CHAPTER ONE

Near infrared (NIR) spectroscopy as a rapid and cost-effective method for nutrient analysis of plant leaf tissues

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Contents

Abstract

The efficient use of nutrients by plants can significantly improve the economic profitability and environmental sustainability of agricultural enterprises. Near infrared spectroscopy (NIRS) can provide a real-time, rapid, and non-destructive crop nutrient monitoring method to improve the timing of plant nutrient delivery. This review provides an analysis of the use of NIR (700–2500 nm) spectrometer for measuring

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macro- and micronutrients in leaf tissues. It firstly discusses the history of NIRS in agriculture and the principle of NIRS in estimating leaf nutrient content. The review then discusses factors that influence the effectiveness of NIR spectra in estimating leaf macro- and micronutrient contents: sample preparation, the spectral range used, pre-processing and multivariate analysis methods, and conditions of application. Key findings are: (1) macronutrients (N, P, K, S, Ca, Mg) and micronutrients (Fe, Zn, Mn, Cu) can be predicted accurately using NIRS, (2) macronutrients are better predicted compared to micronutrients, (3) NIRS can detect macronutrients such as N, P, and S directly because they are major constituents of NIR-sensitive organic compounds, whereas micronutrients and macronutrients that exist mostly in inorganic forms such as Ca, Mg, and K are detected through association with organic compounds and indirect correlations with organic compounds, (4) dried and ground samples result in a better calibration compared to fresh leaf samples due to the standardization of moisture and particle size, (5) Partial least squares regression (PLSR) yields better model accuracy and robustness compared to other linear regression methods, (6) there are not many studies that use machine learning methods for calibration, and (7) NIRS performed better in a laboratory condition compared to field conditions due to interfering external factors such as moisture, temperature, solar radiation and leaf orientation. The overall review suggests that there is a great potential for the field application of NIRS to be used for in situ nutrient analysis of plant leaf tissue.

1. Introduction

Crop nutrient management is one of the most important factors that determine the success of any agriculture enterprise (Ali et al., 2008; Beegle et al., 2000; Dobermann, 2007). The application of fertilizers that has occurred for over 100 years has been successfully used to fulfill the nutritional requirements of crops to increase yields and enable crop production to meet the demands of a continuously growing population (Stewart et al., 2005). However, these fertilizers are often used excessively and inefficiently by growers (Dobermann, 2007). Nutrient fertilizer use efficiency is approximately 20–40% for N, 15–20% for P and 30–50% for K and mainly attributed to losses from the system (Roberts, 2008; Samborski et al., 2009). The low efficiencies increase the cost of crop production and have a negative impact on the environment (Roberts, 2008). Improving NUE in crop production ensures the future economic sustainability and environmental soundness of agriculture enterprises.

The key to improving fertilizer efficiencies is to manage a congruence between the supply of nutrients from the soil and the demand of the crop at different phenological stages (Fageria and Baligar, 2005; Ulissi et al.,

2011; Van Noordwijk and Cadisch, 2002). This concept considers the crops' dynamic demand for nutrients relative to their stage of development. Split application of nutrients is one practice that takes account of this dynamic demand of the crop (Hallikeri et al., 2010). Theoretically, split application improves the fertilizer efficiency because it allows nutrient application rates to be adjusted when crop demand decreases reducing any excess input, consequently reducing input costs and the environmental footprint of the crop production system (Hallikeri et al., 2010).

This split or timely application method relies on the ability to frequently and accurately monitor the crop's nutrient status (Samborski et al., 2009; Tarpley et al., 2000). However, current methods of monitoring a crop's nutrient status, as shown in Table 1, are costly, inefficient, and require hazardous chemical reagents (Kalra, 1997; Menesatti et al., 2010; Rossa et al., 2015; Samborski et al., 2009). This inefficiency forces growers to be reactive in their nutrient management where nutrients are applied when a deficiency is observed, consequently reducing yield potential and returns (Fageria and Baligar, 2005). Therefore, a cheaper, non-destructive, and more accessible tool that can provide a real-time estimate of the crop's nutrient status is required (Van Maarschalkerweerd and Husted, 2015).

Near infrared spectroscopy (NIRS) is an emerging technique for soil and plant nutrient analysis. This spectroscopy technique, which used the reflectance at wavelength range of 700–2500 nm, offers a rapid, non-destructive, cheap, less labor-intensive, and a real-time plant nutrient analysis (García-Martínez et al., 2012; Van Maarschalkerweerd and Husted, 2015). Currently, numerous studies have focused on the use of NIRS for soil analysis (e.g., Ng et al., 2019; Nocita et al., 2015; Stenberg et al., 2010). Most studies indicate that NIRS can be used to predict soil properties

Table 1 List of the current standard methods used for plant tissue nutrient analysis with the associated nutrient analyzed (Kalra, 1997).

Methods	Nutrients
Inductive coupled plasma-optical emission spectrometry (ICP-OES)	P, B, K, Ca, Mg, Cu, Zn, Na
Atomic absorption spectrometry	K, Ca, Mg, Cu, Zn, Fe
Kjeldahl distillation	N
Dry combustion	C, N, S
UV–visible spectrophotometer of extract	Nitrate-N, P

that relate to organic materials and surface reactions, e.g., clay content, carbon content, cation exchange capacity (Stenberg et al., 2010). Some studies suggest that NIRS can be used as a tool for rapid soil nutrient analysis (Recena et al., 2019). However, there are uncertainties over the actual plant availability of these soil nutrient analyses and the ability of NIR to detect them (He et al., 2007; Singh et al., 2019).

Using NIRS at a leaf level allows a direct measurement of the crop's nutrient status, which bypasses soil nutrient analysis and allows growers to use this information for fertilizer management. Moreover, NIRS enables the detection of hidden deficiencies and prevents any excess application of fertilizers (Van Maarschalkerweerd and Husted, 2015). This would allow growers to be proactive in their nutrient management by maintaining the synchrony between nutrient demand from the crop and the supply from the soil, consequently reaching optimum yield and increasing profits, while reducing unnecessary input costs and environmental footprint of agriculture enterprises.

Currently, remote sensing at canopy level has been used extensively to measure a crop's health (plant's greenness) via an index called NDVI (Bausch and Duke, 1996; Jones et al., 2007; Serrano et al., 2000). There are also extensive studies on multi- or hyperspectral camera mounted on an unmanned aerial vehicle (Wang et al., 2015). However, the NDVI and other spectral indices are limited by the restricted wavelengths and become less reliable as they reach saturation in high canopy levels (Jiang and Huete, 2010; Ramoelo et al., 2011). Proximal leaf analysis using NIRS is advantageous as it overcomes these limitations. Studies on estimating macro- and micronutrients at a leaf level are emerging, and most studies were conducted on forages and hay (Clark et al., 1987; McLellan et al., 1991; Shenk and Westerhaus, 1985), as well as other grasses (De Aldana et al., 1995). Studies have shown that NIRS can be a useful predictive tool in isolation or in combination with the visible spectra (Vis-NIR) in agriculture. Therefore, assessing the potential of estimating macro- and micronutrients of plant leaf tissue as a tool for fertilization management in a crop production system will be beneficial.

This review aims to

- review the overall success rate of the NIRS method in predicting the concentrations of different leaf macro- and micronutrients in various plant species,
- examine the principle of NIRS in estimating the nutrient status of plant leaf tissue,

- assess the effect of sample preparation, spectral range, and multivariate methods of analysis, and
- compare laboratory and field suitability of NIRS for estimating leaf nutrient content.

2. NIR spectroscopy principle and application for plant nutrient analysis

2.1 History of NIRS for plant nutrient analysis

The earliest study on using NIRS on plants was Knipling (1970) who assessed the physical and physiological basis for the reflectance of visible and NIR radiation of vegetation. The use of NIRS in plant leaf tissue analysis only started in the mid-1970s (Norris et al., 1976). Early studies of NIRS focused mostly on forage qualities such as digestibility, crude protein contents and acid detergent fiber (Abrams et al., 1987; Clark et al., 1987; McLellan et al., 1991; Norris et al., 1976; Shenk and Westerhaus, 1985). Out of these early studies, Shenk et al. (1979) were one of the first studies that successfully estimated concentrations of nutrients such as N, P, Ca, K and B in forage grasses using NIRS. Most research on NIRS in 1980–1990s focused in estimating protein in forages and grains. NIRS application for N analysis of rice crop tissue for better fertilizer application strategies was developed in the 1986 by Batten and Blakeney (1991). While there are increasing number of papers on NIRS application on leaf tissues (e.g., Hattey et al., 1994; Rotbart et al., 2013), studies on leaves are much less compared to NIRS application in soil (e.g., Nocita et al., 2015).

2.2 Principles of NIRS

NIRS is a sensing technique that relies on the variability of chemical and physical compositions between different samples (Ludwig and Khanna, 2001). The variability between samples differ in their proportion and combination of absorption energy that is attributed to the stretching and vibrations of different bonds such as C—H, N—H, S—H, C—C, C═C, C—N, and O—H in the NIR spectral range (700–2500 nm) (Fig. 1) (Foley et al., 1998). These NIR-active bonds are typically present in organic compounds such as carbohydrates and proteins, which suits NIRS for organic compound analysis (Galvez-Sola et al., 2015; Ludwig and Khanna, 2001). NIR radiation interacts differently with different bonds, resulting in different combinations of peaks and troughs in the spectra which are unique to a sample (Richardson et al., 2004).

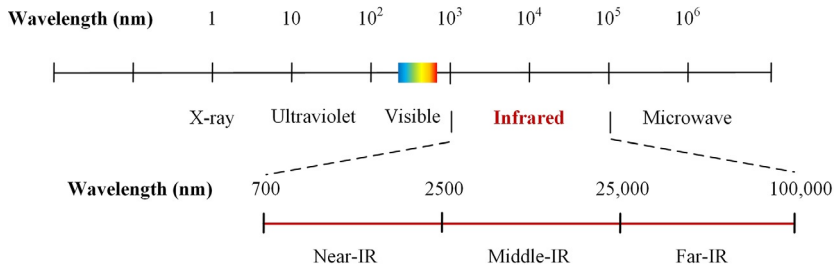

Fig. 1 The electromagnetic spectrum, showing the spectral range and location of near infrared (NIR) relative to other types of electromagnetic radiation.

However, there are still some limitations associated with NIRS. For instance, the NIR spectrum (wavelength 700–2500 nm) does not have distinct and sharp peaks compared to the mid-infrared spectrum (2500–25,000 nm) due to the combinations and overtones, resulting in broad and overlapping peaks which is harder to detect and analyze (Ludwig and Khanna, 2001; Richardson et al., 2004). Moreover, NIRS is highly affected by particle size and moisture content of the samples, which will be discussed further in Sections 3.3 and 3.4. Despite this, NIR used in isolation or in combination with the visible spectra (Vis-NIR) still provides a substantial amount of information on the sample's biochemical constituents (Richardson et al., 2004).

2.3 Plant leaf spectra

Plant leaf tissue has a unique reflectance or absorbance spectrum in the visible (400–700 nm) and NIR (700–2500 nm) spectral ranges compared to other materials (Richardson et al., 2004) (Fig. 2). Furthermore, each plant species has its unique reflectance spectra; however, there is a general trend that can be observed (Fig. 2).

