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THE GEOCHEMISTRY OF MAJOR AND SELECTED TRACE ELEMENTS IN SOIL FROM NORTHERN AREA OF IAȘI CITY (ROMANIA)

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Abstract: The major and selected trace elements of soil and parent material were used for the assessing of main geochemical features along soil profile and within soil layers. The composition of different soil layers relatively change comparing with parent material. The loss of major oxides during soil developments is low for Si, Al, Fe and K, while the gain depends on their ability to form new compounds as the mass transfer method infers. The high losses of Ca, Na and Mg are responsible for the main mineralogical changes. The loss or gain of trace elements are firstly related to Fe and Al behaviour under soil forming conditions and secondly to Mn and organic material enrichment trend. The high carbonate amount of parent material and its dissolution over the long term could maintain almost neutral pH condition which promotes a low mobility of certain major and trace elements. The major elements distributions and correlations along soil profile and within sampled layer support the predominance of clay fraction which consists of illite, smectite, chlorite or vermiculate, and their percent in soil layers change upward.

Keywords: soil geochemistry, mass transfer coefficients, mineralogical interpretation, Iasi, Romania

1. INTRODUCTION

The soil is one of the most complex open systems and its geochemistry result from the interaction of many factors such as climate conditions, soil organism, vegetation, time, landscape, parent material lithology and not only. Within a soil profile the contribution of different factors gradually change and consequently the geochemical composition is more or less variable. Generally, the upper mineral soil layers (A and B horizons) are enriched in organic matter and their composition can be affected by anthropogenic input as well. The deeper mineral layer, known as C-horizon is comparatively unaffected by the pedogenic processes operative in A and B horizons, except the accumulation of Ca and Mg-carbonates and the more soluble salts (Florea & Munteanu, 2003).

The history of compositional changes during soil developments can be featured using mass transfer coefficient method (Brimhall & Ditrich, 1987; Egli & Fitze, 2000; Oh & Richter, 2005; Jin et al., 2010). This geochemical approach emphasizes the relative gain or loss in the concentration of a certain elements within soil profile in relation with parent material. The advantage of this method comes from the correction of pedogenic effects as expansion/compaction (strain factor) and those related to the change of element concentration due to the changes of other elements. Also, the method assumes the parent material from which soil derived is homogenous.

Within soil profile, the composition changes due to mineral reactivity as response to theirs trend of attaining the more stable state. Thus, the distribution and relation among elements reflect the current mineralogy within sampled layer and its variation along soil profiles.

The investigated area is places between 47°.10' – 47°14'20''N and 27°30'30''-27°43'E (Fig.1) in the northern sector of suburban zone of Iasi city.

The soil has formed under continental temperate conditions, trough intense bioaccumulation processes, being predominantly represented by chernozems (Iancu & Buzgar, 2008; Lăcătuşu et al., 2008). The pervious studies on soil from investigated

area emphasized the physical-chemical proprieties of soil along profiles (Lăcătuşu et al., 2005) and the abundance of major and selected trace elements within 0-20 cm soil layer (Lăcătuşu et al., 2008) or 0-40 cm soil layer (Iancu & Buzgar, 2008). Thus, the soil reaction is found to be slight acid to weak alkaline, the carbonate concentration is low (often under 1%) in upper soil layer and increases downward (over 8%), the organic carbon content denotes a good supply with organic mater in soil and the texture is clayey or clayey-silty.

Geological setting is related to the Moldavian Platform which represents the south-western part of East European Platform. The soil is developed on the top of Sarmatian sedimentary deposits consisting of brownish and greenish fissile shale-clays and thin and discontinuous sand or silty-sand layers located in the upper part. The mineralogy of Sarmatian shale-clays mainly consist of illite (I), smectite (S), I/S interstatification, chlorite and kaolinite (Grasu et al., 2002), while the silty-sand layers represent a mixture of quartz, calcite, micas, low amount of feldspars and heavy minerals (e.g. rutil, anatase, garnet, zircon) (Dill et al., 2012).

In few profiles, the contact between Sarmatian deposits and soil C-horizon was found at between 120 and 200 cm in depth, and soil parent material collected under these depths are classified as saprock and belongs to weathering profile (water-rock interaction) according to Velde & Meunier (2008). In other profiles the thickness of C-horizon is higher than 200cm. As the soil thickness is variable, the upper limit of C-horizon occurs under 60-80 cm. This soil-horizon shows a yellow-brownish colour and a porous clay aspect. The soil upper layer between 0-40 cm depths corresponds to A-soil horizon.

In this study, the major and trace element concentrations were used for the modeling of soil geochemical evolution from parent material and also for the mineralogical interpretations of soil sampled layers.

2. MATERIALS AND METHODS

The sampling was performed in open hand made or excavated profiles and consist of two soil samples from 0-20 cm and 20-40 cm depths (A-horizon) and a corresponding one from the depth below 60-80 cm (C-horizon). A total number of 18 profiles were sampled (Fig. 1). Moreover, a number of 12 parent material samples were collected from the excavated profiles (Fig. 1).

The soil was air-dried in the laboratory and the fraction < 2 mm was separated by sieving. The soil layer <60-80 cm having a fine-grain texture were only crushed and not sieved.

The total concentrations of Co, Ni, Cu, Zn, Cd, Pb and As were determined using ED-XRF spectrometer (Epsilon 5, PANanalytical). The samples were mixed with binder at a ratio of 5:1 and homogenized for 20 minutes in agate mortal at mechanically mill. The resulting powder was pressed in aluminum pellets of 40 mm diameter using a hydraulic press under 20t/cm^2 strength.

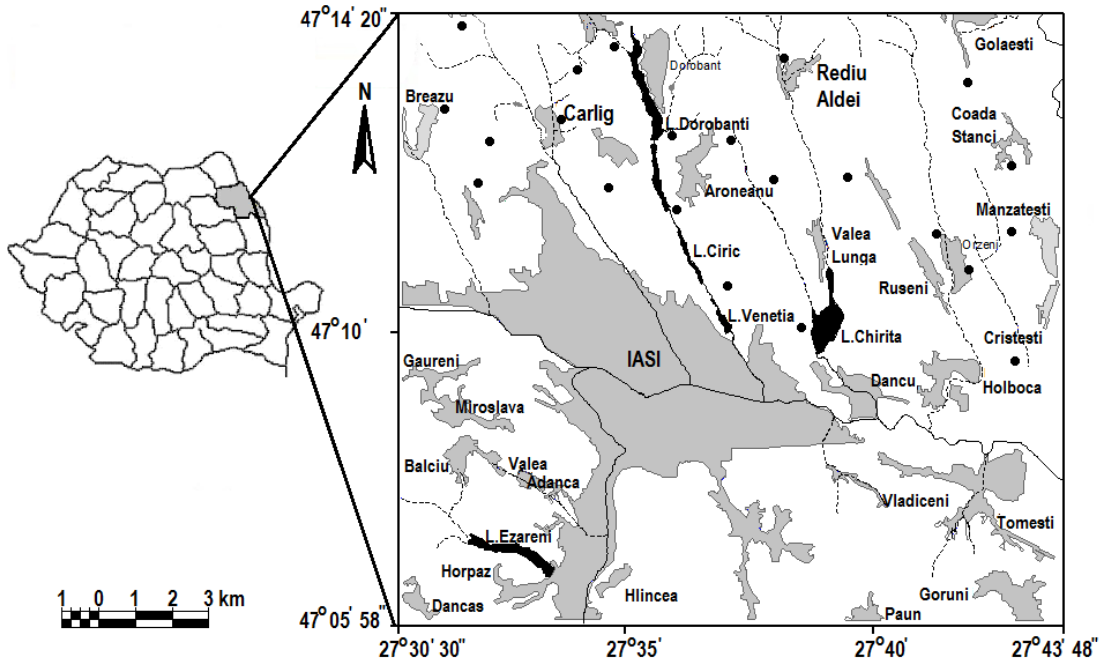

Figure 1. The location of samples in the northern area of Iasi city (modified from Iancu & Buzgar, 2008).

