In Situ Measurement of Soil Carbon with Depth using Near Infrared (NIR) Spectroscopy

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Abstract. Information on soil carbon (C) content is necessary in order to figure out the amount of C stock in soil, as the emission of CO₂ from soil pool can increase CO₂ concentration in the atmospheric pool, causing global warming. However, methods to measure this soil property are labour intensive and time-consuming. This study is aimed to investigate the ability of near infrared spectroscopy (Vis-NIRS) to in situ measure soil C from 0 to 50 cm depth. Soil cores from a Luvisol in Manawatu Region New Zealand were collected using a metallic cylindrical corer and scanned using a soil probe attached to the spectrometer at 1-cm interval from 0 to 50 cm depth. Reference data were generated by measuring soil C of the sliced soil cores using dry combustion technique. Pre-processed spectral data and the reference data were used to build partial least square regression (PLSR) model. The model was able to predict soil C with depth from surface to subsurface horizons. Thus, the Vis-NIRS-soil coring technique can be rapidly used to measure in situ soil C content with depth that can be used to measure the amount of soil C stock.

1. Introduction
Attention on the dynamics of soil carbon (C) increases in recent years, as the emission of CO₂ from soil accumulated in the atmosphere has been one of several greenhouse gases causing global warming [1]. Sequestering large amount of C for long period of time in soil is one of the encouraging ways to mitigate global warming [2]. Storing C in deep soil layer is intended to increase the residence time and this can postpone C transformation into CO₂ to the atmosphere [3]. The challenge is how to create a method that can be used to measure or monitor the variations of soil C concentration with soil depth, as the conventional procedures are tedious and time consuming.

Visible near-infrared spectroscopy (Vis-NIRS), which is known as a rapid and inexpensive technique, has been reported able to measure soil C concentrations both in laboratory [4] and in the field [5]. This technique has been used to assess horizontal variability of soil C concentrations in a small [6] and a large area [7]. Not only for small and large area, global spectra of Vis-NIR library involving many countries has been used for predicting soil attributes, including soil organic C [8].

Besides for soil C prediction, the use of Vis-NIR technique has been reported also for prediction other soil chemical and physical properties, such as total N, NH₄-N, NO₃-N, CEC, P, K, Ca, Mg, pH, moisture, and soil particle size [9], with accuracies from poor to excellent. Malley and Martin [10] reported that this technique is mostly successful for predicting total C, organic C, total N, CEC, and moisture. Study
of Vis-NIRS technique has also been used for testing the root density [11-13] and biochar stability indices [14].

As the limited information reported on the ability of this technique to figure out soil C concentration with soil depths, this paper is aimed to investigate the ability of Vis-NIRS soil coring technique in measuring total soil C variations with soil depths in a grassland of Manawatu region New Zealand.

2. Materials and methods

2.1. Sample collection

Twelve soil cores (0-50 cm depth) were collected in a grassland of a Luvisol (Typic Fragiaqualf) the Manawatu region, New Zealand, using a metal cylindrical corer with a 4.6 cm diameter. The distance of each core was ~10 m in between. The Luvisol has developed on loess with a layer of Aokautere ash and is rich in silt and clay; the clay is dominated by 2:1 clay minerals [15].

2.2. Spectral collection and total C measurement

Spectral reflectance (UV, visible and near-infrared range; 350 – 2500 nm) of the soil cores was acquired using a soil probe attached to an ASD FieldSpec 3 V-NIR Spectrometer (Analytical Spectral Device, Boulder, CO, USA). The soil cores were scanned at 1 cm interval from 0 to 50 cm depth, and the spectral data collected were then saved in an ASCII text file.

The soil cores were air dried, ground and sieved to pass a 0.180 mm-diameter sieve and the total C content was then measured using elemental analyser (Elemental, Vario MACRO, Germany).

2.3. Spectral pre-processings

Initially, the UV bands (350-399 nm) were excluded from the spectral data. Then, the 1-cm interval spectral data were averaged for every 5 cm from 0 to 30 cm, and for every 10 cm from 30 to 50 cm depth of soil cores. The averaged data were later exported to a chemometric analysis software – ParLeS [16] – for several pre-processing steps as follows [17, 18]: the spectral data were (1) transformed from reflectance to Log (1/R) unit; then (2) treated using wavelet detrending; (3) smoothed using a Savitzky-Golay filter with a 3rd order polynomial algorithm and window size of 7 nm; (4) transformed into the first derivative, and then (5) finally treated using mean centering.

