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HEAVY METALS ABUNDANCE IN THE SOILS FROM RARĂU MASSIF

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KEY WORDS: pedogeochemistry, soil, heavy metals, Rarău Massif, geochemical abundance.

Introduction

Rarău Massif is situated in the north side of Central Eastern Carpathian group, in the eastern side of crystalline-mesozoic area, to the inner flish boarder (between 47°32′47″ and 47°32′32″ northern parallels, 25°28′06″ and 25°39′30″ eastern longitude). Moldova and Şandrului valleys - Gemenea gorge – Babei valley – Slătioara creek – Hogea valley, Chiril and Bistriţă valleys – Colbu creek – Colbu crest – Izvorul Giumalăului valley represents the demarcation borders of Rarău Massif (figure 1) and between these limits he have 164.35 km^2.

Because the geological basement represents one between the factors accountable for actual aspect of Rarău Massif, this it consists of sedimentary (exotically limestone, dolomite, shale, claystone, jasper, sandstone etc.), igneous (diabaze) and metamorphic rocks (middle to low regional P/T metamorphic degree: schist, metatuff, micaschist, quartzite etc.), widely or remotely affected by tectonic elements.

Rarău Massif has a proportional relief with grouped forms. He have a central unit with plane aspect, where the peaks get by 1500 m (Rarău Peak – 1650.5 m, Lady's Stone Peak – 1634 m, Popii Rarăului Peak – 1627.9 m, Tihăraiei Peak – 1576.7 m), which continue to west with a low altitude's mountain area.

Relief forms and geographic position tell on the climatic conditions. Therefore, two climatic levels are distinguished: first and the most important of middle and low mountains and second of very low mountains (proper to Eastern Carpathians). Also, another two climatic areas are situated to the northern massif where the continental air masses are heat (summer) and cold (winter), and southern part of massif where come in the clammy maritime air masses. The temperature limits are sized between -14°C and 14.3°C (7.4°C average value) and 663.4 l/m^2 – 901.5 l/m^2 precipitations, with 750 l/m^2 average value. Vegetation has same altitudinal multi-staged. Whereas these assignations aren't distinguished, the assortment forest (beech, fir and spruce), spruce (predominantly) and subalpine stages can be identified.

Under the pedogenetic factors influence, early mentioned its, in Rarău Massif was developed a few types and sub-type of soils from the *Cernisol* (rendzine), *Cambisol* (eutricambisol and districambisol), *Spodisol* (prepodzol and podzol), *Umbrisol* (nigrosol), *Protisol* (litosol, regosol and alluviosol) and Atrisol (erodosol) classes.

