Geochemical and Spatial Distribution of Heavy Metals in Forest Soils Adjacent to the Tinovul Mare Poiana Stampei Peat Bog

BOGDAN CONSTANTIN CAZACU, NICOLAE BUZGAR[1], OVIDIU GABRIEL IANCU*

Alexandru Ioan Cuza University of Iasi, Faculty of Geography and Geology, Department of Geology, 20A, Blvd. Carol I, Iasi 700505, Romania

Tinovul Mare Poiana Stampei is situated in the northern group of the Oriental Carpathians within the Dornelor Depression, one of the richest peat areas in Romania. In this study we have performed analyses of certain heavy metals (Cr, Co, Ni, Cu, Zn, Pb, As and Cd) found in the forest soils adjacent to the Tinovul Mare Poiana Stampei peat bog. The analyses performed through X-ray fluorescence spectrometry indicated the following variation limits (mg/kg): Cr: 20-66; Co: 8-29; Ni: 16-78; Cu: 16-42; Zn: 36-199; Pb: 21-229; As: 5.5-36 and Cd: 0.01-1.4. The outcomes of the present study indicate high concentrations for certain (Ni, Pb and As). These concentrations exceed the alert threshold established by the Romanian Law, according to Order no. 756 of November, 3rd 1997.

Keywords: heavy metals, soils, Poiana Stampei, pH, XRF

The site is located at the foot of the Calimani Mountains, source of the Dorna and Dornisoara Rivers, which flow to the east and west of the peat bog. The highest peaks in the neighbourhood are Tamau (1861 m) and Lucaciu (1769 m) in the Calimani Mountain Range, and Tihuta (1200 m) in the Bargau Range. The Dorna and Dornisoara Rivers border the reservation to the east and west. The Calimani Mountains represent the northern most and largest volcanic area amongst the 160 km long Calimani-Gurghiu-Harghita range in Romania. Medium-K andesites prevail in the Calimani Mountains, as in the whole CGH, while rock types range from basalt to rhyodacite. Low-K dacites are rarely found in the southern half of the area. The volcanic rocks are typically porphyritic with microcrystalline or glassy groundmass and frequent glomerophyric accumulations of phenocrysts. Afanitic andesites are characteristically present in the northwestern Calimani area. Cognate xenoliths are widespread, commonly including orthopyroxene, amphibole, feldspar and opaque minerals. Upper crustal xenoliths displaying lithologies of the local prevolcanic basement are also frequent [1].

The Bargau Mountains are characterized by intrusive magmatism and lack of volcanic activity. The magmatic products are represented by cone-shaped intrusive bodies composed of andesites, microdiorites, dacites and rhyolites [2].

The peat bog is of natural origin, and the peat accumulation process started in the post-glacial period, on an existing eutrophic fen. The peat bog appeared by miring a spruce forest, a fact proved by the existent trunks horizon. The peat thickness exceeds 1 m and is still active. The water level shows seasonal fluctuations and the water is acidic, with a *p*H of 3.6-5.0. Thermic annual water levels vary from - 1° to 14°C. Water transparency has low values, depending mainly on precipitation levels and the amount of peat particles released from the substrate. Annual precipitation input ranges from 600 to 800 mL. The colour is tawny (brown), due to humic compounds and peat particles in suspension [3].

Experimental part

From the forest area adjacent to the Tinovul Mare Poaina Stampei peat bog 90 samples were collected (fig. 1). The samples were extracted using a stainless steel probe from depths between 0 and 25 cm. Each sample weighed 2.2 and 2.8 kg. Soil samples were grinded and sifted into 2 mm fractions in order to eliminate excess materials and vegetal remains.

For each sample *p*H measurements were performed using a Hach Lange GmbH pH meter with glass electrode (model HQ40D, USA), through the potentiometer method, in an aqueous solution using a soil: water ratio of 1:2.5 [4]. For each analysis there were used 10 g of sample and 50 mL of distilled water.

