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**Humus state of Bulgarian Chernozems**

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*Abstract.* Content, composition and morphology of soil organic matter are important diagnostic indicators which provide valuable information in the study of soils and soil processes. Data for content and composition of soil organic matter from statistical profiles of subtypes of Chernozem are presented in the study. Micromorphological characteristics of studied soils are developed. Micromorphological indicators confirm the identified chemically - humus type and humic acids condensation.

*Keywords:* Chernozems, soil organic matter, humic acids, fulvic acids, micromorphology, humons.

**Гумусное состояние черноземов Болгарии**
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*Аннотация.* Содержание, состав и морфология органического вещества почвы являются важными диагностическими показателями, которые дают ценную информацию при изучении почв и почвенных процессов. Представлены данные по содержанию и составу органического вещества из статистических профилей подтипов черноземов. Получены микроморфологические характеристики изученных почв. Микроморфологические индикаторы подтверждают идентифицированные тип гумуса и содержание гуминовых кислот. Микроморфологическое исследование позволило определить основные диагностические критерии, характеризующие состояние почвенного органического вещества с целью оценки количества и степени превращения органических остатков, активности почвенной биоты, количества и состояния гуминовой плазмы. Результаты показали, что процессы биогенного накопления являются основными и форматирующими процессами. Процесс гумификации проходит с высокой интенсивностью до очень глубокого уровня и определяет темный цвет коагулированного гумуса или локально концентрированный стабильный гумус. Как следствие этого преобладание гуминовых кислот над фульвокислотами, высокая степень конденсации и ароматизации гуминовых кислот, что в свою очередь создает предпосылки благоприятных физико-химических условий в этих почвах.

*Ключевые слова*: черноземы, почвенное органическое вещество, гуминовые кислоты, фульвокислоты, микроморфология, гумоны.

**Introduction**

Organic matter in soil, its content, composition and morphology are important diagnostic features, which are valuable information on the study of soils and soil processes. Information on humus state is base for studies on soil genesis, soil monitoring and in developing strategies for agriculture, soil conservation and fertility, and sustainable land management.

Moreover, information on soil organic matter can be obtained not only chemically [23, 26], but by morphological characteristics, applying micromorphological study in thin soils sections. The micromorphological method allows studying the current status, internal organization and profiling distribution of soil organic matter. [12, 15]. It expands and enriches indicative possibilities for diagnosis of biogenic processes, evaluation of their intensity and determination of their place in the soil profile.

This study aims to generalize the existent information of the humus state of subtypes of Chernozems.

**2. Objects and Methods**

Data on the content and composition of soil organic matter (SOM) were submitted from summarized representative soil profiles of Chernozems' subtypes [7—9].

SOM composition was determined by the method of Kononova-Belchikova [23, 10]. The following parameters are presented: a) Content of total organic carbon (TOC) in the alkali extract (extraction with mixed solution of 0.1M $Na_4P_2O_7$ and 0.1 M NaOH); b) Content of organic carbon (OC) in HAs (Ch) and FAs (Cf), "free" and bounded with $R_2O_3$, after extraction with 0.1 M NaOH and c) the most dynamic, low molecular fraction of SOM, so-called "aggressive" FAs fraction, extracted with 0.05 M $H_2SO_4$.

Optical characteristics $E_4/E_6$ show the degree of condensation and aromatization of HAs measuring their extinction at λ 465 и 665 nm.

Preparation of soils thin sections of representative soil samples were made in the Laboratory of "Soil Micromorphology", Institute of Soil Science, Agrotechnology and Plant Protection "Nicola Poushkarov", Sofia. Micromorphological observation is carried out of soils thin sections using microscope "Amplival" with integrated camera "ProgRes" (Project SoilTrEC – FP7 Cooperative Work Programme, 2009). Micromorphological way to diagnose soil organic phase is to establish the presence, quantity and degree of transformation of several important markers: plant residues – plant tissues, plant cells etc.; faecal material – the various types of excrements, produced by soil fauna; microorganisms – fungal form - hyphaes and/or spores; diatoms, phytoliths, molluscs; humus (humus plasma) – clay-size organic matter that may exist separately or intimately associated with the clay fraction; humons – the smallest particles of dark coloured humus [28, 29, 11].

