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The geochemical distribution of the heavy metals in the forestlands of the moor Şaru Dornei

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Abstract

Industrial activities such as burning coal and gasoline are the main factors which contribute to the more increasing emissions of heavy metals in the atmosphere. Once they have reached the atmosphere, these are easily dissolved in the precipitation water and they can be deposited at local, regional and global level, leading to the disturbance of the biogeochemical cycles of the trace elements. A series of heavy metals (Cr, Co, Ni, Cu, Zn, Pb, As and Cd) from the forestlands adjacent to the moorland from Șaru Dornei moor were investigated within this study. The samples were analyzed with an X-ray fluorescent spectrometer with energy dispersion (ED-XRF). Following the analysis, we obtained the following average values (mg/kg): Cr (49.31), Co (5.56), Cu (30.88), Ni (27.69), Zn (48.38), Pb (57.13), As (12.76) and Cd (0.17). The values of their pH varied between 3.5 (very strongly acid) and 4.68 (strongly acid). The results of the study showed that the following elements, Cr, Co, Zn and Cd, had concentrations inferior to the minimum value, while those of Pb and As exceeded the alert threshold (50 mg/kg) and the intervention one (25 mg/kg) respectively, according to the HG 756/1997.

Keywords: trace elements, Şaru Dornei, heavy metals, organic horizon, anthropogenic pollution.

1. Introduction

Soil is a key element of the forest ecosystem, providing support, water, nutrients and oxygen for the growth of the forest; thus, preserving the quality of soil is essential for the durable development of forest (Karim et al., 2014). The soil is acting like a container of heavy metals (Akan et al., 2013; Zadrożny et al., 2015) emitted to the environment by the anthropogenic activities, a behaviour also favoured by their property of accumulating over time (Marchand et al., 2011; Qingjie and Jun, 2008). The capacity of the soil to store heavy metals is associated to its type and physical properties (texture, structure or clay content),

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chemical properties (pH and Eh), as well as the nature of the polluting heavy metal (Kabata-Pendias, 2011).

The sources of metals provenance in the environment may be of natural origin as well as anthropogenic. The main natural sources are represented by atmospheric deposits of particles emitted by forest fires, biogenic emissions and volcanic activity (Cachada et al., 2013), and the main anthropic sources derive from the social and economic activities such as metallurgy, exploitation of various metals (Cu, Pb, Zn, Au, Ag), burning of fossil fuel and domestic waste, road traffic, agriculture (Herrero-Hernandez et al., 2012).

The accumulation of heavy metals in the superficial layers of soil is directly or indirectly linked to the human activity. Heavy metals of anthropic origin may be carried out by atmospheric currents and deposited at the surface of the soil, and may reach the inferior part of the soil profile by means of precipitations (Chen et al., 2007). The increasing of the heavy metal concentration may be correlated with the proximity of industrialized areas or routes of transportation.

The soils situated in urban areas have the largest heavy metal concentrations, but these can also be found at a far distance from the emission source (Acosta et al., 2015), being carried out by atmospheric currents. Among the most exposed areas to contamination with heavy metal are the protected areas, such as national parks or natural reservations (Dudzik et al., 2010; Tomaškin et al., 2013). The soils in the natural reservetions areas were often subject to the influence of urban areas expansion, mining activities or metallurgic industry (Dharani et al., 2007). They are also exposed to domestic waste disposal from major urban centers (Dudzik et al., 2010). Soil contamination in protected areas may also take place by means of agricultural activities (inappropriate fertilization or use of pesticides) (Tomaškin et al., 2013).

1.1 Description of the study area

The moor Şaru Dornei is part of a vaster marsh complex situated in the Dornelor Basin from the northern sector of the Oriental Carpathians. The latter represent the longest segment of the Carpathians on Romanian territory, with a maximum height of 2303 m (Pietrosu Rodnei). The moor (Fig. 1) is located at 800-900 m altitude, having all the characteristics of a northern moorland, such as a cold climate and a large quantity of rainfall. The annual average temperature is 4.2 ºC , with the highest temperature of 13.8 ºC and the lowest of -9.1 ºC; the precipitation regime exceeds 900-1000 mm/year.

Şaru Dornei township and Vatra Dornei town are located near the studied area, with populations of 2077 inhabitants and 14.429 inhabitants, respectively. The closest urban agglomeration is the town of Suceava (105.624 inhabitants), situated at approximately 174 km.

1.2. Geological setting of the study area

The studied area is situated in the South-Western part of the Dornelor Depression, where deposits belonging to the Quaternary Age can be found predominantly. Quaternary deposits represent the majority of the Dornelor Depression area. These have various thicknesses and are inharmoniously arranged over the older formations of the post-tectonic crys-

