# Estimating mineral content of indigenous browse species using laboratory spectroscopy and Sentinel-2 imagery

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# ABSTRACT

Trees provide low-cost organic inputs, with the potential to improve livelihoods for rural communities. Understanding foliar nutrients of tree species is crucial for integration of trees into agroecosystems. The study explored nitrogen (N), phosphorus (P), potassium (K) and calcium (Ca) concentrations of nine browse species collected from the bushveld region of South Africa using wet analysis and laboratory spectroscopy in the region 400-2500nm, along with partial least squares (PLS) regression. We further explore the relationship between canopy reflectance of Sentinel-2 image and foliar N, P, K & Ca. Laboratory spectroscopy was significant for N estimation, while satellite imagery also revealed useful information about the estimation of nitrogen at landscape level. Nitrogen was highly correlated with spectral reflectance ( $R^2$ =0.72, p<0.05) for winter and ( $R^2$ =0.88, p<0.05) for summer, whilst prediction of phosphorus potassium and calcium were considered not accurate enough to be of practical use. Modelling the relationship using Sentinel-2 data showed lower correlations for nitrogen (R<sup>2</sup>=0.44, p<0.05) and the other nutrients when compared to the dried samples. The findings indicate that there is potential to assess and monitor resource quality of indigenous trees using nitrogen as key indicator. This multi-level remote sensing approach has promise for providing rapid plant nutrient analyses at different scales.

# Keywords:

Laboratory spectroscopy; Hyperspectral data; Multispectral data; Wet analysis; Nitrogen; Sentinel-2; Continuum removal; Partial least squares regression

# 1. Introduction

# 1.1 Trees and livelihoods

Trees are important natural assets, which play vital economic and environmental roles. They constitute fodder for livestock or they can be incorporated into the soil to improve fertility (Chepape *et al.*, 2011; Akinnifesi *et al.*, 2010). Fodder trees and shrubs contain appreciable amounts of nutrients that are deficient in other feed resources such as grasses especially during dry seasons (Lukhele & van Ryssen, 2000). The integration of trees in production landscapes is known as agroforestry. The system bestows a wide range of ecosystem benefits to improve the quality of life of rural households (Mbow *et al.*, 2014).

Due to the persistent threat of food shortages, projected climate change and rising prices of agricultural inputs, agroforestry has experienced special interest from research and development communities (Garrity *et al.*, 2006). It is considered a cost-effective and ecologically sound approach to enhance food security particularly in the era of adverse environmental conditions (Mbow *et al.*, 2014).

Indigenous trees demonstrate the potential to supplement exotic species due to the minimal impact they have on the environment (Mukolwe, 1999; Lukhele & van Ryssen, 2000; Tegegne, 2008). Possible applications include establishment of indigenous multipurpose trees on agro-ecological systems and on sensitive sites such as riparian zones, water-stressed catchments and land cleared of alien plants to improve land management and protect biodiversity (Everson *et al.*, 2011).

#### 1.2 Science-based agroforestry

The resource quality varies with the plant species, plant parts, the stage of maturity and whether the plant nodulates and fix nitrogen or not (Palm *et al.*, 2001). Plant materials are classified by taxonomic family, genus and species. The nutrient composition of some browse species has been investigated using conventional wet techniques (e.g. Lukhele & Ryssen, 2000). Methods based on tissue analysis have been widely applied due to their reliability. However, they are costly because they require use of reagents, time-consuming and destructive (Muñoz-Huerta *et al.*, 2013). A significant barrier to plant mineral analysis in general is the price versus the

perceived value by farmers (Rossa *et al.*, 2015). To overcome these limitations, efforts have been directed to the study and development of spectroscopy.

# 1.3 Laboratory spectroscopy

Absorption of electromagnetic radiation in the near infrared (NIR) and other parts of the electromagnetic spectrum reflects the molecular composition of a sample (Rossa *et al.*, 2015). The technique is widely accepted as a tool for analysis in fields such as agriculture and the food industry (İlknur ŞEN, 2003). The equipment used can record spectra for solid and liquid samples with no pre-treatment, provide spectra quickly and predict the physical and chemical parameters (van Maarschalkerweerd *et al.*, 2015).

Quantification of macronutrients and micronutrients by NIR spectroscopy in soils has been demonstrated by various studies (e.g. İlknur ŞEN, 2003; Awiti *et al.*, 2007). It is reported that measurement of soil N demonstrated good results whilst calibrations for P and K in soil were less successful (Ward *et al.*, 2011). Leaf spectroscopy has been used in analysis of macro- and micronutrients content in various crops (Riley & Cánaves, 2002; Yarce & Rojas, 2012).