The reflectance in the visible spectral range (Vis) of leaf tissue is relatively low, and the reflectance in the NIR spectra is relatively high (vice versa for the absorbance) and flattens at a wavelength of 800–1300 nm called the NIR plateau (Fig. 2) (Grant, 1987; Jie et al., 2014). This unique spectrum is a result of the complex scattering and absorption pattern by various biochemical and structural components present in the tissue (Grant, 1987; Richardson et al., 2004). In the visible spectral range, absorbance by pigment structures (e.g., chlorophyll and carotenoids) is the major contributor to the reflectance (Grant, 1987; Richardson et al., 2004). Pigments absorb visible

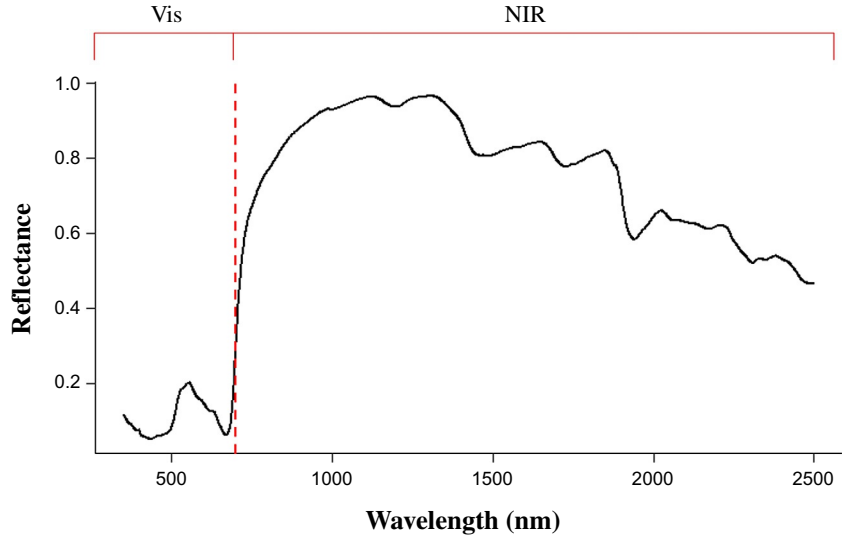

Fig. 2 Reflectance spectra of a cotton leaf in the visible part of the spectra (400–700 nm) and the NIR part of the spectra (700–2500 nm).

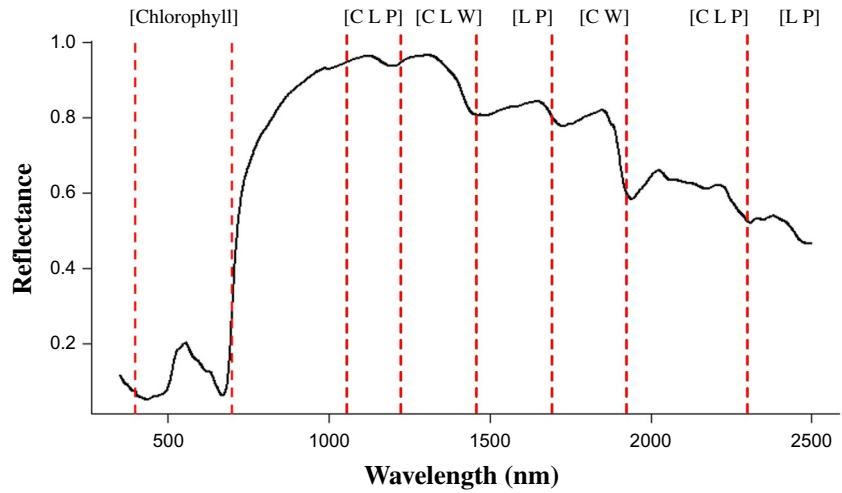

Fig. 3 The sensitivity range of different compounds (Chlorophyll = Chlorophyll, C = Carbohydrate, L = Lipid, P = Protein, W = Water) in the Vis-NIR spectra.

light as a primary process of photosynthesis (Sims and Gamon, 2002), whereas internal structure and organic compounds such as carbohydrates and proteins have a higher contribution to the absorbance in the NIR range through different chemical bonds (Fig. 3) (Richardson et al., 2004).

2.4 Nutrient estimation of plant leaf tissue using NIRS

Nutrients and minerals in plants exist in both the organic and inorganic fractions (Clark et al., 1987). Nutrients that are present in organic form can be measured directly by NIRS, as these compounds contain chemical bonds that have signature peaks in the NIR spectrum and their abundance can be correlated to the intensity in those particular peaks (Richardson et al., 2004). For example, N which is mainly present in organic form is an important component of (1) Chlorophyll, which can be detected by the Vis spectra due to its C—C and C═C bonds in the porphyrin ring and the magnesium ion; however, there is also a correlation in the NIR spectra through the C—H bond in the phytol tail of chlorophyll (Min et al., 2006; Sims and Gamon, 2002) and (2) Protein, which can be detected largely in the NIR spectra due to its C—H and N—H bonds (Bojović and Marković, 2009; Kokaly, 2001; Min et al., 2006).

Despite the better suitability of NIR in detecting organic compounds, NIRS can still extract information on the inorganic fraction of leaf samples such as Ca, K, and other micronutrients. Shenk et al. (1979) reported that Ca in diverse hay samples could be estimated with reasonable accuracy. Galvez-Sola et al. (2015) produced a reliable calibration for predicting Ca (validation R^2 (Rv) = 0.98), and reasonable calibrations for K, Mg, Fe, and zinc (Zn) in citrus leaves. Yarce and Rojas (2012) also successfully produced reliable calibrations for the estimation of N, P, K, Ca, Mg, copper (Cu), iron (Fe), Zn, and manganese (Mn) of sugarcane leaves.

There are two main mechanisms in which inorganic materials can be detected by NIRS:

(1) the association between inorganic compounds with organic compound functional groups or directly to the organic matrix (Huang et al., 2008; Yarce and Rojas, 2012) and

(2) through indirect measurements from other compounds that can be measured directly by NIR spectroscopy (Sims and Gamon, 2002).

An example is in the estimation of K content in leaf tissues. K is an essential macronutrient for plants as it controls or stimulates more than 50 enzymes and functions in plants (Ciavarella et al., 1998; Galvez-Sola et al., 2015). However, it is not incorporated into the chemical structure of plant tissues as other nutrients, and it is most influential in K^+ ion form; therefore, it is most abundant in inorganic form in plant tissues (Ciavarella et al., 1998; Prajapati and Modi, 2012). Despite this, it was suggested that K could be associated with organic molecules such carbohydrate and organic acids

(e.g., Malic acids) (Clark et al., 1987), because K^+ ions influence photosynthesis, and translocation of assimilates (Mechanism 2) (Ciavarella et al., 1998). Moreover, K forms cation-carbohydrate complexes, which can be analyzed via NIRS (Mechanism 1) (Cadet and Offmann, 1996). This assumption was supported by the findings of Ciavarella et al. (1998) which successfully calibrated K by focusing on wavelengths that had the strongest association with carbohydrates such as sucrose, starch, and cellulose.

Numerous studies have assessed the potential of NIRS in estimating leaf nutrient status of different plants such as tomato (Ulissi et al., 2011), sugarcane (Chen et al., 2002; Larrahondo et al., 2001; Yarce and Rojas, 2012), natural grass (De Aldana et al., 1995), cotton (Hattey et al., 1994; Tarpley et al., 2000), red fescue and perennial ryegrass (Gislum et al., 2004), coniferous, deciduous and shrub woody tree foliage (Bolster et al., 1996; Card et al., 1988; Petisco et al., 2005, 2008; Wessman et al., 1988), olive (Rotbart et al., 2013), rocket (Villatoro-Pulido et al., 2012), citrus (Ciavarella et al., 1998; Galvez-Sola et al., 2015; Menesatti et al., 2010; Min and Lee, 2005), yerba mate (Rossa et al., 2015), moringa (Rébufa et al., 2018), Chinese cabbage (Min et al., 2006), fingered citron (Liao et al., 2012), rice (Ciavarella et al., 1998; Shao and He, 2013), alfalfa (González-Martín et al., 2007; Halgerson et al., 2004), pear (Jie et al., 2014), oil palm (Santoso et al., 2019), and grape (Ciavarella et al., 1998). These studies varied in sample preparation, spectra pre-processing, the spectral range used, and the applied multivariate analysis methods which will be discussed in the following sections.

2.5 NIR calibration and validation for estimating plant leaf nutrient status

2.5.1 Calibration and validation

The calibration process in NIRS aims to convert spectral information into chemical information of the leaf sample (Mark et al., 2002) via mathematical models. The quality of the calibration determines the accuracy and precision of the NIRS technique in estimating the chemical properties or in this case, the leaf nutrient contents (Nicolai et al., 2007).

In the modeling procedure, usually three datasets are required: calibration, validation, and test dataset. The calibration dataset was used to build the model. The mathematical model usually contains a set of parameters that need to be optimized. The validation dataset is used to adjust or optimize parameters of the model. Moreover, to ensure that the calibration can be used outside the calibration dataset, assessment of the calibration's ability

to predict external data, called the test dataset, is required (Mark et al., 2002). In practice, most studies only divide the data into the calibration and validation dataset.

The accuracy and fit of calibration, validation, and test data can be assessed using accuracy parameters as described in Nicolai et al. (2007), such as the coefficient of determination (R^2), root mean squared (RMSE), standard error of prediction (SEP) and bias.

Coefficient of determination (R^2) is calculated from Eq. (1), shows the proportion of the variance of the calibration or validation dataset explained by the model,

$$\mathrm{R}^2 = 1 - \frac{\text{Sum of Squared Error}}{\text{Sum of Squared Total}} = 1 - \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} (\widehat{\mathrm{y}}_\mathrm{i} - \mathrm{y}_\mathrm{i})^2}{\sum_{\mathrm{i}=1}^{\mathrm{n}} (\overline{\mathrm{y}} - \mathrm{y}_\mathrm{i})^2} \tag{1}$$

with n the number of observations used in the calibration or validation, $\overline{y}$ the average of the observation, and $\widehat{y}_i$ and y_i the predicted and measured value of the ith observation, respectively.

Root mean squared (RMSE) calculated by Eq. (2) measures the accuracy of the prediction,

$$\mathrm{RMSE} = \sqrt{\frac{1}{\mathrm{n}} \sum_{\mathrm{i}=1}^{\mathrm{n}} (\widehat{\mathrm{y}}_\mathrm{i} - \mathrm{y}_\mathrm{i})^2} \tag{2}$$

In the NIR spectroscopy literature, RMSE calculated on the calibration dataset is usually called RMSEC or SEC (standard error of calibration), while this accuracy measure on the validation dataset is commonly called RMSEP or SEP (standard error of prediction).

Model bias, which is represented by Eq. (3) is the average difference between the predicted and the measured concentration values, where a positive bias value indicates over estimation of the model and a negative value indicates under estimation of the model,

$$\mathrm{Bias} = \frac{1}{\mathrm{n}} \sum_{\mathrm{i}=1}^{\mathrm{n}} (\widehat{\mathrm{y}}_\mathrm{i} - \mathrm{y}_\mathrm{i}) \tag{3}$$

Other parameters such as the ratio of RMSE to standard deviation of data (RPD) and the ratio of RMSE to interquartile range of the data (RPIQ) are also commonly calculated (Bellon-Maurel et al., 2010).

