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CONTENT AND STOCK OF ORGANIC CARBON IN SOILS ON THE TERRITORY OF VITOSHA NATURE PARK

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Abstract

A complex of humus parameters was studied and a database was created about the content of soil organic matter and org. C stock in the surface 20 cm layer of Umbrisols in order to monitor the relationship ‘climate changes – organic C stock’ over time. Geo-coordinated stations located near the Cherni Vrah meteorological station were used, where the temperatures and precipitation have been observed since 1935. Higher acidity (pH_{H2O}), higher amount of total carbon and free low-molecular humic acids were determined in the surface 10 cm soil layer in comparison with the 10–20 cm layer. The share of humic and fulvic acids in the total carbon of the two layers did not differ and was characterized by stable values. The org. C stock in the surface 10 cm layer was 7.00 ±1.31 $t.ha^{-1}$ and 15.55 ±2.72 $t.ha^{-1}$ in the 10–20 cm layer. The total org. C stock in the surface 20 cm layer of Umbrisols was 18594.15 t. The obtained results allow future statistical evaluations of information about monitoring the relationship ‘climate changes – org. C stock’ over time.

Key words: Ca complexed humic acids, fulvic acids, humic acids, optical characteristics, org. C stock, Umbrisols.

Introduction

One of the most topical issues, related to conservation of soil fertility, is the loss of soil organic matter (SOM). There are many reasons for these losses – tillage, land use changes, erosion, climate changes, etc. Modern challenges for SOM protection are largely related to climate changes. It is assumed that the SOM decomposition rate will increase with rising temperatures (Tate et al. 1993, Orlova and Vasilievskoi 1994, Simmons et al. 1996). Climate changes and their effect on soil depend on different biotic, abiotic and anthropogenic factors. The variation of org. C stock has been accepted as an indicator of their impact on SOM (IPCC GPG 2003, IPCC 2006). It is expected that the rising temperatures will have an impact on the content of org. C in soil in long term, but it is more likely that short-term changes, caused by the applied management practices and land use changes, will occur (EEA 2017). Examples of such changes include increased soil compaction rates, erosion, pollution, etc. The contemporary evaluation reveals that the information about the org. C stock in the arable land may be greatly increased – by about 25 %

(EEA 2017). In most studies this stock is estimated for the organic and surface soil layers which occupy the upper 30 cm soil. Worldwide, soils contain about 1500 Pg org. C (Batjes 1996), which is about three times the amount of carbon in plants and twice as much in the atmosphere (IPCC 2000, GFOI 2016). According to Jansen (2003) soils contain approximately 2344 Pg C in the first 3 m layer, 1502 Pg C of which are in the first meter.

The soils in the forest territories of Bulgaria, which are not affected by degradation processes, are comparatively rich in organic matter (Rousseva and Marinov 2014). According to Boyadgiev et al. (1994) the org. C stock in soils in the country is about 1.3 Gt, and according to Filcheva and Rousseva (2004) – 1.5 Gt. Different studies were carried out – estimates for different soil depths of 25 cm, 50 cm and 100 cm, by soil groups (Filcheva et al. 2002, Filcheva and Rousseva 2004), by climate zones (Hristov and Filcheva 2016), etc. The creation of databases can contribute to the monitoring of changes in org. C stock, caused by climate changes, but in the IPCC methodological guidelines for evaluation of org. C stock (Guidance 2003, 2006) it is recommended to create permanent monitoring sites in order to collect regular information over time. In the forest area of the country there is only one such site, located in the field station for intensive monitoring of forest ecosystems in Yundola. The collected database refers to *Dystric Cambisols* (Malinova et al. 2011). Disadvantage of this site is the short-term monitoring of temperature and precipitation – since 1998 (Kolarov et al. 2002).

The aim is analysis and evaluation of the soil organic matter content and org. C stock in a specially designed experimental plot on the territory of Vitosha Nature Park, located near a meteorological station. A database on the content of soil organic matter and org. C stock in the top 20 cm soil layer of Umbrisols was created in order to monitor their relationships to climate changes over time.

Subject and method of the research

The Cherni Vrah area was selected for the purpose of the present study, where measurements of the temperature and precipitation have been carried out since 1935. It is the highest peak of Vitosha Mountain. Apart from the presence of the meteorological station, the fact that soils of the high mountain areas are considered the most sensitive to temperature increase due to the combination of this process with the acidification of atmospheric depositions (Kulhavý et al. 2009), is also significant for selecting the location for creation of the experimental site.

