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Visible Near-Infrared Reflectance and Laser-Induced Breakdown Spectroscopy for Estimating Soil Quality in Arid and Semiarid Agroecosystems

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Abstract: Visible near-infrared reflectance spectroscopy (VNIRS) and laser-induced breakdown spectroscopy (LIBS) are potential methods for the rapid and less expensive assessment of soil quality indicators (SQIs). The specific objective of this study was to compare VNIRS and LIBS for assessing SQIs. Data was collected from over 140 soil samples taken from multiple agricultural management systems in New Mexico, belonging to arid and semiarid agroecosystems. Sampled sites included New Mexico State University Agricultural Science Center research fields and several commercial farm fields in New Mexico. Partial least squares regression (PLSR) was used to establish predictive relationships between spectral data and SQIs. Fifteen soil measurements were modeled including the soil organic matter (SOM), permanganate oxidizable carbon (POXC), total microbial biomass (TMB), total bacteria biomass (TBB), total fungi biomass (TFB), mean weight diameter of dry aggregates (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe). Overall, calibrations based on measurements irrespective of locations performed better for LIBS and combined VNIRS-LIBS. Measurements separated according to locations highly improved the quality of prediction for VNIRS as compared to combined locations. For example, the prediction R^2 values for regression of VNIRS were 0.19 for SOM, 0.30 for POXC, 0.24 for MWD, 0.15 for AGG > 2 mm, and 0.13 for EC in combined datasets irrespective of location. When separated according to locations, for one of the locations, the predictive R^2 values for VNIRS were 0.48 for SOM, 0.70 for POXC, 0.67 for MWD, 0.60 for AGG > 2 mm, and 0.51 for EC. The prediction values varied with the sampling time for both LIBS and VNIRS. For example, the prediction values of some SQIs using VNIRS were higher in samples collected in winter for measurements, including SOM (0.90), MWD (0.96), WAS (0.66), and EC (0.94). Using the VNIRS, the corresponding predictive values for the same SQIs were lower for samples collected in the fall (SOM (0.61), MWD (0.45), WAS (0.46), and EC (0.65)). While this study illustrates the prospects of VNIRS and LIBS for estimating SQIs, a more comprehensive evaluation, using a larger regional dataset, is required to understand how the site and soil factors affect VNIRS and LIBS, in order to enhance the utility of these methods for soil quality assessment in arid and semiarid agroecosystems.

Keywords: visible near infra-red spectroscopy; laser-induced breakdown spectroscopy; soil quality indicators; arid; semiarid; agroecosystems; soil measurements

1. Introduction

Soil quality is the capacity of a specific kind of soil to function within its natural or managed ecosystem boundaries to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation [1,2]. Conventional assessments of soil quality rely on laboratory and field measurements known as soil quality indicators (SQIs) [3,4]. However, the necessary laboratory and field soil analyses for determining SQIs are usually expensive, destructive, time-consuming, often complicated, and can require extensive chemical use [5]. Therefore, other methods to estimate SQIs would be useful to reduce costs and improve efficiency.

Visible-near infrared spectroscopy (VNIRS) and laser-induced breakdown spectroscopy (LIBS) have been considered as possible rapid, precise, non-destructive, portable and cost-efficient methods to replace conventional soil analysis and characterization of a wide range of soil materials [6–8]. Visible near-infrared reflectance spectroscopy (VNIRS) includes the visible (400–700 nm) and near-infrared (700–2500 nm) spectral regions [8] while LIBS spectra are measured in the spectral region between 200–1000 nm [9].

The fundamentals of VNIRS as described by Viscarra et al. [8] and Bo Stenberg et al. [10] rely on generating a soil spectrum where radiation containing all relevant frequencies is directed to the soil of interest. Based on the elemental and structural composition of the soil, the radiation will be absorbed or reflected because of the vibration and rotation of molecular bonds in the soil materials caused by the incident radiation. These bonds will absorb the radiation to different degrees, with a specific energy quantum, corresponding to the differences between the two energy levels. The energy quantum is directly related to the frequency and inversely related to the wavelength. The absorbed or reflected radiation will generate characteristic spectra that can be used to infer the physical and chemical composition of the soil.

Fundamentally, LIBS detects emitted light in the range of 200–1000 nm, and thus LIBS spectrum contains information about the concentration of most of the elements in the periodic table [11]. LIBS analyzes the light produced from the interaction of the sample with laser radiation and records the light emitted from the decay of electrons to lower-energy orbitals during the cooling of laser-induced ablation plasmas [6,11] (Figure 1).

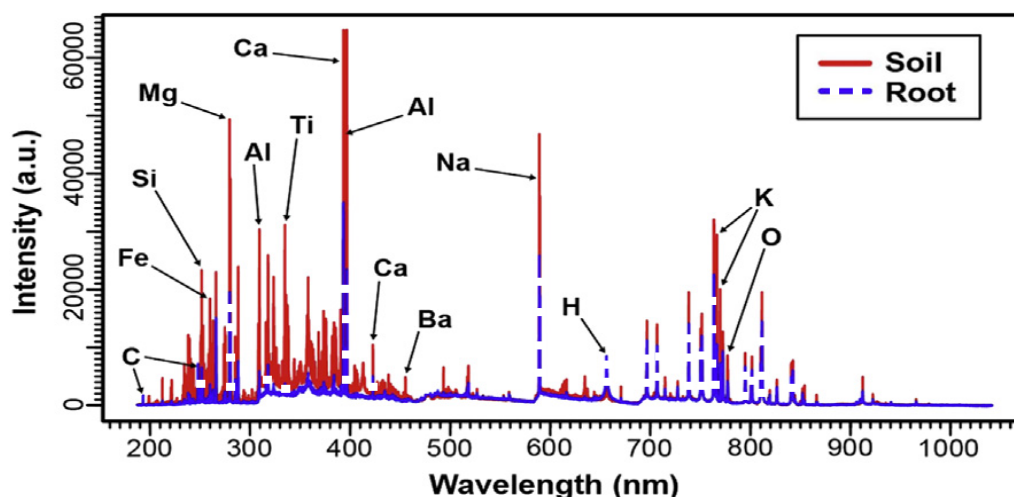


Figure 1. Representative broadband laser-induced breakdown spectroscopy (LIBS) spectra of single soil and root ablations with characteristic elemental peaks identified. Signal intensity values are in arbitrary units (a.u.). Reprinted from Soil Biology and Biochemistry, 131, [12]. High-resolution elemental mapping of the root-rhizosphere-soil continuum using LIBS, 119–132. Copyright 2019, with permission from Elsevier.