2.5.2 Review of past studies

This review evaluates 35 publications published between 1988 and May 2019 that used Vis and NIR spectroscopy in estimating leaf nutrients contents based on keywords (NIR spectroscopy for plant nutrient analysis, real-time plant nutrient analysis, NIR leaf nutrient analysis) searches in the Web of Science. Appendix A lists the accuracy parameters of those studies for Vis-NIR or NIR calibrations in estimating macro- (N, P, K, S, Ca, and Mg) and micronutrients (Fe, Zn, Cu, Al, B, Na, and Mn) content in leaves of different plant species.

To understand the accuracy of NIRS in predicting macro- and micronutrient of plant leaf tissues, the statistical distribution of the calibration and validation accuracy parameters were calculated. From numerous studies listed in Appendix A (Table A1), a series of tables were constructed which portrays the overall performance of NIRS calibrations in predicting concentrations of various macro- and micronutrients.

A summary of calibration accuracies is shown in Table 2, built using NIR in isolation and NIR in combination with Vis (Vis-NIR). Tables 3–7 show the statistical distribution of the accuracy parameters of the calibrations and validations built for N, P, K, Ca and Mg in plant leaf tissues. In this review, Rc refers to calibration R^2, Rv = validation R^2, and SEC/RMSEC = standard error calibration/root mean square error of calibration, and SEP/RMSEP = standard error prediction/root mean square error of prediction (on validation data).

2.5.3 Spectral range used in calibration for estimating plant leaf nutrient status

From Table 2, it can be observed that:

- Among the nutrients, total N content in leaf tissues is most accurately predicted by Vis-NIR and NIR. This was shown by the high median R^2 value for both the NIR (median R^2 (Rc) = 0.98) and validation (median R^2 (Rv) = 0.94) and Vis-NIR (median Rc = 0.90, median Rv = 0.83).
- Other macronutrients, i.e., P, K, Ca, and Mg had median R^2 (Rv) > 0.64 for Vis-NIR except for Ca, and > 0.62 for NIR.
- For micronutrients, Fe is the only nutrient that had an acceptable median R^2 for both NIR (0.72) and Vis-NIR (0.74), Zn had an acceptable median R^2 for NIR. Other micronutrients had a relatively low median R^2 for both NIR and Vis-NIR.

Table 2 The median and range of the calibration and validation parameters of N, P, K, Ca, Mg (%) and Fe, Mn, Zn, Cu (mg kg^{-1}) predictions using spectra of NIR (700–2500 nm) and in combination with Visible (Vis-NIR) range (400–2500 nm). Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error of prediction (Appendix A, Table A1).

	NIR			Vis-NIR		
	Rc	**Rv**	**SEC/RMSEC**	**Rc**	**Rv**	**SEP/RMSEP**
N	0.98	0.94	0.12	0.89	0.82	0.19
	(0.90–0.99)	(0.84–0.99)	(0.01–0.29)	(0.48–0.98)	(0.71–0.98)	(0.05–0.64)
P	0.91	0.62	0.02	0.91	0.68	0.02
	(0.70–0.99)	(0.52–0.99)	(0.01–0.05)	(0.80–0.92)	(0.43–0.69)	(0.02–0.03)
K	0.94	0.64	0.17	0.83	0.86	0.34
	(0.70–0.99)	(−0.10–0.98)	(0.01–0.47)	(0.59–0.99)	(0.73–0.99)	(0.06–0.78)
Ca	0.93	0.85	0.10	0.72	0.47	0.30
	(0.77–0.98)	(0.42–0.98)	(0.01–0.57)	(0.39–0.99)	(0.22–0.95)	(0.07–0.95)
Mg	0.86	0.85	0.02	0.71	0.64	0.05
	(0.77–0.98)	(0.47–0.97)	(<0.01–0.07)	(0.44–0.98)	(0.27–0.94)	(0.04–0.22)
Fe	0.81	0.72	16.00	0.81	0.74	17.28
	(0.71–0.99)	(0.56–0.97)	(0.02–237)	(0.62–0.95)	(0.57–0.92)	(6.05–92.00)
Mn	0.81	0.59	23.37	0.41	0.57	11.47
	(0.68–0.98)	(0.35–0.98)	(0.54–303.00)	(0.37–0.84)	(0.21–0.93)	(1.64–21.30)
Zn	0.85	0.62	3.45	0.67	0.40	4.30
	(0.02–0.98)	(0.62–0.98)	(0.04–11.38)	(0.32–0.90)	(0.24–0.89)	(0.97–8.30)
Cu	0.86	0.52	0.89	0.52	0.44	2.90
	(0.02–0.99)	(0.00–0.99)	(0.05–10.37)	(0.39–0.73)	(0.26–0.62)	(2.30–3.50)

Table 3 The statistical distribution of N calibration and validation parameters of NIRS, where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error of prediction (%) (constructed from Appendix A, Table A1).

	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias
Average	0.913	0.146	0.895	0.197	0.028
Median	0.948	0.106	0.930	0.124	0.007
SD	0.105	0.104	0.079	0.158	0.047
25th interval	0.882	0.090	0.834	0.102	<0.001
75th interval	0.980	0.154	0.945	0.300	0.024
IQR	0.083	0.064	0.103	0.198	0.024
Min	0.480	0.012	0.710	0.009	<0.001
Max	0.990	0.430	0.990	0.640	0.110

Table 4 The statistical distribution of P calibration and validation parameters of NIRS, where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error (%) (constructed from Appendix A, Table A1).

F	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias
Average	0.877	0.017	0.642	0.024	0.006
Median	0.910	0.015	0.635	0.018	0.008
SD	0.087	0.011	0.153	0.014	0.005
25th interval	0.845	0.010	0.540	0.015	0.004
75th interval	0.925	0.026	0.688	0.033	0.009
IQR	0.080	0.016	0.148	0.018	0.004
Min	0.700	0.004	0.429	0.007	0.001
Max	0.988	0.038	0.988	0.051	0.009

Overall, the review indicates that both NIR and Vis-NIR spectra can be used for accurately measuring the concentration of N, P, K, S, Ca, Mg (further discussed in Section 2.5.2), and Fe on leaves. There is still uncertainty on micronutrients such as Zn, Cu, Mn, and B which may be case dependent.

Based on the examined studies, there seems to be an indication that calibration using NIR spectra is better than Vis-NIR, which may be attributed to the larger amount of spectra variables used in Vis-NIR that may cause

Table 5 The statistical distribution of K calibration and validation parameters of NIRS, where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error (%) (constructed from Appendix A, Table A1).

	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias
Average	0.881	0.147	0.653	0.232	0.022
Median	0.933	0.111	0.720	0.172	0.011
SD	0.110	0.151	0.312	0.188	0.030
25th interval	0.860	0.087	0.435	0.117	0.005
75th interval	0.950	0.137	0.885	0.303	0.028
IQR	0.090	0.050	0.450	0.145	0.023
Min	0.590	0.013	- 0.100	0.009	0.001
Max	0.995	0.680	0.991	0.780	0.066

Table 6 The statistical distribution of Ca calibration and validation parameters of NIRS, where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error (%) (constructed from Appendix A, Table A1).

	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias
Average	0.851	0.133	0.734	0.275	0.025
Median	0.900	0.086	0.850	0.110	0.009
SD	0.177	0.157	0.256	0.275	0.033
25th interval	0.850	0.056	0.580	0.065	0.006
75th interval	0.970	0.137	0.929	0.282	0.036
IQR	0.100	0.081	0.230	0.217	0.030
Min	0.390	0.009	0.220	0.007	0.002
Max	0.995	0.590	0.980	0.950	0.063

Table 7 The statistical distribution of Mg calibration and validation parameters of NIRS, where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error (%) (constructed from Appendix A, Table A1).

	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias
Average	0.813	0.042	0.696	0.053	0.005
Median	0.840	0.024	0.745	0.042	0.005
SD	0.157	0.052	0.254	0.063	<0.001
25th interval	0.765	0.012	0.485	0.014	0.005
75th interval	0.910	0.045	0.928	0.058	0.005
IQR	0.145	0.033	0.443	0.043	<0.001
Min	0.440	0.009	0.270	0.004	0.005
Max	0.982	0.180	0.974	0.220	0.006

overfitting, or the redundancy of the visible spectra (Xu et al., 2008). There is a lack of study that compares the prediction performance of models calibrated using NIR and Vis-NIR spectra. Future research into this area would clarify this issue and improve the accuracy of calibration.

2.5.4 Macronutrients

2.5.4.1 Nitrogen (N)

Nitrogen content in leaf tissues found in reviewed studies ($n = 22$) varied with different plant species and growth stages, and ranged from 0.36 (Card et al., 1988) to 7.2% Total N (Zerner and Parker, 2019) with median values ranging from 1.55% to 4.55% (Appendix C, Table A5). Overall, NIRS was reported to be outstanding in estimating leaf N content with a 25th and 75th interval of Rc and Rv between 0.882 and 0.980 and between 0.834 and 0.945, respectively, where the 25th and 75th interval for SEP/RMSEP ranged from 0.102% to 0.300% (Table 3). These results show that there is a strong correlation between Total N in leaf tissues and the Vis-NIR spectra.

Chlorophyll and proteins are the main compounds that are sensitive in Vis and NIR spectra, respectively, for N content estimation in leaf tissue (Al-Abbas et al., 1974; Johnson, 2001; Min et al., 2006; Shao and He, 2013). Chlorophyll affects the visible spectra at the blue region (430 and 450 nm), red region (650 and 660 nm) and green region (550 nm), where it reflects the green region and absorbs the remaining two (Min et al., 2006), whereas proteins affect the NIR spectra at wavelengths of 2054 nm and 2172 (Min et al., 2006), which was similar to the findings of Johnson (2001) (2075, 2160 and 1675 nm) due to the C—N and N—H bonds in protein compounds (Kokaly, 2001; Min et al., 2006).

2.5.4.2 Phosphorus (P)

Phosphorus is another important nutrient due to its involvement in key metabolic processes in plants and the role it plays in controlling key enzymatic reactions (Vance, 2001). P content found in reviewed studies ($n = 11$) varied with different plant species and stages and ranged from 0.012 (Chen et al., 2002) to 0.40% with the median values ranging from 0.13% to 0.31% (Appendix C, Table A5). Overall, the interquartile range for the prediction of P had Rc between 0.845 and 0.925 (Table 4). Despite the relatively high Rc, the interquartile range for Rv was lower ranging from 0.540–0.688 with a median of 0.642 (Table 4). The largest RMSEP was 0.051%, which is still quite large, considering it is five times

the minimum P content found in the reviewed studies. Calibrations for P estimates were considered acceptable in some studies (Clark et al., 1987; Petisco et al., 2005; Yarce and Rojas, 2012) but not successful in others (De Aldana et al., 1995).

Organic P is the dominant form of P in plant tissues (De Boever et al., 1994; Foley et al., 1998). It is an important component of organic molecules such as phytates (50–70%), nucleic acids, phosphoproteins, phospholipids (20–30%) and the remaining is in inorganic forms such as calcium or potassium phosphate (Chen et al., 2002; De Boever et al., 1994). NIRS is sensitive to these organic compounds (De Boever et al., 1994); however, it does not have signatures for calcium or potassium phosphate (Clark et al., 1987). The presence and abundance of the less dominant organic P are seasonal, depending on phenology and species (Foley et al., 1998), which might restrict the use of organic P as a representative P content in leaf samples.

