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Assessment of soil macronutrients using near-infrared reflectance spectroscopy: A review

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ABSTRACT

Soil macronutrients namely, nitrogen, phosphorus and potassium are critical elements for crop growth and yield. Their reliable assessment at varying space and time domains is an essential pre-requisite with regard to site-specific soil and crop management perspective. The classical methods of their assessment are very expensive, time consuming and laborious and hence not appropriate for their characterization at different space and time domains.Near-infrared reflectance spectroscopy (NIRS)operating in 400–2500 nm wavelength range appeared to be a promising alternative for the purpose due to its inherent advantages; rapid, non-destructive, non-invasive and acquiescence to both proximal and remote sensing modes of operation. Over the last two decades, several studies have demonstrated the potential of NIRS approach to estimate soil macronutrient contents. This review intent to provide an overview of NIRS approach and collate information with regard to its performance in the estimation of soil macronutrient contents. The performance evaluation of NIRS models was based on residual prediction deviation (RPD) value. It was noted that the NIRS approach successfully yielded moderate (1.4<RPD<2.0) to accurate (RPD>2.0) estimation of soil macronutrient contents in many studies.Thus, NIRS technique promise rapid, reliable and cost-effective analysis of soil macronutrient contents at varying spatio-temporal scales.

Keywords: Near infrared reflectance spectroscopy, proximal sensing, remote sensing, soil macronutrients, nitrogen, phosphorus, potassium

INTRODUCTION

Soil macronutrients namely, nitrogen (*N*), phosphorus (*P*), and potassium (*K*), are vital elements for crop growth and yield. Their reliable assessment in a rapid manner at varying space and time domains is an essential pre-requisite of site-specific soil and crop management programs or precision agriculture(Kim *et al.*, 2009). It enable actions to optimize macronutrient supply for improved soil fertility and reduce environmental pollution risk due to their excess concentration in soil. However, classical soil macronutrient testingbased on colorimetry or atomic emission spectroscopy techniques are very expensive, time consuming and laborious as it involve intense extraction and analytical procedures. These limitations confound their application to characterize spatial or temporal variability of soil macronutrient contents even within an individual field. Over the last few decades, near-infrared reflectance spectroscopy (NIRS) has been acknowledged as a rapid, non-destructive and non-invasive technique for soil characterization(Shepherd and Walsh, 2002; Stenberg *et al.*, 2010). In NIRS approach, spectral reflectance of soil in the visible, near-and shortwave-infrared portion of the electromagnetic spectrum (400–2500 nm) is related with attribute of interest. The NIRS spectral range is mainly characterized by electronic transitions, overtones and combinations of fundamental vibrations related to *C–H*, *N–H* and *O–H* functional groups(Stenberg *et al.*, 2010). So, soil attributes such as organic carbon, clay, mineral and moisture contents which have direct linkage with these spectrally active functional groups (referred as chromophores) became prime targets of NIRS approach. In addition, other soil attributes such as soil nutrient contents which has co-variation with chromophores are also estimated via NIRS (Kinoshita *et al.*, 2012; Sarathjith *et al.*, 2014)despite their insignificant direct association with spectrally active components (referred as non-chromophores). With inherent advantages and ability to characterize soil nutrient contents, the NIRS approach appeared to be a promising solution to the aforementioned concerns. Several studies have investigated the potential of NIRS approach to assess soil macronutrient contents. With advancements in multivariate data modelling over the last two decades, the linkage

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between soil spectral signature and macronutrients could be established with reasonable level of accuracy. However, the estimation accuracy of macronutrients via NIRS vary across different studies as influenced by multiple factors including soil type, reference analytical method, data modelling, among others. This article collated the outcome of those studies and examined the status of soil macronutrient contentestimation via NIRS. In addition, it briefly addressed the potentials and limitations of NIRS approach along with an attemptto identify different factors affecting its performance in macronutrient content assessment.

