POTENTIALITY OF LABORATORY VISIBLE AND NEAR INFRARED SPECTROSCOPY FOR DETERMINING CLAY CONTENT IN FOREST SOILS: A CASE STUDY FROM HIGH FOREST BEECH (*FAGUS SYLVATICA*) IN CALABRIA (SOUTHERN ITALY)

POTENTIEL DE LA SPECTROSCOPIE VISIBLE ET PROCHE INFRAROUGE POUR PRÉDIRE DE LA TENEUR DE L'ARGILE DANS LES SOLS FORESTIERS: UNE ÉTUDE DE CAS DANS UN FUTAIE D'HETRE (FAGUS SYLVATICA) DANS LA CALABRE (ITALIE DU SUD)

POTENZIALITÀ DELLA SPETTROMETRIA VIS-NIR PER LA DETERMINAZIONE DEL CONTENUTO DI ARGILLA IN SUOLI FORESTALI: UN CASO STUDIO IN UNA FUSTAIA DI FAGGIO (*FAGUS SYLVATICA*) DELLA CALABRIA MERIDIONALE (SUD ITALIA)

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Abstract

Clay content is the most important textural fraction because affects soil fertility and productivity. Reflectance spectroscopy in the visible and near infrared (Vis-NIR, 350-2500 nm) spectral region could be an alternative to laboratory standard methods. This paper was aimed to develop a calibration model with laboratory-based soil Vis-NIR spectra for clay content determination and mapping clay content using a geostatistical approach. Soil samples were collected at 235 locations in a forest area of southern Italy and analyzed in laboratory for clay content and Vis-NIR spectroscopic measurements. Partial least squared regression (PLSR) was applied to establish a relationships between reflectance and clay content. Calibration model was developed using only 175 samples, while the remaining 60 samples were used for testing the model. The results of PLSR were satisfactory and ordinary kriging was used for spatial interpolation of clay content determined both using conventional method and the PLSR model.
Key words: *Soil clay content, Vis-NIR spectroscopy, PLSR, Ordinary kriging, Southern Italy.*

Résumé

La teneur en argile est la partie la plus importante de la texture parce qu'elle influence la fertilité et la productivité du sol. La spectroscopie visible et proche infrarouge (350-2500 nm, Vis- NIR) pourrait être une alternative aux méthodes traditionnelles de laboratoire. L'objectif de l'étude a été le développement d'un modèle prédictif de la teneur en argile dans le laboratoire en utilisant la

spectroscopie Vis- NIR et la cartographie avec une approche géostatistique. Dans une zone de forêt (sud de l'Italie) 235 échantillons de sol ont été collectés et analysé en laboratoire pour la détermination de la teneur en argile et l'acquisition des spectres de réflectance. Les spectres, divisé en un ensemble de calibrage (175) et à une validation (60), ont été analysées par la régression des moindres carrés partiels (PLSR). Les résultats ont été satisfaisants et les données d'argile avec les deux méthodologies ont été interpolées par krigeage ordinaire.

Mot-clés: *Teneur de l'argile, spectroscopie Vis-NIR, PLSR, krigeage ordinaire, Sud de l'Italie.*

Riassunto

Il contenuto in argilla è la più importante frazione tessiturale perché influenza la fertilità e la produttività del suolo. La spettroscopia nell'intervallo compreso tra il visibile e l'infrarosso vicino (350-2500 nm, Vis-NIR) potrebbe essere una alternativa ai metodi di laboratorio tradizionali.

L'obiettivo dello studio è stato lo sviluppo di un modello predittivo del contenuto di argilla mediante l'utilizzo in laboratorio della spettroscopia Vis-NIR e la successiva mappatura con un approccio geostatistico.

All'interno di un'area forestale (sud Italia) sono stati prelevati 235 campioni di suolo e analizzati in laboratorio per la determinazione del contenuto in argilla e l'acquisizione degli spettri di riflettanza.

Gli spettri, suddivisi in un set di calibrazione (175) ed in uno di validazione (60), sono stati analizzati attraverso la regressione parziale ai minimi quadrati (PLSR). I risultati sono stati soddisfacenti e i dati di argilla determinati con entrambe le metodologie sono stati interpolati mediante il kriging ordinario.

