by Tukey (1977) divides the data into four equal numbers of values based on the median, quartile 1, and quartile 3, and can directly determine abnormalities. Reimann et al. (2005) also states that in the case of boxplot charts, 50% of the values of the distributions can be found in the "box" with limits represented by quartiles 1 and 3. The boundaries between the normal distribution and abnormal values are represented by $Q3 + 1,5 \times IQR$ in the upper part of the barrier, respectively, and by $Q1 - 1,5 \times IQR$ on the lower side of the barrier.

4.3. Multivariate analysis results

4.3.1. Hierarchical clustering analysis (HCA)

To differentiate distinct groups of heavy metals as tracers of natural or anthropic sources, we performed an explorative HCA, which maximises the variance between groups and minimizes the variance between members of the same group. The obtained results are reported in the form of a hierarchical dendrogram in Fig. 6, which allows the identification of five groups of elements. Cr, Cu, and Cd were clustered independently of other elements, while the rest of the elements appear grouped in one cluster containing As, Co, and Ni and a second cluster containing Zn and Pb. The similarity axes represent the degree of association between the elements, with greater values meaning more significant association. The cluster formed by Zn and Pb may reflect anthropogenic pollution, while the cluster of As, Co, and Ni seems to be associated with geogenic or pedogenic sources. Except for influences from geogenic or pedogenic sources, Ni concentrations can also be easily influenced by fertilizers. Like Zn and Pb, Cd may be affected by anthropogenic pollution, while Cr may originate from the soil parent materials. Among other possible sources, phosphate fertilizers and metallurgical industries could also represent an input into the soils for Cd and Cr (Maas et al., 2010). Cu is in a cluster that may originate from the influence of the fertilizers or fungicides in the soil samples that surpass the alert thresholds.

4.3.2. Principal component analysis (PCA)

For further investigation of the relationships among the elements, PCA was performed (Fig. 7). For easier interpretation of the

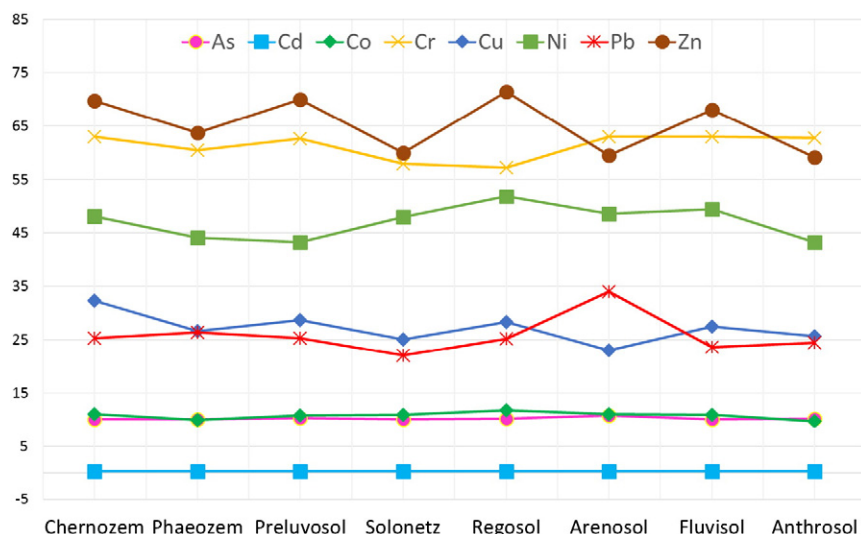


Fig. 5. Average contents of measured heavy metals (mg/kg) for each type of soil.

