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Soil organic matter characterization in rubber based systems in central Kerala - A spectroscopic approach

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Abstract

Land use and agro-management practices influence the quantity and quality of soil organic matter. Soil properties to a large extent are influenced by the content and nature of soil organic matter. A field study was conducted in two locations, one at Amayannoor and the other at Mundakayam in Kottayam district, Kerala to undertake the spectroscopic characterization of soil organic matter. The four rubber systems investigated at Amayannoor were mature rubber, immature rubber with cover crop *Pueraria phaseoloides,* immature rubber with inter-crop banana and immature rubber with inter crop pineapple. At Mundakayam, mature rubber, immature rubber with cover crop *Mucuna bracteata,* immature rubber with inter crop banana, and immature rubber with inter crop pineapple were investigated. Both, UV-Vis and FTIR spectroscopic studies were carried out. Soil organic matter under mature rubber was observed to be more aromatic than soil under immature systems at both locations. Among the different immature systems, the soil organic matter in rubber-*Pueraria* system showed the presence of more carbohydrates and polysaccharides than rubber-pineapple and rubber-banana systems. However, rubber-*Mucuna* system showed relatively higher aromaticity than rubber-pineapple and rubber-banana systems. This study confirms the earlier reports about the faster decomposition of soil organic matter in rubber-*Pueraria* system and slower decomposition of soil organic matter in mature rubber plantation. This spectral investigation also revealed the specific nature *viz*., higher aromaticity of the soil organic matter in rubber-*Mucuna* system which contributed towards the buildup of soil carbon in the system.

Keywords: Aromaticity, characterization, cover crop, rubber, spectroscopy

Introduction

Soil organic matter (SOM) is a complex mixture of organic materials derived from plant litter/crop residues, roots and micro-organisms and it mainly comprises of carbohydrates, amino acids, proteins, lipids, and lignins. It is the primary soil component that influences physico-chemical as well as biological properties of soil. Maintaining or increasing SOM is important from an agronomic as well as an environmental perspective as it influences soil fertility and crop productivity and functions as a source and sink of atmospheric CO_2-C.

Many of the soil functions such as storage and supply of nutrients and water depend on the nature and content of organic matter in the soil. The quality and quantity of SOM are influenced mainly by vegetation and management practices such as tillage, organic amendments, *etc.* (Solomon *et al*., 2002; Wander, 2004; Kaiser and Ellerbrock, 2005). The chemical composition of SOM is an important determinant of the nutrient supplying capacity of soils. Information on the chemical structure of SOM contributes to the understanding of bio-available and stable forms of SOM also.

Spectral investigations are useful in the characterization of SOM. Spectroscopic techniques such as ultraviolet-visible (UV-Vis) and Fourier-transform infrared (FTIR) are employed for qualitative and quantitative characterization of SOM (Barancikova *et al.,* 1997; Rivero *et al.,* 1998). Schnitzer and Khan (1972) observed that the presence of aromatic chromophores and other such organic components in soil organic matter leads to strong absorbance in the UV-Vis range (190-800 nm), especially in the UV region. The ratio of absorbance at 250 and 365 nm (E_2/E_3) and 465 and 665 nm (E_4/E_6) were often used for the characterization of SOM (Chin *et al*., 1994; Chen

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et al., 1977). Purmalis and Klavins (2013) reported that UV absorbance ratios in different wavelengths indicate the extent of the humification of organic matter. In the studies conducted in Czech soils by Fasurova and Pospisilova (2010) also UV-Vis spectroscopy was employed to understand the degree of humification and nature of organic matter.

FTIR spectroscopy also enables the characterization of SOM as absorbance intensity in the mid-infrared region (4000-400 cm^{-1}) can be used to fingerprint the components in SOM. Ellerbrock *et al*. (1999a, 1999b, 2001a, 2001b) and Gerzabek *et al.* (2006) used FTIR spectra to identify components of SOM under various land-use systems and management practices. In Ethiopian soils, using FTIR spectra, Solomon *et al.* (2005) studied the impact of various land-use systems on different organic components in different size fractions of soils. Haberhauer *et al.* (2000) also reported that FTIR spectroscopy is a powerful tool for the investigation of the quality of organic matter in soils under different vegetation.