Fundamentals of near-infrared reflectance spectroscopy

Near-infrared absorption

At ambient temperature, molecules of matter are in a state of their fundamental vibrational energy levels with amplitudes in nanometers scale. The frequency of vibration is depended on the strength of the bond and the mass of the individual bonded atoms or their groups. Upon incidence of electromagnetic radiation of given wavelength, the amplitude of these vibrations increasesdue to transfer of photon energy to the molecule (Pasquini, 2003). For infrared absorption to happen, a) frequency of the radiation matches the natural frequency of the vibration and b) molecular vibration should impose a change in the dipole moment of the molecule. The intensity of a given absorption band depends on the magnitude of the dipole change (during the displacement of atoms in a vibration) and its degree of anharmonicity. Both phenomena are typically associated with bonds involving the hydrogen atom and some other heavier element such as carbon, nitrogen and sulphur. Thus, *O–H*, *C–H*, *N–H* and *S–H* bonds tend to have fundamental absorptions in the mid-infrared (3000–4000 nm) region. The overtones and combinations of the fundamental vibrations of these functional groups occur in the region of energy associated with near-infrared photons. The spectral characteristics (in terms of reflectance) of soil within NIRS operation range (Fig. 1a) typically consist of three prominent absorption peaks centered on 1400, 1900 and 2200 nm which are linked with clay minerals (Wetterlind and Stenberg, 2010). The spectral features around 1400 and 1900 nm can be assigned to the O–H group associated with water while metal-hydroxyl stretching characterize the absorption around 2200 nm (Bricklemyer and Brown, 2010).

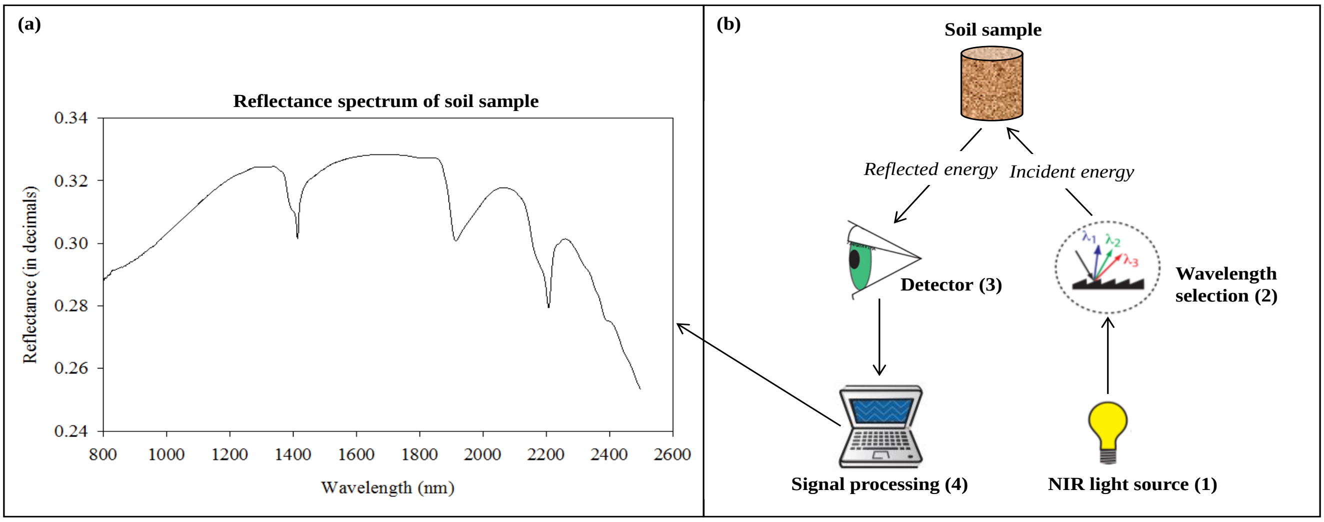

Fig. 1a) Spectral reflectance of soil; b) Conceptual diagram showing components of a NIRS instrument

Instrumentation

NIRS instruments essentially comprised of a light source, detector, wavelengths selection component and micro-controller unit to perform necessary signal processing for a desired output spectrum (Fig. 1b). A tungsten coil or a halogen lamp is the mostly used light source in NIRS instruments. The detectors based on silicon, lead sulphide and indium gallium arsenide materials which impart a very high signal-to-noise ratio are commonly used. Based on the technology employed for wavelength selection, NIRS instruments are classified as filter, light-emitting diode (LED) source self-band selection, dispersive grating and interferometric (Fourier transform) instruments. Instrument selection must be guided by end application. Low cost instruments, based on filters and LEDs, suffice for many dedicated laboratory and routine in field applications. Instruments based on fixed dispersive optics and sensor arrays have proven to be a robust solution when multi-wavelength spectral data for in field applications are required. Fourier-based instruments must be the choice when research, wide application spectra and calibration transference are of concern as they exhibit the best resolution and signal-to-noise ratios.

Data modelling

Figure 2 depicts a basic flow chart of NIRS data acquisition and modelling. The main objective NIRS approach is to link NIRS spectra (acquired using NIRS instrument) and target attribute (determined by classical reference method) of the materials. The spectral data consists of the information on both the composition (absorption) and scattering of incident electromagnetic radiation.