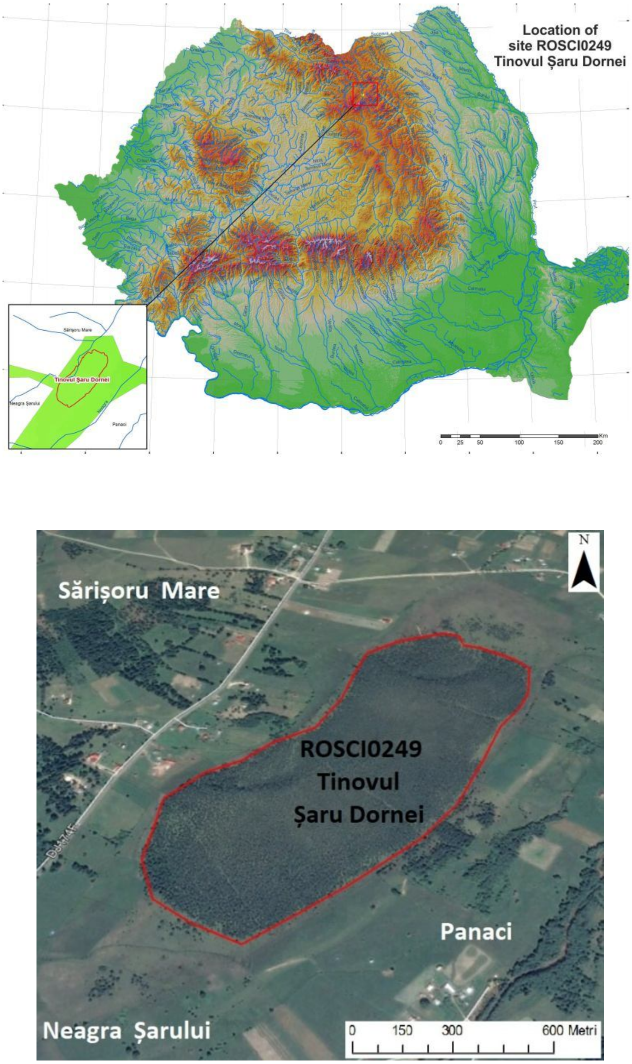

Fig. 1 Localization of Tinovul Şaru Dornei area.

talline, eruptive or sediments. The Quaternary Age is represented by four genetic types of deposits: alluvial, diluvial-proluvial, proluvial and moorland (oligotrophic moors) (Chiriţă, 2003).

Neogene and Quaternary lavas delineate Dornelor Depression from West to South, along the mountain frame corresponding to the Eastern part of the Bârgăului Mountains and North of Călimani Mountains, extending to the center of the depression. There are massive volcanic roks, pyroclastic rocks and volcanic agglomerates which are part of lavas, resulting from a staged magmatic activity, each of them leading to the formation of a volcanic compartment with a different petrography (Mihalca, 2014).

The fundament of the volcanic area is represented by inferior crystalline and sedimentary formations from Mesozoic and Paleogene-Miocene. Crystalline rocks are mainly meso-metamorphic and in a lesser measure epi-metamorphic (chlorite-sericite schists, paragneisses, mica schists, limestone and crystalline dolomites), which belong from a petrographic point of view to Rebra and Tulgheş lithogroups. The fundament of the eruptive is covered by formations of the interior volcanic compartment, volcanogenic sediment or andesitic and dacitic lava flows. Also, the fundament occurs at the surface in some isolated areas (Chiriţă, 2003).

The crystalline formations in the basement are associated with epiclastic deposits, subaerially or subaquatically accumulated, during the periods without volcanic activity. Eruptive rocks show a varied andesitic composition, of the pyroxene andesites and amphiboles type. These stretch over an important area in the South-central part of the Dornelor Depression. The oldest eruptions of a subvolcanic type are in the western region of the mountain frame, corresponding to Bârgău, characterized by a varied mineralogic composition and different levels of schistosity, which appear in the Western part of the massif, surpassing the limits of Dornelor Basin (Chiriţă, 2003).

Volcanic rocks include, in order of the importance of their spatial distribution in the Călimani Mountains, the following petrographic types: pyroxenic andesite, horblendic andesite, basaltic andesite, pyroxene and horblende andesite and/or horblende and pyroxene andesite, biotite ± quartz, dacite, quartz-ferrous andesite, pyroxenic andesite ± olivine ± hornblende ± biotite ± quartz. These belong to the igneous stages during the Panonian, in the case of the amphibolic andesites, hornblende andesites, pyroxene and amphibole andesites and during Meotian-Pontian-Dacian and inferior Pleistocene in the case of hornblende ± pyroxene andesites and basaltic andesites (Chiriţă, 2003).

Mineralogically, dacites have a low potassium content. Typical volcanic rocks are porphyritic, with a micro-crystalline or vitreous binder, showing frequent glomerophiric accumulations of phenocrysts. Aphanitic andesites are characteristic to the North-Western area of Călimani. Xenoliths are also widely spread, usually including ortho-pyroxenes, amphiboles, feldspars and opaque minerals. The comparison between the chemical composition, according to the criterion of the mineralogic diagnosis (petrotype) and the affiliation to the main geographic units of the Călimani-Gurghiu-Harghita mountain chain, does not reveal significant differences. In the Northern part of Călimani, the andesites are predominant among volcanic rocks, followed by basaltic and dacitic andesites (Mihalca, 2014).

2. Materials and methods

2.1 Sampling methodology

From the forest area, adjacent to the Tinovul Saru Dornei peat bog, 36 samples were collected (Fig. 2). The samples were extracted using a stainless steel sample, from depths between 0 and 25 cm. Each sample weighed 2.0–2.5 kg. The testing equidistance was of approximately 150 m. The samples were stored in tightly sealed plastic bags and properly numbered. The

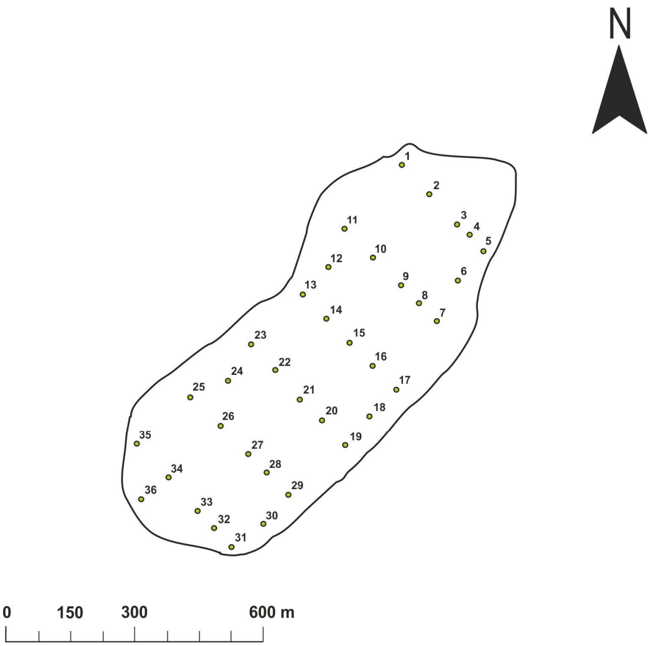

Fig. 2 The sampling network.

collection sites were identified by means of a GPS tracker device.