2.5.4.3 Potassium (K)

Potassium content in reviewed studies ($n = 14$) is in the range of 0.15 (Petisco et al., 2008)—7.1% (Villatoro-Pulido et al., 2012) with the median values ranging from 1.04% to 5.00% (Appendix C, Table A5). Similar to N and P, reasonable prediction of K in leaf tissues was reported with a relatively high Rc 25th and 75th interval of 0.860 and 0.950; however, the Rv are quite variable in different studies with a 25th and 75th interval value of 0.435–0.885 (Table 5). The median SEP/RMSEP is relatively high approximately half of the minimum K content found in the reviewed studies. Half of the studies reported successful in estimating K using NIRS (Ciavarella et al., 1998; Menesatti et al., 2010; Yarce and Rojas, 2012).

Potassium can be measured indirectly via NIRS through carbohydrates and organic acids (e.g., Malic acids) (Clark et al., 1987) and it can also be detected in cation-carbohydrate complexes (Cadet and Offmann, 1996). Thus, an accurate NIR calibration can potentially be built for K by putting more attention to carbohydrate affected regions in the spectra as shown in Fig. 3.

2.5.4.4 Sulfur (S)

Sulfur content was only studied in few studies ($n = 3$), which ranged from 0.01% (Stubbs et al., 2010) to 1.78% (Halgerson et al., 2004) with median values ranging from 0.09% to 1.11% (Appendix C, Table A5). Out of the studies, one generated a reasonably accurate calibration ($Rc = 0.73$, $Rv = 0.64$), while another was unsuccessful ($Rc = 0.18$) (Appendix A,

Table A1). The study that produced reasonable calibration (Rébufa et al., 2018) used only NIR. Another study (Halgerson et al., 2004) used Vis-NIR which coincided with the findings of Stubbs et al. (2010) that found a reasonable calibration (Rc = 0.80) for S in wheat and barley straw residue. Thus, there may be potential in utilizing the NIR spectra in predicting sulfur; however, the accuracy of prediction could be improved with a well-distributed S content range. As S is the only macronutrient not commonly assessed using NIRS, it may be beneficial to conduct more research to understand the performance of NIRS in estimating S.

2.5.4.5 Calcium (Ca) and magnesium (Mg)

Calcium ($n = 12$) concentration found in the reviewed studies ranged between 0.012% (Rossa et al., 2015) and 10.3% (Menesatti et al., 2010) with the median values ranging between 0.28% and 5.31%. Studies on magnesium ($n = 10$) had concentration values between 0.018 (Petisco et al., 2008) and 0.955 (Rossa et al., 2015) with median values ranging from 0.12% to 0.57% (Appendix C, Table A5). NIRS calibration for both Ca (median Rc = 0.851) and Mg (median Rc = 0.813) was found to be relatively good (Tables 6 and 7).

The strong correlation that is generally displayed in the prediction can be potentially attributed to the strong association of both of these nutrients to NIR-sensitive organic compounds in particular components of the cell structure (Chen et al., 2002; De Aldana et al., 1995). For example, De Aldana et al. (1995) reported that Ca pectate binds to plant cells and are sensitive in the NIR region. Moreover, De Aldana et al. (1995) also reported that Mg was strongly correlated to the chlorophyll band which was found in NIR region found in Clark et al. (1987) (1768, 1818, 1850, 2076, 2304, 2350 nm) instead of the visible spectra found in Masoni et al. (1996) which could explain the better calibration built using NIR in isolation. Thus, NIRS has a high potential to be used as a monitoring system for Ca and Mg.

2.5.5 Micronutrients

Several studies predicted micronutrients ($n = 13$), include Iron (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu), Boron (B), and Aluminum (Al). Overall, micronutrient predictions were not as good as those reported on macronutrients, which may be due to the lower concentration of micronutrients, especially at concentrations lower than 100 mg kg^{-1} (Clark et al., 1987; Liao et al., 2012; Van Maarschalkerweerd and Husted, 2015). Higher correlations can be obtained from a higher concentration of nutrients

(Ramoelo et al., 2011). This was shown by the higher median Rc (macronutrient = 0.92, micronutrient = 0.79) and Rv (macronutrient = 0.84, micronutrient = 0.59) of macronutrients (Appendix B, Table A2). Nevertheless, the results derived from different studies for micronutrients were highly variable with a range of Rc from 0.02 to 0.989 (Appendix A, Table A1).

Fe (median Rc = 0.81, Rv = 0.72, RMSEP = 16 ppm) and Zn (median Rc = 0.80, Rv = 0.62, median RMSEP = 3.45 ppm) were the only micronutrients that were reported to be well predicted. Mn, Na and Cu had reasonable calibrations with a median Rc ranging from 0.68 to 0.87 but had poor validations (median Rv < 0.6) (Appendix B, Table A2). Aluminum had a reasonable calibration; however, no validation parameter was provided (Halgerson et al., 2004). Generally better micronutrient NIRS calibration was obtained from using NIR in isolation except for Fe and B. There were only two studies that assessed B (Santoso et al., 2019).

Despite the relatively poor prediction of micronutrients reported in a few of the studies, there are associations between micronutrients and other leaf components that can assist in understanding the effect of micronutrients on NIR spectra. Shao and He (2013) found that Fe and Mn are strongly correlated to variation in chlorophyll concentration, as both are fundamental components of chlorophyll along with S and Mg (Al-Abbas et al., 1974). The study also found that Fe is correlated to wavelengths 560–580 nm (green spectral range), whereas Zn is correlated to wavelengths 680–720 nm (Red edge position). Van Maarschalkerweerd et al. (2013) concluded that Cu deficiencies could be related to lignin composition which can be detected using NIRS at 1887–1923 nm and 1405–1470 nm. In summary, NIRS is less accurate in estimating micronutrients, mainly due to their low concentrations in plant tissues and the lack of spectral signatures. Nevertheless, several studies such as Clark et al. (1987), Menesatti et al. (2010), and Rossa et al. (2015) show the potential of NIRS in estimating micronutrients for certain plant species.

3. Spectral analysis for the prediction of leaf tissue nutrients

3.1 Pre-processing of raw NIR spectra

Spectroscopy methods rely on information in the reflectance spectrum (Knipling, 1970). The reflectance spectrum of a sample serves as predictive variables used to estimate the chemical composition of the sample (Abdi,

2010). However, due to the large number and high collinearity of the predictive variables (i.e., reflectance spectrum), it needs to be processed and analyzed using multivariate methods (Tobias, 1995).

Various spectra pre-processing methods were used in various studies for different nutrients. Raw spectra possess significant noise and can be affected by background light (Xu et al., 2008). The noise in raw NIR spectra may arise from interfering physical and/or chemical factors, technical errors or random factors. High signal-to-noise ratio (SNR) reduces the accuracy of the calibration (Xu et al., 2008). Moreover, background and reflectance scatter add unwanted variables to the spectral data that lead to biased and low accuracy models (Xu et al., 2008). Thus, the pre-processing of raw NIR spectra before multivariate analysis is fundamental.

However, there is no general rule on which pre-processing method is best, it depends on spectral range and instruments, and thus the optimal method is commonly determined via trial and error (Xu et al., 2008). Pre-processing on the NIR wavelength variables is the common method, but pre-processing the response variable (nutrient values) is also possible, as shown by Menesatti et al. (2010). Transforming reflectance (R) into absorbance ($A = \log(1/R)$) is the first pre-processing step conducted on most of the studies, as using absorbance resulted in better calibrations compared to reflectance (Min and Lee, 2005). This transformation can be seen in Fig. 4. Other spectra pre-processing methods include (Hassan et al., 2015; Xu et al., 2008):

1) Signal smoothing to remove noise:
   a. Savitzky-Golay (S-Golay)
2) Normalization or baseline removal:
   a. First derivative (FD) (Fig. 4D)
   b. Second derivative (SED) (Fig. 4D)
   c. Standard Normal Variate (SNV) (Fig. 4E)
   d. Vector normalization (VN)
   e. Minimum-maximum normalization (MMN)
   f. Straight line subtraction (SLS)
   g. Constant offset elimination (COE)
3) Detrending (Fig. 4C):
   a. Multiple scatter correction (MSC)
   b. Orthogonal signal correction (OSC)
4) Peak enhancement or feature extraction:
   a. Continuum removal

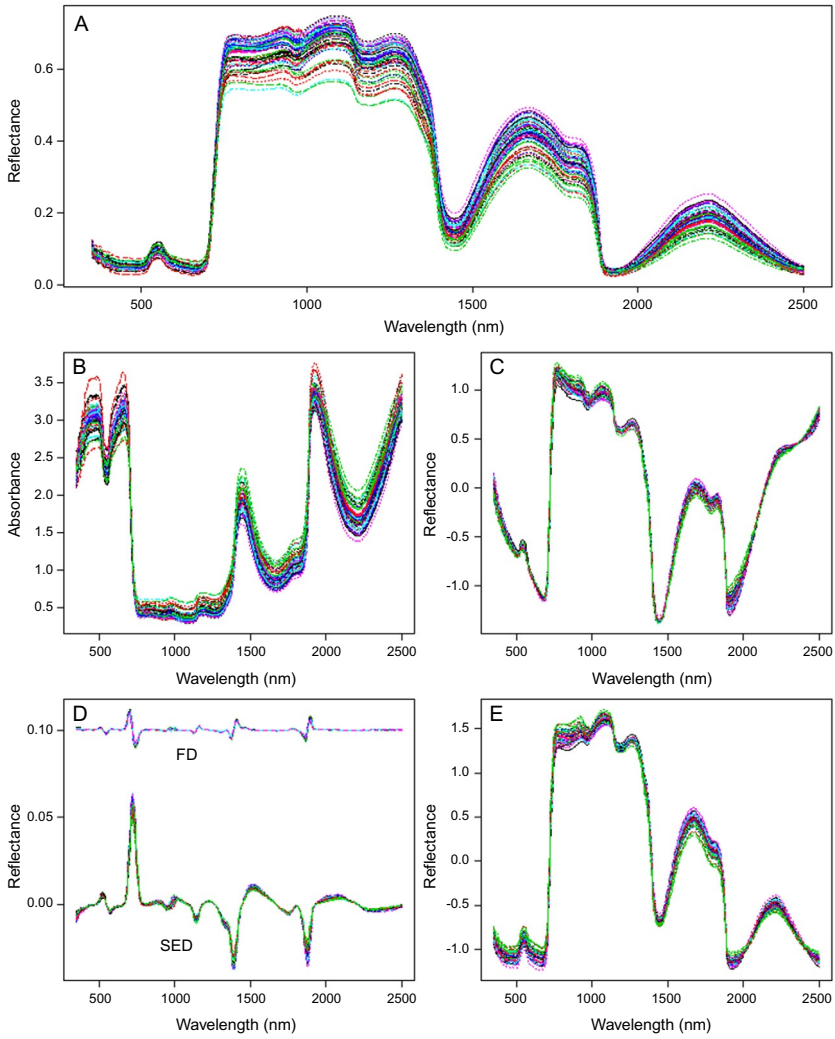

Fig. 4 Effect of pretreatment; (B) absorbance; (C) detrending; (D) first (FD) and second derivative (SED); and (E) standard normal variate (SNV) on cotton leaf reflectance spectra compared to raw untreated cotton leaf reflectance spectra (A).

