

INVESTIGATION AND EVALUATION OF TOTAL ORGANIC CARBON IN SOIL

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Abstract. Soil – is one of the most important natural resources, on its structure and condition not only the aesthetical and cultural earths landscapes productivity depend, but also the ability of the top stratum to accumulate coal even in the long term, when different migration cycles (large and small Carbon migration cycles) take place. The soil also influences the quantity of gas in the atmosphere that causes the green house effect. This paperwork will start the series of publications on the accumulation of carbon in the Lithuania's soil and the change dynamics due to the ongoing climate change. The paperwork presents the soil sample collecting methods and the general methods of measurement of carbon level using the Shimadzu SSM-5000A device. The first general carbon level research of the soil of the meadow of Užpaliai and the forest of Paliepis.

Key words: Soil, general carbon, carbon cycle, organic material.

1. Introduction

Soil – is the special formation of the natural biosphere, natural body, that formed in the top levels of the Earth-crust with the influence of the climate, soil forming rock, relief, plants and other live organisms in the formation period of the country [1]. It is very hard to separate the priority factors of the soil forming, because they are closely bonded. The complex of different factors form different soils.

The surface of lithuanian territory, with the exception of a small southern part, has formed by the Valdajus icing glacier bedsores, that were left by the melted glacier about 12-20 thousand years ago. According to the genetic type of the relief in Lithuania about 30% are the formations of the glacier bottom, 27% - glacier outskirts, 23% - *limnoglacialis* (lot.), 11% - *fluvialis* (lot.) ir 7% - *fluvioglacialis* (lot.) formations [2].

The organic material of soil is one of the most important elements that influence the potential fertility of the soil. As one of the main accumulator of the solar energy it is involved in the fundamental processes and predetermines the physical characteristics of the soil, that has the influence on the plant nutrition regime and vital to the plant growth. [3]. The organic materials of soil consist of: humus (80-85%), non disintegrated plant remnants and roots (10-15%), and other live organisms (up to 15%). The

ratio of the organic remnants in the cultivated meadows and forests are: fir-grove – 32, pine forest – 66, cultivated plant crop 16-31 [3, 4].

The main source of the organic material of soil in the ecosystem – organic materials are produced during the plant photosynthesis and in very small amounts by *autotrophos* (lot.) soil bacteria. When organic bacteria gets into the soil ecosystem they can: 1) completely mineralogise and by that enrich the supply of carbon and minerals. 2) be used for the nutrition of the microorganisms and to assimilate in the microbic biomass. 3) be included in the newly formed humus materials. The speed and direction of these changes depend on many aspects, such as the quantity of the soil microorganisms and the intensity of their work, the climatic conditions of the soil, the quantity of the plant remainder and their chemical structure [5].

Bacteria, aktinomicets, invertebrate animals and plants increase the ferments that are important catalizators in the soil as they increase the disintegration of organic materials and the processes of synthesis. The micro organisms and animal, by dying, increase the organic materials 100 – 200 kg/ha on average annually in the soil [6].

The accumulation of nitrogen and organic materials in the top horizon and the level of it in the soil – is one of the most important soil fertility indicator, that influence the agrochemical and

physical characteristics of the soil, its biologic activity and buffering. In the organic material it is accumulated 98% soil nitrogen, 80 % sulphur, 60 % phosphorus, a large quantity of other macro and micro elements. Joined in the organic combination these elements are saved from being flushed out [7, 8].

In Lithuania the soil is separated in the 5 groups according to the level of humus in it.

Table 1. The evaluation of the humus level in soil [8]

The level of humus in soil	Humus %		
	Sand	Sandy loam, Clay loam, clay	Forest soil
Very low level of humus	Less than 0,5	Less than 1,0	Less than 1,0
Low level of humus	0,6 - 1,5	1,1 - 2,0	1,1 - 2,0
Medium level of humus	1,6 - 2,5	2,1 - 3,0	2,1 - 4,0
High level of humus	2,6 - 3,5	3,1 - 4,0	4,1 - 6,0
Very high level of humus	More than 3,5	More than 4,0	More than 6,0

Lithuanian soil depending on the humus reserve are divided as: containing less than 30 t/ha of humus, occupy 1.3 %, 31 – 40 t/ha 3,9 %, 41 – 50 t/ha 15,3 %, 51 – 60 t/ha 13,7 %, 61 – 70 t/ha 6,4 %, 71 – 80 t/ha 7,7 %, 81 – 90 t/ha 26,4 %, more than 120 t/ha 6,9% of the countries territory [9].

Carbon as one of the main macro element of the soil is a part of the humus acid, fulvo acid and non hidrolized remainder – humid acid [10].

The characterized by high productivity soils, as a rule, are rich in humus (7-10 %) and respectively by carbon (2-3,5 %). Simultaneously they are one of the natural drains of carbon, which regulate concentration in the atmosphere of the Earth of this greenhouse gas as carbonic acid. The distribution of carbon on its basic reservoirs in the lithosphere and the external mantle of the Earths according to is shown in table (table 2) [11].