Most soil materials have distinct spectral fingerprints, and there are three major soil chromophores (materials that absorb incident radiation) including minerals, organic matter, and water [13,14]. For instance; absorption in the visible (VIS) region (400–700 nm) is associated with minerals containing primarily iron, while multiple absorption features in the near-infrared (NIR) region (700–2500 nm) are due to OH, SO₄, CO₂, and CO₃ groups and band combinations of H₂O and CO₂. Some absorption peaks in the MIR (mid-infrared) region (2500–25,000 nm) can be attributed to aliphatic CH₂ and CH stretching [10]. Thus, identifying a specific spectrum may be a challenge as many organic and inorganic molecules may absorb/reflect light in the VIS and NIR regions [10].

The LIBS technology is a more elemental technique and is suitable for measuring the elemental composition of different solid and liquid materials, and only small amounts of the materials are needed for the analysis [9]. However, LIBS is a costlier and more complex system compared to the VNIRS system. On the other hand, visible near-infrared reflectance spectroscopy (VNIRS) is a more molecular technique that is better suited for detecting essential constituents of the soil such as clay minerals and organic materials. While VNIRS is less costly and complex compared to LIBS, one of the limitations of VNIRS is that the positions of absorption features for various soil materials and minerals are not unique and often overlap [6].

Subsequently, the use of VNIRS and LIBS methods in soil quality assessment requires advanced statistical, spectral, and soil knowledge for calibration of spectra with SQIs. Various calibration methods have been used for relating soil spectra to soil properties including principal component regression (PCR), multiple regression analysis (MRA), partial least squares regression (PLSR), stepwise multiple linear regression (SMLR), multivariate adaptive regression splines (MARS), Fourier regression, locally weighted regression (LWR), and multivariate regression with covariance estimation (MRCE) [6,8,9]. There is no universal agreement on the use of a specific calibration method for VNIRS and LIBS spectra.

Many studies have shown the capability of VNIRS and LIBS in agriculture and natural resource applications and for investigating specific soil materials including the mineral fraction, iron oxides, organic matter, water, carbonates, soluble salts, and particle size distribution [6,9,15,16]. More than fifteen SQI measurements were predicted simultaneously by VNIRS at different levels of success by Idowu et al. [17]. The same study also reported a successful prediction ($R^2 > 0.80$) for soil organic matter, permanganate oxidizable carbon, soil pH, and exchangeable acidity. Other studies have suggested that VNIRS used as a tool for integrating soil measurements may provide accurate estimates for soil organic carbon, soil water, clay content, cation exchange capacity, some plant nutrients, and soil pH, thus reducing the time and costs associated with analyzing the individual soil measurements [7,18]. It is worth noting that complete elimination of standard and/or conventional soil analytical procedures may not be possible as those are still necessary for calibrating VNIRS and LIBS investigations.

Soil quality assessment in the Southwestern United States has unique challenges that are associated with spatial, temporal, and crop management variations which make such an assessment arduous and complicated. Soil quality or soil health assessment relies on identifying key soil measurements known as soil quality indicators. These indicators are a combination of the physical, chemical, and biological soil attributes that interact in a complex way to determine how effectively the soil will function. Some common physical, chemical, and biological interactions that occur in the soil include those between soil biota and soil particles and biochemical interactions between soil biota and soil organic constituents. Some research has shown the potential and acceptable performance of VNIRS, LIBS, and combined VNIRS-LIBS for soil carbon determination [6], one of the most important SQIs. Therefore, there is a need for establishing soil spectral libraries based on data gathered at local and regional scales that offer the potential to compare sensor data with traditional laboratory analysis. Currently, little is known about the performance of the sensors and/or spectroscopies across a wide range of soil and environmental conditions in the study area, for making soil quality assessment more rapid, cost-effective, and environmentally friendly as well as facilitating digital soil mapping. Therefore, the overall goal of this research is to explore the potential for VNIRS and LIBS to reduce or

replace laboratory analysis. The specific objective of this study was to compare VNIR and LIBS for assessing SQIs.

2. Materials and Methods

2.1. Soil Sampling and Laboratory Analyses

Soil samples were collected from different fields from multiple agricultural management systems in 2015 and 2016 as part of a soil quality assessment study in the arid agroecosystems of New Mexico. Two New Mexico State University (NMSU) Agricultural Science Centers (Los Lunas and Leyendecker) were sampled, with 36 samples collected from each location, and 71 samples were collected from another six commercial fields across New Mexico, resulting in a total of 143 soil samples (Table 1, Figure 2).

At the NMSU Los Lunas site, soils were collected from long-term (≥ 5 years) replicated soil and crop management systems which included permanent grass with tall fescue, a peach orchard with clover understory, an alfalfa field, and conventional management with varied annual crops (Table 1). At the Leyendecker Plant Science Research site in Las Cruces, NM, samples were collected under different crop management systems including alfalfa, pecan, and cotton fields (Table 1). Additionally, SQIs at the NMSU Leyendecker site were sampled over four seasons: fall (October 2015), winter (January 2016), spring (April 2016), and summer (July 2016).

Table 1. The number of samples, time of sampling, soil texture, and crop management practices of the sampled agricultural fields.