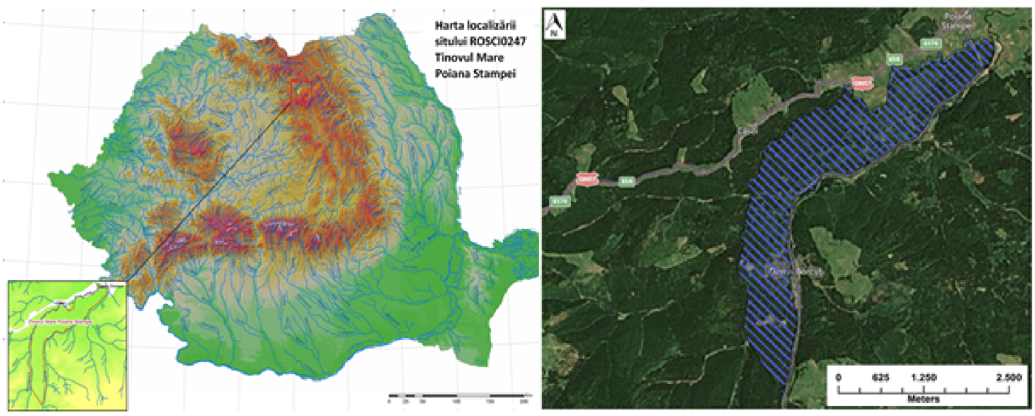

Fig 1. Localization of Tinovul Mare Poiana Stampei

* email: ogiancu@uaic.ro

After the samples were sifted and brought to a granulation below 2 mm, a quantity of approximately 15 g from each sample was mixed with epoxy resin (3 g) in a proportion of 5:1, the mixture being homogenized for 20 minutes, at 180 rotations per minute, using an agate ball mill. Following homogenization, 9 g of mixture of soil and resin were placed in aluminium capsules, subsequently pressed for 30 s under a force of 20 t/cm^2 in a hydraulic press.

The chemical analysis of Cr, Co, Ni, Cu, Zn, As, Cd and Pb was done using an EDXRF Epsilon 5 Spectrometer. It has the following characteristics: Gd anode, rating 25-100 kV, 0.5-24 mA, maximum power 600 W, Be window (300 μm), Ge-X-ray detector, 30mm^2, 5 mm thick, Be window (8μm), spectral resolution 140 eV, polarizing optics with 3-dimensional design, secondary targets Al, Ti, Fe, Co, Cu, Zn, Ge, Zr, Mo, Ag, Ce_2O_3, Al_2O_3, BaF_2, CsI and KBr. The standardization was performed using 24 CRM ($LKSD_{1-4}$, $STSD_{1-4}$, $Till_{1-4}$ SO_{1-4}, JLk_{1-3}, GSD, RTH, RT etc.). The exposure time was 60 s, with the exception of As and Cd, in which case the exposure time was 100 s. The lower limit of detection for measured elements is cca 2 mg/kg (Cr, Co, Ni, Cu, Zn and Pb), 1 mg/kg for As and 0.1 mg/kg for Cd. 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 instrument (0.1 mg/kg).

Results and discussions

Table 1 displays the values of the main statistic parameters of the elements found in the study area as well as of the normal values to be found in soils (VN), the alert threshold (AT) and the intervention threshold (IT) as established by the Romanian legislation [5].

According to the research conducted by various authors [6], the variation coefficients for heavy metals resulted from natural sources are lower than those of the heavy metals resulted from anthropic activities. Thus, based on their variation coefficients, heavy metals can be divided into two groups: i) with values below 0.40 for Cr, Co, Cu, Zn and As, and ii) with values above 0.40 for Ni, Pb and Cd. This explains why the concentrations of the elements belonging to the first group seem to be associated with natural sources while the concentrations for Ni, Pb and Cd seem to be influenced by anthropic activities.

In the research area, the *p*H values are between 4.09 and 5.89. The lowest value (*p*H = 4.09) indicates a highly acid environment, while the highest value (*p*H = 5.89) indicates a weakly acid environment [7]. Over 54% of the samples belong to a strongly acid environment, with a pH below 5, while 35 % of the samples indicate a moderately acid environment, with a *p*H between 5 and 5.5. Approximately 12.2 % of the samples indicate a highly acid environment, displaying a pH below 4.5, while a percentage of 1% represents the samples with a *p*H close to 6.

