Vibrational spectroscopy techniques are extremely well suited to be used as portable or handheld. Their simplicity, speed, selectivity, and ability make them ideal to be used outside the lab. In this work the potential of NIR spectroscopy using portable instrumentation to determine chemical compounds was evaluated for studying some Mediterranean soils from Sardinia (Italy). Forty-five soil samples were collected in three different areas (a; b; c) of Sardinia (Italy): a) in the North-Eastern Sardinia (Typic Dystroxerept); b) in the west-coast of Sardinia (Psammentic Palexeralfs); c) in the North-Western Sardinia (calcareous clay-loam).

A microNIR 1700 spectrometer (Diessechem Srl, Italy) was used in reflectance mode (900 to 1600 nm, 50 scans; 125 reading points). PCA applied to the whole set of spectra allowed the discrimination among the three different soils. PLSR in cross validation was used to calculate models for quantitatively determination of the organic C and the total N contents, found to vary according to the kind of soils. The organic C content was well predicted (R²=0.849) using first derivative as pretreatment (7 LV), total N content was calibrated using 2nd derivative as pretreatment and 5 LV (R²=0.743).

The use of portable NIR instrumentation to fast measure N and C contents in different soils is not widely diffused in Italy. The identification of soil type in desertification areas suggest useful tools for the analysis of soil characteristics and classification to better understand “in loco” how to proceed with dedicated actions.

KEYWORDS: NIRS, reflectance, soil, portable instrumentation
opments in positioning, sensing, and control systems have opened a new era in which many traditional agricultural practices are being left behind. Hence, high-throughput and cost-effective methods of SOC analysis should be developed to support the implementation of effective soil inventories and production of digital soil maps at the continental scale from which the state of the SOC can be determined in a consistent manner. Replacing them are ‘precision farming' techniques that manage variability within a field by applying agronomic inputs in the right place, at the right time, and in the right quantity to reduce the environmental impact of crop production. Visible and near-infrared spectroscopy (NIRS) has emerged as one of these techniques, enabling the rapid and non-destructive analytical correlation of diffusely reflected NIR radiation with chemical and physical properties of soil components. A large number of papers have shown the advantage of using NIRS combined with pedometrics or soil science, or the application of mathematical and statistical methods for the study of the distribution and genesis of soils, mainly for the quantification of soil parameters. However the diversity of mineral composition of the soils and the weak content level of organic matter make their detection and quantification by NIRS a real challenge. Reflectance spectroscopy is a promising, nondestructive technique for rapid analysis of soil physical and chemical properties to fulfill these requirements. Numerous laboratory studies have demonstrated the effectiveness of NIRS in performing quantitative analysis of soils, including soil C. Vibrational spectroscopy techniques are extremely well suited to be used as portable or handheld. Their simplicity, speed, selectivity, and ability to operate without sample preparation make them ideal to be used outside the lab in more difficult environments. Recent evidence supports using visible-near infrared reflectance spectroscopy for sensing soil quality; advantages include low-cost, non destructive, rapid analysis that retains high analytical accuracy for numerous soil performance measures. Research has primarily targeted agricultural applications (precision agriculture, performance diagnostics), but implications for assessing ecological systems are equally significant. In this work the potential of reflectance spectroscopy using portable instrumentation to determine chemical compounds was evaluated for studying some Mediterranean soils from Sardinia (Italy).

MATERIALS AND METHODS

Forty-five soil samples were collected in three different land uses (a; b; c) of Sardinia (Italy):

a) a Mediterranean agro-silvo-pastoral system, located in the North-Eastern Sardinia at Berchidda (40° 47’ 0” N 09° 10’ 0” E) at 320 m above sea level. The soil of the area developed from a granite and was classified as Typic Dystrochrept. Soil texture in the Ap horizon is sandy loam with average pH of 5.7.

b) an intensive forage system for dairy cattle, located in a Nitrate Vulnerable Zone in the district of Arborea, (39°47’ N 8°33’ E, 3 m a.s.l.) on the west-coast of Sardinia. The soil was classified as Psammentic Palexeraufs. In the Ap horizon (0-45 cm), the soil of the experimental field had a sandy texture (97% sand) with pH 6.3;

c) an artichoke organic cropping system located in an experimental farm of the Agriculture Faculty of the University of Sassari at Ottoman (Sassari) in the North-Western Sardinia at 225 m above sea level (40° 46’ 31” N 8° 29’ 22” E). The soil was a calcareous clay-loam with pH 7.7.