The pre-processing method selection depends on the nature of the spectra, and it is important to note that some of these pre-processing methods may degrade the spectral data when used incorrectly (Xu et al., 2008). Thus, care must be taken when applying the pre-processing method.

3.2 Multivariate analysis

NIR spectra data contains hundreds to thousands of reflectance values as a function of wavelengths. These spectra values are also highly correlated. Partial least squares regression (PLSR) is a method that combines generalized principal component analysis and multi linear regression which can be used for predicting dependent variables from large, highly collinear sets of independent variables (Abdi, 2010; Tobias, 1995). PLSR is particularly useful for a large number of predictor variables such as in NIRS because it extracts orthogonal factors that have the best predictive power called latent variables (Abdi, 2010). PLSR reduces the number of multivariate variables and reduces the risk of overfitting (Tobias, 1995). Other methods that can be used to reduce the number of multivariate variables prior to regression modeling include principal component analysis (PCA) and independent component analysis (ICA) (Barnes et al., 1989; Shao and He, 2013; Xu et al., 2008).

From the various studies examined, PLSR and stepwise multilinear regression (SMLR) were the most commonly used method with a few studies also incorporating principle component regression (PCR) (Gislum et al., 2004; Hattey et al., 1994; Rébufa et al., 2018; Shao and He, 2013). It was found that NIRS calibrations for macronutrients generated using PLSR were more reliable compared to SMLR and PCR in terms of median Rc (PLSR = 0.93, SMLR = 0.87) and median Rv (PLSR = 0.87, SMLR = 0.76) (Appendix B, Table A4). This finding is also true for micronutrient NIRS calibrations, providing a generally lower median Rc and Rv (Appendix B, Table A4). The SEP/RMSEP median was higher for SMLR of both macro- (PLSR = 0.12%, SMLR = 0.58% ppm) and micronutrients (PLSR = 5.59 $mg\,kg^{-1}$, SMLR = 10.88 $mg\,kg^{-1}$) (Appendix B, Table A4). Surprisingly, SMLR has been widely used for NIRS foliar nutrient analysis (Grossman et al., 1996; Huang et al., 2004), although it is well-known that this method has limitations in spectral modeling (Jie et al., 2014; Ramoelo et al., 2011). Only a few studies used machine learning methods for modeling, for example, Shao and He (2013), suggested the use of least squares-supported vector machine (LS-SVM) combined with ICA as a procedure in estimating micronutrients in rice leaves. In contrast, many studies in soil spectroscopy used machine learning models on large soil spectra library (e.g., Ng et al., 2019). Studies on leaf samples are still limited in sample size, with a minimum of 10 and maximum of 1550. The leaf of different plant species would be different and cannot be combined as done in soil spectra.

3.3 Dry vs fresh samples

Three sample preparations for NIRS was found from reviewed studies, namely (1) fresh and intact leaves directly in the field (fresh, intact leaves), (2) fresh leaves removed from the plants which were scanned in laboratory conditions (fresh, removed leaves), or (3) dried and ground leaf samples (dried, ground leaves). The ability to non-destructively measure plant leaf nutrients in situ and bypass time-consuming laboratory analysis is the main target of NIRS investigation (Van Maarschalkerweerd and Husted, 2015); hence, scanning fresh, intact leaves would be the most ideal aim. Most reviewed studies conducted NIRS on dried, ground leaf samples, except for Menesatti et al. (2010), Ulissi et al. (2011), Rotbart et al. (2013), Tarpley et al. (2000), and Zerner and Parker (2019). In the few studies that assessed fresh leaves either intact or removed, it was found that the calibrations generated were generally reliable; however, within these studies, there were poor calibrations such as ones built by Rotbart et al. (2013), the P calibration of Menesatti et al. (2010), and the N calibration of Tarpley et al. (2000) which show the inconsistencies of using fresh leaf samples.

Only a few studies compared the calibration of fresh leaf samples and dried, ground leaf samples (Zerner and Parker, 2019; Rotbart et al. 2013). Zerner and Parker (2019) assessed the NIRS calibration of fresh and intact wheat leaf to estimate nitrogen content ($Rc = 0.82$, $SEP = 0.64\%$) which performed slightly lower compared to dried and ground wheat leaves ($Rc = 0.94$, $SEP = 0.35\%$); however, no validation was provided in this study. Rotbart et al. (2013) assessed calibrations of dried, ground olive leaves, and fresh removed leaves, which showed that dried, ground samples produced a significantly better calibration. Both studies demonstrated that dried and ground samples produce a more accurate calibration for NIRS compared to fresh leaf samples (Rotbart et al., 2013; Van Maarschalkerweerd and Husted, 2015).

This poorer calibration of fresh and intact samples can be attributed to the surface condition, particle size, and moisture effect which affect the strength of the NIR absorption. This can be seen in Fig. 5, where the reflectance spectra of dried, ground leaves are quite different in terms of pattern and have a much higher reflectance compared to the spectra of fresh. Moreover, Fig. 5 shows that there is more consistency in dried, ground leaf spectra, where the spectra of fresh, intact leaves are more scattered and variable between replicates. Removing moisture and decreasing the leaf samples to a finer and more uniform particles size improved the path length for

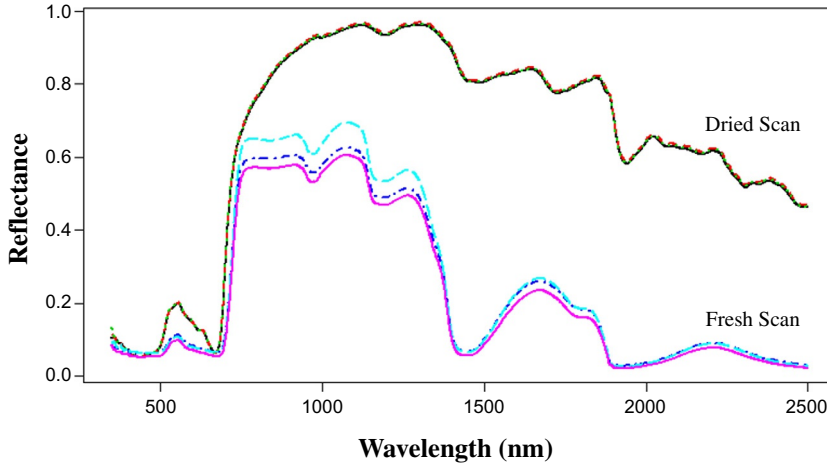

Fig. 5 Reflectance spectra (three replicates) of fresh, intact cotton leaves taken in-glasshouse conditions (field conditions) and reflectance spectra of the same leaves after it was dried, ground, and scanned in laboratory conditions. The reflectance spectra of both samples are quite different in pattern, and the dried, ground leaf samples appear significantly higher.

incidence light and reduced the disturbance from O—H vibrations of water (Galvez-Sola et al., 2015; Ludwig and Khanna, 2001).

3.4 Field vs laboratory application

Most studies that assessed NIRS on fresh leaves were done for removed leaves, whereas studies on fresh, intact leaves are rare and only found in two studies (Tarpley et al., 2000; Zerner and Parker, 2019). As mentioned previously, Zerner and Parker (2019) found that NIRS calibration for predicting N content of fresh, intact wheat leaves was reasonable compared to the more accurate dried, ground leaf samples. The other study that assessed field application of NIRS was Tarpley et al. (2000) on cotton leaves, which also showed reasonable success; however, the study only used a small number of samples. Although calibrations from fresh, intact leaf samples are good, there are still several issues that arise from field application of NIRS:

1) moisture significantly affects the NIR spectral data (Lobell and Asner, 2002; Rotbart et al., 2013),
2) temperature changes the composition of organic compounds in leaf tissue which creates biases in the model (Nicolai et al., 2007; Roger et al., 2003),

3) leaf structure and orientation affects the spectra data and obscuring the readings (Rotbart et al., 2013), and
4) unpredictable solar radiation (Rotbart et al., 2013; Tarpley et al., 2000).

Water is one of the most limiting factors in NIRS (Ramoelo et al., 2011; Soriano-Disla et al., 2017). It strongly affects the NIR spectra at certain wavelengths (centered at 1200, 1400 and 1900 nm) (Fig. 7) (Alchanatis et al., 2005; Jie et al., 2014; Rotbart et al., 2013). These water-affected regions are reported to have a high standard deviation which could lead to misinformation regarding any correlative relationship between a nutrient and the NIR spectra (Cozzolino and Moron, 2004). Temperature, on the other hand, affects the abundance of organic substances and the relative absorbance of the different chemical bonds in the compounds (Nicolai et al., 2007) which creates variability in the readings (Minasny et al., 2011; Roger et al., 2003). The effect of moisture and temperature has mainly translated into bias, and it was suggested that calibrations should include samples with variable moisture and temperature to overcome this issue; however, it is complicated and impractical. Minasny et al. (2011) and Roger et al. (2003) suggested an adjustment method to remove the external effects from NIR spectra, such as moisture from soil samples and temperature in sugar cane analysis, using the external parameter orthogonal (EPO) algorithm. A combination of EPO and PLSR would allow the development of a robust model that can be used in the field.

Removing leaves from the plants and conducting scans in a controlled environment (fresh, removed leaves) would be a better method as it avoids external factors found in the field, mostly temperature. Current studies have not assessed the effect of removing leaves from plants on NIR spectra, which would be essential in understanding the reliability of fresh, removed leaf samples. As can be seen in Fig. 6, removing leaves from the plant increases the reflectance in the NIR range, and it continues to increase after removal. Although it alters the reflectance, the spectra patterns are relatively unmodified compared to the change in the spectra of dried and ground leaf spectra in Fig. 5.

The current availability of low cost, miniaturized NIRS with limited wavelengths offer the possibility for scanning in-field or glasshouse conditions (Bogue, 2016; Sharififar et al., 2019; Walsh et al., 2000). Moreover, the automation of these low cost and portable NIR spectrometers can potentially provide a high throughput analysis of nutrient contents in leaves, where current high throughput analysis are restricted inside glasshouse conditions for estimating physiological traits such as stress level, chlorophyll content, etc. (Pandey et al., 2017).

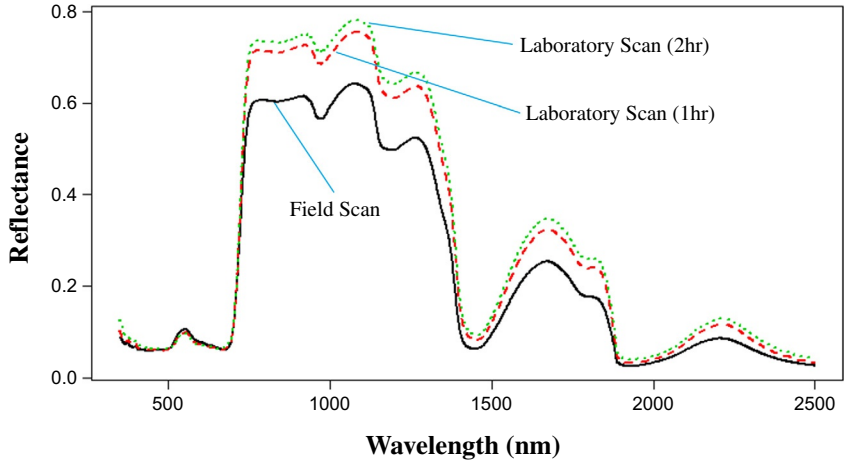

Fig. 6 Reflectance spectra of intact cotton leaves taken in-glasshouse conditions (field conditions) and laboratory condition at 1 and 2 h after removal from plants. The overall reflectance at wavelength 750–1400 nm, 1500–1800 nm, and 2200–2300 nm appears to be higher as the leaves are removed from the plants and continues to increase after removal.

