



Spectroscopy of canopy chemicals in humid tropical forests

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ABSTRACT

Remote sensing of canopy chemistry could greatly advance the study and monitoring of functional processes and biological diversity in humid tropical forests. Imaging spectroscopy has contributed to canopy chemical remote sensing, but efforts to develop general, globally-applicable approaches have been limited by sparse and inconsistent field and laboratory data, and lacking analytical methods. We analyzed leaf hemispherical reflectance and transmittance spectra, along with a 21-chemical portfolio, taken from 6136 fully sunlit humid tropical forest canopies, and developed an up-scaling method using a combination of canopy radiative transfer, chemometric and high-frequency noise modeling. By integrating these steps, we found that the accuracy and precision of multi-chemical remote sensing of tropical forest canopies varies by leaf constituent and wavelength range. Under conditions of varying canopy structure and spectral noise, photosynthetic pigments, water, nitrogen, cellulose, lignin, phenols and leaf mass per area (LMA) are accurately estimated using visible-to-shortwave infrared spectroscopy (VSWIR; 400–2500 nm). Phosphorus and base cations are retrieved with lower yet significant accuracy. We also find that leaf chemical properties are estimated far more consistently, and with much higher precision and accuracy, using the VSWIR range rather than the more common and limited visible to near-infrared range (400–1050 nm; VNIR). While VNIR spectroscopy proved accurate for predicting foliar LMA, photosynthetic pigments and water, VSWIR spectra provided accurate estimates for three times the number of canopy traits. These global results proved to be independent of site conditions, taxonomic composition and phylogenetic history, and thus they should be broadly applicable to multi-chemical mapping of humid tropical forest canopies. The approach developed and tested here paves the way for studies of canopy chemical properties in humid tropical forests using the next generation of airborne and space-based high-fidelity imaging spectrometers.

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1. Introduction

Canopy chemistry both reflects and predicts the functional status of vegetation and ecosystems, expressing processes ranging from primary production to decomposition and nutrient cycling. Canopy chemistry is also often indicative of functional and biological diversity in ecosystems (Townsend et al., 2008). As a result, chemical remote sensing has been a focus of research for many years, and much progress has been made in developing methods for the detection and mapping of plant chemicals with field, airborne and space-based technologies (reviewed by Kokaly et al., 2009; Ustin et al., 2009). The most important technology in this arena continues to be imaging spectroscopy, also known as hyperspectral remote sensing.

Remote sensing of plant chemistry has a relatively long scientific history (Gates et al., 1965). Early work focused on linking leaf visible-to-infrared spectra with leaf photosynthetic pigments, water, nitrogen (N), cellulose and lignin. This fueled a well-known synthesis

by Curran (1989), who listed the spectral features associated with these and other leaf chemical constituents. Meanwhile, airborne imaging spectroscopy was pursued in an effort to estimate concentrations of foliar N, lignin, and other chemical constituents in forest canopies (Peterson et al., 1988; Wessman et al., 1988). In the 1990s, additional studies were undertaken with the goal of generalizing the methods for spectroscopic remote sensing of canopy chemicals. The NASA Accelerated Canopy Chemistry Program worked to associate leaf and canopy spectra with N and lignin content in foliage of 96 forest species (ACCP, 1994). Yet at that time, development of a general approach to foliar chemical mapping was stymied by methodological limitations. One major problem was the statistical overfitting of high-dimensional, collinear spectral data with each chemical trait. Another problem occurred when attempting to apply a set of predictive equations derived from one dataset to another (Grossman et al., 1996).

In parallel with ACCP, the Leaf Optical Properties Experiment (LOPEX) generated a spectral and chemical dataset spanning about 50 species, with the main intention of advancing leaf optical models (Fourty et al., 1996). LOPEX supported the development of several models, the most notable being PROSPECT (Jacquemoud and Baret,

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1990), which is currently in its fifth version (Feret et al., 2008). While these leaf models greatly advanced our understanding of photosynthetic pigment, water and total carbon contributions to the optical spectroscopy of foliage (Jacquemoud et al., 2009), they were not intended to incorporate all known chemical sources of variability in leaf spectra. In particular, the models often lack a mechanistic treatment of N, carbon fractions such as lignin and cellulose, and other secondary metabolites such as phenols.

