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Predictions of soil surface and topsoil organic carbon content through the use of laboratory and field spectroscopy in the Albany Thicket Biome of Eastern Cape Province of South Africa

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ABSTRACT

In recent years it has been shown that laboratory and field visible near infrared spectroscopy (VNIRS) allows for the accurate prediction of soil organic carbon (SOC) — more rapidly, less expensively, and at larger scales than conventional soil laboratory methods. VNIRS might find application in the restoration assessment of the degraded, semi-arid subtropical thickets of the Albany Thicket Biome (ATB) of the Eastern Cape Province of South Africa. During the twentieth century, the semi-arid forms of the ATB suffered heavy browsing by goats, transforming the dense closed-canopy shrubland into an open savannah-like system. This paper presents a study dealing with SOC estimation of soil surface (0–5 mm) and topsoil (0–200 mm) in the degraded ATB, through the combination of soil spectroscopy and partial least square regression (PLSR). Spectroscopic measurements and soil samples were collected along a transect in the ATB. The PLSR models developed with laboratory and field spectra gave good predictions of SOC, with root mean square error of validation (RMSEV) <5.0 and 5.5 g C kg^{-1}, respectively. The use of the full visible near-infrared spectral range gave better SOC predictions than using either visible or near-infrared separately. The resampling simulation of the field surface spectra to the 232 channels of the satellite-born EnMAP sensor gave good SOC predictions for laboratory conditions (RPD>2), but low accuracy (RMSE: 9.88 g C kg^{-1}) for field model. The results of this research study indicated that, for the ATB, (i) combining soil spectroscopy and PLSR does favor accurate prediction of SOC, (ii) the predictions of surface SOC can be used as a proxy of topsoil SOC, and (iii) there is potential for future application of satellite-born hyperspectral data for SOC content predictions.

1. Introduction

The rising carbon dioxide (CO_2) concentration in the atmosphere, and the climate change have precipitated the possibility of sequestering CO_2 into soils by increasing soil organic carbon (SOC) stocks (Lal, 2004). It has been widely demonstrated that SOC stocks are linked with management practices and land use changes (Guo and Gifford, 2002; Johnson and Curtis, 2001; West and Post, 2002). For example, during the 20th century, 800,000 ha of semi-arid subtropical thickets (Lloyd et al., 2002) of the Albany Thicket Biome (ATB) (Hoare et al., 2006) of Eastern and Western Cape Provinces of South Africa were affected by goats' heavy browsing which transformed the dense closed-canopy shrubland into an open savannah-like system (Lechmere-Oertel et al., 2005). The carbon lost, as a result of vegetation removal in succulent thicket, was approximately 4.0 kg m^{-2} yr^{-1} in soils to a depth of 500 mm and 4.5 kg m^{-2} yr^{-1} in biomass (above and below-ground) (Mills et al., 2003). The restoration of ATB ancient vegetation matrix might return more than 8.5 kg C m^{-2}, due to the reduction of surface erosion, and the decreases of surface temperature and mineralization rate of soil organic matter (Mills and Cowling, 2006). The estimation of SOC sequestration rate would be very difficult with the time-consuming and expensive conventional sampling methods and chemical analyses because of the large amount of samples to be processed in order to accurately calculate SOC stocks (McCarty and Reeves, 2001). In the ATB, soil spectroscopy might be valuable alternative technique for measuring SOC in a more rapid and less expensive way, and at higher sampling density compared to the conventional soil laboratory methods (Shepherd and Walsh, 2002).

In the past soil spectroscopy has been demonstrated to be a non-destructive and versatile technique to accurately quantify SOC, both in the laboratory under controlled conditions (Ben-Dor and Banin,

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1995; Chang and Laird, 2002; Cozzolino and Moron, 2003; Fidencio et al., 2002; Kooistra et al., 2001; Reeves et al., 1999; Salgo et al., 1998; Sørensen and Dalsgaard, 2005), and in the field (Christy, 2008; Kooistra et al., 2003; Stevens et al., 2008). Moreover, the possibility to test several spectral ranges for both laboratory and field spectroscopy might be an asset for the prediction of SOC. The sensitivity of the near-infrared (NIR, 700–2500 nm) and visible (VIS, 400–700 nm) parts of electromagnetic spectrum to organic and inorganic phases of the soil is due to intense fundamental molecular frequencies related to soil components occurring in the middle infra-red (MIR: 2 500–25,000 nm) wavelengths (Viscarra Rossel et al., 2006). Previous studies used either the full visible near-infrared (VNIR, 400–2500 nm) spectral range or VIS and NIR near-infrared separately to predict SOC. For instance, Stevens et al. (2010) and Morgan et al. (2009) predicted SOC in the field, using the full VNIR spectral range, with a mean error of 2.4 g C kg^{-1} and 4.1 g C kg^{-1}, respectively. Other experiments where VNIR has been used to predict SOC gave coefficients of determination (R^2) ranging between 0.60 and 0.92 (Brown et al., 2005; Dunn et al., 2002; Islam et al., 2003; Shepherd and Walsh, 2002; Udelhoven et al., 2003; Vågen et al., 2006). The adoption of just NIR or VIS spectral bands to predict SOC reduces error probability and computational time, making these regions particularly useful for measuring different forms of carbon (Morra et al., 1991). Dalal and Henry (1986) predicted SOC in the wavelength range 1100–2500 nm with a very low standard error of prediction (SEP) of 0.16%. Islam et al. (2003) investigated VIS and NIR to predict accurately SOC, getting R^2 of 0.68 and 0.76, respectively. Henderson et al. (1992), testing the response of different soil properties to laboratory VNIR, noted that several NIR wavelengths were sensitive only to differences in SOC. Christy et al. (2003) successfully tested NIR spectroscopy (780–2500 nm) in the field to produce SOC maps on a field scale, obtaining R^2 of 0.87.