Parole chiave: *Contenuto in argilla, spettroscopia Vis-NIR, PLSR, kriging ordinario, Sud Italia.*

Introduction

Soil mineral particles are classified according to their size into sand, silt, and clay (Osman, 2013). Since soil particles vary widely in their shapes, they are classified on their *effective diameter*: the diameter of a sphere that has a velocity of fall in a liquid medium equal to the particle in question. Sand and silt particles consist of primary minerals such as quartz, feldspars, and mica, while clay particles are mainly secondary minerals such as kaolinite, smectite, vermiculite, illite, chlorite, and hydrated oxides of iron and aluminium (Osman, 2013). Clay particles have large surface area and electrical charges, both negative and positive, on their surfaces. Because of these properties, clays they have high water- and nutrient-holding capacity and they participate in chemical reactions in the soil. Therefore, to determine soil clay content and to capture its variability is essential for utilizing and managing forest soils, particularly, when a large number of samples have to be analysed.

In the last two decade laboratory visible, near infrared (Vis-NIR, 350 - 2500 nm) spectroscopy has been widely used and accepted as alternative to traditional laboratory methods because Vis-NIR spectroscopy is rapid, relatively inexpensive, require minimal sample preparation and no hazardous chemicals, is non-destructive and several soil properties can be measured from a single scan (e.g. Reeves et al., 2001, 2002; Shepherd & Walsh, 2002; Demattê et al., 2006; McBratney et al., 2006; Viscarra Rossel et al., 2006; Stenberg et al., 2010; Conforti et al., 2012).

The determination of clay content by Vis-NIR measurements depend on the distinctive spectral signatures of common clay minerals (Waiser et al., 2007). The spectral signatures include overtones and combination of bands due to chemical bonds within soil minerals (Clark, 1999; Stenberg *et al*., 2010).

Vis-NIR reflectance spectroscopy requires only a few seconds to analyze a soil sample, but the relevant information needs to be mathematically extracted from the spectra so that it can be correlated with soil clay content. Therefore, the successful application of Vis-NIR spectroscopy to quantification and evaluate the relationships between soil reflectance and soil clay content depends largely on the development of accurate and robust calibration models. To investigate the relationships between reflectance spectra and soil clay content, chemometrics techniques and multivariate statistical methods (Martens and Næs, 1989; Viscarra Rossel and Behrens, 2010; Stenberg *et al*., 2010) have to be used.

In addition, clay content predictions are made only at the sampled locations, so for producing accurate continuous maps, clay content needs to be estimated spatially. Geostatistical methods (Matheron, 1971) are commonly used to generate maps of soil properties and they provide a valuable tool to study the spatial pattern of soil properties, taking into account spatial autocorrelation of data to create mathematical models of spatial correlation structures, commonly expressed by semivariograms. The interpolation technique of the variable at unsampled locations, known as kriging, provides the 'best', unbiased, linear estimate of a regionalized variable in an unsampled location, where 'best' is defined in a least-square sense (Chilès and Delfiner, 2012).

The paper was aimed at: 1) developing a calibration model with laboratory-based soil Vis-NIR spectra for soil clay content determination; and 2) mapping soil clay content using a geostatistical approach.

Material and methods

Study area
The study area was a high forest beech (Fagus sylvatica) located in the Serre Massif (Calabria, southern Italy) between 4,262,231N to 4,261,333N latitude and 607,788E to 608,583E longitude (Figure 1). It covers an area of about 332,000 m^2, with elevation ranging from 1,155 to 1,205 m above sea level.

The climate is typical upland Mediterranean (Csb, sensu Koppen 1936) with a long-term (1928-2012) average annual precipitation equal to 1,810 mm distributed on 110 rainy days and an average mean annual temperature of 11.3 °C.