The standardization was performed by using 23 Certified Reference Materials (SO_{1-4}, RT, RTH, GSD and LKSD). Each pellet was two times counted. Thus, the final concentration represents the average of both counts. The detection limits for the elements analyzed are the following: Pb = 2.92 mg· kg^{-1}, Ni = 4.65 mg·kg^{-1}, Cu = 1.64 mg·kg^{-1} Zn = 2.27 mg·kg^{-1}, As= 1.13 mg·kg^{-1}. Accuracy was checked by analysing some of CRMs.

The estimation of soil organic material was performed by loss on ignition at 500°C (the temperature was gradually increased, and porcelain crucibles were heated in oven for 12 hours).

3. RESULTS AND DISCUSSIONS

The development of soil layers from parent material implies physical and chemical changes mainly due to weathering and pedogenic processes over the long term. If the evolution of soil in relation with parent material can be described by mass transfer coefficients, the distributions and relations of major and trace elements within and among different soil layers show the current geochemistry of soil profile.

3.1 Mass transfer coefficients

The loss or gain can be assessed comparing the concentration of an immobile element with that of a more mobile element, according to the following formula (Brimhall & Ditrich, 1987; Egli & Fitze, 2000; Oh & Richter, 2005; Jin et al., 2010):

$$\tau_{i,j} = \frac{C_{j,w}}{C_{j,p}} \cdot \frac{C_{i,p}}{C_{i,w}} - 1$$

where: C – represent the concentrations of immobile (i) and mobile (j) elements in weathered material (w) (soil) and parent material (p). Mass transfer coefficients ($\tau_{i,j}$) can take either positive values indicating the gain of element in soil or negative values when the element is lost from soil. The value of zero means that element j is in fact immobile in weathered profile.

Herein, the parent material composition is considered to be represented by saprock. The homogeneity of saprock is denoted by descriptive statistic parameters. Thus, the average and median values are close to each other, and the standard deviation of major components ranges from 0.03 for TiO_2 to 0.71 for Al_2O_3 (Table 1). Base on these observations, the average concentration of saprock was used as parent material composition for the following determinations.

Among the major components of saprock, the concentration of TiO_2 shows the minimum variation reflected by the low values of standard deviation. Therefore, Ti was assumed as reference immobile (conservative) element in order to assess the relative loss or gain of a more mobile element. The behaviour of Ti during weathering depend on mineralogy of parent material and on porewater composition (e.g. Jin et al., 2010), but its immobile character comes from its high ability to generate new Ti-bearing phases (e.g. Kabata-Pendias, 2011) as anatase or to be incorporated in new formed Fe oxides during soil formation.

Table 1. Parent material (saprock) chemical composition (%)

sample number	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5
sr.14.2	57.308	0.702	14.999	5	4.203	0.078	6.94	1.29	2.776	0.137
sr.11.2	57.608	0.756	14.866	6.13	4.362	0.098	6.929	1.703	3.177	0.177
sr.10.2	56.796	0.743	15.080	5.29	5.514	0.093	7.106	2.209	3.106	0.17
sr.9.6	56.242	0.791	15.308	5.89	4.33	0.08	6.185	1.604	3.156	0.139
sr.9.5	57.611	0.775	15.888	5.73	5.049	0.072	6.458	2.002	3.233	0.147
sr.9.4	57.820	0.722	14.357	5.17	4.703	0.093	7.731	2.232	3.001	0.183
sr.3.4	57.179	0.750	15.279	5.47	4.561	0.081	6.762	1.82	3.102	0.155
sr.2.3	56.528	0.766	15.807	5.73	4.959	0.078	6.587	1.814	3.255	0.199
sr.2.2	57.582	0.777	16.373	5.4	4.954	0.074	6.696	2.202	3.302	0.2
sr.2.1	57.257	0.785	16.241	5.79	4.978	0.075	6.551	1.949	3.35	0.164
sr.1.6	56.627	0.730	14.635	5.3	3.398	0.063	6.395	1.493	2.89	0.116
sr.1.5	57.563	0.706	14.457	4.74	3.789	0.085	6.792	1.559	2.888	0.129
average	57.177	0.750	15.274	5.470	4.567	0.081	6.761	1.823	3.103	0.160
median	57.283	0.753	15.180	5.435	4.632	0.079	6.729	1.817	3.131	0.160
stdev	0.511	0.030	0.674	0.400	0.589	0.010	0.400	0.306	0.180	0.027

Therefore, the concentration of TiO_2 does not significantly change in soil profile comparing with parent material. Generally, the mass transfer coefficients of the major oxides denote the same trend of depletion or enrichment for an element within soil profiles (Table 2). Most of the elements are lost from profiles, but there are two main trends. The low loss corresponds to transfer coefficient between -0.01 and -0.30, while the higher loss consists of values up to -0.92.

The highest loss is noted for CaO in soil 0-20 cm and 20-40 cm layers with the gain of CaO in <60-80 cm layer, where the coefficient takes positive values and sometime higher than one (Table 2). This trend of CaO suggests the dissolution of carbonates in soil upper layers (0-40 cm) and their partial precipitation within deeper layer (<60-80 cm, C-horizon). The evolution of Na_2O and MgO transfer coefficients with negative values increasing upward (Tabel 2) seems to be similarly. However, in upper soil layers (0-20 cm and 20-40 cm) the loss of correlation between Na_2O and MgO transfer coefficients (r = 0.43) suggests that the compositional change of Na+Mg and Mg-bearing mineral phases (such as 2:1 smectite and chorite-vermiculate) is not congruent.