Sites	Number of Samples	Time of Sampling	Soil Texture	Management Practices
Commercial agricultural farms	71 samples [‡] from 6 sampling areas [†]	Fall of 2016	Sandy loam, clay loam, clay, loam, sandy clay loam, and loamy sand	Flood or sprinkler irrigated annual field crop systems, Flood or sprinkler irrigated vegetable systems and Flood or drip-irrigated orchards
NMSU Agricultural Science Center, Los Lunas	36 samples	Fall of 2016	Sandy loam, sandy clay loam, sandy clay, clay loam, and clay	(a) Grass field with tall fescue (<i>Lolium arundinaceum</i> (Schreb.)); (b) Alfalfa (<i>Medicago sativa</i> L.) field; (c) Conventionally tilled with varied annual crops; (d) Peach (<i>Prunus persica</i> (L.) Batsch) orchard with white clover (<i>Trifolium repens</i> L.) understory; (e) Young cottonwood (<i>Populus deltoides</i> W. Bartram) tree orchard
NMSU Leyendecker Plant Science Center, Las Cruces	36 samples per sampling season	<ul style="list-style-type: none"> Fall 2015 Winter 2015 Spring 2016 Summer 2016 	Sandy loam and clay loam	Alfalfa fields, upland cotton (<i>Gossypium hirsutum</i>) fields and pecan (<i>Carya illinoensis</i>) orchards

[‡] Four replicate fields per crop management system (field crop systems, vegetable systems, and orchards) were sampled in four areas (Area 1, Area 2, Area 4, and Area 5) (total samples = 48); for Area 6, seven replicate samples were collected for field crop systems while four replicate samples were collected for vegetable systems and orchards (total samples = 15); for Area 3, four replicate samples were collected only for field crops and vegetable crops (total samples = 8). Different farm fields selected within each region were regarded as replicates. [†] Sampling areas represent the major land resource areas (MLRA) in New Mexico included Southern Desert Basins, Plains, and Mountains (MLRA 42) (Area 1), Southern High Plains, Southern Part (MLRA 77C) (Area 2), Central New Mexico Highlands (MLRA 70C) (Area 3), Upper Pecos River Valley (MLRA 70B) (Area 4), Colorado Plateau (MLRA 35) (Area 5) and Southwestern Plateaus, Mesas, and Foothill (MLRA 36) (Area 6) [19].

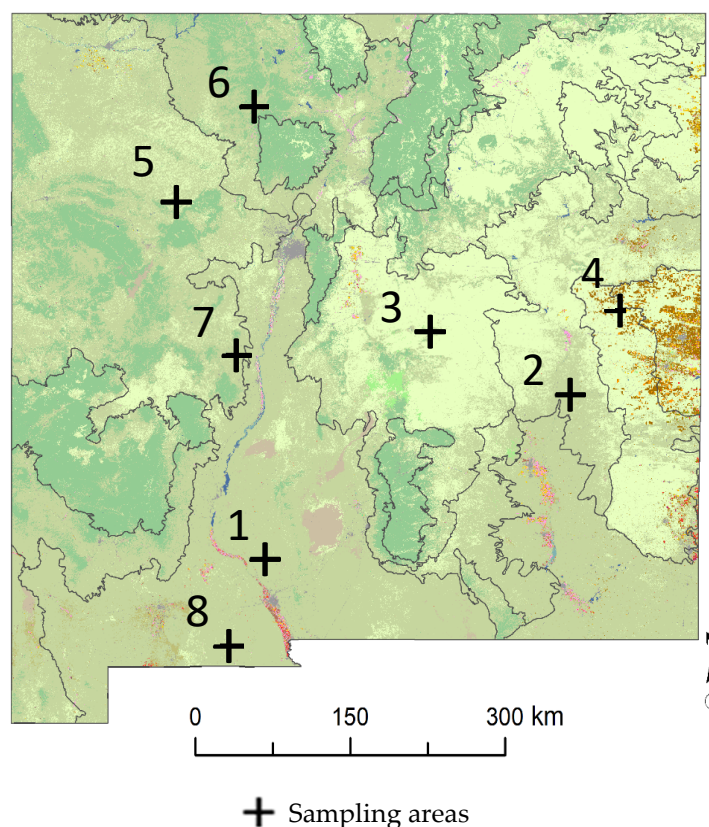


Figure 2. Sampled fields from different Major Land Resources Areas (MLRA) and areas in New Mexico included Southern Desert Basins, Plains, and Mountains (MLRA 42) (Area 1), Southern High Plains, Southern Part (MLRA 77C) (Area 2), Central New Mexico Highlands (MLRA 70C) (Area 3), Upper Pecos River Valley (MLRA 70B) (Area 4), Colorado Plateau (MLRA 35) (Area 5), Southwestern Plateaus, Mesas, and Foothill (MLRA 36) (Area 6) [19], Los Lunas Agriculture Science Centers, Los Lunas (Area 7), and Leyendecker Plant Science Center (Area 8).

Surface soil samples (0–0.15 m) were collected from the field, air-dried, and analyzed for 15 SQI measurements. Soil samples were collected in a zig-zag pattern using a standard soil auger and ten random soil cores were collected per each sampled field to form a composite sample. Soil organic matter (SOM) was measured by Walkley–Black method [20], permanganate oxidizable carbon (POXC) was measured using the technique developed by Weil et al. [21], dry aggregate size distribution analysis resulted in mean weight diameter of dry aggregates (MWD), aggregates between 2–4 mm ($AGG > 2$ mm), and aggregates less than 0.25 mm ($AGG < 0.25$ mm), all of which were measured using a Tyler RX-29 Rotap sieve shaker (W.S. Tyler, Mentor, OH, USA) [22], wet aggregate stability (WAS) was measured using the Cornell sprinkle infiltrometer method [23].

Electrical conductivity (EC), pH, calcium (Ca), magnesium (Mg), and sodium (Na) were measured on the saturated paste extract using the US Salinity Lab method [24]. Soil iron (Fe) was measured using the DTPA extract method [25]. Additionally, during field sampling, separate soil samples (~200 g per sample) were collected in plastic bags, transferred into coolers and stored at -20 °C before they were shipped to Ward Laboratories (WARD Laboratories, Inc., Kearney, NE, USA) for phospholipid fatty acid (PLFA) analysis to estimate the total microbial biomass (TMB), total bacteria biomass (TBB), and total fungi biomass (TFB) [26].