The precipitation pattern shows a rainy period from November to February in which occurs more than 60% of total annual precipitation.The pedoclimate shows a mesic soil temperature regime associated with a udic soil moisture regime (ARSSA, 2003).
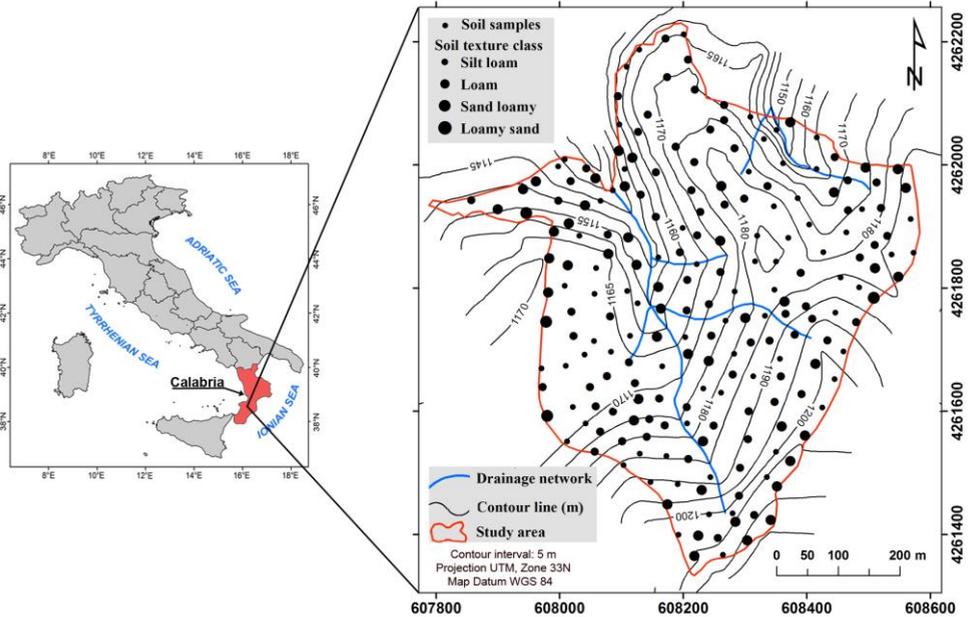

Figure 1 - *Location of the study area and soil samples distribution in the soil texture classes.*

Geologically the study area is characterized by Palaeozoic granitoid rocks deeply fractured, weathered and frequently covered by a thick regolith and/or colluvial deposits (Borsi *et al*., 1976; Calcaterra *et al*., 1996). Morphology is dominated by a mountains landscape with deep, V-shaped valleys and summit Paleosurfaces that represent the remnants flat or gently-sloping highlands, often sharply separated by steep slopes (Sorriso-Valvo, 1993; Calcaterra and Parise, 2010).

According to USDA (2010) soil classification, the most frequent soils are Inceptisols and Entisols (ARSSA, 2003). Generally, soil depth ranges from shallow to moderately deep (0.20 to 1m) and soil profiles have A-Bw-Cr and/or A-Cr horizons (ARSSA, 2003). The soils have acidic pH (3.7–5.8), are coarse-textured, because are mainly classified as sandy loam, loam and silt loam and the bulk density ranges from 0.5 to 1.6 g cm^{-3}.

Accumulation of organic matter in upper A horizons (umbric epipedon, USDA, 2010) is among the dominant pedogenetic processes.

Soil sampling and analysis

Soil samples were collected at 235 locations within the study area (Figure 1). At each site, surface litter was removed and soil was sampled to a depth of 20 cm

using a metallic core cylinder having a diameter of 7.5 cm and a height of 20 cm (883.1 cm^3). Soil sampling locations were georeferenced using a differential global positioning system (DGPS), with a precision of about 1m.

The soil samples were brought to the laboratory, oven dried at 45°C for 48 hours, gently crushed in an agate mortar to break up larger aggregates and visible roots were removed; afterwards each sample was sieved at 2 mm, homogenized and quartered. Soil clay content was determined using the hydrometer method after a pre-treatment with sodium hexametaphosphate as a dispersing agent (Sequi and De Nobili, 2000).

Spectral measurements

Vis-NIR spectral measurements were acquired in the laboratory using an ASD FieldSpec IV 350–2500 nm spectroradiometer (Analytical Spectral Devices Inc., Boulder, Colorado, USA). Prior to the determination of the spectral data, soil samples, sieved at 2 mm, were placed in Petri dishes, 9.5 cm in diameter and 1.2 cm in height, and levelled with the edge of a spatula to obtain a smooth surface. The spectral measurements were collected in a black room to better control irradiance conditions. The spectroradiometer combines three spectrometers to cover the solar reflected portion of the spectrum between 350 and 2500 nm, with a sampling interval of 1.4 nm for the 350-1000 nm region and 2 nm for the 1000-2500 nm region. FieldSpec IV provided spectra collected with a sampling resolution of 1 nm, thus producing 2151 spectral bands. A 50-Watts halogen lamp with a zenith angle of 30°, located at a distance of approximately 25 cm from the soil sample was used as artificial illumination. The instrument was located in a nadir position with a distance of 10 cm from the sample, allowing the radiance measurements within a circular area of approximately 4.5-cm diameter to be done. The noise level in the spectral signal was reduced averaging 50 spectra for each soil sample. In addition, to eliminate any possible spectral anomalies due to geometry of measurement, four replicate scans were acquired for every soil sample by rotating the soil sample by 90° and were averaged in post-processing. A Spectralon panel (20 x 20 cm^2, Labsphere Inc., North Sutton, USA) was used as white reference to compute reflectance values. A reference spectrum under the same conditions of measurement was acquired immediately before the first scan and after every set of five samples.