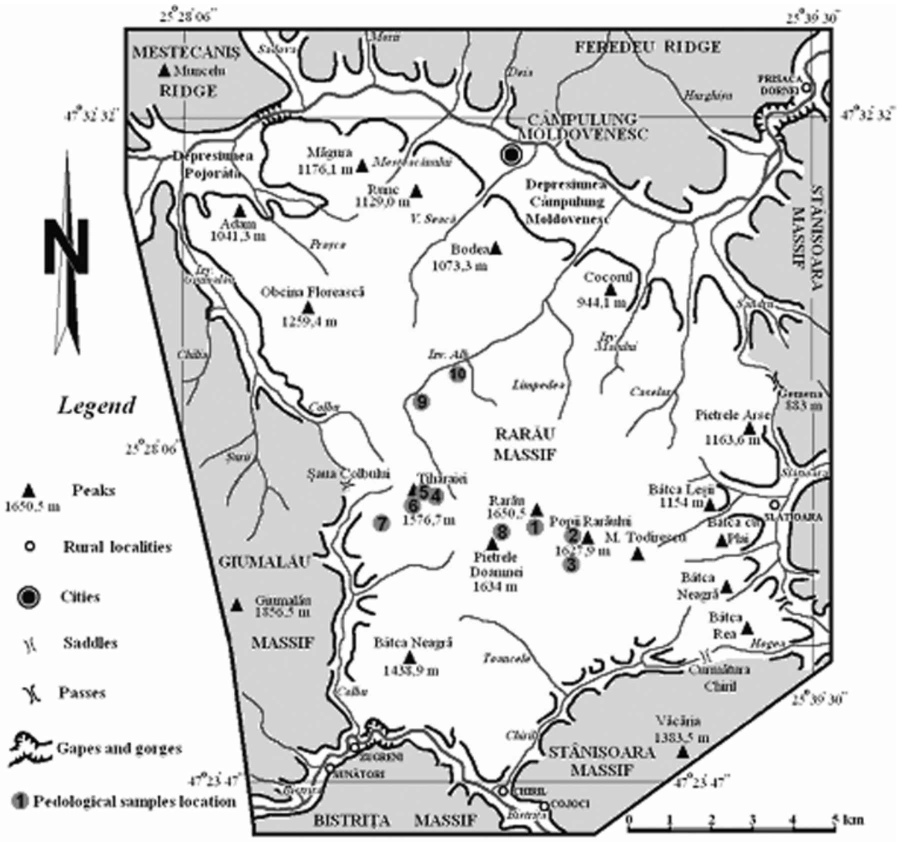

Fig. 1. Geographical position and borders of Rarău Massif

Material and research methods

To the appreciation of pedogeochemical process that leads the soils evolution from Rarău Massif, it was drawing sample-sounding (table 1) that correspond to the different basement. Ten different samples from twenty centimeter depth was analyzed and determinate conform the I.C.P.A. methodology (Florea *et al.*, 1987).

Table 1. Samples location

Sample	**Soil type**	**Lithological basement**	**Sample places**
1	Cernisol – Cambic rendzine	limestone	Rarău Peak
2	Cernisol – Typical rendzine	limestone	Popii Rarăului Peak
3	Cambisol – Typical districambosol	wildflish	SW versant of Popii Rarăului Peak
4	Umbrisol – Typical nigrosol	augen gneisses	Tihăraiei Peak
5	Umbrisol – Typical nigrosol	augen gneisses	Tihăraiei Peak
6	Spodisol – Typical podzol	micaschist	Tihăraiei Peak
7	Spodisol – Typical prepodzol	sericite – chlorite quartzitic schist	Pietrele Stânei Peak
8	Cambisol – Typical eutricambosol	wildflish	Rarău Plateau, NE part of Lady’s Stone (Tâlharului Creek)
9	Cambisol – stagnic eutricambosol subrendzinic	wildflish	Izvorul Alb Valley
10	Cambisol – Stagnic eutricambosol	wildflish	Ruginosu Creek

Granulometric analyses (dropping – Kacinski method) consist the physical description of samples. The contain the potentiometer determination of pH in H_2O (1:2.5 soil/solution), hydrolytically acidity (Ah) from 1 N sodium acetate extract, Kappen method of basic change cations sum (SB), changeable hydrogen (SH $A_{8.3}$) by 1 N potassium acetate percolation at 8.3 pH, total capacity of cationic changeable (T) and bases saturation degree (V %) represent the suit of sample’s chemical analyses.

Total contain of soil’s heavy metals (Zn, Cu, Mn, Pb, Ni, Cr, Co, Cd) was determinate at I.C.P.A. Bucharest, using atomic absorption spectrometry (air-acetylene flame). The I.M.N.R. Bucharest used same method for rock’s heavy metals contains. The samples were leaching with perchloric and azotic acid and the residue was soluble with 0.5 N HCl solutions.

Cartographically, was used some topographical, pedological and geological regional maps (scale 1:50 000).

3. Results and discussions

The *cambisols* are dominating in the Rarău area, over 50% from pedological field, and that have evaluated on wildflish basement. In Rarău Massif, the eutricambosols are majority from the cambisol class (samples 8, 9, 10). This samples has a standard morphology (Ao-Ao/Bv-Bv/C-C(R)) (Rusu, 2002), with medium structure (SS) and chemical composition characterized by a moderate acid to neuter reaction. The basic change cations sum has 24.39-31.8 me/100g soil, and very low values of acidity (0.83-3.58 me/100g soil). These chemical characteristics explain the eubasic character of soils. The *districambosols* (sample 3) have a reduced distribution. Chemical, they have a below chemical characteristic as the eutricambosols. The soil has o low acid reaction, with 34.3% basic saturation degree that indicates a big rate of changeable acidity (SH = 16.38 me/100g soil), but very low level of changeable bases (SB = 8.55 me/100g soil). The *eutricambosols* are characterized by a high level (43.6%-49.6%) of dust (0.002-0.02 mm), the increase of clay (<0.002 mm) contain (till 17.76%) and decrease of coarse sand contain to 0.83%.

