

# RAPID DETECTION OF SOIL ORGANIC CARBON USING SHORTWAVE NEAR INFRARED (SW-NIR) SPECTROSCOPY

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**Abstract**— Soil organic matter content is a primary indicator of quality over measuring soil organic carbon (SOC). Demand has been created for quick and real time multiple analysis methods for SOC instead of available laborious, time consuming and expensive methods. There are developed Near Infrared Spectroscopy (NIR) methodologies for detecting SOC, however imply either expensive full scale NIR instruments or considerable work on sample preparation. There are attempt in narrow range vehicle mounted NIR detections in precision agriculture on the go mode SOC very low accuracy. This study develops a rapid method for the detection of SOC for laboratory scale. Soil samples (n=144) were collected from a range of sites at Mapalana research farm, University of Ruhuna in three different depths including 3 replicates from each depth. Seventy-two air-dried, sieved and finely ground soil samples were prepared in conventional dry sample presentation method. Four spectra per sample were taken by holding them into sample cups. Soil samples, saturated with distilled water were kept for 30min and similar process were followed for new wet sample presentation approach. Direct probe NIR Spectrometer FQA-NIR Gun (588-1100 nm) (Shibuya Seiki, Hamamatsu, Japan), was used to acquire NIR reflectance spectra. Standard Walkey-Black method was used to detect the organic carbon contents of spectra acquired soil samples as the respective reference data to validate the approach. For both wet and dry soil sample types, Partial Least Square (PLS) regression models were developed to predict the SOC. The validation results of both experiments were successful for the prediction of SOC where 0.95 of  $R^2$  and 0.248 of SEV for dry sample test and 0.91 of  $R^2$  and 0.245 of SEV for new wet sample approach. Sample preparation time and procedures were substantially reduced by the newly introduced wet method (30 min) when it is compared to the conventional spectroscopic methods (24 hrs). Average spectra investigation shows that 770 nm was strongly correlated with the SOC which could possibly be employed in further simplified instrumentation. The research revealed that the potential of using NIR technology as a nondestructive and rapid detection method for soil organic carbon with quick multiple field level detection facilities.

**Index Terms**— Soil, Organic Carbon, Near Infrared, Spectroscopy, PLSR, Walkey-Black, Non Destructive.

## 1 INTRODUCTION

The Soil is among three major natural resources accompanied with air and water. It is an amazing product of Mother Nature without which there would be no life. Composition of soil creates immense important attributes in soil for nutrient management for crop growth and consideration of various engineering constructions. A typical soil consists of mineral, organic matter, water, air. Soil organic matter (SOM) plays important role in the maintenance and improvement of soil properties. SOM is composed of three major components i.e. plants residues, animal remain and dead remains of microorganisms & mainly consists moisture and dry matter. This 25% made up of Carbon, Oxygen, Hydrogen, Nitrogen and mineral matter. Generally, 10-12% of Carbon present in the soil [1]. Soil organic carbon (SOC) is an important constituent of soil organic matter (SOM) and also plays a major role in the soil cation-exchange capacity, retention of base ions, soil aggregation, and nutrient availability. Thus, quantifying SOC is of a great interest to soil management, soil mapping, and grassland management. In laboratories, soil organic matter is estimated in terms of soil organic carbon as it is the most reliable and easy method. The

perocedure is extending of the measured soil organic carbon is converted in to soil organic matter based on the assumed percentage of carbon in the organic matter. This can vary and the conversion can range from 1.72 to 2.0 depending on the source of the materials for the soil organic matter. In practice, the value of 1.72 is used [2], [3] for more precise scientific work only the values of soil organic carbon are used. Standard methods for detecting of SOC have been developed during recent years. There are several methods performed for estimation of SOC. Some of them are destructive and others are non-destructive. Prevailing methods for SOC are Wet oxidation method, Hydrogen peroxide method, Dry combustion method, Loss-On-Ignition method etc. [2]. However, conventional laboratory methods are expensive, slow, and often imprecise. In addition, these methods consume chemical reagents and cause environmental pollution. Therefore, a rapid, chemical-free measurement method for determination of SOC is of great significance. The application of spectroscopy as a viable solution for SOC, especially in the near-infrared (NIR) region, has shown a high potential [4], [5].