The heavy metals concentrations in the studied areas

Chrome concentration in the analysed samples varies between 20 mg/kg and 60 mg/kg, with an average content of 45.93 mg/kg. All the studied samples exceed the normal values for the soil (30 mg/kg). However, none of the samples exceeds the alert threshold (100 mg/kg) as

Table 1

STATISTICAL PARAMETERS OF ELEMENTS CONTENTS (mg/kg) OBTAINED THROUGH THE ED-XRF ANALYSIS FROM THE RESEARCH AREA SOILS (TINOVUL MARE POIANA STAMPEI)

	Element	Cr	Co	Ni	Cu	Zn	Cd	Pb	As	pH
Statistics	Mean (mg/kg)	45.93	18.64	22.14	23.56	87.61	0.31	41.3	10.99	4.82
	Median	45	19	16	23	87	0.31	36.5	10.5	4.81
	Mode	45	20	16	23	79	0.27	37	12	4.45
	Minimum (mg/kg)	20	8	16	16	36	0.01	21	5.5	4.07
	Maximum (mg/kg)	66	29	78	42	199	1.4	229	36	5.89
	Variance	75	7.06	146.64	12.96	389.45	0.027	641.31	13.25	0.15
	Skewness (Pearson)	-0.004	-0.506	2.650	1.728	2.044	3.054	5.114	3.746	-0.474
	Kurtosis (Pearson)	0.462	4.610	7.181	7.761	11.139	19.212	34.629	24.372	0.253
	Variation coefficient	0.18	0.13	0.54	0.15	0.22	0.51	0.61	0.31	0.08
	Inferior quartile	41	17	16	22	78	0.25	30	9	4.48
	Superior quartile	50	20	23	25	96	0.38	46	12	5.10
Order no. 756 of November, 3rd, 1997	Normal value	30	15	20	20	100	1	20	5	-
	Alert threshold	100	30	75	100	300	3	50	15	-
	Intervention threshold	300	50	150	150	700	5	250	25	-

stipulated in the Romanian legislation. Consequently, high Cr values are rather mostly influenced by the natural phenomena in the area than by the anthropic factor.

Cobalt concentration in the analysed samples varies between 8 mg/kg and 29 mg/kg, with an average content of 18.64 mg/kg. Out of the total number of analysed samples, six are below the normal value for the soil (15 mg/kg), while the rest exceed the normal value, yet remain below both the alert threshold (30 mg/kg) and the intervention threshold (50 mg/kg) as established by order HG 759/1997.

In the analysed soil samples the *nickel* concentration varies between 16 mg/kg and 78 mg/kg, with an average value of 22.14 mg/kg. All analysed samples exceed the normal soil values (20 mg/kg). However, only one sample exceeds the alert threshold (75 mg/kg) as established by the Romanian legislation. Since basically all samples exceed the normal soil values we can conclude that the nickel ion is influenced by the use of fertilizers in agriculture-related activities.

The content values determined for *copper* in the soils from Tinovul Mare Poiana Stampei area vary between 16 mg/kg and 42 mg/kg, with an average content of 23.56 mg/kg. Most analysed samples exceed the normal soil value (20 mg/kg), yet none of them exceeds the alert threshold (100 mg/kg) according to the Romanian legislation. Less than 8% of the samples are below the normal value. Since none of the samples exceeds the alert threshold we can state that the researched area does not display a significant copper contamination.

In the analysed soil samples *zinc* concentration varies between 36 mg/kg and 199 mg/kg, with an average value of 87.61 mg/kg. None of the analysed samples exceeds the alert threshold (300 mg/kg), while only 15 samples exceed the normal soil value (100 mg/kg). We can thus conclude that the zinc ion does not represent a significant pollutant for the researched area.

Content values for lead in the soils from Tinovul Mare Poiana Stampei vary between 21 mg/kg and 229 mg/kg, with an average value of 41.3 mg/kg. All analysed samples exceed the normal soil value (20 mg/kg), while 14 samples exceed the alert threshold (50 mg/kg) established according to HG 756/1997. The samples exceeding the alert threshold were collected from the vicinity of the national road DN 17. We can thus infer that pollution is due to fuel combustion resulted from internal combustion engine vehicles.

