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Predicting macronutrient concentrations from loblolly pine leaf reflectance across local and regional scales

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Given the economic importance of loblolly pine (*Pinus taeda*) in the southeastern US, there is a need to establish efficient methods of detecting potential nutrient deficiencies that may limit productivity. This study evaluated the use of remote sensing for macronutrient assessment in loblolly pine. Reflectance-based models were developed at two spatial scales: (1) a natural nutrient gradient across the species' range, and (2) localized fertilization and genotype treatments in North Carolina and Virginia. Fascicles were collected regionally from 237 samples of 3 flushes at 18 sites, and locally from 72 trees with 2 fertilization treatments and 6 genotypes. Sample spectral reflectance was calculated using a spectroradiometer, and nutrient concentrations were measured with dry combustion and wet chemical digestion. Results were analyzed statistically using nutrient correlations with reflectance and common vegetation indices, and partial least squares regression (PLSR). PLSR performed well at the regional scale, with R^2 values for nitrogen, phosphorus, potassium, calcium, and magnesium of 0.81, 0.70, 0.68, 0.42, and 0.51, respectively. No model successfully predicted nutrients at local sites for any treatment or canopy stratum. This discrepancy implies that a large nutrient range and/or spatial scale may be necessary to model loblolly pine nutrients with spectral reflectance.

Keywords: remote sensing; spectroradiometer; nutrients; loblolly pine; partial least squares regression; spatial scale

Introduction

Loblolly pine (*Pinus taeda*) is the most commercially productive species for timber in the southeastern US (SE US), covering over 13 million hectares in the region (Susaeta et al. 2012). However, soil nutrient limitations are common, particularly in nitrogen (N) and phosphorus (P). Along with potassium (K), these nutrients form the primary nutrient requirements of plants; secondary nutrients are calcium (Ca), magnesium (Mg), and sulfur (S). N, P, K, and Mg are required in photosynthesis and respiration, while Ca is used in cell division and cell walls (Taiz and Zeiger 2010). Insufficient macronutrients can stunt plant growth, injure organs, and lead to mortality (Pallardy 2008).

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When nutrient stress is detected early, forest managers can reduce the likelihood of damage by applying fertilizer or other silvicultural treatments (Svotwa et al. 2012). However, field measurements to determine nutrient concentrations are time- and labor-intensive (Gong et al. 2012). With such a vast area allocated to loblolly pine production, remote sensing may offer advantages over current field methods for nutrient assessment (Im et al. 2009; Svotwa et al. 2012). Satellite hyperspectral sensors, such as NASA's Hyperion sensor and ESA's Compact High Resolution Imaging Spectrometer (CHRIS), collect high resolution spectral data that is sensitive to biophysical characteristics in vegetation. The upcoming launches of the Environmental Mapping and Analysis Program (EnMAP) satellite in Germany and the NASA Hyperspectral Infrared Imager (HyspIRI) mission necessitate a greater understanding of the relationship between macronutrients and reflectance across species' ranges to maximize data benefits.

Effective use of hyperspectral data relies on field-derived relationships between spectral reflectance patterns and chemical composition. The chemical constituents of foliage reflect unique amounts of radiation in the visible and NIR portions of the spectrum. Since the 1970s, researchers have used spectral signatures to identify foliar biochemicals and nutrients (Al-Abbas et al. 1974). After Hinzman, Bauer, and Daughtry (1986) found differences in visible, near infrared (NIR), and mid-infrared reflectance from fertilizer treatments, Peterson et al. (1988) predicted leaf nitrogen concentrations from reflectance measurements. Studies of other nutrients followed a similar trajectory, as researchers used observed spectral patterns to predict nutrient quantities (Curran 1989; Ferwerda and Skidmore 2007; Gholz et al. 1997).

Relationships between reflectance and nutrients vary significantly by element and plant species. For this reason, interspecific models are often quite successful at predicting nutrients across diverse areas (e.g. Asner et al. 2011; Ollinger et al. 2008). Im et al. (2009) used airborne imaging spectroscopy to quantify macronutrient concentrations in several species, including loblolly pine. However, interspecific models may not be appropriate for individual species, which often have a much narrower range in nutrient concentrations. Research on other plants suggest that relatively low intra-site variability necessitates a large environmental gradient for monospecific models (Ferwerda and Skidmore 2007; Pimstein et al. 2011). Currently, few studies have examined loblolly pine reflectance beyond nitrogen or leaf area index (Gong et al. 2012; Nelson, Gjerstad, and Glover 1986; Tsay, Gjerstad, and Glover 1982); so, the necessary nutrient range is undefined. Even given the known nutrient limitations, there are no remote-sensing models specifically for loblolly pine macronutrients.

The objective of this study is to use reflectance measurements to develop models for loblolly pine macronutrient concentrations (N, P, K, Ca, and Mg) across two settings: (1) a natural nutrient gradient across the SE US, and (2) localized experimental fertilization treatments in Virginia and North Carolina. The goal is twofold: to determine the relationship between spectral reflectance and nutrient concentration in loblolly pine, and to investigate the role of geographic scale in model accuracy. To achieve these aims, the study considers several treatments and leaf characteristics known to affect nutrient concentration, and in some cases, the spectral signature. These variables include fertilization, genotype, canopy stratum, and flush (Im et al. 2009; Zhang and Allen 1996). Determination of the appropriate spatial scale for loblolly pine nutrient models can improve current methods for modeling and mapping nutrient quantities in the SE US. Relationships between flush and spectra will demonstrate the effectiveness of representing total foliage, both nutritionally and spectrally, with a given flush. In addition, results may provide insight into the possibility and potential limitations of scaling algorithms up to landscape-level analysis using satellites.

Methodology

Study sites

Regional analysis

The 18 regional study sites are located across the SE US. These sites range latitudinally from Virginia to Florida, with a longitudinal range to East Texas and Oklahoma (Figure 1). They consist of loblolly pine plantations across the species' environmental habitat gradient. Sites represent 5 US Environmental Protection Agency Level II ecoregions and 13 Level III ecoregions (US Environmental Protection Agency 2010). Site conditions are extremely varied, including differences in soils, stress, and climate. Stands range in soil properties, tree age, level of thinning, and amount of understory. Mean annual daily average temperatures are 12 to 21°C, and mean annual precipitation is 101 to 178 cm (National Climatic Data Center 2005).

Local analysis

The two local sites are within the Reynolds Homestead Forestry Research Center in Patrick County, Virginia, US (36°40′ N, 80°10′ W), and Bladen Lakes State Forest in Bladen County, North Carolina, US (34°41′ N, 78°36′ W, Figure 1). Reynolds Homestead is in the Virginia Piedmont and has well-drained Fairview series soils. For a more detailed description of the topography, climate, and soils at Reynolds Homestead, please refer to Stovall et al. (2011). Bladen Lakes, in the North Carolina Coastal Plain, has poorly drained soils of the Rains series. The NSF Center for Advanced Forestry Systems established the genotype and fertilization plots in 2009. Preliminary results in the first three years of the experiment indicate silvicultural and site differences in loblolly pine growth (Yanez, forthcoming).