Cherni Vrah is located at an altitude of 2290 m. The terrain of Vitosha is layered due to the multiple mountain elevations during the Neogene and Quaternary. The Vitosha pluton is composed of Upper Cretaceous intrusive rocks – gabro, monzonite and leucosyenite (Management Plan … 2014). The vegetation is meadow.

The experimental site is located on the territory of the Sofia State Forest Enterprise in section 1178, subsection 10, in the immediate vicinity of Cherni Vrah (Pic. 1), at an altitude of 2260 m. The soil is Umbrisols, formed under the impact of meadow vegetation including *Nardus stricta, Vaccinium* sp., *Juniperus* sp. The soil-forming rock is leucomonzonite. No soil erosion is observed. An area with flat terrain is selected in order to prevent the occurrence of erosion processes. No

Pic. 1. Soil sampling area near Cherni Vrah.

signs of human impact are determined.

The experimental plot consists of 10 geo-coordinated sampling points, located at a distance of 1 m in the north-south direction. Soil samples from depths 0–10 cm and 10–20 cm were collected from each sampling point.

The following soil parameters were analysed: total carbon; total content of org. C extracted with a double solution of sodium pyrophosphate and sodium hydroxide; extractable carbon with 0.1M NaOH; ‘aggressive’ fraction of fulvic acids (0.1 N H_2SO_4); content of org. C in humic acids and fulvic acids; ‘free’ and R_2O_3 complexed humic acids; optical characteristics of humic acids. The E_{465}/E_{665} ratio was calculated as the ratio of absorbance at 465 nm and 665 nm wavelength. The content and composition of soil organic matter was determined by the modified Tyurin method (i.e. 120 ^{o}C, 45 min. and Ag_2SO_4 as a catalyst) and by the Kononova-Belchikova method (Kononova 1966, Filcheva and Tsadilas 2002), and bulk density according to ISO 11272.

Results

The soil at the experimental plot is Umbrisols with a profile A*sod* – A – C. A*sod* is with a soil depth of about 5 cm. The lower limit of the *umbric* horizon is at 38 cm depth, with a clear transition to a C horizon. In a fresh state the soil is characterized by from 10 YR 2/4 colour in *Ah* to 10 YR 2/1 in the A horizon. Soil texture is loam, aggregates – barely observable and soil does not react under the influence of a 10 % HCl solution.

The soil has a highly acidic reaction (see Table 1). It is the most acidic in the surface 10 cm layer (pH=4.53 ±0.06), where active decomposition processes of grass vegetation residues occur. The pH values show strong acidification of this soil layer. The difference in pH between layers 0–10 cm and 10–20 cm is statistically significant (Fig. 1). The median splits the data sets for the two layers in intervals that completely deviate (Fig. 1).

The higher acidity of the surface soil layer is due to the higher presence of free low-molecular humic acids in it (see Table 1). The significance of the difference with the 10–20 cm layer is demonstrated by *p*=0.02 (calculated of free low-molecular humic acids as a % of the soil sample) and by *p*=0.03 (calculated as a % of the total carbon). It can be assumed that the values are above the critical limit of pH=4.0, after which the carbon mobilization is enhanced (Funakawa et al. 2006).

The total carbon amount is very high. It is differentiated in depth as in the surface 10 cm layer it is the highest (17.29 ±1.51 %) and sharply decreases in depth – 10–20 cm layer. The difference between the two layers is also statistically significant p=0.00 (Fig. 2).

Taking into consideration the humic and fulvic acid amounts (extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH) as a percentage of the soil sample, it is determined that they accumulate more actively in the surface 10 cm soil layer and in depth their content decreases (figs 3 and 4). However, their share in the total carbon does not differ in the two layers, which indicated their stability (figs 5 and 6).

The humus type, determined by the ratio between the org. C in humic (Cha) and fulvic (Cfa) acids is estimated as fulvic-humic.

The ratio varies from 0.77 to 1.61. The results do not clearly outline the reason for the presence of the reversed hu-

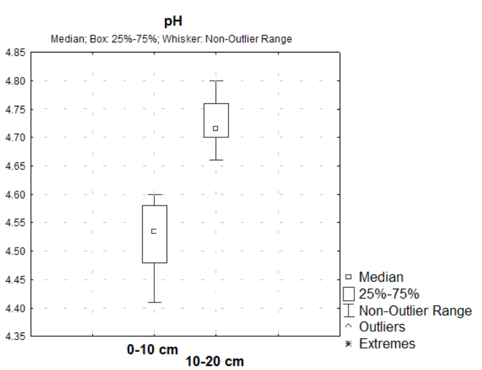

Fig. 1. Reaction of soil solution in layers 0–10 cm and 10–20 cm in Umbrisols.