Although the promising results obtained in previous studies, field spectroscopy, as well as remote sensing, can only provide estimations of surface SOC (0–5 mm). This technical limit is more important in natural rangelands, like the ATB, due to the absence of plough layer. The assessment of topsoil (0–200 mm) SOC content is the most significant indicator of soil restoration, because 33% of the SOC content of the first meter is located in the topsoil, and this amount is strictly linked with plant root density (Jobaggy & Jackson, 2000).

The objectives of this study were (i) to test the accuracies of VIS, NIR, and VNIR spectral ranges in predicting SOC, (ii) to explore the potential of laboratory and field soil spectroscopy to predict surface SOC as a proxy of topsoil SOC, and (iii) to simulate a resampling of field and laboratory spectral data to EnMAP satellite spectral resolution (Müller et al., 2009).

2. Methodology

2.1. Study area

The ATB is a dense formation of evergreen and weakly deciduous succulent shrubs (e.g., *Portulacaria afra*), spinescent shrubs (e.g., *Azima tetracantha, Gymnosporia polycantha, Putterlickia pyracantha, Rhus longispina*), and low-growing trees (2–5 m) (e.g., *Pappea capensis, Euclea undulata, Schotia afra*) (Cowling et al., 2005). The ecosystem carbon storage exceeds 20 kg m^{-2} (Mills, et al., 2003). The study area was a transect of approximately 130 km running in a south east (SE)-north west (NW) direction within the ATB (SE extreme: 25.38 E; NW extreme: −32.59 S). The study area was characterized by geological formation of mudstone, shales and sandstones (Mills et al., 2005). Soil types included Calcaric Cambisols, Calcic Luvisols, Rhodic Luvisols, and Calcaric Regosols (FAO, 1998).

The transect was selected analyzing ATB vegetation types, rainfall and contour data. The three datasets were overlaid, obtaining a stratified map. Based on the highest possible variability of biome classes, transect and sampling points were pre-selected. Fig. 1 shows the 113 points sampled along the transect, crossing 6 vegetation types (Fig. 1a), with altitude ranging from 100 to 1100 m.a.s.l. (Fig. 1b), and rainfall between 300 and 500 mm yr^{-1} (Fig. 1c).

2.2. Field data collection

A total of 113 topsoil samples up to 200 mm depth (C0-200) were collected from a 20×20×20 cm excavation. After being homogenized, the soil was divided into two parts: the first destined to chemical analyses, and the second to laboratory spectral analyses. One month later the same plots were revisited to collect soil spectral reflectance, with an ASD Fieldspec-Pro radiometer (ASD, Boulder, Co), 1 nm step in the 350–2500 nm wavelength range. A contact probe device, with a viewing area of 2-cm-diameter circle and its own light source, was used in order to eliminate the effect of vegetation on the soil spectra, and to avoid weather condition limitations (Waiser et al., 2007). A 50×50 cm plot was defined, and five spectral measurements collected, according to the following scheme: one in the center and one at every corner of the plot. After collection of the spectra, a soil surface sample up to 5 mm depth (C0-5) of the plot was taken, homogenized, and divided into two bags, one for chemical analyses and one for laboratory spectral analyses.

2.3. Soil sample analyses

SOC was chemically determined using the Walkley–Black method (Walkley and Black, 1934). Soil spectral reflectance was acquired under laboratory controlled conditions, with the same spectrometer used in the field, for sub-sampling portions of the ground (<2 mm soil, ~20 g) (Viscarra Rossel et al., 2006). All samples were illuminated with two-quartz halogen lamps (1000 W each), mounted on a tripod with zenith angle of 30^0 and a distance of about 30 cm between the fiber optic of the radiometer and the soil sample. The instantaneous field of view (IFOV) was 8°, corresponding to about 12 cm^2. The reflected light was assessed from nadir position. Four measuments were taken for every sample, rotating in the same direction: clockwise and 90°.