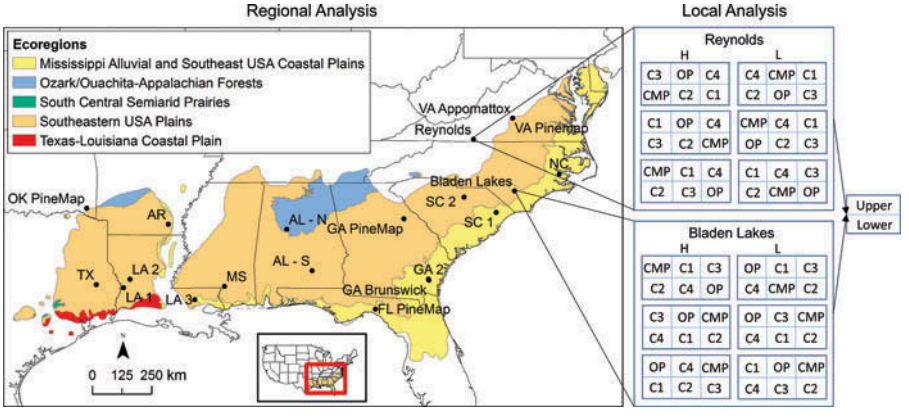

Figure 1. Study site locations in the southeastern US for analyses at the regional and local scales, with the local sampling scheme. Sites span the geographic range of loblolly pine (Little 1971). Regional sites represent a diversity of environmental characteristics and cover multiple ecoregions, as characterized by the US Environmental Protection Agency's Level II ecoregional classification (US EPA 2010). At the local scale, an in-depth analysis was conducted across canopy levels ("Lower" and "Upper"), fertilization treatments ("H" = High, "L" = Low), and genotypes (C1-C4 = distinct genotypes, "CMP" = controlled mass pollination, "OP" = open pollination).

Field and laboratory measurements

Data collection and sampling procedures differed by the scale of analysis. Separate field campaigns were conducted for the regional analysis and localized genotype and fertilization experiments.

Regional sampling across loblolly range

A FieldSpec 3 Rapid and Portable Spectroradiometer (ASD Inc., Boulder, CO) was used to take measurements at the SE US study sites. The spectroradiometer has a spectral range of 350–2500 nm and records 2150 spectral channels at 1.4–2 nm resolution. At each site, branches were shot down from the upper canopy of one or two loblolly pine trees. One to six foliar samples consisting of multiple adjacent fascicles were collected from the most recent flush, previous flush, and previous year's flush. Prior to data collection, the spectroradiometer was calibrated with a white reference panel (Spectralon Labsphere Inc., North Sutton, NH, US). Consequently, the entire view surface of the plant probe was covered with fascicles. An average of 10 spectral readings for each wavelength in the range were collected for each sample. The presence and quantity of particular flushes varied across branches. Measurements were taken in the summer of 2012.

Local sampling for fertilization treatment and genotype

At Reynolds Homestead and Bladen Lakes, leaf samples and reflectance measurements (n = 144) were collected in the upper and lower canopies of 72 trees. The experimental design consists of three replicates of two levels of silvicultural treatments (high and low intensity) and six loblolly genotypes: C1, C2, C3, C4, Controlled Mass Pollination (CMP), and Open Pollination (OP). At Reynolds Homestead, high silvicultural plots were fertilized with a phosphate-coated urea fertilizer (CUF: 39% N, 4% P, 0.16% B; 239 g/tree) in March, 2010, and herbicide was applied in April 2010 and 2011 (4 oz Arsenal AC + 2 oz Oust XP + 0.25 oz Escort per ac). At Bladen Lakes, herbicide and fertilizer were applied in March 2010, and herbicide was re-applied in May 2011 (Yanez, Forthcoming). Measurements were taken in September and October, 2012, in the fourth growing season.

Reflectance at the needle-level for each canopy stratum were measured with the aforementioned spectroradiometer. Three sunlit branches in the lower and upper canopies were selected for sampling. One fascicle was detached from the latest flush on each branch in the canopy stratum, producing two sets of three fascicles per tree. The spectroradiometer was calibrated with a white reference (Spectralon Labsphere Inc., North Sutton, NH), and then each set of fascicles was arranged on the plant probe. An average of 10 reflectance measurements was immediately recorded for samples. Additionally, 25 fascicles were collected from the same branches for nutrient analysis.

Laboratory procedures

Fascicles were immediately refrigerated and stored in a dry room prior to conducting laboratory analyses. Macronutrient concentrations were assessed for all foliage samples through the dry ash procedure using a spectrometer (Jones and Steyn 1973). Samples were ground with a Wiley mill and oven-dried for 24 hours. Desiccated samples of 0.5 g were poured into ignition tubes and heated in a muffle furnace at gradually increasing temperatures up to 500°C. Samples were mixed with 10 mL 6N HCl and 40 mL distilled water, shaken, and analyzed with an inductively

coupled plasma-optical emission spectrometer (ICP-OES) on a Varion Vista-Max (Varion, Palo Alto, CA, US). For C and N concentrations, oven-dried samples were measured by dry combustion with a vario MAX CN Analyzer (Elementar, Hanau, Germany).

Statistical approach

First derivatives and 28 common reflectance indices for vegetation analysis were calculated from the reflectance data (Table 1). These indices were selected due to

Table 1. Common vegetation reflectance indices and their formulas calculated for correlation with and prediction of foliar macronutrient concentrations (Gökkaya et al. 2014; Schlemmer et al. 2013; Stagakis et al. 2010; Ustin et al. 2009). "R" denotes reflectance and "D" the derivative for a given wavelength (nm).