All soil samples were air-dried, milled and sieved to 2 mm to remove stones, coarse materials, and other debris; the samples that still required drying were dried for 12 h in an oven, at 60 °C. After the homogenization with an agate mortar, the total amount of sample (2.0–2.5 kg) has been separated in four equal parts (quartation).Three parts were stored as a blank, and one part was used to perform ED-XRF and pH analyses.

2.2 Determination of pH

For each sample, pH was measured using a standard pH-meter, by the potentiometric method in an aqueous solution; the sample:water ratio was 1:2.5 (STAS 7184/13-88). For this study, a Hach Lange GmbH pH-meter, model HQ40D, was used. The sample-distilled water mixture was intermittently stirred with a glass rod for homogenization, left 1 h to settle and then analysed. The calibration of the pH-meter was carried out with buffer solutions of pH 4 and 7 at the beginning of each set of analysis.

2.3 X-ray fluorescence analysis

A quantity of approximately 15 g of each sample was mixed with epoxy resin (3 g) in a proportion of 5:1. The mixture was stirred for 15 min at 180 rpm/min using an agate mill (Frisch Pulverisette Planetary Mill 5). After homogenization, 9 g of the mixture was placed in aluminum caps and pressed into pellets at 20 t/cm^2, for 30 s, using a hydraulic press. ED-XRF analyses were performed using an ED-XRF spectrometer (Epsylon 5, Panalytical N.V.).

Calibration of the detection device was performed 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 one standard produced by the United States Geological Survey (RGM-1: rhyolite powder).

The detection limits for each analyzed element are as follows: As = 1.13 mg/kg, Cd = 0.05 mg/kg, Co = 1.14 mg/kg, Cr = 7.03 mg/kg, Ni = 10.65 mg/kg, Pb = 2.92 mg/kg, Zn = 2.27 mg/kg. The exposure time was 60 s, except for As and Cd, for which the exposure time was 90 s.

Quality control and quality assurance were assessed using the SO-4 certified reference material. The standard was measured after each 10 sample measurements. The results for Cr, Co, Ni, Cu, Zn, Pb and As indicated an analytical precision better than 5% relative standard deviation (RSD) and accuracy was within 4%. For Cd, the results were slightly higher (precision 22% RSD and accuracy 12%) due to the low concentrations of this element in CRM (0.34 mg/kg) very close to the detection limit of the device (0.1 mg/kg).

2.4 Statistical analysis

The main descriptive parameters of each element were calculated by means of statistical analysis (standard deviation, minimum, maximum, mean, median, mode, skewness and kurtosis etc).The multivariate statistical analysis and desciptive statistics used for this study were performed using XLSTAT 12 software. Principal component analysis (PCA) and hierarchical clusters analysis (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).

3. Results and discussions

3.1 Leaching tests

According to previous investigations (Adriano, 2001), 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 accesibility of elements Cu, Mn, and Zn; thus, their availability for plants decreases as the pH increases in the range of 5 to 8 (Teng et al., 2015).

The pH values in the study area range from 3.5 to 4.68. The lowest value (pH = 3.5) is found in very strongly acid environment, and the highest value (pH = 4.68) in a strong acid environment. More than 52.77 % of the samples are from an extremely acid environment, with a pH lower than 4.30, while 47.23 % of the samples indicate a strong acid environment, with a pH lower than 5.

The pH values correlate with the heavy metals concentrations. Most of the analyzed samples fall within the very strongly acid soil category (3.5–4.3). Thus, at low pH values, the majority of the heavy metals (Cu, Pb, Zn, Co and Ni) will be related to the content of organic matter (Skwaryło-Bednarz et al., 2014).

3.2 Heavy metal concentrations in the study area soils

In order to identify a possible contamination and/or soil pollution, minor element values obtained through ED-XRF 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.

Table 1 presents the values of the main statistical parameters of the elements found in the study area (Cr, Co, Ni, Cu, Zn, Pb, As and Cd), as well as the normal values (NV) of the soil and alert (AT) and intervention thresholds (IT) according to the Romanian legislation. Moreover, for comparison, table 1 outlines the intervals of variation of the same metals as estimated by Salminen (2005) and Adriano (2001).

The concentration ranges of Co, Cu, Cr, Ni, Cd, Pb, As and Zn were: 2.9–11,

Tab. 1 Statistical parameters contents (mg/kg) of the research area soils (Tinovul Şaru Dornei)

		Cr	Co	Ni	Cu	Zn	Cd	Pb	As	pH
Mean		43.91	5.56	27.69	30.88	48.38	0.17	57.13	12.76	4.18
Median		47	5.25	26	26	46	0.16	47	9.75	4.29
Mode		49	5	26	19	46	0.14	38	8.5	4.53
Variance		90.07	2.80	56.21	137.87	66.98	0.08	639.78	35.55	0.11
Skewness		1.296	2.549	1.158	0.563	1.371	-0,095	0.022	1.857	-0.657
Kurtosis		-1.351	1.297	1.128	1.024	1.016	0.100	1.037	1.624	-0.589
Minimum		18	2.9	16	19	35	0.02	29	7.6	3.5
Maximum		56	11	46	65	74	0.38	122	28.7	4.68
CV		0.21	0.30	0.27	0.38	0.16	0.52	0.44	0.46	0.07
Q1		42.5	4.57	23	21.75	42.5	0.12	37.75	8.77	3.97
Q3		49.5	6.52	30.25	39.25	53	0.25	70.75	14.67	4.41
IQR		7	1.95	7.25	17.5	10.5	0.13	33	5.9	0.44
Nr. of samples		36	36	36	36	36	36	36	36	36
Order no. 756/1997	VN*	30	15	20	20	100	1	20	5	-
	PA**	100	30	75	100	300	3	50	15	-
	PI***	300	50	150	150	700	5	250	25	-
Adriano (2001)	means	70.00	8.00	50.00	30.00	90.00	0.35	35.00	6.00	-
Salminen (2005)		60.00	7.78	18.00	13.00	52.00	0.145	22.60	7.03	-
Tinovul Mare		45.93	18.64	22.14	23.56	87.61	0.31	41.3	10.99	