2.2. Reflectance Measurements

VNIRS measurements were made on ≤ 2 mm fractions of air-dried soils with a Fieldspec 2500 spectrometer (Analytical Spectral Devices [ASD], Boulder, CO, USA) with a spectral range

of 350–2500 nm, acquired at 1 nm increments [27]. The optical setup was done as recommended by the instrument's manufacturer and following the methodology developed by the US Natural Resources Conservation Service (NRCS) for Rapid Carbon Assessment [27]. Soil sampler holders were filled to capacity with air-dried, ≤ 2 mm sieved soils, and the excess soil was scraped off using a blade to ensure a flat surface flush with the top of the holder. Afterward, the sample holder was directly, gently, and firmly slid onto the ASD high-intensity mug light attachment of the spectrometer, and there was no gap between the sample holder and mug light. Baseline measurements were taken before scanning every sample as the thermoelectric coolers take time to stabilize. Ten spectra were collected for every sample to minimize instrument noise and the average of the ten spectra were then recorded [2]. Scanning of the samples using VNIRS equipment was performed at USDA–NRCS Soil Survey office in Las Cruces, New Mexico.

The LIBS sample preparation involved compressing approximately 11 g of air-dried, ≤ 2 mm sieved soil inside a 38 mm Spec-Cap using a 15 ton hydraulic press for one minute to ensure that the soil sample would not be scattered by the pulses of laser light focused on the sample, once it was placed on the LIBS sample platform. In this study, the LIBS spectra were recorded with an average of 200 laser shots as the sample was rotated, and the result was a spectrum with 13,700 variables where each variable was the intensity of one of the 13,700 channels of light collected over a range between 198 and 969 nm [9].

2.3. Data Calibration and Modeling

In addition to testing VNIRS and LIBS independently, spectra from both VNIR and LIBS were combined to test their ability for predicting soil quality indicators (SQIs). This was accomplished by first independently mean-centering and variance-scaling the VNIR and LIBS spectra and then merging both spectra into a single combined LIBS-VNIRS predictor dataset.

Spectral pre-treatments were applied to remove any noise in the spectra caused by subtle variations in sample preparation and measurement [28]. All spectra were filtered using the Savitzky–Golay filter and were trimmed to remove noisy regions at the edge of the detector limits, especially in the regions of 350–500 nm and 2450–2500 nm for VNIRS, 1–150 nm and 13,652–13,701 nm for LIBS, and 1–150 nm and 15,801–15,850 nm for combined VNIRS-LIBS. Multiplicative scatter correction was used to correct the spectra to an ideal spectrum to ensure that the baseline and amplification effects were the same average level in every spectrum [28]. Continuum removal and wavelets were applied to the spectra to fit a convex hull to each spectrum and for multiscale examinations of the spectra, respectively [28]. The number of predictors (i.e., individual bands) after preprocessing were 1950, 13,500, and 15,650 for VNIRS, LIBS, and combined VNIRS-LIBS, respectively. In this study, 75% of the dataset was used for calibration and 25% for validation.

Our modeling strategy was based on samples collected from previous soil quality studies that presented a unique opportunity to study how different spectroscopic methods would perform in relating measured soil quality indicators to spectral data (Table 2). Model 1 (a statewide library) was used to explore a regional prediction of soil measurements from spectral reflectance measurements. Model 2 (a local spectral library) was used to explore soil spectra from soils collected from long-term crop management practices in an agricultural research center. Model 3 (a temporal spectra library) was used to understand the variations in the soil spectra as a function of the sampling dates that corresponded to the fall, winter, spring, and summer.

Partial least squares regression (PLSR) was used to model the relationship between spectra and SQIs. The number of PLSR components was selected based on R-square values, the cumulative percentage of variance, and scree plots for VNIRS, LIBS, and VNIRS-LIBS. The PLSR model was used to fit the calibration data and afterward used to predict the validation dataset. Model performance for both the calibration and validation datasets was assessed using the coefficient of determination (R^2) and root mean square error (RMSE) computed using both datasets [29]. All analyses were performed

using the R statistical software, and multiple R packages/libraries including signal, plyr, wavethresh, spectroscopy, Cubist, pls, and devtools (R version 3.4.4, 64-bit) [30].

Table 2. Locations used for developing the partial least squares regression (PLSR) models.

Models [†]	Locations	Sample Size
Model 1	All the data irrespective of locations across the state of New Mexico 71 commercial farm samples from 6 regions, 36 samples from NMSU Agricultural Science Center in Los Lunas, and 36 fall season samples from NMSU Leyendecker Plant Science Center in Las Cruces	143
Model 2	Data from NMSU Agricultural Science Center in Los Lunas, New Mexico, (34°46′00.34″ N, 106°45′31.95″ W, Elevation 1478.28 m)	36
Model 3	Data from NMSU Leyendecker Plant Science Center in Las Cruces, New Mexico, (32°11′5″ N, 106°44′26″ W, Elevation 1175.00 m)	
• Winter		36
• Spring		36
• Summer		36
• Fall		36

[†] Soils were collected from different management systems and were modeled irrespective management systems.

3. Results

3.1. Calibration-Model 1 (A Statewide Library)

Descriptive statistics of SQIs for all samples are presented in Table 3. Most SQIs had positive skewness, however, WAS (−0.27) and pH (−0.65) had negative skewness. Similarly, most SQIs had positive kurtosis, except POXC, AGG < 0.25, and WAS, which had negative kurtosis (Table 3). Although transformations of the data could reduce the impact of skewness, no transformations of the data were undertaken in this study because the downside of the transformations would be a loss of interpretability of the individual values, and the SQIs would not be in the original units.

Table 3. Descriptive statistics for laboratory-measured soil quality indicators (SQIs) using a dataset from all locations in New Mexico (n = 143).