Table 2. Mass transfer coefficients of major oxides along soil profiles

sample number	depth	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	MnO	Total loss
85	0-20 cm	-0.001	-0.295	-0.199	-0.272	-0.700	-0.830	-0.710	0.372	***-3.007***
	20-40 cm	**0.038**	-0.245	-0.177	-0.247	-0.698	-0.830	-0.707	0.442	***-2.904***
	<60-80 cm	**0.102**	-0.017	-0.082	-0.182	-0.470	**1.960**	-0.453	0.158	***-1.203***
82	0-20 cm	**0.028**	-0.118	-0.061	-0.096	-0.572	-0.532	-0.584	0.383	***-1.962***
	20-40 cm	**0.020**	-0.112	-0.053	-0.129	-0.352	-0.542	-0.561	0.383	***-1.750***
	<60-80 cm	**0.021**	0.020	-0.019	-0.134	-0.458	0.753	-0.348	0.359	***-0.959***
47	0-20 cm	**0.034**	-0.244	-0.154	-0.228	-0.425	-0.489	-0.631	0.370	***-2.172***
	20-40 cm	**0.023**	-0.245	-0.143	-0.236	-0.642	-0.173	-0.576	0.316	***-2.016***
	<60-80 cm	**0.108**	-0.221	-0.181	-0.163	-0.654	**0.321**	-0.296	0.338	***-1.515***
43	0-20 cm	-0.035	-0.368	-0.147	-0.211	-0.594	-0.622	-0.651	0.261	***-2.628***
	20-40 cm	**0.009**	-0.252	-0.120	-0.156	-0.531	-0.044	-0.527	0.283	***-1.630***
	<60-80 cm	**0.034**	***0.073***	***0.073***	-0.084	-0.581	**0.875**	0.064	0.268	***-0.665***
37	0-20 cm	-0.128	-0.335	-0.108	-0.243	-0.556	-0.828	-0.750	0.371	***-2.949***
	20-40 cm	-0.075	-0.252	-0.119	-0.231	-0.641	-0.691	-0.640	0.271	***-2.650***
36	0-20 cm	-0.028	-0.221	-0.099	-0.152	-0.658	-0.784	-0.671	0.492	***-2.613***
	20-40 cm	-0.052	-0.206	-0.122	-0.192	-0.659	-0.706	-0.657	0.197	***-2.595***
	<60-80 cm	**0.002**	-0.186	-0.112	-0.203	-0.325	**0.634**	-0.539	0.215	-1.366
33	0-20 cm	-0.106	-0.209	-0.031	-0.208	-0.675	-0.836	-0.661	0.365	***-2.726***
	20-40 cm	-0.079	-0.164	-0.040	-0.237	-0.446	-0.845	-0.634	0.330	***-2.446***
	<60-80 cm	-0.105	-0.127	-0.036	-0.194	-0.583	-0.789	-0.467	0.389	***-2.303***
24	0-20 cm	-0.023	-0.098	-0.015	-0.094	-0.699	-0.694	-0.595	0.331	***-2.218***
	20-40 cm	**0.018**	-0.093	-0.028	-0.118	-0.716	-0.828	-0.600	0.174	***-2.383***
	<60-80 cm	**0.043**	***0.147***	***0.037***	**0.012**	-0.261	**0.458**	-0.312	0.193	***-0.573***
23	20-40 cm	**0.028**	0.032	0.068	-0.040	-0.415	-0.708	-0.509	0.357	***-1.671***
	<60-80 cm	**0.069**	-0.087	-0.082	-0.074	-0.056	-0.046	-0.090	0.186	***-0.435***
21	20-40 cm	-0.063	-0.176	0.004	-0.170	-0.616	0.171	-0.469	0.297	***-1.494***
	<60-80 cm	-0.040	*-0.031*	*-0.002*	*0.002*	-0.069	0.034	-0.018	0.196	***-0.160***
18	0-20 cm	-0.061	-0.296	-0.147	-0.202	-0.599	-0.751	-0.716	0.311	***-2.773***
	20-40 cm	-0.063	-0.237	-0.117	-0.275	-0.676	-0.853	-0.702	0.146	***-2.922***
	<60-80 cm	**0.033**	-0.159	-0.143	-0.253	-0.401	**0.723**	-0.411	0.128	***-1.367***
17	0-20 cm	**0.070**	-0.162	-0.012	-0.015	-0.491	-0.050	-0.525	0.162	***-1.256***
	20-40 cm	**0.026**	**0.127**	***0.087***	0.002	-0.456	0.825	-0.296	0.241	***-0.752***
	<60-80 cm	**0.104**	***0.011***	*-0.121*	*-0.010*	-0.037	**0.093**	**0.065**	0.059	***-0.168***

Table 2 continued										
sample number	depth	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	MnO	Total loss
16	0-20 cm	-0.033	-0.282	-0.095	-0.165	-0.517	-0.747	-0.682	0.321	***-2.521***
	20-40 cm	-0.006	-0.159	-0.067	-0.147	-0.708	-0.493	-0.576	0.261	***-2.155***
	<60-80 cm	-0.071	*-0.033*	*-0.023*	*-0.030*	0.047	-0.136	**0.032**	-0.021	***-0.293***
13	0-20 cm	-0.077	-0.109	0.017	-0.072	-0.570	-0.411	-0.616	0.158	***-1.855***
	20-40 cm	**0.012**	-0.007	***0.067***	-0.029	-0.354	0.603	-0.518	0.134	***-0.909***
	<60-80 cm	**0.105**	*-0.024*	*-0.042*	*-0.037*	-0.161	**1.078**	-0.133	-0.040	***-0.400***
12	0-20 cm	-0.005	-0.092	-0.022	-0.017	-0.416	0.185	-0.406	0.255	***-0.958***
	20-40 cm	-0.041	-0.040	***0.035***	0.029	-0.626	-0.201	-0.430	0.207	***-1.338***
	<60-80 cm	-0.003	***0.004***	*-0.052*	**0.058**	-0.093	**0.202**	-0.015	0.638	***-0.163***
9	0-20 cm	-0.173	**0.041**	**0.096**	-0.064	-0.701	-0.924	-0.605	0.143	***-2.467***
	20-40 cm	-0.073	-0.115	**0.173**	0.042	-0.424	-0.261	-0.371	0.197	***-1.244***
	<60-80 cm	**0.014**	*-0.023*	*-0.018*	*0.005*	0.272	**0.188**	0.070	0.193	***-0.041***
1	0-20 cm	-0.048	-0.295	-0.133	-0.242	-0.544	-0.802	-0.685	0.364	***-2.749***
	20-40 cm	-0.009	-0.308	-0.132	-0.240	-0.540	-0.807	-0.730	0.328	***-2.765***
	<60-80 cm	**0.025**	*-0.064*	*-0.079*	-0.011	-0.091	0.068	-0.118	0.115	***-0.363***

The similarities in transfer coefficient values and variation trend are observed for Al_2O_3 and K_2O (Table 2). The loss of Al_2O_3 and K_2O are low and the minimum depletion seems to be typical of <60-80 cm layer, where a slight gain is also found for both elements. Comparing with the total loss of <60-80 cm layer, there are profiles where the loss of Al_2O_3 and K_2O can attain up to 18 %. The Fe_2O_3 depletion is lower than for Al_2O_3 and K_2O, with the trend of slight enrichment in <60-80 cm layer (C-horizon) or in soil 20-40 cm layer (A-horizon) where the transfer coefficients take positive values (Table 2). Even if the loss of MgO (23 – 57 % of total loss) is much higher than of K_2O and Al_2O_3 in soil upper layers, there are similarities in variation of their transfer coefficients which bring to high correlation of transfer coefficients ($r = 0.85$ MgO-Al_2O_3; $r = 0.86$ MgO-K_2O) which suggest a congruent dissolution of chlorite and illite during soil development (e.g. Jin et al., 2010). The silicon more often is gain than lost. Thus, the negative values of transfer coefficient are very low (-0.0X), while positive values suggest a slight enrichment of <60-80 cm (C-horizon) and 20-40 cm (A-horizon) soil layers (Table 2). These trends infer that SiO_2 released from mineral structure evolves toward silica precipitation within the same layer or its removal as solute is limited and brings to accumulation of amorphous SiO_2 in deeper layer. The transfer coefficients also suggest that in soil conditions SiO_2 has a low mobility. MnO is the only major component which is systematically gains from <60-80 cm to 0-20 cm layer. The mass transfer coefficients take values above 0.1 in <60-80 cm layer (C-horizon) and tend to increase upward (Table 2).