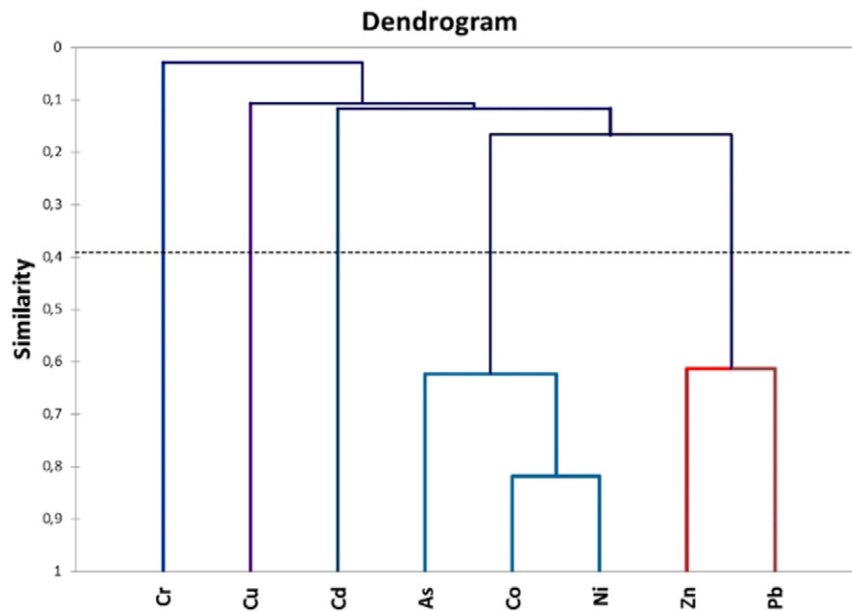


Fig. 6. Cluster analysis by Ward linkage method and Euclidean distance.

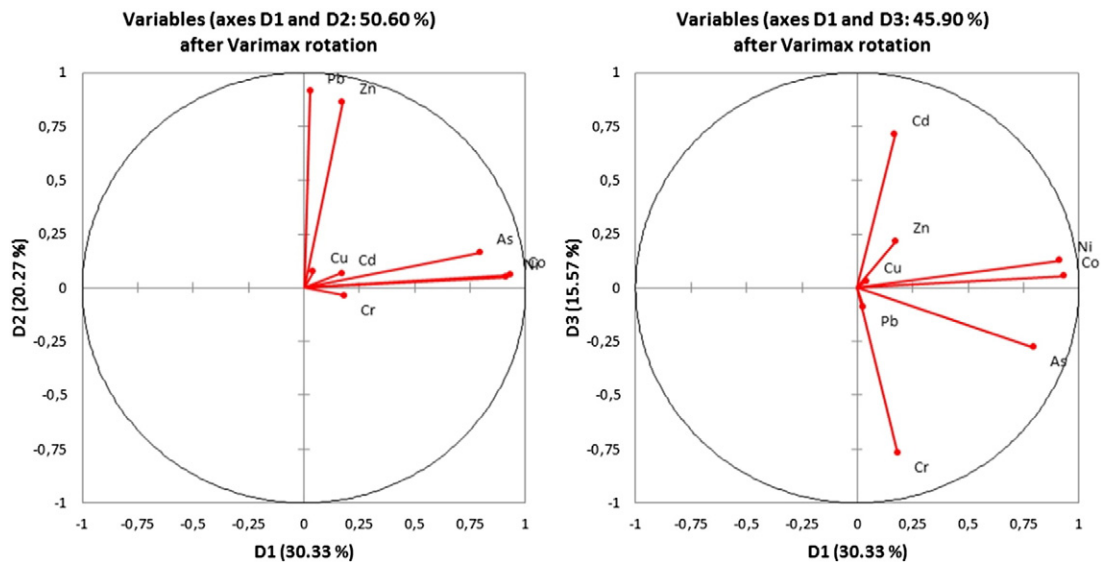


Fig. 7. Projection of the variables of the PCA.

principal component loadings and for maximization of the variance explained by the extracted factors, the obtained factors were rotated using a varimax normalized algorithm (Table 2). Four components were extracted from the available dataset that explained a total

Table 2
Varimax-rotation factor matrix for metals in the study area.