The *cernisols* represented by rendzine (samples 1, 2) have developed on calcareous rocks and the derivates of them and all this rocks represent 10% of rendzine contain. The samples have a grained texture and a medium structure (sandy clay-powdery) with a relative constant contain of clay (12%), from 44.88% (sample 1) to 35.12% (sample 2) of dust and 5.58% to 13.76% contain of coarse sand contains. The chemical characteristics are influenced by altitude, the vegetation type and the relief. The soil reaction is low acid (pH = 5.27) to neuter (pH = 7.13), according to soil type. Between the changeable basic cations Ca is dominant and come next after by Mg. Basic saturation degree is oligomesobasic (sample 1) and eubasic (sample 2).

From *umbrisol* class was assayed two nigrosol samples (4, 5) evaluated on augen gneisses basement. The *nigrosols* appear on small areas and have a coarse structure. The clay contain is very low (<3.68%) and the dust have a variation between 22% and 26.12%. The sandy fraction has a significant participation (average is 72.69%) from which the fin sand represents approximately 50%. These soils have a moderate-acid to very acid reaction with a reduced bases saturation degree (17.03% and the other one have 9.09%). The changeable basic cations are low represented in against with changeable acidity (19.54me/100g soil versus 34.22me/100g soil).

The *spodosols* formed in mountain boreal climatically condition, cold (2-4^{o}C) and wet, on an intense alterated acid rocks basement (metamorphic predominant). These soils appear on very small areas, to altitudes over 1400m and have a medium to coarse structure, a pH that gives to the soil a high acidity character, oligobasic. The sample assayed from Tihăraiei Peak (7) has a high dust (45.20%) and low fin sand concentrations. These have a low basic elements contain (SB = 4.21me/100g soil, 5.39 me/100g soil) and rich in acidophil fraction (SH=25.69 me/100g soil and respective 23.58 me/100g soil). The most important physic-mechanical and chemical characteristics are represented in tables 3 and 4, and their dynamic parameters are plotting on diagrams from figures 2.

The structural classes and subclasses were defined according the I.C.P.A. system which is based on Atterberg classification correlated with Kacinski classification. The granulometric soils composition (figure 3) depend on nature of geological basement (mineralogical and chemical proprieties of parental materials), and such as the soil improve on in situ rocks, the structural type been more evident. Function on pedogenetical processes, the structure can present altitudinal variations, in the same type of profile, but even for the same lithological basement. Therefore, the soils evaluated on hard rocks (from Tihăraiei Peak) have a high level of sand contain (70.2-78.84%) and a low percent of clay fraction (<4%).