The average reflectance curves were translated from binary to ASCII using ViewspecPro software (Analytical Spectral Devices, Inc., Boulder, CO, 80301) and re-sampled each 10 nm, reducing the number of wavelengths from 2151 to 216, which smooths the spectra and reduces the risk of over-fitting (Kemper and Sommer, 2002; Shepherd and Walsh, 2002).

Prediction model

In this study, as multivariate statistical procedure to develop a calibration model based on spectra and laboratory soil clay content data, partial least squares regression (PLSR) methodology (Geladi and Kowalski, 1986) was used. PLSR is a

technique widely used in chemometrics (e.g. Aïchi *et al*., 2009; Cozzolino and Moron 2003; Viscarra Rossel *et al*., 2006; Conforti *et al*., 2013) when there are many predictor variables, highly collinear. PLSR is based on latent variable decomposition of two sets of variables: the predictors **X**, which, in our case, are the spectral reflectance bands and the responses **Y**, that are the soil clay content data. PLSR selects orthogonal factors that maximize the covariance between the independent (**X**) and the dependent variables (**Y**), where the limited number of PLSR factors selected explains most of the variation in both predictors and responses. More details can find in Martens and Naes (1989) and Næs *et al*. (2004). PLSR analysis was carried out using the PArLeSvs3.1 software developed by Viscarra Rossel (2008).

Before performing quantitative statistical analysis, to reduce noise and enhance the absorption frequencies, some spectral data pre-processing techniques were performed (Martens and Næs, 1989; Næs *et al*., 2004). The measured reflectance (R) spectra were transformed in absorbance through log(1/R) to reduce noise, offset effects, and to enhance the linearity between measured absorbance and soil clay content. The absorbance spectra were mean-centred to ensure that all results will be interpretable in terms of variation around the mean and then they were smoothed using a Savitzky–Golay filter algorithm with a first derivative to remove an additive baseline (Viscarra Rossel, 2008).

To test the accuracy of the PLSR regression models the dataset were randomly split into two subset: a training set (175 samples = 75% of the total database) for developing the prediction model, and a validation set (60 samples = 25% of the total database) to test the accuracy of model.

Leave-one-out cross-validation was performed (Efron and Tibshirani, 1993) to test the predictive significance of each PLSR component and to determine the number of factors (latent variables) to be retained in the calibration model. In the leave-one-out cross-validation, one sample was left out of the global data set and the model was calculated on the remaining data points. Then the value of left-out sample was predicted and the prediction residual computed. The process was repeated with another sample of the data set, and so on, until every sample had been left out once. In this study, 20 bilinear factors were tested. To check the goodness of prediction of the leave-one-out cross-validation models were using the coefficient of determination (R^2) and root mean square error (RMSE).

The validation set was used to test the calibration model through the coefficient of determination of validation (R^2_{val}) and root mean square error of validation ($RMSE_{val}$).

Geostatistical approach

To produce accurate continuous maps, both measured and spectrally predicted values of soil clay content were modelled as an intrinsic stationary process using a geostatistical approach where each datum $z(\mathbf{x}_\square)$ (measured or spectrally predicted) at different location $\mathbf{x}_\square$ ($\mathbf{x}$ is the location coordinates vector and $\square$ the sampling points = 1, ..., *N*) is interpreted as a particular realization of a random variable

Z($\mathbf{x}_\square$). Interested readers are referred to Chilès and Delfiner (2012), Goovaerts (1997), Wackernagel (2003), Webster and Oliver (2007), among many others.

The quantitative measure of spatial correlation of the regionalized variable $z(\mathbf{x}_\square)$ is the experimental variogram $\square\square\mathbf{h}$) which is a function of the distance vector (**h**) of data pairs values $[z(\mathbf{x}_\alpha), z(\mathbf{x}_\alpha + \mathbf{h})]$. A theoretical function, called variogram model, is fitted to the experimental variogram to allow one to estimate the variogram analytically for any distance **h**. Experimental variograms can be modelled using only functions that are conditionally negative definite, in order to ensure the non-negativity of the variances. The objective is to build a permissible model that captures the major spatial features of the attribute under study. The variogram model generally requires two parameters: range and sill. The range is the distance over which pairs of the three soil textural fractions are spatially correlated, while the sill is the variogram value corresponding to the range. The optimal fitting will be chosen on the basis of cross-validation, which checks the compatibility between the data and the structural model considering each data point in turn, removing it temporarily from the data set and using its neighbouring information to predict the value of the variable at its location. The estimate is compared with the measured value by calculating the experimental error, i.e. the difference between estimate and measurement, which can be standardized by estimating the standard deviation. The goodness of fit was evaluated by the mean error (*ME*) and the mean squared deviation ratio (*MSDR*). The mean error (*ME*) proves the unbiasedness of estimate if its value is close to 0. The mean squared deviation ratio (*MSDR*) is the ratio between the squared errors and the kriging variance (Webster and Oliver, 2007) and if the model for the variogram is accurate, the *MSDR* value should be 1.