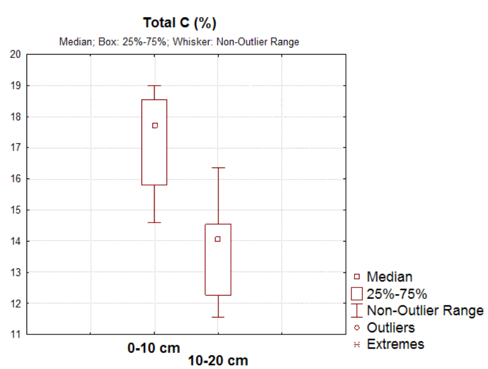

Fig. 2. Total carbon content in layers 0–10 cm and 10–20 cm in Umbrisols.

Table 1. Soil organic matter content and composition.

Sampling point No	Soil depth, cm	pH H_2O	Total C, %	Organic carbon extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			Ratio C_h/C_f	Organic carbon humic acid fractions, %		Nonextracted org. C, %	Extracted org. C 0.1N H_2SO_4 %	Optical properties, %		Org. C NaOH, %
				Org. C, %	C_h, %	C_f, %		Free and R_2O_3 complexed	Ca complexed			Total humic acids E_{465}/E_{665}	Free humic acids E_{465}/E_{665}	
1	0–10	4.4	18.54	8.89 47.95	4.14 22.33	4.75 25.62	0.87	100.00	0.00	9.65 52.05	0.74 3.99	4.95	4.78	8.34 44.98
	10–20	4.7	14.54	6.82 46.91	3.82 26.27	3.00 20.64	1.27	100.00	0.00	7.72 53.09	0.80 5.50	4.84	4.75	5.95 40.92
2	0–10	4.5	18.99	7.25 38.18	3.27 17.22	3.98 20.96	0.82	100.00	0.00	11.74 61.82	0.72 3.79	4.89	4.40	6.93 36.49
	10–20	4.7	16.36	5.84 35.70	3.05 18.64	2.79 17.05	1.09	100.00	0.00	10.52 64.30	0.67 4.09	4.86	4.72	5.78 35.33
3	0–10	4.6	15.45	6.27 40.58	3.27 21.17	3.00 19.41	1.09	100.00	0.00	9.18 54.42	0.78 5.05	4.83	4.86	5.89 38.12
	10–20	4.8	12.27	3.65 29.75	1.96 15.97	1.69 17.77	1.16	100.00	0.00	8.62 70.25	0.70 5.70	5.19	4.63	3.44 28.04
4	0–10	4.5	17.27	6.53 37.81	2.84 16.44	3.69 21.37	0.77	100.00	0.00	10.74 62.19	0.70 4.05	4.77	4.67	6.16 35.67
	10–20	4.7	14.27	3.87 27.12	2.07 14.51	1.80 12.61	1.15	100.00	0.00	10.40 72.88	0.68 4.76	5.17	4.47	3.55 24.89
5	0–10	4.5	18.18	6.60 36.30	3.60 19.80	3.00 16.50	1.20	100.00	0.00	11.58 63.70	0.63 3.46	4.74	4.91	6.60 36.30
	10–20	4.8	13.95	4.25 30.47	2.62 18.78	1.63 11.69	1.61	100.00	0.00	9.70 69.53	0.74 5.30	4.86	4.77	3.87 27.74
6	0–10	4.5	18.74	6.21 33.14	3.83 20.40	2.38 12.70	1.61	2.48 64.75	1.35 35.25	12.53 66.86	0.53 2.83	5.27	5.22	6.16 32.87
	10–20	4.7	13.62	6.76 49.63	2.76 20.26	4.00 29.37	0.69	1.45 52.54	1.31 47.46	6.86 50.37	0.43 3.16	4.95	4.93	3.12 22.71
7	0–10	4.5	17.66	6.43 36.41	3.83 21.69	2.60 14.72	1.47	2.79 72.85	1.04 27.15	11.23 63.59	0.49 2.77	5.31	5.28	5.24 29.67
	10–20	4.7	14.17	5.23 36.91	2.79 19.69	2.44 17.22	1.14	2.28 81.72	0.51 18.28	8.94 63.09	0.49 3.46	4.60	5.02	4.30 30.35