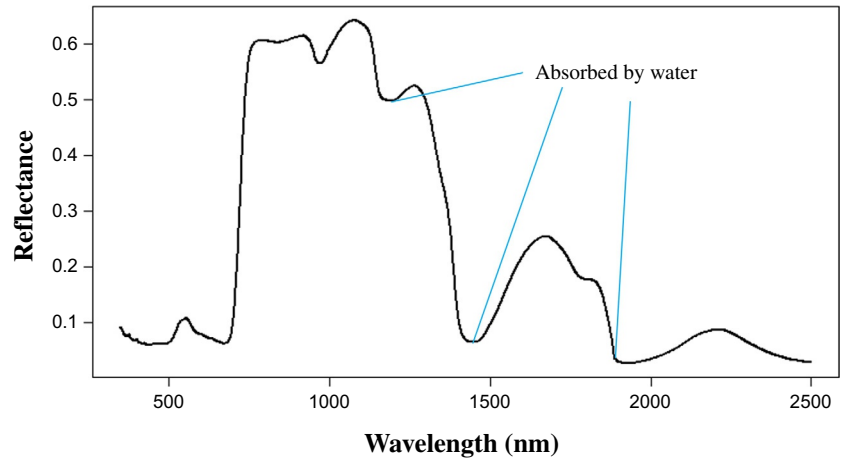

Fig. 7 Reflectance spectra of a cotton leaf showing part of the spectra that are correlated with the absorbance of water (O—H bond) at 1200, 1400 and 1900 nm. *Based on Jie, W., Hua-Bing, Z., Chang-Wei, S., Cai-Xia, D., Yang-Chun, X., 2014. Determination of nitrogen concentration in fresh pear leaves by visible/near-infrared reflectance spectroscopy. Agron. J. 106, 1867–1872.*

4. Conclusions

Current studies have shown that NIRS has a large potential to be used to measure crop nutrients at a crop/leaf level. Calibrations for various macronutrients (N, P, K, Ca, Mg) and micronutrients (Fe, Mn, Zn, Cu, Al, Na, and B) have been reported for different plants with good success. Predictions were more accurate and robust for macronutrients due to the higher concentrations and stronger correlations with NIR-active organic compounds in the leaf. Nevertheless, several micronutrients were also reported to be well predicted by NIR spectra, especially Fe.

Due to the large number of wavelength variables used in NIR spectra and reflectance scatter, these raw spectra are subjected to various transformations prior to multivariate analysis to increase the signal to noise ratio, improving the robustness of the consequent calibration. Partial least squares regression (PLSR) was found to be universally better compared to multiple linear regression and principal component regression in prediction accuracy. There are novel approaches that are still not explored in leaf studies, such as the use of machine learning algorithms combined with variables selection methods that were found to outperform PLSR in soil studies.

Most studies on leaf nutrient analysis using NIRS focused on dried and ground leaves. The few studies that assessed nutrient assessment on fresh leaves were under laboratory conditions. The application of NIRS in-field conditions is still restricted due to external limiting factors such as moisture, temperature, leaf orientation, and unpredictable solar radiation that prevent the development of robust calibration. The review strongly indicates that NIRS has the potential for in-field or in-glasshouse application, as a reliable and rapid method that can be used by farmers or consultants for crop nutrient management.

Appendix A. Compiled data from reviewed studies used to calculate the statistical distributions of Tables 2–7

Table A1 Shows the different nutrients assessed by various studies with their calibration and validation parameters (calibration R^2 = Rc, standard error of calibration/root mean squared error of calibration = SEC/RMSEC, validation R^2 = Rv, standard error of prediction/root mean squared error of prediction = SEP/RMSEP and bias).

Nutrient	Type	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias	Spectral range	Analysis	Dried/ fresh	Reference
P	Macronutrient	0.988	0.008	0.988	0.007	0.009	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
P	Macronutrient	0.94	0.005	0.62	0.016		NIR	PLSR	Dried	Rossa et al. (2015)
P	Macronutrient	0.74	0.038	0.52	0.051	0.008	NIR	SMLR	Dried	Liao et al. (2012)
P	Macronutrient	0.92	0.013	0.65	0.014		NIR	PLSR	Dried	Petisco et al. (2005)
P	Macronutrient	0.94	0.011	0.74	0.011		NIR	SMLR	Dried	Petisco et al. (2005)
P	Macronutrient	0.86	0.03	0.57	0.04		NIR	SMLR	Dried	Larrahondo et al. (2001)
P	Macronutrient	0.7	0.027	0.53	0.031	0.0005	NIR	SMLR	Dried	De Aldana et al. (1995)
P	Macronutrient	0.909	0.024		0.034		NIR	PLSR	Dried	González-Martín et al. (2007)
P	Macronutrient	0.915	0.004	0.429	0.018		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
P	Macronutrient	0.91	0.015		0.018		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
P	Macronutrient	0.9	0.017	0.69	0.027		Vis-NIR	PLSR	Dried	Chen et al. (2002)
P	Macronutrient	0.80		0.68			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)

Continued

Table A1 Shows the different nutrients assessed by various studies with their calibration and validation parameters (calibration R^2 = Rc, standard error of calibration/root mean squared error of calibration = SEC/RMSEC, validation R^2 = Rv, standard error of prediction/root mean squared error of prediction = SEP/RMSEP and bias).—cont'd

Nutrient	Type	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias	Spectral range	Analysis	Dried/fresh	Reference
N	Macronutrient	0.97	0.106	0.93	0.14		NIR	PLSR	Dried	Bolster et al. (1996)
N	Macronutrient	0.98	0.09	0.99	0.06	0.0004	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
N	Macronutrient	0.99	0.106	0.97	0.15	0.11	NIR	PLSR	Dried	Hattey et al. (1994)
N	Macronutrient	0.98	0.09	0.9	0.12		NIR	SMLR	Dried	Larrahondo et al. (2001)
N	Macronutrient	0.9	0.106	0.84	0.121		NIR	SMLR	Dried	Liao et al. (2012)
N	Macronutrient	0.99	0.059	0.94	0.076		NIR	PLSR	Dried	Petisco et al. (2005)
N	Macronutrient	0.99	0.066	0.94	0.079		NIR	SMLR	Dried	Petisco et al. (2005)
N	Macronutrient	0.96	0.24	0.92	0.29		NIR	PLSR	Dried	Rébufa et al. (2018)
N	Macronutrient	0.95	0.117	0.95	0.122		NIR	PLSR	Dried	Rossa et al. (2015)
N	Macronutrient	0.98	0.11	0.98	0.11		NIR	SMLR	Dried	Wessman et al. (1988)
N	Macronutrient	0.989	0.012	0.989	0.009		NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
N	Macronutrient	0.98	0.077	0.94	0.079	0.0071	NIR	SMLR	Dried	De Aldana et al. (1995)
N	Macronutrient	0.81	0.43	0.94	0.35		Vis	PLSR	Fresh	Ulissi et al. (2011)
N	Macronutrient	0.94	0.233	0.9	0.33	0.024	Vis-NIR	SMLR	Dried	Card et al. (1988)
N	Macronutrient	0.98	0.18	0.98	0.19		Vis-NIR	PLSR	Dried	Gislum et al. (2004)
N	Macronutrient	0.945	0.09	0.909	0.051	0.0004	Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)

N	Macronutrient	0.889	0.106	0.828	0.12		Vis-NIR	PLSR	Dried	Min and Lee (2005)
N	Macronutrient	0.916	0.094	0.816	0.126		Vis-NIR	SMLR	Dried	Min and Lee (2005)
N	Macronutrient	0.854	0.356	0.776	0.44		Vis-NIR	SMLR	Dried	Min et al. (2006)
N	Macronutrient	0.866	0.34	0.818	0.4		Vis-NIR	PLSR	Dried	Min et al. (2006)
N	Macronutrient	0.48	0.11		0.12		Vis-NIR	PLSR	Fresh	Rotbart et al. (2013)
N	Macronutrient	0.9	0.12		0.15		Vis-NIR	PLSR	Dried	Rotbart et al. (2013)
N	Macronutrient	0.88		0.71			Vis-NIR	PLSR	Fresh	Tarpley et al. (2000)
N	Macronutrient	0.961	0.127	0.847	0.448		Vis-NIR	PLSR	Fresh	Jie et al. (2014)
N	Macronutrient	0.82			0.64		Vis-NIR	PLSR	Fresh	Zerner and Parker (2019)
N	Macronutrient	0.85		0.77			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
K	Macronutrient	0.94	0.09	0.88	0.12	0.0063	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
K	Macronutrient	0.979	0.013	0.979	0.009	0.0013	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
K	Macronutrient	0.95	0.078	−0.1	0.303		NIR	PLSR	Dried	Rossa et al. (2015)
K	Macronutrient	0.7	0.225	0.37	0.331	0.066	NIR	SMLR	Dried	Liao et al. (2012)
K	Macronutrient	0.94	0.079	0.48	0.136		NIR	PLSR	Dried	Petisco et al. (2008)
K	Macronutrient	0.86	0.12	0.42	0.117		NIR	SMLR	Dried	Petisco et al. (2008)
K	Macronutrient	0.99	0.11	0.64	0.469		NIR	PLSR	Dried	Rébufa et al. (2018)

Continued

Table A1 Shows the different nutrients assessed by various studies with their calibration and validation parameters (calibration R^2 = Rc, standard error of calibration/root mean squared error of calibration = SEC/RMSEC, validation R^2 = Rv, standard error of prediction/root mean squared error of prediction = SEP/RMSEP and bias).—cont'd

Nutrient	Type	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias	Spectral range	Analysis	Dried/fresh	Reference
K	Macronutrient	0.943	0.111	0.852	0.172		NIR	PLSR	Dried	Ciavarella et al. (1998)
K	Macronutrient	0.951	0.131	0.929	0.179		NIR	PLSR	Dried	Ciavarella et al. (1998)
K	Macronutrient	0.933	0.101	0.887	0.116		NIR	PLSR	Dried	Ciavarella et al. (1998)
K	Macronutrient	0.88	0.11	0.37	0.11		NIR	SMLR	Dried	Larrahondo et al. (2001)
K	Macronutrient	0.78	0.189	0.71	0.195	0.0158	NIR	SMLR	Dried	De Aldana et al. (1995)
K	Macronutrient	0.899	0.118		0.165		NIR	PLSR	Dried	González-Martín et al. (2007)
K	Macronutrient	0.995	0.039	0.991	0.058		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
K	Macronutrient	0.79	0.68	0.73	0.78		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)
K	Macronutrient	0.86	0.155		0.248		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
K	Macronutrient	0.59			0.43		Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
S	Macronutrient	0.18	0.042		0.043		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
S	Macronutrient	0.73	0.19	0.64	0.24		NIR	PLSR	Dried	Rébufa et al. (2018)
S	Macronutrient	0.8	0.01	0.49	0.013		Vis-NIR	PLSR	Dried	Stubbs et al. (2010)