2.4. Pre-processing and models construction

Spectralon was used as white reference for all spectra collected in the field and in the laboratory. Spectra were corrected for the ASD "jump" at 1000 nm (additive correction method), and averaged for subsequent processing. The dataset was sorted according to SOC content (from the lowest to the highest content), and then divided into training (2/3) and test (1/3) sets. Prior to performing the statistical analyses, spectral band ranges (350–399, 796–814, and 2401–2500 nm) that were insensitive or influenced by artifacts produced by the spectrometer were removed (Viscarra Rossel et al., 2006). The following pre-processing techniques, commonly used in soil spectroscopy, were tested for the enhancement of spectral features: transformation of reflectance (R) spectra in log (1/R), to reduce possible spectra non-linearities; spectral normalization performed using multiplicative spectral correction (MSC), to correct for light scattering variations in reflectance spectroscopy (Geladi and Kowalski, 1986); random noise reduction and signal to noise ratio (SNR) improvement using the Savitzky–Golay filter (Savitzky and Golay, 1964); spectral resolution enhancement and background effect elimination with first derivative and mean-center function applications (Viscarra Rossel et al., 2006).

The models to estimate SOC from the measured spectral reflectance were built using PLSR (Cozzolino and Moron, 2003). The leave one-out cross-validation (CV) of the training set was used to choose the number of factors to include in the PLSR (Reeves et al., 2002). The test set was used for an independent validation of the established PLSR models.

After eliminating the negative predicted values, the coefficient of determination (R^2) between measured and predicted values, and

