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## Estimation of oxidizing ability of organic matter of forest and arable soil

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### Abstract

The unique method of multi-stage chemodestruction (11 fractions) of soil organic matter (SOM) for the estimation of its quantitative-qualitative composition of forest and arable soils was applied. Substantial differences in oxidative ability of organic matter in the 0–40 cm soil layer of old oak wood and arable land were determined. The forest soil distinguished by more resistant to oxidation and thus more stable SOM as compared with the soil of arable land. A small content of medium-oxidative part up to its complete disappearance in the 31–40 cm layer is the feature of arable soil. The differences in quantitative-qualitative composition of SOM enable the use of the method of multi-stage chemodestruction for the estimation of resistance of SOM to the destruction at different land use.

Key words: soil organic matter, labile SOM, stable SOM, forest soil, arable soil, multi-stage chemodestructive analysis.

### Introduction

Recent concerns about the role of carbon (C) in climate change and the implications about soil organic matter (SOM) for sustainable use of soils have underlined the need to examine the role of SOM in different ecosystems (Cheng, Kimble, 2001; Janušienė, Šlepetienė, 2001; Buciene et al., 2003; Slepetiene, Slepetys, 2005; Cunha et al., 2009; Ryan et al., 2009).

Most conventional methods used in soil organic carbon determination have been developed to maximize oxidation and recovery of C. However, total organic carbon measurements might not be sensitive indicators of changes in soil quality: small changes in total SOC are often difficult to detect because of natural soil variability and background carbon levels (Blair et al., 1995). Therefore, many attempts have been made to differentiate SOC into various pools of varying lability and the more labile pools have been used as sensitive indicators of changes in response to land use management (Blair et al., 2001; Chan et al., 2001; Weil et al., 2003; Lutzow et al., 2007; Oyonarte et al., 2007).

Chemical fractionation of SOC, based on its susceptibility to oxidation with  $\text{KMnO}_4$  solutions of various concentrations (33–333 mM), was introduced by Loginow et al. (1987) on the premise that microbiological decomposition of organic matter in the soil is also largely associated with an oxidation process of enzymatic character. Blair et al. (1995) modified the procedure using a single concentration of  $\text{KMnO}_4$  (333 mM) as the oxidizing agent. Subsequently, several publications dealing with the use of this method to determine short-term changes in the labile C fraction have appeared (Blair et al., 1997; 2001; Shrestha et al., 2002).

However, soil C oxidized by neutral  $\text{KMnO}_4$  or permanganate-oxidizable C (POC) was better correlated with total C ( $P < 0.01$ ), than with water-soluble C ( $P < 0.05$ ) and was not correlated with microbial biomass C. Carbon oxidized by  $\text{KMnO}_4$  is not a reliable measure of labile C and should be referred to as POC when used as a parameter for characterizing soil C (Tirol-Padre, Ladha, 2004).

Popov, Tsyplenkov (1994) proposed a method that differs from previously described permanganate method (Loginow et al., 1987) in the following: as oxidants are used solutions of  $K_2CrO_4$  with the identical concentration of 0.4 N in eventual volume and with increasing oxidizing ability, created due to the use of series of sulphuric acid solutions, concentrations of which in eventual volume are 5, 10, 15, 20, 25, 30, 35, 40, 45, 50%. The offered method allows selection of 11 fractions of constituents of SOM that differ from each other by stability to oxidation. The active or labile forms of SOM are oxidized more easily, relatively steady (passive) forms of SOM – more difficult.

The aim of the present study was to estimate the features of oxidizing ability of organic matter of forest and arable soil with the use of method of multi-stage chemodestructive fractionating (Popov, Tsyplenkov, 1994) for the control of resistance of soil organic matter to the destruction as affected by different land use.

## Materials and methods

Research of SOM was conducted in protected forest natural boundary of “Kornalovychi” Sambir district of Lviv area (Ukraine), and also on adjoining agricultural territories.

The first experimental area was approximately 40 year-old forest array with predominance of oak (*Quercus robur* L.) and European hornbeam (*Carpinus betulus* L.) and common hazel (*Corylus avellana* L.) in an undergrowth. The second area was a plough-land located near the forest. This territory was also covered by the forest in the past; however, for more than 70 years it has been used in agriculture. The most widespread soils on the given territories are different varieties of loamy sod-podzolic soils (*Gleyic Albelvisols*, ABg). Within the limits of experimental areas, soil samples were taken with the help of a bore to the depth of 40 cm through each 10 cm, the forest litter was removed. The sampling sites were separated in two groups before analysis: forest soils under forest (n = 5), arable soils under cultivation (n = 5).