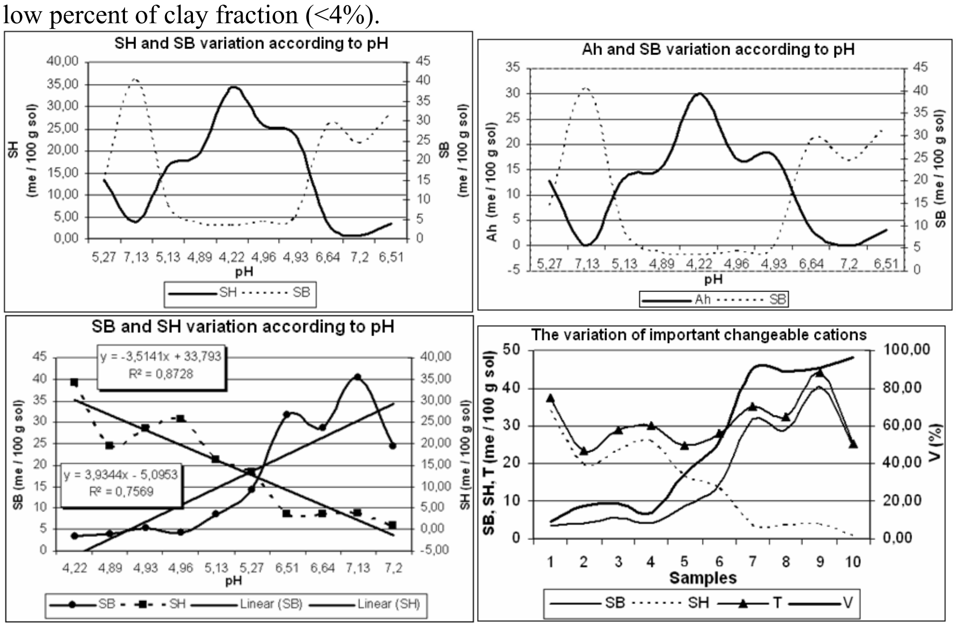

Fig. 2. The variation of important soil's chemical parameters

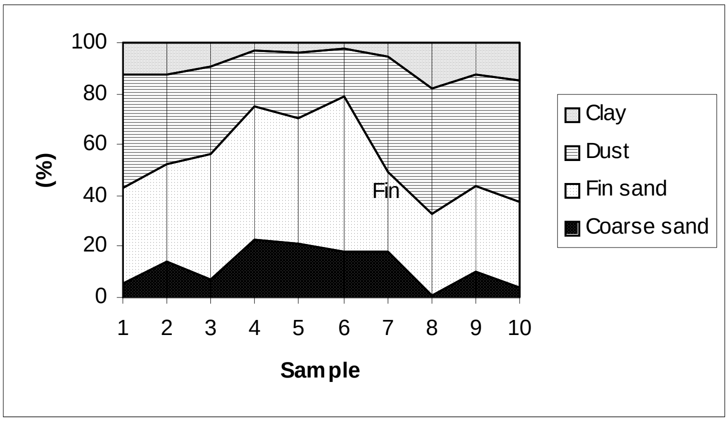

Fig. 3. Granulometric composition of Rarău Massif's soil

Table 2. Structures type of Rarău's soils

Sample	Structure type
1	Medium structure; Sandy– dusty clay class
2	Medium structure; Sandy– dusty clay class
3	Medium structure; Sandy– dusty clay class
4	Coarse structure; Sand class; Medium sand subclass
5	Coarse structure; Sand class; Medium sand subclass
6	Coarse structure; Sand class; Medium sand subclass
7	Medium structure; Sandy– dusty clay class
8	Medium structure; Sandy– dusty clay class
9	Medium structure; Sandy– dusty clay class
10	Medium structure; Sandy– dusty clay class

Altogether, the medium structures are predominantly (figure 4) and where the medium clayey sand predominating. The diminution of pedogenetical processes intensity is reflected by the proportional decrease of clay contain and the increase of coarse fraction (fin sand and coarse sand). Between the chemical aspects of soils can be observed same aspect of SH/SB and Ah/SB relationships (figure 2). The changeable acidity is due to hydrogen and aluminum cations (Al^{3+} create a difference between SH and Ah values) (table 3).

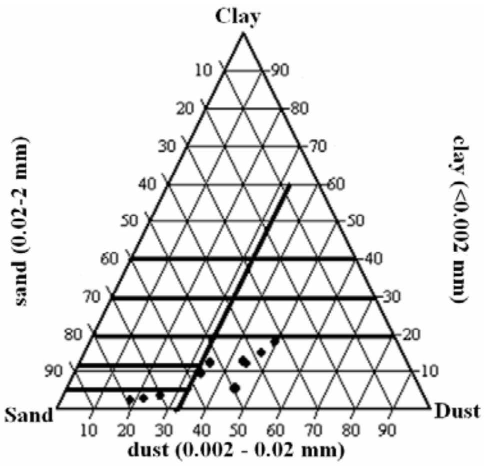

Fig. 4. The triunghiular diagram of structures

Table 3. Soils classification according to chemical proprieties

Sample	Soil reaction	Changeable bases sum (SB)	Hydrolytic acidity (Ah)	Changeable cationic capacity (T_{SH})	Bases saturation degree (V_{SH})
1	low acidity	lowly	very highly	medium	oligo-mesobasic
2	neuter	very highly	highly	-	eubasic
3	low acidity	lowly	very highly	medium	oligo-mesobasic
4	medium-high acidity	very lowly	very highly	medium	oligobasic
5	very high acidity	extreme lowly	very highly	highly	extremely oligobasic
6	moderate high acidity	very lowly	very lowly	medium	oligobasic
7	moderate high acidity	very lowly	very highly	medium	oligobasic
8	moderate acidity	highly	lowly	medium	eubasic
9	neuter	medium	-	medium	eubasic
10	moderate acidity	highly	lowly	medium	eubasic

