International Journal of Innovative Studies in Sciences and Engineering Technology (IJISSET)

ISSN 2455-4863 (Online) www.ijisset.org Volume: 2 Issue: 7 | July 2016

# Mineral composition of soils formed on massive limestone of Pivska Planina

Raičević Petar[1], Tomić Zorica[1], Vasin Jovica[2], Jakšić Snežana[2], Đorđević Aleksandar[1]

[1] Department of Soil Management, Faculty of Agriculture, University of Belgrade, Serbia

[2] Laboratory for Soil and Agroecology, Institute of Fields and Vegetable Crops, Novi Sad, Serbia

**Abstract:** *Research paper presents the results concerning the study of mineral composition in the geological substrate, insoluble residue, and calcomelanosol (Mollic Leptosols) and calcocambisol (Cambisols) soils in the region of Pivska planina, Republic of Montenegro. Forty pedological profiles were examined and identification of soil systematic categories was performed at 14 locations. Two profiles were selected among the most widespread calcomelanosol and calcocambisol soil types (26 Barni Do and 29 Babići). Besides the basic analyses, the research also included the examination of mineral composition of the geological substrate (carbonate rocks), mineral composition of insoluble residue, and particularly mineral composition of mechanical fractions of soil (sand, silt, and clay). Mineral composition was determined using Philips PW 1710 automated powder diffractometer.*

**Keywords:** *calcomelanosol, calcocambisol, kaolinite, vermiculites, Republic of Montenegro*

## 1. INTRODUCTION

Montenegro is mainly characterized by the hilly and mountainous terrain and steep slopes of the land. Carbonate rocks are the most widespread geological substrates in Montenegro (about 80% of the total territory), where mostly calcomelanosol and calcocambisol soil types are formed (Fuštić, 2000).

Calcomelanosol is the first evolutionary phase of soil formation on limestone and dolomites (Đorđević, 1993). Profile texture is Ah-C and belongs to the class of automorphic and humus-accumulative soils, according to the national classification. These soils are characterized by very specific genesis. The most important natural pedogenetic processes in calcomelanosol soil type are: dissolution and leaching of earth-alkali carbonates, slow mineralization and accumulation of organic matter, and quite strongly expressed denundation processes. Unlike other types of soil, minerals in calcomelanosol soil type are formed in the insoluble residue i.e. residuum, and not in the basic mineral mass of rocks i.e. calcite (dolomite).

Calcocambisol is the second evolutionary phase of soil formation on calcareous rocks. Profile texture is Ah - (B) rz - C and, according to the national classification, it belongs to the class of automorphic and cambic soils. Pedogenesis is similar to the calcomelanosol soil type, with difference in the formation of (B)rz horizon.

The bulk of minerals in this soil also originates from the insoluble residue – residuum.

Very few data are present in research literature concerning the mineral composition of insoluble residue in the carbonate substrate and the soils which were formed on it.

The aim of this study was to review the mineral composition of insoluble residue of carbonate rocks and the soils formed on its surface, at the mountain Pivska Planina in Montenegro, in order to confirm the abovementioned theoretical considerations on the formation of soils on carbonate rocks.

## 2. MATERIALS AND METHODS

Forty pedological profiles were opened at 14 locations on Pivska Planina. Two profiles were selected among the most wiseapread calcomelanosol (soil profile 29 Babići) and calcocambisol soils (26 Barni Do). The main physical and chemical characteristics were examined using standard methods.

Mechanical fractions of sand and silt were separated by wet sieving, while decantation method was used for the mechanical clay fraction.

Survey was conducted using Philips PW 1710 automated powder diffractometer. Diffractograms (diagrams) were obtained by CuKα radiation, using copper anticatodes with the value of the wavelength $\lambda = 1.54184$ Å generated in an X-ray tube, under current I=30 mA, with tube operating voltage U=40 kV. Diffracted radiation was registered with a scintillation counter, and electronic test equipment was used to determine the measurement of intensity. Mechanical fractions of sand and silt were recorded in the range 2Θ from 3 to 60 °, with a step 0.025 °, and retention period of 0.5 s (0.02 ° / 0.5 s). Mechanical clay fraction was recorded in the range of 3–15 ° 2Θ, with a step 0.02 ° / 0.5 s, as an oriented sample, air-dried (AD), saturated with ethylene glycol (EG), or annealed at 550 ˚C (550 ˚C). Insoluble residue was determined by treating geological substrate with cold 10% HCl during 24 hours. Diffraction profiles and semiquantitative analysis were analyzed by DRXWin 1.4 software.