Data on the physicochemical characterization of representative Chernozems profiles are presented. The profiles are part of a soil study under a project funded by the European Social Fund. The methodology is described in a manual issue [32]. The comparison is made the both subtypes of Chernozems – Vertic and Haplic. The samples are prepared by standard protocol [5] and follow physicochemical characteristics are determined: pH [18], CEC [4], distribution of particle size [19].

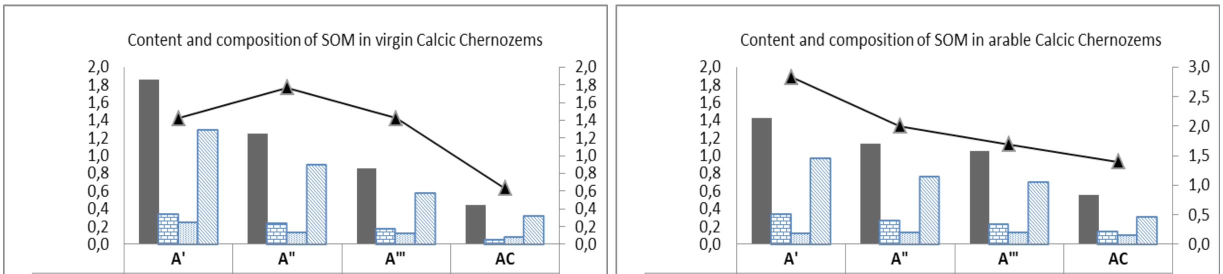
## 3. Results and Discussion

### 3.1. Calcic Chernozems

Chernozems occupied around 2 300 000 ha, which is 21 % of the total area of the country [20]. Calcic and Haplic Chernozems covered 830 000 ha which is 36% of Chernozems area. Soil formation processes in these soils, as well as in all Chernozems, determined relatively good conditions for humus formation and its accumulation. These processes in Bulgarian Chernozems are expressed significantly less compared to classical Chernozem zone of Russia. Virgin Calcic Chernozems, pastures used are characterized by relatively high humus content in the upper humus-accumulation horizon. Humus content is from 3.5 to 5% by gradually reducing along the profile depth of its content on 90 cm, it's about 1.0% [7—9].

The type of humus is humic to fulvic-humic around the profile depth. The degree of humification (Ch/Ct)x100 is high throughout the soil profile. HAs are bound with calcium and ratio $E_4$: $E_6$ presents a high degree of condensation, "free" and bind with mobile forms of $R_2O_3$ HAs absent in the entire depth of the profile. The content of an aggressive faction of FAs, extracted with 0.1 n $H_2SO_4$ is negligible.

Features of generalized profiles of Calcic Chernozems virgin and arable are presented in Figures 1. The data show a gradual decrease in the humus content along the profile depth and confirmed by other authors obtained results about the influence of the type of land use [7—9].




| | A' | A'' | A''' | AC |
|---|---|---|---|---|
| Ct,% | 1,86 | 1,25 | 0,86 | 0,44 |
| Ch,% | 0,34 | 0,23 | 0,17 | 0,05 |
| Cf, % | 0,24 | 0,13 | 0,12 | 0,08 |
| Cres,% | 1,29 | 0,89 | 0,57 | 0,32 |
| Ch/Cf | 1,42 | 1,77 | 1,42 | 0,63 |

| | A' | A'' | A''' | AC |
|---|---|---|---|---|
| Ct,% | 1,42 | 1,14 | 1,05 | 0,56 |
| Ch,% | 0,34 | 0,26 | 0,22 | 0,14 |
| Cf, % | 0,12 | 0,13 | 0,13 | 0,10 |
| Cres,% | 0,97 | 0,76 | 0,70 | 0,31 |
| Ch/Cf | 2,83 | 2,00 | 1,69 | 1,40 |

Fig.1 – The SOM content, composition and distribution along the profile depth at different land use Calcic Chernozems

Distribution of humus is in accordance with the distribution of total HAs, those bound with Ca and FAs. The absence of "free" HAs in Calcic Chernozems determines their favourable water-physical properties. For the more detailed approximation of SOM composition along the profile, depth requires more observations (sub horizons) and application of appropriate methodology [31].