## 1.4 Nutrient estimation using remote sensing

Monitoring foliar nutrients using traditional methods of leaf harvesting and transportation to laboratories for analysis implies a number of difficulties. Species of interest are sometimes inaccessible, because of dense overgrowth or they could be located in swamps (van Deventer *et al.*, 2015). Remote sensing techniques complement ground based monitoring systems. They essentially involve the ability to detect and characterise unique patterns of nutrient phenology across species, seasons and regions (Cho *et al.*, 2012).

In spite of the advances made in mapping foliar nutrients using remote sensing, the relationship between foliar nutrient concentration and spectral reflectance across species, season and ecosystems remains poorly understood (Ramoelo *et al.*, 2015). The relationship between foliar nutrients and spectral information of multipurpose trees in relation to seasonal variation is of significance in resource characterisation (van Deventer *et al.*, 2015).

The recent availability of time series of Sentinel-2 imagery at fine spatial resolution (10m) and high temporal frequency represents a significant step in the use of satellite data for monitoring forest resources (Simonetti *et al.*, 2017). The study therefore tested this method. The results offer an opportunity for monitoring and mapping nitrogen rich species that could be promoted in agroecosystems.

# 1.5 Study aim

The aim of the study was to investigate the utility of spectral data at the laboratory level and space-borne platforms in predicting the leaf nitrogen (N), phosphorus (P), potassium (K) and calcium (Ca) content of leguminous and non-legumes species in the Lowveld region of South Africa.



Figure 1: The workflow conceptualizing the processes followed in the study.

# 2. Materials and methods

# 2.1 General description of the study area

The study was conducted at the Wits Rural Facility (24°33'S; 31°1'E), in the central Lowveld, South Africa. The soil type is predominantly shallow sandy lithosols. The vegetation is typically lowland savanna, dominated by members of the Combretaceae (e.g. *Combretum collinum, C. apiculatum* and *Terminalia sericea*); and Mimosoideae (e.g. *Vachellia gerrardii, V. swazica* and *Dichrostachys cinerea*). The mean annual rainfall is 665±123mm, received mostly during the summer months. The mean annual temperature is approximately 22°C (Shackleton, 2001).

# 2.2 Data collection

2.2.1 Plant species investigated in the study

The data comprised of three (3) broad-leaved leguminous, 3 fine-leaved leguminous trees and 3 non-legume species, hereafter referred to as "**groups**" (Table 1).

Table 1:	Tree species	investigated	in the	study
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Species	Family	Group	Foliage
Bauhinia galpinii	Fabaceae	Broad-leaved,	Deciduous
		leguminous	
Philenoptera violacea	Fabaceae	Broad-leaved,	Deciduous
		leguminous	
Schotia brachypetala	Fabaceae	Broad-leaved,	Evergreen
		leguminous	
Peltophorum africanum	Fabaceae	Narrow-leaved,	Evergreen
		leguminous	
Dichrostachys cinerea	Fabaceae	Narrow-leaved,	Evergreen
		leguminous	
Vachellia gerrardii	Fabaceae	Narrow-leaved,	Evergreen
		leguminous	
Combretum apiculatum	Combretaceae	Broad-leaved,	Deciduous
		non-leguminous	
Terminalia sericea	Combretaceae	Broad-leaved,	Deciduous
		non-leguminous	
Euclea natalensis	Ebenaceae	Broad-leaved,	Evergreen
		non-leguminous	

(Van Wyk & Van Wyk, 2013; http://pza.sanbi.org/ [accessed: 22 September, 2016]).

## 2.2.2 Leaf sampling and handling

Leaf samples were collected on 22 August 2016 (dry season) and again on 13 January 2017 (wet season). Leaf samples were, as much as possible, collected from different positions and directions of the crown (top, middle, south, east, etc.). Five samples were collected for each species. Samples were put in paper bags and labelled. Sampling points (waypoints) were recorded using Garmin *eTrex*30, global positioning system (GPS) instrument. In the laboratory the samples were oven-dried at 60°C for 48 hours, and then ground and sieved through a 1mm screen (Campbell & Plank, 1997). Samples were placed in polythene bottles and stored in a cabinet, pending chemical and spectral analyses (Lukhele & van Ryssen, 2003).

# 2.3 Chemical analysis

Foliar nitrogen was determined following the Dumas dry oxidation combustion method (Dumas, 1831). The finely milled sample was used directly on a Carlo Erba NA 1500 Carbon/Nitrogen/Sulphur Analyzer, using approximately 10mg sample, weighed into a tin foil container for each determination. The instrument uses gas chromatography (GC) to separate the gases and yield nitrogen in the form of N<sub>2</sub> gas (Jimenez & Ladha, 1993).

Potassium, calcium and phosphorus were determined by optical emission spectroscopy using the Spectro Genesis inductively coupled plasma optical emission spectrometer (ICP-OES). Approximately 0.3g of each sample was digested in the Kjeldahl wet oxidation process as described by Kovacs *et al.* (1996). The elements are then determined by optical emission spectroscopy with inductively coupled plasma excitation.