## 3. RESULTS AND DISCUSSION

The examined soil profiles 29 Babići and 26 Barni Do exhibited differences between the mineral composition of their geological substrate and insoluble residue, observed in the content of quartz, mica, and secondary phyllosilicates.

Pedogenesis on carbonate geological substrate was significantly different than soil formation on silicate rocks (Sedov et al., 2008).

### 3.1 Geological Substrate and Insoluble Residue

Geological substrate of the soil profile 26 Barni Do, (Figure 1a) chiefly consists of the same content: 42% calcite (3.85, 3.03, 2.49, 2.28, 2.09, 1.91,... Å) and 40% $MgCO_3$ (3.69, 2.88, 2.67, 2.40, 2.19, 2.01, 1.80,...Å), with a significantly lower content of feldspar (about 7% ) and phyllosilicates (about 8%) (Table 1). The insoluble residue of soil in the profile 26 Barni Do (Figure 2a) had the high content of phyllosilicates, quartz and dolomite, lower content of feldspar, and the lowest content of hematite (Table 1). Presence of dolomite in insoluble residue comes, most likely, from the use of cold 10% HCl. We did not use hot 1:1 HCl in order not to deteriorate structure of some minerals (Fe).

Geological substrate of soil profile 29 Babići (Figure 1b) contains 84% calcite (C) (3.85, 3.03, 2.49, 2.28, 2.09, 1.92, 1.87 Å) and about 11% phyllosilicates (10.0, 5.16), minimum content of dolomite (D) (2.88, 2.01 Å) and feldspar (or) (3.31, 3.29 Å) Unlike geological substrate, the insoluble residue (Table 1) had an increased content of quartz, feldspar and phyllosilicates (Figure 2b).

The degree of dissolution of calcite and dolomite is very similar. Both minerals dissolve very quickly in comparison to silicate minerals. However, the degree of dissolution of calcite is 5 times larger than that of dolomite (Stumm and Morgan, 1996). This probably explains the differences in carbonate dissolution between the geological substrate of 29 Babići and 26 Barni Do, as well as differences in the content of calcite and dolomite between the geological substrate and the insoluble residue of soil samples 29 Babići and 26 Barni Do. Quartz content was evident in the insoluble residue of both soil profiles.

### 3.2 Mechanical Fractions of Sand and Silt

The dominant minerals of the mechanical fraction of sand in soil profile 26 Barni Do (Figure 3a) were quartz, phyllosilicates (muscovite), K-feldspar (orthoclase), and hematite (Table 2). Amo horizon of the mechanical fraction of sand in soil profile 29 Babići (Figure 3b) consisted mostly of quartz, muscovite, and feldspar, while the content of hematite was lower (Table 2). (B)rz horizon had a slightly lower content of quartz, feldspar, and muscovite, compared to the Amo horizon, while the content of phyllosilicates increased. According to research literature, two reasons cause this behaviour. The first reason is the dissolution of carbonate, which leads to an increase in insoluble minerals and therefore increases quartz and muscovite content (Egli et al., 2008), and the second is deposition of material by wind which lead to concentration of quartz and mica in Amo horizon (Egli et al., 2008).

Mechanical fraction of silt in soil profile 29 Babići (Figure 3b) consisted of the same minerals as the mechanical fraction of sand, only their prevalency, i.e. their participation was different. Illite was the dominant mineral of silt fraction in Amo and (B)rz horizon of soil profile 29 Babići. There was a significant increase of phyllosilicates (76%) in (B)rz horizon, while quartz and feldspar are decreased (Table 2).

Silt particles are typically present in the atmosphere of Eastern Mediterranean, while the soils formed in these areas were certainly complemented with the particles from the deserts of North Africa, as indicated by many authors (Muhs et al., 2010; Macleod, 1980).

The content of Fe oxides and hydroxides (goethite and hematite), as well as minor amounts of boehmite, increased in the silt fraction. There was a sharp reduction in the same fraction of the content of quartz and feldspar, muscovite transformation to illite, and increase in the total content of illite and other phyllosilicates. In addition, there was an increase in hematite / goethite and boehmite / gibbsite, compared to the sand fraction.