SQIs [‡]	Mean	S.D.	C.V. (%)	Min.	Max.	Skewness	Kurtosis
SOM (%) [†]	1.37	0.86	62.3	0.76	4.83	1.62	3.14
POXC (mg·kg ^{−1})	426	63.8	15.0	379	591	0.72	−0.09
TMB (ng·g ^{−1})	2163	1849	85.5	891	11266	2.09	6.39
TBB (ng·g ^{−1})	1038	937	90.3	442	4841	2.07	5.19
TFB (ng·g ^{−1})	227	267	117	34.9	1280	1.91	3.79
MWD (mm)	0.74	0.51	67.5	0.31	2.65	0.91	0.83
AGG > 2 mm (%)	24.1	18.9	78.3	6.24	80.5	0.70	0.04
AGG < 0.25 mm (%)	34.1	18.3	53.6	19.6	87.2	0.62	−0.43
WAS (%)	54.6	17.2	31.7	43.5	93.9	−0.27	−0.40
pH	7.44	0.27	3.60	7.30	8.10	−0.65	0.55
EC (dS·m ^{−1})	1.60	1.53	95.5	0.67	8.28	2.18	4.96
Ca (mg·kg ^{−1})	8.86	7.90	89.1	4.17	46.6	2.19	4.99
Mg (mg·kg ^{−1})	2.88	3.06	106	1.08	18.4	2.51	7.25
Na (mg·kg ^{−1})	6.56	9.13	139	1.75	62.6	3.19	12.6
Fe (mg·kg ^{−1})	4.16	3.58	85.9	2.09	21.2	2.46	7.52

[‡] Standard deviation (S.D.), Coefficient of variation (C.V), Minimum (Min.) and Maximum (Max.). [†] Soil organic matter (SOM), permanganate oxidizable carbon (POXC), total microbial biomass (TMB), total bacteria biomass (TBB), total fungi biomass (TFB), mean weight diameter (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe).

Calibration R^2 and RMSE values for the SQIs are presented in Table 4. The R^2 ranged from 0.13 for EC, Mg, and Na to 0.76 for pH. The calibration using LIBS alone showed that few SQIs had $R^2 > 0.90$ except the microbial components (TMB, TBB, and TFB) which had $R^2 = 0.96$ (Table 4). The calibration R^2 for combined VNIRS-LIBS was ≥ 0.80 for pH, TMB, TBB, and TFB (Table 4). The combined VNIRS-LIBS yielded a better prediction for all the SQIs as compared to VNIRS alone. Moreover, the R^2 for combined VNIRS-LIBS improved for SOM, pH, EC, Mg, and Na as compared to LIBS alone (Table 4). The decline in R^2 values using the combination VNIRS-LIBS in comparison with LIBS alone for some soil quality indicators may be related to fundamental basis, elemental, and molecular responses of each sensor. Combined VNIRS-LIBS may have affected the stoichiometric relationships in the data used by PLSR, and molecular and elemental information may not be successfully integrated in some cases either [6].

Table 4. Calibration R^2 and root mean square error (RMSE) values of soil quality indicators (SQIs) using visible-near infrared spectroscopy (VNIRS), laser-induced breakdown spectroscopy (LIBS), and combined VNIRS-LIBS for all samples ($n = 143$).

SQIs	VNIRS		LIBS		VNIRS-LIBS	
	R^2	RMSE	R^2	RMSE	R^2	RMSE
SOM (%) [†]	0.19	0.66	0.61	0.43	0.65	0.54
POXC (mg·kg ⁻¹)	0.30	51.5	0.81	26.4	0.68	36.2
TMB (ng·g ⁻¹)	0.44	1211	0.96	430	0.82	835
TBB (ng·g ⁻¹)	0.45	649	0.96	214	0.81	499
TFB (ng·g ⁻¹)	0.41	189	0.96	68.8	0.80	120
MWD (mm)	0.24	0.48	0.72	0.27	0.57	0.34
AGG > 2 mm (%)	0.23	16.1	0.72	9.66	0.58	12.6
AGG < 0.25 mm (%)	0.15	16.2	0.68	9.64	0.56	11.6
WAS (%)	0.16	16.1	0.73	8.72	0.54	11.6
pH	0.76	0.11	0.89	0.11	0.92	0.07
EC (dS·m ⁻¹)	0.13	1.20	0.33	1.20	0.54	1.10
Ca (mg·kg ⁻¹)	0.17	5.84	0.61	5.44	0.61	4.86
Mg (mg·kg ⁻¹)	0.13	2.25	0.61	1.72	0.67	1.62
Na (mg·kg ⁻¹)	0.13	7.80	0.58	4.59	0.59	6.41
Fe (mg·kg ⁻¹)	0.15	2.66	0.69	1.38	0.63	2.12

[†] Soil organic matter (SOM), permanganate oxidizable carbon (POXC), total microbial biomass (TMB), total bacteria biomass (TBB), total fungi biomass (TFB), mean weight diameter (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe).

3.2. Calibration-Model 2 (A Local Spectral Library)

Considering the soil measurement data collected from a single location (NMSU Agricultural Science Center at Los Lunas), the assessment of univariate normality for soils at this location showed that only POXC (−0.17) was negatively skewed, while the rest of the SQIs had positive skewness (Table 5). The SQIs with negative kurtosis include AGG > 2 mm (−0.57), AGG < 0.25 mm (−0.74), and WAS (−0.50), while the rest of the SQIs had a positive kurtosis (Table 5).

Calibration R^2 and RMSE values are presented in Table 6. The R^2 values ranged from 0.48 for SOM to 0.75 for soil pH using VNIRS alone. For LIBS alone, the R^2 ranged from 0.66 for POXC to 0.95 for TFB. The R^2 values using LIBS alone showed that some SQIs had $R^2 \geq 0.90$ including TFB ($R^2 = 0.95$), Mg ($R^2 = 0.94$), TMB ($R^2 = 0.91$), and TBB ($R^2 = 0.90$). The R^2 for combined VNIRS-LIBS ranged from 0.57 for Ca to 0.95 for pH (Table 6).

Table 5. Descriptive Statistics for laboratory-measured soil quality indicators (SQIs) using a dataset from NMSU Agricultural Science Center in Los Lunas, NM (n = 36).

