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HUMUS QUALITY OF ANTHROPOGENIC SOILS FROM FLYSCH DEPOSITS. CASE STUDY: KAŠTELA BAY, CROATIA

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ABSTRACT

The study aimed to evaluate the humus quality of anthropogenic soils derived from flysch deposits. A total of 10 samples were collected in the top-soil horizon (0-20 cm) of olive groves in Kaštela Bay in Middle Dalmatia, Croatia. Five samples were taken from traditional low-input olive groves (TOG), and the other five samples were from intensive ones (IOG). The soil samples were analysed for basic soil properties: particle size distribution, pH, carbonate content, P_2O5, K_2O, and soil organic carbon (SOC) content. Humic substance isolation was done following the procedure given by Schnitzer (1982). Spectroscopic characterization of humic substances was carried out by measuring absorbances in VIS spectral range (400-700 nm). Optical index E_4/E_6 (ratio of optical absorbance at 465 and 665 nm for humic substances in solution) was calculated. The mean value of SOC content in soils of TOG was lower than in soils under IOG (1.20 and 1.60%, respectively). The absorption spectrum of the studied soils showed a monotonous decrease of absorbance from 400 to 700 nm. The E_4/E_6 indices for soils under TOG varied from 4.60 to 5.00, while for soils under IOG were in the range of 4.83 – 6.89. The E_4/E_6 indices > 4 revealed low humus quality in studied soils. However, soils under TOG have lower mean values E_4/E_6 index in comparison to soils under IOG (4.76 and 5.70, respectively), indicating slightly higher humus quality.

Key words: *E_4/E_6 index*, *olive groves, VIS spectroscopy.*

INTRODUCTION

Soil organic matter supports multiple soil ecosystem functions underpinned by processes such as C sequestration, N mineralization, aggregation, promotion of plant health and compound retention (Hoffland et al., 2020.) It is a heterogeneous mixture of organic compounds that differ in stability, decomposition degree, and turnover rate (Huang et al., 2008). Humic substances are generally classified into humic acid, fulvic acid, and humin based on their solubility in water as a function of pH (MacCharthy et al., 1990). Although numerous methods have been developed for isolation and quantification of humic substances (van Zomeren and Comans, 2007), method of Schnitzer (1982) is the most widely used. It is successful in maximizing extraction of humic compounds and minimizing their degradation, and suitable for all soil types regardless of carbonate content.

Numerous non-destructive spectroscopic techniques (UV–Vis, DRIFT, SFS, FTIR, and ^{13}C-NMR) provide valuable information on humic substance structure and properties (Chen et al., 2002). Since humic substances show strong absorption in the UV-Vis range (190-700 nm) due to the presence of aromatic chromophores (Schnitzer and Khan, 1975) the UV-Vis spectroscopy is one of the most frequently used methods for humic substance characterization (Shirshova et al., 2006). The E_4/E_6 index calculated as the ratio of optical absorbance at 465 to 665 nm for humic substances in solution is commonly used to evaluate humus quality (Aranda et al., 2011; Reddy et al., 2014; Bensa et al., 2016). It is negatively correlated to the content of condensed aromatic structures (Stevenson, 1994) and decreases as condensation, aromaticity, and molecular weight of humic substances increase.

The impermeable or poorly permeable flysch deposits are especially prone to erosion by torrential watercourses (Pollak et al., 2010) which increases the loss of organic matter from top-soil. Therefore, many authors reported low humus content in soils derived from flysch deposits (Miloš and Maleš, 1998; Bogunović et al., 2009; Aranda et al., 2011). However, restricted data are available on humus composition and quality in these soils. In addition, anthropogenic activities such as tillage, fertilization, and the use of pesticides affect humus quality in agricultural soils.

The aim of the paper is: (i) spectroscopic characterization of humic substances and (ii) evaluation of humus quality of anthropogenic soils derived from flysch deposits under traditional low-input and intensive olive groves.

MATERIAL AND METHODS

The study was conducted in the olive growing area of Kaštela Bay in Midldle Dalmatia, Croatia, Figure 1a. The study area is characterized by a Mediterranean climate (Csa) with hot and dry summers and mild rainy winters (Filipčić, 1998). Kaštela Bay coastal area is built of Eocene Flysch marls, sandstones, and siltstones with lenses of calcirudites and calcarenites (Marinčić et al., 1971). Impermeable clastic flysch deposits and sloping terrain (mainly 10-30%) make this area vulnerable to erosion. Soils of the study area have an alkaline reaction, high carbonate content, very low to medium humus content, and silty loam texture (Miloš and Maleš, 1998). According to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015) studied soils can be classified as Regosols (Calcaric, Siltic/Loamic, Escalic). The olive growing in the study area characterizes dry farming, including traditional low-input and intensive growing systems.

A total of 10 top-soil samples (0-20) cm were collected as composite samples. The five samples were taken in the olive groves under the traditional low-input system, and the other five from the olive groves with the more intensive growing system, Figure 1b. Soils in the traditional olive groves (TOG) are rarely tilled, fertilized, and treated with pesticides. The intensive olive growing system (IOG) includes more intense fertilization (mineral and organic), plant protection, and regular soil tillage.