Table 2. Carbon amount in Earth ecosystems [11]

Reservoir	Carbon amount	
	10 ⁹ t	%
Atmosphere	668	0,0006
Land fitomas	900	0,0008
Pedosphere	1550	0,0013
Ocean	40643	0,0344
Earth crust	118000000	99,9629
Full amount	118043761	100

As is evident, the overall share of carbon, find in the Earth's atmosphere and in the biomass of land, it is very small - only order 0,0014% of its overall mass in

all reservoirs of the earth's crust and external mantle of the earths. Approximately so many carbon it is concentrated in pedosphere of the land, where soil humus is its majority carrier (77,4%). In this case the general reserves of carbon in the forest bedding and the soils of boreal forests 2 times approximately exceed its reserves in the biomass of the ground-based vegetation of tropics, in portion of which are fallen more than 40% biomass of the vegetation of land [12].

Considerably larger carbonic capacity possesses the World ocean, where in the composition of living organisms, the weighed dead organic, the dissolved organic and inorganic (HCO₃⁻) matter are located about 40 643 Gt carbons, i.e., approximately more 13 times than in the atmosphere, the phytomass of land and pedosphere together. Let us note that the basic form of the presence of carbon in the World ocean is the dissolved inorganic - bicarbonation HCO₃⁻ (94,8%) [12].

Bulk of carbon of its reservoirs mentioned above is concentrated in the earth's crust - more than 99,96 mass %. this means that the masses of carbon, enormous are at first glance, find in the atmosphere, World ocean, living substance of planet and to pedosphere (almost 44 000 Gt) in actuality comprise less than 0,04 mass % from its overall mass, one way or another, the more or less actively implicated in the global geological rotation of substance planet [12].

Ocean – atmosphere. The atmosphere is natural medium relatively low-inertia with respect to a change in its composition and carbon in the form CO₂ constantly participates in the gas exchange in the system the *ocean- atmosphere*. Since solubility CO₂ in the water rises with a decrease in its temperature (in the fresh water with 0°C 1,71, and with 25°C - only 0,76 ml/l) and the decrease of the concentration of the dissolved salts, the cold and relatively weakly mineralized water of polar seas contain more dissolved CO₂, than the warmer and stronger mineralized water of the equatorial belt of World ocean. Therefore cold oceanic (thermohaline) flows are carriers CO₂ into the equatorial belt, where with heating of waters its release and isolation into the atmosphere occurs [13].

In the system *ocean - the atmosphere* functions the having the greatest ecological value buffer system of the carbonate equilibrium: with the growth of partial pressure CO₂, for example, in the atmosphere carbonic acid is dissolved in the sea water and, being connected with it, it gives carbon acid H₂CO₃, which usually dissociates on H⁺ and HCO₃⁻. A drop in the concentration CO₂ in the atmosphere, on the contrary, in accordance with the Le Chatelier principle is caused its emission by ocean and disintegration in the sea water of carbon acid on CO₂ and H₂O [13].

By the most important functions of this conglubulation are the maintenance of pH of oceanic water and partial pressure CO₂ in the atmosphere, the regulation of concentration CO₂ in the oceanic water,

including with a change in its temperature and mineralization, absorption isolatable into the atmosphere with the differentiation of the substance of the Earth volcanic CO₂. To these functions was at present added one more - absorption of carbon dioxide, isolated into the atmosphere and which participates in the ionic drain from the land in connection with the technogenic processes. Since mass CO₂ in the ocean is considerably more than in the atmosphere, as the most important regulator of its concentration in the atmosphere protrudes precisely ocean [13].

Biological rotation. By living organisms in the biomass of the Earth are yearly connected about 140 Gt carbons, i.e., approximately 21 % from that being containing in the atmosphere. Since the process of decompositions of the dead organic matter, which are accompanied by the formation of carbon dioxide, simultaneously in the biosphere proceed, the losses of the latter in the Earth's atmosphere as a whole does not occur.

From other side, not all organic matter, synthesized by the organisms of the Earth, after their loss undergoes complete destruction with the release of carbon in the form CO₂ and in the form of its other connections. Analysis tabl. 1 shows that only mass of carbon in the forest beddings, the peat and in the humus of soils is about 1550 Gt, i.e., 11 times it approximately exceeds its mass in the annual production of biosphere. Furthermore in the water of ocean constantly find about 2 100 Gt dissolved and weighed organic carbons [13].

The part of the not experienced destruction inanimate organic matter undergoes burial, being included in the composition of sedimentary geological formations and remaining in them in one or other form or another during hundreds of millions and billions years. According to the available estimations (A.B. Ronov, A.A. Yaroshevskiy, A.A. Dobrovolskiy and other) sedimentary mantle of the Earth contains, at least $15 \cdot 10^{15}$ t of organic carbon, i.e., its mass here more than 10 000 times exceeds the mass of carbon in the biomass of the Earth. The absolutely large part of this carbon is the scattered organic matter of the rocks, whereas in the portion of its concentrated accumulations in the form of the layers of coal and oil are felt only about 0,04% ($6,2 \cdot 10^{12}$ t). If to coal and oil are added even and the layer of the bituminous shale (more than $26 \cdot 10^{12}$ t in the conversion to schistose resin), then this estimation, apparently, will be doubled. However, the general degree of concentration of organic carbon in stratisfere of the Earth remains low – one order with the average degree of concentration of the majority of metals in the lithosphere, i.e., of about 0,1% [14].

