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(RESEARCH ARTICLE)



Reserves of nutrients and soil organic components of Haplic Chernozems

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Abstract

The focus of this investigation is to present the reserves, soil nutrients and organic matter components along the profile depth of Haplic Chernozems near village Krupen, Kavarna municipality, South Dobrudzha region. The data confirm our previous investigations that they are one of the most fertility soils in Bulgaria. The profile is also marked by a variation of nutrients reserves according to the genetic horizon. All investigated reserves gradually decreased which is typical for the group of izohumic soils. The N_{total} reserves varied from 66.37% in $A_{horizon}$ to 8.86% in $C_{horizon}$ of the total stocks counting to 3.247 kg/ha. The reserves of total phosphorus in $A_{0-84\text{ cm}}$ add up to 1.723 kg/m², which is 45.94% from the total reserves of through profile, while in soil formation material horizon ($C_{horizon}$) they reached to 0.782 kg/m² (20.85%). The C_{org} reserves in the study profile (0-195 cm) are 326.131 kg/m² and 67.50% of the stocks are concentrated in the humus accumulative horizon. In transition horizon (B_{84-152}) all nutrient reserves gradually decreased and reached lowest values in soil formation material horizon ($C_{152-195}$). These two genetic horizons have a higher degree of enrichment of humus with nitrogen compared to the humus-accumulative horizon. Throughout the depth of the profile, the degree of enrichment of humus with nitrogen is defined as "average". We established essential correlations between the investigated indices as follows: Reserves of C-total are in a strong correlation with reserves of N-total (0.993**); Cres. (0.982**); C_{-THS} (0.949**); Mineralization ability after 56 days incubation (0.665**) and exchable potassium.

Keywords: Virgin profile; Haplic Chernozems; organic carbon reserves

1. Introduction

A primary understanding of soil is achieved through the study of the soil profile, interactions of soil material with organisms, and the movement of water through the soil profile by leaching. An essential function of soil is the break down of organic material to form soil humus and release nutrients that can be utilized by soil organisms and growing plants. Soil is also an important reservoir of the Earth's biodiversity, containing higher species and functional biodiversity than any other portion of terrestrial ecosystems.

As the interface between the atmosphere, biosphere, and lithosphere, soil undergoes an intense vertical exchange of materials resulting in steep chemical and physical gradients from surface to bedrock. The type, thickness, and position of horizons can yield information about soil forming factors such as climate, topography, and vegetation type [1]. Soils represent the most important long-term organic carbon (OC) reservoir in terrestrial ecosystems, as they contain more C than plant biomass and the atmosphere [2]. The large soil reservoir is not permanent results from a dynamic equilibrium between organic and inorganic material entering and leaving the soil. Soil C is further sensitive to environmental changes such as global warming or nitrogen deposition [3]. Soils represent the most important long-term organic carbon (OC) reservoir in terrestrial ecosystems, as they contain more C than plant biomass and the atmosphere [4, 5]. The large soil reservoir is not permanent but results from a dynamic equilibrium between organic

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and inorganic material entering and leaving the soil. Therefore, C stored in soils is affected by changes in vegetation and plant growth, removal of biomass by harvest, and mechanical soil disturbances such as plowing.

The manifold importance of nutrients and organic matter in soil formation and soil fertility has been demonstrated by the experience of agriculture over many centuries and by numerous investigations, in which the role of organic matter in soil processes (weathering, soil profile formation, soil structure formation, etc.) as well as in supplying plants with nutrients and biologically active substances has been elucidated [6, 7].

Dokuchaev [8, 9] defined Chernozem as a zonal soil formed under steppe and dry continental climates on loess parent material. In literature, the “Chernozem” was probably mentioned for the first time in 1645 by Salmon Gubert [10]. Chernozem is an iconic soil. Because Chernozem is a symbol of fertility, it has always been a centre of high interest for agronomists and pedologists [11]. Chernozems cover an estimated 230 million hectares worldwide, mainly in the middle latitude steppe of Eurasia and North America, north of a zone with Kastanozems. Traditionally, Chernozems are ranked as undifferentiated by the material composition of soil. Under conditions of circulation of hydrocarbonate-calcium solution in Chernozems, its aggressiveness is bare enough to wash out and redistribute calcium carbonates in the soil profile. At the same time, soil processes that actively destroy and redistribute the silicate part of the mineral composition of Luvic Greyzemic Chernozems seem not to take place (such as podzolization) or are slightly noticeable (gleyzation, lessivage, mole draining). In general terms, these statements are true only for Haplic Chernozems [12].