The soil samples were oven-dried at 40°C and sieved at 2 mm to remove skeletal particles, large roots and organic debris. The C and N contents in the soil samples were determined using an elemental analyser (LECO CHN 628, LECO Italy Srl, 20060 Cassina De’ Pecchi, Milan, Italy). Prior to TOC measurements, carbonates were systematically removed by HCl acid treatment. Spectra of soil samples were collected in duplicates using a microNIR 1700 spectrometer (Diessechem Srl, Milan, Italy) in reflectance mode over the range 900 to 1600 nm, (50 scans; 125 reading points).

Prior to performing the statistical analyses, spectral bands that were insensitive or influenced by artifacts produced by the spectrometer were removed. The following pre-processing techniques, commonly used in soil spectroscopy, were tested for the enhancement of spectral features: i) transformation of reflectance (R) spectra in log (1/R), to improve linearity; ii) spectral normalization using multiplicative spectral correction (MSC), to correct for light scattering variations in reflectance spectroscopy; iii) random noise reduction and signal to noise ratio (SNR) improvement using the Savitzky–Golay filter; iv) spectral resolution enhancement and background effect elimination with first derivative and mean-center function applications. This transformation procedure generally intensifies the absorption characteristics indicative of soils properties, and diminishes variation among spectra. Multivariate data analysis was performed using PLS_Toolbox (Eigenvector research Inc., USA). PCA
was calculated applying a Savitzky Golay 1st derivative, 15-point pretreatment on the spectra and a venetian blind cross-validation (9-data split) was used. Raw spectra were then pretreated applying a Savitzky Golay 2nd derivative, 15 points. Partial Least Squares (PLS) regression with venetian blind cross validation was used to calculate models in order to quantitatively determine the SOC and the SN contents. A test set was used for an independent validation of the established PLSR models.

RESULTS AND DISCUSSION

These samples had a wide range of soil characteristics due to variations in land use, vegetation cover and specific climatic conditions which indicates the presence of significant differences in the soils characteristics (Fig. 1a, b, c). The average of C contents (g kg\(^{-1}\)) in the 0-20 cm soil depth in the different land uses were: 29.19; 13.71; 15.16 respectively for agro-silvo-pastoral area, intensive forage system and artichoke organic cropping system. Instead the average of N contents (g kg\(^{-1}\)) in the soil samples were: 1.98 at Berchidda (a), 1.25 at Arborea (b) and 1.44 at Ottava (c).

![Figure 1. a) Agro-silvo-pastoral system; b) Intensive forage system; c) Artichoke organic cropping system.](image1)

The reflectance spectra collected showed similar profiles. All the spectra have three large absorption peaks in the NIR region around 1400 nm (Fig.2), which corresponded with the highest absorbance peaks obtained testing soil by Chang and Laird\(^{12}\) and Fidencio et al.\(^{13}\), and some few small peaks in the region between 1000~1100 nm.

![Figure 2. NIR spectra of analyzed soil samples](image2)

![Figure 3. SOC content prediction](image3)

![Figure 4. SN content prediction](image4)

The organic C content was better predicted (R\(^2\) 0.849) using first derivative as pretreatment (7 LV), than total N content calibrated using 2nd derivative as pretreatment and 5 LV (R2 0.743), as shown in Figs. 3-4. Data represented in Fig. 5, showed a very good ability to discriminate between groups, and the variability explained by the first two components is over 88%. In this model, two samples were eliminated as outliers. The obtained results were very similar to those reported in literature under laboratory measurement condition\(^{14-17}\).
Differences in soils profiles were well highlighted in the graph of Fig. 6, where the PC2 loadings allowed the identification of 8 bands characterizing the profile of the three different soils. In particular these bands seemed to be associated with the following vibrational groups: 927 (Hydrocarbons -Aliphatic), 989 (Phenolic OH ), 1026 (Aromatic amines), 1051 (Hydrogen Bonding), 1075 (- OH combination band with water), 1348 (Hydrocarbons Aliphatic), 1379 (CH - Methyl), 1447 o CH aromatic o NH aromatic / 1448 NH aromatic , 1459 (NH amide urea o OH intramolecularly band) 1676 (– ketones) according to literature. A greater number of observations, can definitely confirm the NIR potential in this field of applications.

**CONCLUSION**

The use of portable NIR instrumentation to fast measure N and C contents in different soils is not widely diffused in Italy. This new possibility to identify the kind of soil in desertification areas suggest high prediction power useful for rapid and non destructive analysis of soil characteristics and classification to better understand “in loco” how to proceed with dedicated actions. In addition, areas with low SOC were identified and mapped, thus facilitating the development of remediation strategies in terms of application of fertilization environmental protection and method for modeling soil properties with great potential for diagnosing the nutrient deficiency, assessing the risk of soil parameters on the environment.

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