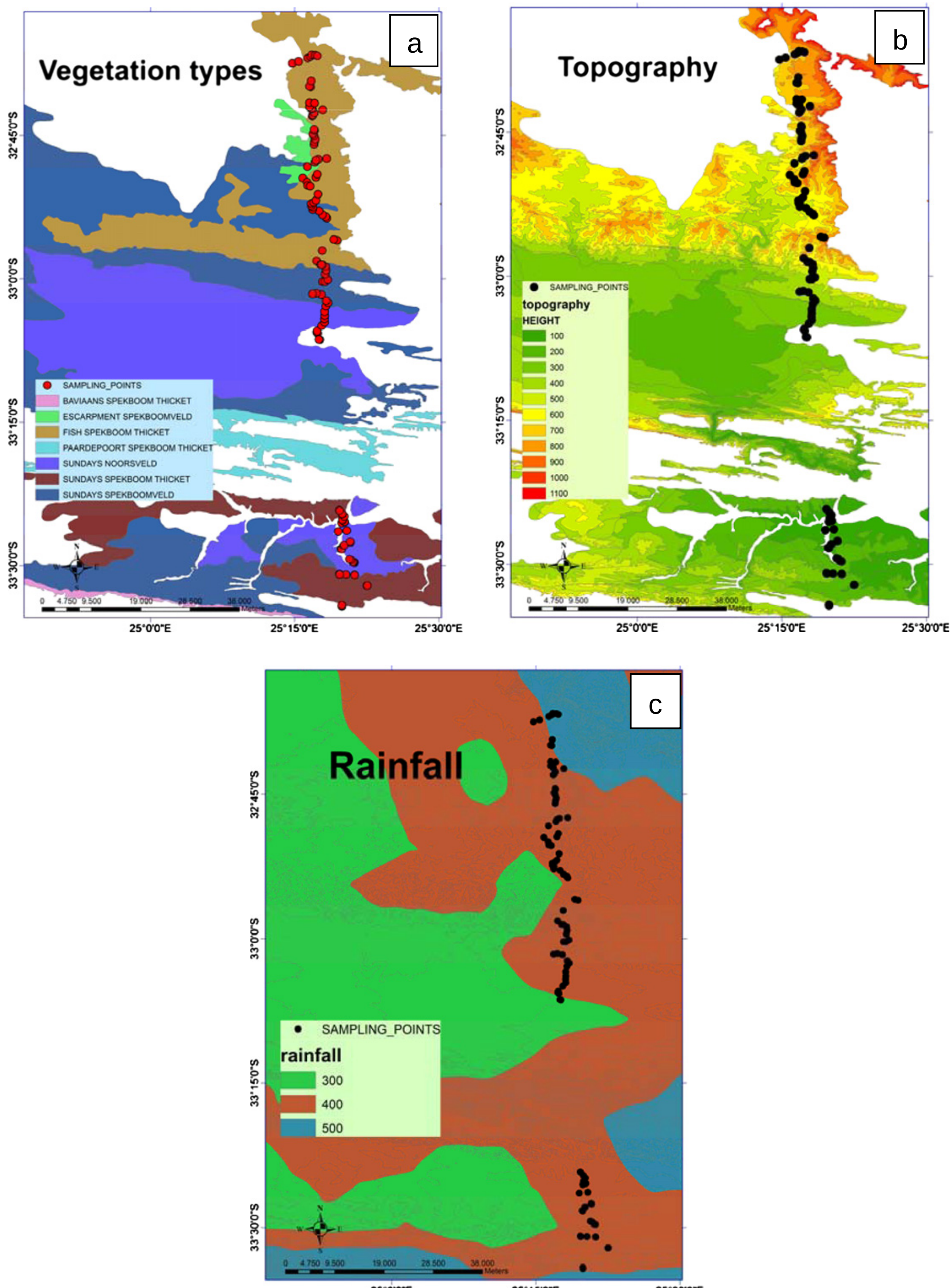

Fig. 1. Spatial distribution of a) sample points and vegetation types, b) sample points and topography, c) sample points and rainfall ranges for the Albany Thicket Biome (ATB) of the Eastern Cape Province of South Africa.

the root mean square error of validation (RMSEV) measured the quality of the model (Kooistra et al., 2003), while the ratio of performance to deviation (RPD) was used to test the SOC prediction ability of the PLSR models. Based on the value of RPD, Chang and Laird (2002) defined three classes: RPD > 2 are models that can accurately predict the soil property in question; RPD between 1.4 and 2 is an intermediate class which regroups models that can be possibly improved; RPD < 1.4 has no prediction ability. The VIS (400–700 nm), NIR (700–2400 nm), and VNIR (400–2400 nm) spectral ranges were tested to determine the most accurate spectral range for SOC prediction (Viscarra Rossel et al., 2006). The software "ParLes 3.1" was used to develop the PLSR models (Viscarra Rossel, 2008).

2.5. Resampling simulation to EnMAP spectral resolution

The resampling simulation to EnMAP spectral resolution was realized using C0-5 spectra collected both in the field and in the laboratory. The resampling process was characterized by the transformation

Table 1
Organic carbon content of topsoil and soil surface.

Statistics	Soil organic carbon (%)	
	C0-200	C0-5
Mean	1.32	1.35
Max	5.05	6.03
Min	0.20	0.18
Median	1.17	1.00
St. dev.	0.91	1.25

C0-200: topsoil; C0-5: soil surface.

of the 2150 bands of the ASD field spectrometer to the 233 simulated bands of EnMAP, from 420 to 2450 nm, with 6–10 nm band ranges (6 nm till 900 nm, 10 nm till 2450 nm). In order to increase the test significance, instrument noise was added, which impacted the signal to noise ratio (SNR). EnMAP characteristics indicate SNR of about 500:1 in the VIS and about 150:1 in the NIR (Guanter et al., 2009). The instrument noise applied in this research was a SNR of 100:1 for all EnMAP simulated channels, to recreate the worst possible scenario of sensor signal quality. All the PLSR models for estimating SOC, based on the EnMAP simulated spectra, were built following the same procedure as described in 2.4.

3. Results and discussion

3.1. Chemical analyses

The chemical analysis showed that C0-5 had a higher SOC content than C0-200, nevertheless the two layers had similar mean SOC contents (Table 1). The Pearson correlation coefficient (r) of 0.77 between SOC of C0-5 and C0-200 (Fig. 2) indicated a strong link between SOC content of surface and topsoil. Meersmans et al. (2009) developed the SOC depth distribution model, stating that SOC stock of surface/topsoil is mainly dependent on land use and management practices. The estimation of C0-200 and C0-5 through VNIRS would not provide the full profile SOC stock, but might be used as a proxy of the estimation of the restoration impact of ATB.

3.2. Interpretation of soil spectral reflectance

The differences of mean spectral reflectance between (i) laboratory and field spectra, and (ii) C0-200 and C0-5 samples are shown in Fig. 3. The highest reflectance value was detected for C0-200, under laboratory controlled conditions. The difference between C0-5 laboratory (C0-5L) and C0-5 field (C0-5F) was smaller than expected, probably due to the contact probe device, which reduces the gap between laboratory and field in terms of light stability (Waiser et al., 2007).

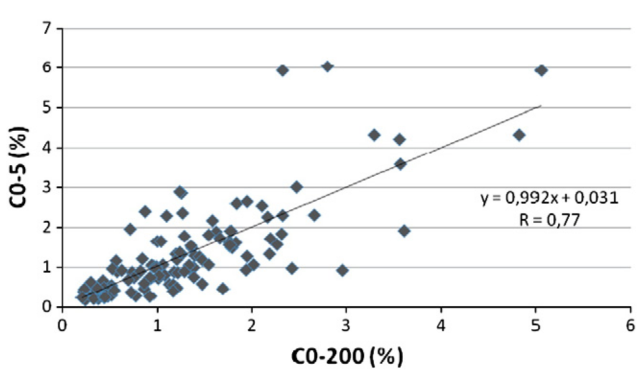

Fig. 2. Correlation between mean soil surface and topsoil organic carbon content.