Hevea brasiliensis, the main source of natural rubber, is cultivated in about 8.1 lakh hectare area in India and the major portion is in Kerala (Rubber Board, 2017). In immature rubber plantations, the establishment of legume covers (*Pueraria phaseoloids/ Mucuna bracteata*) is a recommended agro-management practice. Intercropping in immature rubber plantation is also a common practice and banana and pineapple are the popular intercrops. The content and composition of SOM in the various rubber-based systems may vary (Abraham, 2015) as plant residues are the primary source of SOM in any system. The agro-management practices followed in different rubber-based systems also vary. Naturally, a variation in relative size and composition of SOM pools in these systems is expected. Even though there are many reports available on the effect of intercrop/cover crop on soil properties in rubber growing soils (Jessy *et al.*,1996; Philip *et al.*, 2005; George *et al.*, 2012) information on chemical structure of organic matter in various rubber-based systems in the traditional rubber growing areas in south India is lacking. Hence, the present study was conducted to characterize SOM in different rubber-based systems through a spectroscopic approach.

Materials and methods

Site description/characteristics

The study was conducted at two locations in the Kottayam district in Central Kerala. One location was in a smallholding sector (Amayannoor village in Kottayam, 9^0 37' N, 76^0 36' E) and the other in an estate sector (Harrisons Malayalam Limited, Mundakayam, 9^0 31' N, 76^0 52' E). The systems and associated management practices in each location are briefed in Table 1.

Table 1. Management practices followed in different rubber-based systems

Location	Systems	Planting cycle	Age (years)	Input of organic manure	Soil disturbances (Tillage/pitting)
Amayannoor	Mature rubber	Second	23	12 kg FYM* in the pit at the time of planting	Pitting at the time of planting rubber
	Rubber-*Pueraria*	Third	3	12 kg FYM in the pit at the time of planting rubber	Pitting at the time of planting rubber
	Rubber-banana	Third	2	For rubber-12 kg FYM in the pit at the time of planting rubber. For banana- 10 kg FYM/plant in each year	Pitting at the time of planting rubber Manual tillage of inter-row area of rubber plants for planting banana
	Rubber-pineapple	Third	2	For rubber-12 kg FYM in the pit at the time of planting rubber. For pineapple- 25 t ha^{-1} organic manure as basal dose	Pitting at the time of planting rubber Mechanical tillage of the entire area before planting pineapple

	Mature rubber	Second	20	12 kg FYM in the pit at the time of planting	Pitting at the time of planting rubber
	Rubber-*Mucun*a	Third	3	12 kg FYM in the pit at the time of planting rubber	Pitting at the time of planting rubber
Mundakayam	Rubber-banana	Third	2	For rubber-12 kg FYM in the pit at the time of planting rubber	Pitting at the time of planting rubber
				For banana- 10 kg FYM/plant in each year	Manual tillage of inter-row area of rubber plants for planting banana
	Rubber-pineapple	Third	2	For rubber-12 kg FYM in the pit at the time of planting rubber	Pitting at the time of planting rubber
				For pineapple - 25 t ha^{-1} organic manure as basal dose	Mechanical tillage of the entire area before planting pineapple

*FYM- Farmyard manure

Other nutrient inputs (kg ha^{-1}) in rubber plantations during-

First year NPKMg @ 20:20:8:3

Second year NPKMg @40:40:16:6

Third year NPKMg @50:50:20:7.5

Fourth year NPKMg @40:40:16:6

Fifth year onwards NPK @30:30:30

The under-flora in mature rubber plantation was scanty and the litter turnover was negligible in both locations, whereas thick litter layers of *Pueraria*/*Mucuna* were observed in the respective immature fields. Incorporation of crop residues of the previous banana planting was noticed in the rubber-banana system. Litter or crop residues were observed to be very meager in the rubber-pineapple fields compared to other studied systems. The fertilizers were supplied separately to intercrops.

Soil sampling and analyses

Soil samples (0-10 cm) were collected on a random basis from five different sites in each system in each location. From each sampling site, three samples were collected and composited. Samples were sieved (2 mm), air-dried and used for the analysis. Carbon content in these samples was estimated by dry combustion method using an automated elemental analyzer (Leco, Truspec-CN) and the data generated were subjected to a one-way analysis of variance (Gomez and Gomez, 1984).

The organic compounds in the soil were extracted with 0.05 M $NaHCO_3$ in the ratio 1:5 and used for the UV-Vis spectroscopic characterization as described by Schnitzer (1982). Absorbance was measured at 254 (E_2), 365 (E_3), 465 (E_4) and 665 (E_6) nm using a UV-Vis spectrophotometer (UV-1601, Shimadzu). Then E_2/E_3 and E_4/E_6 ratios were worked out.