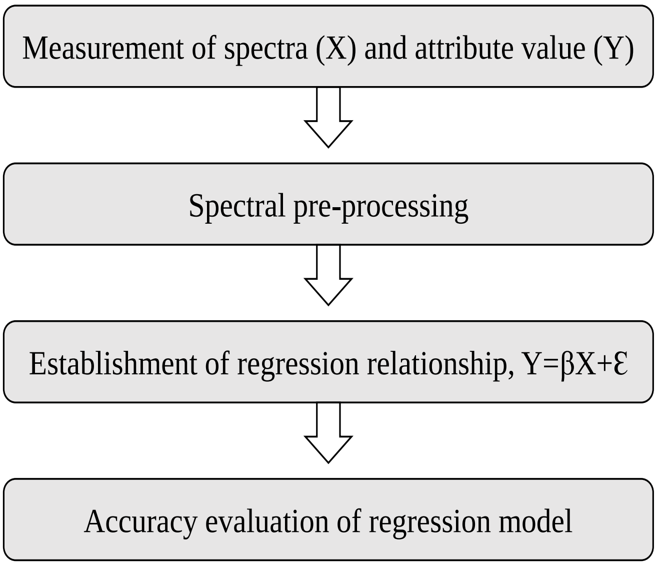

Fig. 2: Flow chart of near infrared reflectance spectroscopic data acquisition and modelling. β and Ɛ denotes regression coefficient and residual, respectively

The scattering component is of least significance in the context of compositional analysis as it does not have energy transfer with the sample. But it cause undesired variations (baseline shifts and non-linearity) in the spectra which can be effectively removed using spectral pre-processing. The pre-processing techniques may be categorized either as scatter correction methods or as spectral derivatives. The former category consist of multiplicative scatter correction (*MSC*), detrending (*DT*), standard normal variate (*SNV*) and normalization while first (*FD*) and second derivatives (*SD*) constitute the latter category (Rinnan *et al.*, 2009).

The NIRS spectra generally has weak and complex absorptions due to overlap of spectral features related to constituent functional groups.The regression model should be capable of extracting relevant spectral information and link with the desired attribute. Over years, several multivariate statistical algorithms have been used to establish spectra-attribute linkage (also referred as regression model or calibration function). They mainly includestepwise multiple linear regression (SMLR), principal component regression (PCR), partial least square regression (PLSR), support vector machine regression (SVR) and multi adaptive regression splines (MARS), among others. Accuracy evaluation consider simple linear relationship between the observed (determined using classical reference analysis) and model predicted values as expressed in terms of coefficient of determination (R^2), root mean squared error (RMSE) and residual prediction deviation (RPD). It may be noted that no statistical limits have been defined for any of these indicators for model evaluation. Although, no fixed criterion has been followed in the NIRS literature to judge model performance, RPD criteria as proposed by Chang *et al.* (2001)has been widely used in soil NIRS studies. Accordingly, NIRS models are categorized into accurate (RPD>2.0), moderate (1.4<RPD<2.0) and poor (RPD<1.4) classes.

Estimation of soil macronutrient contents

Model performance

Over the past few decades, several studies across the globe have investigated the potential of NIRS to estimatemacronutrients and often yielded mixed results. Table 1, 2 and 3 lists

Table 1: Details of selected studies on near infrared reflectance based estimation of soil nitrogen content

Country/ Region	Wavelength range (nm)	Regression algorithm	Calibration			Validation/Cross-validation				Reference
			n	R^2	RMSE	*n*	R^2	RMSE	RPD	
Spain	830–2630	PLSR	-	-	-	393	0.95	0.41	-	Zornoza *et al.* (2008)
China	400–2450	PLSR	-	-	-	26	0.86	24.76	2.49	Wenjun *et al.* (2014)
Israel	380–2500	PLSR	-	-	-	50	0.79	-	2.34	Paz-Kagan *et al.* (2015)
Israel	380–2500	PLSR	-	-	-	50	0.82	-	1.94	Paz-Kagan *et al.* (2015)
China	800–2564	PLSR	60	0.602	0.051	30	0.63	0.06	1.838	Zhang *et al.* (2016)
China	800–2564	SVR	60	0.823	0.034	30	0.81	0.05	2.219	Zhang *et al.* (2016)
China	900–1700	PLSR	60	0.93-0.99	0.15-0.51	30	0.94-0.97	0.34-0.50	-	He *et al.* (2017)
France	350–2500	PLSR	-	-	-	146	0.92	0.10	3.57	Vaudour *et al.* (2018)