Since recent past, NIR spectroscopy has been extensively applied in various fields including, agriculture, geology, medicine and soil science. In soil science, numerous studies have demonstrated that the NIR spectral range combined with multivariate calibration methods could be used as a non-destructive rapid analytical technique for simultaneous estimation of several soil compositional constituents and soil quality attributes with acceptable accuracy in a very short time.

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The trend all over the world now is to develop chemical free green non-destructive protocols for all possible scientific techniques and so does the measuring quality attributes of soils. Near infrared reflectance spectroscopy (NIRS) is a nondestructive and rapid technique applied increasingly in soil quality evaluation in recent years. It provides the information to research the quality parameters of soil such as moisture content, soil minerals and organic carbon content are increasingly in NIR applications. However, in all these applications either NIR use its full scale spectrum from 350-2500nm with expensive INGAs sensors or employees in on the go field measurements with low accuracy [6], [7]. However, at present, there are number of innovative commercial versions in different kind of near infrared spectrometers, such as Fourier transform, FOG (fiber optic probe & moving grating), NCDA (non-contact reflectance diode array), RED-wave NIR instruments. In this research we used short wave near infrared (SW-NIR) instrument (550nm to 1100nm) which is operated with relatively low cost Si diode array sensor inside to investigate the performances of organic carbon content in soil.

Therefore, the aim of this work was to develop quick and low cost Short Wave Near Infrared Spectroscopic (SWNIR) methodology for the laboratory scale detection of organic carbon in soil.

## 2 MATERIALS AND METHODS

### 2.1 Location

Soil samples were obtained from sixteen different locations in Mapalana Research farm, Faculty of Agriculture, University of Ruhuna in a manner that those samples represent a wide range of Soil organic matter content in the samples. The mean annual precipitation is 2500mm and average monthly temperature is 29.420C. The soil type was classified as red yellow podzolic according to the USDA soil classification.

### 2.2 Soil sampling

Soil samples were collected from different sites of study at three different depths of 0-5cm, 5-10cm & 10-15cm and including 3 replicates from each depth (9 soil samples per location). The samples were packed up to polythene bags labeled and securely kept until further processing for the experiments. One hundred forty-four soil samples were used in the research. Seventy-two samples were used for dry sample test and seventy-two samples were used for wet sample test.

### 2.3 Experiment 01 – Dry sample test

The first experiment assessed the impacts of model configurations to detect soil organic carbon using SWNIR spectrometer for dry soil samples. Thus, the experiment was used to develop a calibration model to find the best data pretreatment, math transformation, number of factors etc. to detect soil organic carbon. The samples were air dried for 24 hours and then passed through a 2mm sieve to remove plant debris and large root matter. Soil samples thoroughly ground using mortar and pestle for homogeneity and to reduce physical variability between replicates. A custom made plastic cup with 4.5 cm in diameter and 1 cm in depth was constructed to hold the soil samples. The plastic sample cup was filled with ground soil

sample and the excess sample surface was trim with a spatula. A quart glass screen attached to a plastic plate was placed on the top of soil samples to keep the spectrometer probe at the spectra acquisition. The NIR spectra from 588nm to 1100nm were acquired and recorded from all the samples as four spectra per sample (one spectrum per one direction) fig.1. The integration time of the spectra was recorded as 115 milliseconds.

