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EARLY PROCESSES IN SOIL FORMATION ON THE OLD DUMP FROM WESTERN VULCAN COALFIELD

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Abstract: The coal mining in Petroşani Basin (South Carpathians, Romania) led to build up of huge sterile dumps. Some of them were planted with *Hippöphae rhamnoides* (sea buckthorn). The dump mineralogy studied by X-ray diffractions and microscopy showed quartz, calcite, potassium feldspars, and biotite. Comparative investigations carried out on these samples show a random arrangement in the mineral particles in the areas devoid of small trees. In the other areas, the majority of the minerals – mainly calcite and biotite - are adsorbed on plant root surfaces. This fact is proved by the X-ray elementary fluorescence analysis, which points out a faint increase of Ca and Mg contents for the samples originating from root soil and a slow decrease of quartz content. The genesis activity of the sea buckthorn is observed in the higher content of Ca and lower content of Mg in fruits compared with the average standard value, documenting that the dump soil is richer in calcium than in magnesium. The presences of the ascorbic acid in sea buckthorn fruits revealed in the thin layer chromatogram in sufficient amount indicate relative normal plant synthetic activity of organic substances, but running relatively slow due to humus scantiness. For accelerating the formation of a fertile soil, it would be useful to distribute aqueous dispersion of manure, which would lead to faster humus formation, needed for faster growing of planted small trees.

Keywords: South Carpathians**,** Petroşani Basin, coal dumps, rehabilitation, sea buckthorn.

1. INTRODUCTION

The mining works are inducing sometimes significant damages to the native environment. Such dumps are usually located nearby the mining fields. If there is a large choice for potential dump fields, it is chosen the one inducing the smallest harm to the environment and lowermost costs for dumping (Onica, 2001; Tufescu & Tufescu, 1981). These kinds of soils are considered entiantrosols according to the current taxonomy (Florea & Munteanu 2003). The major damages induced by the coal dumps to the environment concern: distasteful views; losses of lands with fertile soil and vegetation; pollution of surface and underground water by chemical elements or only by solid particles in suspension trended from the dump by rainfalls or seepage waters; air pollution by gases stored into the dumps or originating from mineral oxidation; material damages and human losses, because of the dumps insecurity (Fodor & Baican, 2001). Some of industrial landfill, such those affected to metallurgical industry, are very dangerous due to the heavy metal content (Damian, 2008; Damian et al., 2010). Some of mining dumps presents environmental risk due to heavy metals and acid leaks (Lacatusu, et al, 2009; Dragastan, et al, 2009; Horaicu, et al, 2010; Stumbea, 2010). The coal sterile dumps present low danger for heavy metal contamination due to their pedogenesis.

Petroşani Basin is among the sedimentary basins located in South Carpathians (Săndulescu, 1984) occurred after the Upper Cretaceous („Laramian”) tectogenesis. It is filled by Paleogene and Miocene (Givulescu, 1996) molasses. It was and still remains an illustrative area for the coal mining in Romania. Among the coalfields, Vulcan is a main one.

The basin basement refers to various metamorphic rocks belonging to the Danubian Units and Getic Nappe (Săndulescu, 1984). There are found several formations containing clays, marls, and oil shale corresponding to three stages: first stage Rupelian (Moisescu, 1980), second stage Egerian (Givulescu, 1996; Pop, 1993), and the third stage late Chattian (Rebrişoreanu et al., 2002; Belkin et al. 2010).

The Quaternary is largely exposed, hiding the underlying deposits. It concerns terraces, alluvia, and debris fans. On its western side the Petroşani Basin stress out an asymmetric syncline. There, the coal bearing layers are NV-SE, N-S, or NE-SV trended (Givulescu, 1996).

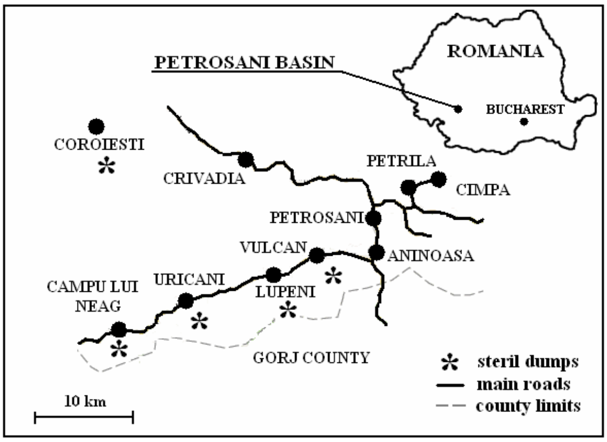

Figure 1. The map of main sterile dump placed in Petroşani Basin.