The pH condition of soil solution during weathering and pedogenic processes in soil open system represents an important factor in elements migration and retention. The high carbonate content inherited from parent material can act on the pH conditions during soil formation and evolution. Thus, the carbonate dissolution can buffer the acidity of soil solution due to rain water infiltration maintaining the pH conditions at almost neutral values. The relatively low transfer coefficients of K_2O, Fe_2O_3, SiO_2 and Al_2O_3 in soil layers consist with their low to very low mobility which is typical of light acid to weak basic pH conditions in soils. Also, the good correlations of transfer coefficients of CaO with K_2O ($r = 0.66$), Al_2O_3 ($r = 0.54$), Fe_2O_3 ($r = 0.53$), MgO (0.77), Na_2O (0.72) and SiO_2 ($r = 0.59$) within 0-20 cm and 20-40 cm soil layers denote that carbonate dissolution progressed simultaneously with clay minerals transformations.

The depletion or enrichment patterns of Co, Ni, Cu and Zn (transition trace elements - TTE, excluding Cd with very low concentration and higher depletion trend) in relation with parent material (saprock) are generally similar along soil profiles and within sampled layer. Thus, the mass transfer coefficients infer a negligible or low loss for each TTE ranging between -0.001 to -0.2 (Table 3). Although the total loss can show a higher depletion for <60-80 cm layer comparing with the soil layers of A-horizon, there are profiles in which transfer coefficients of <60-80 cm layer have positive values at list for one of TTE. This kind of enrichment of <60-80 cm layer (C-horizon) is

not compulsory followed by the gain of TTE in soil upper layers which can be characterized by a depletion trend (negative coefficients; Table 3). The enrichments with TTE can also occur either in 20-40 cm or 0-20 cm soil layers, with the higher gain of all TTE for 20-40 cm soil layer. The Cu contamination of four samples from 0-20 cm layer is suggested by their transfer coefficients above 0.5 which correspond to depleted soil layers in the depth (Table 3).

The patterns of TTE gain in soil profiles are similar with that of Fe_2O_3 and Al_2O_3. Thus, the enrichment of TTE is found in sampled layers where mainly Fe_2O_3 and subordinately Al_2O_3 show the accumulation trend (positive mass transfer coefficients) (Table 2 and 3).

The clay fraction is the most important source of TTE in sampled layers as their transfer coefficients correlation with major soil elements suggests (Table 4). Also, the release of TTE from mineral structure seems to be promoted mainly by Fe, Al and Mg dynamic during mineral weathering.

Table 3. Mass transfer coefficients of trace elements along soil profiles

sample number	depth	Co	Ni	Cu	Zn	Pb	As	Cd	Total loss
85	0-20 cm	-0.228	-0.278	-0.189	-0.199	*0.119*	*0.133*	-0.443	-1.337
	20-40 cm	-0.208	-0.276	-0.114	-0.223	*0.225*	*0.183*	-0.316	-1.136
	<60-80 cm	-0.246	-0.236	-0.301	-0.181	*0.131*	*0.187*	0.015	-0.965
82	0-20 cm	-0.037	-0.105	-0.071	-0.083	*0.113*	*0.292*	0.010	-0.296
	20-40 cm	-0.037	-0.068	-0.087	-0.066	*0.041*	*0.212*	-0.486	-0.743
	<60-80 cm	-0.138	-0.062	-0.085	-0.037	*0.175*	*0.252*	-0.237	-0.560
47	0-20 cm	-0.223	-0.160	-0.212	-0.228	*0.100*	*0.223*	-0.425	-1.248
	20-40 cm	-0.177	-0.213	-0.160	-0.197	*0.074*	*0.221*	-0.244	-0.992
	<60-80 cm	-0.212	-0.240	-0.209	-0.223	*0.074*	*0.126*	-0.223	-1.107
43	0-20 cm	-0.249	-0.197	-0.109	-0.085	*0.242*	*0.356*	-0.567	-1.207
	20-40 cm	-0.168	-0.191	-0.137	**0.006**	*0.240*	*0.367*	**0.105**	-0.496
	<60-80 cm	-0.042	**0.033**	**0.096**	**0.061**	*0.179*	*0.382*	-0.030	-0.072
37	0-20 cm	-0.150	-0.190	**0.880**	-0.140	*0.194*	*0.387*	-0.703	-1.183
	20-40 cm	-0.160	-0.206	0.205	-0.184	*0.082*	*0.401*	-0.405	-0.955
36	0-20 cm	-0.087	-0.148	**1.445**	-0.020	*0.231*	*0.359*	-0.348	-0.603
	20-40 cm	-0.143	-0.229	-0.136	-0.164	*0.128*	*0.184*	-0.698	-1.370
	<60-80 cm	-0.243	-0.300	-0.196	-0.131	*0.101*	*0.299*	**0.386**	-0.870
33	0-20 cm	0.001	-0.019	**0.605**	**0.026**	*0.133*	*0.462*	-0.657	-0.676
	20-40 cm	-0.024	-0.021	-0.098	-0.090	*0.100*	*0.353*	**0.239**	-0.234
	<60-80 cm	-0.036	-0.084	-0.146	-0.051	*0.088*	*0.329*	-0.511	-0.828
24	0-20 cm	-0.082	0.019	0.015	-0.019	*0.208*	*0.400*	-0.400	-0.501
	20-40 cm	-0.082	-0.009	-0.165	-0.076	*0.161*	*0.346*	-0.104	-0.436
	<60-80 cm	**0.004**	**0.129**	**0.277**	**0.096**	*0.093*	*0.306*	-0.235	-0.235
23	20-40 cm	0.088	0.108	0.034	0.052	*0.166*	*0.358*	-0.113	-0.113
	<60-80 cm	-0.118	-0.008	-0.075	-0.090	*0.139*	*0.250*	-0.553	-0.844
21	20-40 cm	-0.015	-0.022	-0.110	-0.005	*0.135*	*0.379*	-0.438	-0.590
	<60-80 cm	-0.004	0.044	-0.002	0.022	*-0.001*	*0.069*	-0.038	-0.045
18	0-20 cm	-0.061	-0.234	**6.350**	**0.593**	*0.885*	*0.397*	-0.249	-0.863
	20-40 cm	-0.096	-0.288	-0.218	-0.189	*0.143*	*0.240*	-0.197	-0.988
	<60-80 cm	-0.232	-0.259	-0.194	-0.181	*-0.028*	*0.196*	-0.217	-1.110
17	0-20 cm	-0.001	-0.113	**0.003**	0.102	*0.321*	*0.418*	-0.168	-0.282
	20-40 cm	-0.019	0.110	**0.064**	**0.080**	*0.084*	*0.175*	-0.739	-0.758
	<60-80 cm	-0.176	-0.138	0.000	-0.060	*-0.075*	*0.024*	-0.030	-0.479