	PC1	PC2	PC3	PC4
Cr	0.033	0.001	0.586	0.030
Co	0.867	0.004	0.003	0.000
Ni	0.835	0.002	0.016	0.000
Cu	0.002	0.006	0.001	0.918
Zn	0.030	0.744	0.048	0.001
Cd	0.029	0.005	0.507	0.058
Pb	0.001	0.833	0.008	0.015
As	0.630	0.027	0.076	0.017

Values in bold correspond for each variable to the factor for which the squared cosine is the largest.

variance of approximately 79%. Factor I is formed by Co, Ni, and As, and based on the previous discussions, the distribution of these elements is mainly controlled by geogenic and pedogenic sources. In case of Ni, in addition to geogenic and pedogenic sources, Ni

Table 3
Pearson's correlation matrix for the metal concentration.

Variables	Cr	Co	Ni	Cu	Zn	Cd	Pb	As
Cr	1							
Co	0,085	1						
Ni	0,071	0,817	1					
Cu	0,020	0,087	0,070	1				
Zn	-0,123	0,245	0,226	0,092	1			
Cd	-0,152	0,117	0,191	0,097	0,191	1		
Pb	0,039	0,066	0,078	0,154	0,613	0,080	1	
As	0,261	0,656	0,590	0,140	0,159	0,004	0,229	1

Values in bold are different from 0 with a significance level $\alpha = 0.05$.

concentration can also be easily influenced by fertilizers. Factor II is composed of Pb and Zn and may reflect anthropogenic pollution caused by traffic or human activities. Factor III is represented by Cr

and Cd and may be affected by both lithogenic control and anthropogenic sources, such as phosphate fertilizers and metallurgical industries (Maas et al., 2010), even if they do not surpass the normal

