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Analysis of Soil Organic Carbon Functional Groups by FTIR Method among Land Use Types in Semi-arid Region of Kadapa, Andhra Pradesh

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Abstract: Soil organic carbon is an important component of soils as it determines the soil fertility and soil carbon sequestration potential. The SOC comprises of components of plant and animal litter present at varied decomposition stages. FTIR Spectroscopy was used to identify different functional groups of soil organic carbon components across the four land use types. FTIR method measures the absorbance of IR radiation (4000 cm^{-1} - 400 cm^{-1}) by which functional groups (C-O, C=O, C=C, C-H, N-H) associated with soil organic carbon. A total of 72 soil samples were randomly collected from the four selected study areas and composite soil sample was prepared. Aliphatic -CH stretching was found in all land use types at 2925 - 2300 cm^{-1}. The presence of aromatic phenolic compounds 1410-1380 cm^{-1}with (-CO, OH) groups of humic acid, Si-O mineral groups 798-779cm^{-1}were reported in all four land use types. While the band 779-798 cm^{-1} which corresponded to the stretching vibrations of the Si-O mineral group is observed in all the four land use types. The results suggest that although SOC content is varied across the four study sites, the decomposition products featured more or less same re-synthesized products showing similar peaks in the FTIR spectral graphs.

Keywords: Soil organic carbon, FTIR, Humic substances, Aliphatic components, spectroscopy, persistence of SOC

Soil allows plants to live and grow by providing suitable substratum, water and essential nutrients. It is mainly possible by the presence of an important constituent - soil organic carbon in the soil, which comprises of plant, animal and microbial origin components at different stages of decomposition (Rao and Reddy 2023). The organically-binded carbon and nutrients are released as inorganic nutrients by soil microorganisms, fungi and soil fauna present in the soil through decomposition and mineralization processes (Ramana and Reddy 2021). Further, SOC possess binding sites for essential nutrients to be made available for plants in solution. In addition SOC consists of humic substances that are usually adsorbed on clay mineral surfaces by different mechanisms and become less accessible to microbial decomposition and thus exhibits high persistence nature (Kaushal et al., 2021). This kind of varied stability nature of SOC will influence the global carbon cycle (Schmidt et al., 2011). Thus, the amount of SOC content strongly influence soil fertility as well as the soil properties like water holding capacity, soil structure nutrient availability and carbon sequestration (Denef et al., 2009).

The decomposing material of the soil organic carbon resulting from the un-decayed plant and animal tissues comprises of diverse organic compounds such as carbohydrates, polysaccharides, proteins-polypeptides, lipids and nucleic acids and recalcitrant materials like waxes, cutins, suberin (Huang and Hardie 2009). Each type of organic matter along with resynthesized polymers of fulvic acid and humic acids components present in SOC possess functional groups like carbonyl - C=O, alcoholic C-OH, phenolic –OH, amino = NH and amine - NH_2 hydroxyl -OH, methyl-CH_3, phosphate, sulphydryl –SH (Schnitzer and Monreal 2011). The objective of the study is to identify the functional groups associated with soil organic components in soil organic carbon across the four land use types and test the hypothesis that there are no differences in functional groups across the four land use types.

MATERIAL AND METHODS

Study area: The analysis of soil organic carbon functional groups was conducted in four land use types: Guvvalacheruvu forest (GF;14˚16' 28.3" N 78˚51'57.6" E) belonging to Palakonda hill ranges, Miyawaki plantation in Yogi Vemana University campus (YVU) (plantation;14˚28 10.8 N, 78˚42' 43.56,' E), agricultural crop land (AG;14˚2810.8' N, 78˚42' 43.56' E) and barren land with sparse vegetation in the YVU campus (barren land; 14°28' 10.8” N, 78°42' 43.56”E;). Total of six soil samples in three replicates were collected randomly from each of the four land use types, resulting in 72 soil samples, from 0-30 cm soil depth by randomly laying quadrats in each of the four land use types for the quantification of soil organic carbon. The soil samples of each site are air dried and thoroughly mixed to form a composite mixture and was passed through 2mm sieve for the estimation process. The same soil samples are used for the identification of functional groups.10 mg of soil sample was mixed with 40 mg of KBr FTIR grade, the mixture was finely ground in a mortar and pestle. The milled sample mixture was transferred to the sample holder. By using a vacuum pump at ten metric tons per minute pressure, the KBr pellet is prepared. The pellet was collected on the microscopic glass slide and subjected to the characterization work mid-infrared region on FTIR spectroscopy (Reddy et al, 2018). The FTIR spectroscopy technique tries to measure these molecular vibrations of organic compounds supposed to present in the different land use type soils. (Silverstein et al, 2014).

RESULTS AND DISCUSSION

Among the four land use types forests have high SOC average of 13.9g/kg followed by Miyawaki plantation soils (7.1 g/kg) the lowest mean SOC (4.8 g/kg) was in barren land.