Concerning the relationship between the individual minerals, there was a directly proportional relationship between quartz content (54% in Amo horizon and 48% in (B)rz horizon in the soil sample 29 Babići, and 56%

in 26 Barni Do) and the content of coarse particles, i.e. coarse sand (10.14 and 1.69% in 29 Babići, and 10.27% in 26 Barni Do) (Table 2 and 3).

### 3.3 Mechanical Clay Fraction

Mechanical clay fraction in soil profile 26 Barni Do (Figure 4a) is characterized by the reflection of 7.35 Å in the air-dried sample, which remained in the same position after saturation (7.19 Å) and collapsed after annealing, indicating the presence of kaolinite. The reflection moved from 14.80 Å of AD sample to 17.71 Å after saturation, and 10.44 Å after annealing, which indicates the presence of smectite. Another part of the same reflection (14.80 Å) remained in the same position after saturation (14.61 Å) or moved to 10.44 Å after annealing, thus indicating the presence of vermiculite. In addition to these minerals, a very small reflection was observed at 10.73 Å in the air-dried

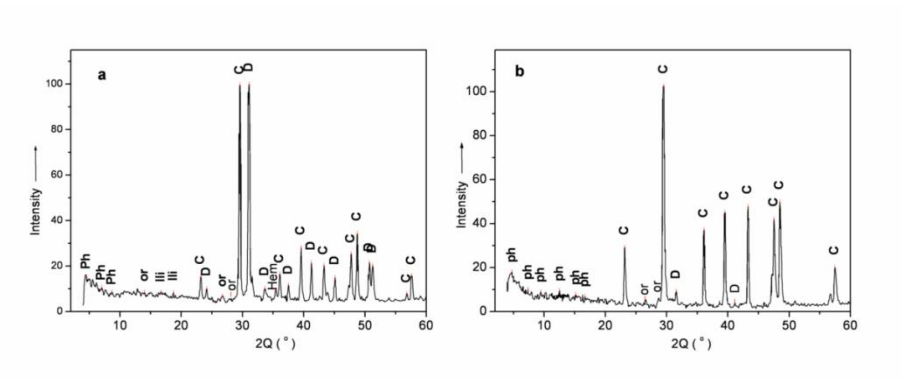


**Fig 1:** *X-ray diffractogram of the geological substrate in soil profiles 26 Barni Do (a) and 29 Babići (b).*

**Table 1:** *Mineral composition of geological substrate and residuum (%)*

| | 29 Babići N 43°16′34.6″ E 18°51′57.2″ | | 26 Barni Do N 43°15′42.1″ E 18°52′14.6″ | |
|---|---|---|---|---|
| Minerals | Geological substrate | Residium | Geological substrate | Residium |
| Quartz (Q) | / | 37 | / | 22 |
| Feldspar (Fl) | 3 | 10 | 7 | 10 |
| Phyllosilicates | 11 | 32 | 8 | 44 |
| Hematite/goethite | / | 7 | tr | 2 |
| Boehmite/gibbsite | / | 5 | / | 2 |
| Calcite | 84 | 2 | 42 | 1 |
| Dolomite ($CaCO_3 \cdot MgCO_3$) | 2 | 2 | 40 | 19 |

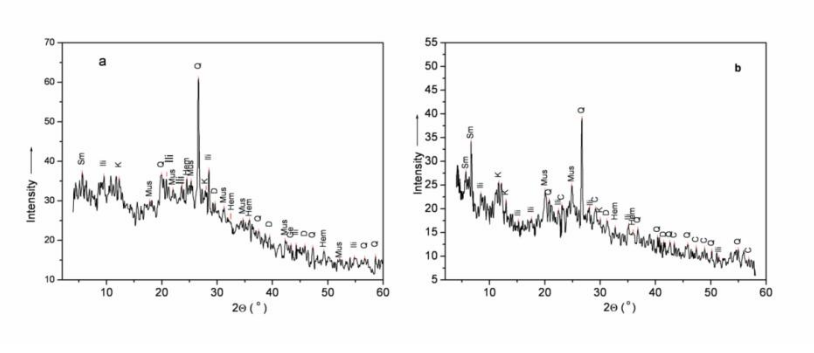


**Fig 2:** *X-ray diffractogram of residuum of geological substrate in soil profile 26 Barni Do (a) and 29 Babići (b)*

sample at the same position after saturation (10.87 Å) and after annealing (10:44 Å), which is in conformity with the low contents of illite. Part of the same reflection moved to 11.62 Å after annealing, which suggests low content of mixed-layer silicates (MLS).