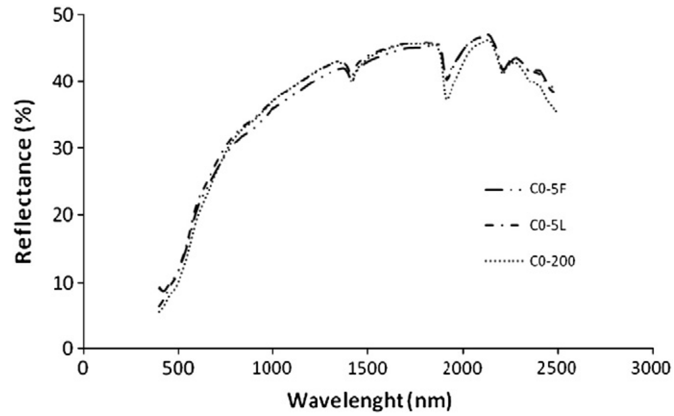

Fig. 3. Mean laboratory and field spectra obtained from soil surface and topsoil samples.

Before and during spectral measurements collection no precipitation was registered and soil surface was considered dry. This was proved by the similar reflectance values of C0-5L and C0-5F (Fig. 2) indicating that field spectra were not influenced by soil moisture.

Examples of mean field spectra clearly illustrated differences of SOC content (Fig. 4). Plots 67, 78 and 106 were characterized by the same land use, but a surface SOC content of 3.01, 6.03, and 0.25%, respectively. Plot 106 reflected much more light than plot 67 and 78, confirming what was observed by Stoner and Baumgardner (1981), who found out that soil reflectance decreases with increasing organic matter content. The difference was particularly appreciable in the 600–750 nm spectral range, where the spectrum slope of plot 106 was more pronounced than plot 67 and 78 (Fig. 4). This trend was also observed by Bartholomeus et al. (2008), who analyzed 40 spectra originating from soil samples of different climatic zones, and discovered the highest correlation between SOC and reflectance value around 600 nm. Plot 67 showed lower reflectance values than plot 78, due to its approximately double SOC content. This was appreciable around 600–700 nm spectral range, and more evidently after 1500 nm (Fig. 4).

3.3. Calibration and validation of SOC prediction models

The comparison between PLSR models based on laboratory and field spectra for SOC prediction indicated better results for C0-200 than C0-5L (Table 2), probably due to the lower standard deviation

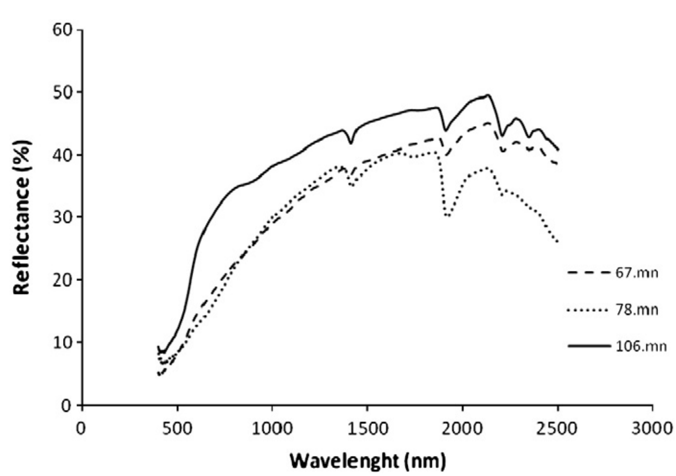

Fig. 4. Soil surface field spectra of plots 67, 78, and 106.

Table 2
Results of calibration and validation of PLSR models for SOC prediction, using VNIR, VIS, and NIR spectral ranges.

Spectral data	Training	Test	Calibration			Validation		
			R^2CV	RMSECV (g C kg^{-1})	Factors	R^2	RMSEV (g C kg^{-1})	RPD
C0-200_VNIR	76	37	0.811	3.70	6	0.930	2.87	3.70
C0-200_VIS	76	37	0.738	4.35	4	0.897	3.30	2.79
C0-200_NIR	76	37	0.731	4.41	4	0.906	3.23	3.20
C0-5L_VNIR	75	36	0.880	4.40	8	0.872	3.30	2.96
C0-5L_VIS	75	36	0.834	5.18	9	0.820	4.67	2.31
C0-5L_NIR	75	36	0.855	4.85	7	0.853	3.65	2.60
C0-5F_VNIR	75	36	0.831	5.26	10	0.837	4.03	2.51
C0-5F_VIS	75	36	0.757	6.27	5	0.770	5.06	2.10
C0-5F_NIR	75	36	0.830	5.25	7	0.860	3.64	2.42