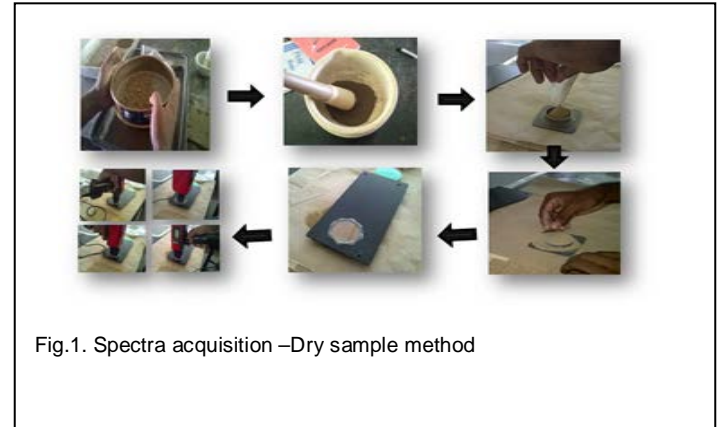


Fig.1. Spectra acquisition –Dry sample method

### 2.4 Experiment 02 – Wet sample test

The second experiment was designed to reduce the need of sample preparation further by assessing the possibility of using wet soil sample for detecting SOC. This methodology eliminates the need of sieving; drying and grinding which substantially reduce the time while further enhance the rapid nature of detection.

The soil samples after removing large gravels and debris by hand kept in to a crucible. Then the samples were saturated adding distilled water and thoroughly mixed using spatula and homogenized to reduce variability between replicates. A filter paper was placed inside the perforated bottom of the sample cup to let the excess water out.

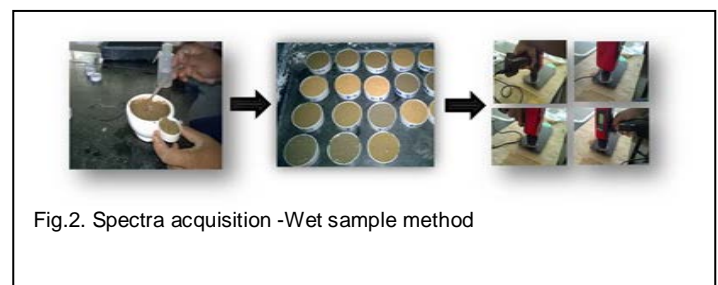


Fig.2. Spectra acquisition -Wet sample method

The plastic sample cup was filled with saturated soil sample and the sample surface was leveled. Soil samples were kept for 30 min to standardize. After 30 min, the NIR spectra from 588 nm up to 1100 nm were collected by the same spectrometer. The spectra were recorded from all the samples as four spectra per sample (one spectrum per one direction) fig.2. The integration time of the spectra was recorded as 115 milliseconds.

## 2.5 Acquisition of Reference Data

Standard Wet oxidation (Walkey-Black Method) [8] was used to obtain reference data. After spectra acquisition, tested samples were subjected to determine the organic carbon content by wet oxidation method.

## 2.6 Data Analysis

The acquired spectra were first evaluated by Principal Component Analysis (PCA) to remove possible outliers. The selected spectra were applied in the Partial Least Square (PLS) calibration models for the class identification in Pirouette 4.5 software. PLS models were developed to predict the organic carbon content of soil. Calibration model performance was assessed in terms of coefficient of determination ( $R^2$ ) and standard error of validation (SEV).

## 3 RESULTS AND DISCUSSION

### 3.1 Preprocessing of the Spectra

NIR Spectra taken from all dry & wet samples were evaluated by principal component analysis (PCA) to remove possible outliers. The sample plots of PCA with the removed outliers are shown the fig.3. A substantial baseline variation between the spectra was present even after removing the outliers. This baseline effect is usually present due to sample presentation variations and environmental noise which is undesirable for data analysis. Thus, different data pretreatments were applied to the outlier removed spectra to reduce the baseline effect.