Index	Abbreviation	Formula
Chlorophyll Absorption In Reflectance Index	CARI	$(R_{700} - \rho_{670}) - 0.2(R_{700} - R_{550})$
Modified CARI	MCARI	$(R_{700} - R_{670}) - 0.2(R_{700} - R_{550})(R_{700}/R_{670})$
Red Edge Chlorophyll Index	CI RE	$R_{NIR}/R_{RE} - 1$
Photochemical Reflectance Index	PRI	$(R_{531} - R_{570})/(R_{531} + R_{570})$
Normalized Difference Vegetation Index	NDVI	$(R_{NIR} - R_{Red})/(R_{NIR} + R_{Red})$
Modified NDVI	mNDVI	$(R_{750} - R_{705})/(R_{750} + R_{705})$
Simple Ratio Index	SR	R_{NIR}/R_{Red}
Modified Red Edge Simple Ratio Index	mSR705	$(R_{750} - R_{445})/(R_{705} - R_{445})$
Enhanced Vegetation Index	EVI	$2.5(R_{NIR} - R_{Red})/(1 + R_{NIR} + 6R_{Red} - 7.5R_{Blue})$
Greenness Index	GI	R_{554}/R_{677}
Structure Insensitive Pigment Index	SIPI	$(R_{800} - R_{445})/(R_{800} - R_{680})$
Pigment Specific Simple Ratio 675	PSSR 675	R_{800}/R_{675}
Pigment Specific Simple Ratio 650	PSSR 650	R_{800}/R_{650}
Pigment Specific Normalized Difference 675	PSND 675	$(R_{800} - R_{675})/(R_{800} + R_{675})$
Pigment Specific Normalized Difference 650	PSND 650	$(R_{800} - R_{650})/(R_{800} + R_{650})$
Plant Senescence Reflectance Index	PSRI	$(R_{680} - R_{500})/R_{750}$
Carotenoid Reflectance Index 1	CRI1	$(1/R_{510}) - (1/R_{550})$
Carotenoid Reflectance Index 2	CRI2	$(1/R_{510}) - (1/R_{700})$
Anthocyanin Reflectance Index 1	ARI1	$(1/R_{550}) - (1/R_{700})$
Anthocyanin Reflectance Index 2	ARI2	$((1/R_{550}) - (1/R_{700}))R_{800}$
Red Green Ratio Index	RGRI	R_{Red}/R_{Green}
Gitelson & Merzlyak 2	G&M2	R_{750}/R_{700}
Lichtenthaler Index 1	Lic1	$(R_{800} - R_{680})/(R_{800} + R_{680})$
Vogelmann Index 1	Vog1	R_{740}/R_{720}
Vogelmann Index 2	Vog2	$(R_{734} - R_{747})/(R_{715} + R_{726})$
Derivative Chlorophyll Index	DCI	D_{705}/D_{722}
Maximum Derivative of Red-Edge	DmaxRE	$Dmax_{RE}$
Maximum Derivative of Red-Edge Divided by Derivative at 703 nm	Dmax703	$Dmax_{RE}/D_{703}$

their repeated use in the related literature. Data was tested for normality and determined to require non-parametric statistics. Three correlation-based statistical approaches were conducted: (1) correlation analysis using reflectance, derivatives, and absorbance transformations (Asner 2008; Smith et al. 2003); (2) correlation analysis with indices (Im et al. 2009); and (3) partial least squares regression (PLSR) with reflectance, derivative, and absorbance values (Asner et al. 2011; Martin et al. 2008). The purpose of the correlational analyses was to determine any regions of the spectrum (i.e. real features across multiple wavelengths) or indices that are consistently correlated with loblolly pine nutrient status. As a powerful modeling technique increasingly used in spectroscopy and remote sensing, PLSR offers the ability to model nutrient concentration across the full spectrum. Reflectance (R) values were transformed to absorbance (A) using the equation, $A = \log(1/R)$ (Smith et al. 2003).

Spearman's rank correlation coefficients (r_s) were calculated between nutrient concentrations and wavelength reflectance values and indices. Next, PLSR was conducted with centered and scaled variables using leave-one-out cross-validation (LOOCV). LOOCV is effective on small data sets and has low bias, variance, and error rates compared to other cross-validation techniques (Cawley and Talbot 2003; Mevik and Cederkvist 2004). For each nutrient, the PLSR model with the minimum root mean PRESS was selected. For flush model comparison, the model with the least number of latent factors with a van der Voet T^2 significance level greater than 0.10 was selected (Townsend et al. 2003). The van der Voet T^2 is a test statistic that indicates whether model residuals are significantly greater than residuals in the model with the lowest error (Tobias 1995). For models with 15 latent factors and no minimum PRESS, the model with 1 latent factor was selected, indicating no valid model. PLSR models were also calculated using major indices (Table 1); and various subsets of the spectrum, consisting of different numbers and combinations of wavelengths derived from the variable importance for the projection (VIP) and correlation analyses. Differences between the various strata – flush, canopy level, genotype, and fertilization treatment – were examined to assess the value in developing treatment-specific models (Figure 2). Tukey–Kramer HSD groupings indicated significant differences between strata (Table 2). Consequently, models were also calculated across each stratum. For all models, centered and scaled regression coefficients and VIP were calculated. VIP indicate the contribution of each variable to the model fit across all latent factors for the predictors and response variables. Wold's criterion of 0.8 was used as the threshold for variable significance (Wold 1994). Predicted versus observed and residuals versus predicted plots were evaluated for model fit.

Results

Nutrients and reflectance

Foliar nutrient concentrations varied between sites within and across ecoregions (Figure 3). Correlation coefficients of the nutrient concentrations and spectra also varied substantially, as shown in Figure 4. There were many significant correlations in the regional samples ($p < 0.05$). Ca has the strongest relationship with reflectance (730 nm, $r_s = -0.62$), followed by K (733 nm, $r_s = 0.45$). The NIR plateau (750–930 nm) was moderately correlated with N, K, and Ca (average $r_s = 0.41, 0.42, -0.57$); this was also the best-performing region for P, but correlations were weaker (average $r_s = 0.28$). K and Ca were also strongly related to wavelengths in the red-edge and green regions. Mg was best, albeit weakly, correlated with mid-IR wavelengths (1380–2500 nm, average $r_s = -0.23$).