n: number of samples; R^2: coefficient of determination; RMSE: root mean squared error (unit differ across studies); RPD: residual prediction deviation; PLSR: partial least square regression; SVR: support vector machine regression

the details of selected studies related to NIRSbasedestimation of *N*, *P* and *K,* respectively. The NIRS approach was found to be suitable for moderate (1.4<RPD>2.0) to accurate (RPD>2.0) estimation of *N*among all the studies compiled. The highest accuracy (in terms of R^2) was noted in case of He *et al.* (2017) which investigated the effect of soil moisture on the detectability of *N* using NIRS. They noted an optimum soil moisture content of 1.03% at which the validation performance of generated PLSR model was found to the highest for *N* estimation (R^2=0.97; RMSE=0.34 gKg^{-1}).Although, PLSR appeared to be the most commonly used algorithm for *N* estimation, Zhang *et al.* (2016) reported superior results of SVR than that of PLSR. In case of *P*, NIRS approach yielded accurate models as reported by Malley *et al.* (1999)(RPD=3.44) and Sarathjith *et al.* (2016b) (RPD=2.27). The former study noted superior performance of PLSR compared to SMLR in conjunction with different pretreatments. The latter study endorsed SVR models for better results compared to PLSR counterpart, both based on discrete wavelet transformed spectra. Among other studies, bothMouazen *et al.* (2007)(RPD=1.80) and Paz-kagan *et al.* (2015)(RPD=1.92) estimated *P* with moderate accuracy under PLSR framework and all the remaining studies failed to achieve *P* estimation with reasonable accuracy. Among different studies compiled, accurate NIRS models of *K* were obtained for Malley *et al.* (1999) and Sarathjith *et al.* (2014) while Abdi *et al.* (2012), Chang *et al.* (2001) and Debaene *et al.*(2014) yielded those with moderate performance. All the remaining studies reported poor estimation of *K* via NIRS.

Covariation assumption- Reason for NIRS based estimation of macronutrients

The NIRS wavelength domain is characterized mainly by the overtones and combinations of fundamental vibrations related to *C–H, N–H* and *O–H* functional groups. Those attributes that has direct linkage with these spectrally active functional groups (referred as chromophores) are more likely to be the most suitable candidate for NIRS based estimation. This may justify the estimation of *N* using NIRS as itis directly related to amino (*N–H*) group. But, this may not be valid with other attributes (such as *P* and *K*, among others) with no direct linkage with spectrally active functional groups (termed as non-chromophores). The predictability of a non-chromophore via NIRS is assumed to be associated with its covariation with appropriate chromophores (Stenberg *et al.*, 2010). Chang *et al.* (2001) assessed the co-variation assumption bycomparing the performance of NIRS and pedotransfer function (generated using chromophores) based models. Some otherstudiesused Pearson correlation coefficientbetween the target non-chromophore and chromophores as a measure of co-variation(Kinoshita *et al.*, 2012; Nduwamungu *et al.*, 2009).Both these methods describe linear relation of a non-chromophore with chromophores and may fail to characterize their non-linear linkage. Recently, Sarathjith *et al.* (2014)suggested an average dependency index (ADI) to be used as a measure of co-variation. The index computation is versatile to both linear and non-linear dependency measures. They obtained good relationship (R^2=0.93) between non-chromophore model performance (in terms of RPD) and ADI values (based on adjacency values of mutual information) computed using iron, clay and organic carbon contents.

Table 2: Details of selected studies on near infrared reflectance based estimation of soil phosphorus content