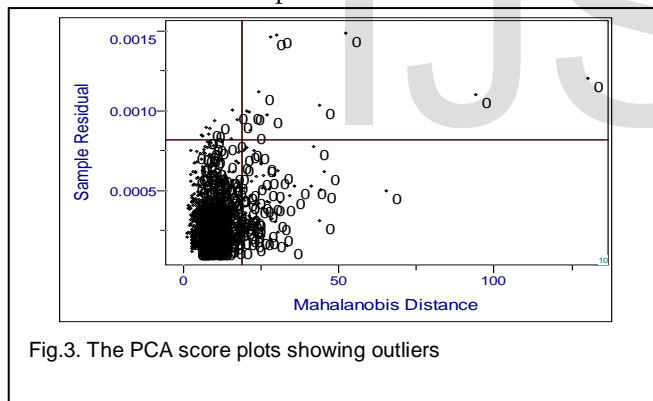


Fig.3. The PCA score plots showing outliers

### 3.2 Variation of SOC Content in Different Layers

Average soils Organic Carbon Contents (SOC) in the investigated layers are shown in the fig.4. When comparing the means of SOC content in different soil layers, there were typical gradient of SOC from the top to bottom were found. As shown in the Figure SOC values of soil were decreased gradually from top to bottom layer. Therefore, SOC content is different from each layer of the soil. The SOC levels were statistically significant at the probability 0.05 level. Therefore, in the first attempt the PLS models were developed for each soil layer separately.

### 3.3 Experiment 01 – Dry sample test

The result of PLS prediction for dry sample test with four spectra leaving out validation is shown in the Table 1. In the

first attempt of the data analysis the PLS prediction models constructed for middle layer soil were performed better (SEV 0.18) to the top and bottom soils (Table 1). After the validation of Top, Middle and Bottom layer soils, it was noticed that a range of SOC was lack in the obtained separate layers profiles missing in the Y fit. The missing SOC data ranges in Y fit of the PLS model for Top soil was between 1.4-1.6 %, for Middle soil was between 1.4-1.8 % and for Bottom soil was between 1.1-1.5 %. In order to avoid the impacts of missing range combined PLS model was developed for all dry soil samples to predict SOC.

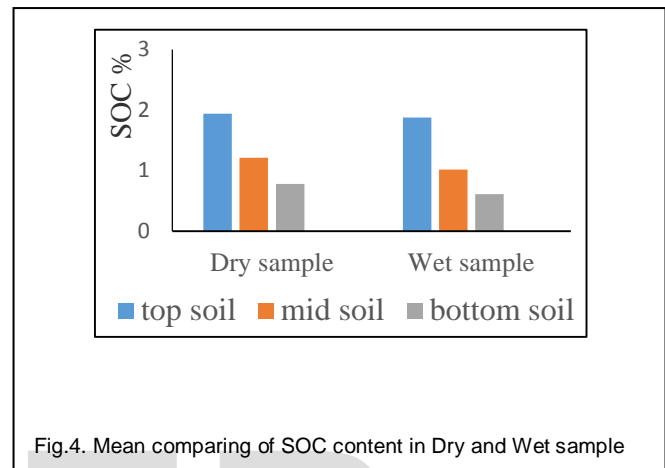


Fig.4. Mean comparing of SOC content in Dry and Wet sample

TABLE 1  
 SUMMARIZE OF THE SEV AND  $R^2$  VALUES OF BEST PRE-TREATMENT SET FOR DIFFERENT LAYERS (DRY SOILS)

	SEV	$R^2$
Top Soil	0.255	0.922
Middle Soil	0.180	0.966
Bottom Soil	0.191	0.90

### 3.3.1 Best model configurations for SOC prediction in dry sample presentation

PLS model was developed for dry soil samples with different data pre-treatments and math transformations. According to the given results, mean centering pre-treatment with 2nd derivatives indicated lowest standard error of validation (SEV = 0.2480) and Highest  $R^2$  validation ( $R^2 = 0.9481$ ) value. After the validation of dry sample presentation, it was noticed that there was no missing data range in the Y fit (Fig.5). Therefore, mean center pretreatment with 2nd derivatives were best to predict SOC in dry soil samples.