Descriptive statistics on foliar nutrients (N, P, K and Ca) were computed using ANalysis Of VAriance (ANOVA) programmed into the R statistical software. Statistical tests compared nutrient variation between (i) the species; (ii) dry and wet seasons; and (iii) between broad-leaved legumes, narrow-leaved legumes and non-legumes.

# 2.4 Spectral measurements

#### 2.4.1 Recording of spectra

The spectral reflectance of dried and ground foliage was measured using FieldSpec<sup>®</sup> 3 spectroradiometer (Analytical Spectral Devices Inc., Boulder, Colorado, USA). The instrument has a sampling interval of 1nm from 350nm to 2500nm spectral region (Awiti *et al.*, 2007). Samples were placed on a spectrally black surface to minimize the background spectral noise. The radiance spectra were normalized against a 99% white reference to produce relative reflectance spectra for each measurement. Five spectral measurements were taken on each sample, which were then averaged to obtain representative spectra.

#### 2.4.2 Data pre-treatment

Due to some noise in the 350-399nm spectral region, the interval was excluded from the analyses (Awiti *et al.*, 2007). The raw data were subjected to "continuum removal" using the prospectr package of the R software (Stevens & Ramirez-Lopez, 2015). The treatment is necessary for minimization of the scattering effect (Curran *et al.*, 2001) and it standardises isolated absorption features for comparison purposes (Clark & Roush, 1984; Clark, 1999; Kokaly & Clark, 1999). The continuum-removed spectra were used to develop models through the method of chemometrics (Garcia & Filmoser, 2017).

#### 2.4.3 Constructing the models

Partial least squares regression (PLSR) was used to model relationship between the chemical and spectral measurements of samples. Forty-five (45) samples were used to build the models for winter and summer respectively. Chemical data determined by the reference methods were pasted alongside spectra (400-2500nm). Functions of the following packages programmed into the R software were used: pls, chemometrics, ChemometricsWithR, prospectr and inspectr.

Validation of the model was done using "leave one out" cross validation (LOOCV) because of small number of observation (Mevik & Wehrens, 2007). The root mean square error (RMSE), the coefficient of determination ( $R^2$ ) and the *p* values were

considered as statistic measure of precision and accuracy (Garcia & Filmoser, 2017; Ramoelo & Cho, 2018).

The script for fitting the model was:

NleafChem <- plsr(Nitrogen ~ crALLSPECTRA, ncomp = 10, data = leafTrain, validation = "LOO").

This fits a model with 10 components and includes leave-one-out (LOO) crossvalidated predictions. We then get an overview of the fit and validation results with the summary method as follows: summary(NleafChem). The optimum number of components was determined using the local minimum of RMSE of the model developed using 10 components (Mevik & Wehrens, 2007).

# 2.5 Sentinel-2 data

# 2.5.1 Image acquisition and pre-processing

Sentinel-2 images covering the study area were downloaded from <u>http://glovis.usgs.gov/</u> [retrieved: 28 June, 2017]. Atmospheric correction was performed using Image Correction Plugin for Snap Toolbox Software (iCOR), previously known as OPERA (Sterckx *et al.*, 2015). The iCOR plugin for the Sentinel-2 Snap Toolbox is scene and sensor generic atmospheric correction algorithm that can handle land and water targets (VITO, 2017).

All input data required for the atmospheric correction are derived from the image itself or delivered through pre-calculated look-up-tables. Through the use of a single atmospheric correction implementation, discontinuities in the reflectance between land and the highly dynamic water areas are reduced (Ramoelo & Cho, 2018).

#### Table 2: List of Sentinel-2 images used in the study

Product ID	Date
S2A_OPER_MSI_L1C_TL_MPS20160812T112604_A005952_T36JUT_N02.04	2016-08-12
S2A_MSIL1C_20170119T074231_N0204_R092_T36JUT_20170119T075734	2017-01-19

(https://glovis.usgs.gov/app [accessed: 28 June 2017]).

In order to extract multispectral data, the images were pre-processed wherein digital numbers were converted to surface reflectance.



Figure 2: Workflow of iCOR atmospheric correction algorithm. (Adapted from: <a href="https://blog.vito.be/remotesensing/icor\_available">https://blog.vito.be/remotesensing/icor\_available</a> [accessed: 12 Jan 2018]).

LUT = Look-up-Table, SZA = Solar Zenith Angle, VZA = View Zenith Angle, RAA = Relative Azimuth Angle, DEM = Digital Elevation Model, TOA = Top-of-Atmosphere, AOT = Aerosol Optical Thickness, SIMEC = Similarity Environment Correction, L2 = Level 2 Atmospherically Corrected.