C0-200_VNIR: topsoil visible near infrared laboratory; C0-200_VIS: topsoil visible laboratory; C0-200_NIR: topsoil near-infrared laboratory; C0-5L_VNIR: soil surface visible-near infrared laboratory; C0-5L_VIS: soil surface visible laboratory; C0-5L_NIR: soil surface near-infrared laboratory; C0-5F_VNIR: soil surface visible near infrared field; C0-5F_VIS: soil surface visible field; C0-5F_NIR: soil surface near-infrared field.

of SOC content of C0-5 samples than C0-200 (Table 1). The differences detected between C0-5L and C0-5F models are in line with what was observed by Kooistra et al. (2003), who noticed a decrease of accuracy passing from laboratory to field conditions. The results of C0-5F showed that field spectroscopy can be very accurate, even in soils with a wide topsoil SOC content range, as proven by Stevens et al. (2006), who attained their best SOC prediction model from field data.

The analyses of the different parts of the spectrum indicated (Table 2 and Fig. 5) that the models produced with VNIR, gave better results than the predictions developed using NIR or VIS spectral bands. All C0-5 models gave very accurate predictions. In particular, C0-200 produced with VNIR (C0-200_VNIR) was the best SOC prediction model obtained in this study, with a RPD of 3.70 and a RMSEV of 2.87 g C kg^{-1}. C0-200_NIR was slightly more accurate

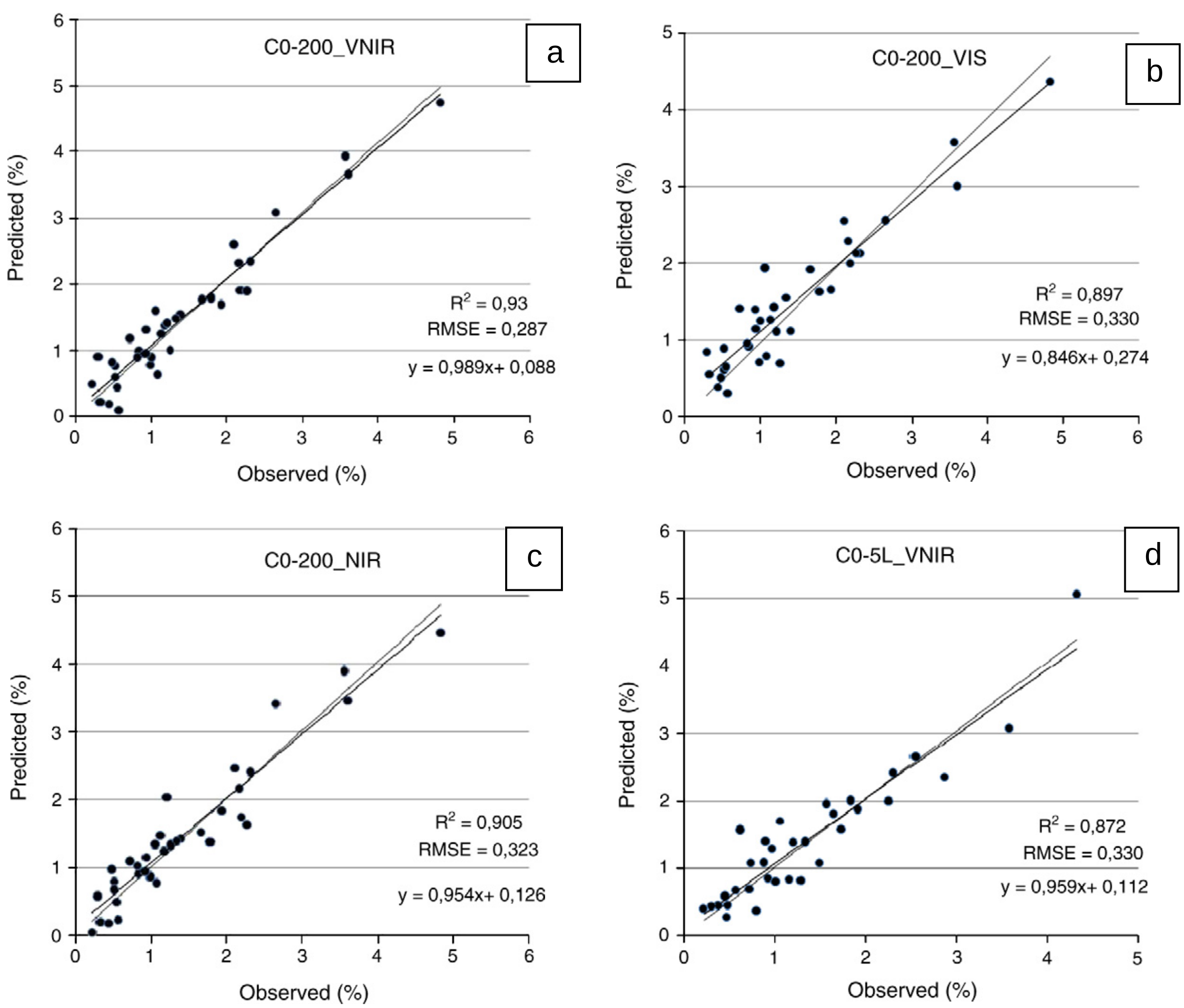

Fig. 5. SOC predicted vs. observed values developed with VNIR, VIS, and NIR laboratory and field spectra.