From analytical data determination of heavy metals the maxim values of Cu (12.64 ppm), Mn (476.9 ppm), Ni (44.75 ppm), Cr (42.4 ppm), Cd (0.6 ppm) have a normal values of contains. Zn (109.66 ppm), Pb (35.61 ppm) and Co (27.8 ppm) exceed by 1.75 and 3 times the normal values, but not over the maximal admissible values limit (Kloke, 1980). Other statistics parameters of heavy metals are presented in table 4.

Table 4. Statistic parameters of soils heavy metals contains

Parameters	Zn	Cu	Mn	Pb	Ni	Cr	Co	Cd
n	10	10	10	10	10	10	10	10
x_{min}	35.81	2.02	67.71	13.91	22.98	13.98	13.84	0.05
x_{max}	109.66	12.64	476.9	35.61	44.75	42.4	27.8	0.6
x_{med}	62.59	7.58	192.21	27.29	33.72	27.55	21.59	0.2
σ	22.69	3.47	154.33	7.24	6.81	9.24	5.37	0.19

If it's consult the reference values of 756 Order of M.A.P.P.M. from 1997 referred to alert deadline and intervention for a low soil's sensibility usage, can be observe that the heavy metals concentration are between the normal admitted and the alert limit values.

The soils with a fin texture (clayey) contain a high microelements accumulation as the soil with coarse or clayey structure (Lăcătuşu, 1994). It can be observed the directly relation and the very good correlation between the Cu and Zn contains and clayey fraction (figure 5). Also, Pb and the clayey fraction haven't this correlation. The soil sample 6 that has the high sand contain (78.84%) has a very low heavy metals value, Mn and Pb exceptive (figure 6).

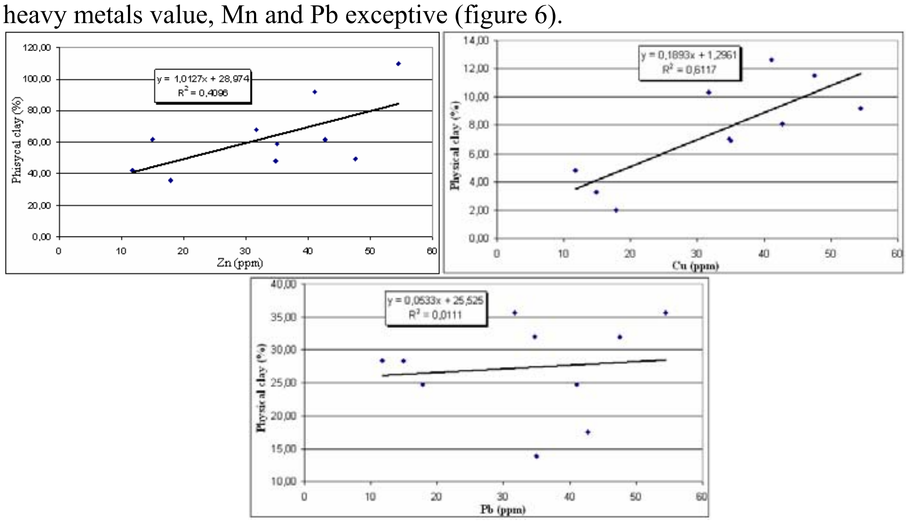

Fig. 5. The relationship between Zn, Cu and Pb contain and physical clay from 0-20 cm depth of soils orisons

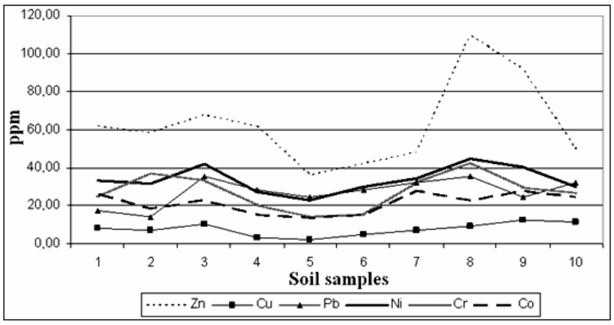

Fig. 6. The heavy metals contain from Rarău Massif's soils

Between some heavy metals contain determinate in 0-20 cm soil depth is recorded an important Cu/Zn (R=0.57), Cd/Co (R=0.68) and Co/Ni (R=0.65) and a very important Cr/Ni (R=0.79) correlations (figure 7).