8	0–10	4.6	14.60	5.56 / 38.08	3.00 / 20.55	2.56 / 17.53	1.17	2.69 / 89.67	0.31 / 10.33	9.04 / 61.92	0.49 / 3.36	4.084	5.06	3.98 / 27.26
	10–20	4.7	14.60	4.15 / 28.42	1.96 / 13.42	2.19 / 15.00	0.89	1.76 / 89.80	0.20 / 10.20	10.45 / 71.58	0.49 / 3.36	5.13	4.97	3.44 / 23.56
9	0–10	4.6	17.76	6.00 / 33.78	3.31 / 18.64	2.69 / 15.15	1.23	2.48 / 74.92	0.83 / 25.08	11.76 / 66.22	0.71 / 3.99	4.61	5.25	5.56 / 31.31
	10–20	4.7	11.55	4.58 / 39.65	2.28 / 19.74	2.30 / 19.91	1.00	1.76 / 77.19	0.52 / 22.81	6.97 / 60.35	0.54 / 4.67	5.38	4.85	3.65 / 31.60
10	0–10	4.6	15.80	5.89 / 37.28	2.90 / 18.36	2.99 / 18.92	0.97	2.07 / 71.38	0.83 / 28.62	9.91 / 62.72	0.43 / 2.72	5.06	5.30	5.02 / 31.77
	10–20	4.8	11.66	3.49 / 29.93	1.96 / 16.81	1.53 / 13.12	1.28	0.93 / 47.45	1.03 / 52.55	8.17 / 70.07	0.39 / 3.34	5.22	4.86	2.73 / 23.41

Notes: In columns of organic carbon extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH: underlined number shows the share of org. C of soil sample mass, in % and not underlined number shows the share of org. C of total carbon, in %. In columns of org. C in humic and fulvic acid fractions: underlined number shows the share of org. C of soil sample mass, in % and not underlined number shows the share of org. C of total carbon, in %. C_h is humic acids; C_f is fulvic acids; E_{465}/E_{665} ratio of absorbance at wavelength of 465 nm and 665 nm.

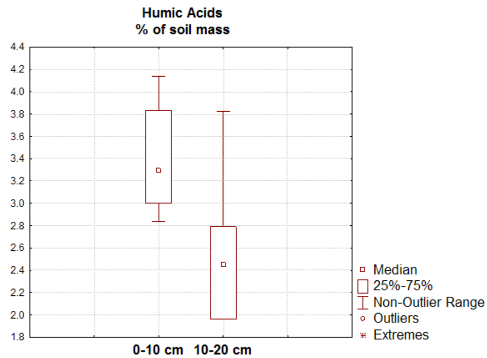

Fig. 3. Humic acid content (% of soil mass) in layers 0–10 cm and 10–20 cm.

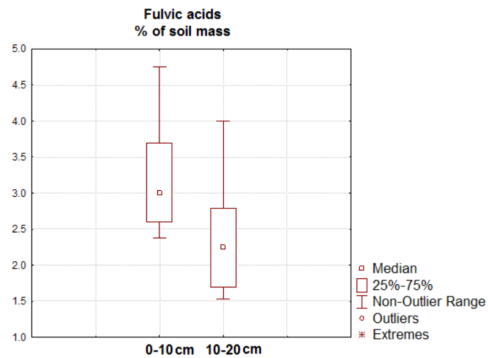

Fig. 4. Fulvic acid content (% of soil mass) in layers 0–10 cm and 10–20 cm.

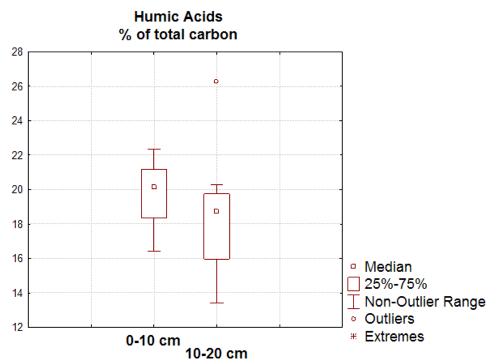

Fig. 5. Humic acid content (% of total carbon) in layers 0–10 cm and 10–20 cm.