The fitted variograms for the measured and predicted data of the soil clay content data were used to estimate their values at unsampled locations using Ordinary kriging (Webster and Oliver, 2007). Finally, the values of soil clay content of laboratory measured data and predicted values from spectroscopic data were estimated at the nodes of a 1 m x 1 m interpolation grid.

All statistical and geostatistical analyses were performed using the software Isatis®, release 2013.3 (http://www.geovariances.com).

Results and Discussion

The basic statistics for exhaustive data set, training and validation sets of soil clay content are reported in Table 1. The percentage of clay content in the samples of the exhaustive data set ranges from 2.8% to 23% with a mean value of 11.5% (Table 1), indicating that most samples have overall low clay content. The data distribution appear almost normal (Figure 2) and is characterized by a positive value skewness (0.23). Descriptive statistics of clay content for training set and validation set are quite similar to those of the exhaustive data set (Table 1, Figure 2).

	Exhaustive set	Training set	Validation set	**Table 1**
Count (-)	235	175	60	*Descriptive statistics*
Minimun (%)	2.80	2.80	3.70	*of the exhaustive,*
Maximum (%)	23.00	23.0	20.20	*training and*
Mean (%)	11.50	11.50	11.70	*validation data sets*
Stand. dev. (%)	3.60	3.60	3.50	*of clay content*
Skewness (-)	0.23	0.20	0.32	
Kurtosis (-)	0.11	0.17	-0.24	

Figure 2

Distribution of clay content for exhaustive, training and validation data sets.
Bars = histogram,
Line = normal fit.
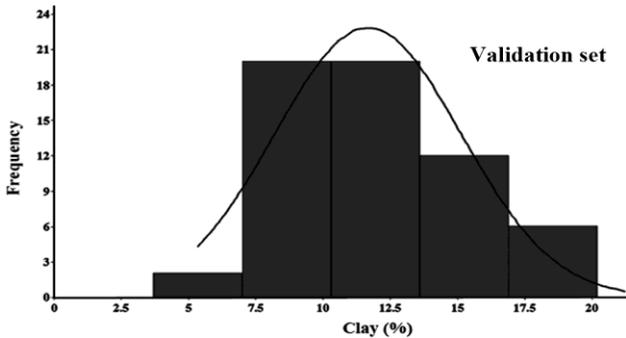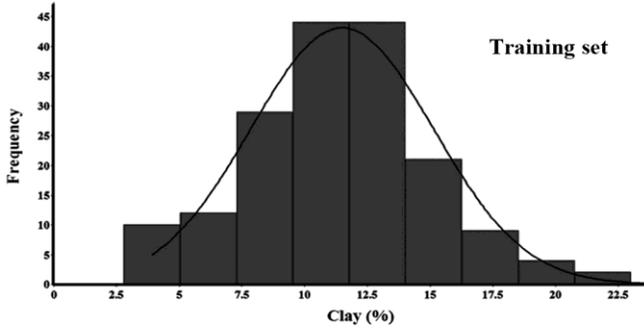
The raw spectra of all soil samples analyzed in laboratory are plotted in Figure 3a. The soil spectra showed the typical pattern in each region of wavelength domain, in