SQIs ‡	Mean	S.D.	C.V. (%)	Min.	Max.	Skewness	Kurtosis
SOM (%) †	1.28	0.81	63.4	0.29	4.47	2.09	5.99
POXC (mg·kg ⁻¹)	381	32.7	8.58	288	452.1	−0.17	0.76
TMB (ng·g ⁻¹)	1489	1633	109	105	7943	2.27	6.38
TBB (ng·g ⁻¹)	736	829	112	26.0	4152	2.38	7.56
TFB (ng·g ⁻¹)	145	225	155	0.00	956	2.55	6.81
MWD (mm)	0.64	0.49	77.0	0.13	2.03	1.00	0.24
AGG > 2 mm (%)	19.3	18.7	96.6	0.28	65.1	0.81	−0.57
AGG < 0.25 mm (%)	32.5	16.1	49.6	6.65	64.2	0.35	−0.74
WAS (%)	64.0	11.3	17.7	43.4	87.1	0.07	−0.50
pH	7.58	0.15	2.00	7.30	7.90	0.31	0.07
EC (dS·m ⁻¹)	0.69	0.34	48.8	0.30	2.00	1.91	5.55
Ca (mg·kg ⁻¹)	4.53	1.94	42.9	2.05	10.9	1.34	2.12
Mg (mg·kg ⁻¹)	1.13	0.56	49.3	0.44	2.68	1.43	1.85
Na (mg·kg ⁻¹)	2.39	1.33	55.6	1.08	7.83	2.42	7.45
Fe (mg·kg ⁻¹)	1.80	1.02	56.4	0.72	4.79	1.34	2.11

‡ Standard deviation (S.D.), Coefficient of variation (C.V), Minimum (Min.) and Maximum (Max.). † Soil organic matter (SOM), permanganate oxidizable carbon (POXC), total microbial biomass (TMB), total bacteria biomass (TBB), total fungi biomass (TFB), mean weight diameter (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe).

Table 6. Calibration R² and RMSE values for visible-near infrared spectroscopy (VNIRS), laser-induced breakdown spectroscopy (LIBS), and combined VNIRS-LIBS using data from NMSU Agricultural Science Center in Los Lunas, NM (n = 36).

SQIs ‡	VNIRS		LIBS		VNIRS-LIBS	
	R ²	RMSE	R ²	RMSE	R ²	RMSE
SOM (%) †	0.48	0.61	0.89	0.27	0.69	0.45
POXC (mg·kg ⁻¹)	0.70	14.7	0.66	5.23	0.77	32.04
TMB (ng·g ⁻¹)	0.55	1107	0.91	510	0.71	1058
TBB (ng·g ⁻¹)	0.55	576	0.90	274	0.76	480
TFB (ng·g ⁻¹)	0.67	134	0.95	48.4	0.77	131
MWD (mm)	0.67	0.26	0.85	0.15	0.73	0.25
AGG > 2 mm (%)	0.66	10.1	0.85	6.26	0.73	9.00
AGG < 0.25 mm (%)	0.60	9.95	0.80	6.35	0.71	9.73
WAS (%)	0.72	5.55	0.77	5.11	0.69	9.27
pH	0.75	0.07	0.85	0.05	0.95	0.06
EC (dS·m ⁻¹)	0.51	0.24	0.82	0.14	0.65	0.85
Ca (mg·kg ⁻¹)	0.55	1.29	0.78	4.14	0.57	4.73
Mg (mg·kg ⁻¹)	0.55	0.35	0.94	0.14	0.63	1.93
Na (mg·kg ⁻¹)	0.63	0.83	0.77	0.63	0.67	5.08
Fe (mg·kg ⁻¹)	0.54	0.72	0.80	0.38	0.66	1.62

‡ The soils of this location were collected from different soil and crop management systems including permanent grass with tall fescue, a peach orchard with clover understory, an alfalfa field, and conventional with varied annual crops. † Soil organic matter (SOM), permanganate oxidizable carbon (POXC), total microbial biomass (TMB), total bacteria biomass (TBB), total fungi biomass (TFB), mean weight diameter (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe).

3.3. Calibration-Model 3 (A Temporal Spectra Library)

Sampling seasons affected the correlation between soil spectra and SQIs (Table 7). The VNIRS calibration showed that the R² values were less than 0.90, except for pH (R² = 0.94), in the fall. In the winter, the R² values for some SQIs, including MWD, Fe, EC, and SOM, increased to ≥0.90. The R²

values ranged from 0.61 for the Fe to 0.92 for soil pH in the spring while the R^2 values ranged from 0.51 for POXC to 0.92 for soil pH in the summer (Table 7).

Table 7. Calibration R^2 and RMSE for visible-near infrared spectroscopy (VNIRS) over four measurement seasons at Leyendecker Plant Science Center, Las Cruces, NM ($n = 36$ for each season).

SQIs ‡	Fall		Winter		Spring		Summer	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
SOM (%) †	0.61	0.22	0.90	0.10	0.75	0.19	0.68	0.14
POXC ($\text{mg}\cdot\text{kg}^{-1}$)	0.62	27.1	0.70	13.4	0.75	9.68	0.51	20.6
MWD (mm)	0.45	0.45	0.96	0.07	0.68	0.24	0.81	0.31
AGG > 2 mm (%)	0.47	16.6	0.66	8.31	0.63	9.28	0.83	8.50
AGG < 0.25 mm (%)	0.46	14.8	0.66	6.09	0.67	9.30	0.90	5.86
WAS (%)	0.46	10.5	0.66	8.41	0.62	7.97	0.52	7.73
pH	0.94	0.06	0.67	0.08	0.92	0.01	0.92	0.03
EC ($\text{dS}\cdot\text{m}^{-1}$)	0.65	0.67	0.94	0.26	0.65	0.64	0.68	0.47
Ca ($\text{mg}\cdot\text{kg}^{-1}$)	0.61	4.27	0.82	2.77	0.69	3.43	0.59	2.58
Mg ($\text{mg}\cdot\text{kg}^{-1}$)	0.63	1.03	0.82	0.77	0.68	1.09	0.65	0.67
Na ($\text{mg}\cdot\text{kg}^{-1}$)	0.71	3.09	0.89	2.11	0.63	4.45	0.74	2.27
Fe ($\text{mg}\cdot\text{kg}^{-1}$)	0.71	0.97	0.95	0.28	0.61	0.91	0.84	0.42

‡ The soil samples were collected in the fall (October 2015), winter (January 2016), spring (April 2016), and summer (July 2016) from three replicate fields of the three tested crop production systems [5]. † Soil organic matter (SOM), permanganate oxidizable carbon (POXC), mean weight diameter (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe).