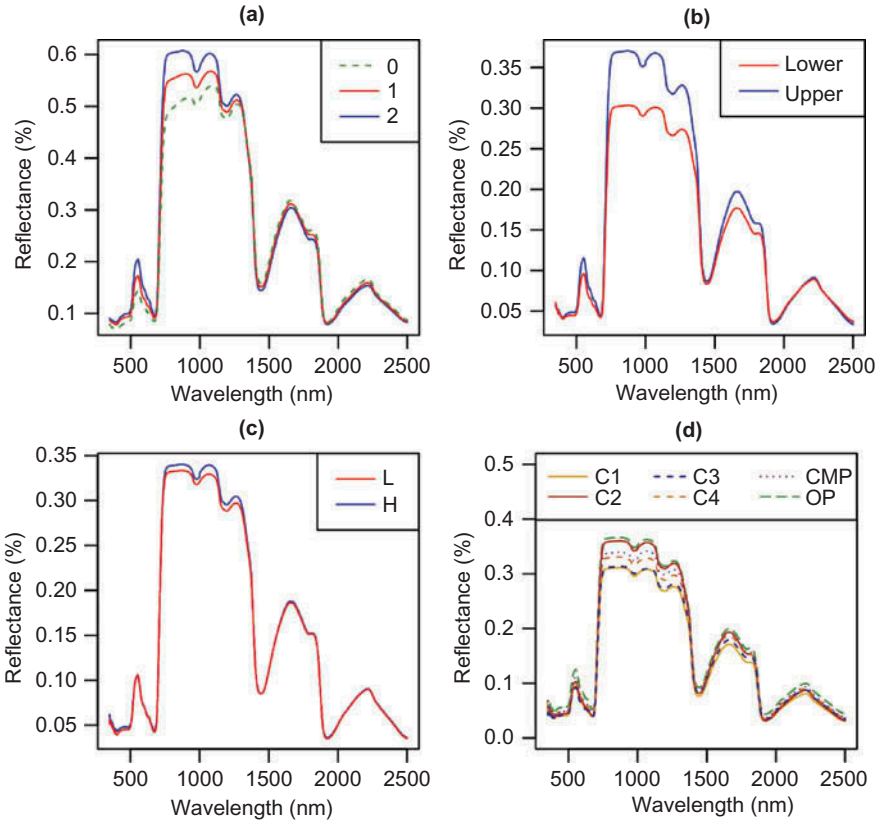

Figure 2. Significant differences exist in average reflectance across strata: (a) flush ("0" = older flush, "1" = previous flush, "2" = most recent flush), (b) canopy level, (c) genotype (C1-C4 = distinct genotypes, "CMP" = controlled mass pollination, "OP" = open pollination), (d) fertilization treatment ("H" = high, "L" = low).

Table 2. Tukey–Kramer groupings of average foliar nutrient content by flush in loblolly pine samples across the southeastern US. Statistically significant nutrient differences ($p < 0.05$) are shown by different groups and exist between flushes for nearly all nutrients.

	Grouping (A, B or C), Mean (%)				
Flush	Nitrogen	Phosphorus	Potassium	Calcium	Magnesium
0	A, 1.08	A, 0.11	A, 0.62	A, 0.27	A, 0.11
1	B, 1.21	B, 0.10	B, 0.51	B, 0.19	A, 0.11
2	B, 1.25	C, 0.09	C, 0.36	C, 0.14	A, 0.10

Correlations have inverse signs for reflectance and absorbance. Derivative correlations fluctuated greatly across the spectrum, with peaks in similar locations across nutrients. K and Ca best correlated with the derivative spectra in the NIR plateau (average $r_s = -0.44$ and 0.56, respectively). The derivative correlation with N peaked at 740 nm ($r_s = 0.68$, $p < 0.001$).

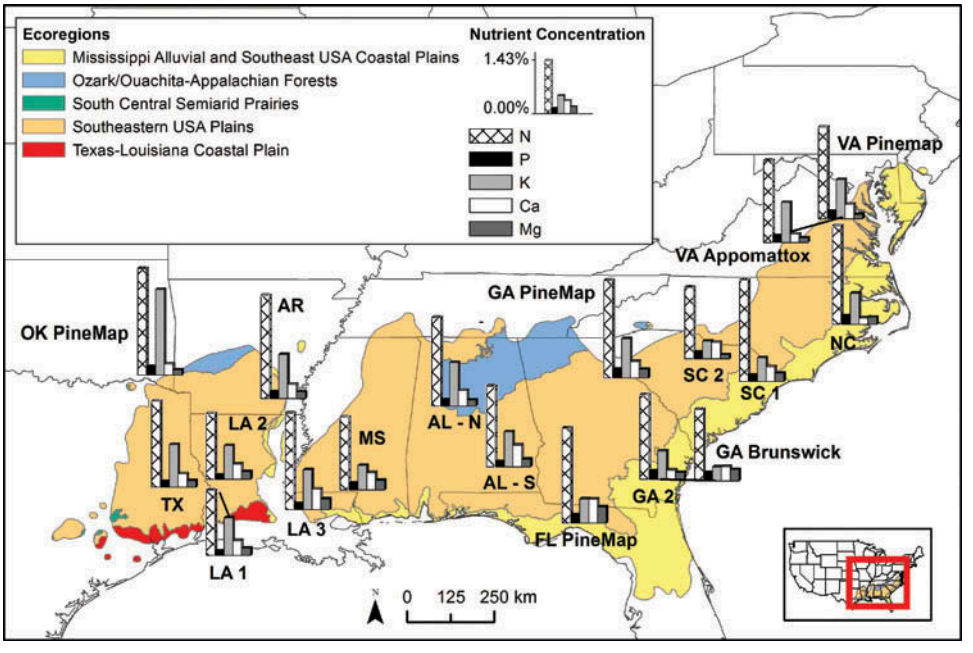

Figure 3. Map of the spatial distribution of loblolly pine foliar macronutrient concentrations (%) across sites in the southeastern US. High variability in nutrient content exists between and within the US Environmental Protection Agency's Level II ecoregions (US EPA 2010).

There were many significant correlations between nutrients and indices ($p < 0.001$). Figure 5 shows the top correlations between each nutrient and a common vegetation index. As Table 3 depicts, no one index was best for all five nutrients; however, several indices and wavelengths have moderate relationships with multiple nutrient concentrations.

Nutrient models

Regional analysis

Partial least squares regression models range in their predictive capabilities by nutrient (Table 4). The r^2 values for N, P, K, Ca, and Mg are 0.81, 0.70, 0.68, 0.42, and 0.51, respectively. Figures 6 and 7 depict model fit using the predicted versus observed values and residuals versus predicted values. PLSR models for the SE sites by flush are shown in Table 5. According to O'Brien's test for equal variances, there is no significant difference between the flush models for N or P ($p = 0.96$ and $p = 0.07$), so the model with the lowest PRESS was selected. For nutrients with a significant difference between the models ($p < 0.001$, $p = 0.02$, and $p = 0.004$ for K, Ca, and Mg, respectively), the model with the least residual variability was selected.

Predictive capabilities of the models generally improve when stratified by flush. However, flush model selection varies by nutrient. The most recent flush produced the selected model for N, Ca, and Mg, while the oldest flush produced models for P and K. Table 4 also displays the PLSR models for the derivatives. Derivative models for all nutrients except Ca have five factors, with a mean R^2 of 0.70. PLSR models with selected