particular, reflectance is generally lower in the visible range (350-700 nm) and higher in the near infrared (700-2500 nm). In accord with Demattè *et al.*, (2014), on the spectral curves can be observed three main features: variation of the overall reflectance intensity (albedo), absorption bands (depth and amplitude), around 1400, 1900 and 2200 nm, and changes in the spectral shape (Figure 3a). The soil reflectance spectral characteristics are closely related to the physical, chemical and mineralogical properties of soil. Variations in reflectance intensity and shape of the spectral curves were mainly due to differences in soil clay content. Soil reflectance was relatively higher for low content of clay content, throughout the 350 nm to 2500 nm wavelength range (Figure 3b).
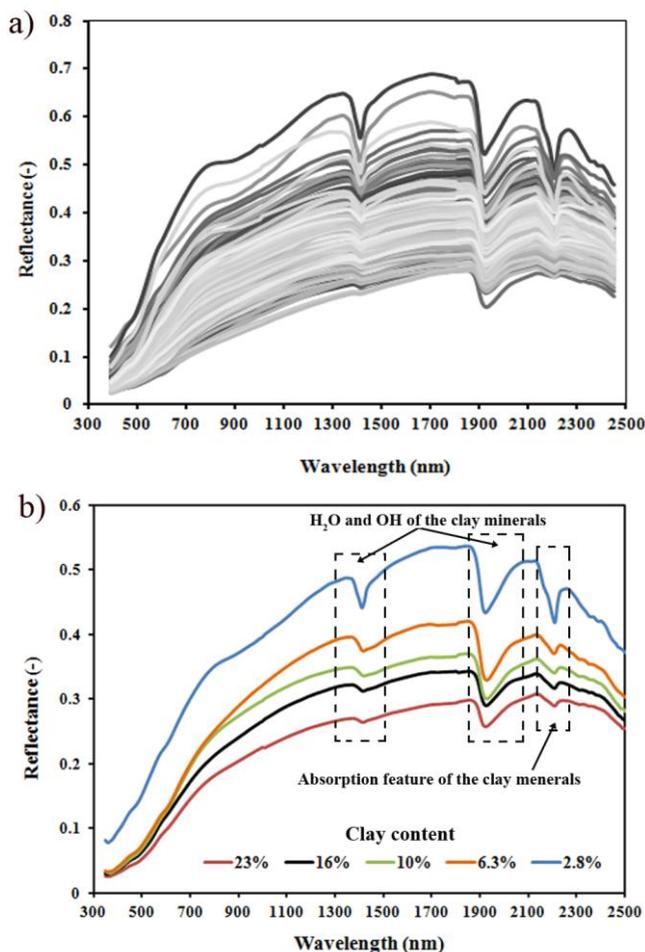
Figure 3

a) Reflectance curves for each soil sample scanned.

b) Reflectance curves of soils with different clay content.

Note the differences in shapes of spectral curves; slopes; overall reflectance intensity; position of absorption bands, diagnostic of the clay minerals.

Relationship between the spectral reflectance of each soil and the soil texture classes (Figure 1) showed that soils with higher clay content, which fall in the loam and silt loam textural classes showed low values of albedo (Figure 4). On the contrary, high values of albedo occurred in the soil samples with loamy sand

texture (Figure 4), which have a content of sand more than 70% and a clay content very low (< 6%). In addition, the reflectance curve of soils with low clay content had a convex shape indicated by a steep reflectance rise between 500 nm and 800 nm of wavelength (Figure 3a).
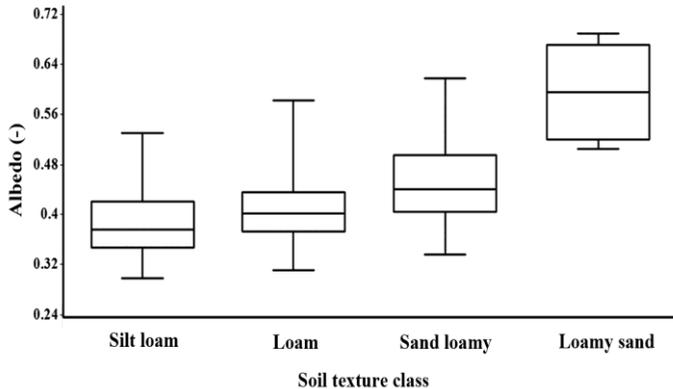
Figure 4
Box-plots of clay content for the different soil textural classes. The lower and upper limits of each box are the 25th and 75th percentiles, the whiskers show the data range and the horizontal line in each box represents the median.