In the analysed soil samples *arsenic* concentration varies between 5.5 mg/kg and 36 mg/kg, with an average value of 10.99 mg/kg. Almost all samples exceed the normal soil value (5 mg/kg); however, only three samples exceed the alert threshold (15 mg/kg). The samples exceeding the alert threshold can be influenced by agriculture-related activities such as the use of fertilizers or by the intensive farming activities such as animal breeding.

Content values for *cadmium* in the soils from Tinovul Mare Poiana Stampei vary between 0.01 mg/kg and 1.4 mg/kg, with an average value of 0.31 mg/kg.

Hierarchical cluster analysis (HCA)

Following the hierarchical cluster analysis, cadmium was separated from the other elements which were grouped into three clusters (fig. 2): cluster I (Pb and As), cluster II (Cr and Ni) and cluster III (Zn, Co and Cu). Similarity axes represent the degree of association between the elements. The higher the axes values, the higher the degree of association between the elements.

Pb, Zn and Cu concentrations could be influenced by both road traffic and phosphate fertilizers used in agriculture

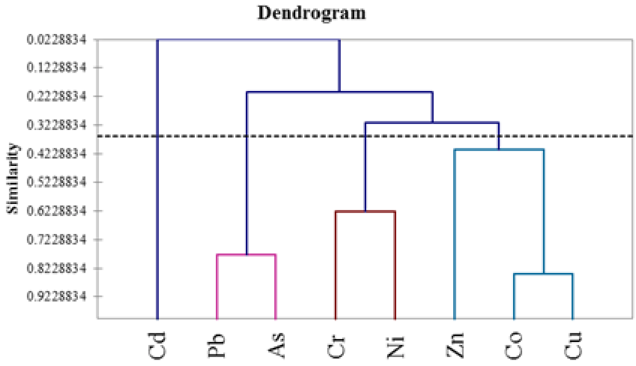

Fig 2. Cluster analysis through ward's method and Euclidean distance

[8-11], while nickel and arsenic concentrations can be influenced by the use of fertilizers. Nevertheless, the analysis identifies three clusters, namely Pb and As, Cr and Ni, and Zn, Cu and Co [12-15]. This hierarchy indicates that besides the geogenous contribution, pollution also results from a combined contribution (for instance, Pb and As – road traffic and pesticides).

Main components analysis

Four components were extracted from the set of available data (fig. 3) which explain a total variation of over 81.61%. The first factor is represented by Co, Cr, Cu and As (table2). High concentrations of cobalt and chrome can be influenced by agriculture-related activities such as the use of various fertilizers, while arsenic concentrations can be influenced by both agriculture-related activities [12, 13, 16, 17] (use of fertilizers and pesticides) and animal