Figure 1 Location of the study area (A) and soil sampling sites (B). Locations of traditional olive groves are symbolised by yellow triangles and intensive ones by red circles

The disturbed soil samples were prepared for analysis according ISO 11464:2006. Basic soil analyses included: particle size distribution (ISO 11277:2009), pH (ISO 10390:2005), carbonate content (ISO 10693:1995), P_2O_5 and K_2O (Egner et al., 1960) and humus content (method of Tjurin, JDPZ, 1966). Soil organic carbon (SOC) content was calculated by dividing the humus content with the Van Bemmelen factor (1.724). The isolation of soil humic substances (HS) was made by the Schnitzer method (1982). The VIS spectra were measured by Shimadzu UV 1700 spectrometer in the range of 400-700 nm. The extracts were prepared as a mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7$.

RESULTS AND DISCUSSION

Alkaline soil reaction (pH_{KCl} >7.2) was established in the soils under both types of olive production with minor differences, Table 1. The studied soils were highly calcareous (mean values of $CaCO_3$ in soils under TOG and IOG 58.6 and 47.9%, respectively). The SOC content was low in the soils under TOG (0.90-1.60%) and low to medium in the soils under IOG (1.09-2.12%), Table 1. The mean value of P_2O_5 in the soils under TOG (7.1 mg/100 g of soil) pointed to a poor supply with P_2O_5, with high variation (CV 45.5). The soils under IOG were moderately supplied with P_2O_5 (mean value 14.8 mg/100 g of soil), Table 1. Even more pronounced differences were observed for K_2O concentrations. The soils under TOG contained medium K_2O content (mean value 16.4 mg/100 g of soil), while the soils under IOG were richly supplied with K_2O (mean value 48.1 mg/100 g of soil), Table 1. It can be attributed to mineral fertilization applied in higher doses to soils under IOG.

Table 1 Descriptive statistic for basic chemical properties of studied soils

	pH_{H2O}		pH_{KCl}		$CaCO_3$ %		SOC %		P_2O_5 mg/100 g of soil		K_2O	
	TOG	IOG	TOG	IOG	TOG	IOG	TOG	IOG	TOG	IOG	TOG	IOG
Min	8.35	8.28	7.48	7.23	56.5	31.6	0.90	1.09	4.6	11.3	12.8	34.5
Max	8.50	8.54	7.72	7.58	64.1	61.6	1.60	2.12	13.4	18.1	19.2	73.5
Mean	8.43	8.40	7.59	7.48	58.6	47.9	1.20	1.60	7.1	14.8	16.4	48.1
Med	8.45	8.39	7.59	7.54	56.6	50.5	1.16	1.68	5.8	15.1	17.0	47.4
SD	0.06	0.09	0.08	0.13	0.23	10.1	0.23	0.34	3.21	2.41	2.09	13.9
CV	0.75	1.1	1.0	1.8	5.0	21.1	19.3	21.5	45.5	16.3	12.8	28.9

Min – minimum; Max maximum; Med- median; SD- standard deviation; CV coefficient of variation

Particle size distribution analysis revealed the domination of silt particles for soils under both management types. However, soils under IOG have a higher content of clay particles in comparison to soils under TOG (mean values 24.24 and 15.72%, respectively). The texture classes of soils under TOG were loam and silty loam, while soils under IOG were silty loams and clay loams, Figure 2.

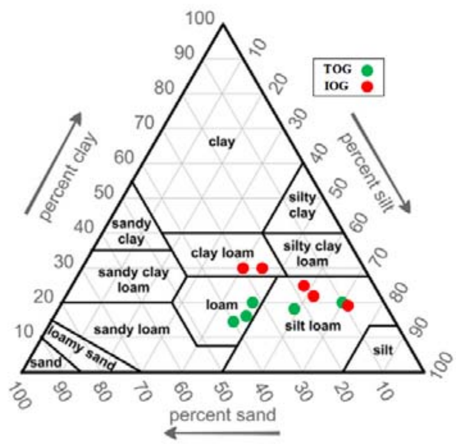

Figure 2 Distribution of soil samples on texture triangle (FAO/UNESCO, 1990)

The established properties of studied soils correspond to literature findings for soils on flysch deposits in Middle Dalmatia (Miloš and Maleš 1998; Bogunović et al., 2009; Miloš and Bensa, 2019).

Humic substances showed strong absorption in the UV-Vis range (Schnitzer and Khan, 1975). UV-Vis spectra of humic substances can characterize their quality, maturity, and condensation degree (Fuentes et al., 2006). The UV-Vis spectral lines of humic substances extracted from studied soils are shown in Figure 3. In general, lower absorbances and a milder decline in the spectral curves were observed for the soils under TOG compared to IOG. It implies the domination of aromatic over aliphatic structures (Pospíšilová and Fasurová, 2010; Fasurová and Pospíšilová, 2010) in the soils under TOG.