Soil nutrition reserves including and carbon stocks are strongly controlled by the climate and land cover. These main drivers, especially the land use patterns are changing rapidly by human activities. The climate and land-use changes are significantly visible, and their impacts on terrestrial ecosystems are increasingly being studied [13]. Climatic conditions have the main impact on vegetation and crop management, which also has influence over soil organic matter content [14].

Soil formation processes in all Chernozems, determined relatively good conditions for humus formation and humus accumulation. These processes in Bulgarian Chernozems are expressed significantly less compared to classical Chernozem's zone of Russia. Soil organic matter has a favourable composition and properties. The subtypes of Chernozems with their specific characteristics and in accordance with the humus distribution along the profile depth, organic carbon stocks were detailed described in the well known Bulgarian researchers Artinova, Gribachev, Jolevski; Krastanov, Gerasimov, in Soil survey; Filcheva [15, 16, 17], Petrova, Shishkov and especially for Dobroudja region – articles, published of Nankova [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37].

Features of generalized profiles of subtypes of Chernozems in different land use: arable, virgin and under forest with profile distribution of organic carbon, organic matter fraction, organic carbon stocks were described in details (Filcheva, 2004, 2007, 2015). The latest investigation grouped the Chernozems in the group of Izohumic soils and was presented their main characteristics [15, 16, 17, 38, 39, 40, 41].

The focus of our investigation is to present the reserves of soil nutrients and organic matter components of a virgin Haplic Chernozems profile, situated in the eastern part of geographical region South Dobrudzha (Bulgaria) near the village of Krupen municipality of Kavarna town.

2. Material and methods

The investigation was carried out on the territory of AGROSPECTOR LTD in the region of Village Krupen municipality of Kavarna town (N 43°34'22.43"- E 28°14'45.59") at elevation of 173 meter. Complete characteristics of the virgin profile was made from Prof. Shishkov [42].

In geological terms, this region of the Dobrudzha plateau is built on the lower and the middle-Sarmatian sediments, made up of alternating sandy limestones and marls with the aquiferous flow that run through in them (Figure 1).