# 2.5.2 Point extraction

Spectral reflectance of georeferenced ground points (GPS coordinates of the sampled trees) were extracted from the image. Trees with larger canopies were purposively sampled (Ramoelo *et al.*, 2014); and their chemical, hyperspectral and multispectral spectral (Sentinel-2) measurements were modelled. Due to the fewer number of trees with large canopies, the dataset comprised of combined dry and wet seasons' measurements.

# 2.5.3 Spectral bands and indices

This study utilised eight Sentinel-2 MSI bands that are critical for characterisation of vegetation (Skidmore *et al.*, 2010; Ramoelo *et al.*, 2014). The bands are centred at 490nm, 560nm, 665nm, 705nm, 740nm, 783nm, 842nm and 865nm (Table 3).

Spectral Band	Central wavelength (nm)	Band width (nm)	Resolution	
Band 2 – blue	490nm	65nm	10m	
Band 3 – green	560nm	560nm 35nm		
Band 4 – red	665nm	30nm	10m	
Band 5 – vegetation red edge	705nm	15nm	20m	
Band 6 – vegetation red edge	740nm	15 nm	20m	
Band 7 – vegetation red edge	783nm	20nm	20m	
Band 8 – NIR	842nm	115nm	10m	
Band 8b – vegetation red edge	865nm	20nm	20m	

Table 3: Description of Sentinel-2 bands used in the study

ESA (2015); retrieved from <u>http://www.gdal.org/frmt\_sentinel2.html [</u>15 September, 2017]).

Conventional and red-edge based vegetation indices such as modified simple ratio mSR705 (B06 - B01) / (B05 - B01); normalized difference vegetation index - NDVI (B08 - B04) / (B08 + B04); red-edge normalized difference vegetation index - RE NDVI (B08 - B06) / (B08 + B06); NDVI-Green (B03 \* (B08 - B04) / (B08 + B04), were computed (Ramoelo *et al.*, 2014; http://www.sentinel-hub.com/eotaxonomy/indices [accessed: 26 October, 2017]). A total of eighteen bands and vegetation indices were used as an input into the model.

# 2.5.4 Modelling nutrient composition using Sentinel-2 data

Partial least squares regression (PLSR) was used to model relationships between leaf chemical composition and multispectral data from Sentinel-2. The model was implemented using the pls package in R programming language. Validation of the model was done using 'leave one out' cross validation (Mevik & Wehrens, 2007).

The root mean square error (RMSE), coefficient of determination ( $R^2$ ) as well as *p* values were considered as statistic measures of precision and accuracy (Garcia & Filmoser, 2017; Ramoelo & Cho, 2018).

# 3. Results and discussion

# 3.1 Descriptive statistics

The composition of the foliage from the different species is presented in Table 4.

	Nitro (g/1	ogen 00g)	Phosphorus (g/100g)		Potassium (g/100g)		Calcium (g/100g)	
Season	D	W	D	W	D	W	D	W
n	45	45	45	45	45	45	45	45
Max	2.43	3.54	0.22	0.23	1.02	1.67	3.27	1.82
Mean	1.753	2.372	0.098	0.135	0.619	0.916	1.562	0.852
Min	0.71	1.55	0.06	0.07	0.33	0.47	0.52	0.30
SD	0.405	0.514	0.030	0.043	0.179	0.290	0.607	0.328
CV (%)	23.1	21.7	30.2	31.4	28.9	31.6	38.8	38.5

Table 4: Descriptive analysis of the chemical data

SD = standard deviation; CV = coefficient of variation; D = dry season; W = wet season

Figure 3 shows the boxplots of the nutrient levels among the species in both seasons. The highest concentration of nitrogen was recorded in in *Philenoptera violacea* specimen during summer; and the lowest was in *Terminalia sericea* specimen during winter. Phosphorus concentration was highest in *Dichrostachys cinerea* during summer, whilst the lowest was recorded in *Terminalia sericea* during winter. Potassium was highest in *Philenoptera violacea* foliar during summer, and was lowest in *Combretum apiculatum* during winter. The highest amount of calcium was recorded in *Dichrostachys cinerea* leaves during winter, while the lowest was recorded in *Combretum apiculatum* during summer.



Figure 3: Foliar nutrient variation by species in the dry (D) and wet (W) seasons

The Shapiro–Wilk test showed that nitrogen was normally distributed, while phosphorus, potassium and calcium were not. There was more variability in nitrogen content during winter (CV=23.1%) compared to summer (CV=21.7%).

*Philenoptera violacea* contain significantly higher (p<0.05) levels of nitrogen compared with other species except with *Dichrostachys cinerea*. The findings corroborate the work by du Toit (2003), which showed foliar nitrogen concentrations for *Philenoptera violacea* in the Lowveld savanna were more than 3% in summer. The non-leguminous species *Terminalia sericea* contained significantly lower (p<0.05) amounts of nitrogen compared with most species, except for *Peltophorum africanum* and *Euclea natalensis*.