### 3.3.2 Important wavelength for detection of SOC content

The regression vector coefficients were observed to get the most important wavelength variables involved in the detection of SOC content and illustrated in the fig.6. According to the Graph, positive and negative regression coefficient values were found. Highest regression coefficient values are considered to be more influential in the detection of SOC. According to the fig.6, most of the regression vectors are observed in visible region (440-700nm- visible range) when it is compared to the NIR range which indicates in the dry soil samples method

soil color is one of the primary important parameter for detecting soil SOC.

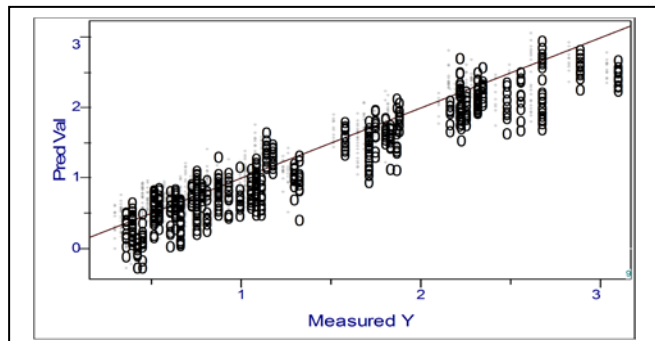


Fig.5. Y fit of the PLS model for Dry sample presentation

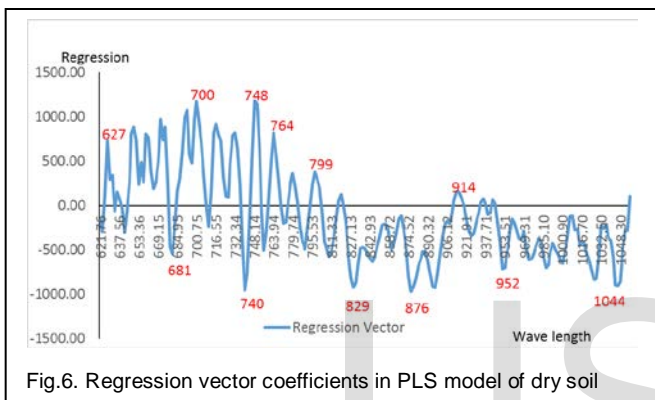


Fig.6. Regression vector coefficients in PLS model of dry soil

**3.3.3 Spectra investigation**

The average spectra were investigated to observe the difference of radiation absorbance in soils with different levels of SOC. Three sets of spectra were assigned in the order of their levels of absorbance as high (3.1-1.8) medium (1.8-0.9) and low (0.9-0.3). Average spectra calculated separately from three different levels of SOC contents were transformed in to first derivative spectra to avoid the baseline effects and are shown in the fig.7. According to the graph, the average spectra order was observed to be arranging in the similar order of the SOC classes at 770 nm. As such, the average spectra investigation shows that 770 nm was strongly correlated with the SOC which could possibly be employed in simplified instrumentation. Therefore, this wavelength region would be usable to develop single wave length low cost device for detecting SOC in dry soil samples presentation method.

**3.4 Experiment 02 – Wet sample presentation method**

The result of PLS prediction for wet sample test with four spectra leaving out validation is shown in the Table 2. In the first attempt of the data analysis the PLS prediction models constructed for bottom layer soil were performed better (SEV 0.204) to the top and middle soils. After the validation of Top, Middle and Bottom layer soils, it was noticed that range of SOC was lack in the observed samples in the models in the Y fit. The missing SOC data ranges in Y fit of the PLS models for Top soil was between 1.5-2.0 %, for Middle soil was between

0.8-1.2 % and for Bottom soil was between 0.4-0.7 %. In order to get the representative samples for the missing range, PLS model was developed for all wet soil samples to predict SOC.