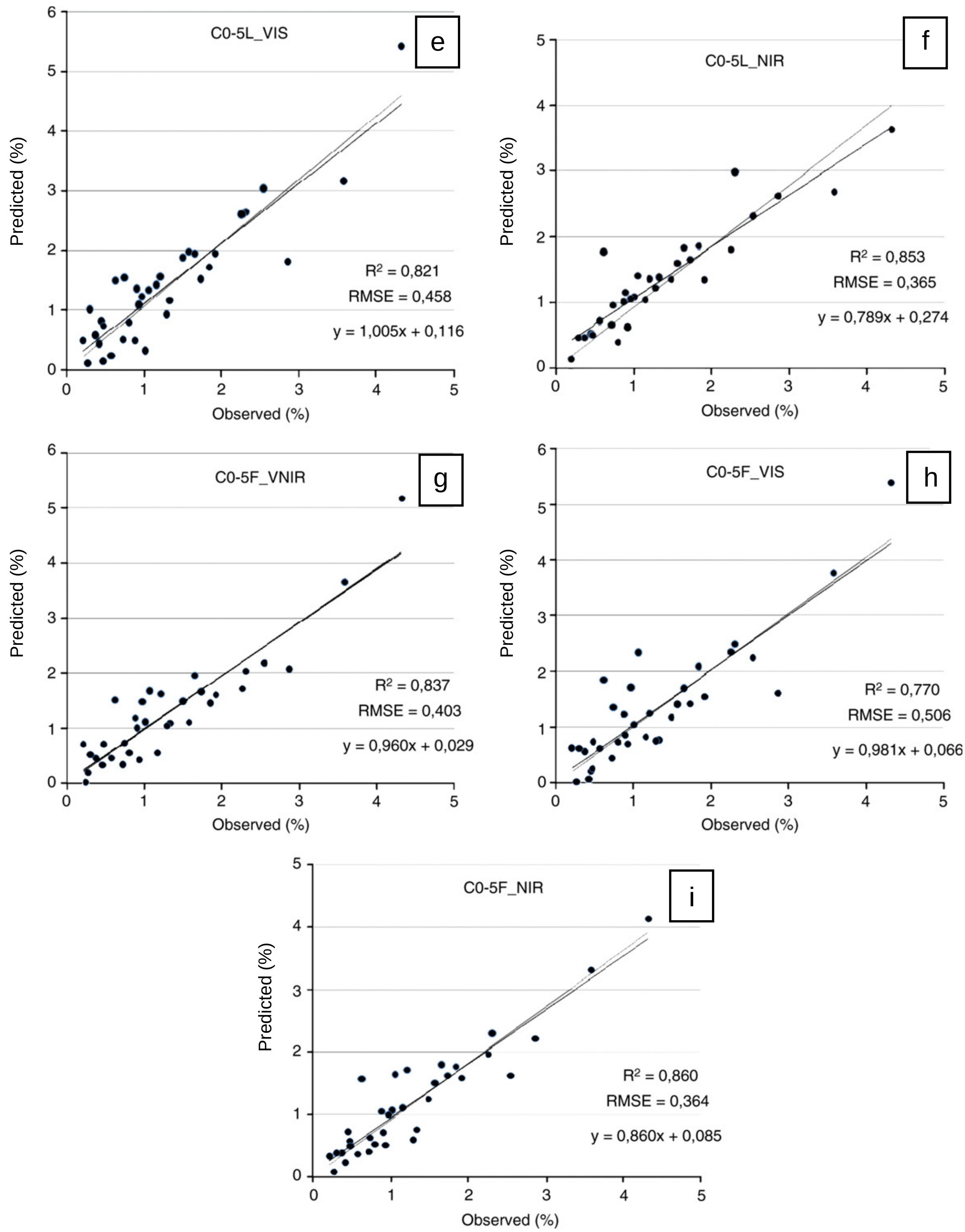

Fig. 5 (*continued*).

than C0-200_VIS, and both presented very high SOC prediction ability (Fig. 5b and c). The C0-5L and C0-5F models presented the same trend as C0-200 predictions, with VNIR giving better accuracies than NIR and VIS spectral ranges (Table 2 and Fig. 5). According to the classification system developed by Chang and Laird (2002) all the models developed in this study pointed out good predictive abilities. In summary, it was demonstrated that, although the use of either VIS or NIR spectral range reduces error probability, calibration–validation procedures, and computational time, in an environment such as the degraded ATB, characterized by low water content and small herbivores overstocking land use, the application of full VNIR spectral range could generate a lower error for the prediction of SOC content.