The results of foliar nitrogen variation between groups are shown in Figure 4. The concentration was significantly lower (p<0.05) in non-leguminous plants than in leguminous plants during summer, while the difference between broad-leaved and narrow leaved legumes was not significant. During winter, nitrogen concentration was significantly lower (p<0.05) in non-legumes than in broad-leaved legumes while the difference in mean nitrogen between narrow-leaved legumes and non-legumes was not significant.

Leaf nitrogen is related to protein (Majeke *et al.*, 2008). The higher protein content in leguminous plants is due to the action of nitrogen-fixing bacteria that habitat root nodules of leguminous plants (Hungria & Franco, 1993; Jacobs *et al.*, 2007). Nonetheless, the potential to fix nitrogen needs to be explored for each species due to significant variability among leguminous spiecies. For instance the results revealed that the nitrogen content of *Peltophorum africanum*, which is a leguminous plant, was among the lowest of the plant species investigated.

In terms of phosphorus, broad-leaved legumes contained significantly higher (p<0.05) concentration than narrow-leaved legumes and non-leguminous species. The difference between narrow-leaved legumes and the non-legumes was not significant. Differences in potassium and calcium between the three groups were not significant. Seasonal effect was significant (p<0.05) for all the four nutrients. Concentrations of nitrogen, phosphorus and potassium were significantly higher (p<0.05) in summer than in winter, whereas calcium was significantly higher (p<0.05) in winter (Figure 5).

Green plants generally have higher nutrient concentrations due to active metabolic activities (e.g. photosynthesis) portraying vigour and health of vegetation. During dry periods, nutrients are generally translocated from leaves to the roots (Majeke *et al.*, 2008). The interaction effect between the **groups** and **seasons** was significant (p<0.05) for nitrogen; this could be attributed to changes soil conditions (temperature and humidity) on the activity of nitrogen-fixing bacteria in leguminous species (Jacobs *et al.*, 2007).





BLL.D = Broad leaved legume – dry season; NLL.D = Narrow leaved legume – dry season; NOL.D = Non-legume – dry season; BLL.W = Broad leaved legume – wet season; NLL.W = Narrow leaved legume – wet season; NOL.W = Non legume – wet season.



Figure 5: Foliar nutrient concentration between dry and wet seasons.

# 3.2. Nutrient concentration and spectral reflectance of dried leaf samples.

Table 5 is a summary of the performance of the statistical models developed to relate foliar nutrients measured by reference methods to hyperspectral data obtained from laboratory spectroscopy. Figures 6 to 9 show the graphical output of the models. There was a significant relationship between foliar nitrogen concentration and hyperspectral reflectance of ground leaf samples for both summer ( $R^2$ =0.88, p<0.05) and winter seasons ( $R^2$ =0.76, p<0.05).

The coefficient of variation for nitrogen was lower in summer (CV=21.7%) compared to winter (CV=23.4%); consequently the predictive accuracy was higher in summer ( $R^2$ =0.88) than in winter ( $R^2$ =0.76). A similar trend was observed with the prediction of phosphorus. The study corroborates the findings by Ramoelo *et al.* (2014), that prediction of leaf N is higher during the period of peak productivity. During the wet season, plants have more vigour and high levels of nutrients and photosynthetic pigments such as chlorophyll (Kumar *et al.*, 2003; Majeke *et al.*, 2008).

The relationships between foliar phosphorus, potassium and calcium concentrations and hyperspectral reflectance of ground leaf samples were generally low (Table 5). . The predictive capability of Ca was reasonably higher in winter ( $R^2$ =0.43) than in summer ( $R^2$ =0.01).

Season	n	Nutrient	RMSEP	R <sup>2</sup>	<i>p</i> values < 0.05	Commented [Moses@1]: Verify your p values
		Ν	0.21	0.76	Yes	
Winter	45	Р	0.02	0.49	Yes	
		К	0.17	0.08	Yes	Commented [Moses@2]: Are u sure the p was < 0.05
		Ca	0.45	0.43	Yes	
Summer 45	Ν	0.18	0.88	Yes		
	45	Р	0.03	0.41	Yes	
		К	0.26	0.20	Yes	
		Ca	0.32	0.01	Yes	Commented [Moses@3]: Are u sure the p was < 0.05

 Table 5: Performance of the models on the estimation of foliar nutrients

 using spectrometer data

The results demonstrate that spectral reflectance of dried and ground leaf samples, coupled with partial least squares regression can be applied as a fast analytical technique to evaluate nitrogen content of species in the lowveld ecosystem. Work by Galvez-Sola *et al.* (2015) using dry leaf spectroscopy on lemon, mandarin, orange and grapefruit found high accuracy ( $R^2$ =0.96) regarding the estimation of nitrogen as well as acceptable estimates for potassium, iron and zinc. In yerba mate plants (*llex paraguariensis*), the prediction was good for phosphorus and copper but not for potassium and calcium (Rossa *et al.*, 2015). These data show that the leaf spectral response depends on the species studied; thus for each species it is necessary to make the appropriate calibrations.