Micromorphological observation shows that in these soils rapid transformations of organic residues and strongly decomposed plant tissue predominate. There are often signs of active work of the soil mesofauna. Humus plasma is dark-coloured, observed with different crowding density and shape humons (fig.2: photos 1 and photos 2).

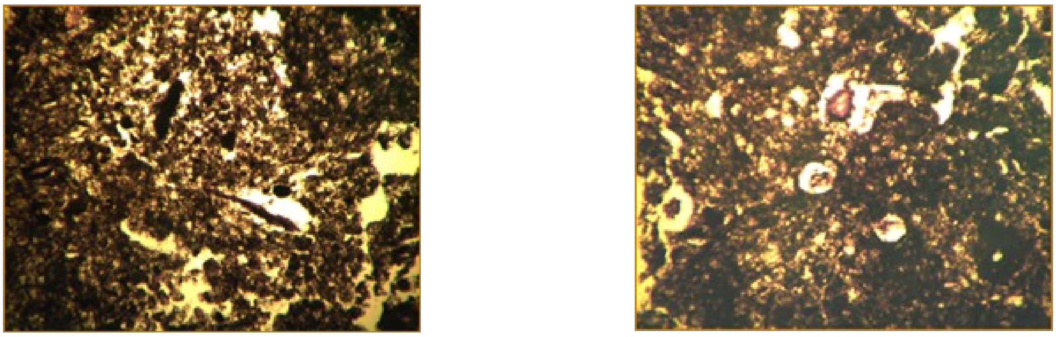
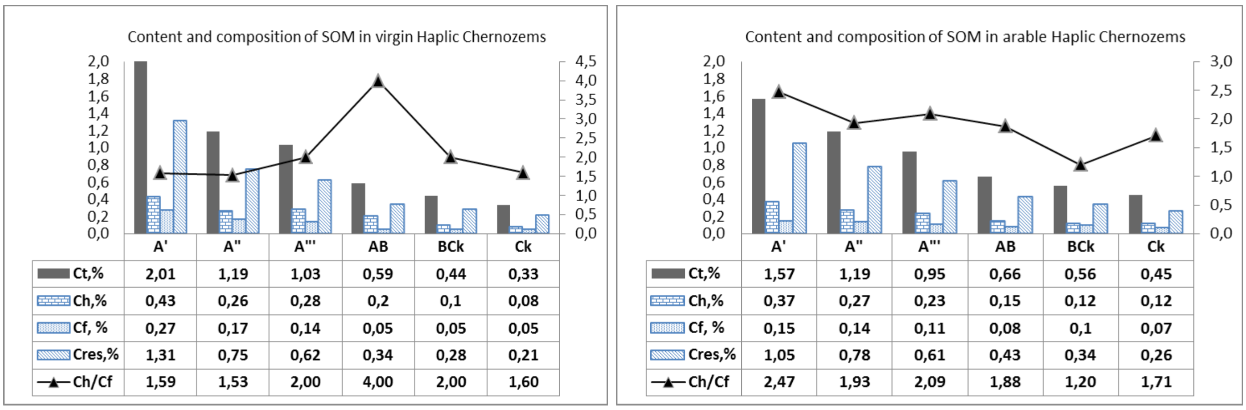


Photo 1 Photo 2

Fig.2 – Humus plasma is dark-coloured, observed with different crowding density and shape humons

### 3.2. Haplic Chernozems

Haplic Chernozems occupied around 1 075 000 ha or 43.8 % of the Chernozems area [20]. The type of humus on top of the humus-accumulation horizon is fulvic-humic, in the middle of the profile is humic and in the bottom is humic-fulvic. The degree of humification for the whole profile is high by classification of Grishina and Orlov [13] and reached higher values by Artinova [1, 2]. Free HAs and binds with mobile $R_2O_3$ forms are 10-25% in the humus-accumulation horizon and distinguishes Haplic Chernozems from Typical Chernozems (Epicalcic Chernozems [33, 34]). In the profile depth of Haplic Chernozems, HAs are bound with calcium and have a high degree of aromaticity and condensation. Participation of aggressive FAs fraction is negligible and unextractable OC is 50-60%. The Figure 3 presents the SOM content, composition and distribution along the profile depth at different land use.