2.4. Developing calibration models

PLSR was used to develop calibration models between the pre-processed spectral data and the reference data (soil C measured using elemental analyser). In order to avoid overfitting, the PLSR models were developed using a number of factors (principal components) that produce the lowest root mean square error (RMSE) and the lowest Akaike Information Criterion (AIC) [16].

2.5. Parameters for testing the accuracy of the model

The ability of the PLSR model to predict soil C was assessed using the following statistics [17, 18]: (i) RMSE (root mean square error) of measured and predicted soil C, (ii) coefficient of determination (R²), and (iii) RPD (ratio of prediction to deviation); RPD is calculated as the standard deviation of the reference data divided by root mean square error (SD/RMSE). The best model has the largest RPD and R², and the smallest RMSE.

3. Results and discussion

3.1. Soil C data with depth

The summary of soil C data with depth (0-50 cm) is shown at Table 1. The topmost soil (0-5 cm depth) contains the highest amount of C, and the C concentration tends to decrease with soil depth, as Kusumo et al. [13] also found. Besides that, the top 20 cm soil layers contain more C than that of below the 20 cm. Large amount of C in the top 20 cm soil layer seems associated with the accumulation of plant
debris and roots in this layer. Evans [19] reported that most grass roots occurred on the top 20 cm of grassland in New Zealand. The decay of these roots leaves C which is accumulated in soil.

Table 1. Data of soil C (%) with depth.

| Soil depth (cm) | Range Min. | Range Max. | Mean | Median | Standard deviation | Variance | Coeff. of variation |
|----------------|------------|------------|------|--------|--------------------|----------|--------------------|
| 0-5            | 2.84       | 4.72       | 3.81 | 3.79   | 0.57               | 0.32     | 0.15               |
| 5-10           | 2.20       | 3.34       | 2.75 | 2.84   | 0.37               | 0.14     | 0.13               |
| 10-15          | 2.09       | 3.48       | 2.61 | 2.40   | 0.46               | 0.21     | 0.18               |
| 15-20          | 1.64       | 3.14       | 2.43 | 2.49   | 0.53               | 0.28     | 0.22               |
| 20-25          | 1.14       | 2.62       | 1.77 | 1.78   | 0.50               | 0.25     | 0.28               |
| 25-30          | 0.77       | 1.79       | 1.12 | 1.12   | 0.29               | 0.09     | 0.26               |
| 30-40          | 0.37       | 1.22       | 0.80 | 0.77   | 0.26               | 0.07     | 0.33               |
| 40-50          | 0.24       | 0.87       | 0.54 | 0.52   | 0.19               | 0.04     | 0.35               |

3.2. Variations of soil spectral reflectance with soil depth

The shape of soil reflectance in each depth is depicted at Figure 1. As can be seen that there is a contrast appearance of soil reflectance of 0-20 cm depth and 20-50 cm depth. Soil reflectance from 0 to 20 cm depth do not show a concave shape at wavelength around 950 nm, while soil reflectance of 20-50 cm depth do show. Concave contour of soil reflectance on 20-50 cm depth is probably due to iron oxides content, as reported by Dematte et al. [20]. There is no concave shape on the soil reflectance of 0-20 cm depth probably due to the organic matter content. As the soil layer close to the surface, the organic matter content tends to increase (as shown by the mean data of soil C concentration at Table 1), and this organic matter masks the effect of iron oxide which then remove the concave shape from the soil reflectance [13, 20, 21].