Mechanical clay fraction of soil profile 29 Babići in Amo horizon (Figure 4b) of air-dried sample (AD), first order reflection, d(001), at 7.17 Å, after saturation with ethylene glycol, remained in the same position 7.20 Å, and collapsed after annealing at 550 ˚C, which indicates

ISSN 2455-4863 (Online) www.ijisset.org Volume: 2 Issue: 7 | July 2016

a significant content of kaolinite. Besides kaolinite, reflection in the air-dried sample (AD) also occurred at 14.23 Å, and remained in the same position after saturation (14.44 Å). On the other hand, the reflection split into two reflections after annealing, after which one part moved to 10.72 Å, indicating the presence of vermiculite, while the other part moved to 12.40 Å, indicating the presence of mixed-layer silicates (MLS).

(B)rz horizon of soil profile 29 Babići (Fig. 4c) reflection at 7.16 Å, of the air-dried sample, which remained in the same position after saturation (7.23 Å) but collapsed after annealing, thus indicating a significant content of kaolinite. The second most intense reflection was at 14.71 Å which split into two reflections after saturation. The first part of the reflection remained in the same position after saturation (14.8 Å) and split into two reflections after annealing, when one part moved to 10.19 Å, indicating the presence of vermiculite, and the other moved from 16.80 Å to 10.19 Å after annealing indicating lower content of smectite. Part of the reflection remained in its position after annealing 14.75 Å indicating lower content of chlorite.

In addition to kaolinite both soil profiles show contents of vermiculite, while insoluble residue of the geological substrate (limestone) does not contain vermiculite. Similar results were reported by Durn et al. (1999, 2001, 2003) while studying the red soils of Istria.

It is possible that the dissolution of mica leads to the release of K+, and calcite dissolution leads to the release of Ca2+. This is how the exchange from Ca2+ to K+ in the interlayer of clay is transformed into vermiculite (Bassett, 1959).

The dominant mineral of clay fraction is certainly kaolinite. Some authors explain the prevalence of kaolinite over illite rather by a geochemical transformation of kaolinite into illite than sedimentation, deposition, or materials from external sources (Moresi and Mongelli, 1988).

The content of smectite, vermiculite and mixed-layer silicates (MLS) in a mechanical clay fraction of soil profile 26 Barni Do exhibited the highest total adsorption capacity (T) 62.11 cmol/kg, while high content of kaolinite and low content of smectite and vermiculite in Amo horizon of soil profile Babići 29 exhibited lower general adsorption capacity (T) 35.06 cmol/kg (B)rz horizon of soil profile 29 Babići exhibited the lowest total adsorption capacity (T) 34.41 cmol/kg, because it is affected only by a low content of vermiculite and MLS (Table 3).

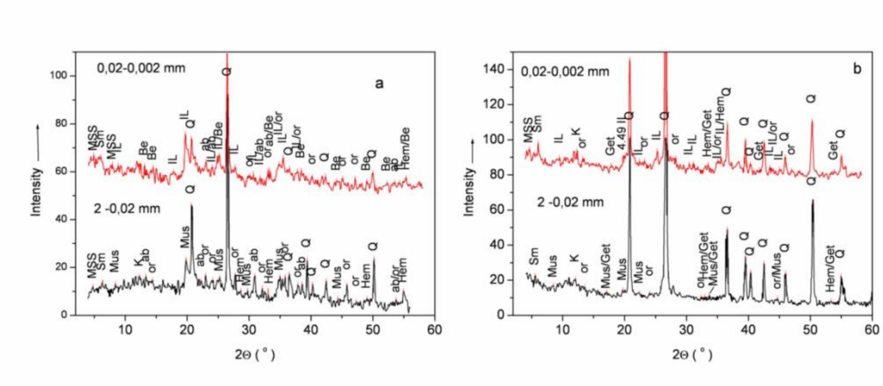


**Fig 3:** *Mechanical fractions of sand and silt in soil profile 26 Barni Do (a) and 29 Babići (b).*

**Table 2:** *Mineral composition of sand and silt mechanical fractions (%)*

| | 29 Babići | | | | 26 Barni Do | |
|---|---|---|---|---|---|---|
| | Amo (0-20 cm) | | (B)rz (20-47 cm) | | Amo (0-27 cm) | |
| **Minerals** | Sand | Silt | Sand | Silt | Sand | Silt |
| Quartz (Q) | 54 | 20 | 48 | 10 | 56 | 8 |
| Feldspar (Fl) | 16 | 10 | 13 | 8 | 6 | 10 |
| Phyllosilicates | 26 | 64 | 35 | 76 | 41 | 73 |
| Hematite/Goethite | 3 | 4 | 2 | 3 | 4 | 6 |
| Boehmite/Gibbsite | 1 | 2 | 2 | 3 | 1 | 3 |
| Calcite | / | / | / | / | | |
| Dolomite ($CaCO_3 \cdot MgCO_3$) | / | / | / | / | | |