| | A' | A" | A"' | AB | BCk | Ck |
|---|---|---|---|---|---|---|
| Ct,% | 2,01 | 1,19 | 1,03 | 0,59 | 0,44 | 0,33 |
| Ch,% | 0,43 | 0,26 | 0,28 | 0,2 | 0,1 | 0,08 |
| Cf, % | 0,27 | 0,17 | 0,14 | 0,05 | 0,05 | 0,05 |
| Cres,% | 1,31 | 0,75 | 0,62 | 0,34 | 0,28 | 0,21 |
| Ch/Cf | 1,59 | 1,53 | 2,00 | 4,00 | 2,00 | 1,60 |

| | A' | A" | A"' | AB | BCk | Ck |
|---|---|---|---|---|---|---|
| Ct,% | 1,57 | 1,19 | 0,95 | 0,66 | 0,56 | 0,45 |
| Ch,% | 0,37 | 0,27 | 0,23 | 0,15 | 0,12 | 0,12 |
| Cf, % | 0,15 | 0,14 | 0,11 | 0,08 | 0,1 | 0,07 |
| Cres,% | 1,05 | 0,78 | 0,61 | 0,43 | 0,34 | 0,26 |
| Ch/Cf | 2,47 | 1,93 | 2,09 | 1,88 | 1,20 | 1,71 |

Fig.3 – The SOM content, composition and distribution along the profile depth at different land use of Haplic Chernozems.

The micromorphological observations confirmed the analytical data of SOM composition in Haplic Chernozems (Fig.4). The quantitative and qualitative evaluation of micromorphological indicators in the Haplic Chernozems show both processes: a) the biogenic-destructive decomposition of organic residues and b) biogenic-accumulative formation of humic substances.

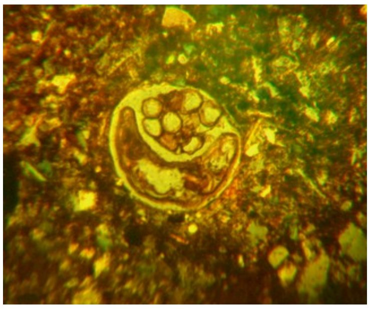


Photo 1

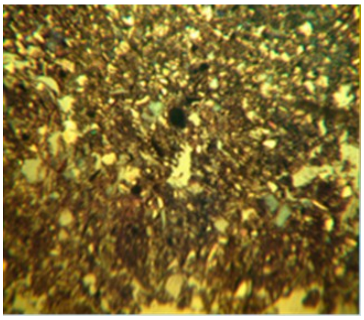


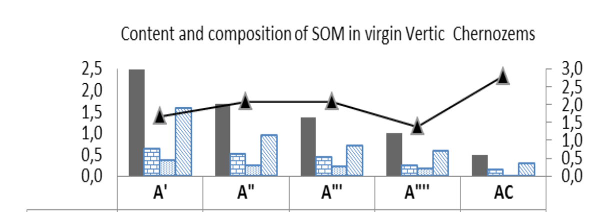
Photo 2

Fig.4 – Residues of the soil mesofauna in the Humus horizon of Chernozems (photo 1); Humus plasma in the Humus horizon of Chernozems (photo 2)

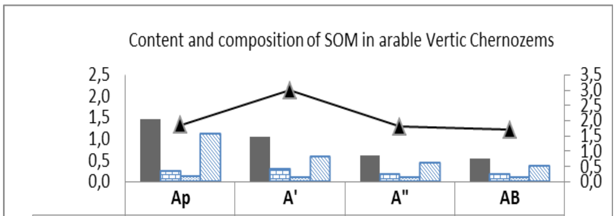
The surface humification and humus formation along the profile depth proceed with high intensity. The established prevailing HAs over FAs determines the formation of dark, coagulated or locally concentrated, stable humus type Mull.