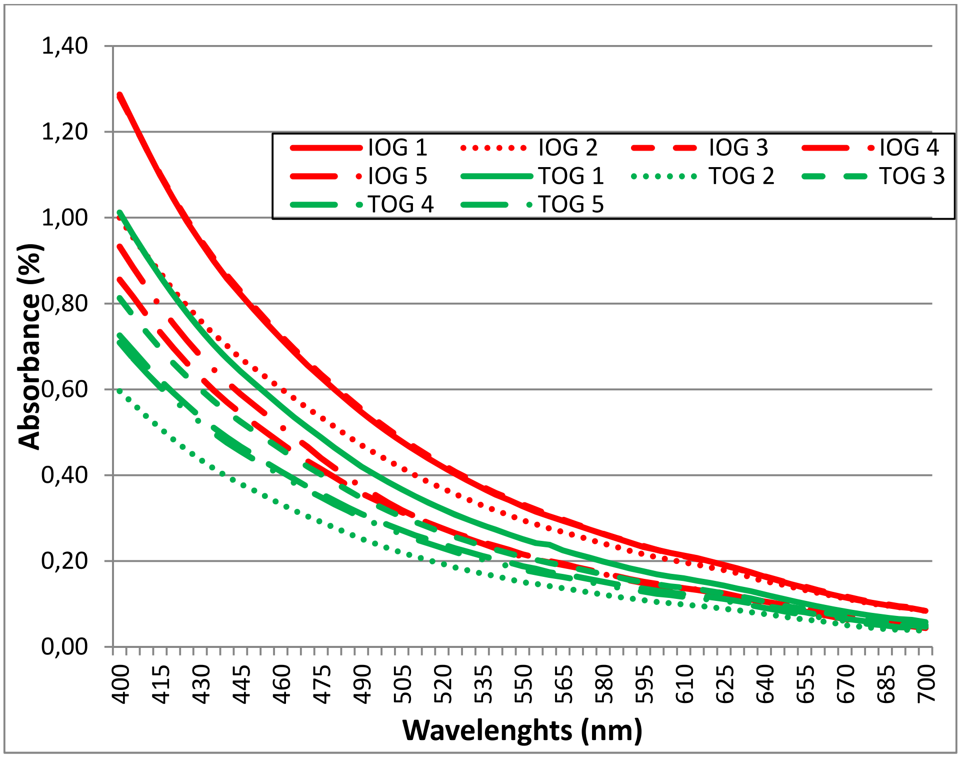

Figure 3 UV-Vis spectra of exctracted humic substances in the studied soils

The absorbance of humic substances at the wavelength of 465 nm is associated with the first phase of the humification process (fulvic acids), while absorption at 665 nm is related to well-humified substances (humic acids) (Stevenson, 1994). Therefore, the calculated optical index E_4/E_6 (ratio of optical absorbance at 465 to 665 nm for humic substances in solution) is negatively correlated to the content of condensed aromatic structures (Stevenson, 1994; Fuentes et al., 2006). It decreases as condensation, aromaticity, and molecular weight of humic substances increase. The E_4/E_6 indices of humic substances isolated from studied soils are shown in Table 2.

Table 2 The E_4/E_6 indices of humic substances isolated from the studied soils

Management type	Soil sample number 1	2	3	4	5	Mean value
TOG	5.00	4.68	4.73	4.60	4.78	4.76
IOG	5.63	4.83	5.55	5.59	6.89	5.70

In soils under TOG E_4/E_6 indices were 4.60 to 5.00, with mean value of 4.76. Soils under IOG had E_4/E_6 indices in the range of 4.83 – 6.89, with mean value of 5.70. The E_4/E_6 indices above 4 in all studied soils indicated low humus quality (Chen et al., 2022; Pospišilova et al., 2010; Reddy et al., 2014). However, a narrower range and lower mean value of E_4/E_6 in soils under TOG (Table 2) indicated slightly higher and a more uniform humus quality. It can be ascribed to a less soil cultivation since tillage is unfavourable for humification and the formation of stable humic substances. It is consistent with the study of Murage and Voroney (2008) and Seddaiu et al. (2013), who also found higher humus quality in less tilled soils. Aranda et al. (2011) reported similar E_4/E_6 indices in soils under olive groves derived on marls in Spain (4.37-5.15). Authors established lower values (higher humus quality) in soils under organic farming compared to conventional olive production.

CONCLUSIONS

Spectroscopic characterization of humic substances isolated from the anthropogenic soils derived on flysch deposits under olive groves revealed domination of aliphatic over aromatic structures. In general, studied soils have low humus quality. However, lower E_4/E_6 indices in soils under traditional low-input olive groves indicate slightly higher humus quality. Therefore, it can be concluded that agricultural practices in intensive olive production (mainly tillage) negatively affected humus quality. The results of the study point to the need for improvement of humus quality (and content) in anthropogenic soils on flysch deposits under olive groves in fragile Mediterranean environment.

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