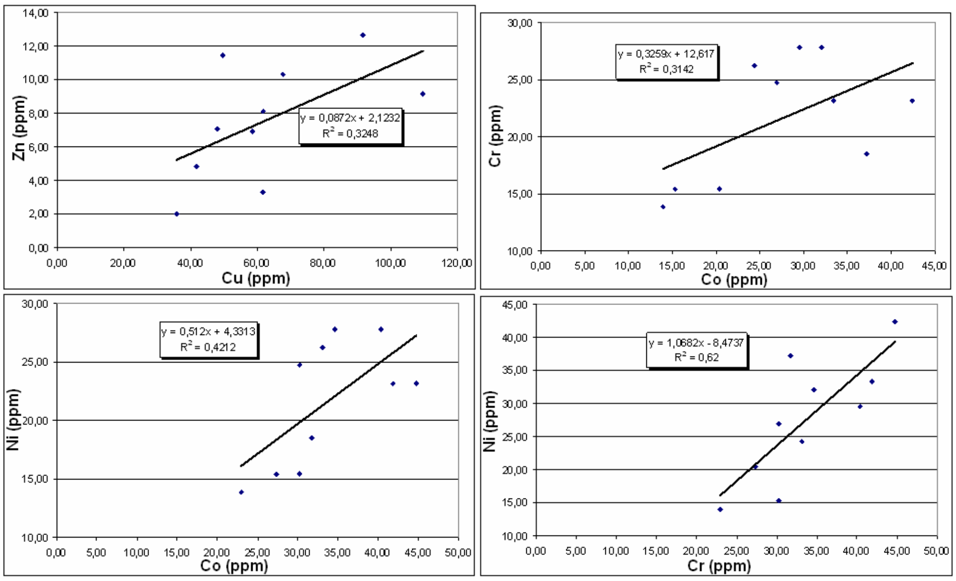

Fig. 7. The relationships from total contain of heavy metals in Rarău Massif's soils

To the abundance appreciation of some chemical elements from Rarău Massif's soils it's used there contain in parental materials (table 5) and soils (table 6), to global or local level. The anthropogenic influence was excluded because the area is dominated by forest and grass land which haven't supported important amendaments. The indicators calculated are represented by *local geochemical abundance indicator* (LGAI), *regional geochemical abundance indicator* (RGAI), *global coefficient of geochemical abundance* (GCGA) and *regional concentration degree* (RCD).

The *local geochemical abundance indicator*s (LGAI) represent the values of chemical element from soil and his parental material ratio. The over-unitary values reflect a chemical elements migration from rock to pedological horizons.

The *regional geochemical abundance indicators* (RGAI) reflect the chemical concentration degree of soil's elements as local level parental rocks.

The *global coefficient of geochemical abundance* (GCGA) or *geochemical abundance indicators* (GAI) represent the global soil's (Sposito, 1989) and superior earth crust (Emsley, 2003) concentrations ratio, where the sub-unitary values indicate a high abundance of element in soil.

The *regional concentration degree* (RCD) reflects the geochemical regional and global abundance ratio. I this case is distinguished the next situations:

- to sub-unity values, the elements have a low concentration, sometimes by reason of streaming;
- between 1 and 2, the elements have a reduced concentration;
- between 2 and 5, have a medium concentration;
- values that exceed 5 reflect a high concentration.