The total content of humus was determined by Tyurin method modified spectrophotometrically by Nikitin. Fractions of organic matter were determined by the method, developed by Popov and Tsyplenkov (1994). This method is based on different resistance of soil organic matter to the action of oxi-

dant in the form of solutions with the identical concentration of  $K_2Cr_2O_7$ , but with growing oxidizing ability. Oxidizing ability of these solutions depends on the concentration of  $H^+$ , provided with the different amount of  $H_2SO_4$  and described by the Hammett acid function. The greater oxidative ability of oxidant, the more intensive chemical destruction of organic matter is taking place. Accordingly, labile forms of SOM are oxidized by solutions with low oxidative ability, and stable ones – with high ability. On this basis labile and stable parts of SOM are differentiated. As this method is insufficiently elucidated in literature we present the detailed description of the procedure of chemodestruction of SOM: identical ( $\pm 5$  mg) samples of soil are brought into 11 heat-resistant retorts (volume of 50–100 ml); then all retorts are refilled by 5 ml 0.8 N water solution of  $K_2Cr_2O_7$  (40 mg  $K_2Cr_2O_7$  on 1 ml of water). Hereupon 5 ml 0.1 M solution of  $H_2SO_4$  are added to the 1<sup>st</sup> retort; 5 ml of 10% solution of  $H_2SO_4$  – to the 2<sup>nd</sup> retort; 5 ml of 20% solution of  $H_2SO_4$  – to the 3<sup>rd</sup>, 5 ml of 30 % solution of  $H_2SO_4$  – to the 4<sup>th</sup> retort and so on – consistently different retorts are refilled by solutions of  $H_2SO_4$  with a concentration increase by 10%; and finally 5 ml of concentrated  $H_2SO_4$  – into the 11<sup>th</sup> (last) retort. All retorts are placed in a thermostat heated to 140°C and maintained for 20 minutes. The amount of oxidized organic matter is determined colorimetrically (by intensity of the green colouring, predefined by  $Cr^{3+}$ ) (Tsyplenkov, Popov, 1979). Every fraction (part of oxidized SOM) is expressed in percentage from  $C_{total}$ . Results are presented in a differential form, which is more convenient to interpret.

The variability of the determination of the different fractions of C was measured as the relative standard deviation. Statistical data analysis was carried out using *Microsoft Excel 2003* software.

## Results and discussion

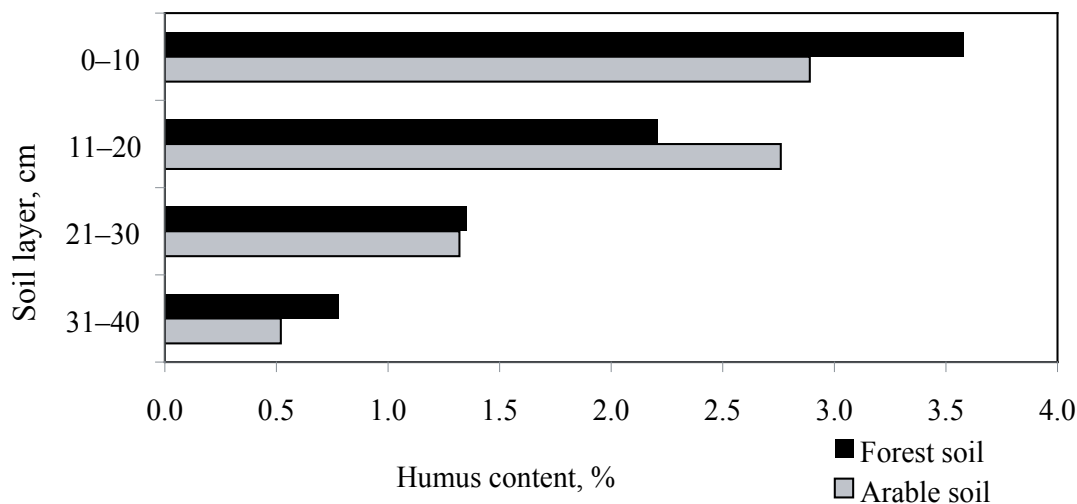
The features of the quantitative distribution of organic matter in the profiles of forest and arable soils are shown in Fig. 1.