Country/ Region	Wavelength range (nm)	Regression algorithm	Calibration			Validation/Cross-validation				Reference
			n	R^2	RMSE	*n*	R^2	RMSE	RPD	
Canada	400–2498	PLSR	-	-	-	28	0.92	0.02	3.65	Malley *et al.* (1999)
USA	400–2498	PCR	-	-	-	802	0.40	32.28	1.18	Chang *et al.* (2001)
ESA	350–2500	MARS	511	0.32	17.00	-	-	-	-	Shepherd and Walsh (2002)
Mississippi	351–2398	SMLR	191	0.46	-	82	0.51	18.60	-	Ge and Thomasson (2006)
Belgium	400–1700	PLSR	-	-	-	175	0.69	1.35	1.80	Mouazen *et al.* (2007)
Zhejiang	350–2500	PLSR	135	0.42	26.31	30	0.29	29.43	-	He *et al.* (2007)
Spain	830–2630	PLSR	-	-	-	393	0.46	2.02	-	Zornoza *et al.* (2008)
Missouri	450–2500	PLSR	104	0.32	6.00	104	0.26	6.30	1.15	Sudduth *et al.* (2009)
Kenya	350–2500	PLSR	-	-	-	227	0.47	22.57	1.34	Kinoshita *et al.* (2012)
Poland	400–2200	PLSR	199	0.36	6.50	199	0.39	6.27	1.30	Debaene *et al.* (2014)
China	400-2450	PLSR	-	-	-	26	0.29	19.33	1.17	Wenjun *et al.* (2014)
India	400–2450	PLSR	175	0.54	0.57	59	0.30	0.70	1.20	Sarathjith *et al.* (2014)
Israel	380–2500	PLSR	-	-	-	50	0.74	-	1.92	Paz-Kagan *et al.* (2015)
India	350–2500	SVR	176	0.82	3.88	59	0.80	4.09	2.27	Sarathjith *et al.* (2016b)
France	350–2500	PLSR	-	-	-	48	0.12	0.01	1.08	Vaudour *et al.* (2018)

Factors affecting NIRS based estimation of macronutrients

***Soil type*:** The estimation accuracy of a macronutrient rely on its direct (in case of *N*) or indirect (in case of *P* and *K*) co-variation with spectrally active functional groups. Such linkages vary across soil types due to their inherent difference in characteristics. Hence, the estimation accuracy of macronutrients using NIRS may differ across different soil types irrespective of wavelength range, pre-processing and regression algorithms implemented (Table 1, 2 and 3). This was evident in the study reported by Sarathjith *et al.* (2014) which they examined soil attributes of two different soil types namely, Alfisols and Vertisols. They noted accurate and poor estimation of *P* and *K,* respectively in Vertisols. On the other hand, *K* was estimated accurately while poor result was noted for *P* in case of Alfisols. This contrasting result noted for both *P* and *K*across different soil groups were due to disparity of their co-variation with chromophores considered in their study.

***Reference method*:** Usually, attribute values determined using a primary reference method may differ from those obtained using another method. Consequently, NIRS performances also vary depending on the type of primary reference method as the approach is unique to spectra-attribute linkage. The variation in NIRS performance noted in case of extractable *K*(Table 3) determined using ammonium acetate (R^2=0.55; RPD=1.44) and Mehlich III (R^2=0.64; RPD=1.64) extraction methods (Chang *et al.*, 2001)is an example that emphasize the selection of suitable reference method for NIRS based analyses.

***Spectral pre-processing and regression algorithm*:** Different studies have tested several spectral pre-processing techniques for their suitability to estimate soil macronutrients, but only the best results obtained in those studies are only presented in Table 1, 2 and 3.It may be noted that the best pre-processing techniqueis not consistent across different studies.This is due to variation in scattering and noise

Table 3: Details of selected studies on near infrared reflectance based estimation of soil potassium content

Country/ Region	Wavelength range (nm)	Regression algorithm	Calibration			Validation/Cross-validation				Reference
			n	R^2	RMSE	*n*	R^2	RMSE	RPD	
Canada	400–2498	SMLR	-	-	-	28	0.94	0.54	4.21	Malley *et al.* (1999)
USA	400–2498	PCR	-	-	-	802	0.64	132.43	1.64	Chang *et al.* (2001)
ESA	350–2500	MARS	512	0.66	0.25	-	-	-	-	Shepherd and Walsh (2002)
Mississippi	351–2398	SMLR	191	0.40	-	82	0.16	16.00	-	Ge and Thomasson (2006)
Zhejiang	350–2500	PLSR	135	0.61	30.95	30	0.58	32.98	-	He *et al.* (2007)
Spain	830–2630	PLSR	-	-	-	60	0.79	0.11	-	Zornoza *et al.* (2008)
Missouri	450–2500	PLSR	104	0.41	40.10	104	0.36	41.8	1.25	Sudduth *et al.* (2009)
Turkey	350–2500	PLSR	359	0.44	0.19	153	0.32	0.21	1.21	Bilgili *et al.* (2010)
Canada	400–2500	PLSR	150	0.79	25.00	38	0.62	44.6	1.59	Abdi *et al.* (2012)
Kenya	350–2500	PLSR	-	-	-	227	0.25	160.96	1.14	Kinoshita *et al.* (2012)
Poland	400–2200	PLSR	199	0.46	3.67	199	0.46	3.31	1.40	Debaene *et al.* (2014)
China	400–2450	PLSR	-	-	-	26	0.07	20.82	0.77	Wenjun *et al.* (2014)
India	400–2450	PLSR	174	0.87	0.28	58	0.75	0.37	2.03	Sarathjith *et al.* (2014)
Israel	380–2500	PLSR	-	-	-	50	0.614	-	2.00	Paz-Kagan *et al.* (2015)
India	350–2500	SVR	175	0.42	0.26	58	0.32	0.27	1.22	Sarathjith *et al.* (2016b)