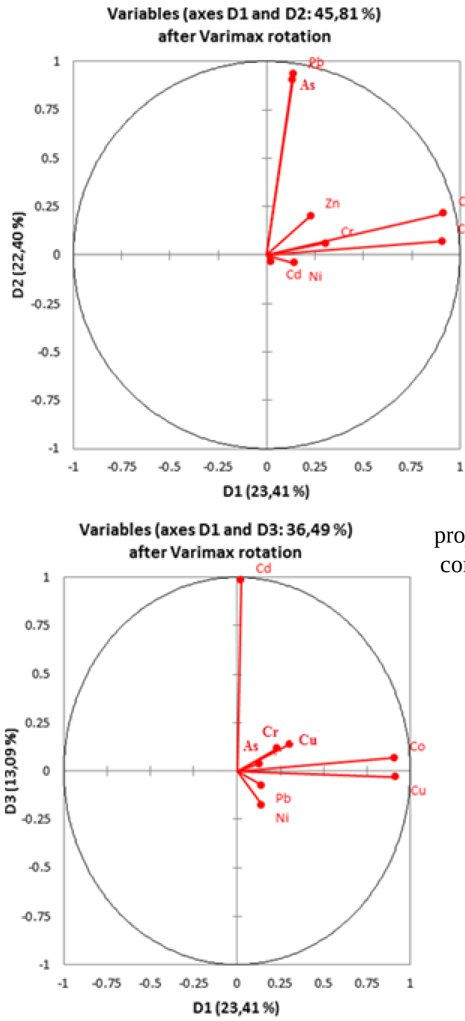

Fig 3. Variables projection in the main components analysis

Table 2
VARIMAX-MATRICE ROTATION FACTOR FOR METALS IN THE STUDY AREA

Factors	F1	F2	F3	F4
Elements	Cr, Co, Cu, As	Ni, Pb	Cd	Zn
Cr	**0.433**	0.265	0.001	0.006
Co	**0.665**	0.038	0.033	0.003
Ni	0.215	**0.396**	0.119	0.000
Cu	**0.697**	0.015	0.000	0.028
Zn	0.403	0.042	0.135	**0.404**
Cd	0.006	0.004	**0.781**	0.108
Pb	0.248	**0.549**	0.084	0.030
As	**0.429**	0.351	0.036	0.007

breeding (cattle, sheep, etc.) activities specific to the area [18]. The 2nd factor is represented by Ni and Pb. High Ni concentrations may be associated with agriculture-specific activities in the area such as the use of fertilizers and fungicides [16, 17], while high lead concentrations can be associated with road traffic [19, 20]. The 3rd factor is represented by Cd, which can be associated with the following anthropic activities: non-ferrous metals industry, forest fires and coal combustion [21, 22]. The 4th factor is represented by zinc. As resulting from the previous discussion, it can be associated with agriculture-related activities in the area, such as the use of fertilizers and fungicides [16, 17].

Spatial distribution of heavy metals in the study area

In order to draft the distribution maps for heavy metals (Ni, As, Pb, Cd, Zn, Cu, Co and Cr) in the soils belonging to the research area (fig. 4), we used the inverse distance weighting method (IDW) of the ArcGis (ArcMap) software, version 10.2.2.

Lead and zinc concentrations displayed high levels in the vicinity of inhabited areas and the national road DN 17 that connects the areas of Moldavia and Transylvania through the Tihuta Pass (1201 m), characterized by intense road traffic. As compared to various other studies [23, 24] our study indicates that high levels of lead are associated with road traffic, while high levels of zinc are the result of phosphate fertilizers use.

Since Dornelor Depression is well-known as an intensive animal breeding area, high concentrations of arsenic were detected (3 of the samples exceeding the alert threshold) in the vicinity of animal farms and agricultural fields. This aspect could be the result of inappropriate filtering of the evacuation system of the farms [18].

The spatial distribution of the other heavy metals (Co, Ni, Cu and Cr) indicates that these elements display higher concentrations than the normal soil values (VN = 20 mg/