It is evident from Fig. 1, that the highest humus content is typical of the upper forest soil layer, where it is 3.58%. Downward the profile humus content gradually diminishes to 0.78% in the 31–40 cm layer.

Humus content in the upper 0–10 cm arable soil layer is less (2.89%), which is typical of culti-

vated soil. In this soil profile humus content is to some extent different than the forest variant: in two upper 0–10 and 11–20 cm layers the humus content is almost identical (2.89 and 2.76%, accordingly),

and downward in the soil profile there is the sharp (on 1.44%) decreasing of humus content in the 21–30 cm layer. In forest soil this change of organic matter content in the soil profile is 0.86%.



**Figure 1.** Profile changes of humus content in soils of experimental areas of forest and agroecosystems

Such differences are explained by the feature of land use: the root systems of grasses are of different structure and power mechanism than those of forest vegetation. Accumulation of organic matter in the upper part of the soil profile of areas, covered by native forest, is caused by the fact, that forest successfully counteracts an eluvial process, forming an almost closed biological cycle. According to Migunova (Migunova, 1993), the protracted growth of foliage forest vegetation, even on chernozems, is accompanied by an increase of humus supplies in soil. It is also shown by this author that in the soil of long ago deforested territories the maximum of humus is accumulated in the upper horizon that is connected with the presence of the forest litter. Power of humus horizons under the forest is substantially greater, compared with the open areas.

Due to the substantial differences of the quantitative distributing of humus in the profile of forest and arable soils the features of fraction composition of organic matter were investigated. The results of chemodestructive analysis of SOM were presented in Fig. 2–5.

As is evident from Fig. 2, the quantitative distributing of fractions in the 0–10 cm forest soil layer is characterized by the presence of few maximums. The 11<sup>th</sup> fraction content reached 24% of

organic matter ( $C_{total}$ ). Practically identical content was determined also in the 1<sup>st</sup> and 10<sup>th</sup> fractions with values 15.4 and 15.7%, accordingly. Other fractions did not exceed 10%.

Analyzing the quantitative-qualitative distributing of SOM by intensity of chemodestruction, Popov et al. (Popov et al., 2004) separated its three parts: labile, with 1–4 fractions, medium-oxidative – 5–7 fractions, and stable – 8–11 fractions.

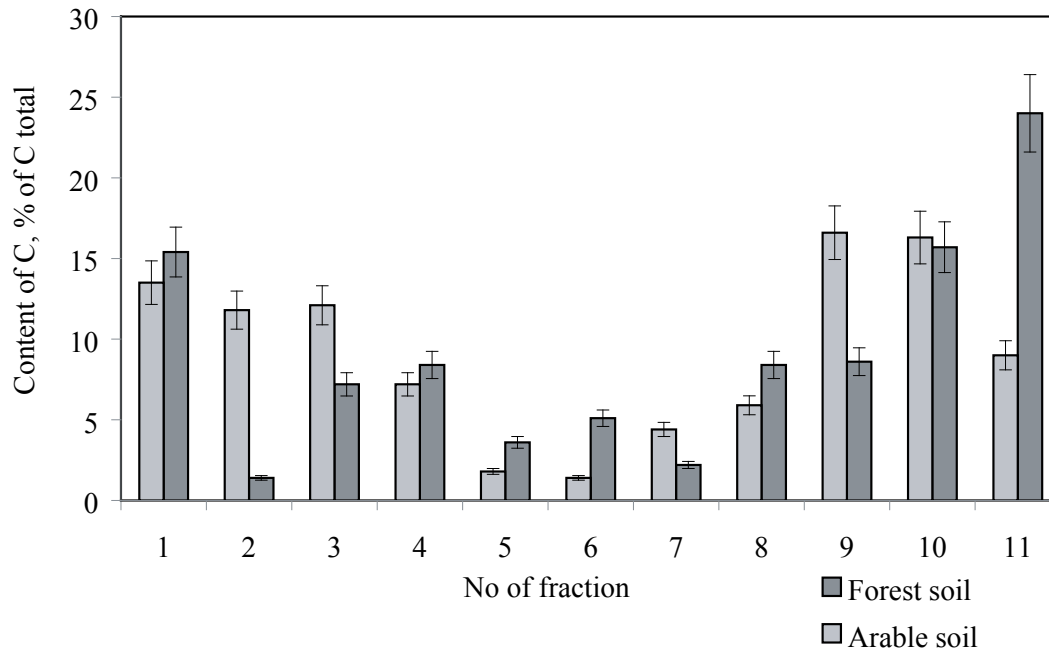
Some other differentiation of fractions, got as a result of chemodestruction of SOM, carried out by Mazur (Mazur, 2007), who divided 1–2, 3–4, 5–8 and 9–11 fractions in separate groups, differ in the structure and stability. This led to the conclusion that in the 0–10 cm forest soil layer a stable part of organic matter prevailed.