Ca	Macronutrient	0.98	0.25	0.98	0.25	0.0627	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
Ca	Macronutrient	0.974	0.009	0.974	0.007	0.009	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
Ca	Macronutrient	0.93	0.039	0.42	0.123		NIR	PLSR	Dried	Rossa et al. (2015)
Ca	Macronutrient	0.878	0.146		0.275		NIR	PLSR	Dried	González-Martín et al. (2007)
Ca	Macronutrient	0.95	0.063	0.91	0.06		NIR	PLSR	Dried	Petisco et al. (2005)
Ca	Macronutrient	0.9	0.087	0.85	0.067		NIR	SMLR	Dried	Petisco et al. (2005)
Ca	Macronutrient	0.88	0.092	0.85	0.097	0.0022	NIR	SMLR	Dried	De Aldana et al. (1995)
Ca	Macronutrient	0.77	0.06	0.69	0.06		NIR	SMLR	Dried	Larrahondo et al. (2001)
Ca	Macronutrient	0.97	0.134	0.76	0.567		NIR	PLSR	Dried	Rébufa et al. (2018)
Ca	Macronutrient	0.995	0.085	0.947	0.304		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
Ca	Macronutrient	0.85	0.044		0.068		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
Ca	Macronutrient	0.39	0.59	0.22	0.95		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)
Ca	Macronutrient	0.59		0.47			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
Mg	Macronutrient	0.84	0.05	0.89	0.05		NIR	PLSR	Dried	Galvez-Sola et al. (2015)
Mg	Macronutrient	0.976	0.009	0.974	0.004	0.005	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
Mg	Macronutrient	0.94	0.066	0.94	0.068		NIR	PLSR	Dried	Rossa et al. (2015)

Continued

Table A1 Shows the different nutrients assessed by various studies with their calibration and validation parameters (calibration R^2 = Rc, standard error of calibration/root mean squared error of calibration = SEC/RMSEC, validation R^2 = Rv, standard error of prediction/root mean squared error of prediction = SEP/RMSEP and bias).—cont'd

Nutrient	Type	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias	Spectral range	Analysis	Dried/fresh	Reference
Mg	Macronutrient	0.88	0.01	0.48	0.011		NIR	PLSR	Dried	Petisco et al. (2005)
Mg	Macronutrient	0.86	0.011	0.47	0.013		NIR	SMLR	Dried	Petisco et al. (2005)
Mg	Macronutrient	0.84	0.016	0.85	0.018	0.0055	NIR	SMLR	Dried	De Aldana et al. (1995)
Mg	Macronutrient	0.77	0.03	0.5	0.06		NIR	SMLR	Dried	Larrahondo et al. (2001)
Mg	Macronutrient	0.982	0.02	0.944	0.048		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
Mg	Macronutrient	0.66	0.028		0.036		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
Mg	Macronutrient	0.44	0.18	0.27	0.22		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)
Mg	Macronutrient	0.76		0.64			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
Fe	Micronutrient	0.77	44	0.96	60.4	−3.23	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
Fe	Micronutrient	0.989	0.15	0.974	0.623	1.171	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
Fe	Micronutrient	0.98	0.658	0.75	0.022		NIR	PLSR	Dried	Rossa et al. (2015)
Fe	Micronutrient	0.71	28.41	0.69	28.67	−7.45	NIR	SMLR	Dried	Liao et al. (2012)
Fe	Micronutrient	0.948	111		237		NIR	PLSR	Dried	González-Martín et al. (2007)

Fe	Micronutrient	0.79	10.05	0.67	8.46		NIR	PLSR	Dried	Petisco et al. (2008)
Fe	Micronutrient	0.81	9.1	0.64	8.25		NIR	SMLR	Dried	Petisco et al. (2008)
Fe	Micronutrient	0.74	50	0.56	16	3.39	NIR	SMLR	Dried	De Aldana et al. (1995)
Fe	Micronutrient	0.98	61	0.81	16.5		NIR	PLSR	Dried	Rébufa et al. (2018)
Fe	Micronutrient	0.946	4.38	0.917	6.054		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
Fe	Micronutrient	0.619			20.65	−12.35	Vis-NIR	PLSR	Dried	Shao and He (2013)
Fe	Micronutrient	0.84	71		92		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
Fe	Micronutrient	0.78	7.6	0.57	13.9		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)
Mn	Micronutrient	0.77	4.99	0.53	5.55	−0.392	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
Mn	Micronutrient	0.976	0.034	0.976	0.543	0.8	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
Mn	Micronutrient	0.91	105.5	0.35	303.0	0.976	NIR	PLSR	Dried	Rossa et al. (2015)
Mn	Micronutrient	0.843	5.4		9.6		NIR	PLSR	Dried	González-Martín et al. (2007)
Mn	Micronutrient	0.74	50	0.71	54	6.82	NIR	SMLR	Dried	De Aldana et al. (1995)
Mn	Micronutrient	0.68	31.75	0.59	37.14	−5.35	NIR	SMLR	Dried	Liao et al. (2012)
Mn	Micronutrient	0.84	3.064	0.925	1.637		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
Mn	Micronutrient	0.41	15.2	0.21	21.3		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)

Continued

Table A1 Shows the different nutrients assessed by various studies with their calibration and validation parameters (calibration R^2 = Rc, standard error of calibration/root mean squared error of calibration = SEC/RMSEC, validation R^2 = Rv, standard error of prediction/root mean squared error of prediction = SEP/RMSEP and bias).—cont'd

Nutrient	Type	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias	Spectral range	Analysis	Dried/fresh	Reference
Mn	Micronutrient	0.37	9			10	Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
Zn	Micronutrient	0.84	3.23	0.88	3.34		NIR	PLSR	Dried	Galvez-Sola et al. (2015)
Zn	Micronutrient	0.979	0.002	0.979	0.035	0.96	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
Zn	Micronutrient	0.91	1.081	0.07	3.29		NIR	PLSR	Dried	Rossa et al. (2015)
Zn	Micronutrient	0.72	3.8	0.62	3.4	−0.66	NIR	SMLR	Dried	De Aldana et al. (1995)
Zn	Micronutrient	0.853	2		3.5		NIR	PLSR	Dried	González-Martín et al. (2007)
Zn	Micronutrient	0.02	28.41	0	11.38	−1.22	NIR	SMLR	Dried	Liao et al. (2012)
Zn	Micronutrient	0.9	8.27	0.72	7.17		NIR	PLSR	Dried	Petisco et al. (2008)
Zn	Micronutrient	0.76	5.98	0.53	6.69		NIR	SMLR	Dried	Petisco et al. (2008)
Zn	Micronutrient	0.905	1.107	0.889	0.972		Vis-NIR	PLSR	Fresh	Menesatti et al. (2010)
Zn	Micronutrient	0.673			5.592	1.523	Vis-NIR	PLSR	Dried	Shao and He (2013)
Zn	Micronutrient	0.32	2		3		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)

Zn	Micronutrient	0.71	5.9	0.4	8.3		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)
Zn	Micronutrient	0.45		0.24			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
Cu	Micronutrient	0.22	1.29	0.36	1.47	0.12	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
Cu	Micronutrient	0.98	0.223	0.89	0.563		NIR	PLSR	Dried	Rossa et al. (2015)
Cu	Micronutrient	0.987	0.015	0.987	0.045	0.993	NIR	PLSR/SMLR	Dried	Yarce and Rojas (2012)
Cu	Micronutrient			0.5	5.7		NIR	PLSR	Fresh	Van Maarschalkerweerd et al. (2013)
Cu	Micronutrient	0.82	0.84	0.59	0.89	−0.18	NIR	SMLR	Dried	De Aldana et al. (1995)
Cu	Micronutrient	0.02	5.34	0	10.37	0.17	NIR	SMLR	Dried	Liao et al. (2012)
Cu	Micronutrient	0.89	0.8	0.32	1.03		NIR	PLSR	Dried	Petisco et al. (2008)
Cu	Micronutrient	0.71	1.1	0.52	0.74		NIR	SMLR	Dried	Petisco et al. (2008)
Cu	Micronutrient	0.39	2		2.3		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
Cu	Micronutrient	0.52	2.3	0.26	3.5		Vis-NIR	PLSR	Dried	Villatoro-Pulido et al. (2012)
Cu	Micronutrient	0.73		0.62			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
B	Micronutrient	0.56	59	0.47	53.2	0.0521	NIR	PLSR	Dried	Galvez-Sola et al. (2015)
B	Micronutrient	0.8	9.9		13		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)

Continued

Table A1 Shows the different nutrients assessed by various studies with their calibration and validation parameters (calibration R^2 = Rc, standard error of calibration/root mean squared error of calibration = SEC/RMSEC, validation R^2 = Rv, standard error of prediction/root mean squared error of prediction = SEP/RMSEP and bias).—cont'd

Nutrient	Type	Rc	SEC/RMSEC	Rv	SEP/RMSEP	Bias	Spectral range	Analysis	Dried/ fresh	Reference
B	Micronutrient	0.71		0.57			Vis-NIR	PLSR	Fresh	Santoso et al. (2019)
Na	Micronutrient	0.94	0.002	0.29	0.007		NIR	PLSR	Dried	Rossa et al. (2015)
Na	Micronutrient	0.63	125		147		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)
Na	Micronutrient	0.79	710	0.44	620	−0.18	NIR	SMLR	Dried	De Aldana et al. (1995)
Na	Micronutrient	0.979	92.8		195		NIR	PLSR	Dried	González-Martín et al. (2007)
Al	Micronutrient	0.79	74		93		Vis-NIR	PLSR	Dried	Halgerson et al. (2004)

Furthermore, the table shows whether the studies used visible spectral range (400–700 nm) or NIR spectral rang or in combination (400–2500 nm), used dried or fresh leaf tissue samples, and the multivariate analysis (partial least squares regression (PLSR) or stepwise multilinear regression (SMLR)).

Appendix B. Statistical distribution of calibrations and validations: accuracy parameters for different nutrient types and methodologies

Table A2 The median of the calibration and validation parameters of macronutrients (N, P, K, Ca, Mg (%)) and micronutrients (Fe, Mn, Zn, Cu (mg kg^{-1})), where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error.

	Macronutrients				Micronutrients		
	Rc	Rv	SEP/RMSEP		Rc	Rv	SEP/RMSEP
N	0.95	0.93	0.12	Fe	0.81	0.72	16.00
P	0.91	0.62	0.02	Mn	0.77	0.59	9.60
K	0.94	0.72	0.17	Zn	0.80	0.62	3.45
S	0.73	0.57	0.04	Cu	0.71	0.50	1.25
Ca	0.92	0.85	0.11	Na	0.87	0.37	171.00
Mg	0.85	0.85	0.04	B	0.68	0.47	33.10
Total	0.91	0.79	0.08	Total	0.79	0.55	16.00

Table A3 The median of the calibration and validation parameters of macronutrients, micronutrients and total sample using different sample preparation, i.e., dried or fresh, where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error.