In recent years, some of these issues have been overcome, and an ever more consistent set of approaches is being reported. For example, Martin et al. (2008) used Airborne Visible and Infrared Imaging Spectrometer (AVIRIS) and space-based EO-1 Hyperion satellite data to estimate N content of forest canopies. With partial least squares regression (PLSR) techniques, which directly address data dimensionality and collinearity issues (Martens, 2001), Martin et al. (2008) showed that canopy N content can be estimated in different ecosystems. This was a major step forward, yet it focused on N, and we do not know whether this approach would work for other foliar chemicals. Moreover, they spatially integrated leaf N data across species and with canopy leaf area, thereby going for direct relationships between plot-scale spectral measurements and canopy-N. This approach left open the question of whether the spectral variation was driven solely by leaf N, or by covariances among leaf chemical and structural properties such as leaf area index (LAI), canopy architecture (e.g. needle vs. broadleaf), and composition (plant families, genera and species).

In 2007, the Spectranomics Project was undertaken to address these and similar issues by combining chemometric methods, such as PLSR, with extensive field-based measurements of leaf optical properties and physical models needed to scale from leaf to canopy levels (Asner and Martin, 2009). The effort focuses on humid tropical forest canopies, and therefore is limited to mostly broadleaf species. Nonetheless, humid tropical forests span a wide range of environments, and the spectranomics database currently stores about 10,000 tropical forest canopy specimens collected from sites spanning elevations from sea level to 3660 m, and ranging in mean annual temperature and precipitation of 8–28 °C and 1200–6100 mm yr⁻¹, respectively (<http://spectranomics.ciw.edu>).

Previously we reported on the use of high-fidelity leaf spectroscopy (400–2500 nm) to estimate six foliar chemicals and leaf mass per area (LMA) in 162 canopy species found along an elevation gradient in Australian tropical forests (Asner et al., 2009). We found that chlorophyll-a and -b (chl-a, chl-b), carotenoids, water, N, phosphorus (P) and LMA could be estimated with high precision and accuracy using PLSR. Combining PLSR with a canopy reflectance model, we also found that variation in canopy LAI, architecture, and solar and view geometry has a minimal effect on leaf pigment and LMA estimates from high-fidelity spectroscopy (Asner and Martin, 2008). However, variation in canopy structure imparts a larger degrading effect on the accuracy of leaf N and P estimates from canopy spectra.

Despite the progress made to improve the link between leaf and canopy spectroscopy and chemical traits in tropical forests, our previous studies, like others, fell short in providing a general approach that might be transportable to new settings. Chemometric approaches such as PLSR, whether used at the leaf level, or embedded in a canopy model, are subject to instability when calibrations developed with one dataset are used to predict the chemicals from spectra in another dataset (Boulesteix and Strimmer, 2006; Martens, 2001). This suggests that a very large set of predictors, spanning as wide a range of leaf chemical and spectral traits as possible, is required to build the most general models. This is particularly challenging in humid tropical forests, where canopy chemical properties have proven to be among the most diverse on Earth (Fyllas et al., 2009; Townsend et al., 2008). A second problem with past work involves the application of “noise-free” PLS regressions to airborne or space-based spectral data, which does not work well because random and systematic

noise is invariably embedded in the spectral images. Systematic noise in imaging spectrometer data is dominated by high-frequency errors and artifacts that remain following atmospheric modeling to convert radiance spectra to reflectance.

To develop a general approach to high-fidelity spectroscopic mapping of canopy chemistry in tropical forests, we analyzed leaf hemispherical reflectance and transmittance spectra, along with a 21-chemical portfolio, in 6136 humid tropical forest canopies, and developed up-scaling methods using a combination of canopy radiative transfer, PLSR and high-frequency noise modeling techniques. With this dataset, we ask: (i) What is the precision and accuracy of 21 chemical determinations using high-fidelity spectroscopy at the leaf level? Are there global models that can effectively represent all tropical forest canopies, independent of ecoregion, site, lifeform or taxon? (ii) With what precision and accuracy can the chemical traits be estimated at the canopy scale, and against a backdrop of varying canopy structure? (iii) What is the effect of sensor noise, including both random and systematic sources of error, on chemical estimates from canopy spectroscopy?