Figure 6: Cross-validated RMSEP curves for hyperspectral vs chemical: winter



Figure 7: Cross-validated predictions for hyperspectral vs chemical data: winter.



Figure 8: Cross-validated RMSEP curves for hyperspectral vs chemical: summer



Figure 9: Cross-validated predictions for hyperspectral vs chemical data: summer

# 3.3. Relationship between foliar nutrient concentrations and Sentinel-2 data

Table 6 shows the performance of models relating chemical composition to spectral reflectance. The graphical output of the model is shown as Figure 10.

 Table 6: Performance of models for estimating foliar nutrients using data from

 both dry and wet seasons

Season	n	Nutrient	RMSE	R <sup>2</sup>	p values < 0.05
þ	19	Ν	0.22	0.44	Yes
oine aset	19	Р	0.04	0.04	Yes
omk data	19	К	0.27	0.23	Yes
0	19	Ca	0.41	0.25	Yes



Figure 10: Cross-validated predictions for Sentinel-2 data: wet and dry seasons.

Using Sentinel-2 data, the prediction accuracy for nitrogen was higher compared to that of potassium, phosphorus and calcium. Phenology is a major factor of this outcome; most of the vegetation indices particularly Red Edge based indices depend on the vegetation vigour and greenness (Kumar *et al.*, 2003). There was weak correlation ( $R^2$ =0.44, p<0.05) between foliar nitrogen composition and the predictions made by the PLS model. As outlined by Garcia Sanchez *et al.* (2017),  $R^2$  values that are less than 0.75, although not acceptable for practical application, they may be useful for monitoring purposes. It is assumed that the models could perform better with improved sampling techniques and the use of larger datasets.

Estimation of leaf nutrients using Sentinel-2 data yielded low performances, which could be attributed to low dimensionality of the data. PLS regression performs better when number of observations and exploratory variables are in their tens to hundreds and even thousands (Wold *et al.*, 2001). Ramoelo *et al.* (2015) demonstrated that machine learning techniques, such as random forest improved the estimation of leaf nitrogen by 49% and are quite robust if well parameterized.

# 5. Conclusion

Spatial and taxonomic variation in leaf chemistry is recognized as important both for the functional role that trees play in ecosystems as well as their response to environmental change. The study combined field campaigns, chemical analysis, laboratory spectroscopy on dry leaves as well as multispectral data of vegetation to identify opportunities for scaling leaf chemical – spectral relationships to canopies. The analysis was done in the context of the foliar nutrients, as elements of resource quality.

Science based on imaging spectroscopy and techniques has been driven by the assumption that improved identification of particular spectral features leads to better estimation of foliar chemicals. Season specific analysis showed that wet season models performed better than those of dry season. Various literature indicate that performance of models depend on elements being analysed and the plant species. This study demonstrated some potential for hyperspectral data to estimate leaf nitrogen using PLS regression. Nonetheless foliar nutrient estimation using Sentinel-2 data did not show potential for practical application in the estimation of leaf minerals.

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# References

Akinnifesi, F.K., Ajayi, O.C., Sileshi, G., Chirwa, P.W. & Chianu, J. (2010). Fertiliser trees for sustainable food security in the maize-based production systems of East and Southern Africa: a review. *Agronomy for Sustainable Development*, 30: 615–629.

Analytical Spectral Devices Inc. (1997). *FieldSpec user's guide*. Analytical Spectral Devices Inc., Boulder CO.

Awiti, A. O., Walsh, M. G., Shepherd, K. D. and Kinyamario, J. (2007). Soil condition classification using infrared spectroscopy: A proposition for assessment of soil condition along a tropical forest-cropland chronosequence. *GEODER*-09764.

Campbell, C.R. & Plank, C.O. (1997). Preparation of plant tissue for laboratory analysis. In: Kalra, Y.P. (ed). *Handbook of Reference Methods for Plant Analysis*. CRC Press, Florida.

Cho, M.A., Mathieu, R., Asner, G.P., Naidoo, L., van Aardt, J., Ramoelo, A., Debba, P., Wessels, K., Main, R., Smit, I.P.J. & Erasmus, B. (2012). Mapping tree species composition in South African savannas using an integrated airborne spectral and LiDAR system. *Remote Sensing of Environment*, 125: 214–226.

Chepape, R.M., Mbatha, K.R. and Luseba, D. (2011). Local use and knowledge validation of fodder trees and shrubs browsed by livestock in Bushbuckridge area, South Africa. *Livestock Research for Rural Development*, 23 (6).

Clark, R.N. & Roush, T.L. (1984). Reflectance spectroscopy: quantitative analysis techniques for remote sensing applications. *Journal of Geophysical Research*, 89(B7): 6329–6340.