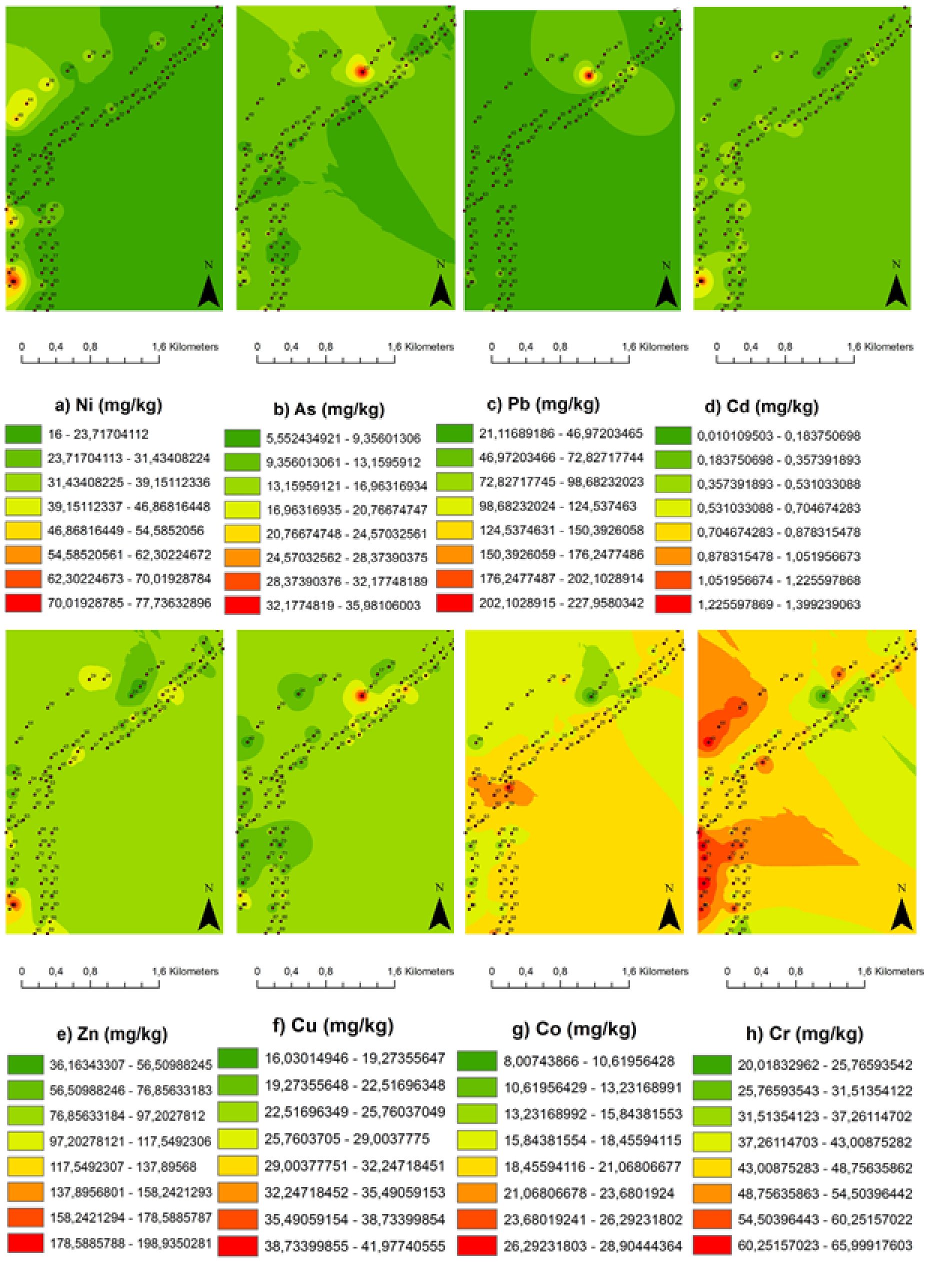

Fig 4. Spatial distribution of heavy metals (Ni, As, Pb, Cd, Zn, Cu, Co and Cr) in the study area

kg), which are, however, slightly lower than the alert threshold as established by Order 756/1997**,** except for Ni which slightly exceeds the alert threshold (AT = 75 mg/kg) with a single value (78 mg/kg). This aspect leads to the conclusion that Co, Cu and Cr are mainly influenced by geogenous and pedogenous sources rather than by anthropic activities.

Conclusions

Within this study we analyzed 90 samples collected from the forest area adjacent to the Tinovul Mare Poiana Stampei peat bog, with the following variation limits (mg/kg): Cr: 20-66; Co: 8-29; Ni: 16-78; Cu: 16-42; Zn: 36-199; Pb: 21-229; As: 5.5-36 and Cd: 0.01-1.4.

Lead concentrations exceed the normal values established for soils, while 14 samples exceed the alert threshold. The samples were collected in the vicinity of the national road DN 17. *Zinc* concentrations are similar to lead concentration, with approximately 16 samples exceeding the normal value for soils, while none of the samples exceeds the alert threshold.

A*rsenic* concentration exceeds the normal soil value, yet only three samples exceed the alert threshold. These soils are situated in the vicinity of agricultural fields and animal farms. *Ni* concentrations also exceed normal soil values, yet only one sample collected from the vicinity of an agricultural field exceeds the alert threshold.

Cu, *Cr* and *Co* contents exceed the normal soil values, yet none of them exceed the alert threshold. These elements are mainly influenced by geogenous and pedogenous sources, except for Cr, which may be influenced by phosphate-based fertilizers. *Cd* concentration exceeds the normal soil value. However, we exclude the possibility of cadmium pollution, since cadmium is associated with the metallurgic industries and can be easily influenced by phosphate-based fertilizers.

As far as the *pH* value of the analysed samples is concerned, it varies between 4.09 (highly acid) and 5.89 (weakly acid). Most soil samples extracted from the researched area belong to the highly acid category (54%) and moderately acid category (35 %).