2. Materials and methods

2.1. Field methods

Samples were collected from 61 sites distributed throughout the humid tropical forest biome, including in the Neotropics (Mesoamerica and Amazonia), Pacific Islands, Paleotropics, Caribbean, Australasia, and Borneo (Fig. 1, Table 1). The dataset is composed of the most common plant habits found in tropical forest canopies, including tree (n=5233), liana (648), palm (74), hemi-epiphyte (109), and vine (51). The dataset also includes 3791 species with two or more replicates collected within a site, and an additional 2870 species with three or more replicates collected across sites. We are only interested in humid forest species, so we controlled for mean annual precipitation (MAP) of 1200 to 6100 mm yr⁻¹ based on long-term climate records. We did not control for mean annual temperature (MAT), which ranges from 8 to 28 °C, and elevations of 0–3660 m. Soil type varies strongly across sites, from extremely nutrient-poor Oxisols (clays) and Entisols (white sands) to nutrient-rich Inceptisols (Table 1). Detailed information and maps for all samples and sites can also be acquired at <http://spectranomics.ciw.edu>.

At each site, individual canopies were carefully selected to control for full sunlight conditions because shading strongly affects leaf chemistry and spectroscopy (Lee et al., 1990; Poorter et al., 1995, 2009), and because canopy reflectance is dominated by upper-canopy, sunlight leaves in highly foliated vegetation canopies (Asner, 2008; Asner and Martin, 2008). This process requires that two or more trained workers agree that the selected canopy has unobstructed exposure to the sky. Individual canopies meeting this criterion were then marked and a voucher specimen was collected. Vouchers were matched by local expert taxonomists to type specimens kept at the National Agrarian University La Molina Herbarium, Peru and the Missouri Botanical Garden, USA. We also matched genus names to information provided by Kew Botanic Gardens, UK. Family-level taxonomy followed the Angiosperm Phylogeny Group III (Stevens, 2001-present). Of the 6136 individuals reported here, 6095 (99%) have been identified to the genus level, and 5786 (94%) have definite taxonomic identifications to the species level. All project reference vouchers are kept at Carnegie Institution facilities, and reference photos of the specimens can be viewed at <http://spectranomics.ciw.edu>.

Leaf collections were conducted using a combination of tree climbing, shooting, crane, and pole-clipping techniques. Only fully sunlit branches of mature leaves were taken and sealed in large polyethylene bags to maintain moisture, stored on ice in coolers, and transported to a local site for processing within 3 h, and often less than 30 min. Leaves with some epiphylls, signs of disease and recent