The predominant form of the presence of carbon in the sedimentary mantle of the earth is carbonate, throughout the mass is more than 5 times that predominating above the organic, which is usually connected with photosynthesis of organic matter by

plants, whereas carbonate - with the formation of the carbonates, whose appearance far from always is associated with the processes of the vital activity of organisms [14].

The estimation of mass of carbon, which falls from the biological rotation as a result of its burial in the sedimentary rocks, are sufficiently approximate and in different researchers significantly disperse. It is possible to assume that this of number on the order of 0,10–0,15 Gt of organic carbon even 0,15–0,30 Gt carbonate. Then the closure failure of the biological cycle of the migration of carbon only on C_{org} can compose 0,07–0,11%, and it is summary on C_{org}+S_k – order 0,18–0,32% [14].

Siliconcarbonic biogeochemical cycle. Besides the exchange of carbon in the system the *atmosphere - ocean* on the Earth successfully functions another most important in ecological sense system the *atmosphere - ocean - lithosphere* with the development in it of the carbonate-silicate cycle of migration. It is possible to consider the weathering of the rocks on the continent and connected with this extension Ca into the World ocean, where occur predominantly the biogenic deposit of its carbonates, connecting CO₂ the beginning of cycle. The accumulation of great thicknesses of carbonate deposits, lowering the sea bottom and caused by this their metamorphism conduct to the binding Ca with Si into silicates and the release CO₂. Freed carbon dioxide in the processes of gas exchange again enters the atmosphere, locking the carbonate- silicate cycle of the migration of carbon [14].

As notes A.A. Marakushev, [14] this cycle possesses the property of autocorrelation and self-regulation, coming out as the factor, which stabilizes the temperature conditions of the ecosphere of the Earth.

The steady functioning of biosphere in the scales of geological time is ensured by the precisely carbonate- silicate cycle of migration. Without the metamorphic mobilization CO₂ from the carbonate rocks contemporary life would cease in time on the order of 1 million years in view of the complete exhaustion by the photos-synthesist of carbon dioxide of the atmosphere. It is necessary to note that this is correct only for the contemporary biomass of the Earth and its contemporary productivity [15].

Balance of those connected with the activity of the man of the flows of carbon in the world in accordance with the data of [15] it appears as follows (Gt in year):

industrial ejections	6,41
cutting down of forests	1,08
erosion of soils	0,91
absorption by the ecosystems of land	4,05
absorption by ocean	1,05
remain in the atmosphere	3,30

Consequently, about 40% of entering the atmosphere from the sources indicated carbon remain in it and together with other greenhouse gases participate in the formation of greenhouse effect. The general entering into the Earth's atmosphere carbon, connected with the consequences technogenesis, in the present time more than 10 times exceeds its entering into the ecosphere from the natural endogenous sources (volcanism, fumarole, etc.) [16].

Exceptional role in the global cycle of carbon belongs to ground-based ecosystems. According to the available estimations at the end of the past century, including as a result of the development of the processes of fertilization, the ecosystems of land on the average absorbed on 0,7 billion t C more than they separated. And although the evaluations of the relative role of World ocean and vegetation of land into the utilizations of anthropogenic CO₂ of the atmosphere, given by different sources and utilized by different models of the calculation of its total balance, significantly are distinguished, important role in this process of soil cover and forests, especially boreal, it is undoubted [16].

The cutting down of the forests of planet is critical at least for 20–25 % the anthropogenic ejections of greenhouse gases – decrease of general biomass and volume of absorbed CO₂ from the atmosphere, the degradation of soil cover, the mineralization of forest bedding, etc [16].

Among the ecosystems of land special position occupy marshy ecosystems, first of all moderate climatic belts. Thus, according to the data of the scientists of Tomsk, in detail investigating Large Vasyuganskoye swamp in West Siberia large in the world by area it is more than 5 million ha, a quantity of carbon, deposited by the vegetation of oligotrophic swamp under the natural conditions, to 60 % exceeds its emission in the same time. The greatest values of emission CO₂ in this case are established for the years with the minimum amount of precipitation – to 170 mg/m²·hour⁻¹. The emission of methane, on the contrary, is maximum in the most moist years – to 11,8 mg/m²·hour⁻¹. In this case with lowering in the level of ground water occur connected increases in the emission CO₂ and the reduction in the emission of methane. The general reserves of peat in this swamp exceed 9 billion t [17], and the fresh water, which contains on the average of 52 mg/l of organic carbon, 400 km³. The mass of deposited by marshy system organic carbon exceeds 5 billion t, and by the peat bogs of entire West Siberia – more than 42 billion T. The processes of improvement, draining of swamps in ecological sense for the deposition of carbon have negative value, including in Lithuania. Analogous value has dehumification of soil cover, as a result of which, for example, in Kazakhstan by the arable layer of soils it is lost by 1,2 billion t of humus, i.e., it is more than 28 % from its total quantity [18].