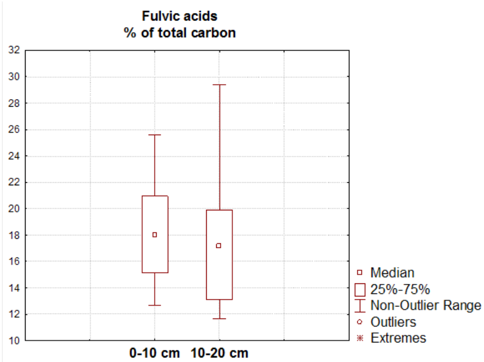

Fig. 6. Fulvic acid content (% of total carbon) in layers 0–10 cm and 10–20 cm.

mic-fulvic humus (see Table 1). According to Bonifacio at al. (2011), humus forms in soil are the first tool characterizing the circulation of soil organic matter and should be related to the stability of org. C stock. The humification degree of soil organic matter is very high (on the scale of Artinova 2014a). It is expressed by the values of percentage of humic acids in the total organic carbon, which are over 20 %. These are found in profiles 1, 2, 3, 6, 7 and 8. In the other cases the humification is high.

The mobile, 'free' and R_2O_3 complex humic acids, expressed as a percentage of the total humic acid content is high and varies within the range 47–100 %. Very low to average content of Ca complex humic acids is determined in the course of the analysis, which is the result of losses of this element in the intensive leaching process. It is demonstrated by the aggressive fulvic acids in soil, extracted with 0.1N H_2SO_4, the amounts of which vary from 2.72 % to 5.70 % of the total org. C. The Ca complex humic acids determine the humus resistance to oxidation processes and stabilize SOM (Bogacz 2011) which is of great importance for Umbrisols due to their soil texture.

The content of non-extracted org. C is high. In the humic acid sum it reaches 50.37 % – 72.88 %, occupying a significant part of them which can be attributed to a number of factors. It is well known that the decrease of temperatures and increase of average annual precipitation quantities slow down the mineralization processes (Bot and Benites 2005). At the same time, the low clay content of these soils (Andreeva 2013) creates a limited adsorbent for establishing the connection between clay particles and organic matter, which is a prerequisite for delayed decomposition.

The results of the humic acid optical density ($E4_{465nm}/E6_{665nm}$) are estimated from medium to high with the prevalence of high values, which indicates an accelerated condensation processes of humic acids. This process was confirmed in Umbrisols by Artinova (2014b). Humus state of the surface soil layer, immediately exposed to atmospheric impact, is estimated as stable. Regardless of its high acidity, the percentage of humic acids, fulvic acids and non-extracted carbon in the total carbon content is stable and does not differ from the underlying soil layer.

The org. C stock (Table 2) in the surface 10 cm layer is 7.00 ±1.31 $t.ha^{-1}$ and 15.55 ±2.72 $t.ha^{-1}$ in the 10–20 cm layer. Much higher values can be found in the relevant literature. In Latvia, for example, the org. C stock in 20 cm soil layer of Umbrisols is 72 ±8.3 $t.ha^{-1}$. According to Turrióna et al. (2009), at equal other conditions the soil-forming rocks have a great importance – soils formed on granite contain less organic matter quantities in comparison with soils developed on shale.

Table 2. Location of sampling points, bulk density, content and stock of org. C.

Point No	WGS 84 coordinates	Depth, cm	Bulk density, kg.m^{-3}	Org. C, g.kg^{-1}	Org. C, t.ha^{-1}
1	42.564767200	0–10	249	18.54	4.62
	23.280099200	10–20	557	14.54	16.20
2	42.564788300	0–10	378	18.99	7.18
	23.280092900	10–20	321	16.36	10.50
3	42.564812100	0–10	365	15.45	5.64
	23.280084500	10–20	546	12.27	13.40
4	42.564823900	0–10	399	17.27	6.89
	23.280086900	10–20	619	14.27	17.67
5	42.564824400	0–10	408	18.18	7.42
	23.280047200	10–20	612	13.95	17.07
6	42.564825000	0–10	480	18.74	9.00
	23.280040200	10–20	708	13.62	19.29
7	42.564831600	0–10	407	17.66	7.19
	23.280031400	10–20	429	14.17	12.16
8	42.564839000	0–10	454	14.60	6.63
	23.280021600	10–20	595	14.60	17.37
9	42.564846700	0–10	498	17.76	8.84
	23.280023300	10–20	701	11.55	16.19
10	42.564851300	0–10	414	15.80	6.54
	23.280020700	10–20	669	11.66	15.60

The difference between org. C stock in the two layers is statistically significant (Fig. 7). It is more than two times and comes mainly from the bulk density values. Under the influence of the grass species root system it is significantly lower in the layer 0–10 cm, compared to the layer 10–20 cm (Fig. 8).