Clark, R. N. (1999). Spectroscopy of rocks and minerals, and principles of spectroscopy. In: *Manual of Remote Sensing, Volume 3: Remote Sensing for the Earth Sciences*, 3-58. John Wiley and Sons, New York.

Curran P.J., Dungan, J.L & Peterson, D.L. (2001). Estimating the foliar biochemical concentration of leaves with reflectance spectrometry: testing the Kokaly and Clark methodologies. *Remote Sensing of the Environment*, 76: 349-359.

du Toit, J.T. (2003). Large herbivores and savanna heterogeneity. In: du Toit, J.T., Rogers, K.H., Biggs, H.C. (Eds.). *The Kruger Experience: Ecology and Management of Savanna Heterogeneity*. Island Press, Washington.

Dumas, J.B.A. (1831). Procedes de l'analyse organic. *Annals of Chemistry and of Physics*, 247: 198–213.

Everson, C.S., Dye, P.J., Gush, M.B. & Everson, T.M. (2011). Water use of grasslands, agroforestry systems and indigenous forests. *Water SA*, 37 (5).

Galvez-Sola, L., García-Sánchez F., Pérez-Pérez, J.G., Gimeno, V., Navarro, J.M., Moral, R., Martínez-Nicolás, J.J. & Nieves, M. (2015). Rapid estimation of nutritional elements on citrus leaves by near infrared reflectance spectroscopy. *Frontiers in Plant Science*, 6 (571). doi: 10.3389/fpls.2015.00571

Garcia, H. & Filzmoser, P. (2017). Multivariate statistical analysis using the R package chemometrics (http://cran.r-project.org [accessed: 20 September, 2017]).

Garrity, D., Okono, A., Grayson, M. & Parrott, S. (2006). *World Agroforestry into the Future*. Nairobi: World Agroforestry Centre.

Hungria, M. & Franco, A.A. (1993). Effects of high temperature on nodulation and nitrogen fixation by *Phaseolus vulgaris* L. *Plant and Soil*, 149: 95-102.

İlknur ŞEN. (2003). Spectroscopic determination of major nutrients (N, P, K) of soil. Masters' Dissertation. İzmir Institute of Technology. İzmir, Turkey.

Jacobs, S.M., Pettit, N.E., Naiman, R.J. (2007). Nitrogen fixation by the savanna tree *Philenoptera violacea* (Klotzsch) Schrire (Apple leaf) of different ages in a semi-arid riparian landscape. *South African Journal of Botany*, 73, 163–167.

Jimenez, R.R. & Ladha, J.K. (1993). Automated elemental analysis - a rapid and reliable but expensive measurement of total carbon and nitrogen in plant and soil samples. *Communications in Soil Science and Plant Analysis*, 24, 1897-1924. http://dx.doi.org/10.1080/00103629309368926

Kjeldahl, J. (1883) Neue methode zur bestimmung des stickstoffs in organischen körper. *Zeitschrift für Analytische Chemie*, 22: 366–382.

Kokaly, R.F. & Clark, R.N. (1999) Spectroscopic determination of leaf biochemistry using band-depth analysis of absorption features and stepwise multiple linear regression. *Remote Sensing of Environment*, 67: 267-287.

Kovacs, B., Gyori, Z., Prokisch, J., Loch, J. & Daniel, P. (1996). *Communications in Soil and Plant Analysis*, 27: 1177–1198.

Kumar, L., Schmidt, K., Dury, S., Skidmore, A. (2003). Imaging spectrometry and vegetation science. In: van der Meer, F.D., de Jong, S.M. (Eds.), *Image Spectrometry*, 3: 111–156. Kluwer Academic Publishers, London, United Kingdom.

Lukhele, M.S. & van Ryssen, J.B.J. (2003). The chemical composition and potential nutritive value of the foliage of four subtropical tree species in southern Africa for ruminants. *South African Journal of Animal Science*, 33 (2).

Majeke, B., van Aardt, J. & Cho, M.A. (2008). Imaging spectroscopy of foliar biochemistry in forestry environments. *Southern Forests*, 70(3): 275–285.

Mbow, C., Van Noordwijk, M., Luedeling, E., Neufeldt, H., Minang P. A. and Kowero, G. (2014). Agroforestry solutions to address food security and climate change challenges in Africa. *Current Opinion in Environmental Sustainability*, 6, 61–67.

Mevik, B. & Wehrens, R. (2007). The pls Package: Principal component and partial least squares regression in R. *Journal of Statistical Software,* 18 (2).

Palm, C.A., Gachengo, C.N., Delve, R.J., Cadisch, G. and Giller, N.E. (2001).Organic inputs for soil fertility management in tropical agroecosystems: application of an organic resource database. *Agriculture, Ecosystems and Environment,* 83: 27–42.