VN*: Normal value
PA**: Alert threshold
PI***: Intervention threshold

19–65, 18–56, 16–46, 0.02–0.38, 0.02–0.8, 29–122, 7.6–28.7 and 35–74 mg/kg, with mean values of 5.56, 30.88, 43.91, 27.69, 0.17, 57.13, 12.76 and 48.38 mg/kg, respectively. The mean concentrations of the heavy metals decreased in the order Pb > Zn > Cr > Cu > Ni > As > Co > 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 Cr, Co, Ni, Cu and Zn are below 0.40, while As, Pb and Cd has a CV value higher than 0.40. Therefore, Cr, Co, Ni, Cu and Zn seem to be associated with natural sources, while As, Pb and Cd seem to be influenced by anthropogenic activities.

As can be noticed in table 1, the concentrations of the metals in the soils of the study area presented similar or higher values for all elements compared with the Geochemical Atlas of Europe (Salminen, 2005). The values reported by Adriano (2001) are comparable or lower for almost all elements, except for Co, Pb and As. The concentration of the elements found within Tinovul Mare Poiana Stampei are higher than those found in Tinovul Şaru Dornei, excepting for Cu and Pb.

3.2.1 Chromium

Limits within which chromium 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 (Lăcătuşu, 2008). Swedish arable soils contain Cr in a range from 3 to 50 mg/kg, at an average value of 22 mg/kg. The median Cr contents in agricultural soils of Japan vary from 56 to 70 mg/kg (Takeda et al., 2004). Dill et al. (2012) indicates average Cr contents in the Basarabian siliciclastic rocks from Eastern Carpathians Foreland Basin of 34 mg/kg (sands), 77mg/kg (silts) and 90 mg/kg (clays).

Chromium concentration in the anlyzed samples from Tinovul Şaru Dornei varies from 18 to 56 mg/kg, with an average content of 43.91 mg/kg. Comparing this average with the results obtained by Dill et al. (2012) in the Bessarabian stones, we found a lower content, regarding the sands (34 mg /kg) and a higher content compared with silts (77 mg/kg) and clays (90 mg/kg). Out of the total number of analyzed samples, four are under the normal value in soil (30 mg/kg), whereas the rest of the samples have concentrations higher than this, but lower than the alert threshold (100 mg/kg). Thus, it can be concluded that the Cr ion is not significantly polluting for the analyzed soils in the study area.

3.2.2 Cobalt

In worldwide soils, the limits of cobalt found in the upper horizon are between 0.1 and 116 mg/kg with a mean value of 9.6 mg/kg (Lăcătuşu, 2008). McGrath and Loveland (1992) have determined cobalt contents between 0.2 and 322 mg/kg in soils from Great Britain. The total Co content in the upper horizon of soils from Romania ranges from 0.2 to 20 mg/kg, with an average value of 6.3 mg/kg (Davidescu et al., 1988).

Cobalt concentration in the analyzed samples varies from 2.9 to 11 mg/kg, with an average content of 18.64 mg/kg. All the analyzed samples have concentrations under the normal limit in the soil (15 mg/kg) for this kind of metal. As a result, the high values of Co are influenced to a large extent by natural phenomena in the area and less by the anthropic factor.

3.2.3 Nickel

The limits of Ni found in the upper horizon of worldwide soils, are between 1 and 450 mg/kg, with a mean value of 23 mg/kg (Lăcătuşu, 2008). In the Earth's crust, the mean Ni abundance has been estimated around 20 mg/kg, whereas in the ultramafic rocks, Ni ranges from 1400 to 2000 mg/kg (Kabata-Pendias, 2011). The average nickel content in soil reported by Fiedler and Rössler (1988) is 20 mg/kg and the value of the global geochemical abundance coefficient is 0.34 (Lăcătuşu and Ghelase, 1992). The highest nickel contents are given for uncontaminated soils from various countries, as follows: Canada (119 mg/kg), China (450 mg/kg), Japan (660 mg/kg) and Italy (3240 mg/kg) (Herselman et al., 2005).

In all the samples of soil analyzed, the nickel concentration varies from 16 to 46 mg/kg, with an average of 27.69 mg/kg. Four samples have contents under the normal value (20 mg/kg), whereas the rest exceed this value, but not that of the alert threshold (75 mg/kg). Since aproximately all samples exceed the normal value in soils, we reached the conclusion that the nickel ion is influenced by the use of fertilizers, during the agricultural activities.

3*.2.4 Copper*

In the upper horizon of worldwide soils, the limits of copper are between 1 and 300 mg/kg, with a mean value of 22.4 mg/kg (Lăcătuşu, 2008). 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. McGrath and Loveland (1992) have determined copper contents between 1.2 and 1508 mg/kg in soils from Great Britain. The concentration of Cu in 3045 samples of surface soil from major agricultural production areas of the United States varies from 0.6 to 495 mg/kg (Kabata-Pendias, 2011).

The content values found for copper in the soils from Tinovul Şaru Dornei vary from 19 to 65 mg/kg, with an average content of 30.88 mg/kg. All the analyzed samples exceed the minimum value in soil (20 mg/kg) for this type of metal, but no sample exceeds the alert threshold (100 mg/kg). Since none of the samples exceeds the alert threshold, we can say that the researched area does not show a significant copper contamination.