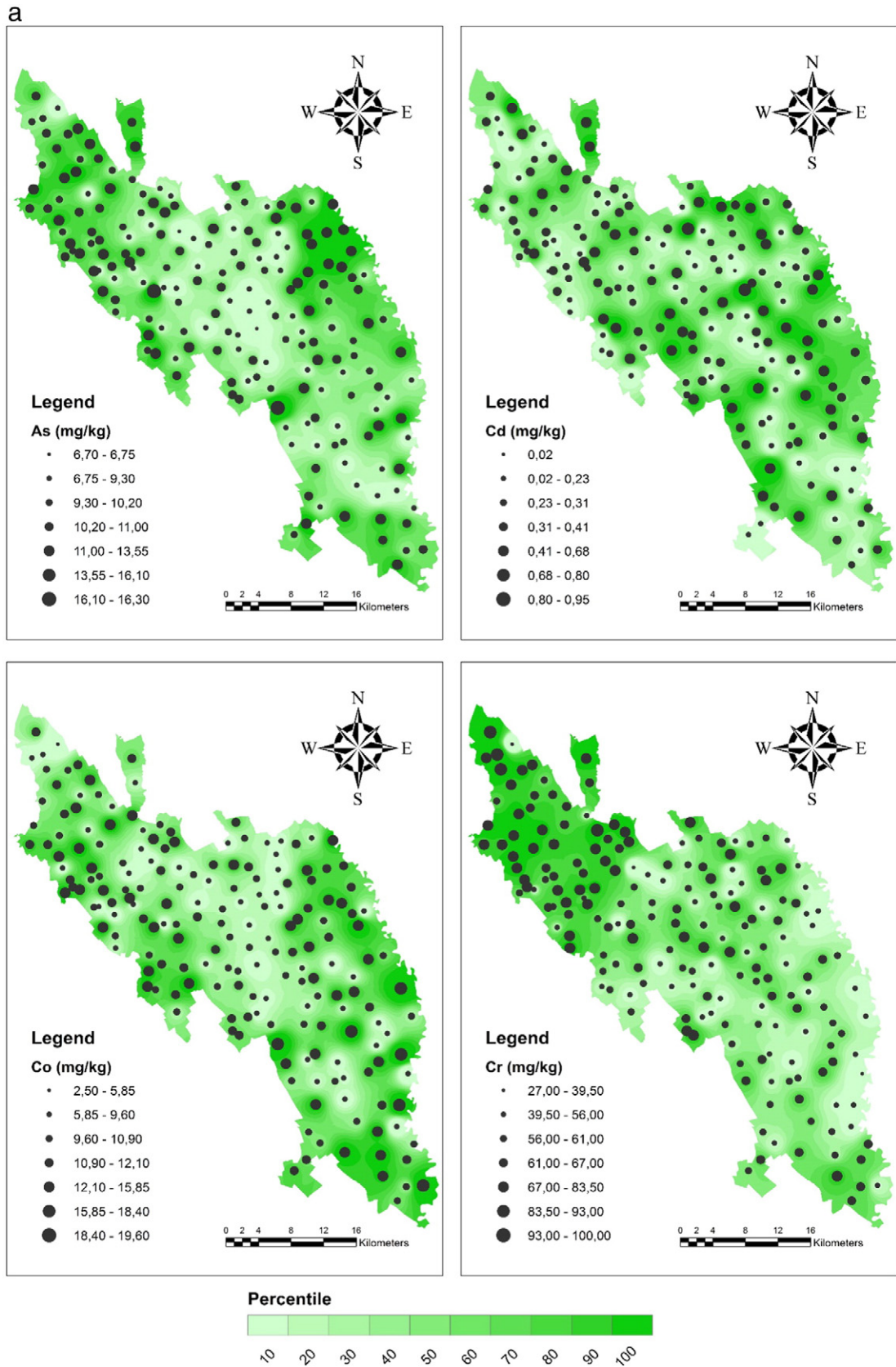


Fig. 8. a. Geochemical distribution of trace elements in topsoils of the study area. b. Geochemical distribution of trace elements in topsoils of the study area.

