EXAMINATION OF HUMIC SUBSTANCES OF COMPOSTS AND DIFFERENTLY AGED SOIL-CHARCOAL SYSTEMS

Gabriella RÉTHÁTI [1] – Viktória LABANCZ[1] – László TOLNER[1] – Zoltán SZALAI[2] – László ALEKSZA[1]

[1]Institute of Environmental Sciences, Faculty of Agricultural and Environmental Sciences, Szent István University, H-2100 Gödöllő, Páter Károly u. 1., E-mail: Rethati.Gabriella@mkk.szie.hu

[2] Institute of Geography and Earth Science, Faculty of Science, Eötvös Loránd University

Abstract: The organic materials, especially the complex structural humic substances that are made of acid-characteristic polymers, are key elements of soils. Despite their small quantity, humic substances have beneficial effects on soil nutrient management, development of optimal soil structure, regulation of soil temperature, and proper water management. Humic substances are much more stable than the original organic materials, however, the adverse environmental effects and cultivation can easily disrupt the sensitive equilibrium of humus formation. To reduce these negative processes an environmental friendly method has been developed in soil carbon management, which impact has already been studied but on humic substances interaction-analysis are still in the initial phase. This study is based on the examination of soil and compost samples with different quality. These measurements are supplemented by samples with various origin and quality, with high organic carbon content. During our examinations, optical density of different brown forest soils, composts, and pyrolyzed organic materials were determined between 465 and 665 nm wavelength. We drew our conclusions about the humus fractions of the samples based on the E_4/E_6 ratio, which is the ratio of the two obtained extinctions.

Keywords: E_4/E_6 ratio, compost, charcoal, bonechar, biochar

Introduction

The organic residues are transformed in the soil by microbiological activity. During the degradation process the macromolecular compounds are transformed to smaller components, while CO_2 and water are produced. The heterotroph microfauna utilize these organic compounds as energy source (Stefanovits et al., 1999). The poorly degradable compounds are polymerized, linked to nitrogenous substances, and transformed to macromolecular, dark-colored compounds, ie. humic substances (Németh, 1996). The separation of the humic substances can be done by fractionation by acids and bases, and the humic substances can be divided into three groups (Filep, 1988). *Fulvic acids* (FA) can be dissolved from soils by alkaline materials while they remain in the acidifying solution. Their molecular weight is low (~2000 Da) and they have light yellow colour. They contain relatively low amount of nitrogen and their oxygen level is the highest. *Humic acids* (HA) have greater molecules and darker colour compared to FA. Their structure consists mainly of condensed aromatic rings. The *humin materials* cannot be dissolved in basic or acidic solvent; their linkage to the soil is the strongest. They have the highest degree of polymerization and nitrogen content, but lowest oxygen level (Filep, 1988; Németh, 1996). The ratio of optical densitiy or absorbance of dilute, aqueous HA and FA solutions at 465 and 665 nm (E_4/E_6) are widely used for the characterization of these materials. E_4/E_6 ratio is related to the degree of condensation of the aromatic carbon network, carbon content, and molecular weight of humic substances (Konova, 1966; Schnitzer and Khan, 1972). FA, with lower molecular weight, have higher (6-8,5); whereas the HA, with higher molecular weight and better quality, have lower (<5) E_4/E_6 ratios (Stevenson, 1994). Chen et al. (1977) concluded, that the E_4/E_6 ratio of FA is greatly influenced by pH, at pH lower than 6.

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They obtained high E_4/E_6 ratio for HA, mainly in compost samples. This phenomenon indicates that the aliphatic structures have higher rate in compost than the aromatic constituents which suggest the early phase of humus formation (Velasco, 2004). The nutrient and toxic element buffering capacity of soils are highly dependent on the organic fraction of soil (Sposito, 1989), thus the replacement of organic matter (OM) and the promotion of humification is indispensable. The level of OM content in soils can be increased by using composts or pyrolyzed organic materials (biochar). Both materials have high carbon content. The mineralization and transformation of composts in soils are faster (~10 years), while the pyrolyzed organic matter (charcoal, bonechar) are only slightly degrading over a century (Lehman et al., 2009). The objective of our research was to determine the absorbance ratios at 465 and 665 nm in some high organic content soil improvers (compost, charcoal, bonechar) and in the soils treated with them. From the obtained E_4/E_6 results, we would like to draw conclusions about the quality of the organic matter.

Materials and methods

For our examinations, the following materials were used: brown forest soils from two different regions of Hungary (Gödöllő, Trizs); topsoil of three brown forest soils collected from charcoal burning piles that were used 25, 35, and 80 years ago; compost made of green wastes; bonechar, and charcoal (Table 1).