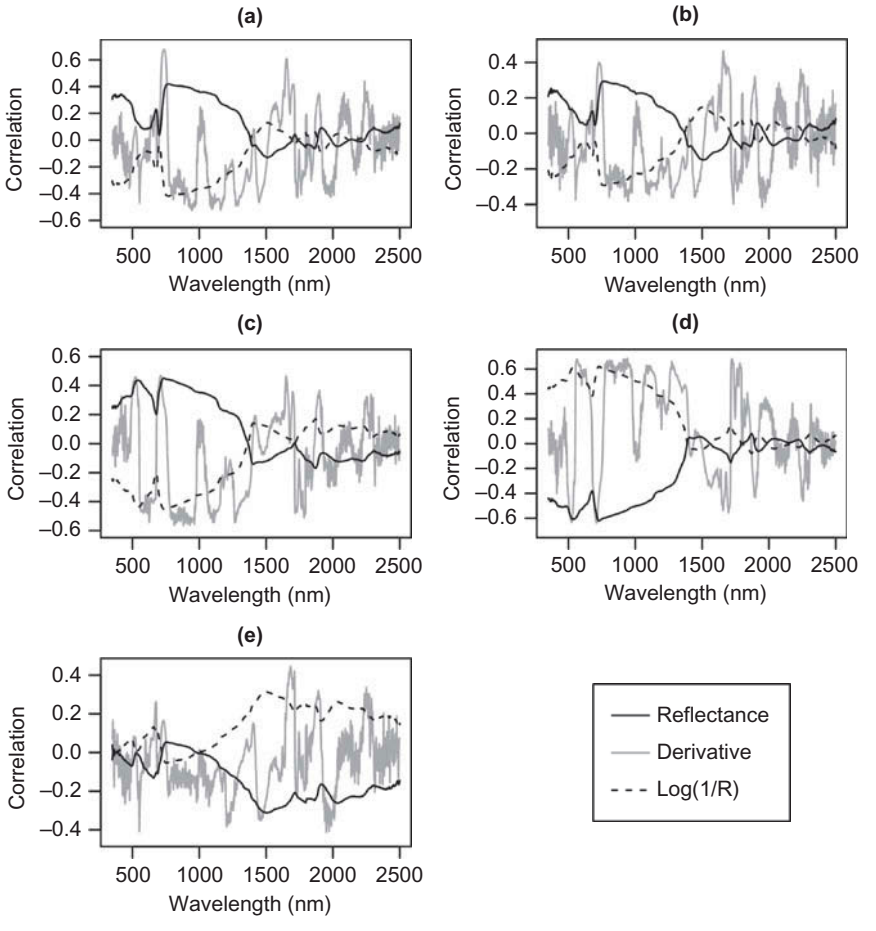

Figure 4. Spearman's rank correlation coefficients (r_s) at the southeastern US sites between original reflectance (R), derivative reflectance, and log(1/R) and nutrient concentrations: (a) nitrogen, (b) phosphorus, (c) potassium, (d) calcium, and (e) magnesium.

indices or wavelengths generally have lower predictive capabilities than the original models.

Similarities and differences in VIP and regression coefficients can be seen in Figures 8 and 9. Flush coefficients generally have similar peaks throughout the spectrum. All nutrients have a peak in the VIP in the visible spectrum between 500–600 nm and near the red edge, around 700 nm.

Local analysis

No stratification produces valid PLSR models consistently across all nutrients or strata, regardless of site, canopy level, genotype, and fertilization treatment. Use of the absorbance transformation, indices, derivatives, and logarithms did not significantly improve models. All derivative models had 0 factors as the lowest PRESS value. This finding is likely due to relatively low variability at the local scale (Figure 10).

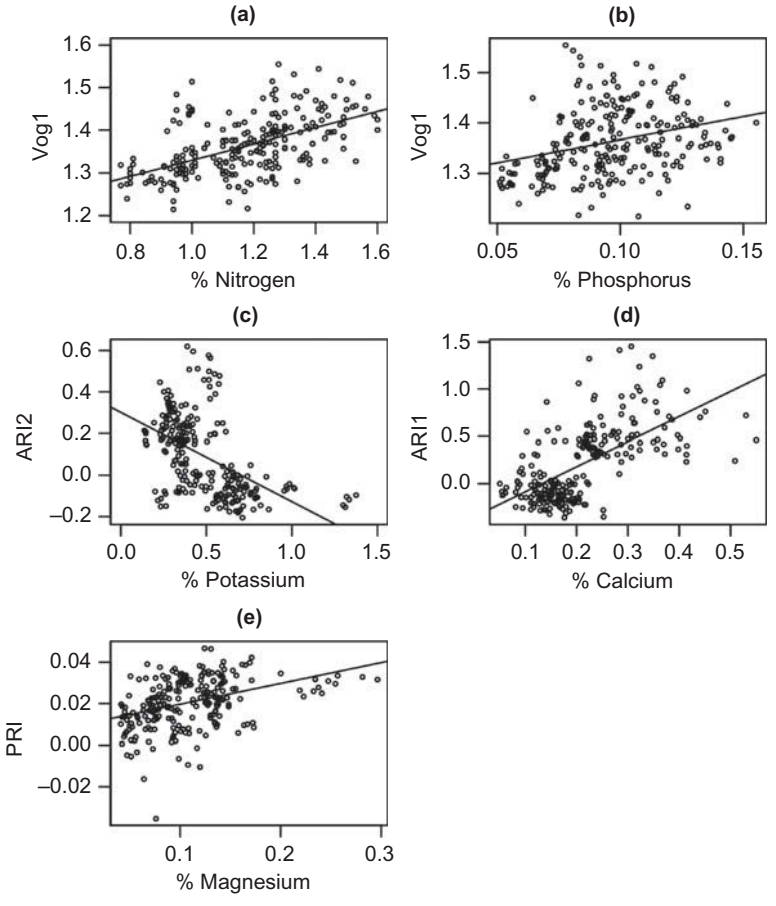

Figure 5. Index versus nutrient plots across all samples at the southeastern US loblolly pine sites: (a) nitrogen and Vogelmann Index 1 (Vog1), (b) phosphorus and Vog1, (c) potassium and the Anthocyanin Reflectance Index 2 (ARI2), (d) calcium and the Anthocyanin Reflectance Index 1 (ARI1), and (e) magnesium and the Photochemical Reflectance Index (PRI).

Discussion

Regional analysis

The PLSR models explain a comparable amount of nutrient variation to prior monospecific studies (Christensen et al. 2004; Pimstein et al. 2011), as well as the related study by Im et al. (2009). However, many studies that model nutrients across multiple species have larger nutrient ranges and produce stronger models. Asner et al. (2011) used PLSR on imaging spectroscopy data to predict macronutrients in tropical forest canopies consisting of several thousand plant species; they obtained R^2 values for N, P, K, Ca, and Mg of 0.77, 0.63, 0.51, 0.65, and 0.57, respectively. Similarly, Petisco et al. (2005) found much higher R^2 values for N, P, and Ca (R^2 = 0.99, 0.94, and 0.95) across 18 different woody plant species in the Iberian Peninsula.

The absorbance transformations, major indices, and subsets of selected wavelengths did not considerably improve the explanatory power of the models. The logarithm transformation produced weaker relationships in the correlation analysis and PLSR.

Table 3. Top correlations between macronutrients and indices for loblolly pine reflectance data from 18 southeastern US sites based on Spearman's rank correlation coefficients ($p < 0.001$). Common vegetation reflectance indices are compiled from prior studies (Table 2).