3.2.5 Zinc

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 (Lăcătuşu, 2008). The average Zn content in soil reported by Fiedler and Rössler (1988) is 50 mg/kg and the value of the global geochemical abundance coefficient is 0.60 (Lăcătuşu and Ghelase, 1992). Kabata-Pendias (2011) estimated the abundance of zinc in the Earth's crust as 72 mg/kg. In soils around the main non-ferrous ore processing units, accumulations of Zn up to 1378 mg/kg (Baia Mare), 400 mg/kg (Zlatna) and 2010 mg/kg (Copşa Mică) have been found (Răuţă et al., 1992).

In the analyzed samples, the concentration of zinc varies from 35 to 74 mg/kg, with an average of 48.38 mg/kg. All the analyzed samples have lower concentrations than the normal value in soil (100 mg/kg) for this type of metal. Since none of the samples exceeds the minimum value in soil, we can say that the zinc ion is not a significant pollutant for the studied area.

3.2.6 Lead

In soils around the world, the limits of lead in the upper horizon are between 5 and 280 mg/kg, with a mean value of 66 mg/kg (Lăcătuşu, 2008). 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 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. In soils around the main non-ferrous ore processing units, there are accumulations of Pb content of up to 1083 mg/kg (Baia Mare), 2248 mg/kg (Zlatna), 3550 mg/kg (Copşa Mică) (Răuţă et al., 1992).

The content values found for lead in the soils from the sudied area vary from 29 to 122 mg/kg, with an average of 57.13 mg/kg. As one can notice, all the analyzed samples exceeded the normal value in soils (20 mg/kg), and 13 samples exceeded the alert threshold (50 mg/kg) established through the Government Decision no. 756 of the Romanian legislation. The samples which exceeded the alert threshold are situated in the proximity of the county road DJ 174 F, which links the localities Şaru Dornei and Gura Haitii.

3.2.7 Arsenic

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 the fossil fuel and waste combustion, metallurgical industry, fertilizers, and volcanic emissions (Tsuji et al., 2004).

In all the analyzed samples, the concentration of arsenic varied from 7.6 to 28.7 mg/kg, with an average content of 12.76 mg/kg. All the samples exceed the normal value in soil (15 mg/kg), and five samples had concentrations superior to the alert threshold (25 mg/kg). Only three samples out of the total of samples exceed the intervention threshold established by the HG 756/1997.

3.2.8 Cadmium

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 (Lăcătuşu, 2008). McGrath and Loveland (1992) have determined cadmium contents between 0.2 and 40.9 mg/kg in soils from Great Britain. The average Cd content in soil reported by Fiedler and Rössler (1988) is 0.3 mg/kg and the value of the global geochemical abundance coefficient is 2.31 (Lăcătuşu and Ghelase, 1992).

The content values of cadmium in the soils from Tinovul Şaru Dornei vary from 0.02 to 0.38 mg/kg, with an average of 0.17 mg/kg. All the samples show concentrations inferior to the minimum value (1 mg/kg) in soil for this type of metal. Since none of the analyzed samples exceeds the normal value, we reach to the conclusion that the cadmium ion is not a pollutant for the researched area.

4. Multivariate analysis results

4.1 Hierarchical cluster analysis (HCA)

To differentiate distinct groups of heavy metals as tracers of natural or anthropic sources, an explorative HCA has been performed, which maximises the

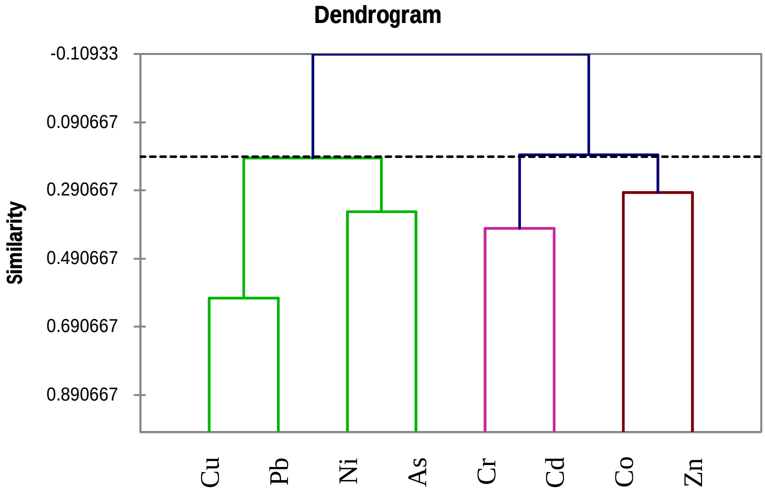

Fig. 3 Cluster analysis through Ward's method and Euclidean distance.

variance between groups and minimizes the variance between members of the same group (Lee et al., 2006).

As can be noticed, the elements were grouped in four clusters (Fig. 3): cluster I (Cu, Pb), cluster II (Ni, As), cluster III (Cd, Cr) and cluster IV (Co, Zn). The similarity axes represent the degree of association between the elements, as follows: the higher their value, the higher the degree of association between the elements. The clusters formed of Cu and Pb as well as that of Ni and As may be influenced by the anthropogenic pollution by means of the activities in the area (agriculture and road traffic), while clusters III and IV seem to be associated with the geogenic (pedogenic included) sources. The high concentrations of Pb, Zn, Ni and Cu in the studied area could be influenced by the road traffic and phosphate fertilisers used in agricultural activities (Maas et al., 2010).

Arsenic concentration might be influenced by fertilisers and the discharge of waste water from the livestock farms (Reimann and de Caritat, 1998), while Cu abundance may be influenced by the fertilisers and fungicides used in agricultural activities. Nickel concentration may be influenced by the bedrock or by fertilisers (Mass et al., 2010). Since there is no cadmium source of pollution in the area, we can say that Cd ion can only come from the geogenic sources of the area.