The infrared spectrum contains specific absorption bands for different functional groups, like aliphatic compounds, aromatic compounds and carboxylic acid groups. The chemical bonds associated with these compounds exhibit vibrational movements like stretching and bending specific to each molecule by which the functional groups can be identified (Thabit et al., 2024). Comprehensive bands that correspond to compounds, functional groups of humic substances present in the SOC was prepared based on the past selective studies on SOC (Carthy 2001, Silverstein et al., 2014, Nuzzo et al., 2020). Mainly include C-H stretching vibrations associated with bands between 2950 and 2800 cm^{-1} corresponds to aliphatic saturated hydrocarbons (Table 1). The spectral region between 1750 and 1660cm^{-1} is attributed to the stretching vibrations of the C=O bond corresponding to carbonyl functional groups such as ketone,

Table 1. Band positions in the FTIR ATR spectra observed among soil samples (up to 30cm) of four land use types

Peak position (cm^{-1})		Assignment
Band-A	Present study	
3200 – 3700 cm^{-1}	3784 cm^{-1}	Stretching of -OH, NH components of humic acids of Soil Organic Carbon
	3711 cm^{-1}	
	3738 cm^{-1}	
Band-B	Present study	Assignment
2300 – 2925 cm^{-1}	2349 cm^{-1}	Vibration of C-H and (CH$_2$-CH) components of soil Organic Carbon
	2353 cm^{-1}	
	2349 cm^{-1}	
	2353 cm^{-1}	
	2349 cm^{-1}	
Band-C	Present study	Assignment
1630 - 1660 cm^{-1}	1639 cm^{-1}	Amide C=O stretching of Humic Acid in SOC
Band-D	Present study	Assignment
1380 – 1410 cm^{-1}	1419 cm^{-1}	The presence of Aromatic phenolic compounds C-O stretch and -OH deformation of Humic Acid in Soil Organic Carbon
	1427 cm^{-1}	
1500 – 1590 cm^{-1}	1519 cm^{-1}	Aromatic C-H deformation,Amide N-H bending and C=N stretch (Amide) components of Soil Organic Carbon
	1597 cm^{-1}	
Band-E	Present study	Assignment
1000 – 1050 cm^{-1}	1002 cm^{-1}	Saturated aliphatic compounds of Soil Organic Carbon
	1018 cm^{-1}	Saturated aliphatic compounds of Soil Organic Carbon
	1010 cm^{-1}	Saturated aliphatic compounds of Soil Organic Carbon
	1006 cm^{-1}	Saturated aliphatic compounds of Soil Organic Carbon
1000 – 1160 cm^{-1}	1033 cm^{-1}	Ester, phenol C-O-C, C-OH stretch, attributed to polysaccharides of Soil Organic Carbon.
Band F	Present study	Assignment
779 - 798 cm^{-1}	775 cm^{-1}	Symmetric Si-O stretching in quartz of clay minerals
	779 cm^{-1}	
	783 cm^{-1}	

esters or carboxylic acids. In addition aromatic compounds can be associated with bands observed from 1600-1490 cm^{-1}. The region < 900cm^{-1} was attributed to quartz and silicates.

The mid IR spectrum is divided into six regions A, B, C D E and (Fig. 1, 2, 3 and 4). The band regions 3629-3618 cm^{1} and 3401-3430 cm^{1} recorded in the spectra in all the four land use types correspond to the -OH groups associated with clay mineral structure. Similarly band 779-798 cm^{-1} which may identify to the stretching vibrations of the Si-O mineral group is observed in all the four land use types. In the same line, the band B (2925-2300 cm^{-1}) having a prominent peak (–CH stretching) suggest the presence of aliphatic compounds are recorded in all the four land use types (Fig. 1, 2, 3, 4). The band C (1660-1630cm^{-1}) suggest to the presence of the amide C=O stretching of the available humic acids. The peak intensity for this band was seen in all the four land use types. In addition, the band 1410-1380cm^{-1} associated with this group may confirm the presence of aromatic phenolic compounds C-O stretch and –OH deformation of humic acids and this band was commonly observed in all the studied four land use types4). The band E (1050-1000 cm^{-1}) corresponding to the stretching vibrations of saturated aliphatic compounds was found in all the four land use types. The band F (798-779 cm^{-1}) was usually associated with Si-O bond of quartz minerals and this band was prominently seen in the FTIR images of all the four land use types.

The occurrence of aliphatic compounds corresponds to labile carbon fractions and this peak is common in all the four land use types. The intensities at 2300-2925 cm^{-1} referred to aliphatic C-H stretch of humic acids. This condition may arise due to the availability of fresh litter content in all the land use types. Such a peak was observed in agricultural crop surface soil (0-10cm) samples in Brazil (Machado et al., 2020). The second peak registered at 1000-1050 cm^{-1} indicates the presence of saturated aliphatic compounds corresponding to polysaccharides and carbohydrates confirming the re-synthesised products from the litter in all the four land use types. Such a FTIR peak with stretching of -OH component of humic acid at the range of 3200-3700 $cm^{-1}$was also identified in the agroforestry soils of Brazil (Thabit et al., 2024). The conspicuous third peak in the range of 779-798 cm^{-1} referred to Si-O stretch in clay minerals is commonly present in all the four land use types suggesting that mineralized carbon is present in the passive carbon pool in all the land use types.