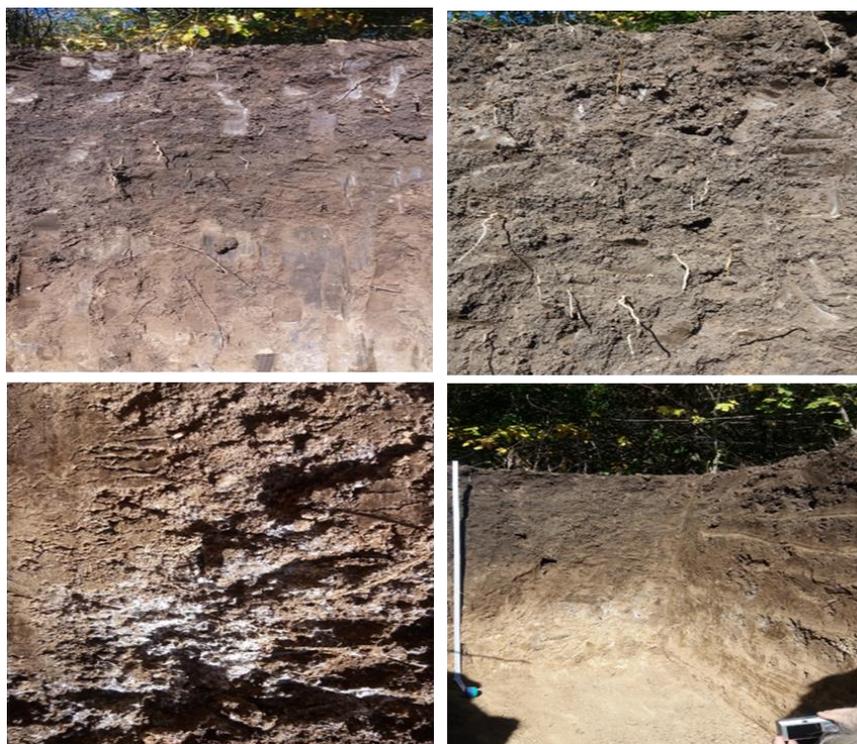


Figure 1 Profile photos

The analytical data for the agrochemical characteristic of the mobile and total forms of the basic macroelements as well as the mineralization capacity and organic C of the soil were prepared according to the requirements of each specific analysis. The content of studied components of soil samples was determined as follow:

- Soil acidity was determined in water and salt suspension (1 n KCl) [43].
- The mineral nitrogen forms in soil and their sum were determined by extraction with 1% K_2SO_4 (mg/1000 g soil). The identification of NO_3-N in the filtrate was done using the disulfophenol method, and ammonium nitrate was determined through the phenol method [44].
- The potential nitrogen-supplying ability of soil was determined through incubation under constant temperature of $30^\circ C$ at 60 % humidity from its total moisture absorption capacity in order to develop optimal conditions for nitrification. Incubation was done in a thermostat to investigate its dynamics at the 14th, 28th and 56th day. The samples were analyzed to determine the amount of nitrate nitrogen in 1 % K_2SO_4 extract. The ability of NO_3-N to form intensive yellow coloration when interacting with disulphurphenolic acid [$C_6H_3OH(HSO_3)_2$] in alkali media was used [44].
- Available phosphorus and the exchangeable potassium were determined by AL-method [45]. Phosphorus available to plants (mg $P_2O_5/100$ g soil) was determined calorimetrically, and the amount of exchangeable potassium (mg $K_2O/100$ g soil) through flame photometry.
- The total nitrogen content in soil (mg/100 g) was determined by the method of Kjeldahl after wet burning with concentrated H_2SO_4 diluted in distilled water at ratio 1:10, followed by distillation of nitrogen in Parnas-Wagner distillation apparatus.
- Total phosphorus content (%) was determined according to Bone method [44].
- Soil organic matter composition was determined by the method of Kononova-Belchikova [6, 46]. Total humic and fulvic acids ($C_{extr.}$) after extraction with mixed solution of 0.1M $Na_4P_2O_7$ and 0.1 M NaOH; “free” and R_2O_3 bounded humic and fulvic acids (C_{NaOH}) after extraction with 0.1 M NaOH and the most dynamic, low molecular fraction of organic matter, so called “aggressive” fulvic acids fraction – 1^a extracted with 0.05 M H_2SO_4 , ratio soil

: solution=1:20 for the three extractions. Humic and fulvic acids in both extracts $C_{\text{extr.}}$ and C_{NaOH} were separated by acidifying the solution with sulfuric acid (0.5 M).

- Nutrient reserves were calculated by [47]: $A = H \cdot V \cdot X$.

Where: A is the reserve of organic matter, kg/ha (t/ha); H is the thickness of soil layer, cm; V is the soil density and X is the element content, %.

The data were analyzed using the software packages Microsoft Excel and SPSS software (Ver. 22, 2013). Relationships between investigated indices were estimated using the mean values, standard errors, analysis of variance (two-way ANOVA) and Pearson's correlation coefficients; significant differences between soil layers were determined at $P \leq 0.05$ and $P \leq 0.01$.

3. Results and discussion

The results from the multifactor analysis of variances, based on the ANOVA, of the reserves of investigated agrochemical indices revealed high statistical significance over soil depth (Table 1).

Precise determination of changes in organic carbon (OC) stocks is prerequisite to understand the role of soils in the global cycling of carbon and to verify changes in stocks due to the management [48].