Nutrient	Index	Correlation coefficient (r_s)
N	Vog1	0.58
	mSR705	0.57
	Vog2	−0.56
	mNDVI	0.55
	G&M2	0.53
P	Vog1	0.37
	mNDVI	0.34
	Vog2	−0.34
	PRI	0.34
	SIPI	−0.33
K	ARI2	−0.55
	ARI1	−0.54
	SIPI	−0.54
	PSRI	−0.54
	EVI	0.45
Ca	ARI1	0.64
	ARI2	0.63
	PSRI	0.63
	SIPI	0.62
	EVI	−0.59
Mg	PRI	0.43
	PSSR 650	0.29
	PSND 650	0.29
	SR	0.27
	NDVI	0.27

Table 4. Partial least squares regression models of reflectance and derivatives by nutrient for the southeastern US sites ($n = 235$) using LOOCV.

Model	Nutrient	Number of factors	R^2	Root mean PRESS	RMSEP
Reflectance	N	14	0.81	0.55	0.08
	P	15	0.70	0.71	0.01
	K	11	0.68	0.64	0.13
	Ca	3	0.42	0.78	0.07
	Mg	10	0.51	0.81	0.11
Derivative	N	5	0.83	0.60	0.08
	P	5	0.77	0.76	0.01
	K	5	0.76	0.70	0.11
	Ca	1	0.44	0.76	0.07
	Mg	5	0.71	0.82	0.02

Derivative models improved predictions and parsimony across all nutrients. This result agrees with a similar study by Petisco et al. (2005) that obtained better results using first and second derivative transformations for N, P, and Ca than the logarithm transformation. Furthermore, Karnieli, Karnieli, and Bonfil (2007) found greater success with derivatives and wavelength selection than the full spectrum of reflectance measurements for N predictions. In this study, selected indices and wavelengths may not have been successful

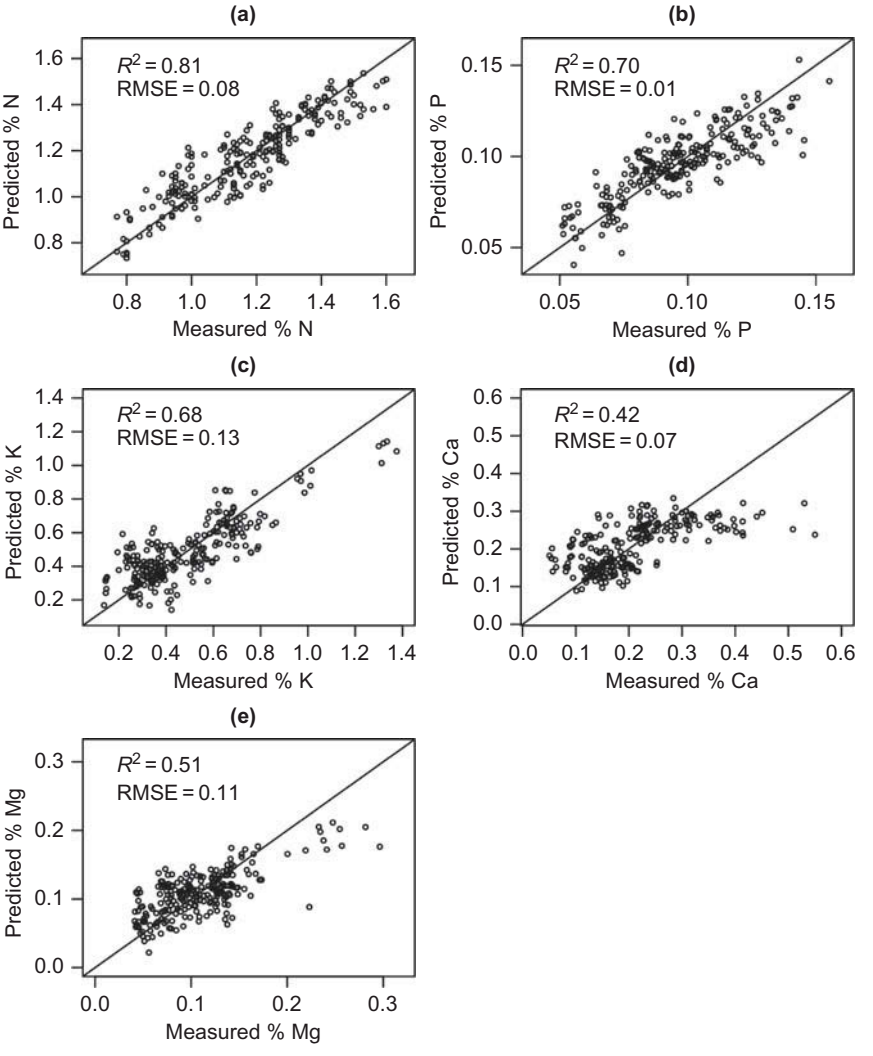

Figure 6. Measured versus predicted plots of partial least squares regression models for 5 nutrients in loblolly pine foliage: (a) nitrogen, (b) phosphorus, (c) potassium, (d) calcium, and (e) magnesium. Models use wavelengths from 350–2500 nm measured with a field spectroradiometer. Samples were collected across the southeastern US.

in the PLSR models because individual wavelengths and/or regions were not strongly correlated with nutrient concentrations.

Flush stratification generally improved parsimony and/or increased explanatory power of nutrient models. The wide range in R^2 values between flushes indicates the importance of flush consideration in sampling. For all nutrients except K, models for the oldest flush used more latent factors and explained more variance than the most recent flush. Likewise, Christensen et al. (2004) used more components in their phosphorus models for older leaves, which they attribute to the greater visibility of nutrient stress in younger leaves. Both Asner (1998) and Christensen et al. (2004) also obtained better N predictions with leaves of later growth stages.