Table 5. Zn, Cu, Mn, Pb, Ni, Cr, Co, Cd and Fe average contains in different Rarău Massif's rocks

Basement rock	**Zn**	**Cu**	**Mn**	**Pb**	**Ni**	**Cr**	**Fe**
Limestone	46,6	23,3	23,3	66,6	12	20	8133,3
Wildflish	91,6	31,6	546,6	103,3	30	26,6	31550
Augen gneisses	70	25	300	130	10	33	30300
Micaschist	120	25	140	230	20	35	36500
Sericite-chlorite quartzitic schist	80	20	300	160	10	20	41200
Media	40,82	12,49	130,99	68,99	8,2	13,46	14768,33

Table 6. Zn, Cu, Mn, Pb, Ni, Cr, Co, Cd and Fe average contains in different Rarău Massif's soils

Sample	Zn	Cu	Mn	Pb	Ni	Cr	Fe
Pd 1	61,59	8,09	411,50	17,53	33,14	24,32	16575,27
Pd 2	58,59	6,92	288,56	13,91	31,69	37,24	13299,14
Pd 3	67,60	10,31	78,00	35,61	41,85	33,36	17082,29
Pd 4	61,59	3,31	246,70	28,38	27,34	20,44	15795,24
Pd 5	35,81	2,02	113,29	24,76	22,98	13,98	14196,18
Pd 6	41,76	4,82	79,29	28,38	30,24	15,27	16263,26
Pd 7	48,07	7,04	68,05	31,99	34,59	32,07	19266,38
Pd 8	109,66	9,14	92,05	35,61	44,75	42,40	18291,34
Pd 9	91,64	12,64	67,71	24,76	40,39	29,48	16770,28
Pd 10	49,57	11,48	476,90	31,99	30,24	26,90	16965,29
Average	62,59	7,58	192,21	27,29	33,72	27,55	16450,47

The values presented in tables 7 and 8 reflect the next characteristics of elements:

- Zn abound in soils evaluated on limestone and wildflish, and RCD reflect a low concentration;
- Cu has a local and regional abundance, but has a low geochemical concentration;
- Mn abound in rendzine (evaluated on limestone) and has a medium regional geochemical concentration;
- Pb abound in parental rocks, this been streaming;
- Ni abound in soils and has a high regional concentration degree;
- Cr abound in some metamorphic rocks (micaschist and augen gneisses), in some soils evaluated on limestone, wildflish and sericite-chlorite quartzitic schist.
- Fe abound in rendzine, but regional has a low concentration in soils.

Table 7. The local geochemical abundance indicator values

Samples	LGAI						
	Zn	Cu	Mn	Pb	Ni	Cr	Fe
Pd 1	1,32	0,35	17,66	0,26	2,76	1,22	2,04
Pd 2	1,26	0,30	12,38	0,21	2,64	1,86	1,64
Pd 3	0,74	0,33	0,14	0,34	1,39	1,25	0,54
Pd 4	0,88	0,13	0,82	0,22	2,73	0,62	0,52
Pd 5	0,51	0,08	0,38	0,19	2,30	0,42	0,47
Pd 6	0,35	0,19	0,57	0,12	1,51	0,44	0,45
Pd 7	0,60	0,35	0,23	0,20	3,46	1,60	0,47
Pd 8	1,20	0,29	0,17	0,34	1,49	1,59	0,58
Pd 9	1,00	0,40	0,12	0,24	1,35	1,11	0,53
Pd 10	0,54	0,36	0,87	0,31	1,01	1,01	0,54

Table 8. RGAI, GCGA, RCD and global average values of soil and Earth crust elements

	Zn	Cu	Mn	Pb	Ni	Cr	Fe
RGAI	1,53	0,61	1,47	0,40	4,11	2,05	1,11
Element's values in Earth crust (Emsley, 2003)	75	50	950	14	80	100	41000
Element's values in soil (Sposito, 1989)	60	25	550	19	19	54	26000
GCGA	0,80	0,50	0,58	1,36	0,24	0,54	0,63
RCD	1,92	1,21	2,53	0,29	17,31	3,79	1,76

Conclusions

In the light of anterior presented, is to speck of that physic-chemical proprieties are strict conditioned by the nature of parental material and his alteration intensity. Also, the remission of pedogenetical process intensity it's evidenced for proportional decrease of clay contains and the increase of coarse fraction (fin and coarse sand). Structurally, the medium structure is predominantly (sandy-dusty clay class), and coarse structure subordinated (sand class, medium sand subclass).

Concerning the heavy metals (Cu, Mn, Ni, Cr, Cd), these have normal values. The Zn, Pb and Co makes an exception of this category; there values are situated between the normal and maxim admissible values, and alert limit for sensible using implicit.

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