Table 1 Varians analysis of the reserves of agrochemical indices

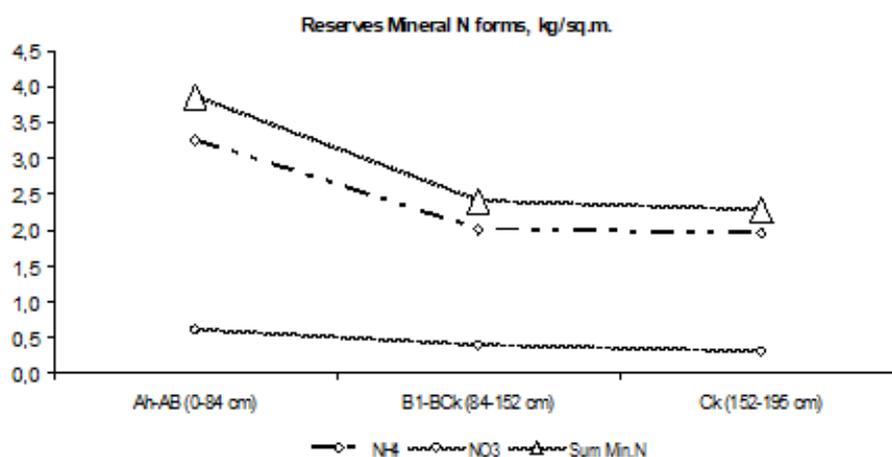
Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
NH ₄	895581.146	9	99509.016	9.777	.001
NO ₃	28431.864	9	3159.096	206.082	.000
Min. N	1174185.641	9	130465.071	12.822	.000
Pure MA-56 days	187.621	9	20.847	135.892	.000
Available P ₂ O ₅	330.608	9	36.734	1446.707	.000
Exchangeable K ₂ O	3128.922	9	347.658	1341273.227	.000
Total C _{org}	4418.506	9	490.945	46693.755	.000
C _{org} in total HS	604.263	9	67.140	18407.977	.000
C _{residue}	1528.617	9	169.846	4214.825	.000
Total N	390240.462	9	43360.051	131.769	.000
Total P	210089.032	9	23343.226	583.232	.000

Mineral nitrogen reserves varied significantly on account of the dynamics of bulk density and depth of the layers constructing respective genetic horizons (Table 2). The data shows increasing of available nitrogen forms and their reserves down the profile at the end of the transition horizon. This data confirm our previous results on Haplic Chernozems (slightly leached) where at the same depth was formed the 1st maximum of accumulation of mireneral nitrogen [29].

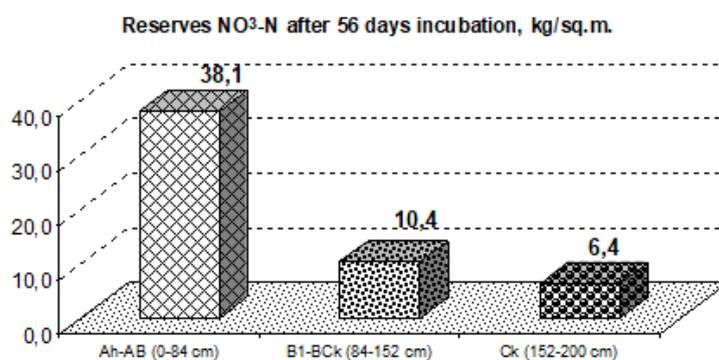
Humus-accumulative horizon ($A_{0-84 \text{ cm}}$) characterized with the greatest reserves of mineral nitrogen accessible for the plants, as well as potential N-supplying ability after 56 days of incubation. More than 80% from the formed reserves were in ammonium form (Fig. 2).

Table 2 Mineral N forms and pure Mineralization ability reserves by genetic horizons down the profile of Haplic Chernozems (Krupen, Kavarna town)

Horizon	Depth, cm	NH ₄ - N g/m ²	NO ₃ - N	Sum	Pure MA after 56 days incubation kg/m ²
Ah	0-8	440.32 a	73.32 a	513.64 a	8.23 e
A ₁	8-24	796.58 cd	122.88 c	919.45 c	10.92 g
A ₂	24-42	801.80 cd	124.58 c	926.38 c	10.10 f
A ₃	42-67	717.60 bc	170.09 g	887.69 bc	6.53 d
AB	67-84	498.17 ab	114.81 b	612.98 a	2.31 a
B ₁	84-105	562.63 ab	133.09 d	695.72 ab	3.14 b
Bk ₂	105-120	456.21 a	69.26 a	525.47 a	2.74 ab
Bck	120-152	987.46 de	195.27 h	1182.73 d	4.54 c
Ck	152-178	1033.62 e	147.16 e	1180.78 d	3.18 b
Ck ₂	178-195	928.84 cde	158.98 f	1087.82 cd	3.23 b