Highlighting the soil reflectance from 0 to 20 cm depth, the reflectance of 0-5 cm depth soil shows the lowest reflectance intensity, followed by 5-10 cm, 10-15 cm and 15-20 cm depth soil (Figure 1). This is strongly related to highest content of soil C (3.81% C) on the 0-5 cm depth soil, followed by 2.75%, 2.61% and 2.43% C of the remaining samples, respectively. As reported by previous researchers [13, 22, 23] that organic matter content causes lower intensity of the soil reflectance. As organic matter increases, overall soil reflectance generally decreases in the band region of 400-2500 nm [22, 23]. However, Mathew et al. [24] reported higher reflectance at 500-1200 nm for soil treated to remove organic matter using 10% H2O2 compared to the non-treated sample, but soil reflectance with no-H2O2 treatment was higher in the 1200-2600 nm band.
3.3. Accuracy prediction of soil C
The accuracy of soil C concentrations predicted using PLSR model of Vis-NIR and NIR bands is shown at Table 2. As can be seen that both models (using Vis-NIR and NIR bands) produce successful prediction accuracy, because of the $R^2$ between 0.90-0.95 and the RPD between 3.0-4.0 as classified by Malley et al. [25]. However, the model produced slightly better soil C prediction ($R^2_{CV}$ 0.931; RPD$_{CV}$ 3.82) when the visible bands (400-780 nm) were amalgamated with the NIR bands (780-2500 nm), rather than using the NIR bands only ($R^2_{CV}$ 0.922; RPD$_{CV}$ 3.60). Variations of the visible bands seems having important factors related to the alteration of soil C concentrations. In this case, the variations of the soil colours have relationship to the variations of soil C. As it is commonly known that higher C content in a soil is usually associated with darker soil colour [26]. Moderately successful prediction of soil C and N in a Gley soil, Kairanga, New Zealand, has been reported by Kusumo et al. [13] when they used the whole Vis-NIR bands for the PLSR model. Ludwig et al. [27] successfully predicted the contents of C, N, and cumulative respiration and N mineralized after 264 days using Vis-NIR region (400-2500 nm). The reason of using the whole Vis-NIR bands because they found the signal of soil C was associated with the visible bands.

![Figure 1](image.png)

**Figure 1.** The shape of soil spectral reflectance with depth.

### Table 2. Prediction accuracy of soil C predicted by PLSR model of Vis-NIR and NIR bands.

| Soil  | Bands used | Number of factors for PLSR model | Cross validation          |
|-------|------------|----------------------------------|---------------------------|
|        |            |                                  | $R^2_{CV}$ | RMSE$_{CV}$ | RPD$_{CV}$ |
| Luvisol| Vis-NIR    | 5                                | 0.931       | 0.298       | 3.82       |
|        | NIR        | 6                                | 0.922       | 0.318       | 3.60       |

Note: Vis-NIR bands = 400-2500 nm; NIR bands = 780-2500 nm; $R^2_{CV}$ = coefficient of determination of cross-validation; RMSE$_{CV}$ root mean square error of cross-validation; RPD$_{CV}$ = SD/RMSE of the cross-validation.

3.4. Measured- and predicted-soil C and distribution of soil C concentration with depth
The relationship between soil C measured by laboratory method (elemental analyser) and predicted by Vis-NIRS technique for all soil depths is shown at Figure 2a. Strong relationship is shown by high coefficient determination ($R^2$ 0.93) between soil C measured by laboratory and predicted by Vis-NIRS.
technique. Low RMSE (0.298) and high RPD (3.82) show the robustness of the Vis-NIRS technique [25]. These parameters indicate that Vis-NIRS technique can be used to measure soil C concentration in various soil depths, which is comparable to the reference method (elemental analyser). Quick scanning of soil cores, no chemical needed and less soil preparation make this technique more superior than the conventional ones, such as elemental analyser and LECO. Vis-NIRS technique can also solve the weaknesses of conventional methods which are known as a tedious procedure and commonly not low-cost.

![Figure 2](image.png)

**Figure 2.** (a) The relationship between soil C measured by laboratory method and predicted by Vis-NIRS technique, and (b) Soil C concentrations with soil depths.

The appearance of soil C concentration with depth, both measured by laboratory and Vis-NIRS technique, is shown at Figure 2b. The pattern of soil C concentration with depth measured by both methods looks similar. This show us that Vis-NIRS technique is able to measure soil C concentrations in various soil depths, which is comparable to the reference method. Vis-NIRS technique is able to show the distribution of soil C concentrations from high at the soil surface and getting smaller at the lower depths, similar to the reference technique. Kusumo et al. [13] also reported the ability of Vis-NIRS technique to predict soil C variations with soil depth, showing reduction trend from high to low, decreasing with depth. In more recent year, the Vis-NIRS-soil coring technique used by Stafford et al. [28] was able to be used to predict variation in total C, total nitrogen (N) and total cadmium (Cd) concentrations with soil depth.

4. Conclusions
Accumulation of soil C was found in a larger amount at the top 20 cm soil depth of the grassland of a Luvisol in the Manawatu region, New Zealand. The soil C accumulation tends to decrease with soil depth, from surface to sub-surface horizons. The Vis-NIRS soil coring technique is able to measure soil C concentrations with soil depth, with the accuracy similar to the reference method. This shows that this technique can be used to rapidly measure and monitor soil C content in soil for accounting the soil C stock in various soil depths.

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