For FTIR characterization, agate milled soil samples were used. Two milligrams of the homogenized powdered sample was thoroughly mixed with 200 mg of KBr (FTIR grade) and pelletized using a hydraulic press at 12 bar. The pelletized KBr samples were dried in an oven (100 °C) for two hours before the analysis to minimize interference from absorbed water. FTIR spectra were recorded in a spectrometer (Varian 660-IR FTIR) with resolution 4 cm^{-1} and 20 scans (Ellerbrock *et al.,* 1999a). Following the subtraction method (Bio Rad, 1996), all spectra were corrected to minimize the effect of mineral contents. The relative absorbance of different components in the spectra was calculated as described by Gerzabek *et al.* (2006):

$$\text{Relative absorbance} = \frac{\text{The peak height of a distinct peak x 100}}{\text{Sum of the heights of all peaks}}$$

Results and discussion

A significant difference was noticed in soil organic carbon (SOC) status of different systems in both locations (Table 2).

Immature rubber with cover crop recorded the highest SOC status in the two locations. At Amayannoor, it decreased in the order rubber-*Pueraria*>rubber-banana>mature rubber>rubber-pineapple. Among the different systems at Mundakayam, it decreased in the order rubber-*Mucuna*>rubber-banana>rubber-pineapple>mature rubber. The higher SOC status in the *Pueraria* system could be due to the higher input of quality litter and faster decomposition of *Pueraria* (Philip and Abraham, 2009). The crop residue addition and high input of organic manure in banana cultivation might have resulted in high SOC status in the rubber-banana system. The intense mechanical tillage during the planting of pineapple and the lesser turnover of crop residues in the system might have resulted in low SOC status in the rubber-pineapple system. George *et al*. (2012) also reported higher SOC in cover cropped and banana intercropped rubber fields than pineapple intercropped fields. The higher SOC status in the rubber-*Mucuna* system at Mundakayam could be due to the higher litter turnover of *Mucuna* compared to other crops.

Table 2. Soil organic carbon status in different systems at different locations

Location	System	SOC (g kg^{-1})
Amayannoor	Mature rubber	20.55
	Rubber-*Pueraria*	23.40
	Rubber-banana	21.63
	Rubber- pineapple	19.36
	SE	0.54
	CD	1.62
Mundakayam	Mature rubber	19.13
	Rubber-*Mucuna*	25.93
	Rubber-banana	23.25
	Rubber- pineapple	21.93
	SE	0.44
	CD	1.32

The absorbance ratio E_2/E_3 (254 and 365 nm) and E_4/E_6 (465 and 665 nm) of organic substances in different systems at Amayannoor and Mundakayam are shown in Table 3 and 4, respectively.

Among the different soil systems at Amayannoor, mature rubber showed a lower E_2/E_3 value than the immature systems (Table 3). The ratio E_2/E_3 increased in the order, mature rubber<rubber-pineapple<rubber-banana<rubber-*Pueraria*. E_4/E_6 values also showed a similar trend. At Mundakayam also a lower E_2/E_3 value was observed for mature rubber than that of immature systems and it increased in the order, mature rubber<rubber-*Mucuna*<rubber-pineapple<rubber-banana (Table 4). The E_4/E_6 values also showed a similar pattern.

Table 3. UV-Vis absorbance ratios of organic substances in different systems at Amayannoor

System	Absorbance ratio	
	E_2/E_3	E_4/E_6
Mature rubber	1.67	2.81
Rubber-*Pueraria*	3.66	4.52
Rubber-banana	2.87	4.22
Rubber- pineapple	2.52	3.26

Table 4. UV-Vis absorbance ratios of organic substances in different systems at Mundakayam

System	Absorbance ratio	
	E_2/E_3	E_4/E_6
Mature rubber	1.50	2.73
Rubber-*Mucuna*	2.80	3.05
Rubber-banana	3.06	4.14
Rubber- pineapple	3.00	3.46

Chin *et al.* (1994) and Peuravouri and Pihlaja (1997) observed that the E_2/E_3 absorbance ratio was negatively correlated with molecular weight and aromaticity of humic substances. The absorbance at higher wavelengths indicates the presence of compounds with more conjugation, which reflects higher aromaticity or more condensation of aromatic constituents. The low E_2/E_3 ratio of mature rubber systems at the two locations indicated that SOM in mature rubber plantation is more aromatic than the other studied systems.