Mineral Nitrogen forms



Pure Mineralization ability reserves after 56- days incubation

Figure 2 Nitrogen reserves by A-B-C horizons down the profile of Haplic Chernozems (Krupen, Kavarna town)

Phosphorus and potassium reserves available for plants are under high dynamic of values (Table 3). The concentration of these macroelements decreased down the profile depth. The main role for the formation of the reserves is both, the depth of the genetic horizons and the bulk density.

Table 3 Available phosphorus and exchangeable potassium reserves by genetic horizons down the profile of Haplic Chernozems (Krupen, Kavarna town).

Horizon	Depth, cm	P ₂ O ₅ g/m ²	K ₂ O
Ah	0-8	6.29 e	27.52 a
A ₁	8-24	4.29 d	53.19 g
A ₂	24-42	2.86 b	47.95 e
A ₃	42-67	3.45 c	64.27 h
AB	67-84	2.45 a	50.67 f
B ₁	84-105	3.09 b	53.21 g
Bk ₂	105-120	3.03 b	38.29 b
BCK	120-152	8.59 f	73.66 i
Ck	152-178	9.05 g	39.99 c
Ck ₂	178-195	16,00 h	43,78 d

In Humus-accumulative horizon were concentrated 26.48% from the phosphorus reserves easy of access for the plants and 48.10% - from those of exchangeable potassium (Fig. 3).

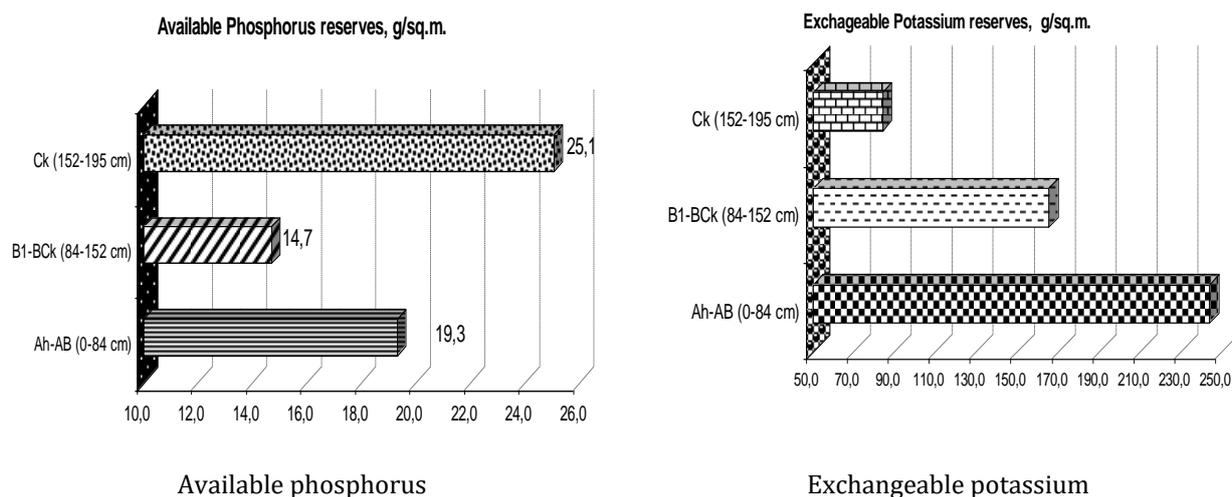


Figure 3 Reserves of available forms of phosphorus and potassium by A-B-C horizons down the profile of Haplic Chernozems (Krupen, Kavarna town), g/m. sq.