Table 3 continued									
sample number	depth	Co	Ni	Cu	Zn	Pb	As	Cd	Total loss
16	0-20 cm	-0.131	-0.127	-0.116	-0.098	*0.140*	*0.234*	-0.296	-0.767
	20-40 cm	-0.094	-0.098	-0.092	-0.086	*0.067*	*0.251*	-0.364	-0.735
	<60-80 cm	**0.006**	-0.086	-0.086	**0.018**	*-0.074*	*-0.007*	-0.080	-0.333
13	0-20 cm	-0.167	-0.034	-0.009	**0.007**	*0.104*	*0.360*	-0.682	-0.892
	20-40 cm	-0.024	0.045	-0.013	**0.065**	*0.216*	*0.331*	-0.485	-0.522
	<60-80 cm	-0.078	-0.088	0.045	-0.017	*-0.005*	*0.196*	-0.128	-0.315
12	0-20 cm	**0.119**	-0.026	**0.008**	**0.088**	*0.191*	*0.265*	-0.200	-0.227
	20-40 cm	**0.051**	**0.005**	**0.053**	**0.214**	*0.273*	*0.373*	-0.268	-0.268
	<60-80 cm	-0.083	**0.007**	-0.009	**0.027**	*-0.021*	*0.067*	-0.144	-0.257
9	0-20 cm	-0.044	**0.236**	-0.047	-0.059	*0.122*	*0.325*	-0.306	-0.457
	20-40 cm	**0.132**	**0.253**	**0.218**	**0.174**	*0.121*	*0.600*	**0.477**	0.000
	<60-80 cm	-0.157	-0.117	-0.135	-0.124	*-0.133*	*0.041*	**0.058**	-0.608
1	0-20 cm	-0.115	-0.160	-0.119	-0.136	*0.271*	*0.371*	-0.390	-0.920
	20-40 cm	-0.138	-0.108	-0.140	-0.158	*0.092*	*0.329*	-0.716	-1.259
	<60-80 cm	-0.115	**0.010**	**0.005**	**0.013**	*-0.056*	*0.010*	0.216	-0.171
15	20-40 cm	-0.205	-0.077	-0.015	-0.245	*0.285*	*0.541*	-0.086	-0.628
	<60-80 cm	-0.302	-0.218	-0.258	-0.281	*0.536*	*0.405*	-0.226	-1.284

The low mobility of TTE suggests that the pH conditions in upper weathering layers during soil formation were light acid to weak alkaline. The higher acidity would generate a higher extraction and mobility of the TTE (e.g. Kabata –Pendias, 2011). As mention above, the almost neutral character of pH could be maintained by the dissolution of carbonates over the long term. The precipitation of secondary carbonates in deeper layers could generates a higher alkalinity which in turn could be involved in increasing adsorption capacity of mineral clay particles and new precipitated iron oxides for TTE (Sipos et al., 2008: Sipos et al., 2011).

The mass transfer coefficients of Cd evolve in different manner than of other TTE (Table 3). Thus, Cd depletion increases from upper soil to depth. The loss of Cd agrees with its high mobility in soil (Kabata-Pendias, 2011). Unlike TTE, the transfer coefficients of Pb and As exhibit a moderate gain with upward enrichment trend (Table 3).

In soil the behaviour of Pb and As mainly depend on both inorganic and organic compound. The high electronegativity of Pb and As should give rise to strong bonds in clay mineral, oxy-hydroxides and organic compounds (e.g. Sipos et al., 2008; Kabata-Pendias 2011). This pattern of Pb and As affinity can explain their accumulation in soil upper layers (0-20 cm and 20-40 cm) and consequently their low mobility. The lack of transfer coefficient correlation of Pb with Fe or Al suggests that the release of major components from minerals do not promote the Pb release, pointing out its immobile behaviour.

Table 4. Correlation of mass transfer coefficients of Co, Ni, Cu and Zn (TTE) with major elements

	Co	Ni	Cu	Zn
0-20 cm soil layer				
Si	0.004	-0.454	-0.176	0.073
Al	**0.619**	**0.734**	-0.254	**0.643**
Fe	**0.579**	**0.926**	-0.245	**0.710**
K	**0.661**	**0.644**	-0.191	**0.796**
Na	0.147	-0.225	-0.126	0.069
Ca	0.470	0.046	-0.195	**0.585**
Mg	**0.657**	0.473	-0.342	**0.711**
Mn	-0.183	-0.521	0.143	-0.426
20-40 cm soil layer				
Si	-0.218	-0.011	-0.263	-0.040
Al	**0.810**	**0.869**	**0.558**	**0.799**
Fe	**0.927**	**0.957**	**0.623**	**0.880**
K	**0.791**	**0.846**	**0.612**	**0.936**
Na	**0.571**	**0.626**	0.372	**0.508**
Ca	0.264	0.429	0.276	**0.570**
Mg	**0.688**	**0.769**	**0.570**	**0.859**
Mn	-0.243	-0.202	-0.112	-0.330

The relation of As and Fe transfer coefficients (r = 0.54) in 20-40 cm soil supports that the accumulation of As is directly related to Fe-oxides development, while the slightly removal of Fe from 0-20 cm disturbs As – Fe association.

3.2. The major and trace elements distribution and relations along soil profiles

The distribution of the major oxides in sampled layer shows little to great variation from <60-80 cm layer (C-horizon) to 20-40 cm and 0-20 cm layers (A-horizon). Thus, the distributions of SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, P_2O_5 and MnO display a narrow range of variations from <60-80cm to 0-20 cm soil layers (Table 5). According to the changes of average concentration along soil profiles, some particular features are observed. Thus, the average contents of SiO_2, Al_2O_3 and K_2O slightly decrease upward. The slight increase in concentrations is found for Fe_2O_3, TiO_2 and MnO from <60-80 cm layer to 0-20 cm layer. The distributions of CaO, MgO and Na_2O significantly change from <,60-80 cm layer to 0-20 cm soil layers (Table 5). In <60-80 cm layer the abundance of CaO is much higher than Fe_2O_3 abundance, and that of MgO exceeds the K_2O abundance. In soil 0-20 cm and 20-40 cm layers, the abundance order change as follows: Fe_2O_3 > CaO > K_2O > MgO.

The distributions of major oxides along sampled layers are in agreement with the usual behaviour of elements in soils under temperate conditions. Therefore, the narrow changes in concentrations along soil profile denote the lower mobility of TiO_2 and Fe_2O_3, while that of SiO_2 and Al_2O_3 is slightly higher. Even if the potassium is known as mobile element in soil, the K_2O distribution in soil profile suggests a low mobility. The distributions of CaO, MgO and Na_2O prove their high mobility during soil formation processes.

The relations among major oxides in soils are often used for mineralogical interpretations.
In <60-80 cm layer (C-horizon), the correlations of Al_2O_3 and Fe_2O_3 with MgO, K_2O, Na_2O and TiO_2 (Table 6) mainly infer their association in clay minerals. Generally, the good correlation of Al_2O_3 with K_2O is attributed to illite (e.g. Bianchini et al, 2002), while that of Al_2O_3 with MgO and also of MgO with Na_2O and K_2O can be firstly related to smectites and secondly to chlorite or its weathering phases. The implication of MgO in carbonate fraction is not supported by its relation with CaO, as long as the correlation between them has a negative trend (Table 6). The negative correlations of CaO with SiO_2, Al_2O_3 and Fe_2O_3 (Table 6) infer that Ca is mainly bound in carbonate fraction of <60-80 cm layer. The origin of carbonate fraction can be either primary or secondary, but the negative correlation between CaO and SiO_2 in <60-80 cm layer (Table 6) suggests the prevalence of primary carbonates and subordinately of secondary carbonates which in turn would brings the loss of negative relation between CaO and SiO_2 (Zhang, 2004, Liu et al., 2009).