The seasonal changes of model calibration values followed a similar trend for some of the laboratory soil measurements. For example, the calibration R^2 values for SOM had a high value in winter spectra measurement, and the SOM content was the highest during the winter sampling [5]. The lowest R^2 values for SOM spectra were found in samples collected during the fall and summer, and the laboratory soil measurements showed that SOM varied significantly in the following order: winter (1.19%), spring (1.05%), fall (0.87%), and summer (0.84%) [5]. Moreover, the R^2 for AGG > 2 mm was the highest in summer sample spectra ($R^2 = 0.83$), corresponding to the highest AGG > 2 mm laboratory measurement for the summer samples [5].

Generally, the relationships between LIBS spectra and SQIs had R^2 values < 0.90, except for soil pH, which had $R^2 > 0.90$ in three out of the four seasons (Table 8). Calibration R^2 values for LIBS in the fall ranged from 0.62 for Na to 0.97 for soil pH while calibration R^2 values ranged from 0.75 for Ca and Mg to 0.96 for pH in the winter. The soil pH was the only SQI which had $R^2 \geq 0.90$ in the spring, while the R^2 values were less than 0.90 for all the SQIs during the summer (Table 8).

Similar to VNIRS, there was a trend between LIBS model calibration values and some soil measurements. For instance, the highest LIBS calibration R^2 value for soil salinity (EC) was 0.86 in the summer, and the highest soil salinity measured ($2.01 \text{ dS}\cdot\text{m}^{-1}$) was also observed during the summer [5]. Some indicators, mostly the physical SQIs, had relatively high calibration R^2 values during the winter including MWD, AGG > 2 mm, AGG < 0.25 mm, and POXC. Many of the chemical SQIs (pH, EC, Ca, Mg, Na, and Fe) had relatively lower calibration R^2 values during the summer using LIBS (Table 8).

Building validation models was not the main focus of this study since we had a small sample size for such a geographically wide and varied region.

Table 8. Calibration R^2 and RMSE values for laser induced breakdown spectroscopy (LIBS) over four measurement seasons at Leyendecker Plant Science Center, Las Cruces, NM ($n = 36$ for each season).

SQIs ‡	Fall		Winter		Spring		Summer	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
SOM (%) †	0.83	0.14	0.81	0.13	0.87	0.14	0.64	0.15
POXC ($\text{mg}\cdot\text{kg}^{-1}$)	0.65	26.0	0.83	10.0	0.77	9.34	0.67	16.9
MWD (mm)	0.72	0.32	0.89	0.12	0.86	0.15	0.85	0.27
AGG > 2 mm (%)	0.74	11.5	0.88	4.79	0.68	7.10	0.85	7.89
AGG < 0.25 mm (%)	0.70	11.0	0.86	3.83	0.81	6.97	0.80	8.38
WAS (%)	0.78	6.73	0.77	6.89	0.85	4.88	0.88	3.73
pH	0.97	0.03	0.96	0.02	0.94	0.01	0.86	0.03
EC ($\text{dS}\cdot\text{m}^{-1}$)	0.63	0.70	0.79	0.47	0.76	0.53	0.86	0.3
Ca ($\text{mg}\cdot\text{kg}^{-1}$)	0.69	3.80	0.75	3.02	0.76	3.01	0.89	1.32
Mg ($\text{mg}\cdot\text{kg}^{-1}$)	0.66	1.00	0.75	0.83	0.77	0.91	0.87	0.39
Na ($\text{mg}\cdot\text{kg}^{-1}$)	0.62	3.57	0.82	2.67	0.79	3.30	0.88	1.56
Fe ($\text{mg}\cdot\text{kg}^{-1}$)	0.81	0.79	0.86	0.59	0.79	0.66	0.89	0.33

‡ The soil samples were collected in the fall (October 2015), winter (January 2016), spring (April 2016), and summer (July 2016) from three replicate fields of the three tested crop production systems [5]. † Soil organic matter (SOM), permanganate oxidizable carbon (POXC), mean weight diameter (MWD), aggregates 2–4 mm (AGG > 2 mm), aggregates < 0.25 mm (AGG < 0.25 mm), wet aggregate stability (WAS), electrical conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), and iron (Fe).

3.4. Validation-Model 1 (A Statewide Library)

The R^2 of the validation dataset of VNIRS ranged from 0.01 for AGG < 0.25 mm, WAS, EC, Ca, Na, and Fe to 0.60 for pH while the R^2 of the validation dataset of LIBS ranged from 0.01 for SOM, TFB, AGG < 0.25 mm and WAS to 0.75 for pH. The R^2 of the validation dataset of VNIRS-LIBS ranged from 0.01 for SOM, AGG < 0.25 mm, WAS, EC, Ca, and Na to 0.57 for pH.

3.5. Validation-Model 2 (A Local Spectral Library)

The R^2 of the validation dataset of VNIRS ranged from 0.02 for TMB and WAS to 0.35 for SOM, while the R^2 of the validation dataset of LIBS ranged from 0.04 for Mg to 0.84 for POXC. The R^2 of the validation dataset of VNIRS-LIBS ranged from 0.01 for TMB, TBM, TFB, MWD, AGG > 2 mm, EC, Ca, Mg, and Na to 0.48 for pH.

3.6. Validation-Model 3 (A Temporal Spectra Library)

The R^2 of the validation dataset of VNIRS ranged from 0.02 for AGG < 0.25 mm to 0.64 for pH in the fall sampling season, while it ranged from 0.10 for POXC, AGG > 2 mm and AGG < 0.25 mm to 0.60 for SOM in winter. The R^2 of the validation dataset of VNIRS ranged from 0.01 for Ca and Na to 0.76 for pH in spring and from 0.03 for POXC to 0.61 for pH in summer.

The R^2 of the validation dataset of LIBS ranged from 0.01 for SOM, EC, and Ca to 0.80 for pH in fall while it ranged from 0.03 for SOM and AGG < 0.25 mm to 0.85 for pH in winter. The R^2 of the validation dataset of LIBS ranged from 0.01 for WAS to 0.51 for pH in spring while it ranged from 0.01 for Na to 0.70 for pH in summer.

4. Discussion

Spectral analysis cannot be perfectly executed without challenges. Challenges particular to this research are highlighted as follows:

- Data visualization and cleaning: Numerous trimming procedures were conducted before the conclusion was finally made.

- Different models were considered before picking the best one for this analysis. Among the models considered were the Forest Regression, the Principal Component Regression, and the Partial Least Square Regression (PLSR).
- Obtaining suitable software for data processing and analysis.