### 3.3. Vertic Chernozems

Vertic Chernozems are distributed in the North-Bulgarian forest-steppe region in the bigger or smaller spots in the Chernozems area. According to the soil map of Bulgaria scale 1:400 000 these soils occupied around 0.069 million ha [21]. Their distribution is in the NE Bulgaria – Dobrich, Varna and Shumen regions well known as “Karasolutsi” which are represented by Calcareous, Typic and Leached "Karasolutsi". In the NW Bulgaria – Vidin, Montana and small areas in Vratsa region, they are known as Heavy-Clayey Chernozems and are represented by Leached-Clayey Chernozems. “Karasolutsi” occupied plain terrenes and less expressed slope forms, while Vertic Chernozems from North Bulgaria – mainly depression forms.
Figures 5 show the distribution of SOC (Ct, %), the content of Has (Ch, %), FAs (Cf, %) and unextractable OC (Cres, %) along the profile depth of virgin and arable soil.




| | A' | A" | A''' | A'''' | AC |
|---|---|---|---|---|---|
| Ct,% | 2,49 | 1,69 | 1,37 | 1 | 0,48 |
| Ch,% | 0,62 | 0,5 | 0,44 | 0,25 | 0,14 |
| Cf, % | 0,37 | 0,24 | 0,21 | 0,18 | 0,05 |
| Cres,% | 1,58 | 0,95 | 0,71 | 0,57 | 0,29 |
| Ch/Cf | 1,68 | 2,08 | 2,09 | 1,39 | 2,80 |




| | Ap | A' | A" | AB |
|---|---|---|---|---|
| Ct,% | 1,47 | 1,06 | 0,61 | 0,53 |
| Ch,% | 0,24 | 0,30 | 0,18 | 0,17 |
| Cf, % | 0,13 | 0,10 | 0,10 | 0,10 |
| Cres,% | 1,11 | 0,57 | 0,44 | 0,36 |
| Ch/Cf | 1,85 | 3,00 | 1,80 | 1,70 |

Fig.5 – The SOM content, composition and distribution along the profile depth at different land use Vertic Chernozems.

Humus content and its stocks decrease about 30% in arable Vertic Chernozems, mainly in the plough layer by data of representative profiles for Vertic Chernozems shown in the above Figures. They represent data for gradual decreasing in the humus content along the profile depth in arable and sharply decreasing in the sublayer of virgin soils which are confirmed by other authors about the influence of the type of land use [3, 7—9].

The conditions for humus formation and accumulation are similar in Vertic and Haplic Chernozems. The heavier particle size distribution of these Chernozems is the reason for accumulation of a large amount of humus [3](Artinova et al, in press). The humus content in Vertic Chernozems is higher than in Haplic Chernozems from those regions developed on lighter soil forming materials. Distribution of humus is gradually decreasing down the profile and in the depth of 100-120 cm, it is more than 1%. The humus type is humic, according to the classification of Grishina and Orlov [26, 1, 2]. Other indicators of humus status are as follows: high degree of humification (25-30%); all HAs are bound with calcium and have a high degree of condensation and aromatisation (E4/E6 is 3.5-3.6); aggressive FAs faction is a minor part approximately 3-4%; the ratio C: N is below 14, which show the complete transformation of organic materials and humus type Mull [24].

Mathematical and statistical analysis of a large number of profiles of Vertic Chernozems and their mean values have to mark the following: Calcareous, Typic and Slightly leached "Karasolutsi" is characterized with middle humus content 3.77; 4.0; 3.76%, respectively; Moderately and Strongly leached "Karasolutsi" have high humus content from 4.12 to 4.43%; Leached Clayey Chernozems from NW Bulgaria is characterized by middle humus content from 2.92 up to 3.31 % [24].

It is established statistically proved difference concerning humus content in Moderately and Strongly leached "Karasolutsi" and Clayey Chernozems. The results established show that Leached "Karasolutsi" has differed with higher humus content from Leached Clayey Chernozems, which confirmed the established results of Filcheva and Krastanov [10]. This could explain with the complex impact of soil-genetical and climatic factors: heavy parent materials, the major role of steppe vegetation in humus horizon formation, changes of humid and dry conditions [24].

Micromorphological diagnostic confirmed active biogenic-accumulative processes of humus formation and accumulation [15—17, 25]. Microscopic observation showed strongly and very strongly decomposed plant tissues. The soil biota is represented by faecal material which is the amorphous or very advanced stage of decomposition. Faecal material from earthworms is observed very frequently. The humus plasma present for the entire soil profile (Fig.6).