The E_4/E_6 ratio also is inversely related to the aromaticity and to the degree of condensation of the chain of aromatic carbons of the organic compounds and could be used as an index of humification (Kononova, 1966 and Chen *et al.,* 1977). Chin *et al.* (1997) also found that a low E_4/E_6 ratio reflects a higher degree of condensation of aromatic structures while a high ratio indicates the presence of more aliphatic structures and less condensed aromatic structures. Albrecht *et al.* (2011) reported that the absorbance at 460-480 nm indicates the presence of organic material in the initial phase of humification and absorbance at 600-670 nm is indicative of strongly humified material with more aromatic condensed groups. The low E_4/E_6in mature rubber systems indicate relatively more condensation of SOM in the mature rubber plantations. Comparatively higher $E_2/E_3$and E_4/E_6 values in the immature systems indicate the presence of relatively more aliphatic compounds in these systems which might be due to the fresh additions of organic matter in the form of legume litter and crop residues. Among the three immature systems at Amayannoor, the higher E_2/E_3 and E_4/E_6 for rubber-*Pueraria* indicated the presence of relatively higher proportions of aliphatic structures. The relatively lower E_2/E_3 and E_4/E_6 values of rubber-*Mucuna* than rubber-banana and rubber-pineapple systems indicated the presence of more condensed organic materials in the rubber- *Mucuna* system.

Vieyra *et al.* (2009) reported that higher values E_4/E_6 could be due to the presence of less condensed forms of organic compounds such as proteins and carbohydrates. Chen *et al*. (2002) also reported a high intensity of absorption in polyphenolic rich fraction than in carbohydrate-rich fraction in the UV-Vis spectra of natural organic matter fractions.

Figures 1 and 2 show the FTIR spectra of bulk soils of different systems at Amayannoor and Mundakayam respectively. In all the systems sharp bands were recorded at about 3690 cm^{-1} (primary N-H stretch), 3400 cm^{-1} (stretching of bonded and non-bonded hydroxyl groups), 1630 cm^{-1} (C=O vibrations of carboxylates and aromatic vibrations) and at 1034 cm^{-1} (C-O stretching vibrations of polysaccharides, carbohydrates). For quantifying the relative variations in the FTIR spectra of different systems in each location, relative absorbance was calculated from peak heights and is given in Tables 5 and 6.

IR characterization

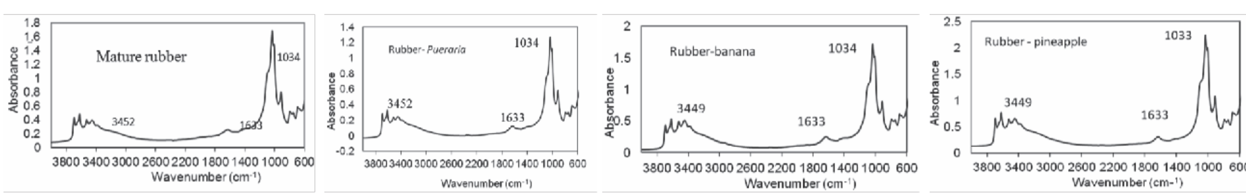

Fig. 1. FTIR spectra of different rubber based systems at Amayannoor

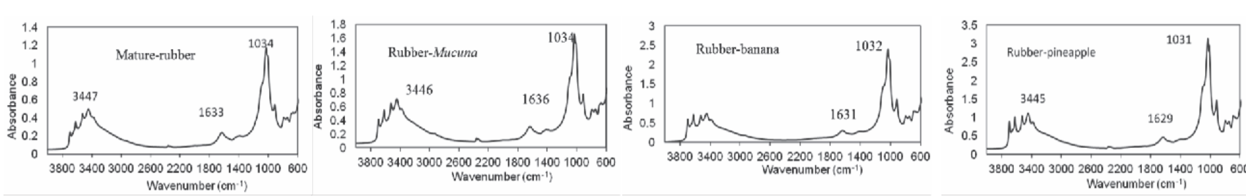

Fig. 2. FTIR spectra of different rubber based systems at Mundakayam

Table 5. Relative IR absorbance of soils in different systems at Amayannoor

System	Relative absorbance at	
	1630 cm^{-1}	**1034 cm^{-1}**
Mature rubber	18.31	81.68
Rubber-*Pueraria*	8.75	91.25
Rubber-banana	12.61	87.39
Rubber- pineapple	11.92	88.00

The rubber-*Pueraria* system at Amayannoor recorded the highest relative absorbance at 1034 cm^{-1} while the lowest was observed in mature rubber system (Table 5). The rubber-banana and rubber-pineapple systems recorded comparable relative absorbance and are intermediate to that of mature rubber and rubber-*Pueraria* system. The results indicate the presence of more carbohydrates and polysaccharides in the rubber-*Pueraria* system compared to other systems. The relative absorbance at 1630 cm^{-1} was highest in mature rubber while the lowest was in the rubber-*Pueraria* system. The other two systems showed almost closer relative absorbance. The strong IR absorbance of mature rubber soils at 1630 cm^{-1} indicated more aromaticity and hence more condensation in the SOM of mature rubber system. The agro- management operations such as tillage carried out in the rubber-pineapple and rubber-banana systems might have resulted in higher aromaticity in these two systems compared to that of the rubber-*Pueraria* system. Tillage of soil leads to loss of more readily decomposable fraction, resulting in an increase in the proportion of the more recalcitrant aromatic C forms in the SOM. Similar observations in tilled and untilled lands were reported by Golchin *et al*. (1995) and Solomon *et al.* (2005).