In the upper layers of arable soil, a clear predominance of the content of separate fractions was not observed as in the case of forest soil. The content of the 9<sup>th</sup> and the 10<sup>th</sup> fractions was the greatest – 16.6 and 16.3% accordingly, however labile and stable parts of SOM were almost equal. The least content was characteristic of the 5<sup>th</sup> and the 6<sup>th</sup> fractions (1.8 and 1.4% accordingly), that testifies to the small part of a medium-oxidative SOM.

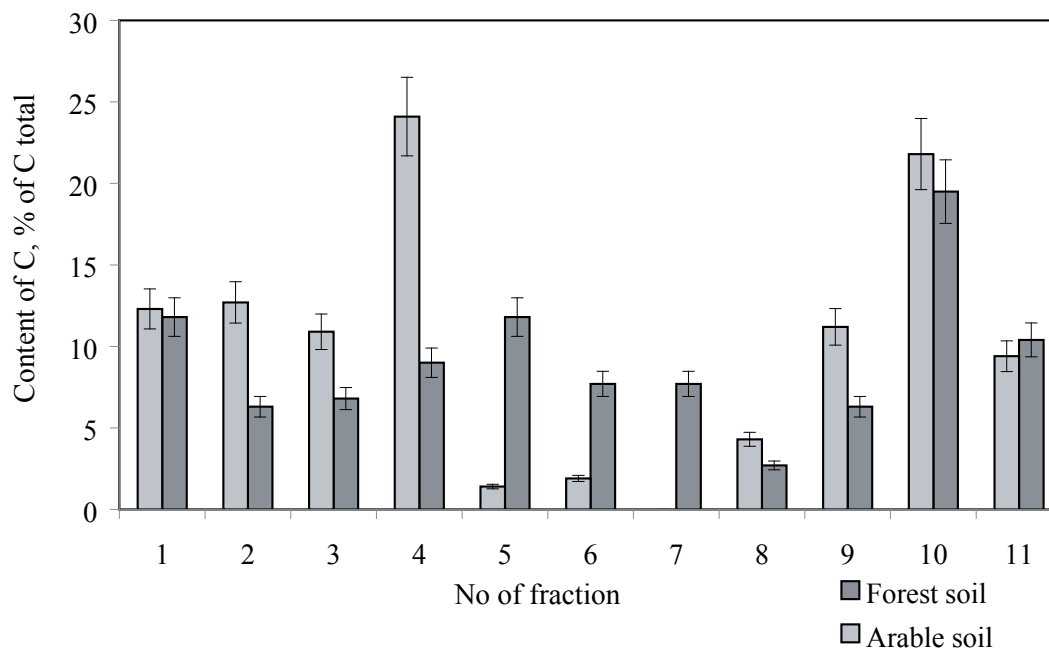
The fractions composition of SOM changed a little in the 11–20 cm layer compared with the upper located layer (Fig. 3). A few maximums are evi-

dent here, however a maximal value is characteristic of the 10<sup>th</sup> fraction (19.5% from  $C_{total}$ ), but not the 11<sup>th</sup>, thus the 11<sup>th</sup> fraction content in the 11–20 cm soil layer decreased by 13.6% compared with the upper horizon. It testifies to the substantial changes of quantitative-qualitative composition of a stable part of SOM of forest soil with a depth.