SOC comprises of not only litter products but also totally transformed litter components into humic molecules. The process of the breakdown of litter fragments usually increases the content of aromatic and aliphatic compounds. Based on this degree of transformation the change in the chemical structure of SOC occurs as well as the protection from microbial bio-decomposition occurs (Schnitzer and Monreal 2011). The aromatic compounds are mainly derived

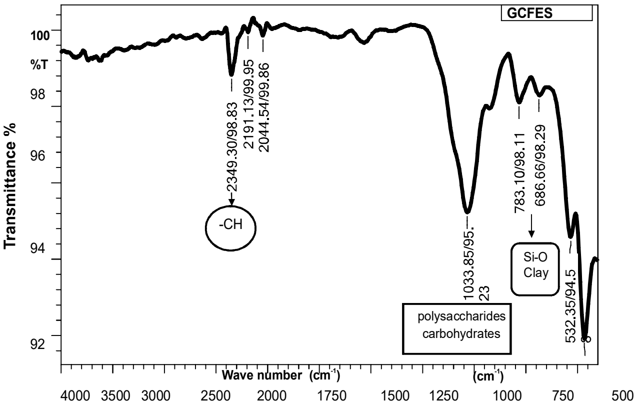

Fig. 1. FTIR spectra showing absorption bands of forest land use soil

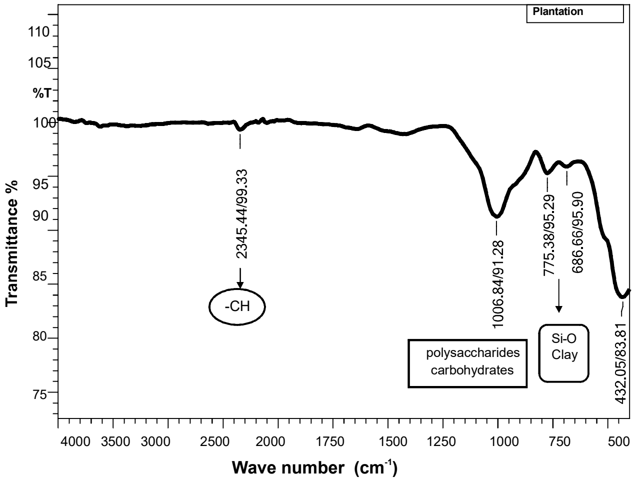

Fig. 2. FTIR spectra showing absorption bands of plantation land use soil

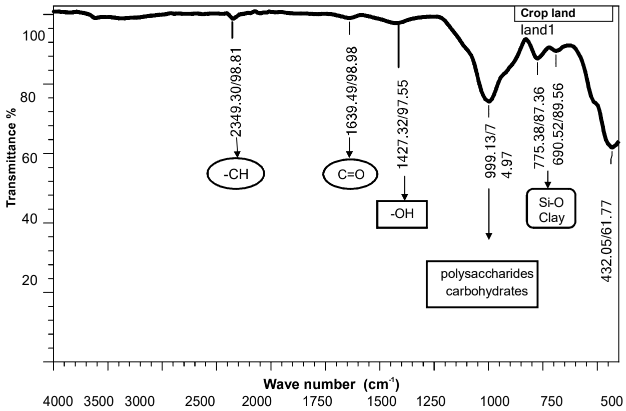

Fig. 3. FTIR spectra showing absorption bands of agricultural crop-land soil

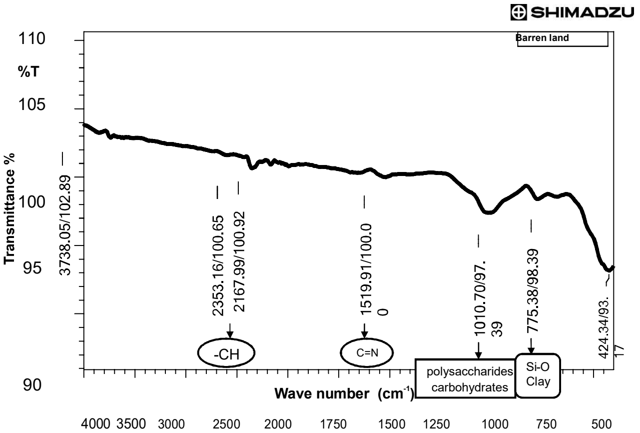

Fig. 4. FTIR spectra showing absorption bands of barren land soil

from lignin and tannin plant products, while alkyl components indicate the resistant products like waxes, cutin and suberins in the SOC (Thabit et al., 2024).The absorption spectra of SOC soil samples collected from four land use types produced similar structure indicating that the decomposition products of the litter comprise of re-synthesised compounds of similar nature although their fresh litter components are different.

CONCLUSIONS

The amount of SOC content is significantly different across the four land use types. But the FTIR data have produced similar functional groups across the land use types. The data indicates that the resulting decomposition products featured more or less same re-synthesised products. The decomposed products of SOC are due to complex interaction between the aboveground litter and its land use patterns. The study suggest that the processes regulating the composition and stability of SOC are related to the ecosystem properties rather than to specific individual plant properties.

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