Coal dump Shaft 7 from Vulcan mine located on Berghii Hill, on the left bank of Crivadia Valley, has a surface of 13.38 ha (Fig. 1). The Eastern side of the dump is covered by sea buckthorn, planted as result of agreement between Jiu Valley National Pit Coal Company (CNH) and National Institute for Research and Development in Mine Safety and Protection to Explosion (INSEMEX) (Givulescu, 1996). The Western side of the dump is covered on 10% with spontaneous plants, as *Populus tremula* and *Crataegus monogina*. The dump is made-up by clay, marl, sandstone, conglomerate, and bituminous shale, mined from the Dâlja-Uricani Formation (Moisescu, 1980; Rebrişoreanu et al., 2002).

There are two mineral sources that could compete in controlling the plant life system on the dump surface: the minerals issued from sterile rocks (dominant) and any others issued from the accompanying elements in the coal mass.

The aim of this study is to clear up the mutual action between the sterile dumped and the sea buckthorn planted on dump surfaces, in order to outline the new fertile soil genesis, a soil more fertile than the primary one.

2. METHOD

The study carried on the soil samples originating from the sterile dump Shaft 7 Vulcan were made using IOR 8 optical microscope (reflected light), with Samsung 8MP digital capture.

X-ray diffraction analyses, using DRON 3 diffractometer with data acquisition module and Matmec VI.0 software were used for mineralogy. The results issued from X-ray diffraction were confirmed by the optical microscopy inspection in polarized light, using Karl Zeiss Jena mineralogical microscope. The soil sample quantitative elements analyses were made by X-ray spectrometry.

The sea buckthorn fruits were collected in the first half of September 2009 from the Vulcan coal dump, to highlight the influence of constituent minerals from sterile dump on the plants. To determine the calcium it was used as indicator Murexid, and for magnesium, Eriocrom T. The ascorbic acid was pointed out by thin layer chromatography using a silica gel chromatographic plate with a 254 µm fluorescence marker.

3. RESULTS AND DISCUSSIONS

Sea buckthorn grows in harsh soils, so it fits for stabilizing the acclivity of sterile dumps (Pilon & Pilon, 2002; Van Aken, 2008). Therefore, it is an intimate connection between soil composition and oligo-elements, and with the essential components hosted into the various structures of plants.

On this ground, several microscopic investigations on sterile soil samples originating from the West dump side had been done, in an area devoid of small trees (Fig. 2a), and on soil samples issued from the small tree roots, planted on the Southwestern side (Fig. 2b).

Figure 2a points out fine soil particles packed in formations with average sizes between 50-70 µm. This morphology is consequence of relative humidity, due to increased rainfall in mountainous areas and longer winters, with heavy snowfall. Therefore, the water is acting as a surfactant between sterile particles forming a dense layer which induces the formation of larger aggregates. On this way, one may observe an equiaxial shape of the particles groupings with irregular shapes, but rounded edges. This particle distribution in the investigated area shows a crowded cluster aggregated under humidity control but bare of binder, fact observed by the presence of fine particles which have the tendency to scrape out the aggregates in areas where the sample start loosing the initial humidity.