References

1. SEGHEDI, I., SZAKACS, A., The Calimani-Gurghiu-Harghita (GCH) Volcanic Chain, in NEDELCU, L., HARTOPANU, I., SZAKACS, A., MOGA, C., PODASCA, I. (eds.): Field Trip Guide (Romanian Jornal of Mineralogy, 78/2), Bucharest, Inst. Geol. Rom., 1997, p. 14.
2. NITOI, E., MUNTEANU, M., MARINCEA, S., An. Inst. Geol. Rom., **72**, 2000, p. 67.
3.*** Information Sheet on Ramsar Wetlands (RIS), 2009-2012 version
4. *** STAS 7184/13-88, 1988.
5. HAN, Y.M., DU, P.X., CAO, J.J., POSMENTIER, E.S., The Science of the Total Environ, **355, No.**1-3, 2006, p. 176.
6.*** USADA. Natural Resources Conservation Service. Soil Quality Indicators: pH (January), 1998.
7.*** Order no. 756 of 3 November 1997 issued by the Minister of Water, Forests and Environmental Protection, 1997.
8. MAAS, S., SCHEIFLER, R., BENSLAMA, M., CRINI, N., LUCOT, E., BRAHMIA, Z., BENYACOUB, S., GIRAUDOUX, P., Environ. Pollut., **158**, 2010, p. 2294.
9. IONESCU, P., RADU, V.-M., DIACU, E., Rev. Chim (Bucharest), **66,** No. 11, 2015, p. 1725.
10. RESETAR-DEAC, A.-M., DIACU, E., Rev. Chim (Bucharest), **66,** No. 9, 2015, p. 1535.
11. BURADA, A., TOPA, C.M., GEORGESCU, L.P., TEODOROF, L., NASTASE, C., SECELEANU-ODOR, D., ITICESCU, C., Rev. Chim (Bucharest), **66,** No. 1, 2015, p. 48.
12. SAHU, P.C., International Journal of Conservation Science, **8**, No. 1, 2017, p. 145.
13. SHAHEDAN, N.F., ABDULLAH, M.M.A., HUSSIN, K., SANDU, I., GHAZALI, C.M.R., BINHUSSAIN, M., YAHYA, Z., SANDU, A.V., Mat. Plast., **51,** no. 3, 2014, p. 258.
14. BURUIANA, D.L., BORDEI, M., SANDU, A.V., CHIRCULESCU, A.I., SANDU, I.G., Mat. Plast., **50,** no**. 2**, 2013, p. 113.
15. ABDULLAH, M.M.A., NORDIN, N., TAHIR, M.F.M., KADIR, A.A., SANDU, A.V., International Journal of Conservation Science, **7**, No. 3, 2016, p. 753.
16. NICHOLSON, F.A., SMITH, S.R., ALLOWAY, B.J., CARLTON-SMITH, C., CHAMBERS, B.J., Sci. Total Environ., **311**, 2003, p. 205.
17. CANG, L., WANG, Y.J., ZHOU, D.M., DONG, Y.H., J. Environ. Sci. China, **16**, 2004, p. 371.
18. REIMANN, C. & DE CARITAT P., Chemical elements in the environment - Factsheets for the geochemist and environmental scientist, Springer-Verlag, Berlin-Heidelberg, 1998, p. 398.
19. ARDITSOGLOU, A., SAMARA, C., Chemosphere, **59**, 2005, p. 669.
20. AL-KHASHMAN, O.A., SHAWABKEH, R.A., Environmental Pollution, **140**, No. 3, 2006, p. 387.
21. NRIAGU, J.O., PACYNA, J.M., Nature, **333**, 1988, p. 134.
22. BAVEYE, P., McBRIDE, M.B., BOULDIN, D., HINESLY, T.D., DAHDOH, M.S.A., ABDEL-SABOUR, M.F., Sci. Total Environ., **227**, 1999, p. 13.
23. IMPERATO, M., ADAMO, P., NAIMO, D., ARIENZO, M., STANZIONE, P., VIOLANTE, P., Environ. Pollut., **124**, 2003, p. 247.
24. SABY, N., ARROUAYS, D., BOULONNE, L., JOLIVET, C., POCHOT, A., Sci. Total Environ., **367,** No**.** 1, 2006, p. 212.

Manuscript received: 7.08.2017