As expected, many SQIs did not show ideal normal distributions, a concern highlighted by Veum et al. [31] who indicated that it may be a challenge to find datasets that exhibit ideal distributions of SQIs, particularly if the measurements come from within a single field or from under similar management practices. Generally, the low prediction values of VNIRS and LIBS for different soil measurements were attributed to the effects of the material's matrices on the intensity of reflectance or emission, including chemical composition, density, hardness and compaction, biological substances, soil moisture, reflectivity, soil organic contents, high dispersion, and appropriate time gating of LIBS signals [32,33].

Additionally, the difference in prediction between LIBS and VNIRS could be a result of fundamental molecular principles on which those spectroscopies are based [6,9]. Generally, calibration dataset R^2 values may be influenced by the high dimensional and co-linear predictors particularly for VNIRS [34,35].

We noticed in this study that validation dataset results were not much different when using data from combined locations or separate sample sets, indicating that the accuracy of prediction models may depend more on the sample size, range of data values, and the degree of autocorrelation rather than on model selection or spectral pretreatments of the data [36].

In our study, only 25% of each dataset was used to build validation models; this, combined with the fact that we had a relatively small number of samples, proves to be inadequate for a robust validation. Therefore, the results may not be faithfully extended beyond the range of calibration models. As reported by many researchers, building robust validation and calibration models requires the use of large soil-spectra libraries, similarity of validation and calibration samples, and pre-screening of the soil samples to limit the effects of within-site heterogeneity and soil diversity especially in agricultural fields [37,38].

Although VNIRS and LIBS have shown predictive relationships with some microbial measurements as compared to the other SQIs, presumably due to the carbon contents of soil microbes, better predictive relationships may be achievable with some other soil measurements by increasing the number of samples evaluated and by taking spectroscopic readings in situ, rather than using disturbed samples measured in the laboratory [39]. In agricultural systems, SQI values may be altered by anthropogenic inputs that may disrupt or change the relationships between soil characteristics that produce soil spectral features [29].

Spectral data might be more suitable in predicting SQIs, especially soil-biological related indicators such as microbial biomass and soil carbon content, which can vary significantly with the season of sampling [5,40]. Previous studies showed the importance of sampling time and related environmental soil factors on soil spectra results and calibration [5,39,41]. The seasonal variability in the soil spectra shows that the results may be applicable only during the time of sampling for which soils were collected. The results may not be regarded as universal and should be interpreted based on the sampling season.

This study demonstrated the feasibility of VNIRS and LIBS spectroscopies as innovative methods for soil quality monitoring, which is fundamental for sustainable agriculture development in arid and semi-arid agroecosystems. In such agroecosystems, soil degradation is widespread, and a key reason for the poor quantification of this degradation is that the conventional methods of soil quality assessment are usually expensive, time-consuming, and often require large numbers of samples to be analyzed across soil types and regions [2].

However, with spectroscopic methods, soil quality assessment may be faster even if many samples have to be analyzed, since the spectroscopic methods do not involve elaborate chemical analyses that often require waiting times for reactions to complete in the laboratory. Moreover, the results of spectroscopic interpretations can be generated more quickly using a previously calibrated dataset.

Another advantage of spectroscopic methods is the absence of chemicals in the process of analysis. Methods used for several soil chemical and biological measurements often involve chemicals that constitute human health and environmental hazards, generating waste products that may need to be handled in special ways to prevent pollution. For example, the SOM analytical method used in New Mexico is the Walkley–Black method [16] which essentially is a chromic acid wet oxidation technique. Chromic acid is a very toxic chemical reagent which is regarded as an environmental pollutant and a carcinogen [42].

Spectroscopic methods are becoming popular and are being gradually embraced by different environmental and agriculture communities, and some examples of applications can be found in soil and plant sciences, water quality, agricultural inputs, livestock health, and food product quality and processing [15]. Although a wide range of spectroscopy applications is possible, the potential use of VNIRS and LIBS applications has not been exploited in the arid regions of the Southwestern USA, and this region in particular can benefit from spectroscopic applications for soil quality assessment considering the vast acreage of land devoted to agricultural production that need monitoring for sustainable production.

The lack of widespread adoption of the spectroscopic techniques for soil management in this region is related to the lack of comprehensive studies that define the relationships of multiple SQIs to spectral data in the region. Another challenge that could possibly limit VNIRS and LIBS applications for assessment of soil quality in the region may be related to handling data pretreatments and the development of effective calibration strategies [43]. Nevertheless, the outcomes of this research serve as a baseline for future studies since our results show the predictive capability of VNIRS and LIBS for various SQI measurements. Rapid and convenient soil analytical methods are crucial for soil quality assessment and precision soil–crop management. Incorporating the use of VNIRS and LIBS for soil management may require active collaborations between growers, land managers, and researchers, to develop effective calibration models that will prove useful for tracking directional changes in soil quality.

At this point in our research, LIBS yielded better prediction over VNIRS, therefore, it may be recommended for estimating soil quality in arid and semiarid agroecosystems. However, more laboratory and field studies are needed to validate this recommendation using larger local and regional datasets.

5. Conclusions

Relationships between multiple soil quality indicator measurements and spectral data generated by visible near-infrared (VNIRS) and laser induced breakdown (LIBS) spectroscopies were studied in selected agricultural soils of the arid Southwestern United States. The results of this study highlight the potential use of spectroscopic techniques for rapid and cost-effective soil assessment. However, predictive accuracies of these methods are location-specific and seasonally dependent in the dataset explored in this study.

The calibrations based on combined measurements irrespective of locations performed better for LIBS and combined VNIRS-LIBS, while measurements separated according to locations highly improved the quality of prediction for VNIRS as compared to combined locations. The prediction values varied with the sampling season for both LIBS and VNIRS. The predictive accuracy of VNIRS and LIBS may be affected by sample size and seasonal variability of soil quality measurements.

While this study shows the promising prospect of the spectroscopic techniques for rapid soil quality evaluations, more comprehensive studies are needed within the study region to create robust calibrations of the relationships between the spectral data and soil quality indicator measurements. Such calibrations will need to consider factors such as location, soil type, and season of sampling to improve predictive accuracy.

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