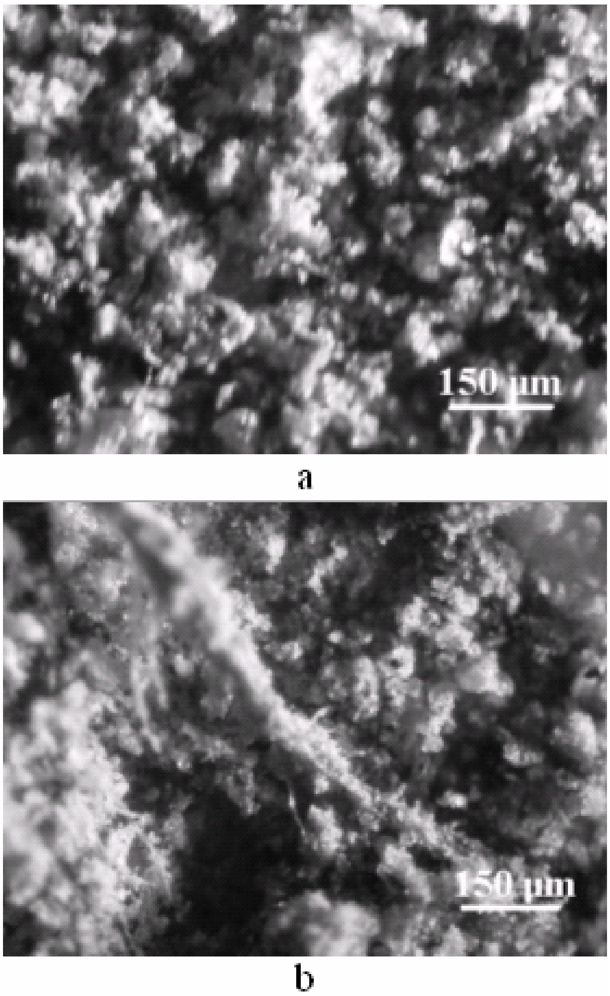

Figure 2. Optical dark field microphotographs: a) sample collected from the western coal dump side; b) sample collected from the southwestern side.

Morphology observed in figure 2a proves to be similar with clay, marl and argillaceous sandstone particles habitus reported by some authors (Arghir, 1986; Ianovici et al., 1980; Mastacan & Mastacan, 1976).

Figure 2b is illustrating a soil sample with sea buckthorn roots taken from Vulcan dump. This image points out the curly distribution of the roots into the ground layer, which had adsorbed on their surface powdery dump material particles with morphology similar to the one observed in Fig. 2a. This fact is high significant, because it testifies the relationship between the plant and dump soil.

Clays are complexes lamellar silicates which include mono-, bi- and trivalent various ions like Na^+, K^+, Ca^{2+}, Mg^{2+}, and Al^{3+}, which act as bond between pseudo-hexagonal shale of base layers. The water is able to infiltrate among these lamellas and in peculiar circumstances, it can change the physical and chemical structures of the clay lamellas (Arghir, 2000; Cordos et al., 2009). We assume that marl contains calcium-carbonated loosened particles which can be washed-out by the rainfall. Therefore, the sea buckthorn roots are spread in Vulcan dumps soil which contains fine particles aggregated in 50 µm diameter groups bounded by water.

The diffractograms (Figs. 3a and 3b) allow observe that the samples from the Vulcan sterile dump have a strong crystalline pattern. One can point out that the diffractograms have alike results for both analyzed samples, indicating crystalline structural uniformity of the Vulcan soil dump.

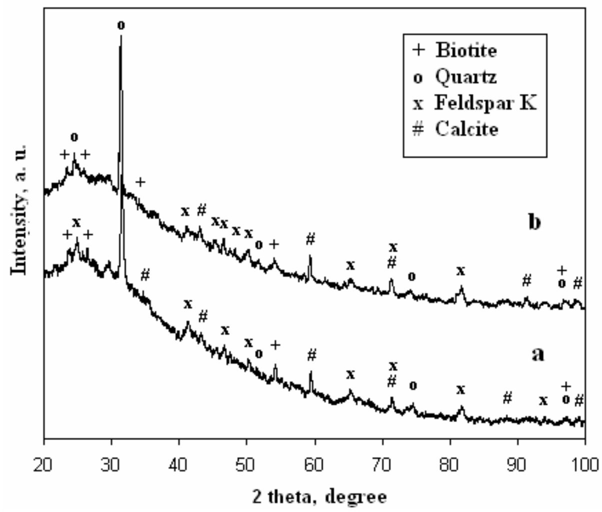

Figure 3. X ray spectra for Vulcan sterile dump soil: a) sample collected from the Western side; b) sample collected from Southwestern side.