Absorption bands at 1400, 1900 and 2200 nm may be associated with clay minerals (Demattê *et al*., 2004; Sørensen and Dalsgaard, 2005; Demattê *et al*., 2014); in particular, 2:1 (smectite, vermiculite, illite/mica) and 1:1 (kaolinite) clay minerals occurring in the soils could be identified at approximately 1400 and 1900 nm (Figure 3b) due to vibrations caused by the interaction of energy in the OH− and H_2O ([H\O\H] +[O\H]) molecules found between unit layers of mineral structures (Ben-Dor *et al*., 2008). The absorption band at 2200, due to interactions with the aluminol group (Al–OH) of clay minerals, e.g. kaolinite and montmorillonite (Clark *et al*., 1990). (Figure 3b). The results of the PLSR are reported in Figure 5, the best cross-validation model was obtained using 9 factors with a RMSE of about 1.6% and a R^2 of 0.82.
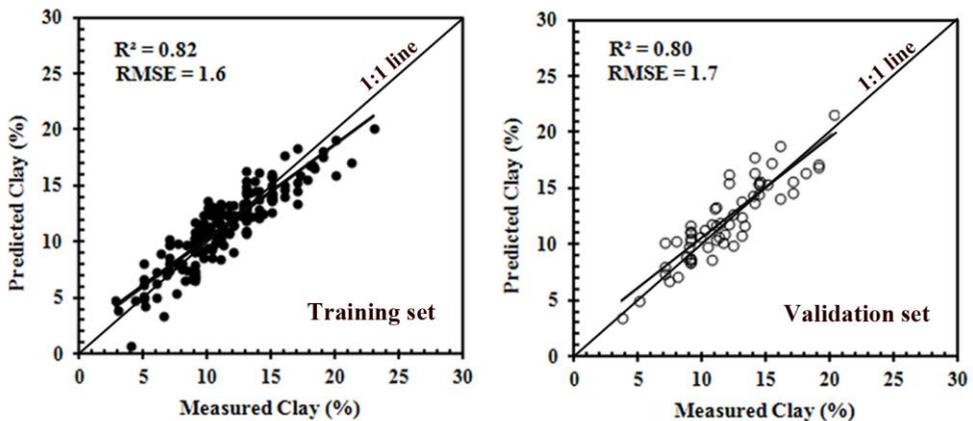

Figure 5 - *Scatter-plots of predicted versus measured clay content for training and validation sets. R^2: coefficient of determination; RMSE: root mean square error.*

Also for the validation set, satisfactory results were obtained with the RMSE equal to 1.7% and the coefficient of determination R^2 equal to 0.80.

No anisotropy was evident in the maps of the 2-D variograms (not shown) to a maximum lag distance of 450 m for both measured and spectrally predicted clay contents.

A bounded isotropic nested variogram model was fitted for each experimental variogram including three basic structures (Table 2): a nugget effect, a spherical model (Webster & Oliver 2007) at short range and a spherical model at longer range. The nugget effect implies a discontinuity in $Z(\mathbf{x})$ and is a positive intercept of the variogram. It arises from errors of measurement and spatial variation within the shortest sampling interval (Webster and Oliver 2007). The spherical model (Webster and Oliver 2007) is given by:

$$\gamma(h) = \begin{cases} c\left[\dfrac{3}{2}\dfrac{h}{a} - \dfrac{1}{2}\left(\dfrac{h}{a}\right)^3\right] & if \quad h \le a \\ c & if \quad h > a \end{cases} \qquad [1]$$

where c is the *sill* and a the range. The presence of two ranges (short and long) in the nested model of variogram means that the physical processes responsible for the variation of soil texture operate and interact at two spatial scales: the short range at about 40-48 m and the longer range at 136-244 m.

Variable	Model	Range (m)	Sill (%^{2})
	Nugget	-	5.4788
Clay$_{meas}$	Spherical	47.89	4.1439
	Spherical	135.54	2.7184
	Nugget	-	6.0568
Clay$_{pred}$	Spherical	38.78	2.3472
	Spherical	243.76	3.2977

Table 2

Variogram model parameters for the values of measured (meas) and spectrally predicted (pred) clay content.

The goodness of fitting for the variogram models was verified by cross-validation and the statistics used, i.e. the mean of the estimation error and variance of the mean squared deviation ratio, showed satisfactory results (quite close to 0 and 1, respectively).

The fitted variogram models were used with ordinary kriging to produce the maps of clay contents for measured and spectrally predicted data (Fig. 6a,b). In addition, comparison of the two maps has revealed that the spectrally predicted data allowed a good reproduction of the spatial pattern of the clay content, as show the map of differences between the measured and predicted interpolated maps (Figure 6c). Therefore, even though 71.8% of the pixels were overestimated and about 28.2%