	Dried			Fresh		
	Rc	Rv	SEP/RMSEP	Rc	Rv	SEP/RMSEP
Macronutrients	0.91	0.83	0.11	0.95	0.94	0.21
Micronutrients	0.79	0.58	8.25	0.91	0.90	3.67
Total	0.85	0.71	4.18	0.93	0.92	1.94

Table A4 The median of the calibration and validation parameters of macronutrients and micronutrients using different multivariate analysis method, i.e., partial least squares regression (PLSR) or stepwise multilinear regression (SMLR), where Rc = calibration R^2, Rv = validation R^2, SEP/RMSEP = standard error prediction/root mean square error.

	PLSR			SMLR		
	Rc	Rv	SEP/RMSEP	Rc	Rv	SEP/RMSEP
Macronutrients	0.93	0.87	0.12	0.87	0.76	0.58
Micronutrients	0.78	0.57	5.59	0.73	0.70	10.88

Appendix C. Sample nutrient content value range of the reviewed studies

Table A5 The macronutrient (N, P, K, S, Ca, and Mg) value (%) range found in the reviewed studies with the associated plant species.

Nutrient	Value range (%)		Sample	Reference
N	**0.69**	**3.51**	**Coniferous, deciduous, and shrub woody tree foliage**	**Bolster et al. (1996)**
N	0.363	3.017	Coniferous, deciduous, and shrub woody tree foliage	Card et al. (1988)
N	0.68	2.9	Natural grass	De Aldana et al. (1995)
N	1.07	3.86	Citrus	Galvez-Sola et al. (2015)
N	0.6	6.26	Red fescue and Perennial ryegrass	Gislum et al. (2004)
N	1.66	4.18	Cotton	Hattey et al. (1994)
N	1.696	4.004	Pear	Jie et al. (2014)
N	1.05	2.91	Sugarcane	Larrahondo et al. (2001)
N	1.776	3.621	Fingered citron	Liao et al. (2012)

Table A5 The macronutrient (N, P, K, S, Ca, and Mg) value (%) range found in the reviewed studies with the associated plant species.—cont'd

Nutrient	Value range (%)		Sample	Reference
N	**0.69**	**3.51**	**Coniferous, deciduous, and shrub woody tree foliage**	**Bolster et al. (1996)**
N	2.8	2.24	Citrus	Menesatti et al. (2010)
N	1.99	3.38	Citrus	Min and Lee (2005)
N	2.47	5.25	Chinese cabbage	Min et al. (2006)
N	0.66	4.5	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2005)
N	3	6.1	Moringa	Rébufa et al. (2018)
N	2.41	4.08	Yerba mate	Rossa et al. (2015)
N	0.59	2.51	Olives	Rotbart et al. (2013)
N	1.80	3.22	Palm oil	Santoso et al. (2019)
N	1.82	4.27	Cotton	Tarpley et al. (2000)
N	0.43	3.06	Coniferous, deciduous, and shrub woody tree foliage	Wessman et al. (1988)
N	0.80	7.20	Wheat	Zerner and Parker (2019)
P	0.012	0.345	Sugarcane	Chen et al. (2002)
P	0.09	0.32	Natural grass	De Aldana et al. (1995)
P	0.111	0.4	Alfalfa	González-Martín et al. (2007)
P	0.28	0.34	Alfalfa	Halgerson et al. (2004)
P	0.11	0.32	Sugarcane	Larrahondo et al. (2001)
P	0.038	0.341	Fingered citron	Liao et al. (2012)
P	0.091	0.224	Citrus	Menesatti et al. (2010)
P	0.024	0.297	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2005)

Continued

Table A5 The macronutrient (N, P, K, S, Ca, and Mg) value (%) range found in the reviewed studies with the associated plant species.—cont'd

Nutrient	Value range (%)		Sample	Reference
N	**0.69**	**3.51**	**Coniferous, deciduous, and shrub woody tree foliage**	**Bolster et al. (1996)**
P	0.08	0.177	Yerba mate	Rossa et al. (2015)
P	0.20	0.80	Palm oil	Santoso et al. (2019)
K	0.48	2.47	Natural grass	De Aldana et al. (1995)
K	0.42	1.92	Citrus	Galvez-Sola et al. (2015)
K	1.49	2.91	Alfalfa	González-Martín et al. (2007)
K	1.6	2.4	Alfalfa	Halgerson et al. (2004)
K	0.81	1.94	Sugarcane	Larrahondo et al. (2001)
K	0.421	2.91	Fingered citron	Liao et al. (2012)
K	0.346	1.73	Citrus	Menesatti et al. (2010)
K	0.15	1.98	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2008)
K	0.26	4.6	Moringa	Rébufa et al. (2018)
K	0.34	1.8	Yerba mate	Rossa et al. (2015)
K	0.86	1.49	Palm oil	Santoso et al. (2019)
K	2.89	7.1	Rocket	Villatoro-Pulido et al. (2012)
K	0.44	2.7	Orange	Ciavarella et al. (1998)
K	0.59	1.9	Grape	Ciavarella et al. (1998)
K	0.23	4.5	Rice	Ciavarella et al. (1998)

Table A5 The macronutrient (N, P, K, S, Ca, and Mg) value (%) range found in the reviewed studies with the associated plant species.—cont'd

Nutrient	Value range (%)		Sample	Reference
N	**0.69**	**3.51**	**Coniferous, deciduous, and shrub woody tree foliage**	**Bolster et al. (1996)**
S	0.35	0.43	Alfalfa	Halgerson et al. (2004)
S	0.43	1.78	Moringa	Rébufa et al. (2018)
S	0.008	0.17	Wheat	Stubbs et al. (2010)
Ca	0.16	1.3	Natural grass	De Aldana et al. (1995)
Ca	0.89	6.77	Citrus	Galvez-Sola et al. (2015)
Ca	0.86	2.47	Alfalfa	González-Martín et al. (2007)
Ca	2.1	2.7	Alfalfa	Halgerson et al. (2004)
Ca	0.16	0.55	Sugarcane	Larrahondo et al. (2001)
Ca	0.318	10.3	Citrus	Menesatti et al. (2010)
Ca	0.1	2.06	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2005)
Ca	0.5	3.7	Moringa	Rébufa et al. (2018)
Ca	0.012	0.545	Yerba mate	Rossa et al. (2015)
Ca	0.42	0.93	Palm oil	Santoso et al. (2019)
Ca	0.28	6.4	Rocket	Villatoro-Pulido et al. (2012)
Mg	0.08	0.26	Natural grass	De Aldana et al. (1995)
Mg	0.14	0.8	Citrus	Galvez-Sola et al. (2015)
Mg	0.38	0.54	Alfalfa	Halgerson et al. (2004)

Continued

Table A5 The macronutrient (N, P, K, S, Ca, and Mg) value (%) range found in the reviewed studies with the associated plant species.—cont'd

Nutrient	Value range (%)		Sample	Reference
N	**0.69**	**3.51**	**Coniferous, deciduous, and shrub woody tree foliage**	**Bolster et al. (1996)**
Mg	0.09	0.42	Sugarcane	Larrahondo et al. (2001)
Mg	0.218	0.927	Citrus	Menesatti et al. (2010)
Mg	0.018	0.217	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2008)
Mg	0.08	0.995	Yerba Mate	Rossa et al. (2015)
Mg	0.16	0.39	Palm oil	Santoso et al. (2019)
Mg	0.24	0.69	Rocket	Villatoro-Pulido et al. (2012)

Table A6 The micronutrient value (Al, B, Cu, Fe, Mn, Na, and Zn) (mg kg^{-1}) range found in the reviewed studies with the associated plant species.

Nutrient	Value range (mg kg^{-1})		Sample	Reference
Al	32	72	Alfalfa	Halgerson et al. (2004)
B	24.22	509.93	Citrus	Galvez-Sola et al. (2015)
B	40	84	Alfalfa	Halgerson et al. (2004)
B	7.52	25.82	Palm oil	Santoso et al. (2019)
Cu	1.3	10	Natural grass	De Aldana et al. (1995)
Cu	0.83	11.24	Alfalfa	Galvez-Sola et al. (2015)
Cu	8	14	Alfalfa	Halgerson et al. (2004)
Cu	0.5	78.63	Fingered citron	Liao et al. (2012)
Cu	2.5	14.7	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2008)

Table A6 The micronutrient value (Al, B, Cu, Fe, Mn, Na, and Zn) (mg kg^{-1}) range found in the reviewed studies with the associated plant species.—cont'd

Nutrient	Value range (mg kg^{-1})		Sample	Reference
Cu	1	44	Yerba mate	Rossa et al. (2015)
Cu	1.52	9.43	Palm oil	Santoso et al. (2019)
Cu	~28		Barley	Van Maarschalkerweerd et al. (2013)
Cu	5.9	18	Rocket	Villatoro-Pulido et al. (2012)
Fe	38	203	Natural grass	De Aldana et al. (1995)
Fe	35.94	637	Citrus	Galvez-Sola et al. (2015)
Fe	110	1870	Alfalfa	González-Martín et al. (2007)
Fe	93	121	Alfalfa	Halgerson et al. (2004)
Fe	43.29	483.59	Fingered citron	Liao et al. (2012)
Fe	66.9	198	Citrus	Menesatti et al. (2010)
Fe	30.5	162	Confierous, deciduous, and shrub woody tree foliage	Petisco et al. (2008)
Fe	50	2250	Moringa	Rébufa et al. (2018)
Fe	8	130	Yerba mate	Rossa et al. (2015)
Fe	39.95	134.25	Rice	Shao and He (2013)
Fe	69	273	Rocket	Villatoro-Pulido et al. (2012)
Mn	38	813	Natural grass	De Aldana et al. (1995)
Mn	18.69	70.48	Citrus	Galvez-Sola et al. (2015)
Mn	18	70	Alfalfa	González-Martín et al. (2007)
Mn	39	61	Alfalfa	Halgerson et al. (2004)
Mn	28.57	280.15	Fingered citron	Liao et al. (2012)

Continued

Table A6 The micronutrient value (Al, B, Cu, Fe, Mn, Na, and Zn) (mg kg^{-1}) range found in the reviewed studies with the associated plant species.—cont'd

Nutrient	Value range (mg kg^{-1})		Sample	Reference
Mn	6.69	42.3	Citrus	Menesatti et al. (2010)
Mn	236	1440	Yerba mate	Rossa et al. (2015)
Mn	3.43	68.1	Rocket	Villatoro-Pulido et al. (2012)
Na	500	7300	Natural grass	De Aldana et al. (1995)
Na	10	40	Alfalfa	González-Martín et al. (2007)
Na	133	543	Alfalfa	Halgerson et al. (2004)
Na	0.1	0.35	Yerba mate	Rossa et al. (2015)
Na	800	2800	Rocket	Villatoro-Pulido et al. (2012)
Zn	10	50	Natural grass	De Aldana et al. (1995)
Zn	9.01	43.92	Citrus	Galvez-Sola et al. (2015)
Zn	132	1950	Alfalfa	González-Martín et al. (2007)
Zn	22	28	Alfalfa	Halgerson et al. (2004)
Zn	11.78	87.97	Fingered citron	Liao et al. (2012)
Zn	6.29	24.8	Citrus	Menesatti et al. (2010)
Zn	7.75	82.8	Coniferous, deciduous, and shrub woody tree foliage	Petisco et al. (2008)
Zn	34	146	Yerba mate	Rossa et al. (2015)
Zn	7.98	26.97	Palm oil	Santoso et al. (2019)
Zn	9.085	49.93	Rice	Shao and He (2013)
Zn	32.7	67.1	Rocket	Villatoro-Pulido et al. (2012)

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