The investigated profile of virgin Haplic Chernozems is also marked by a large variation in total nitrogen and phosphorus reserves throughout the depth (Table 4). The soil formation materials are characterized by the lowest stock size. The largest total nitrogen reserves are concentrated in the A₂ and A₃ sub-horizons. A similar tendency is observed for stocks of total phosphorus, but with the maximum value of the stocks of this nutrient is established at the lower end of the transition sub-horizon (BCK). Moise and Lungu [49] established for the region of Constanta (North Dobrudzha) that in the arable Chernozem humus content was recorded from 3.1 to 4%, 0.145% phosphorus and 0.186% nitrogen contents. These results are relatively similar to those obtained in different research years in Dobrudzha Agricultural Institute for the region of South Dobrudzha [28, 30, 34].

Already in 1896 in the report to the Department of Agriculture of USA Snyder notes that a virgin soil or one recently cleared may show a high state of productiveness for a number of years after it is brought under cultivation. Gradually, however, a decline in fertility is observed, which is slight at first, but more marked after a lapse of fifteen or twenty years [50]. The author points out that agriculturally considered, the two most important points regarding the composition of humus are the presence of nitrogen as a constant constituent, and the chemical union of the humus with potash, lime, and phosphoric acid, forming humâtes.

Soil organic matter is a complex system and composed of organic compounds, differing in mechanisms of their fixation in the soil and in their functions in carbon cycling and soil formation [51, 52]. Literature data about changes in soil carbon stocks due to land use changes are frequently discussed in review articles [53, 54, 55]. The data from our study show that organic carbon stocks in the studied soil profile are gradually decreasing in depth (Table 5). The established carbon stocks of total humic substances (C_{THS}) and carbon of the insoluble residue ($C_{residue}$), as one of the main characteristics of the composition of the soil organic matter, follow the same trend. In their investigations Duchaufour and Kuntze et al. [56, 57] also established the slightly decreasing of organic matter content with depth. This phenomenon is defined as isohumism. The essential process of evolution of this organic matter is a long maturation of various humic compounds, called melanization. [58, 59].

Table 5 Carbon groups reserves by genetic horizons down the profile of Haplic Chernozems (Krupen, Kavarna town).

Horizons	Depth, cm	Org. C _{total} g/m ²	C _{THS}	C _{residue}
Ah	0-8	27.59 d	10.32 d	17.27 e
A ₁	8-24	48.12 h	18.32 h	29.79 h
A ₂	24-42	51.34 i	21.97 i	29.37 g
A ₃	42-67	56.41 j	25.06 j	31.35 i
AB	67-84	36.68 g	18.00 g	18.68 f
B ₁	84-105	31.45 f	15.44 e	16.01 d
Bk ₂	105-120	17.96 c	8.35 a	9.61 b
Bck	120-152	31.15 e	16.80 f	14.35 c
Ck	152-178	12.26 a	8.95 b	7.22 a
Ck ₂	178-195	13.18 b	9.80 c	7.37 a

The use of chernozems in agriculture has caused drastic changes in their properties and the proportion of nearly all soilforming processes. The mass of organic substances that entered the soil and their mineralization changed, the physical properties (for instance, the soil structure) and the water regime were transformed, and acidification and decalcification began to develop. It is therefore imperative that a periodic comparison be made between the state of the virgin land and those under intensive agricultural use. Orlov et al. [60] revised system of the humus status parameters of soils and their genetic horizons. The system of parameters of the soil humus status is an indispensable criterion of soil and land evaluation. The revised and specified system makes it possible to characterize the soil humus status and examine the mechanisms of humus accumulation and formation.

The total organic carbon stocks in the study profile are 326.131 kg/m² (Fig. 5). The redistribution of these stocks across horizons is as follows: in A horizon is focused 67.50% of these stocks, in transition horizon (B) - 24.70% and in soil formation material (C) - 7.80%. In a large scale investigation on the relationship between organic carbon content and soil type in the soils of Serbia Vidojević et al. [61] found out one of the largest SOC stocks for the soil layers 0-30 cm in Chernozems - 230.43 x 10¹² g.

The distribution of total humic substances by genetic horizons in profile Krupen is as follows: in the humus-accumulative horizon (A) - 61.22%, in the transitional (B) - 26.52% and in soil-forming materials (C) - 12.25% of the formed stocks in the order of 153.010 kg/m².