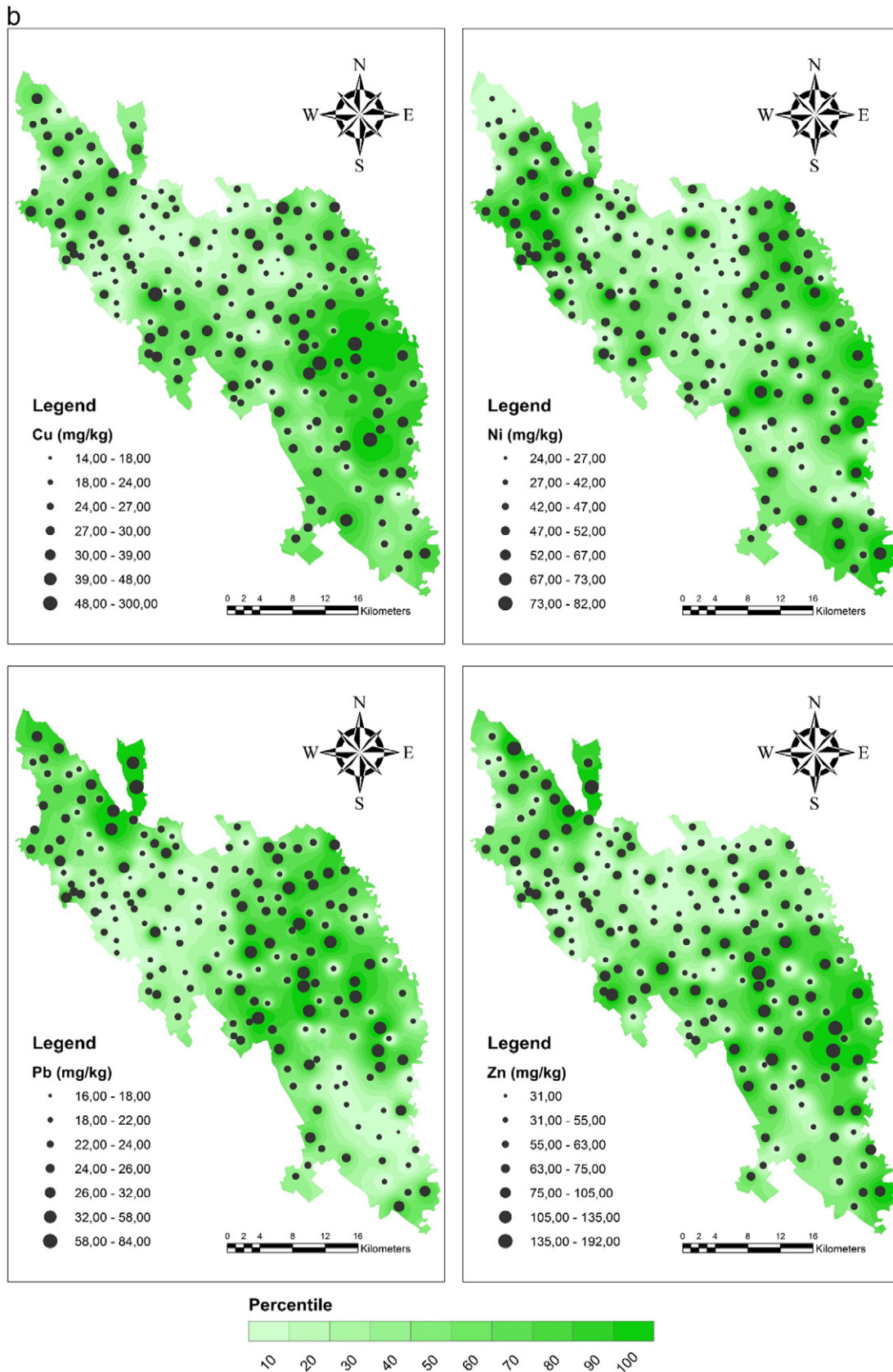


Fig. 8 (continued).

values or the alert threshold in soils. Factor IV is loaded by Cu and can be identified as a tracer of anthropic pollution that may originate from the influence of the fertilizers or fungicides in the soil samples

that surpass the alert thresholds. The heavy metal classification from PCA resembles the results of HCA and thus verifies the interpretation data.

The relationships between the elements from the soil samples in the studied area were also examined with the help of a Pearson correlation matrix (Table 3). The correlation matrix shows a very strong positive correlation between Co and Ni and a relatively high positive correlation between these two elements and As. It also shows a fairly strong positive correlation between Pb and Zn. The results of the descriptive statistics of HCA and PCA agreed well with each other and thus verify the data interpretation.

All the results divided the analyzed elements in four groups: Co, Ni, and As are mainly controlled by geogenic and pedogenic sources, with slight influences by fertilizers in case of Ni contents; Pb and Zn are significantly influenced by anthropogenic pollution caused by the traffic or human activities; Cr and Cd may be affected by both lithogenic and anthropogenic sources; and Cu is influenced by fertilizers or fungicides in the soil samples that surpass the alert thresholds.

4.4. Elemental spatial distribution patterns

Lately, embedded digitized and computerized technologies like geographical information systems (GIS) and GPS are being used more often in the interpretation and presentation of data and geochemical modeling (Wong et al., 2006). GIS software can be used to generate spatial distributions and maps and to identify potential sources of heavy metals (Guo et al., 2012). In order to describe the spatial distribution of the studied elements in soil from the study area, geochemical maps were plotted using ArcMap v.10.2 (ArcGIS) and the Inverse Distance Weighted (IDW) interpolation method with a power of 10 (Fig. 8). A spatial database was developed in ArcGIS, and elemental concentrations were linked to the sampling points. Class intervals were determined by natural breaks using boxplots (Tukey, 1977), and elemental concentrations were established as circles with size increasing as a function of concentration. The interpolated areas were added in the background to improve the visual inspection of the spatial trends (with green being higher and white being lower).