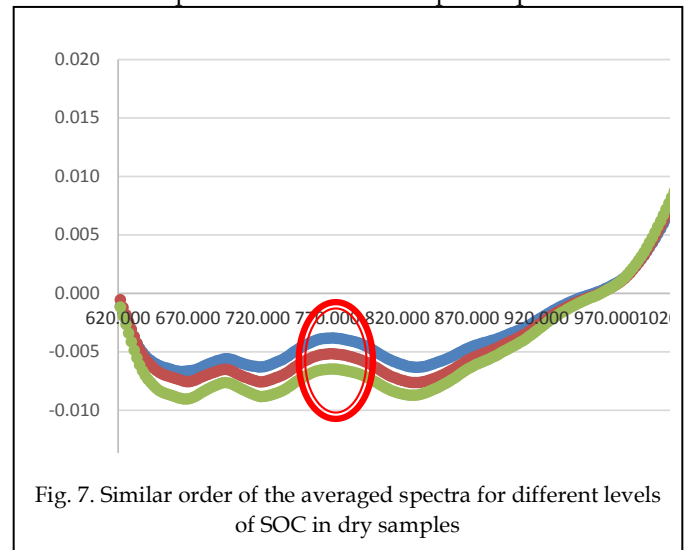


Fig. 7. Similar order of the averaged spectra for different levels of SOC in dry samples

TABLE 2  
 SUMMARIZE OF THE SEV AND R<sup>2</sup> VALUES OF BEST PRE-TREATMENT SET FOR DIFFERENT LAYERS (WET SOILS)

	SEV	R <sup>2</sup> Validated
Top soil	0.478	0.80
Middle soil	0.224	0.90
Bottom soil	0.204	0.819

**3.4.1 Best combination of the wet Soil Samples for SOC prediction**

PLS models were developed for wet soil samples with different data pre-treatments and math transformations. According to the given results, pareto pre-treatment with 2nd derivatives indicated lowest standard error of validation (SEV = 0.2447) and highest R<sup>2</sup> validation (R<sup>2</sup> = 0.9094) value. After the validation of wet sample presentation, it was noticed that a there was no missing data range in the Y fit (Fig.8). Therefore, Pareto pretreatment with 2nd derivatives were best to predict SOC in wet soil samples.

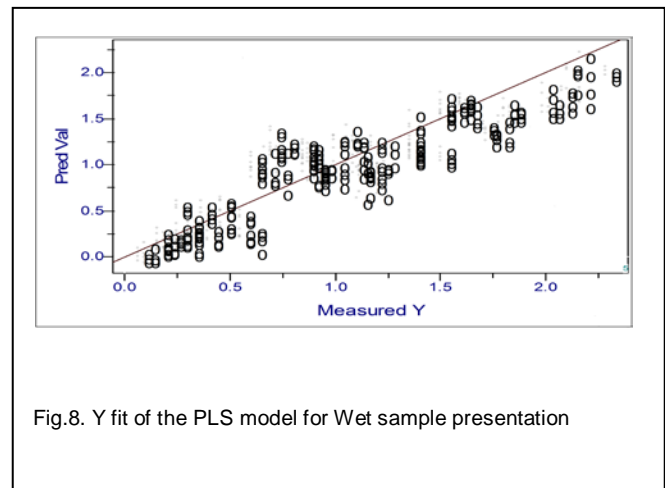


Fig.8. Y fit of the PLS model for Wet sample presentation

**3.4.2 Important wavelength for detection of SOC**

**content**

The most important wavelength variables involved in the detection of SOC content were illustrated in the fig.9. Possible wavelengths to predict SOC in wet soil are given in the graph. According to the Graph, positive and negative regression coefficient values were found. Highest regression coefficient values are considered to be more influential in the detection of SOC. According to the fig.8, the regression vectors were more or less similarly distributed throughout the spectrum unlike concentrating it in the visible region in wet sample presentation method. Thus, soil color may not be a main factor to predict SOC in the wet sample presentation method.