n: number of samples; R^2: coefficient of determination; RMSE: root mean squared error (unit differ across studies); RPD: residual prediction deviation; PCR: principal component regression; MARS: multi adaptive regression splines; SMLR: stepwise multiple linear regression; PLSR: partial least square regression; SVR: support vector machine regression

effects in the measured spectra caused due to different sample preparation (dry, moist, ground, intact, particle size), instrument (type, wavelength range, resolution) and measurement (humidity, temperature, replications) conditions involved in those studies. Thus, this review is not decisive in favor of a particular preprocessing technique to be used for macronutrient estimation. Although utility of several regression algorithms to estimate soil macronutrients (Table 1, 2 and 3) have been tested, PLSR appeared to the most popular and widely used technique among them. The main reason for its popularity may be attributed to its ability to account for multicollinearity pertained in spectra, ease of interpretation and better computational efficiency (Sarathjith *et al.*, 2016a; Viscarra Rossel *et al.*, 2006). Moreover, the PLSR could yield accurate estimation of soil macronutrients(Paz-Kagan *et al.*, 2015; Sarathjith *et al.*, 2014) although SVR outperform it when used in conjunction with spectra subjected to discrete wavelet transformation(Sarathjith *et al.*, 2016b).

Potentials and limitations

The NIRS approach has several advantages compared to conventional primary reference methods. It demands minimum or no sample preparation and does not involve the use of chemicals. The approach is very fast as it takes only fraction of a minute for spectral measurement against the cumbersome and tedious conventional methods. In NIRS approach, the different target attributes can be related to a single spectral signature of soil. Once such linkages (NIRS models) are established, the approach can be suitably used for simultaneous estimation of multiple soil attributes(Sarathjith *et al.*, 2016a). In addition, the NIRS approach involve non-destructive and non-invasive measurements. Moreover, the approach is acquiescent to laboratory, field, airborne and space-borne hyperspectral measurements. For example, spectral measurements or the spectra-attribute linkages developed using a laboratory NIRS instrument may be transferred to other remote sensing modes(Nouri *et al.*, 2017) and vice versa. Hence with the advent of novel hyperspectral measurement systems, the approach would enable rapid estimation of soil attributes at varying space and time scales.

One major limitation of NIRS is the soil specific nature of spectra-attribute linkages (calibration functions). Although several NIRS calibrations of soil attributeshave been developed across the globe, most of themremain valid only for the type of soil used in those studies. Also, NIRS calibration functions are bound within the limits of sample attribute values. Thus, the NIRS estimated attribute value of a sample may not be reliable if it is outside the range of calibration. A possible solution for these problems is to develop robust calibration functions using a large and diverse spectral libraries consisting of samples representing maximum variability in soil types and attribute values. However, this remains a challenging task. The other limitation associated with NIRS approach is that it is not standalone. It has to rely on primary reference methods to develop and test calibration functions. Thus, the quality of reference analysis is decisive of the accuracy of NIRS estimates. Any error associated with reference analysis may get propagated and lead to unreliable calibration functions (Chodak, 2008). The other limitation of NIRS is the high cost of good quality NIRS instruments. The approach would be cost-effective only when very large numbers of samples are to be analyzed during the operational period of the instrument.

Conclusions and future outlook

The NIRS technique promise rapid, reliable and cost-effective analyses of soil macronutrient contents.Statistical algorithms such as PLSR are capable of establishing robust and reliable spectra-macronutrient linkage. However, the use of new machine learning and hybrid (Reichstein *et al.*, 2019) approaches may be investigated in future studies for improved and robust NIRS models for macronutrient estimation. The use of hyperspectral remote sensors (airborne and space borne) may be examined for their potential to estimate soil macronutrients. Nevertheless, the feasibility of transferring calibration functions of soil macronutrients across proximal and remote sensing modes may be examined for better practical utility of the NIRS approach.

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