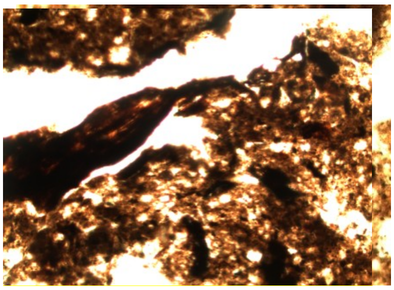
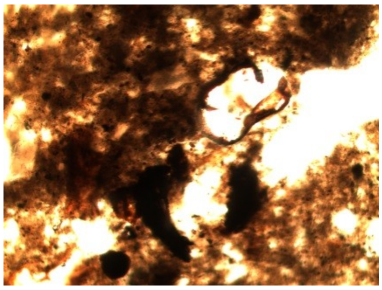


**Photo 1.** Strongly decomposed and humified plant residues and humus. “Mull” type in plasma of A hor., Vertic Chernozems



Ph**oto 2.** Plant residues in the process of decomposition and dark colored humified plasma in the main mass. A hor., Heavy Chernozems

Fig.6 – Micromorphological observation of A hor. in Vertic Chernozems and Heavy Chernozems

Two profiles of Chernozems are presented in the photos below (Fig. 7). The Photo 3.3.3. in the left is Karasoluk – heavy clay, Vertic Chernozems v. Primortsi. The Photo 3.3.4. in the right is Slightly leached Chernozem – moderately deep, Haplic Chernozem, v. Vetrino. The field study and lab analysis found that both profiles have Chernic horizon – thick, very dark-coloured, high base saturation, moderate to a high content of organic matter, well-structured, high biological activity.

**Photo 1.** Karasoluk – *heavy clay.* Vertic Chernozems v. Primortsi

**Photo 2.** Slighty leachet Chernozem –Haplic Chernozem. v.Vetrino

Fig.7 – Profiles of Chernozems

The data for physicochemical characteristics of Chernozem's profiles are presented in Table 1. The proof of vertic properties about the 1st profile is content ≥30 % clay in the depth of more than 100 cm. The second profile is with haplic properties because of a high degree of saturation with bases > 50%.

Table 1 – Physicochemical characteristics of Chernozem's profiles

| Horizont | Depth | pH | SOM | Clay 0.001 | Ph.clay <0.01 | $T_{8.2}$ | V |
|---|---|---|---|---|---|---|---|
| | cm | $H_2O$ | % | mm | mm | cmol.kg$^{-1}$ | % |
| **Vertic Chernozems** | | | | | | | |
| AI орн | 27 | 7.3 | 3.31 | 30.9 | 53.9 | 43.28 | 99.75 |
| AII | 60 | 7.6 | 2.79 | 34.3 | 63.9 | 37.22 | 99.68 |
| AIIIk | 80 | 7.9 | 1.76 | 42.8 | 65.4 | 40.71 | 99.73 |
| aBk | 105 | 8.0 | 1.02 | 42.7 | 72.0 | 34.52 | 99.65 |
| Cк | 130 | 8.0 | 0.52 | 42.9 | 68.1 | 30.01 | 99.63 |
| **Haplic Chernozem** | | | | | | | |
| AI орн | 29 | 7.00 | 2.83 | 29.8 | 53.0 | 34.92 | 99.66 |
| AII | 58 | 7.15 | 2.14 | 34.1 | 58.7 | 32.88 | 99.64 |
| ABk | 73 | 7.55 | 1.60 | 30.2 | 67.2 | 43.71 | 99.75 |
| Bk | 100 | 7.70 | 1.52 | 31.0 | 66.8 | 32.88 | 99.64 |
| Ck | 130 | 7.90 | 0.84 | 32.7 | 67.2 | 24.58 | 99.51 |

The data presented in Table 1 and the correlation matrixes Table 2, help us to detect similarities and differences between two subtypes of Chernozems in relation to the soil organic matter content. Both subtypes are with neutral pH in the surface layers reaching to the slight alkali in depth. Carbonates are found at a depth of 80 cm at Vertic Chernozems and on the depth 73 cm at Haplic Chernozems. Both profiles have SOM accumulation in range 1.02 - 1.52% to a depth of over 100 cm. The profiles are fine texture classes and they saturated with bases in whole investigated depth over 99%.