**Table 3:** *Mechanical composition of soil and basic chemical properties*

| Mechanical composition of soil and MWHC (maximum water holding capacity) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Locality | | Depth (cm) | Coarse sand (%) | Fine sand (%) | Silt (%) | Clay (%) | MWHC (%) |
| 26 Barni Do | Amo | 0-27 | 10.27 | 24.45 | 38.28 | 27.0 | 58.18 |
| 29 Babići | Amo | 0-20 | 10.14 | 32.58 | 31.20 | 26.08 | 55.21 |
| | (B)rz | 20-47 | 1.69 | 11.55 | 8.76 | 78.0 | 54.71 |
| **Basic chemical properties** | | | | | | | |
| Locality | | pH in KCl | pH in $H_2O$ | $H^+$ (cmol/kg) | T-S (cmol/kg) | S (cmol/kg) | T (cmol/kg) |
| 26 Barni Do | Amo | 3.88 | 5.28 | 39.47 | 20.28 | 41.83 | 62.11 |
| 29 Babići | Amo | 4.62 | 5.85 | 21.09 | 13.48 | 21.58 | 35.06 |
| | (B)rz | 4.24 | 6.16 | 16.11 | 13.19 | 21.22 | 34.41 |

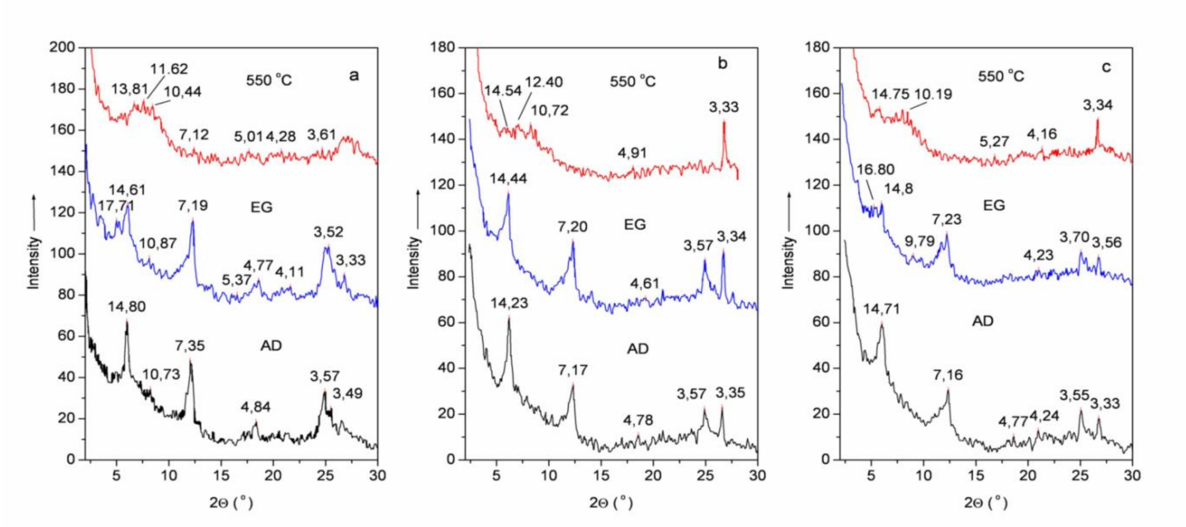


**Fig 4:** *X-ray diffractogram of mechanical clay fraction in soil profile 26 Barni Do (a) and profile 29 Babići (b-Amo, c-(B)rz horizon) (AD-air-dried sample, EG- saturated with ethylene-glycol, annealed at 550 °C - 550 °C).*

## 4. CONCLUSION

The The study of soil profiles (26 Barni Do and 29 Babići) described the differences in mineral composition between geological substrate and insoluble residue, and mineral composition of the mechanical fractions, such as content of quartz, and phyllosilicates. The content of quartz and mica decreased with depth in profile 29 Babići which indicates deflationary processes and their impact on the surface horizon. Kaolinite was the most widespread phyllosilicate in the mechanical clay fraction of both soil profiles, although the geological substrates differed in terms of contents of calcite and dolomite. Both soil profiles revealed the content of vermiculite, while insoluble residue of the geological substrate (limestone) did not contain vermiculite. Content of hematite and goethite was higher in the upper part of the profile (Amo horizon Babići 29) than in the lower, which is explained by deflationary processes.