The lack of correlation of SiO_2 with Al_2O_3 and Fe_2O_3 in <60-80 cm layer (Table 6) could result from quartz dilution effect (e.g. Hardy & Cornu, 2006) upon the concentration of other major oxides. However, the good correlation of SiO_2 with MgO, K_2O and Na_2O (Table 6) infer that SiO_2 is mainly involved in clay minerals structure and just a low percent is bound to quartz or amorphous silica.

Table 5. The concentrations of major oxides (%) in sampled soil layers

Depth	Statistical parameters	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5
0-20 cm	average	52.965	0.725	11.508	4.883	1.597	0.103	2.409	0.730	2.527	0.207
	median	52.95	0.74	11.46	4.95	1.57	0.108	1.73	0.71	2.52	0.19
	min	44.87	0.55	9.26	3.96	1.17	0.069	0.53	0.52	2.24	0.13
	max	61.68	0.81	13.87	6.15	2.24	0.124	6.62	1.02	2.98	0.39
20-40 cm	average	52.790	0.702	12.078	4.856	1.806	0.096	3.455	0.742	2.471	0.158
	median	54.64	0.71	12.38	4.94	1.76	0.098	2.59	0.675	2.46	0.16
	min	42.84	0.56	8.17	4.12	1.09	0.071	1.06	0.49	2.06	0.1
	max	62.5	0.82	14.92	5.56	2.49	0.123	9.21	1.15	2.82	0.21
<60-80 cm	average	53.006	0.673	12.814	4.571	3.448	0.086	8.201	1.332	2.554	0.164
	median	54.332	0.682	12.725	4.46	3.69	0.084	7.75	1.437	2.6	0.17
	min	43.68	0.52	8.95	3.46	1.71	0.065	1.48	0.53	1.76	0.06
	max	57.91	0.8	15.65	5.66	4.99	0.13	13.87	2.38	3.22	0.23

Table 6. Pearson correlation coefficients for major oxides of <60-80 cm soil layer

	SiO_2	TiO_2	Al_2O3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5
SiO_2	1.000	**0.761**	***0.358***	0.417	**0.610**	0.335	**-0.592**	**0.620**	**0.613**	0.391
TiO_2	**0.761**	1.000	**0.703**	**0.844**	**0.688**	**0.584**	-0.736	0.644	**0.796**	0.453
Al_2O_3	0.358	**0.703**	1.000	**0.910**	**0.796**	0.371	**-0.509**	**0.654**	**0.907**	0.248
Fe_2O_3	0.417	**0.844**	**0.910**	1.000	**0.725**	*0.472*	**-0.666**	**0.613**	**0.865**	0.392
MgO	0.610	0.688	**0.796**	**0.725**	1.000	0.231	-0.358	0.826	**0.886**	0.168
MnO	0.335	0.584	0.371	0.472	0.231	1.000	-0.585	0.121	0.408	0.157
CaO	-0.473	-0.736	-0.509	-0.666	-0.358	-0.585	1.000	-0.255	-0.537	-0.269
Na_2O	**0.620**	**0.644**	**0.654**	**0.613**	0.826	0.121	-0.255	1.000	**0.804**	0.411
K_2O	**0.613**	**0.796**	**0.907**	**0.865**	**0.886**	0.408	**-0.537**	0.804	1.000	0.375
P_2O_5	0.391	0.453	0.248	0.392	0.168	0.157	-0.269	0.411	0.375	1.000

Moreover, the low values of SiO_2/Al_2O_3 ratio (3.40-5.32) which are typical of clay rich sediments reflect that the SiO_2 budget of <60-80 cm layer (C-horizon) is controlled by clay minerals over quartz (e.g. Herron, 1988; Meinhold et al., 2007). The illite and smectite seem to be the main clay minerals in <60-80 cm layer according to the K_2O/Al_2O_3 ratio, which take values between 0.14 and 0.22. In shale and mudstones, the K_2O/Al_2O_3 ratio is about 0.3 when illite is the main clay mineral or it is close to zero if other clay minerals (including smectite) prevails (Cox et al., 1995). The mineralogical interpretation on the base of distribution and relations among major oxides in <60-80 cm layer (C-horizon) is inherited from parent material and supported by the mineralogical determinations on shale-clays (Grasu et al., 2002) and intercalated narrow silty-sand layers (Dill et al., 2012) which represent the main parent material of soil on regional scale.

The relations among the major oxides change in soil 20-40 cm and 0-20 cm layers (A-horizon) and are depicted in tables 7. The conservative trend of correlations is observed for Al_2O_3, Fe_2O_3 and K_2O, suggesting that illite is stabilized in upper soil layers (Barré et al., 2009) and also that the amount of Al, Fe rich-clay minerals increase.

The loss of correlations in 20-40 cm and 0-20 cm layers is found for more mobile elements (Table 7). The most significant changes are related to MgO and Na_2O, for which the lack of correlation with Al_2O_3, Fe_2O_3 and K_2O could be related to the decreasing amount of Mg and Na – bearing smectite. However, the relation of MgO with Al_2O_3 in 20-40 cm soil (Table 7) possibly results from the increasing amount of vermiculate at the expense of chlorite. In 0-20 cm and 20-40 cm soil layers, Mg released from smectite or chlorite-vermiculite seems to be included in carbonate fraction as the good correlation of MgO with CaO develops (Table 7). The good relation of TiO_2 with MnO and Fe_2O_3 suggests Ti adsorptions on Mn or Fe oxides or hydroxides in the form of coatings on other soil particle or as nodules (e.g. Kabata-Pedias, 2011).

Table 7. Pearson correlation coefficients for major oxides of 20-40 cm and 0-20 cm soil layers

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5
0-20 cm soil layer										
SiO_2	1.000	**0.727**	0.120	0.029	-0.337	**0.844**	-0.462	0.078	0.008	0.272
TiO_2	**0.727**	1.000	0.333	**0.588**	-0.467	**0.894**	-0.845	-0.147	0.332	0.123
Al_2O_3	0.120	0.333	1.000	**0.781**	0.449	0.211	-0.233	-0.425	**0.868**	-0.142
Fe_2O_3	0.029	**0.588**	**0.781**	1.000	**0.057**	**0.327**	-0.638	-0.460	**0.829**	-0.206
MgO	-0.337	-0.467	0.449	0.057	1.000	-0.462	**0.625**	-0.022	0.386	-0.266
MnO	**0.844**	**0.894**	0.211	0.327	-0.462	1.000	-0.698	-0.020	0.136	0.200
CaO	-0.462	-0.845	-0.233	-0.638	**0.625**	-0.698	1.000	**0.404**	-0.284	-0.016
Na_2O	0.078	-0.147	-0.425	-0.460	-0.022	-0.020	0.404	1.000	-0.426	0.222
K_2O	0.008	0.332	**0.868**	**0.829**	0.386	0.136	-0.284	-0.426	1.000	-0.003
P_2O_5	0.272	0.123	-0.142	-0.206	-0.266	0.200	-0.016	0.222	-0.003	1.000
LOI	0.389	0.439	-0.443	0.011	-0.676	0.529	0.607	0.004	0.228	0.538