3.4. EnMAP simulations

The results of the SOC prediction models developed after resampling laboratory and field spectra to EnMAP channels, and simulating spectral noise showed a promising scenario in relation to potential up-scaling procedures (Table 3). As expected, C0-5L_VNIR produced

Table 3
Results of calibration and validation of PLSR models for SOC prediction, using VNIR and EnMAP resampled spectral data.

Spectral data	Training	Test	Calibration			Validation		
			R^2CV	RMSECV (g C kg^{-1})	factors	R^2	RMSEV (g C kg^{-1})	RPD
C0-5L_EnMAP	76	37	0.815	5.47	4	0.824	4.69	2.04
C0-5L_VNIR	75	36	0.880	4.40	8	0.872	3.30	2.96
C0-5F_EnMAP	75	36	0.013	14.01	6	0.252	9.88	0.97
C0-5F_VNIR	75	36	0.831	5.26	10	0.837	4.03	2.51

C0-5L_EnMAP: laboratory resampled to EnMAP; C0-5L_VNIR: soil surface visible near-infrared laboratory; C0-5F_EnMAP: field resampled to EnMAP; C0-5F_VNIR: soil surface visible near-infrared field.

a higher accuracy than the same model resampled to EnMAP spectral resolution (C0-5L_EnMAP).

Soil surface field model resampled to EnMAP spectral resolution (C0-5F_EnMAP) gave insufficient accuracy with a RPD of 0.97 and a RMSEV of 9.88 g C kg^{-1}. The difference between C0-5L_EnMAP and C0-5F_EnMAP might be caused by the simulated instrument noise, which generated a higher error (Table 3). The general drop in accuracy passing from field to remote hyperspectral sensors has been observed in earlier studies (Gomez et al., 2008; Stevens et al., 2006). Moreover, EnMAP simulation used in this study attempted to recreate the worst possible reality, with the lowest SNR (100:1) for all the EnMAP spectral channels. However, other important factors influencing SOC prediction, like presence of vegetation (spectral mixing), soil crust, soil surface roughness, and pixel size were not taken in consideration. Despite the severe degradation of ATB, there are several areas characterized by intact vegetation. EnMAP spatial resolution (30 m) would collect images of ATB with mixed pixels of soil and vegetation that might not be used for soil properties prediction. Moreover, ATB soils are covered by small stones, which affect the amount of light reflected and detected by remote sensors. Furthermore, the ATB surface is not always flat, smooth, or homogenous and, therefore, high spectral data quality, as collected in the field and in the laboratory, would not be feasible. This leads to problems such as variations in particle size, adjacency, and bi-directional reflectance distribution function (BRDF) effects (Ben-Dor et al., 2008).

4. Conclusions

This study examined the possibility of predicting SOC of soil surface (C0-5 mm) and topsoil (C0-200 mm) of Albany Thicket Biome of Eastern Cape Province of South Africa by combining laboratory and field spectroscopy with PLSR. The results of the chemical analyses indicated that the SOC of C0-5 and C0-200 were correlated ($r=0.77$) and thus the SOC is evenly distributed within the upper soil profile. Hence, the SOC content predictions obtained from soil surface spectra might be used as a proxy of topsoil SOC content. The small differences observed between mean laboratory and field reflectance values pointed out that (i) the use of the contact probe reduced the light stability gap between controlled and field conditions, and (ii) soil moisture did not influence the spectra collected in the field. The PLSR models developed with laboratory and field spectra offered very good results for the prediction of SOC ($R^2>0.75$, RMSEV<5.5 g C kg^{-1}). The analyses of the separate band ranges proved that VNIR wavelengths produced higher accuracy results than VIS and NIR spectral bands for the prediction of SOC. The simulation of EnMAP spectra up-scaling, realized by resampling C0-5 laboratory and field spectra, and including the highest possible system noise (SNR = 100), gave predictions with good accuracies for laboratory data (RMSEV = 4.69 g C kg^{-1}) but insufficient accuracy for field data (RMSEV = 9.88 g C kg^{-1}). The obtained results indicated that, for the ATB, (i) combining soil spectroscopy and PLSR, does favor accurate prediction of SOC, and (ii) there are margins for the application of airborne and satellite based hyperspectral remote sensing to derive spatial patterns of SOC content for the ATB.

Although the good results achieved, it is recommendable to proceed with further investigations in order to understand the factors which decrease the quality of VNIRS applied to SOC prediction.

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