The transformation of feldspar and the newly-formed minerals, such as kaolinite and hematite / goethite, are the typical components of a newly-formed soil which correspond to weather conditions of humid and sub-humid tropical climate. Changes in the fundamental and the newly-formed minerals (kaolinite and hematite / goethite) occur due to leaching in the top part of the profile 29 Babići (Amo horizon), which confirms the content of these minerals in the (B)rz horizon. This interpretation is consistent with the dominant presence of quartz in the sand fraction of the tested soil profile, since quartz is a more stable and more resistant mineral in comparison to other fundamental minerals.

Results of the chemical-mineralogical study leads us to the conclusion that the soil formed on carbonate rocks of Piva valley is partly autochthonous, having inherited its material from the geological substrate, and partly allochthonous, i.e. deposited from external sources, most likely in the form of silt and fine sand particles.

## REFERENCES

[1] Bassett W.A. (1959), "Origin of the vermiculite deposit at Libby, Montana". American Mineralogist, 44: 282-300.

[2] Đorđević A. (1993), "Genesis, classification and characteristics of the soil limestone massif of Rajac as the basis for their rational use". Belgrade, Serbia, Faculty of Agriculture, University of Belgrade.

[3] Durn G. (2003), "Terra Rossa in the Mediterranean Region: Parent Materials, Composition and Origin". Geologia Croatica, 56/1: 83–100.

[4] Durn, G., Ottner F., Slovenec D. (1999), "Mineralogical and geochemical indicators of the polygenetic nature of terra rossa in Istria, Croatia". Geoderma, 91: 125–150.

[5] Durn G., Slovenec D., Čović M. (2001), "Distribution of Iron and Manganese in Terra Rossa from Istria and its Genetic Implications". Geologia Croatica, 54/1: 27-36.

[6] Egli M., Merkli C., Sartori G., Mirabella A., Plötze M. (2008), "Weathering, mineralogical evolution and soil organic matter along a Holocene soil toposequence developed on carbonate-rich materials". Geomorphology, 97: 675–696.

[7] Fuštić B. (2000), "Soils of the Republic of Montenegro". Podgorica, Republic of Montenegro, Univerzitet Crne Gore, Biotehnički institut.

[8] Macleod D.A. (1980), "The origin of the red Mediterranean soils in Epirus, Greece". Journal of Soil Science, 31/1: 125–136.

[9] Markoski M. (2013), "Genesis and properties of soil formed upon lime stones and dolomites in the Republic of Macedonia". Skopje, Macedonia, Ss. Cyril and Methodius University in Skopje.

[10] Moresi M., Mongelli G. (1988), "The relation between the terra rossa and the carbonate-free residue of the underlaying limestones and dolostons in Apulia, Italy". Clay Minerals, 23: 439-446.

[11] Muhs D.R., Budahn J., Avila A., Skipp G., Freeman J., Patterson D.A. (2010), "The role of African dust in the formation of Quaternary soils on Mallorca, Spain and implications for the genesis of Red Mediterranean soils". Quaternary Science Reviews, 29: 2518–2543.

[12] Sedov S., Solleiro-Rebolledo E., Fedick S.L., Pi-Puig T., Vallejo-Gómez E, Flores-Delgadillo M. (2008) "Micromorphology of a Soil Catena in Yucatán: Pedogenesis and Geomorphological Processes in a Tropical Karst Landscape". In: Kapur S., Mermut A., Stoops G. (eds): New Trends in Soil Micromorphology. 1st ed. Heidelberg, Germany, Springer.

[13] Stumm W., Morgan J.J. (1996) "Aquatic chemistry". 3rd ed. New York, John Wiley and Sons, Inc.S. M. Metev and V. P. Veiko, *Laser Assisted Microtechnology*, 2nd ed., R. M. Osgood, Jr., Ed. Berlin, Germany: Springer-Verlag, 1998.