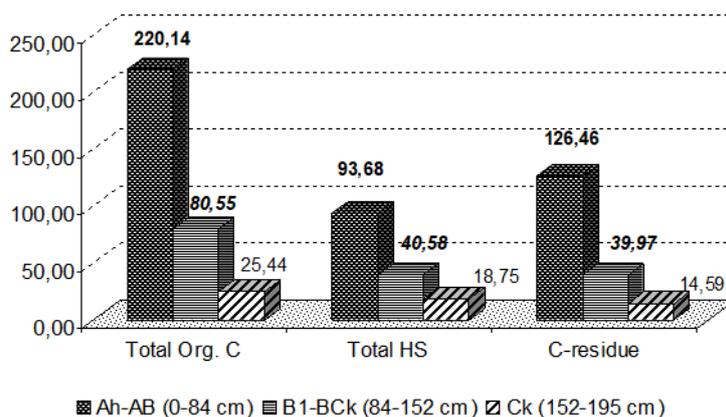


Figure 5 Carbon groups reserves by A-B-C horizons down the profile of Haplic Chernozems (Krupen, Kavarna town)

The insoluble residue ($C_{residue}$) of organic matter in the soil is its essential characteristic. Our results show that, on average, 54.91% of the total organic carbon stocks in this soil profile fall precisely in the humus guardian group. The total amount of $C_{residue}$ in the profile is 181.023 kg/ha, with 69.86% of it being concentrated in the humus accumulative horizon (A).

Based on our research we found that the degree of humus enrichment with nitrogen is "average" along the entire depth of the profile. In humus accumulative horizon (A) the average value is 10.21. In the transition (B - 9.96) and soil-forming materials (C - 8.84) the values decrease, which is an indication of a slight tendency to enrich the organic matter with nitrogen. Summary of soil organic matter in Bulgaria processes of humification and organic carbon stocks by soil groups and types were developed by Professor Filcheva [16, 62, 63].

The analysis of the coefficients of variation showed that the mean values of nitrogen mineral forms and theirs sum, for exchangeable potassium and total phosphorus were approximately homogeneous and is characterized by a mean dispersion of the trait (CV -30%) (Fig. 6). The coefficients for the values of total nitrogen and the composition of the soil organic matter are below 50% and they are sufficiently representative. The highest dispersion was found in the available phosphorus and potential N applying ability after a 56-day incubation values - more than 50%. This means strongly heterogeneous excerpt (large sign dispersing).

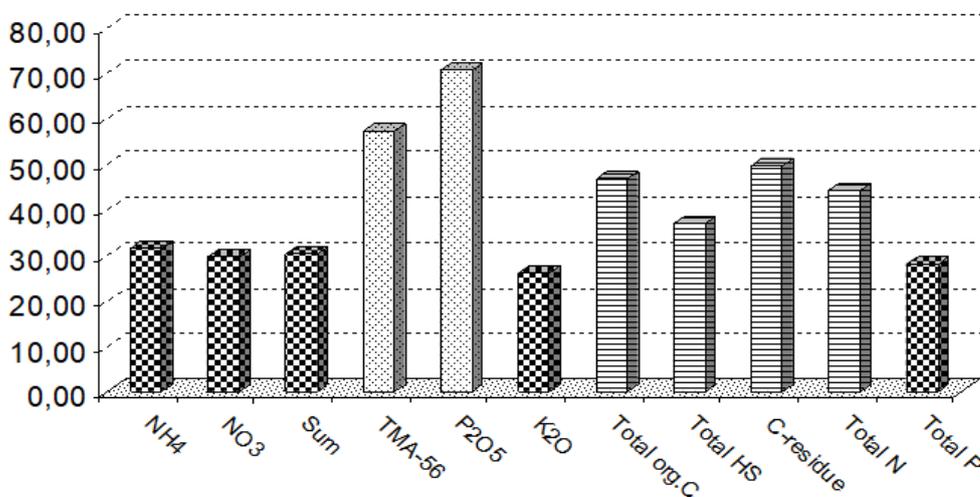


Figure 6 Coefficients of variation by indices for the whole profile

We established very well expressed positive correlations between total org.C reserves with total nitrogen, C-THS and C-residue (Fig. 7). The positive correlations exist also between total organic C reserves with exchangeable K and

potential N-supplying ability. The correlation between total organic C reserves and those with available phosphorus are strongly negative.