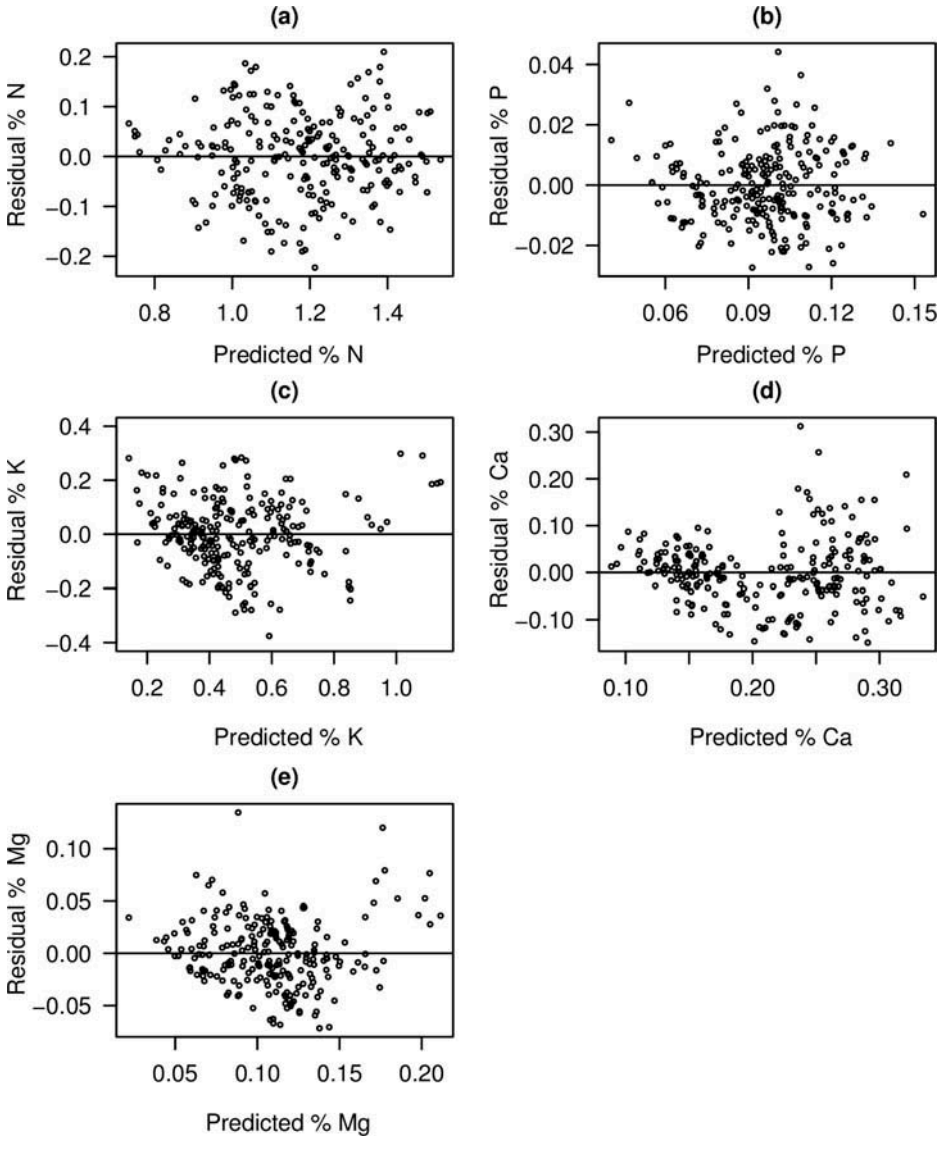

Figure 7. Residual versus predicted plots for 5 nutrients in loblolly pine foliage: (a) nitrogen, (b) phosphorus, (c) potassium, (d) calcium, and (e) magnesium.

Model components

The wavelengths of importance in the PLSR reflectance models are consistent with those in the selected flush models, as well as in prior studies. Given that the flush models use a subset of the data in the reflectance models, this result suggests model stability. The Ca model is the one exception, perhaps due to the relatively low predictive power of the selected flush model. For leaf N status, the N VIP shows the visible, red edge, and NIR regions as the most important reflectance bands (Coops et al. 2003). Wavelengths around 690 nm are particularly related to N due to the absorption of chlorophyll (Christensen et al. 2004).

Table 5. Partial least squares regression models by nutrient and flush for southeastern US sites using LOOCV. Flush 0 indicates the last flush of 2011 (n = 79), Flush 1 indicates the first flush of 2012 (n = 103), and Flush 2 refers to the second flush of 2012 (n = 53).

Nutrient	Flush	Number of factors	R^2	Root mean PRESS	RMSEP
N	0	8	0.82	0.54	0.08
N	1	11	0.78	0.68	0.08
N	2	6	0.81	0.54	0.08
P	0	12	0.78	0.74	0.01
P	1	8	0.54	0.83	0.01
P	2	1	0.18	0.94	0.02
K	0	4	0.34	0.93	0.08
K	1	9	0.74	0.65	0.11
K	2	6	0.73	0.68	0.14
Ca	0	12	0.76	0.83	0.04
Ca	1	7	0.55	0.78	0.06
Ca	2	5	0.46	0.93	0.04
Mg	0	12	0.86	0.63	0.02
Mg	1	10	0.69	0.75	0.00
Mg	2	8	0.73	0.80	0.02

P, K, and Mg showed similar wavelengths of importance in the PLSR models. The P VIP indicates significant contributions from wavelengths near the visible and red-edge regions, 2300 nm, and the 2400–2500 nm range linked to protein, starch, cellulose, and sugar (Curran 1989). The latter connection may be due to the inverse relationship between P content and cellulose or the role of P in protein synthesis (Sawan, Hafez, and Basyony 2001; Specht and Rundel 1990). Visible wavelengths, which are known to indicate K deficiency, had a significant effect on K predictions (Zhai et al. 2013). Furthermore, wavelengths in the chlorophyll absorption features and red-edge are highly related to Mg, which is a chlorophyll component (Gökkaya et al. 2014).

The spectral regions with high correlation coefficients encompass many of the same wavelengths of importance in the PLSR models. However, the degree of similarity between regression coefficients for the reflectance and selected flush models vary by nutrient. Reflectance and flush coefficients for K and Mg models highly match, while P coefficients match moderately. Coefficients for N and Ca models exhibit substantial differences, with high variability in coefficient amplitude and patterns. This disagreement in the Ca models, in conjunction with the discrepancies in the variable importance plots, raise doubts regarding the stability of the Ca model and its physiological underpinnings. Unfortunately, PLSR models are not easily interpretable, particularly with such a large number of variables.

Local analysis

The inability to develop models at Reynolds Homestead or Bladen Lakes is most likely a result of an insufficient environmental gradient. The low nutrient ranges and weak relationships between nutrients and reflectance hinder model development. This finding is consistent with Gong et al's (2012) development of strong local models for sycamore and sweetgum, but inability to do so for loblolly pine. The researchers attribute their difficulty to use red-edge wavelengths exclusively; however, the inclusion of a wide-range