Work objective: identify the amount of total organic carbon in meadow and forest soils.

2. Work methods. The collection of soil samples

The soil samples for the ascertainment of the carbon level have been collected in summer of 2007 in two sites: Užpaliai and the forest of Paliepis (Fig 1, 2). The sample collecting methods were prepared based on the soil sample collecting protocol, prepared by European Union, for the ascertainment of the organic carbon level change. Whes soil samples taken form Užpaliai and Paliepis because its to far from big poliution centres. Soil samples taken from sand soil (Paliepis - pine forest) and clayey soil (Užpaliai - meadow).

In the meadow of Užpaliai and the forest of Paliepis the samples were collected in the 50X50 meters square sites. The samples were collected as shown in the Fig. 1 and 2 defined by 3 sites (cells) 5x5 meters. The main plants in the meadow were – clovers and bent grass.

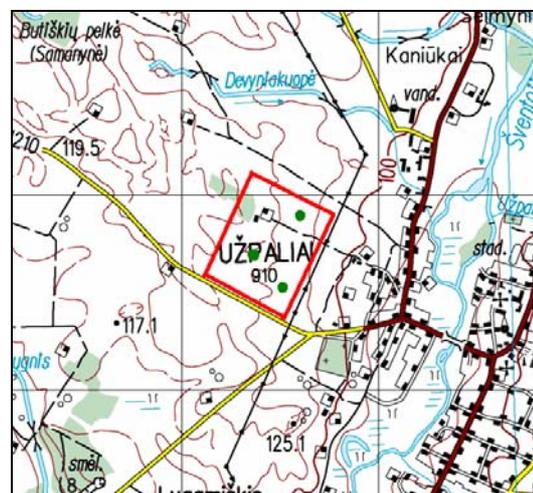


Fig 1. The collection scheme of Užpaliai soil samples (the collection sites are marked in green)

For the collection of the non broken structure soil samples the metal ring was used, 5 cm in high and 15 cm width. The ring is used in order to physically harm the soil as less as possible. To collected soil samples were placed into the numbered plastic bags.

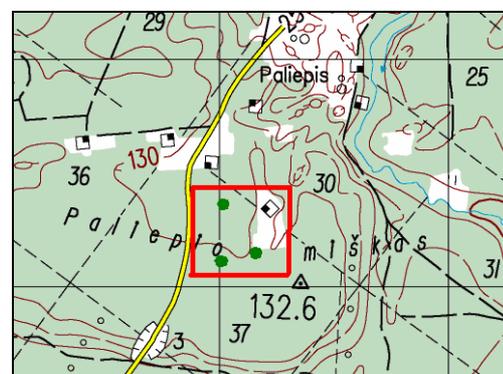


Fig 2. The collection scheme of the forest of Paliepis soil samples (the collection sites are marked in green)

When collecting the samples the net with 100 cells was used, the identification number is selected in accidental order. (Fig 3)

The cell measurements are picked according to the investigated soil site. For example, the explored site is marked by red line (Fig 3), and it has to fit into the used net. The chosen soil site can be rectangle or of any other shape. If the explored site is of the non correct form, then the net corner co-ordinates must be set.

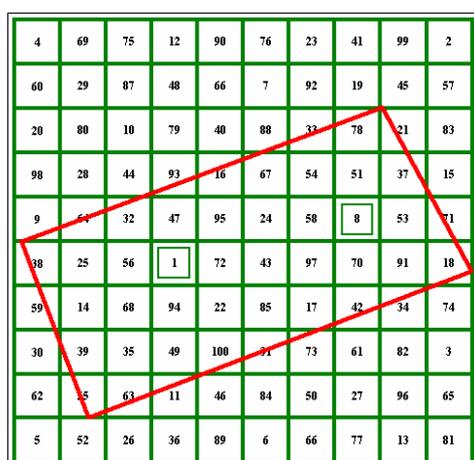


Fig 3. The net of the soil sample collection. The red line marks the boundaries of the explored soil. The cells 1 and 8 are chosen for the sample collection.

The cell measurements are fixed by the nets X and Y borders divided by 10. This way the samples are collected systematically regarding to the explored site size. According to the Fig 3 the chosen cells are number 1 and 8. The choice of cells depend on the size of line number – in the choosing state the cells that have the smallest number and that are a part of the explored site are chosen. The cells that only partially belong to the explored site or the sample gathering is impossible in them are ignored. In such cases the next cell with the higher number is to be chosen.

The choice of the cell numbers depend on the size of the explored soil site (Table 3).