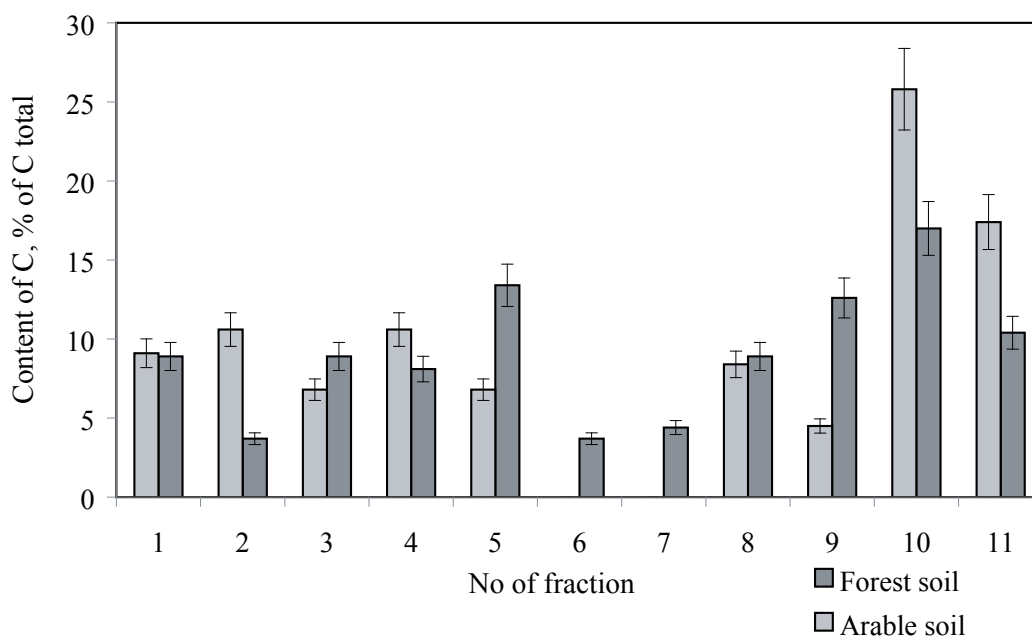
It is worth to notice that the content of labile part of SOM in the 11–20 cm forest soil layer was also high enough: the 1<sup>st</sup> fraction made 11.8%, the 2<sup>nd</sup> – 6.3%. As is evident from Fig. 3, in the 11–20 cm soil layer it is more difficult to select a labile part of SOM, as the content of the first seven fractions changes more droningly.



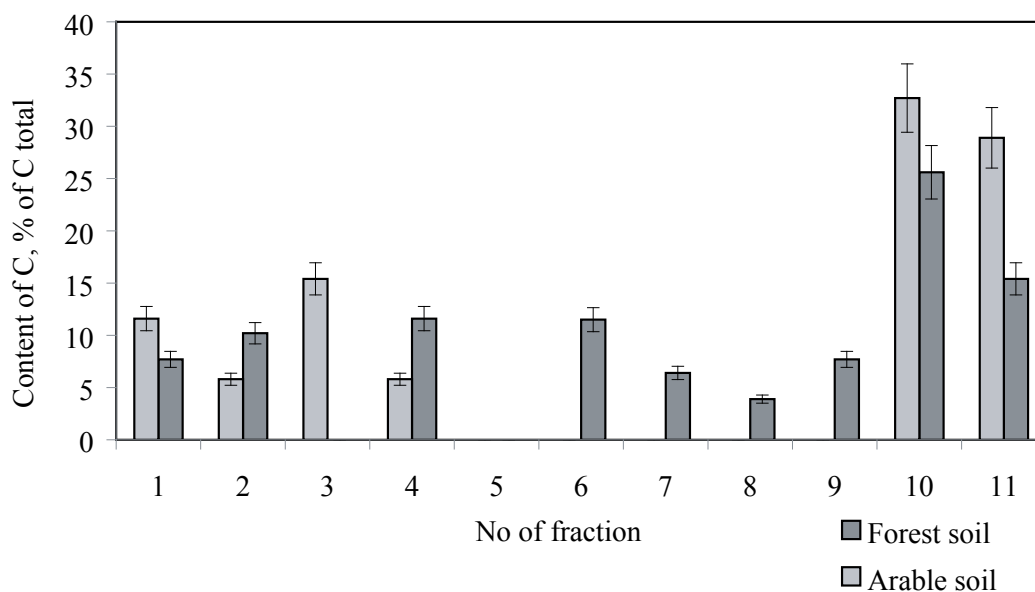
**Figure 2.** Quantitative-qualitative composition of organic matter in the 0–10 cm layer of forest and arable soil



**Figure 3.** Quantitative-qualitative composition of organic matter in the 11–20 cm layer of forest and arable soil



**Figure 4.** Quantitative-qualitative composition of organic matter in the 21–30 cm layer of forest and arable soil



**Figure 5.** Quantitative-qualitative composition of organic matter in the 31–40 cm layer of forest and arable soil

Two fractions of SOM – the 4<sup>th</sup> and 10<sup>th</sup> – were prevailing among others in the 11–20 cm arable soil layer as it was observed in the previous soil horizon. A medium-oxidative part of SOM in that layer was the least, and the other fractions did not differ among themselves.