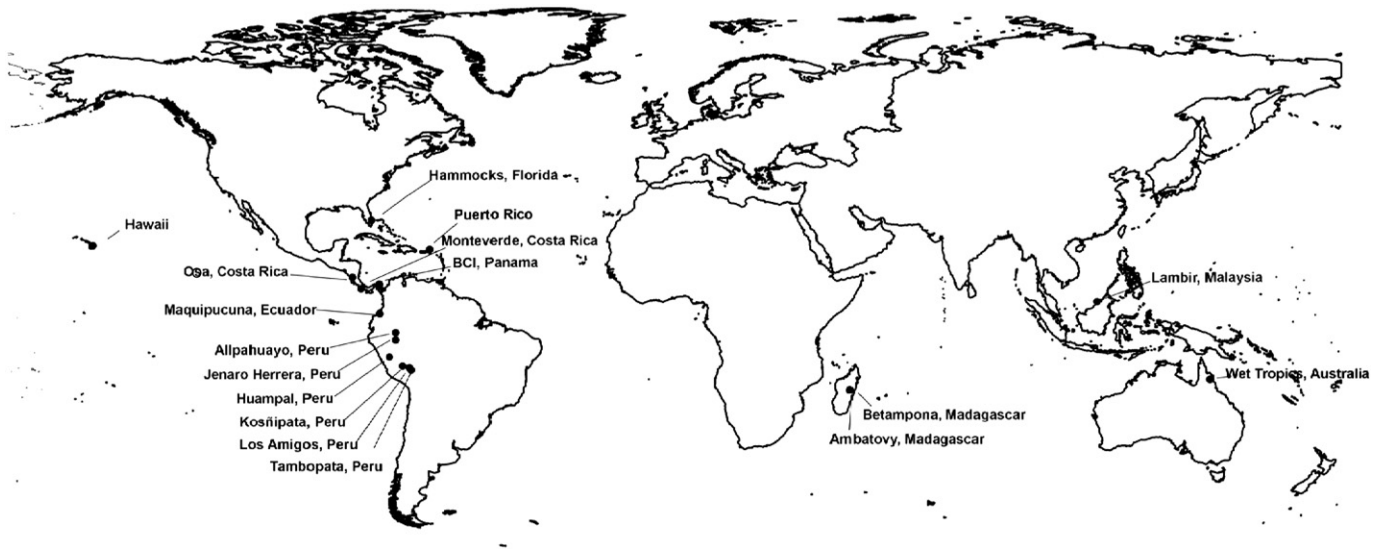


Fig. 1. Map showing the location and number of sites of each canopy leaf sample collection campaign. Full descriptions of the sites and taxa are available on the Spectranomics Project website at <http://spectranomics.ciw.edu>.

flush were permitted to enter the dataset, but only if the leaves remained in whole form and were not overly damaged. For each sample, a subset of leaves was selected from the branches for chemical and LMA determination in the laboratory. With this chemistry sample, hemispherical reflectance and transmittance in the 400–2500 nm range was measured on 12 randomly selected fresh leaf surfaces immediately after acquiring each branch in the field. The spectral measurements were taken at or close to the mid-point between the main vein and the leaf edge, and approximately half-way from petiole to leaf tip. Care was taken to avoid large primary or secondary veins, while allowing for smaller veins to be incorporated into the measurement.

The spectra were collected with a field spectrometer (FS-3 with custom detectors and exit slit configurations to maximize signal-to-noise performance; Analytical Spectra Devices, Inc., Boulder, CO USA), an integrating sphere designed for high-resolution spectroscopic measurements, and a custom illumination collimator (Asner and Martin, 2008). Twenty-five spectra per sample were averaged and calibrated for dark current and stray light, then referenced to a calibration block within the integrating sphere (Spectralon, Labsphere Inc., Durham, NH). An integrating sphere and collimated light source are required if directional-hemispherical reflectance and transmittance measurements are desired, and these measurements are required for use in scaling up to the canopy level using radiative transfer models (Feret et al., 2008; Jacquemoud et al., 2009; Verhoef and Bach, 2007). This up-scaling step cannot be achieved without sphere-based measurements and models that ingest them properly

(Kokaly et al., 2009). In addition, our experience is that these instrument customizations are necessary to provide leaf spectra that require minimal manipulation, such as smoothing that tends to remove critically important spectral features in the data. The high-fidelity measurement capability of our field instruments resulted in calibrated spectra that did not require smoothing or other filters commonly used in leaf optical studies.

2.2. Chemical data

The methods for chemical assays were reported in detail previously (Asner and Martin, 2011). We summarize the minimum, median and maximum values for each chemical and LMA in Table 2. Chemical assay protocols, along with the instruments and standards, are provided on the spectranomics website (<http://spectranomics.ciw.edu>). When the data were non-normally distributed, we applied a natural logarithm (\log_e) transformation. Total C, soluble-C, cellulose, lignin, and phenol and tannins did not require \log_e -transformation for statistical analyses.

It is important to recognize that the range of chemical values incorporated into this study is extremely broad, meeting and often exceeding the range of canopy chemical traits reported for other individual biomes and most biomes combined (McGroddy et al., 2004; Poorter et al., 2009; Reich and Oleskyn, 2004; Townsend et al., 2007; Wright et al., 2004). For example, the range of N and P variation among global terrestrial ecosystems was previously reported as 0.68–4.07% and 0.05–0.23%, respectively (Wright et al., 2004), yet we

Table 1
Collection sites and phylogenetic information for the foliar data set.

Political unit	Num. sites	Elevation ^a range	MAP ^b range	MAT ^c range	Soil orders ^d	Num. samples	Num. families	Num. genera	Num. species
Australia	11	21–1084	1165–3333	18.3–23.7	Alf, Ent, Inc, Oxi, Ult	188	45	121	187
Costa Rica	9	50–1607	2832–4698	17.7–25.8	And, Inc, Ult	746	100	321	607
Ecuador	1	1325–1980	3200	18	Inc	242	51	105	162
Hawaii	9	27–1570	1800–5080	13.2–23.8	And, Inc	180	58	129	156
Madagascar	3	330–1118	1700–3020	17–24.3	Ent, Oxi, Ult	624	72	204	426
Panama	4	84–189	1865–3140	26–27.2	Inc	269	65	180	258
Peru	17	92–3660	2380–6128	8–26.6	Ent, His, Inc, Ult	3338	122	515	2090
Puerto Rico	6	140–910	3460–6096	21.3–25.6	Inc, Ult	104	47	86	101
Sarawak	1	70–80	2680	26.6	Ult	395	51	108	235

^a Elevation (m).