Table 3. The choice of cells according to the explored soil site

The size of the explored site, ha	The number of the chosen cells
<5	3
5 – 10	4
10 – 25	5
>25	6

The recommended number of samples collected in each cell, by the ISO 200a standard, is 25 (Fig 4). The minimum number of samples to be collected in one cell is 9, yet the received data after the analysis cannot be considered as representative. The number of samples is chosen by dividing the side of the cell by 6. These sample collecting sites are to devoted for the

gathering of the compound sample. The non broke samples for the ascertainment of the soil thickness are gathered in the centre of the cell using the ring.

The number of samples taken in the cell's compound and non broken sample gathering sites differ depending on the soil type. There are tree soil types: forest soil, meadow soil and farming soil.

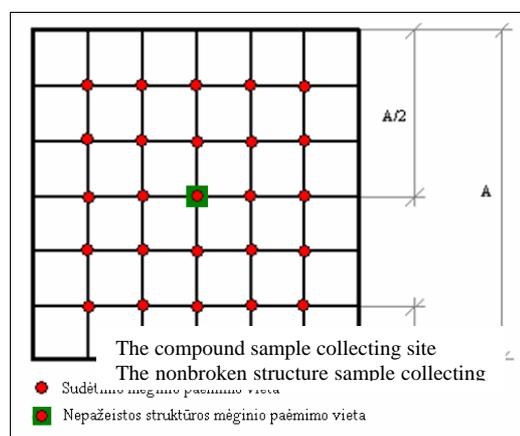


Fig 4. Sample collecting sites in a cell

ICP recommendations were kept when exploring the forest soil (UNECE, 2003). 5 samples of the up to 25cm depth are taken in the cell in non broken structure sample collecting site. Before collecting the sample of non broken structure the sample of the top layer of leaf litter of the 25x25cm size is taken. The compound sample is taken from 0 – 10, 10 – 20 ir 20 – 30 cm depth in all the 25 sample collecting sites, also in the non broken sample collecting site. For the collection of the compound sample a small amount of soil is taken, the amount is around 1 liter. For the analysis 2 compound samples of the forest and farming soil are taken.

For the exploration of the meadow soil the samples are collected of the 30cm in depth. 5 samples of the non broken structure are taken using the ring every 5cm and after removing the top layer of all the verdure. The compound samples are collected in the 0 – 10, 10 – 20 ir 20 – 30 cm depth in all the 25 gathering sites, also in the nonbroken structure sample collection place.

2.1. The methodics of general soil carbon (TOC) ascertainment using the device SSM-5000A.

All samples had been dried before the measurements as water in the sample can have negative influence on the final results of the hard sample form and matrix. The sample is dried for 1 hour in the 100 °C heat till it becomes of the normal weight. All samples (up to 100mg soil) before any measurements have been grinded with the pounder as the carbon combustion oxidation utility factor changes due to the sample type and structure.

In the TOC furnace the working temperature of 900 °C is set.

Before fulfilling the measurements the sample analysis dishes are heated up in the electric laboratory stove so that the carbon in them would oxidate. The sample dish is heated in the stove in the heat of around 500 °C for 20 minutes. The quartz glass filter paper is heated in the stove in the heat of 300 °C for 20 minutes. The tweezers are heated during the heating process. The heated dishes, quartz glass filter paper and tweezers are held in the clean container or box.

The stuck alkali absorb CO₂ from the surrounding and the karbonatai (for example natrium karbonatas or calcium karbonatas), because of that the greater carbon level can be seen in the results, greater then it really is.

The sample grinding:

1. All the material not needed for the experiment are removed.

2. The collected sample is carefully grinded with the pounder.

3. The grinded sample is sifted through the needed thickness of sieve (used 1 mm).

4. The non sieved parts are grinded again. In order to minimise the sample the conoidal distributor or guttered pick up is used.

5. The steps 3 and 4 are repeated for the final sample to be gained, which is sifted through the 200 eye sieve.

In order to gain the accurate data the sample material in the dish has to be spread evenly. Sample quantity is chosen by the optimum weight, taking into consideration the burning temperature and the lack of oxygen during the burn time.

The carbon concentration is presented in percentage in the comparison to the dry soil sample weight..