Table 7 continued										
20-40 cm soil layer										
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5
SiO_2	1.000	**0.901**	0.166	0.326	-0.575	**0.899**	-0.850	0.077	0.273	0.088
TiO_2	**0.901**	1.000	0.296	**0.544**	-0.436	**0.880**	-0.847	0.014	0.357	0.168
Al_2O_3	0.166	0.296	1.000	**0.860**	**0.566**	0.173	**-0.134**	0.360	**0.826**	-0.115
Fe_2O_3	0.326	**0.544**	**0.860**	1.000	0.305	**0.373**	-0.484	0.289	**0.824**	0.095
MgO	-0.575	-0.436	**0.566**	0.305	1.000	-0.444	**0.560**	0.197	0.443	0.006
MnO	**0.899**	**0.880**	0.173	0.373	-0.444	1.000	-0.782	0.000	0.219	0.230
CaO	-0.850	-0.847	-0.134	-0.484	**0.560**	-0.782	1.000	0.014	-0.337	-0.145
Na_2O	0.077	0.014	0.360	0.289	0.197	0.000	0.014	1.000	0.449	0.029
K_2O	0.273	0.357	**0.826**	**0.824**	0.443	0.219	-0.337	0.449	1.000	0.238
P_2O_5	0.088	0.168	-0.115	0.095	0.006	0.230	-0.145	0.029	0.238	1.000

However, anatase inherited from parent material (Dill et al., 2012) could also be responsible for TiO_2 good correlation with MnO and Fe_2O_3. The enrichment of soil with Mn can be related both to organic mater (r = 0.53 Mn-LOI) and silicon – manganese interaction (r = 0.8X, Table 7) due to biogeochemical cycle of these elements in upper soil layers (e.g. Kabata-Pendias, 2011).

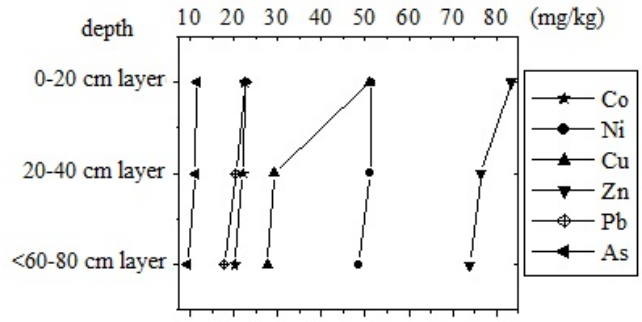

Figure 2. The variation of average concentrations of trace elements along sampled layers.

The distribution of TE along soil profile denotes their general trend to accumulate in soil upper layers (Fig. 2). In 0-20 cm soil layer, the relative higher increases are shown by Cu (24.30-249.27 $mg \cdot kg^{-1}$) and Zn (66.08-143.74 $mg \cdot kg^{-1}$), for which their maximum concentrations enhance the difference between their average and median values (average = 51.03 and median = 29.68 for Cu; average = 83.33 and median = 79.04 for Zn).

The distribution of TE in soil is controlled by several factors, but the most important are clay minerals and oxy-hydroxides of Fe, Al and Mn with high adsorption capacity (e.g. Kabata-Pendias, 2011). The relations of transition trace elements (TTE) with Al, Fe and K in all sampled layer infer their association with clay mineral fraction (Table 8). Since the Fe oxides can be usually found as coatings on soil clay particle (e.g. Sipos et al., 2011), the retention of Co, Ni and Zn on their surface is also suggested by correlation coefficients (Table 8).

In 20-40 cm soil layer, Zn is still correlated with Mg (Table 8), possibly being preserved in Mg-bearing minerals, such as vermiculite. The Cu preference for mineral phases changes from 20-40 cm layer to 0-20 cm layer. Thus, Cu seems to be associated mainly with Fe-oxides in 20-40 cm layer, while in 0-20 cm layer it is mainly related to Mn-oxides. Moreover, the interaction of TTE with soil organic matter (expressed as LOI at 500°C) can enhance TTE accumulation in soil (Table 8).

In <60-80 cm layer (C-horizon), Pb and As do not show a specific trend of associating with major soil elements. In 20-40 cm layer, the correlation of Pb (r = 738) and As (r = 0.592) with Mn denotes their adsorption on Mn-oxides. Unlike lead, in upper soil layers, As also shows the trend to associate with Fe (r = 0.579 in 20-40 cm soil and r = 0.628 in 0-20 cm soil). Thus, there is the possibility for As to be adsorbed by Fe-oxides as well. However, lead in upper 0-20 soil layer developed a good relation with P (r = 72.5) which suggest their interaction due to biochemical processes around plant roots (Kabata-Pendias, 2011). The enrichment of soil upper layers with organic matter could be also responsible for the Pb and As accumulation since both elements have good correlation with LOI (r = 0.571 Pb-LOI; r = 0.765 As-LOI).

4. CONCLUSIONS

The mass transfer approach denotes the soil evolution in relation with parent material over long term. The distribution and correlation of major and trace elements within sampled soil layers mainly depend on current soil mineralogy. According to mass transfer coefficients method, the major oxides are

lost or gain to different extent from upper and deeper soil layers.

The higher reactivity of carbonate fraction, Mg-rich minerals (chlorite) and Na-Mg bearing clay minerals (smectite) is supported by the mass transfer coefficients within 0-20 cm and 20-40 cm soil layers. The loss of MgO and Na_2O from the soil system is also found in <60-80 cm layer, whereas CaO is highly gained. The low loss of Al_2O_3 and K_2O is similarly and infers a partial degradation of illite. Although Fe and Al seem to be simultaneously released from minerals, the Fe ability to form new compounds as oxy-hydroxides is higher. The SiO_2 loss from 0-20 cm layer could gives rise to the increasing amount of amorphous silica in deeper layers so that SiO_2 is partially preserved in the system.

General observations upon the gain and loss of TTE denote that most of the profiles are characterized by a negligible or low loss, with a slightly higher depletion within <60-80 cm layer. The enrichment of <60-80 cm layer (C-horizon) with at least one of the TTE is also found. The behaviour of TTE is determined by Fe_2O_3 and Al_2O_3 mobility. The geogenic origin of Co, Ni, Cu and Zn due to clay minerals is supported by their transfer coefficient correlations with major elements. The anthropogenic input of Cu and Zn for few profiles is reflected by transfer coefficients over 0.5 in 0-20 cm soil layer, since the deeper layers show negative values of transfer coefficients. The Pb and As gain systematically increase upward, being higher than TTE gain. The accumulation of As could result from its affinity for new formed Fe-oxides, while Pb seems to be mainly preserved to the mineral structure.

The carbonate dissolution over long term of soil formation and simultaneously with clay mineral transformation could control the pH values. Consequently, the almost neutral pH conditions would explain the lower mobility of certain major components and TTE in soil. The mass transfer coefficients confirm the low to very low mobility of Si, Fe, Al, K and also of TTE, while Pb and As are preserved and systematically enriched.

According to the distribution of major oxides along soil profiles, a low variation of TiO_2, Fe_2O_3 Al_2O_3, SiO_2 and K_2O is found. The main changes are related to CaO, Na_2O and MgO, their abundances decreasing upward.

The good correlations among Al_2O_3, Fe_2O_3 and K_2O closely reflect the dominance of clay fraction in sampled soil layers. The clay fraction in upper soil layers seems to be enriched in vermiculite and Al, Fe rich-smectite. Part of the MgO released during smectite composition change in 0-20 cm and 20-40 cm layers is bound to the carbonate fraction. The high content of CaO in all sampled layers is related to carbonate fraction.