^b MAP = mean annual precipitation (mm).

^c MAT = mean annual temperature (C).

^d Soil orders: Alf = Alfisol; And = Andisol; Ent = Entisol; His = Histisol; Inc = Inceptisol; Oxi = Oxisol; Ult = Ultisol.

Table 2
Leaf chemical properties and leaf mass per area (LMA) for 6136 humid tropical forest canopies.

Leaf property	Median	Range	Unit of measure
Chlorophyll a	4.78	0.83–15.99	mg g ⁻¹
Chlorophyll b	1.78	0.29–5.83	mg g ⁻¹
Carotenoids	1.41	0.35–4.32	mg g ⁻¹
LMA	100.99	22.21–365.02	g m ⁻²
Water	58.58	37.95–90.79	%
N	1.85	0.56–5.54	%
C	49.1	34.8–57.4	%
Soluble C	45.28	16.19–84.45	%
Hemi-cellulose	11.63	0.00–35.38	%
Cellulose	18.19	5.06–43.59	%
Lignin	22.50	2.71–64.51	%
Phenols	94.58	0.00–309.66	mg g ⁻¹
Tannins	40.13	0.00–205.50	mg g ⁻¹
P	0.10	0.02–0.86	%
K	0.70	0.13–5.64	%
Ca	0.89	0.00–6.87	%
Mg	0.25	0.02–1.50	%
Zn	11.41	1.86–468.40	µg g ⁻¹
Mn	88.03	3.76–7331.67	µg g ⁻¹
B	23.01	2.82–321.89	µg g ⁻¹
Fe	49.44	9.36–9470.68	µg g ⁻¹

compiled foliar data with a range of 0.56–5.54% for N and 0.020–0.86% for P. Our LMA range goes from 22.2 to 365.0 g m⁻², which exceeds the range for nearly all biomes combined, both terrestrial and aquatic (Poorter et al., 2009). As a result, we believe our chemical, and thus spectral, dataset meets or exceeds the range of values found throughout the world's humid tropical biome, and thus we contend that the results presented here are globally applicable.

2.3. Canopy reflectance modeling

We projected the leaf reflectance and transmittance spectra collected in the field to the canopy level using the 4SAIL2 canopy radiative transfer model (Verhoef and Bach, 2007). The model simulates top-of-canopy spectral reflectance based on the measured leaf hemispherical-directional reflectance and transmittance spectra, along with variation of leaf area index (LAI), leaf angle distribution, and other crown geometric-optical properties. Ranges for LAI and other structural parameters for each growth habit (tree, liana, hemi-epiphyte, palm, vine) are provided in Table 3, and were compiled from Asner et al. (2003) and Asner and Martin (2008). For each specimen, a randomly-selected combination of canopy structural parameters based on growth habit was combined with the field-measured leaf spectra to generate a canopy reflectance signature. This was repeated 25 times per specimen, and the resulting 25 reflectance signatures were recorded for each specimen for subsequent analyses.

Table 3
Ranges of canopy structural parameters randomly selected during canopy radiative transfer model simulations. LAI = leaf area index; LAD = leaf angle distribution; Cv = crown covering the ground at nadir; Zeta = ratio of crown diameter to tree height.

Plant habit	LAI	LAD ^a	Cv	Zeta
Tree	3.0–7.0	–0.4 to 0.4 –0.1 to 0.2	0.6–0.8	0.2–0.7
Liana	1.0–4.0	–0.1 to 0.3 0.3 to 0.6	0.7–0.9	0.1–0.3
Palm	2.0–5.0	–0.8 to –0.2	0.7–0.9	0.1–0.3
Vine	1.0–2.5	–0.1 to 0.3 0.3 to 0.6	0.7–0.9	0.1–0.3
Hemi-epiphyte	3.0–7.0	–0.4 to 0.4 –0.1 to 0.2	0.6–0.8	0.2–0.6

^a Leaf angle distribution is described by a two-parameter model, with the first parameter controlling average leaf inclination and the second parameter controlling bimodality of the leaf angle distribution (Verhoef and Bach, 2007).