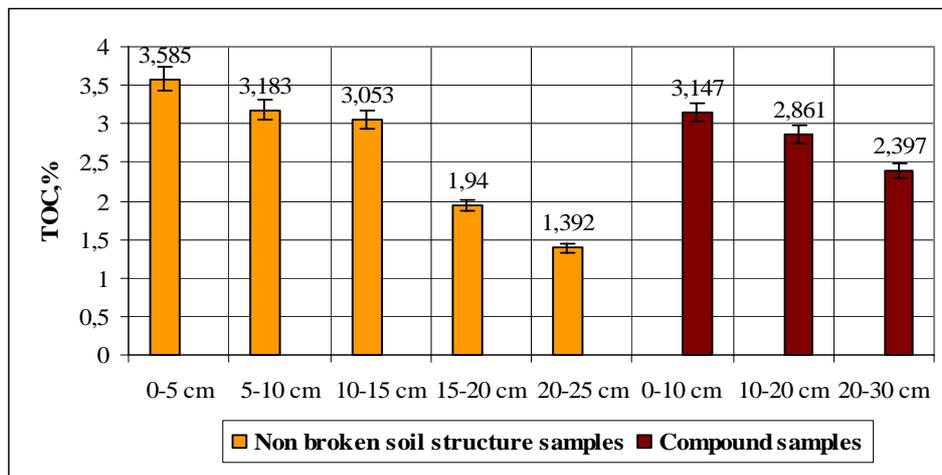


Fig 5. The general carbon (TOC) quantity of the 2nd site of the Užpaliai meadow

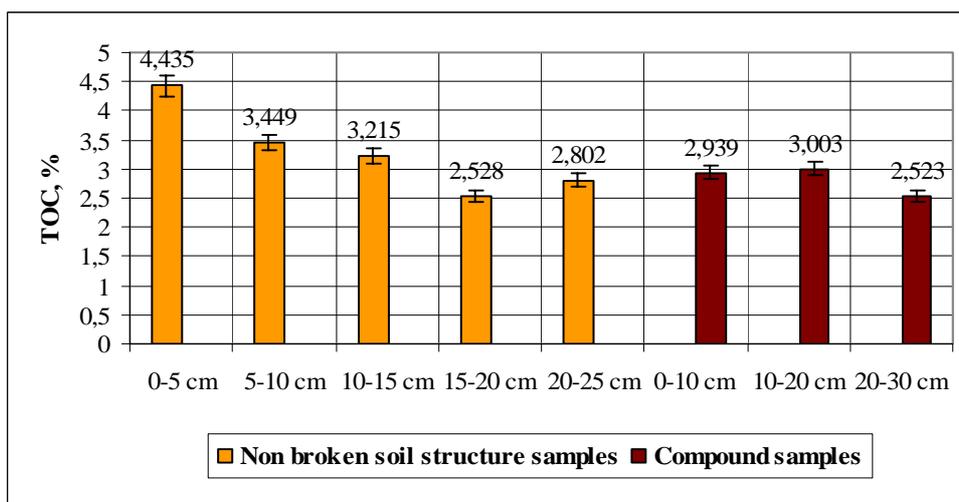


Fig 6. The general carbon (TOC) quantity of the 4th site of the Užpaliai meadow

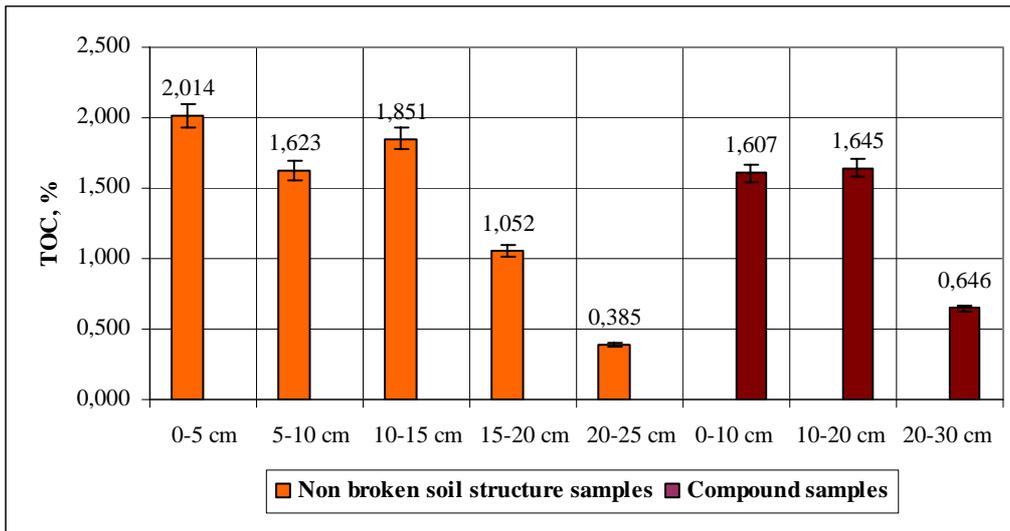


Fig 7. The general carbon (TOC) quantity of the 8th site of the Užpaliai meadow

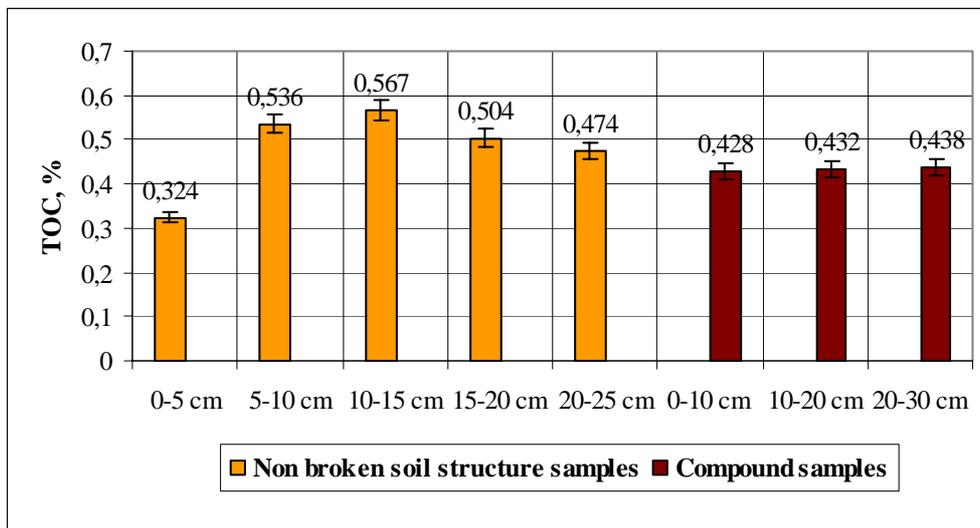


Fig 8. The general carbon (TOC) quantity of the 2nd site of the Paliepis forest

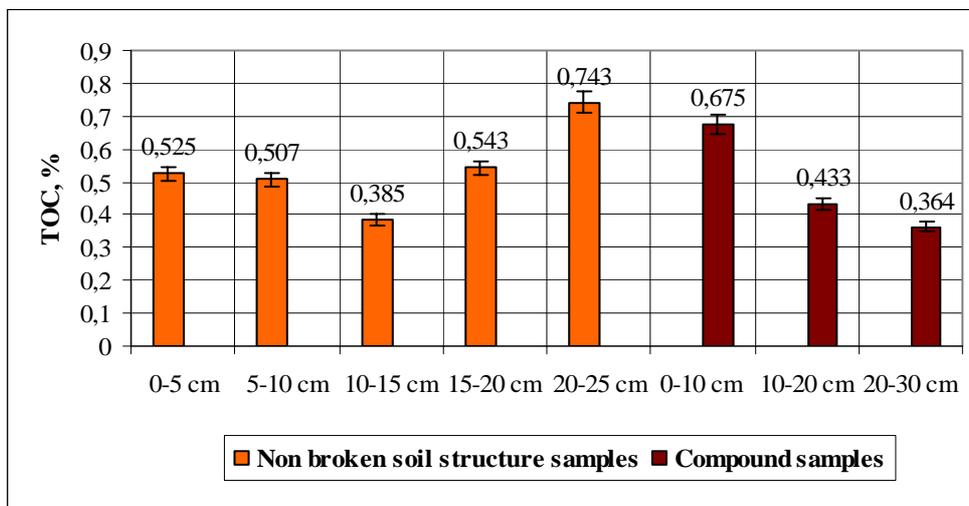


Fig 9. The general carbon (TOC) quantity of the 4th site of the Paliepis forest

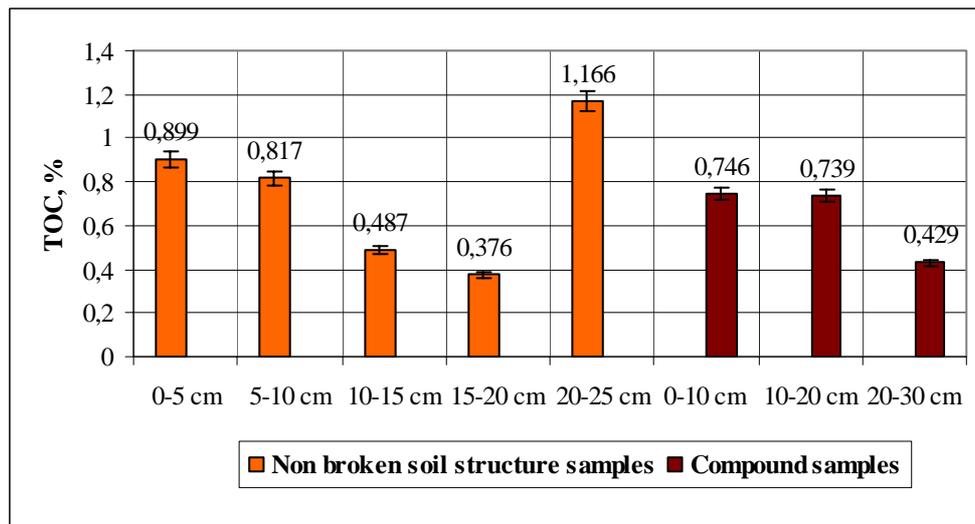


Fig 10. The general carbon (TOC) quantity of the 8th site of the Paliepis forest

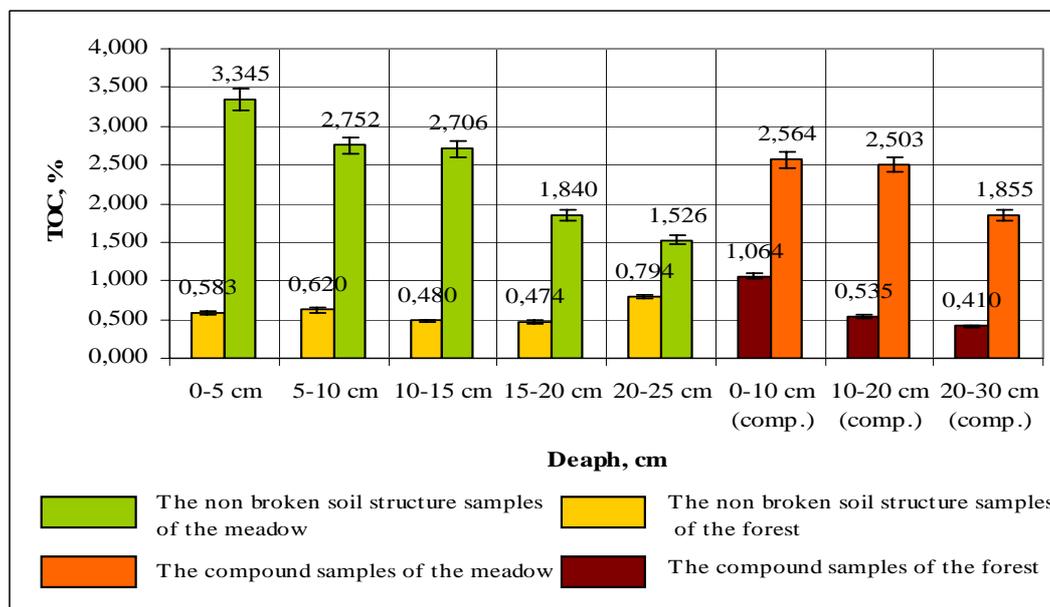


Fig 11. The general carbon (TOC) quantity of mediocre meadow and forest soil

3. Research results

According to the research results the quantity of general carbon in the meadow soil of the non broken samples in the 2nd site changed from 1,392 to 3,585 % (Fig 5).

According to fulfilled research the reduction tendency of the general carbon is noticed when the depth of the collected sample increases. The greatest amount of carbon is detected in the top layers of soil – 3,585 %. In the depth of 20-25 cm the amount of carbon decreased by 2,6 times. The quantity of carbon in the compounded samples changed from 2,397 to 3,147%.

Comparing the non broken structure samples the results differ from 1,1 times less in the top layers and 1,8 times more in the depth of 20-30 cm