Fig. 8 presents Spatial distribution maps of Cr, Co, Cu, Zn, Ni, Cd, Pb, and As in the investigated area. Pb and Zn showed high values in the vicinity of areas inhabited by humans and near a major road carrying large amounts of traffic. Similar to other studies, it is apparent that high concentrations of Pb in urban soils were associated with vehicular exhausts, while Zn compounds are encountered as detergent/dispersant improvers for lubricating oil or antioxidants (De Miguel et al., 1999; Guo et al., 2012; Imperato et al., 2003; Saby et al., 2006). Cu showed high values in the vicinity of the areas planted with vines, which means that the source of high Cu concentration can be represented by the use of fertilizers or fungicides in vineyards. Herrero-Hernandez et al. (2012) note that copper-based fungicides such as the Bordeaux mixture, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot 3\text{CaSO}_4$, have been intensively used in Europe since the end of the nineteenth century to control vine (*Vitis vinifera* L.) fungal diseases, such as downy mildew caused by *Plasmopora viticola*. For instance, the copper content of a typical 1% Bordeaux mixture, would be of 0.25%. Therefore, the use of Copper-based fungicides could represent the source of high Cu concentration. Spatial distribution of Cr, Co, Ni, and As presented less variability and concentrations in the study area; these elements were comparable with background values, suggesting that they were not strongly influenced by anthropogenic activities. Because there is no significant industry and main activity on the research area is represented by agriculture, Ni and Cr contents in soil could be slightly influenced by anthropogenic sources such as fertilizers used frequently in agriculture. The concentration of Cd for soils in the studied area do not exceed 0.8 mg/kg, so even though it is associated with anthropogenic pollution, we cannot speak about it in this case.

5. Conclusions

It has been demonstrated that surface soil metal concentrations are a product of a variety of natural and anthropogenic sources. Cluster

analysis and PCA were combined with spatial distribution patterns to identify the sources of elements and classify them as geogenic or anthropogenic. Results of combined multivariate statistical analyses and spatial variability of heavy metals indicated that vehicle emissions, human activities, and agricultural materials represented the most important sources of Zn, Pb, and Cu contamination. In case of As, Ni, and Co these are mainly controlled by geogenic and pedogenic sources. In addition, Ni concentrations can also be easily influenced by fertilizers. Cr and Cd may be affected by both lithogenic and anthropogenic sources.

With some exceptions, Pb concentrations exceed normal values in soils in a very wide area, but only three values of the analyzed samples are higher than the alert threshold. These contaminated soils are located near a road with high traffic (compared with the rest of the area) and near a village. Zn concentrations resemble those of Pb, and fourteen of the samples exceed normal values in soils, but none of them surpasses the alert thresholds. The highest concentrations were at the same sample points as the highest values for Pb, and the sources of pollution may be caused by traffic or human activities. The Cu content exceeds the normal values in most of the samples, and two of them also surpass the alert thresholds in an area planted with vines. The source of high Cu concentration in these two samples are likely the fertilizers or copper-based fungicides used in vineyards.

The distribution of Co, Ni, and As display a nearly uniform distribution within the area of research and no abnormal contents. The concentration of Cd for soils in the study area is close to or below normal values, so even though it is associated with anthropogenic pollution, we cannot speak about it in this case. Concentrations of Cr do not surpass the alert or intervention thresholds in legislation, and only one of them is within the limits of normal values in soils.

The pH of soil samples ranged from 5.12 (strongly acid) to 9.55 (extremely alkaline). According to the classifications provided by the USDA (1998), soil samples from the study area mostly fit within the class of moderately and slightly alkaline soils (~65%), as well as strongly alkaline and neutral (~20%).

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