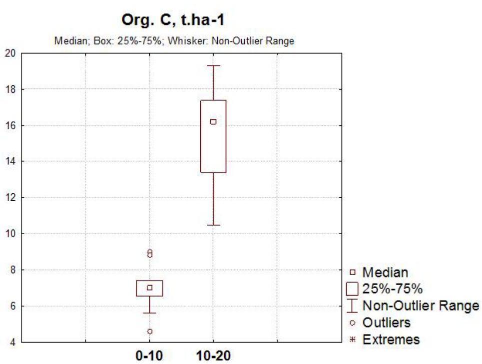

Fig. 7. Org. C stock in layers 0–10 cm and 10–20 cm in Umbrisols.

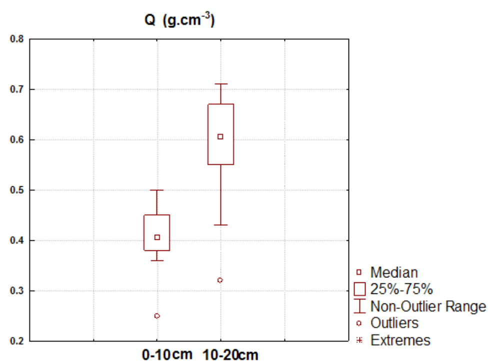

Fig. 8. Bulk density in layers 0–10 cm and 10–20 cm in Umbrisols.

The org. C stock in the surface 20 cm layer is 11.27 ±1.65 $t.ha^{-1}$. Taking into consideration the area of Umbrisols on the territory of the Vitosha Nature Park – 1645.5 ha, the total org. C stock in the surface 20 cm layer of these soils is 18594.15 t.

The current state of the parameters examined in the present study has been formed for a long period of time. No relevant data for soils in the area can be found in the scientific literature, so no comparisons or estimates for the impact of climate changes on the org. C stock can be made.

The first available data about weather conditions (temperatures and precipitation), dates back to 1901, but regular information has been collected since 1935 by the Cherni Vrah meteorological station. Analysing the existing information (Management Plan … 2014, Preparation of water … 2014) it was determined that the variation of the mean annual air temperature T*y* (°C) with the increase of the altitude *H* (m) is linear and can be analytically described by a straight line equation. According to data for the period 1961–1990, this variation can be expressed by the equation $Ty=-0.0055 \cdot H+12.709$ at very high correlation coefficient R=99.8 %. Regarding the period 1961–2010, the analytical expression is $Ty=-0.0055 \cdot H+12.91$ at R=99.7 %.

The minimum and maximum temperature values calculated for the period 1961–2010 are as follows: -10.3 °C (January), -10.2 °C (February) and 5.7 °C (August). Regarding the period 1961–1990 the values are: -10.3 °C (February), -10.0 °C (January), 6.0 °C (July) and 6.2 °C (August).

When comparing the absolute maximum and minimum temperatures for the periods 1961–2010 and 1961–1990, it was determined that the absolute minimums are practically the same, but the absolute maximums are higher in the last 20 years. Temperature is a key factor controlling the rate of decomposition of plant residues. According to some authors, the reaction rates doubled for each increase of 8–9 °C in the mean annual air temperature (Bot and Benites 2005), but others consider that the relationship between decomposition intensity and temperature variation is not linear (Wetterstedt 2010).

Regarding precipitation, results show that for the last 115 years the annual sum of annual precipitation has decreased remarkably mainly in the areas with an altitude of up to 1800–1900 m a.s.l. The decrease of annual precipitation for the higher parts of the Park, where the present study was carried out, is less pronounced.

Conclusions

A complex of humus parameters was studied and a database on the content of soil organic matter and org. C stock was created for the surface 20 cm layer of Umbrisols at geo-coordinated points, located near the Cherni Vrah meteorological station. Higher acidity (pH_{H2O}), higher total carbon content, free low-molecular humic acids, as well as humic and fulvic acids, calculated as a percentage in the soil sample, were determined in the surface 10 cm layer. The share of humic acids in the total carbon did not differ and was characterised by stable values. At that stage the calcium complex humic acids are little or absent and their behaviour over time should be monitored. The obtained results allow future statistical evaluations of information about monitoring the relationship 'climate changes – org. C stock' over time.

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