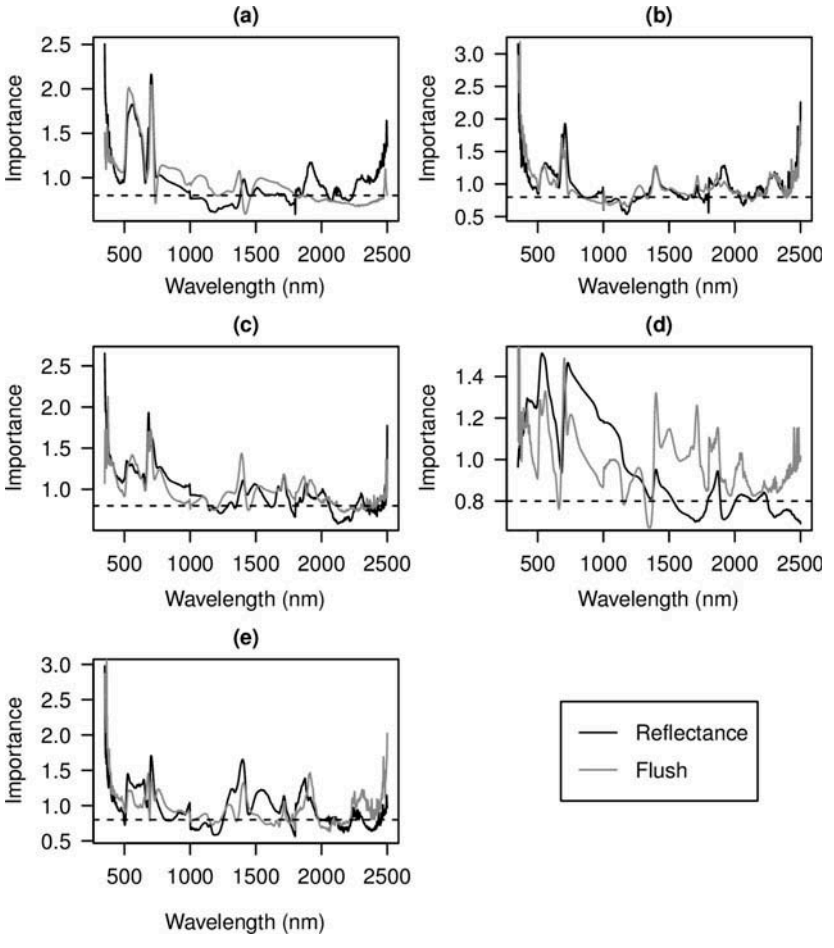

Figure 8. Variable Importance for the Projection (VIP) plots for reflectance and selected partial least squares regression flush models for the following nutrients: (a) nitrogen, (b) phosphorus, (c) potassium, (d) calcium, and (e) magnesium. Dashed line indicates Wold's criterion (0.8). VIP plots indicate the contribution of each variable to model fit across all latent factors in partial least squares regression.

of wavelengths did not resolve the problem. It is possible that the tendency of loblolly pine trees to increase leaf area index when fertilized, rather than foliar N, may confound model development (Gough, Seiler, and Maier 2004). Patterns across the 18 sites in the SE US were apparent because the nutrient ranges were much greater, much as other studies have shown success with interspecific models (Gökkaya et al. 2014; Im et al. 2009).

Spectral differences exist between genotypes and hybrids of different species, as well as in the Bladen Lakes and Reynolds Homestead loblolly pine varieties (Espinoza, Hodge, and Dvorak 2012; Im et al. 2009). However, nutrient differences across genotypes did not match differences in reflectance across genotypes, thus precluding the use of genotype-specific models at Bladen Lakes and Reynolds. Therefore, it is evident that nutrients are not the main driver of spectral differences in these genotypes.

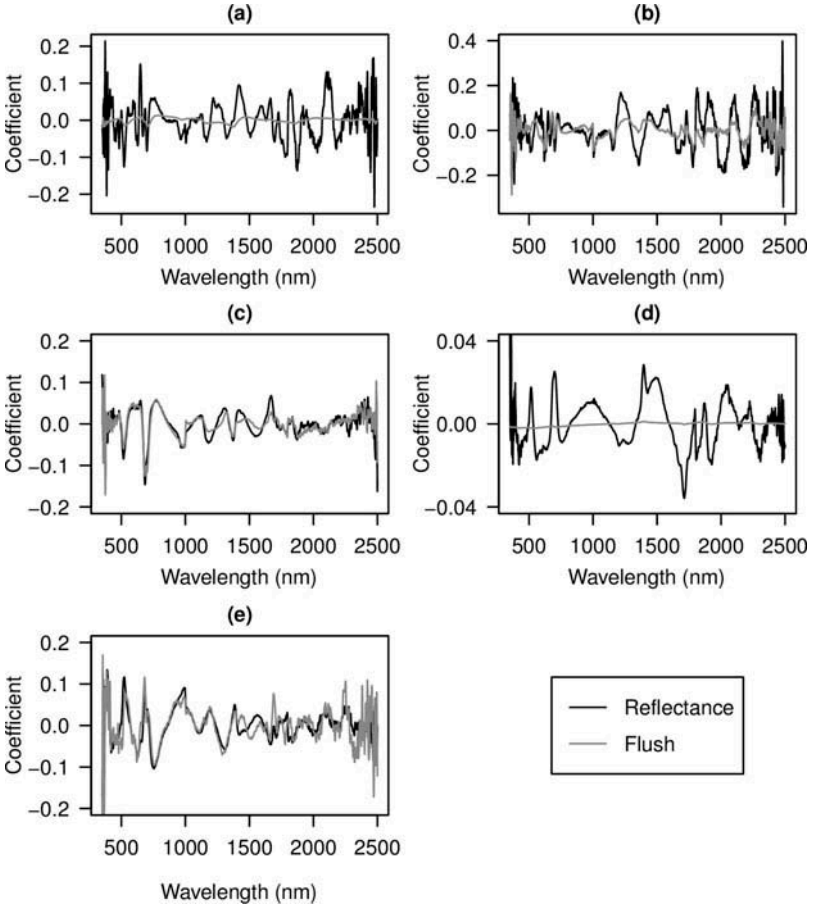

Figure 9. Regression coefficients for reflectance and selected flush partial least squares regression models for nutrients: (a) nitrogen, (b) phosphorus, (c) potassium, (d) calcium, and (e) magnesium. Model coefficients are centered and scaled to improve comparability.

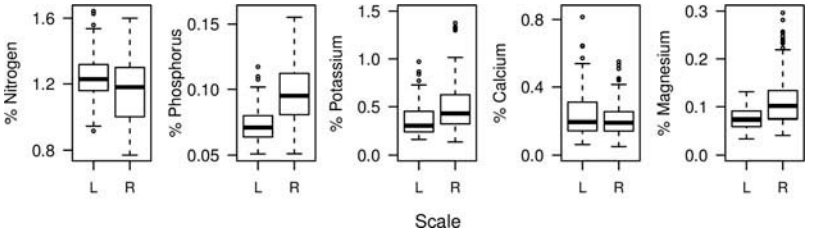

Figure 10. Nutrient distributions of loblolly pine foliar samples across the 18 southeastern US regional ("R") study sites and the localized ("L") study sites in Virginia and North Carolina. Most nutrient ranges are significantly greater at the regional scale.

Conclusion

This study is among the first to successfully identify foliar macronutrients (e.g. N, P, K, Ca, Mg) with spectral reflectance in loblolly pine plantations at the leaf-level scale. Model

accuracies are comparable to those of other species, and the models explain a significant amount of variation in macronutrient concentrations across sites in the SE US. Results indicate that localized loblolly pine nutrient studies, even with fertilization treatments, are less likely to produce successful remote-sensing models than studies across a large geographic region. In addition, the study emphasized the importance of flush in nutrient models using remote sensing. Future work will need to encompass other methods of assessing spectral reflectance, such as continuum-removal or machine-learning techniques. Furthermore, it is critical to determine the relationship between leaf- and canopy-level analyses for future assessment with satellite data.

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