were underestimated, the mean difference between observed and estimated values is -0.3%, whereas the minimum value is -2.4% and the maximum is 2.6%.
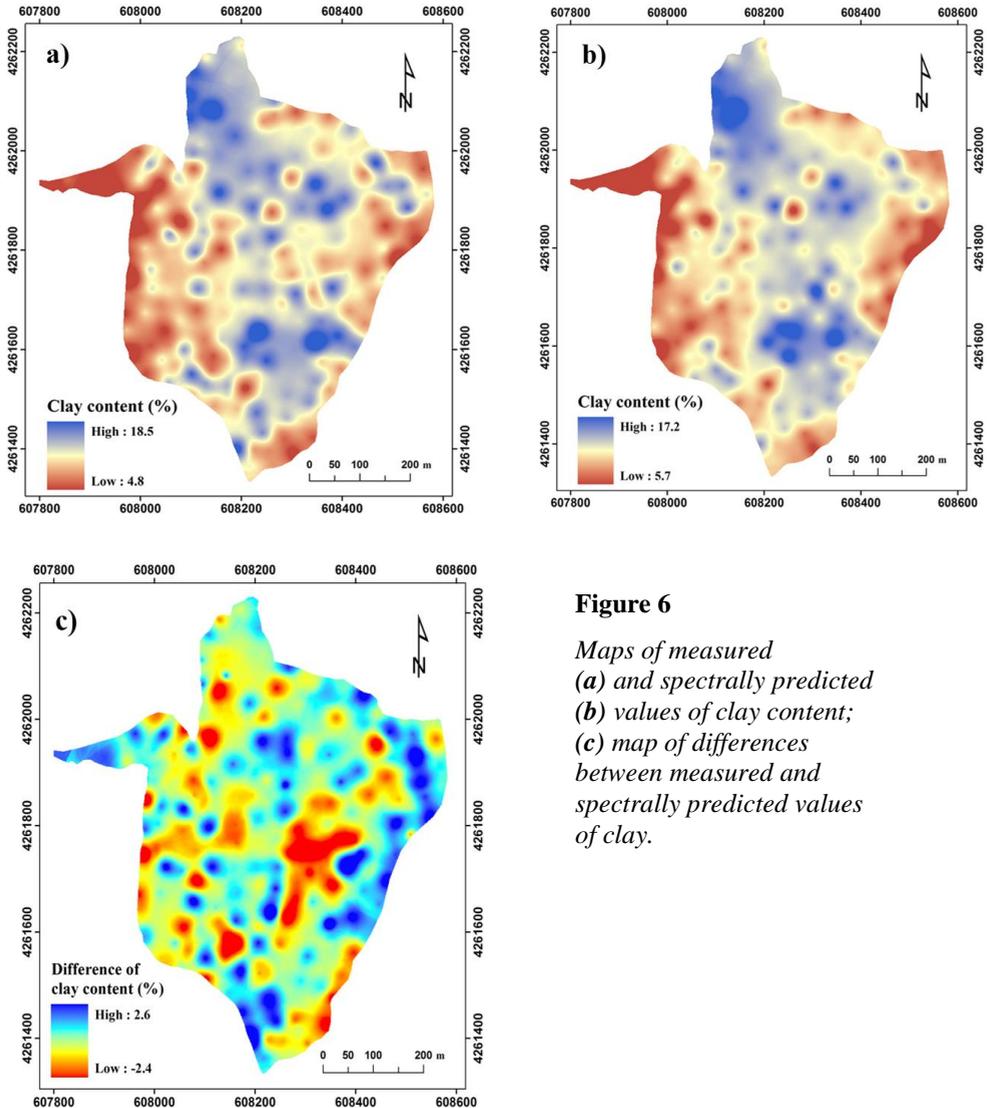
Figure 6

*Maps of measured (**a**) and spectrally predicted (**b**) values of clay content; (**c**) map of differences between measured and spectrally predicted values of clay.*

Conclusions

Several studies have emphasized the ability of Vis-NIR (350-2500 nm) spectroscopy for predicting soil physical, chemical and biological properties. In this study, the potentiality of laboratory reflectance spectroscopy in the Vis-NIR domain for determining soil clay content in forest soils was tested. Reflectance spectroscopy allows detecting soil changes through variations in reflectance

intensity, absorption features and spectral shape. The results showed that soil clay content has an important influence on spectral reflectance in the Vis-NIR range. Therefore, interpretation of spectral curves showed that soil samples could be spectrally separable on the basis of soil textural classes; in particular, it was observed that the reflectance intensity (albedo) was relatively higher, for soils with loamy-sand texture and, relatively, low for silt loam soils, which have an high clay content.

PLSR model allowed an accurate prediction of soil clay content and the same occurred for the validation set.

Accurate continuous maps of soil clay content can be obtained coupling the multivariate calibrations approach with a geostatistical approach. Mapping spatial distribution of soil clay content is critical for understanding and managing forest soils.

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