While the data shown in Table 3.4.1. can hardly distinguish the differences between Vertic and Haplic Chernozems the correlation matrixes between basic soil parameters show some of them. In both Chernozems indicators like pH and contents of physical clay increased proportionally with the profile depth while the content of SOM, CEC and degree of base saturation have an inversional correlation.

Table 2 – Correlation matrix between physicochemical parameters in profiles of Chernozems

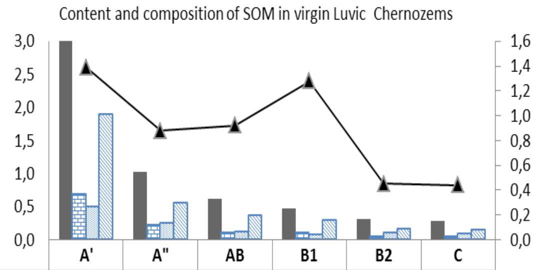
| | pH | SOM | <0.001 | $\sum$<0.01 | $T_{8.2}$ | V |
|---|---|---|---|---|---|---|
| pH | 1 | | | | | |
| SOM | **-0.9479**<br>**-0.9697** | 1 | | | | |
| <0.001 | **0.9802**<br>**0.9313** | **-0.9272**<br>**-0.9207** | 1 | | | |
| $\sum$<0.01 | **0.9418**<br>0.0983 | **-0.8588**<br>-0.3008 | **0.8683**<br>0.0777 | 1 | | |
| $T_{8.2}$ | **-0.7374**<br>-0.3519 | **0.8372**<br>0.3923 | -0.6228<br>-0.5644 | **-0.7631**<br>-0.0445 | 1 | |
| V | **-0.7111**<br>-0.4376 | **0.7843**<br>0.4835 | -0.5741<br>-0.5384 | **-0.8012**<br>-0.1280 | **0.9798**<br>0.9879 | 1 |

* Vertic Chernozems. **Haplic Chernozem

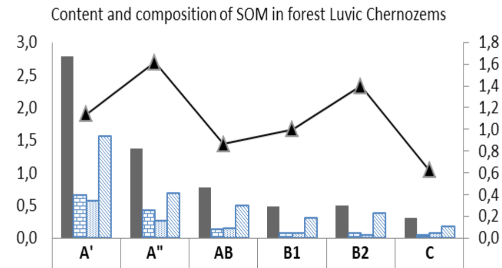
We can conclude for these two examples of Chernozems that the accumulation of soil organic matter is higher in their horizons up to 100 cm where the pH is neutral and the clay content is lower than the underlying layers. Generally, Chernozems fall into the group called izohumic saturated according to the first attempt to group the Bulgarian soils by organic matter content and composition which carried out by Filcheva, 2007 and added later – 2015. That group includes Chernozems as soils with valuable humus – a humic type of humus [8, 9].

## 3. 4. Luvic Chernozems

Luvic Chernozems are formed mainly on deciduous forest vegetation and characterized by low humus content from 2 up to 5%. Profile distribution is characterized with sharply decreasing of OC in the illuvial gleyic horizon approximately 50%. The type of SOM is fulvic-humic, the ratio $C_h/C_f$ is 1.0-1.3 or humic-fulvic, $C_h/C_f$ is 0.7-0.8 in the upper part (fig.8).




| | A' | A" | AB | B1 | B2 | C |
|---|---|---|---|---|---|---|
| Ct,% | 3,06 | 1,03 | 0,61 | 0,47 | 0,31 | 0,28 |
| Ch,% | 0,68 | 0,22 | 0,11 | 0,10 | 0,05 | 0,04 |
| Cf, % | 0,49 | 0,25 | 0,12 | 0,08 | 0,11 | 0,09 |
| Cres,% | 1,89 | 0,55 | 0,37 | 0,29 | 0,16 | 0,15 |
| Ch/Cf | 1,39 | 0,88 | 0,92 | 1,28 | 0,45 | 0,44 |




| | A' | A" | AB | B1 | B2 | C |
|---|---|---|---|---|---|---|
| Ct,% | 2,78 | 1,37 | 0,77 | 0,48 | 0,50 | 0,31 |
| Ch,% | 0,65 | 0,42 | 0,13 | 0,07 | 0,07 | 0,05 |
| Cf, % | 0,57 | 0,26 | 0,15 | 0,07 | 0,05 | 0,08 |
| Cres.,% | 1,56 | 0,68 | 0,50 | 0,30 | 0,38 | 0,18 |
| Ch/Cf | 1,14 | 1,62 | 0,87 | 1,00 | 1,40 | 0,63 |