Table 6. Relative IR absorbance of soils in different systems at Mundakayam

System	Relative absorbance at	
	1630 cm^{-1}	1034 cm^{-1}
Mature rubber	16.67	83.32
Rubber-*Mucuna*	15.80	84.20
Rubber-banana	11.08	88.85
Rubber- pineapple	12.71	87.29

Among the different systems studied at Mundakayam, the relative absorbance at 1034 cm^{-1} decreased in the order rubber-banana>rubber-pineapple>rubber-*Mucuna*>mature rubber (Table 6).

The higher absorbance at 1034 cm^{-1} observed in rubber-banana and rubber-pineapple systems indicated the presence of more carbohydrates and polysaccharides in these two systems compared to the other two systems. The relative absorption at 1630 cm^{-1} was the highest in mature rubber and the lowest in the rubber-banana system. The strong absorption observed at 1630 cm^{-1} for mature rubber indicated more aromaticity as observed in location, Amayannoor. This may be due to the dominance of more recalcitrant aromatic forms in the SOM of mature rubber system.

Wide variation in the quality of litter as indicated by the variation in the content of recalcitrant groups such as lignin and polyphenols and the labile species such as cellulose (Philip and Abraham, 2009) might have also contributed to the observed difference in aromaticity of the different systems. ^{13}C NMR studies (Abraham and Chudek, 2008) also showed the presence of more alkyl-C in rubber litter than in *Mucun*a and *Puerari*a.

The spectroscopic data revealed from the UV-Vis and FTIR studies are complementary. Also, these results were in agreement with that of studies on SOM fractions in different rubber-based systems (Philip, 2014). The presence of relatively more aliphatic components in the rubber-*Puerari*a system was also reflected in higher soil respiration (Philip and Abraham, 2016).

Carbohydrates and polysaccharides are important as bonding agents for soil aggregates and as an energy source for soil microorganisms. These easily degradable SOM components also play a significant role in nutrient mineralization. On the other hand, the presence of aromatic constituents in the SOM leads to slow decomposition of organic matter which in turn helps in minimizing the CO_2 emission to the atmosphere which is an important environmental concern. Higher aromaticity also leads to a build-up of organic matter. The presence of more carbohydrates and polysaccharides in soils under the rubber-*Puerari*a system makes it a better system than the inter-cropped systems in terms of soil quality. Hence, establishing *Puerari*a in the initial growing phase of rubber cultivation is a beneficial management practice. Rubber-banana and rubber-pineapple systems were found better than the rubber-*Mucun*a system in terms of soil quality as these two intercrops contribute more carbohydrates and polysaccharides than the cover crop *Mucun*a. However, higher aromaticity observed in rubber-*Mucun*a systems than that in the intercropped systems is beneficial in retaining/improving the soil carbon status. Hence, establishing *Mucuna* in rubber plantations low in organic carbon status is advantageous. The highest aromaticity of the SOM observed in mature rubber indicates that the organic matter may remain in the system for longer periods, which is environmentally beneficial.

Conclusion

The present spectral studies confirm the results of previous studies indicating that the composition of SOM in rubber plantation varied with land use and management practices. It was found that SOM under a mature rubber system is expressing the presence of relatively more aromatic components than immature systems with cover crop/inter-crop. Among the various immature systems, the SOM in the rubber-*Puerari*a system was found less aromatic than rubber-pineapple and rubber-banana systems whereas the rubber-*Mucun*a system was more aromatic than rubber-pineapple and rubber-banana systems. The presence of relatively larger proportions of aliphatic structures such as carbohydrates and polysaccharides in rubber-*Puerari*a system was also revealed. This may enhance the microbial activity and associated nutrient release in the system compared to other intercropped systems which are advantageous in the growing phase of rubber. Higher aromaticity in the soil under the rubber-*Mucuna* system helps in the buildup of soil carbon. The relative enrichment of carboxylic and aromatic groups in the SOM of mature rubber leads to carbon sequestration which is environmentally beneficial. UV-Vis and FTIR spectroscopic studies were found useful in SOM quality evaluation in rubber plantations.

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