In the 4th site the general carbon quantity decreased from 4,435 in the top layer to 2,528% in the depth of 15-20 cm (Fig 6). In comparison with the compound sample analysis the quantity of general carbon in the top layers was 1,4 times lower. In the depth of 20-30cm the difference between the compound and the non broken structure samples was very low.

The quantity of general carbon in the 8th site changed from 2,014 to 0,385% according to the depth. The maximum quantity of it here was detected in the depth of 10-20cm both in the compound samples and in the non broke structure samples. The difference between them does not exceed 1.04 times (Fig 7).

In the forest soil in the 2nd site the quantity of general carbon was at its maximum in the depth of 5-20cm- from 0,504 to 0,567 % (Fig 8). It decreases a

lot in the lower and higher depth. The minimum concentration (0,324%) was detected in the depth of 0-5 cm. In the compound samples the quantity of general carbon very little depends on the depth (0,428 – 0,438 %).

In the 4th site the non broken structure samples the quantity of general carbon varies from 0,385 to 0,743%, the minimum (0,385) is at the depth of 10-15cm. In the compound samples the highest general carbon quantity (0,675%) was detected in the depth of 0-10cm, the lowest (0,364%) in the depth of 20-30cm.

The greatest fluctuation was detected when analysing the samples from the 8th site, although the general tendency does not change: the minimum concentration is noticed in the depth of 10 – 20 cm. The reason of the great differences noticed in the concentration is not clear, in the non broken soil structure samples and in the compound samples in the depth of 20-30cm – accordingly 1,166 and 0,429%.