Table 1. Parameters of the samples used in our research

	Soil Gödöllő	Soil Trizs	25-year-old Soil-charcoal	35-year-old Soil-charcoal	80-year-old Soil-charcoal	Compost	Charcoal	Bonechar
pH_{KCl}	5,7	3,9	5,0	4,7	3,9	8,3	8,3	7,6
C (%)*	0,75	4,4	12	10	5,1	20	80	10

* carbon content determined by Loss on ignition method

The preparation of the samples was carried out in two steps. First, we centrifuged three grams of the samples with 30 cm^3 2% HCl solution in 50 cm^3 centrifuge tubes (5 minutes, 5000 rpm) in order to dissolve carbonates. This step was repeated one more time after the supernatant was discarded. After discarding the HCl containing supernatant, 30 cm^3 of distilled water was added to the samples and centrifuged again in order to remove the remnant of HCl. The second step was the organic matter extraction, in which after discarding the supernatant of the distilled water, 30 cm^3 0.5 mol NaOH solution was given to the samples, and was put into a rotary shaker for 24 hours. After shaking, the samples were centrifuged (25 minutes, 5000 rpm), then the supernatant was diluted to the required concentration, and the absorbance of the solutions were measured and 465 and 665 nm. The measurements were carried out by Jenway 6405 UV/Vis Spectrophotometer. The analyses were carried out on three replicates and the results were statistically tested. Analysis of variance program was used for data assessment in Microsoft Office Excel Macro. The program was developed based on Sváb's algorithm (1981). It was used in several publications (Kovács et al., 2013; Szabó et al., 2013).

Results and discussion

The average absorbance values of the NaOH extracted humus substances, measured at 465 and 665 nm, can be found in Table 2 and Figure 1. It can be seen that significant amount of humus substances cannot be dissolved by NaOH from the biochar and bonechar samples. This is understandable, since during the pyrolysis of the wood, the small-sized organic molecules disappear in a gaseous form, and the chemical structure of the remaining carbonated material is basically a large molecule, consisting of condensed, aromatic rings. Its molecular structure is nonpolar, it contains only a few functional groups and it does not have acidic character. In case of the bone char, beside the previously mentioned facts, the high phosphate content of the bone forms calcium phosphate due to pyrolysis, which is only soluble in acids. This phenomenon could be already seen on the colour of the NaOH extractions, which were almost colourless in case of the charcoal and bonechar samples, compared to the other samples. The E_4/E_6 ratio was 4.93 for charcoal, and 1.40 for bonechar, which, however, cannot be due to the organic substances present.

Table 2. The average absorbances of the samples, measured at 465 and 665 nm, and the E_4/E_6 ratios

	Soil Gödöllő	Soil Trizs	25-year-old Soil-charcoal	35-year-old Soil-charcoal	80-year-old Soil-charcoal	Compost	Charcoal	Bonechar
465 nm	0,47	0,99	2,79	2,72	2,16	2,86	0,18	0,02
665 nm	0,10	0,17	0,80	1,00	0,64	0,91	0,04	0,01
E_4/E_6	4,94	5,67	3,51	2,71	3,35	3,14	4,93	1,40

The colour of the other NaOH extracted samples was brown, which means that all samples contained some acidic humus material. The E_4/E_6 values of all the samples were below 6, which indicate the presence of humic acids. Since the extraction was carried out by 0,5 M NaOH solution, we do not have to consider great pH-dependence of the E_4/E_6 ratios of the fulvic acids (Chen et al., 1977). The E_4/E_6 ratio of the brown forest soils (Gödöllő, Trizs) were 4.94 and 5.67, respectively, which indicate high amount of fulvic acid compared to the soils treated with charcoal and compost. The humus substances with complicated structure and lower E_4/E_6 values formed in composts (E_4/E_6 = 3.14) and in soil-charcoal system with different ages (E_4/E_6 = 2.71-3.51) can be due to the intensive microbial activity. The lowest E_4/E_6 value was in case of the 35 year-old soil-charcoal system ($E_4/E_{6(35yr)}$ = 2.71), which might be due to the fact that humification process was the most intensive and the most progressed.

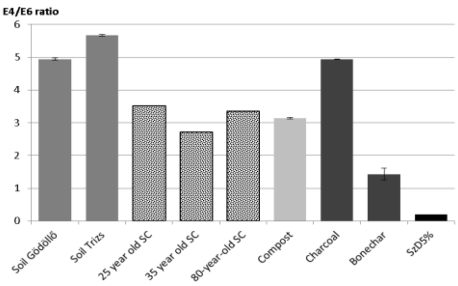

Figure 1. E_4/E_6 values

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Conclusions

As a summary, we can conclude that the E_4/E_6 ratio of the organic substances, which were formed under different circumstances, differed significantly. The forest soil samples had higher (4.97-5.67) E_4/E_6 ratios, while the soil-charcoal systems and the composts (2.71-3.51), that had easily mobilisable organic matter fractions, had lower E_4/E_6 ratios. This can be explained by the intensive biological activity. In case of the soil-charcoal systems, the charcoal provides an excellent habitat for the microorganisms, since it has high surface area, high nutrient and water holding capacity. In case of the composts, the large-scale controlled processes of composting provide optimal circumstances for the decomposition and transformation processes of the organic matter. Among the examined samples, the 35 year-old soil-charcoal system had the lowest E_4/E_6 ratio, from which we concluded that the humification processes were the most intensive and progressed in this sample. The charcoal and the bonechar do not have significant amount of acidic humus substances, the E_4/E_6 ratio could not be evaluated since their absorbance on these two wavelength (465, 665 nm) was nearly zero.

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