4.2 Principal component analysis (PCA)

Principal Component Analysis (PCA) is the most common multivariate statistical method used in environmental studies and is employed to extract a small number of latent factors for analyzing relationships among the observed variables (Manta et al., 2002; Han et al., 2006). As other multivariate statistical methods, PCA is useful in reducing data dimension while retaining important information and representing variables in a form that can be easily interpreted (Lee et al., 2006).

Four compounds were extracted from

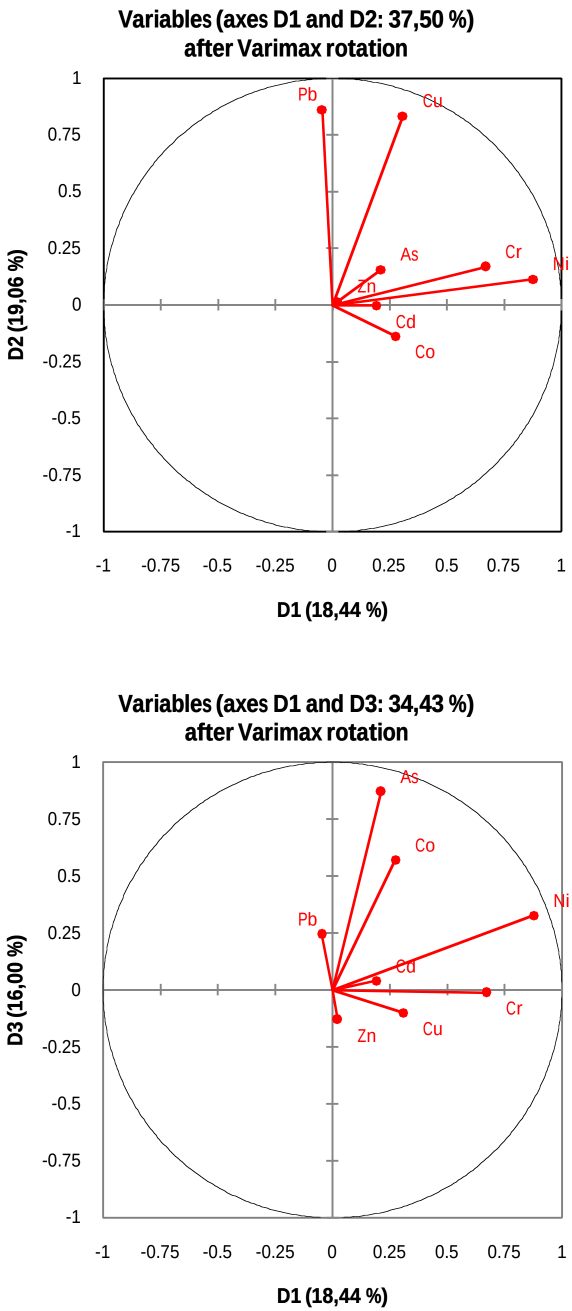

Fig. 4.Variables projection in the main components analysis.

the available data set (Tab. 2; Fig. 4) which explain a total variance of more than 79.64 %. Factor 1 has a variation of more than 33.19 % and refers to Cr, Co and Ni. Chromium has the largest share in this factor, with a concentration of 100 mg/kg in the upper crust (Rudnick and Gao, 2003). The high concentrations of chromium and nickel may be influenced by agricultural activities during which different fertilisers are used, while the concentrations of cobalt may be greatly influenced by the pedogenis sources of the area (Nicholson et al., 2003; Cang et al., 2004). As a result, the factor 1 is influenced by the anthropic sources, i.e. the use of fertilisers in agriculture.

Factor 2 has a variation of more than 19.16 % and it is formed by Pb and Zn. Within this factor, lead has the largest share, with a concentration of 13 mg/kg in the upper crust (Rudnick and Gao, 2003). The high concentrations of Zn can be associated with the agricultural activities, especially the use of fertilisers and fungicides (Nicholson et al., 2003; Cang et al., 2004), whereas high lead concentrations can be associated to road traffic (Arditsoglou and Samara, 2005; Al-Khashman and Shawabkeh, 2006). Factor 2 is influenced by the anthropic activities by means of road transportation and agriculture.

Factor 3 has a variation of more than 14.41 % and it refers to Cu and As. Copper has the largest share within this factor, with a 68 mg/kg in the upper crust (Rudnick and Gao, 2003). The high concentrations of Cu and As may be associated with agricultural (applying fertilisers and pesticides) and zootechnical (inefficient treatment of the waste waters resulted from the regular business) activities in the area (Nicholson et al., 2003; Cang et al., 2004). As a result, factor 3 is influenced by agriculture in the case of copper and by livestock farms in the case of arsenic.

Factor 4 has a variation of 13.83 % and is formed of Cd, with a concentration of 0.1 mg/kg in the earth`s crust (Kabata-Pendias, 2011). This may be associated with the following anthropic activities: non-ferrous metal industry, forest fires, burning of fossil fuel and solid waste incineration (Nriagu and Pacyna, 1988; Baveye et al., 1999). Because the area is lacking completely an industrial activity,

Tab. 2 Varimax-matrice rotation factor for metals in the study area

	F1	F2	F3	F4
Cr	**0.684**	0.075	0.038	0.041
Co	**0.305**	0.147	0.039	0.252
Ni	**0.641**	0.006	0.064	0.002
Cu	0.163	0.289	**0.344**	0.064
Zn	0.094	**0.365**	0.268	0.064
Cd	0.294	0.063	0.007	**0.514**
Pb	0.198	**0.481**	0.056	0.028
As	0.278	0.108	**0.337**	0.066

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

capable of heavy metal pollution, we draw the conclusion that the factor 4 reflects the natural concentrations of the area and is mainly influenced by geogenic, pedogenic included, sources.

5. Spatial distribution of heavy metals in the study area

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 (natural or anthropogenic) of heavy metals from different environments (Guo et al., 2012). In order to draft the distribution maps for heavy metals (Ni, As, Pb, Cd, Zn, Cu, Co and Cr) in the soils from the research area (Fig. 5), we used the inverse distance weighting method (IDW) of the ArcGis (ArcMap) software, version 10.2.2.