The summarised the research results using the separated non broken soil structure and compound samples are presented in the Fig. 11.

4. Conclusions

1. Soil is one of the most important accumulators in the biochemical coal cycle, that regulate the level of CO₂ in the atmosphere. The global warming processed the increase the speed of the mineralization and dehunification of the organic carbon, demand for the monitoring of soil carbon in the pedosphere.
2. The medium quantity of general carbon in the examined meadow soil is 2,31 – 2,42 %, and only 0,52 – 0,59 % in the forest soil, which is 4,1 – 4,4 times less.
3. The general carbon distribution tendency was proven correct – the concentration decreases with the depth. Although it is better noticed in the analysis of the meadow soil when a non broken soil samples are examined in comparison with the compound samples. In the forest soil it is different. It is likely that it depends on the different soil structure evenness to the depth and horizontally in the chosen meadows and forest.
4. In the carbon consideration the forest soil distinguishes with greater variety, due to the micro relief and the verdure peculiarity (eg. The 8th forest site that is in the valley and high carbon concentration in the depth of 20-25cm).
5. Continuing works, connected with the general carbon quantity evaluation in the Lithuanian soil and its balance, the samples must be collected in the depth of no less than 100cm.
6. Determining the general carbon level in the soil of known density, it is possible to limit the compound samples, collected in sections of 10-20cm in depth.

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