Thus, the quantitative-qualitative composition of arable soil differs considerably from that in

the forest soil: a negligible quantity of the 5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> fractions testifies to the different quantitative-qualitative composition of SOM.

In the 21–30 cm forest soil layer (Fig. 4) the quantitative distribution of fractions is somewhat different comparatively with the upper located soil layers; however the main features remained the same. In this layer a stable part of SOM was the

greatest – the 10<sup>th</sup> fraction prevailed and made up 17%. But the content of medium-oxidative part here increased due to the decrease of the content of the labile part of SOM. A high content of the 5<sup>th</sup> fraction (13.4%), which gradually increased with a depth, testifies to it.

For the same layer of arable soil a low content of medium-oxidative part of SOM was characteristic. However, unlike the upper located 11–20 cm soil horizon, a stable part of organic matter was clearly traced here with predominance of the 10<sup>th</sup> fraction that reached 25.8%.

The quantitative distributing of fractions of SOM by oxidizing ability changed substantially in the 31–40 cm forest soil layer, in particular the 3<sup>rd</sup> and 5<sup>th</sup> fractions content, which was zero. Within the limits of labile part of SOM the 2<sup>nd</sup> fraction (10.2%) was prevailing in quantity, although in the upper located soil layers it was less than that of the 1<sup>st</sup> fraction. A stable part of SOM was characterized by the greatest content; in particular the 10<sup>th</sup> fraction content, that reached 25.6%.

As is evident from Fig. 5, a stable part is prevailing in the composition of SOM in the 31–40 cm arable soil layer. Sum of the 10<sup>th</sup> and the 11<sup>th</sup> fractions made up more than 60% of total organic matter. Such increase of stable part content took place due to the minimization of a medium-oxidative part, which in general decreased to zero at this depth. The content of a labile part of SOM practically did not change compared with the upper located soil layers.

## Conclusions

1. On the basis of analysis of the quantitative distribution of SOM fractions by the soil profile, it is possible to specify certain features of forest soils, in particular, predominance of a stable part of organic matter in it, which is related to a high stability of forest ecosystem.

2. Analyzing the changes of the quantitative-qualitative composition of organic matter of arable soil one can see insignificant content of a medium-oxidative part of SOM in the whole soil profile. Also the change of SOM was clearly traced in 21–30 and 31–40 cm soil layers, where the content of a stable part increased.

3. The quantitative-qualitative composition of soil organic matter at different land use differs in the content of labile and stable parts of SOM. During the transformation of forest ecosystems to agroecosystems in soils, there occur substantial changes in the content of SOM fractions by oxidizing ability. The predominance of more resistant to oxidation and accordingly stable part of SOM is typical of the forest soil to the depth of 40 cm. A small content of medium-oxidative part up to its complete disappearance in the 31–40 cm layer is the feature of arable soil.

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## **Miško ir ariamojo dirvožemio organinės medžiagos oksidavimosi galimybės**

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### **Santrauka**

Unikalus daugiapakopis dirvožemio organinės medžiagos (DOM) (11 frakcijų) cheminės destrukcijos metodas taikytas siekiant nustatyti kiekybinę bei kokybinę DOM sudėtį miško ir ariamajame dirvožemyje. Seno ąžuolyno ir ariamojo dirvožemio 0–40 cm sluoksnyje nustatyti dideli organinės medžiagos oksidavimosi skirtumai. Miško dirvožemis pasižymėjo didesniu atsparumu oksidacijai ir dėl to stabilesne DOM, palyginti su ariamuju dirvožemiu. Ariamajam dirvožemiui būdingas nedidelis vidutiniškai besioksiduojančios dalies kiekis ir netgi visiškai jos išnykimas 31–40 cm sluoksnyje. Kiekybiniai bei kokybiniai DOM sudėties skirtumai leidžia taikyti daugiapakopį cheminės destrukcijos metodą tirti įvairiai naudojamoms žemės DOM atsparumą skaidymui.

Reikšminiai žodžiai: dirvos organinė medžiaga, labili DOM, stabili DOM, miško dirvožemis, ariamasis dirvožemis, daugiapakopė cheminė destrukcija.