The following constituent minerals were identified using X-ray diffraction and optical microscopy: quartz – SiO_2: hexagonal crystallization, crystallographic parameters: a = 4.903 Å, c = 5.393 Å the elementary cell volume 112.28 Å^3 (Match 01-0649, 2003); calcite – $CaCO_3$: rhombohedra crystallization, crystallographic parameters a = 4.983 Å, c = 17.019 Å, elementary cell volume 365.97 Å^3 (Match 01-0837, 2003); feldspar K – $K(AlSi_3O_8)$: crystallization in monoclinic system, crystallographic parameters: a = 8.544 Å, b = 12.998, Å c = 7.181 Å, β = 116.16 º, elementary cell volume 715.8 Å^3 (Match 89-8572, 2003); biotite - chemical formula $H_4K_2Mg_6Al_2Si_6O_{24}$, crystallization in monoclinic system, crystallographic parameters: a = 5.3 Å, b = 9.21 Å, c = 10.16 Å, β = 99.5 º, elementary cell volume 489.14 Å^3 (Match 02-0057, 2003).

The minerals pointed out by the X-ray diffraction are structural constituents of sandstone and marl. Highlighting these minerals as structural components allows the fruition of direct connection with the soil formation under the action of sea buckthorn roots in wet environment. Since quartz 101 represents the maximum intensity of 100 % in both diffraction spectra and the other maxima do not exceed 50 % in intensity it may be estimated that the quartz content in Vulcan sterile dump is about 50 %.

The calcium carbonate occurs as calcite. The maximum of calcite presented in figure 3 show its abundance, after quartz. In the presence of water and peculiar conditions, the calcium carbonate can be a powerful source of mineralization, raising the possibility to be relatively integrated by the growing vegetation on one landfill areas. Complex silicates such as potassium feldspar and biotite were also identified. The last one often has a reddish brown color, obvious in sterile samples. Biotite is a mineral which contains 6 Mg ions in each elementary cell. Allowing for the water has a disaggregating action on argillaceous particles in certain conditions it may cross the crystallization plane.