In 2012, a number of 1203 companies with a total of 4826 employees were operating within Dornelor Depression. Among them, 705 companies are specific to the service sector and served by 2129 employees, followed by 355 companies from the secondary sector with 2472 employees and the primary sector represented by 143 companies with 225 employees. This situation shows that a large part of the population is still loyal to traditional occupations such as those in the field of wood processing and food industry (especially that of dairy and bakery products), these substreams holding an important share of the regional economic sector (Mihalca, 2014).

Lead and zinc showed high concentrations in the proximity of inhabited areas and county road DJ 14 F which links the localities Şaru Dornei and Gura Haitii, characterized by high-traffic. Compared to other studies conducted by various authors (De Miguel et al., 1998; Guo et al., 2012), it is obvious that high levels of lead are associated to road traffic, and those of zinc with phosphate fertilisers (Nicholson et al., 2003; Cang et al., 2004).

Arsenic showed high concentrations in the proximity of livestock farms and agricultural lands. Out of the total number of analyzed samples, two samples exceeded the alert threshold (15 mg/kg) and three samples the intervention thereshold (25 mg/kg) according to the HG 756/1997. This might be due to the insufficient filtering of the animal waste within these farms and to the application of various fertilisers (Reimann and de Caritat, 1998).

The spatial distribution of Cr, Ni and Cu presented higher concentrations than the normal value in soil (30 mg/kg; 20 mg/kg; 20 mg/kg), but none of the analyzed samples exceeded the alert threshold (100 mg/kg; 75 mg/kg; 100 mg/kg). The high concentrations of chromium and nickel may be influenced by agricultural activities, by applying different fertilisers, whereas the concentrations of copper may be largely influenced by the pedogenic sources of the area. Cobalt (10.70 mg/kg) and cadmium (0.38 mg/kg) showed concentrations inferior to the minimum value (20 mg/kg; 1 mg/kg), their content being comparable to the background values, which sugests that these were not strongly influenced by anthropic activities.

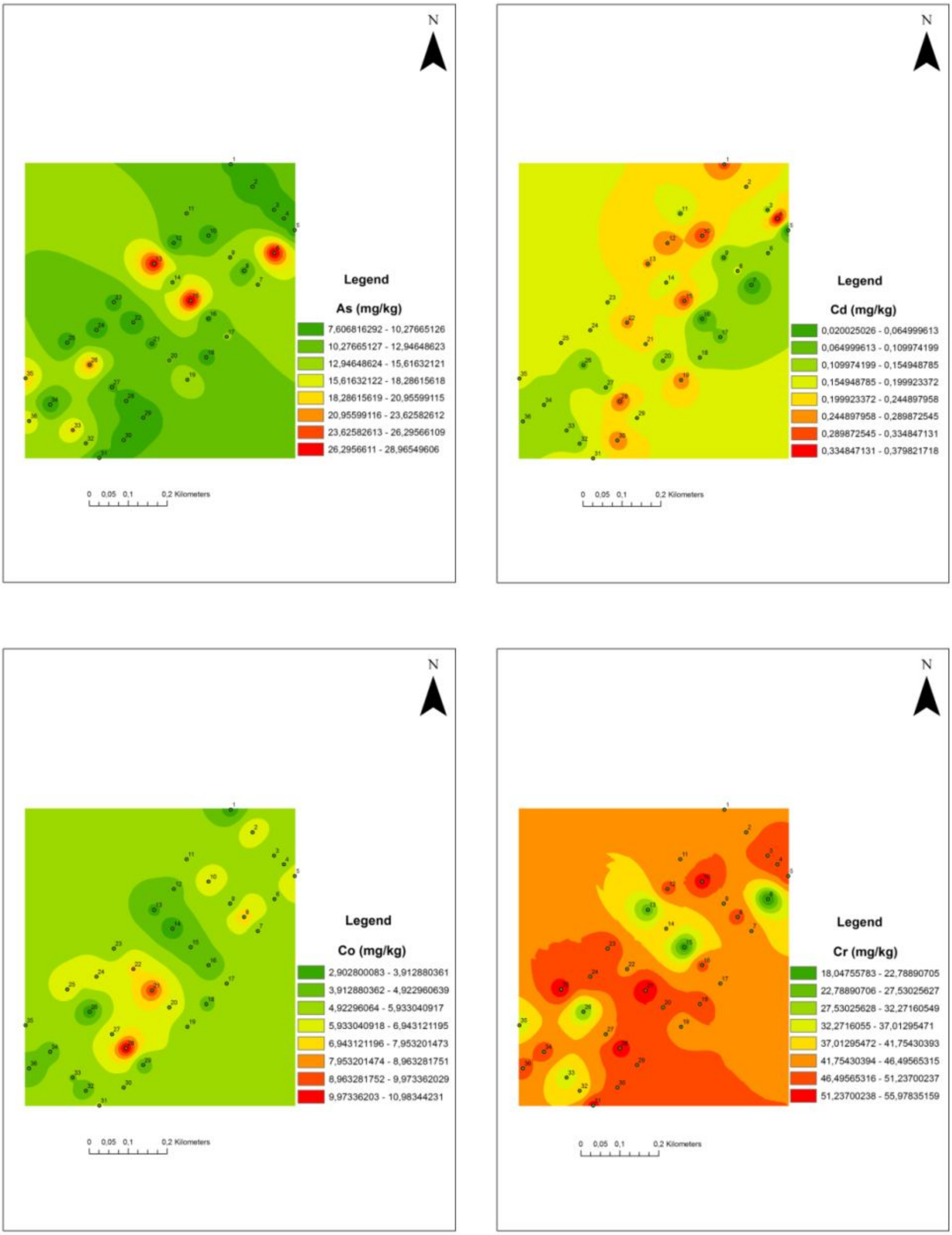

Fig. 5 Spatial distribution of heavy metals (Ni, As, Pb, Cd, Zn, Cu, Co and Cr) in the study area.