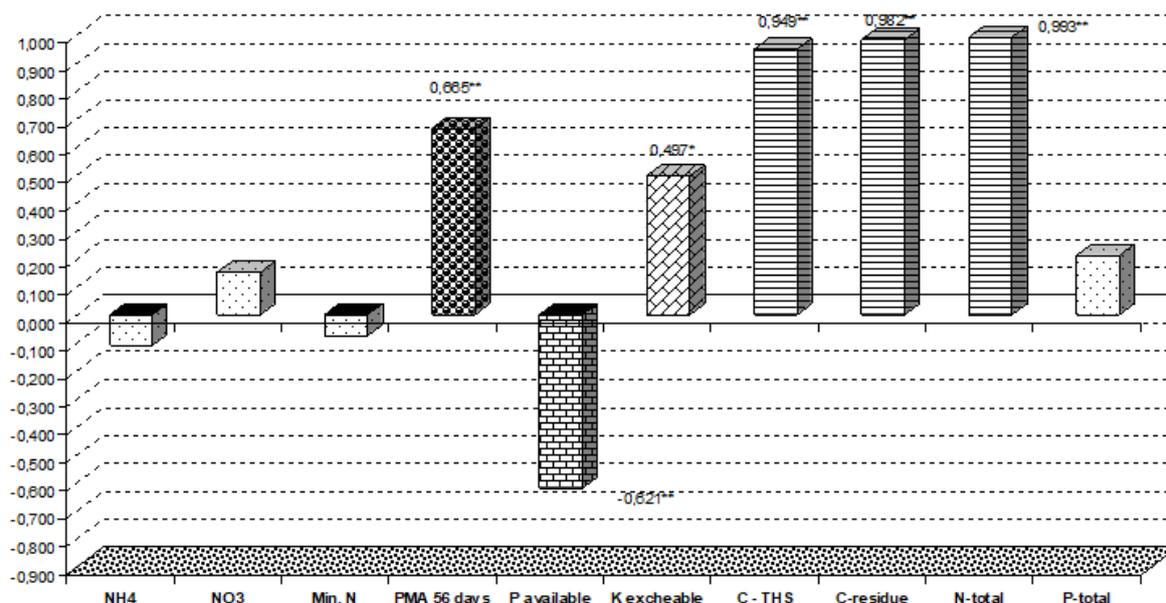


Figure 7 Correlations between total C_{org} reserves with reserves of available and total nutrients and some groups of C_{org} in the investigated profile of Haplic Chernozems

4. Conclusion

Our study on the virgin soil profile is representative of Haplic Chernozems in South Dobrudzha and confirms our previous investigations that they are one of the most fertility soils in Bulgaria. The profile is also marked by a variation of nutrients reserves according to the genetic horizon. The reserves for both, nutrients and soil organic matter gradually decreased which is typical for the group of izohumic soils. The N_{total} reserves varied from 66.37% in A_{horizon} to 8.86% in C_{horizon} of the total stocks amounting to 3.247 kg/ha. The reserves of total phosphorus in A_{0-84 cm} add up to 1.723 kg/m², which is 45.94% from the total reserves of through profile, while in soil forming material horizon (C_{horizon}) reached to 0.782 kg/m² (20.85%). The organic carbon reserves in the studied profile (0-195 cm) are 326.131 kg/m² and 67.50% of the stocks are concentrated in the humus accumulation horizon. In transition horizon (B₈₄₋₁₅₂) all nutrients reserves gradually decreased and reached lowest values in soil formation material horizon (C₁₅₂₋₁₉₅). These two genetic horizons have a higher degree of enrichment of the humus with nitrogen compared to the humus-accumulative horizon. Throughout the depth of the profile, the degree of enrichment of humus with nitrogen is defined as "average". We established essential correlations between the investigated indices as follows: Reserves of C-total are in a strong correlation with reserves of N-total (0.993**); Cres. (0.982**); C-THS (0.949**); mineralization ability after 56 days incubation (0.665**) and exchable potassium.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

There is no any conflict to interest in preparing and publishing the article.

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