Table 8. Pearson correlation coefficients of major and transition trace elements in sampled soil layers

	Co	Ni	Cu	Zn
0-20 cm soil layer				
Si	0.115	-0.105	0.132	-0.106
Ti	0.622	0.411	0.376	0.296
Al	**0.754**	**0.782**	0.145	**0.557**
Fe	**0.977**	**0.948**	0.324	**0.689**
Mg	**0.027**	**0.277**	-0.302	0.163
Mn	0.372	0.143	**0.542**	0.249
Ca	-0.682	-0.487	-0.391	-0.365
Na	-0.410	-0.420	-0.206	-0.604
K	**0.791**	**0.807**	0.191	**0.611**
P	-0.149	-0.301	0.088	-0.239
LOI	**0.517**	0.193	**0.501**	0.263
20-40 cm soil layer				
Si	0.371	-0.003	0.319	-0.008
Ti	**0.592**	0.107	0.490	0.207
Al	**0.809**	**0.707**	0.424	**0.784**
Fe	**0.968**	**0.807**	**0.617**	**0.780**
Mg	0.263	0.422	0.122	**0.618**
Mn	0.450	0.090	**0.441**	0.078
Ca	-0.514	-0.257	-0.422	-0.098
Na	0.248	0.323	0.160	0.265
K	**0.774**	**0.706**	**0.577**	**0.844**
P	0.180	0.061	0.198	0.388
< 60-80 cm layer				
Si	0.486	0.473	0.433	0.437
Ti	**0.871**	**0.764**	**0.688**	**0.822**
Al	**0.896**	**0.911**	**0.915**	**0.951**
Fe	**0.986**	**0.929**	**0.858**	**0.969**
Mg	**0.742**	**0.757**	**0.769**	**0.777**
Mn	0.486	0.487	0.342	0.481
Ca	-0.700	-0.650	-0.580	-0.641
Na	**0.636**	**0.644**	**0.636**	**0.660**
K	**0.883**	**0.906**	**0.880**	**0.918**
P	0.413	0.299	0.329	0.355

The distributions of TTE, Pb and As from <60-80 cm to 0-20 cm soil layers infer their trend to accumulate upward, where the anthropogenic input can also disturbed their geogenic abundance. The higher capacity of clay particle to immobilized TTE is supported by the good relations of TTE with Al, Fe and K in all sampled layers. Also, the Mn and Fe oxides coatings and organic matter could be involved

in TTE, Pb and As retention. Even if the distribution of transition trace elements denotes their slight enrichment in soil upper layers, the mass transfer coefficients point out that the TTE were partially lost from soil upper layer. Thus, the amount of TTE in soil upper layers does not entirely reflect their initial concentration in parent material.

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REFERENCES

Barré, P., Berger, G. & Velde, B., 2009. *How element translocation by plants may stabilize illitic clays in the surface of temperate soils*. Geoderma, 151, 1-2, 22-30.

Bianchini G., **Laviano R., Lovo S. & Vaccaro C**., 2002. *Chemical-mineralogical characterisation of clay sediments around Ferrara: a tool for an environmental analysis.* Applied Clay Sciences, 21, 3-4, 165-176.

Brimhall, G. H. & Dietrich, W. E., 1987. *Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metosomatic hydrochemical systems: results on weathering and pedogenesis.* Geochimica et Cosmochimica Acta, 51, 3, 567–587.

Cox, R., Lowe, D.R. & Cullers, R.L., 1995. *The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States.* Geochimica et Cosmochimica Acta, 59, 14, 2919– 2940.

Dill, D.G., Iancu, G. O., Ionesi, V., Sârbu, S., Balintoni, I. & Botz, R., 2012. *Petrography and mineral chemistry of Bessarabian siliciclastic rocks in the Eastern Carpathians Foreland Basin (Romania and Republic of Moldova)*. Neues Jahrbuch für Geologie und Paläontologie- Abhandlungen, 163, 3, 199-226.

Egli, M.& Fitze, P., 2000. *Formulation of pedologic mass balance based on immobile elements: a revision.* Soil Science, 165, 5, 437–443.

Florea, N. **& Munteanu, I.,** 2003, *Romanian system of soil taxonomy(SRTS)*. Ed. Estfalia, Bucharest, 172 p. (In Romanian).

Grasu, C., Brânzilă, M., Miclăuş, C. & Boboş, I., 2002. *The Sarmatian of foreland basins from Eastearn Carpathians*. Ed. Tehnică, Bucureşti, 407 p. (In Romanian).

Hardy, M. & Cornu, S., 2006. *Location of natural trace elements in silty soils using particle-size fractionation*. Geoderma, 133, 3-4, 295-308.

Herron, M.M., 1988. *Geochemical classification of terrigenous sands and shales from core or log data*. Journal of Sedimentary Petrology 58, 5, 820-829.

Iancu, O.G. & Buzgar, N., 2008. *The geochemical atlas of heavy metals in the soils of the municipality of Iasi and its surrounding areas*. Ed. "Al.I.Cuza" University of Iasi, 48 p.

Jin, L., Ravella, R., Ketchum, B., Bieman, P.R., Heaney, P., White, T. & Brantley, S.L., 2010. *Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory*. Geochimica et Cosmochimica Acta, 74, 13, 3669–3691.

Kabata-Pendias, A., 2011. *Trace elements in soils and plants – Fourth Edition*. CRC Press Taylor & Francis Group, 505 p.

Lăcătuşu, R., Rasnoveanu, I., Breaban, I., Rusu, C., Lungu, M. & Kovacsovics, B., 2005. *Urban soils in Iassy municipium.* Soil forming factors and processes from the temperate zone, 4, 135-143 (In Romanian).

Lăcătuşu, R, Lăcătuşu, A-R, Lungu, M & Breaban, I.G., 2008, *Macro- and microelements abundance in some urban soils from Romania*, Carpathian Journal of Earth and Environmental Sciences, 3, 1, 73–81.

Liu, Z., Zhao, Y., Colin, C., Siringan, F.P. & Wu, Q., 2009. *Chemical weathering in Luzon, Philippines from clay mineralogy and major-element geochemistry of river sediments*. Applied Geochemistry 24, 11, 2195–2205.

Meinhold, G., Kostopoulos, D. & Reischmann, T., 2007. *Geochemical constraints on the provenance and depositional setting of sedimentary rocks from the islads of Chios, Inousses and Psara, Aegean Sea, Greece: implications for the evolution of Palaeotethys.* Journal of the Geological Society, 164, 6, 1145–1163.

Oh, N.H. & Richter, D.D., 2005. *Elemental translocation and loss from three highly weathered soil–bedrock profiles in the southeastern United States.* Geoderma, 126, 1-2, 5-25.

Sipos, P., Németh, T., May, Z. & Szalai, Z., 2011. *Accumulation of trace elements in Fe-rich nodules in neutral - slightly alkaline floodplain soil.* Carpathian Journal of Earth and Environmental Sciences, 6, 1, 13-22.

Sipos, P., Németh, T., Kovács Kis, V. & Mohai, I., 2008. *Sorption of copper, zinc and lead on soil mineral phases*. Chemosphere, 73, 4, 461-469.

Velde, B. & Meunier, A., 2008. *The Development of Soils and Weathering Profile. In: The Origin of Clay Minerals in Soils and Weathered Rocks*. Springer-Verlag Berlin Heidelberg, 113-142.

Zhang, K.J., 2004. *Secular geochemical variations of the Lower Cretaceous siliciclastic rocks from central Tibet (China).* Earth and Planetary Science Letters, 229, 1-2, 73-89.

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