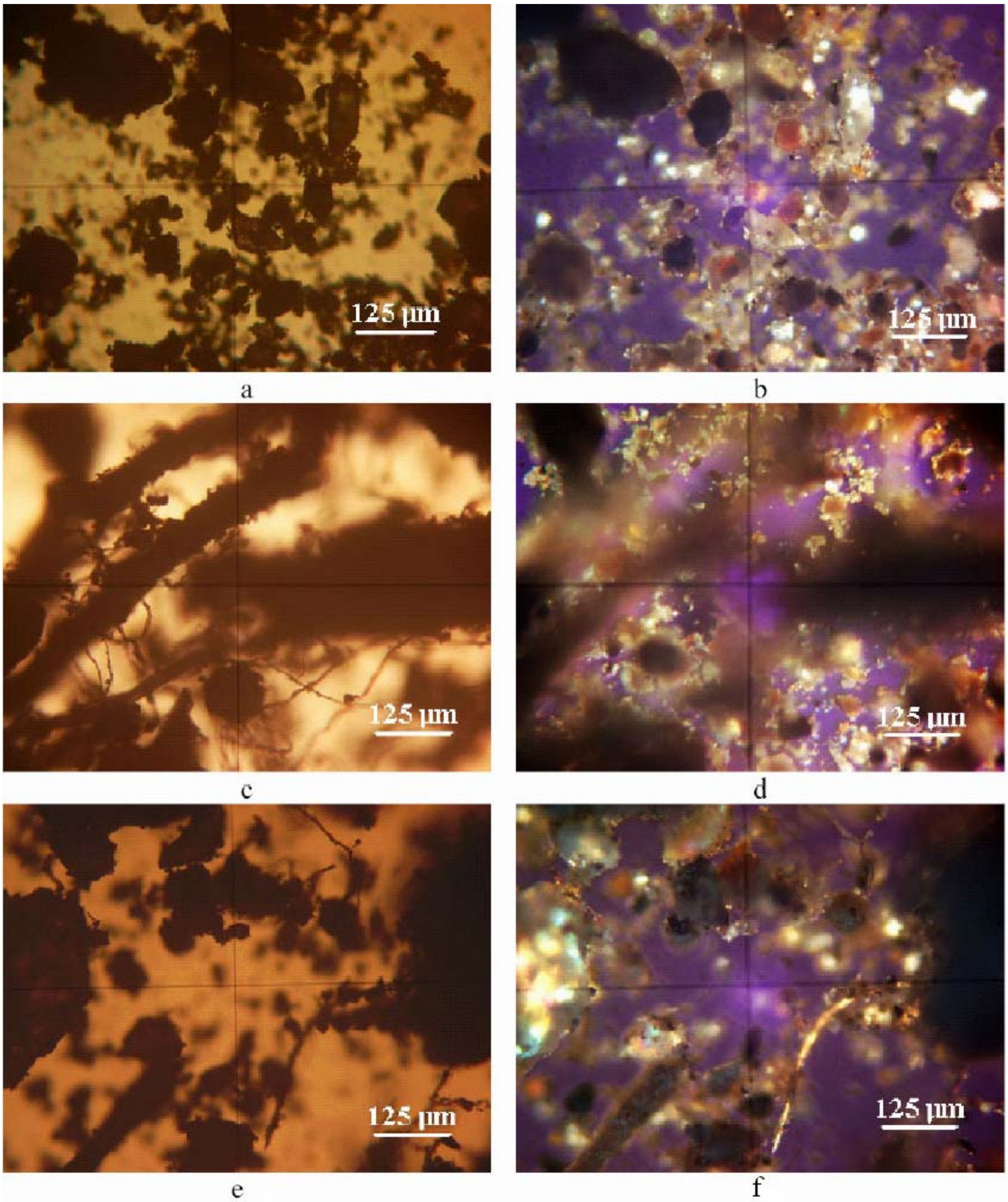

Figure 4. Optical transmission microphotographs and correspondent crossed polarized light for: a, b) soil sample collected from the Western dump side; c, d) Southwestern soil sample with *Hippöphae* roots embedding solid particles; e, f) Southwestern soil sample with fine roots, with adsorbed on surface minerals.

This stimulating effect of relative humidity issued from precipitations leads to magnesium ion source that could also be assimilated by vegetation in dump areas.

Mineralogical study by optical microscopy in transmitted and cross polarized lights (Fig. 4), highlights the interaction between dumps minerals and sea buckthorn roots. In Fig. 4a one may observe the soil particles distribution from the dump area devoid of plants with morphology and pattern similar to the observed one in figure 2a. The behavior concerning the particles shape and dimensions observed by these two different microscopic methods it is in good agreement.

The figure 4b exposes a cross polarized light image showing the mineralogical composition as follows: greenish grey particles are quartz, open white ones the potassium feldspar, red concern biotite and pale yellow are calcite. One can observe their random arrangement in the field sample.

Table.1. Main chemical elements in the soil sample from western dump area

Element	Si	Al	Fe	Ca	K
Content [%]	46.9	20.6	15.8	6.09	5.80
Element	Mg	Ni	Zn	Cu	Pb
Content [%]	1.03	0.06	0.06	0.06	0.02

The elemental composition of the soil sample from the Western side of the dump, determined by X-ray fluorescence, agrees with observations in figures 4a and 4b, the major components are silicium, followed by aluminum, (Table 1). Silicium is the base for quartz but combined with aluminium and potassium forms potassium feldspar. The significant content of calcium and potassium is due to the major presence of calcite and biotite in the soil mineralogical compositions.

Figure 4c feature a peculiar important aspect in understanding soil-plant interaction characterized by the spatial arrangement of the main sea buckthorn roots with the secondary ramifications. In cross polarized light (Fig. 4d), one may observe that these roots adsorbed mineral particles from soil, especially calcite and biotite, lesser quartz and feldspar. The average size of these particles shown ranges from a few micrometers to about 50 µm, fitting with sizes and morphology shown in figure 2b. This preferred orientation obviously points out a peculiar distribution in accordance with the exigency of small trees for samples tapped from their roots (southwest area of landfill). More detailed observations were made in figure 4e, (where are pointed out typical soil particles specific to dumps with small trees which have very thin roots). Spectacular appearance occurs in figure 4f, where fine root in figure 4e is strongly colored in orange areas alternating with yellow ones, highlighted with a light extinction by rotation of optical microscope axis. Normally the root as organic medium should appear dark in polarized light. The presence of pleochroism extinction specific to biotite, alternating with areas colored specifically to calcite, is indicating an adsorption of such very fine particles directly on the fine microscopic ramifications of the roots.