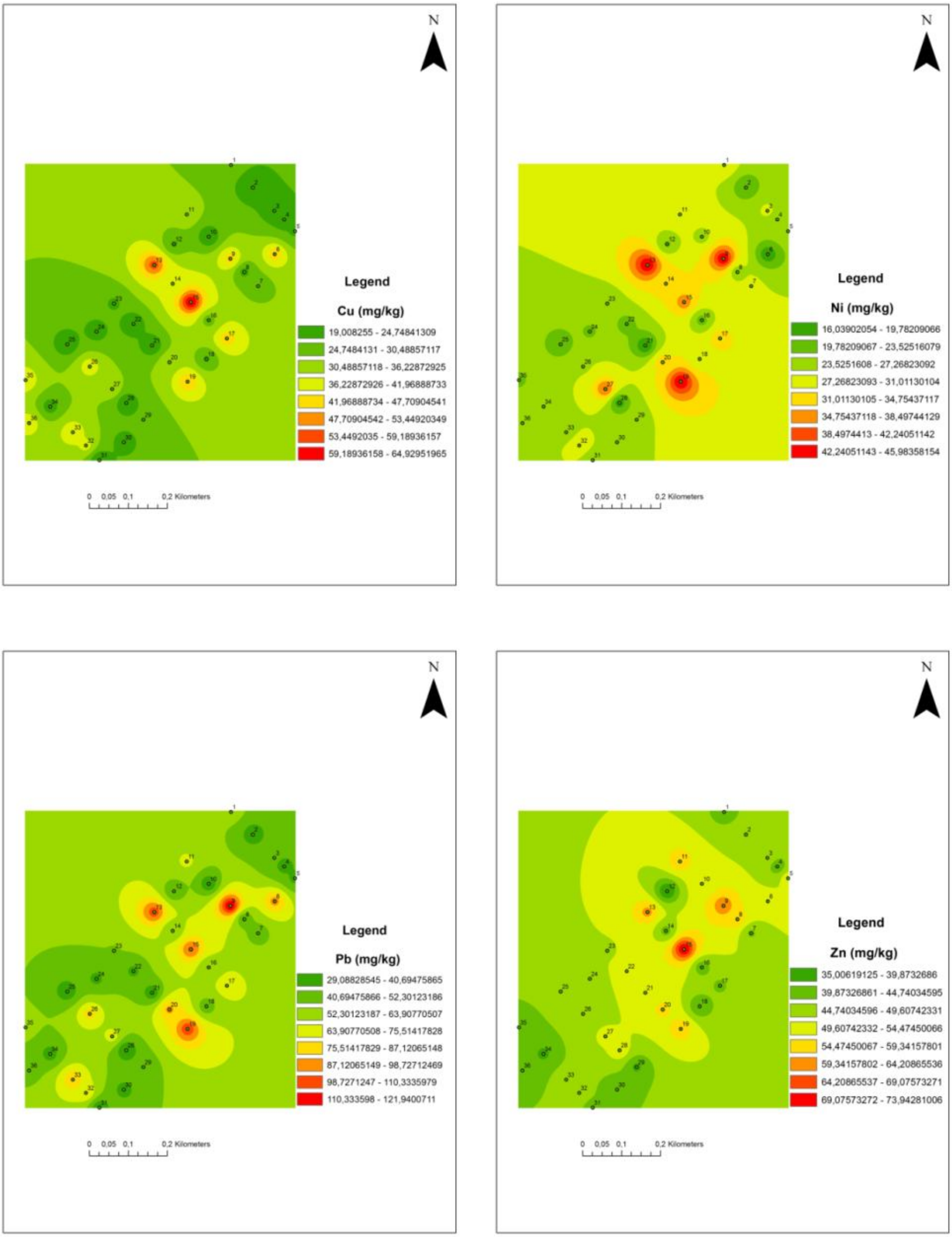

Fig. 5 Spatial distribution of heavy metals (Ni, As, Pb, Cd, Zn, Cu, Co and Cr) in the study area (*continuation*).

6. Conclusions

Within this study, 36 samples were analyzed; they were collected from the forest area adjacent to the moorland of Tinovul Şaru Dornei. The main elements analyzed had the following variation limits: Cr: 18–56 mg/kg; Co: 2.9–11mg/kg; Ni: 16–46 mg/kg; Cu: 19–65 mg/kg; Zn: 35–74 mg/kg; Pb: 29–122 mg/kg; As: 7.6–28.7 mg/kg and Cd: 0.02–0.38 mg/kg.

The results of the combined statistical analyses and spatial variability of heavy metals indicated that the main anthropic activities, which significantly influenced the concentrations of Pb, As, Cr, were road traffic and agricultural activities by the application of fertilisers.

Lead concentrations exceed the normal values in soils and 13 samples exceed the alert threshold, these being situated in the proximity of the county road which links the localities Şaru Dornei with Gura Haitii. The arsenic concentrations exceed the normal value in soil; two samples exceed the alert threshold and three samples have values superior to the intervention threshold.

The concentrations of Cu, Cr and Ni exceed the normal values in soils, but none of them exceeds the alert threshold. These elements are largely influenced by geogenic and pedogenic sources, except for Cr and Ni, which may be influenced by phosphate fertilisers. The Cd and Co concentrations were inferior to the minimum value (20 mg/kg; 1mg/kg) determined for the fundament, which suggests that they were not strongly influenced by anthropic activities.

The pH of soil samples ranged from 3.5 (very strongly acid) to 4.68 (strongly acid). According to the classifications provided by the USDA (1998), soil samples from the study area mostly fit within the class of very strongly acid soils (~53 % of samples), as well as strongly acid (~ 47 % of samples).

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