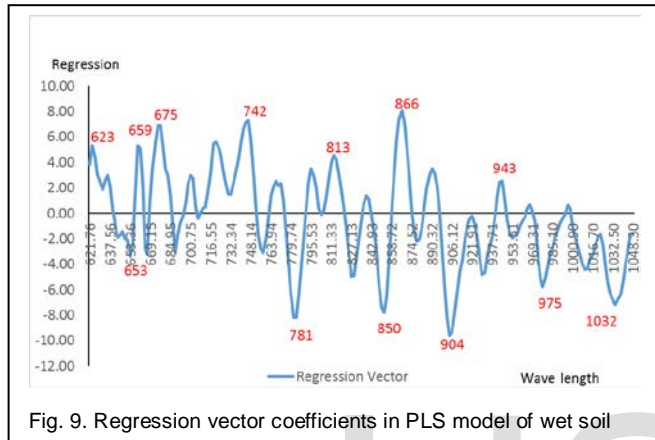


Fig. 9. Regression vector coefficients in PLS model of wet soil

**3.4.3 Spectra Investigation**

In the average spectra investigation, transformed first derivative spectra of three sets of spectra were assigned in the order of their levels of absorbance (Fig.10) as high (2.3-1.5) medium (1.5-0.9) and low (0.9-0.06). According to the graph, wet soil samples have given the average spectra order similar to the order of the SOC classes at 770 nm (Fig.10). Average spectra investigation shows that 770 nm was strongly correlated with the SOC which could possibly be employed in simplified instrumentation. Therefore, this wavelength region would be usable to develop single wavelength low cost device for detecting SOC in wet soil samples.

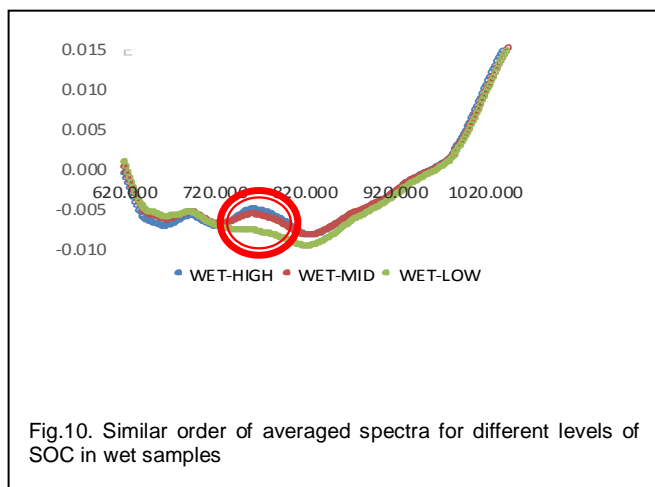


Fig.10. Similar order of averaged spectra for different levels of SOC in wet samples

**4 CONCLUSION**

The developed PLS models for the prediction of soil organic carbon were successful in the dry sample method at the accuracy rate of SEV = 0.248 and, R<sup>2</sup> = 0.95. The new wet sample presentation approach recorded the accuracy rate of SEV = 0.245 and R<sup>2</sup> = 0.91. Sample preparation time for dry sample presentation method (24 hrs.) was about 50 times to the wet sample presentation method (30 min) as the new approach avoids drying, sieving, grinding in the conventional spectroscopic methodology of detection of SOC. Spectra investigation shows that 770 nm was subsequently correlated with the SOC in soil that could possibly be employed in simplified instrumentation. The identified most important wave length for SOC prediction were located at 627 nm, 700 nm, 740 nm, 748 nm, 876 nm, 952nm, 1044 nm in the dry sample method and were located at 623 nm, 653 nm, 675 nm, 742 nm, 781 nm, 850nm, 866 nm, 943nm, 1032nm in wet sample method. The research revealed that the potential of using NIR technology as a non-destructive rapid and chemical free detection tool soil Organic Carbon.

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