The situation may be observed from the results of the elemental X-ray fluorescent analysis made on the sample collected from small tree roots (Southwestern area, Table 2), where one can see small decrease of silicium and aluminum contents corroborate with major increase of calcium, magnesium and iron contents. Iron is pointed out in the chemical analysis but not in the mineralogical one. Hereby, the iron presence in the sterile may be from the iron oxides in the residual coal dust or from iron ions in argillaceous minerals lamellas or feldspar. These oligo-elements are very important in plant growth: calcium interferes in middle layer of cell wall formation (it has a critical role in preserving the integrity of cell membranes); magnesium with iron content is part of the chlorophyll molecule.

Table 2. Main chemical elements in soil sample from Southwestern dump area

Element	Si	Al	Fe	Ca	K
Content [%]	45.4	191	18.7	6.44	5.67
Element	Mg	Ni	Zn	Cu	Pb
Content [%]	1.19	0.07	0.06	0.06	0.01

Hence a differential segregation is highlighted between calcite particles and biotite ones in soil samples from the small tree roots as result of their bio-formatting action. Therefore, interest disaggregated mineral particles in the presence of water supplies oligo-elements ions to the plant needed for vital functions. These are adsorbed by the roots once with water forming raw sap. In the leaves, raw sap is turned into sap drown (through photosynthesis process). Plant development requires also the integration of adsorbed mineral elements in cell structure along with organic reserves integrated. As to the relationship between soil mineral particles and plant, the most important elements are calcium and magnesium due to effect in plant development and also for potential use of plant fruit for healing.

Chemical determinations were made on calcium and magnesium contents of the fruits of sea buckthorn from Vulcan Mine Shaft 7 West, Fig. 5. Three analyses in same conditions for each element had been considered, resulting in final sample average value. Figure 5a shows that the average calcium content ranges above the average medical use reference, and figure 5b the value of magnesium below the specific average.

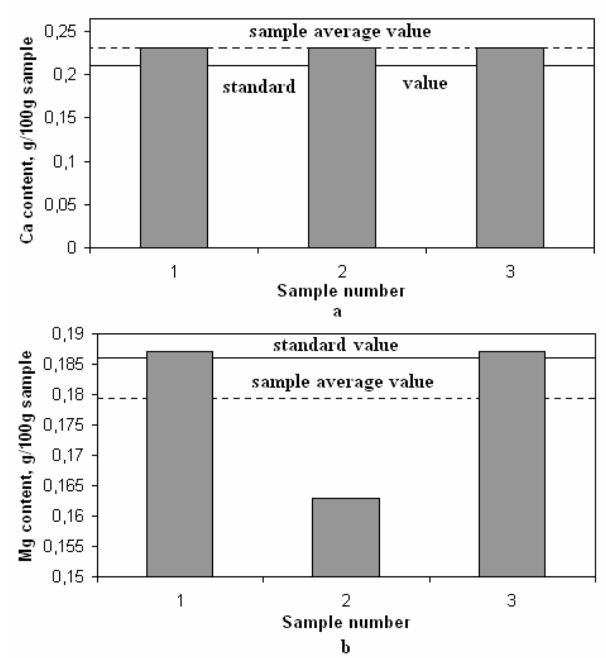

Figure 5. Ca and Mg content variations in fruits compared with standard values

Chemical analysis results of calcium and magnesium in sea buckthorn fruits collected from the dump are directly correlated with the mineral content of the particles pointed out by mineralogical analysis originating from the soil samples from roots. This correlation lies in the richer mineral sources in calcium, calcite being located second from the point of view as quartz and poorer in magnesium sources due to the presence of biotite relatively in small quantities. Hereby the sea buckthorn roots show a tendency to concentrate the useful mineral particles around them on expense biological inert ones.

Small sea buckthorns trees synthesize organic compounds found in plant and also in fruits. One of these important compounds is the ascorbic acid. Therefore, in Fig. 6 one can observe the specific spot for ascorbic acid (middle colon), spot with same location and intensity both in sea buckthorn culture and sterile dump samples. This shows that the sea buckthorn small trees were able to synthesize enough ascorbic acid, so that the spot features are shown in a similar manner to the standard.

This fact indicates a lack of synthesis of organic compounds compared to plants grown in fertile soil. This is explained by the fact that the plant is working to fix that soil and bring it to fertilization stage. Fertile soil is made besides useful material particles and by an organic binder called humus, the result of rotting and desegregation of leaves and fruits fallen on the soil mediated by the humidity in the constituent soil particles. In this case the primary soil lacks humus and the organic products of initial sea buckthorn products (leaves, fruits) were integrated into the forming stage of humus after the first autumn/winter turnover. Hereby leaf-litters first rot ensure first mass of organic material that comes to bind the preferential mineral particles arranged under roots section.