Ramoelo, A., Cho, M.A., Madonsela, S., Mathieu, R., van der Korchove, R., Kaszta, Z. & Wolf, E. (2014). A potential to monitor nutrients as an indicator of rangeland quality using space borne remote sensing. Eighth International Symposium of the Digital Earth (ISDE8), IOP Publishing.

Ramoelo, A., Cho, M.A., Mathieu, R. & Skidmore, A. (2015). The potential of Sentinel-2 spectral configuration to assess rangeland quality. *Journal of Applied Remote Sensing*, 9, 094096.

Ramoelo, A. & Cho, M.A. (2018). Explaining leaf nitrogen distribution in a semi-arid environment predicted on Sentinel-2 imagery using a field spectroscopy derived model. *Remote Sensing*, 10, 269.

Riley, M.L. & Canaves, L.C. (2002). FT-NIR Spectroscopic analysis of nitrogen in cotton leaves. *Biological Systems Engineering: Papers and Publications*. Paper 350.

Rossa, Ü.B., Angelo, A.C., Nisgoski, S., Westphalen, D.J., Frizon, C.N.T. & Hoffmann-Ribani, R. (2015). Application of the NIR method to determine nutrients in yerba mate (*Ilex paraguariensis* A. St.-Hill) leaves. *Communications in Soil Science and Plant Analysis*, 46: 18, 2323-2331.

Shackleton, C.M. (2001). Managing regrowth of an indigenous savannah tree species (*Terminalia sericea*) for fuelwood: the influence of stump dimensions and post-harvest coppice pruning. *Biomass and Bioenergy*, 20: 261–270.

Simonetti, D., Marelli, A., Rodriguez, D., Veselin, V., Strobl, P., Burger, A., Soille P., Achard, F., Eva, H., Stibig, H.J. & Beuchle, R. (2017). Sentinel-2 web platform for REDD+ monitoring, online web platform for browsing and processing Sentinel-2 data for forest cover monitoring over the Tropics. EUR 28658; doi:10.2760/790249.

Skidmore, A.K., Ferwerda, J.G., Mutanga, O., Van Wieren, S.E., Peel, M., Grant, R.C., Prins, H.H.T., Balcik, F.B. & Venus, V. (2010). Forage quality of savannas - simultaneously mapping foliar protein and polyphenols for trees and grass using hyperspectral imagery. *Remote Sensing of Environment*, 114: 64-72.

Sterckx, S., Knaeps, E., Adriaensen, S., Reisen, I., De Keukelaere, L. Hunter, P., Giardino, E. & Odermatt, D. (2015). OPERA: An atmospheric correction for land and water. In Proceedings of the ESA Sentinel-3 for Science Workshop, Venice, Italy, 2–5 June 2015.

Stevens, A. & Ramirez-Lopez, L. (2015). Miscellaneous functions for processing and sample selection of vis-NIR diffuse reflectance data. Retrieved from https://github.com/antoinestevens/prospectr [accessed: 26 September, 2017].

Tegegne, E.D. (2008). Importance of *Ficus thonningii* blume in soil fertility improvement and animal nutrition in Gondar Zuria, Ethiopia. MSc Thesis. University of Natural Resources and Applied Life Science, Vienna.

van Deventer, H., Cho, M.A., Mutanga, O. & Ramoelo, A. (2015). Capability of models to predict leaf N and P across four seasons for six sub-tropical forest evergreen trees. *ISPRS Journal of Photogrammetry and Remote Sensing*, 101: 209–220.

van Maarschalkerweerd, M. & Husted, S. (2015). Recent developments in fast spectroscopy for plant mineral analysis. *Frontiers in Plant Science,* (6), 169.

Van Wyk, P. & Van Wyk, B. (2013). *Field guide to trees of Southern Africa*. Struik Nature, Cape Town.

Vlaams Instituut Voor Technologisch Onderzoek (VITO). (2017). ICOR plugin for snap toolbox software user manual version 1.0., VITO Remote Sensing Unit, Boeretang, Belgium.

http://step.esa.int/main/download/ https://blog.vito.be/remotesensing/icor\_available [accessed: 17 January 2018].

Ward, A., Nielsen, A.L. & Møller, H. (2011). Rapid assessment of mineral concentration in meadow grasses by near infrared reflectance spectroscopy. *Sensors*, 11: 4830-4839.

Yarce, C.J. & Rojas, G. (2012). Near infrared spectroscopy for the analysis of macro and micro nutrients in sugarcane leaves. *Sugar Industry*, 137: 707–710.

http://pza.sanbi.org/ [accessed: 22 September, 2016].

http://www.gdal.org/frmt\_sentinel2.html ([accessed: 15 October, 2017].

http://www.sentinel-hub.com/eotaxonomy/indices [accessed: 26 October, 2017].

https://earthexplorer.usgs.gov/ [accessed: 12 November, 2017]

http://glovis.usgs.gov/ [accessed, 12 November, 2017].