Fig.8 – The SOM content, composition and distribution along the profile depth at different land use Luvic Chernozems

These soils are characterized with: a high degree of humification, increasing of "free" and humic acids bounded with $R_2O_3$ in the surface horizon; high/middle of condensation and aromatization of HAs and negligible part of aggressive FAs [7—9]. Increasing the ratio Ch/Cf (1.8-2.3) and the lack of mobile fraction of HAs in the surface layer is due to the rapid mineralization of the labile soil organic matter. There is a trend of decreasing the $E_4/E_6$ ratio i.e increasing the degree of condensation and aromatization HAs mainly in the upper part of the profile.

### 3.5. Regosols (WRB, 2006) (Shallow Chernozems)

Chernozems with the primitive profile are distributed in the Danube plain, they are strongly and moderately eroded Chernozems ( Koinov et.al., 1964). They occupy 48 500 ha or 2. 01 % of the Chernozems area [20].

Humus content is low from 1% to 1.5 % in the surface horizon and along the depth and decreases to 0.5 %. The ratio C: N varies from 7 to 14, which determine the type of transformation organic materials as Mull. The composition of SOM and distribution along the profile depth are characterized by a high amount of HAs 100 % bounded with alkali-earth metals. Ratio Ch/Cf in the surface horizon is 2.11, which corresponds with a humic type of humus [13, 26, 1, 2]. According to Kalderon [6] ratio, Ch/Cf >1 and (Ch+Cf)/Cres, are in the limits 0.4 to 1 and determined the humic-humin type of humus, which is the most distributed humus in dry arid conditions [14].

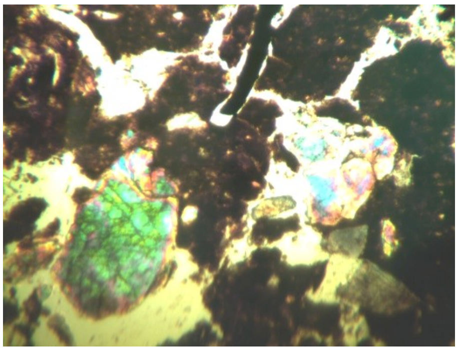
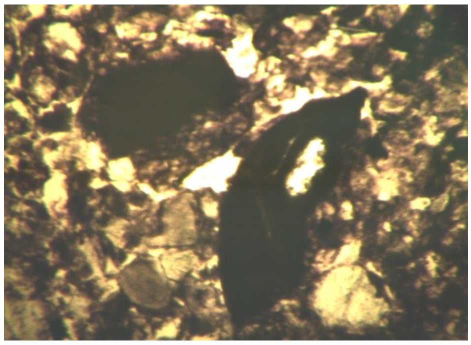
 

Photo 1 and 2. Transformed plant residues. Eroded Chernozems
Fig.9 – Micromorphological observation of Eroded Chernozems

The studied soils have a surface humus horizon with very good micro-aggregation and biological activity. Microbiological analysis confirmed the presence of highly decomposed plant debris and many excrements, the result of the vital activity of soil fauna. Plasma is dark coloured, isotropic, unequally distributed in the soil mass [16].

**Conclusions**

The micromorphological study made possible defining the major diagnostic criteria, characterizing the state of SOM to assess the amount and degree of transformation of organic residues, the activity of soil biota, quantity and condition of humic plasma. In addition with analytical data - quality and quantity of SOM, the study provides more complete and realistic picture of the biogenic processes in soils.
Quantitative and qualitative assessment of chemical and micromorphology indicators of Chernozems subtypes show that the biogenic – accumulation processes are the main and formatting processes. Humification process and in the profile humus formation passes with high intensity to a very deep level and determine the dark-coloured coagulated humus or locally concentrated stable humus [17]. As a result of this it is established prevailing of HAs over the FAs in the SOM composition, a high degree of condensation and aromatization of HAs – the precondition for favourable physic-chemical conditions in these soils.

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