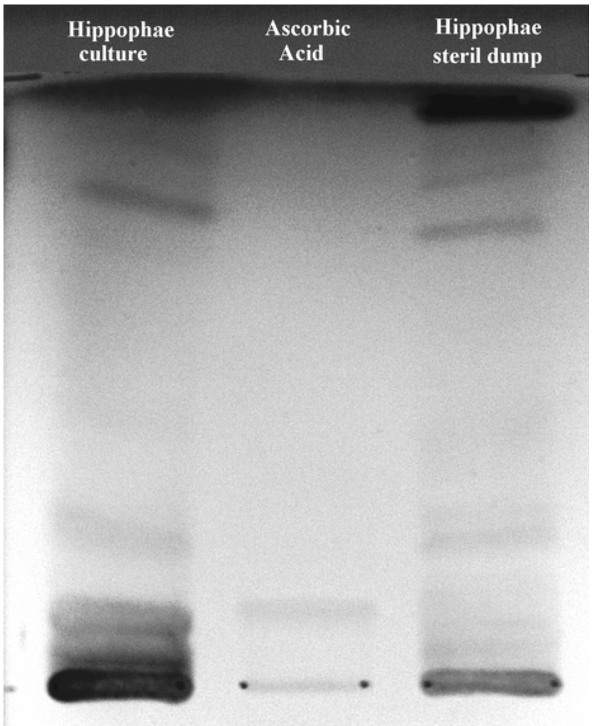

Figure 6. Thin layer chromatography for *Hippöphae rhamnoides* culture, Ascorbic acid standard and a *Hippöphae rhamnoides* grown on the sterile dump (Southwestern region).

The determinations made in this work show in figures 4c and 4d some particle agglomeration which in polarized light appears on dark background, this represents the tendency of humus layer genesis. Therefore, it is obvious the tendency of natural forming of fertile and fixed soil in the planted dump area, compared to the one devoid of plants where soil is infertile.

Given the slow formation process of vegetable humus just by cycling the organic material coming from the existing plants, one can estimate a longer time for the ecological rehabilitation of a planted dump area. The soil formation process can be increased by lying successive strata of animal waste aqueous dispersion (e.g. specific waste product from cattle farms). Some studies uses earth worms for a quick solification of such entiantrosoils (Atyeh et al., 2002). This distribution of natural manure besides being totally organic, allow proper feeding of the plant by the addition of organic matter rough-wrought, which automatically lead to better plant development and the formation of a soil faster, which may soon be covered with greenery.

Elemental analysis performed on soil samples from Vulcan dump Shaft 7 West show low contents of heavy metals such as Ni, Zn, Cu, and Pb, (Tables 1 and 2). Hereby, the underbrush fruits can be used as medical herbs too. The fact may be particularly beneficial justifying mildly the manure fertilization treatment on planted soil areas.

4. CONCLUSIONS

The mineralogical observation indicates preferred orientation of particles of calcite and biotite in the proximal roots area at the expense of neutral biologically particles. This is supported by X-ray fluorescence elemental analysis showing a relative increase of Ca and Mg content for soil samples from root correlated with a decrease in quartz content. The, sea buckthorn roots have an active influence on the arrangement of particles in soil samples, which in the soil samples form areas devoid of plants, occur randomly arranged. Leave-litters during winter are source of organic matter that rots in moist environments, leading to formation of microscopic areas of humus.

Soil-forming activity of sea buckthorn is observed in higher content of Ca and lower of Mg in fruits compared with the average standard value, fully reflecting the facts, sterile soil are much richer in calcium than magnesium. The presence of ascorbic acid in sea buckthorn fruits on the thin layer chromatogram in sufficient amount indicates a synthetic activity of organic substances in the plant relatively normal but relatively slows due to deficiency of humus. To accelerate the formation of a fertile soil would be useful to spread near the sea buckthorn roots an aqueous dispersion of manure.

Elemental analysis shows that the content of the heavy metals in dumps material is low; therefore, the sea buckthorn fruit resulted could be used as medicinal herbs. This aspect may be one more reason to fertilize dump soils and extend the planted areas.

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