2.4. Chemometric analyses

We used PLSR analysis (Haaland and Thomas, 1988) to determine which leaf and canopy properties can be remotely sensed using high-fidelity spectroscopy. Here we repeated the analyses to test two common configurations in imaging spectroscopy: the most common is VNIR (visible to near-infrared; 400–1050 nm) such as the Compact Airborne Spectrographic Imager or CASI (Blackburn, 2002); and the less common VSWIR (visible to shortwave infrared; 400–2500 nm) such as AVIRIS (Green et al., 1998). Leaf reflectance and transmittance were tested using the field-based measurements following re-sampling to 10 nm full-width half-maximum bandwidth spanning the VNIR and VSWIR spectra ranges. To more closely represent airborne data, canopy reflectance was tested in a similar configuration but with the 1350–1450 nm and 1850–1975 nm atmospheric water vapor regions removed from the simulated VSWIR data (Gao and Goetz, 1995).

To avoid overfitting, the number of factors used in the PLSR analysis was determined by minimizing the Prediction Residual Error Sum of Squares (PRESS) statistic (Chen et al., 2004). The PRESS statistic was calculated through a cross-validation prediction for each model. This cross-validation procedure iteratively generates regression models while reserving 10% of the samples from the input data set until the root mean square error (RMSE) for the PRESS statistic is minimized. The models were then used to estimate each leaf property from the original spectral data. Validation statistics were applied to these models to determine the precision and accuracy of each chemical estimate from spectroscopy, as well as to quantify the role of differing spectral configurations in the model (adding noise or multiple spectra with randomly varying structural properties). The coefficient of determination (r^2) was used to assess the precision of the PLSR models developed, while the RMSE between calibration and prediction results yields an assessment of the model accuracy. Similar to Feilhauer et al. (2010), RMSE values were often standardized to the percentage of the response range (%RMSE) to simplify comparison across chemical traits.

2.5. Spectral configurations

PLSR precision and accuracy were first examined using measured leaf reflectance and transmittance, and then using single-canopy simulations based on these leaf spectra ($n = 6136$). Additional variation was subsequently incorporated as explained here. Twenty-five spectra per sample, derived from the canopy modeling described earlier with varying canopy structural parameters were created for each sample ($n = 6136 \times 25 = 153,400$), and were integrated into the PLSR model. Due to processing limitations incurred when all 25 spectra were included for a large number of samples, we tested how many spectra (up to 25) are needed to accurately incorporate canopy structural variability into the spectra using a randomly-selected subset of 853 samples. Three different PLSR models were built and compared based on these 853 samples, one using an average of the 25 spectra per sample as outlined above, a second using five randomly selected spectra per sample, and a third using all 25 spectra. This was tested using both VSWIR and VNIR wavelength regions.

In addition to structural variation, the impact of high frequency noise on PLSR predictions was investigated. This noise is primarily composed of sensor noise and residual artifacts following atmospheric correction. To apply noise to the simulated canopy spectra, data from actual AVIRIS imagery taken over tropical forest was used as a source of noise for VSWIR simulations. A Fast Fourier Transform (FFT) was performed on a set of 400 image pixels of sunlit canopy crowns. The FFT transform was performed in three wavelength segments: 366–1333 nm, 1432–1772 nm, and 2048–2497 nm. For VNIR spectra, the FFT was also performed in 3 segments: 385–678 nm, 687–763 nm, and 772–1055 nm. For each simulated canopy spectrum, the FFT

transform was also performed on the same segments and one of the 400 noise source spectra was randomly selected. The higher frequency components of the selected Fourier transformed noise spectrum were extracted and copied into the Fourier-transformed modeled spectrum for each segment. The inverse of the FFT was then computed on each segment of the composited spectra, and the segments were combined to create a single spectrum. This resulted in noisy canopy spectra that carry the shape and magnitude of the original noise-free spectra, but with higher frequency variation of the spectra collected from the image.

Finally, we assessed the effect of brightness normalization, developed by Feilhauer et al. (2010), on PLSR models containing full structural and spectral variability. The analysis was applied during the creation of two PLSR models, one for the VSWIR and one for the VNIR, utilizing all samples ($n=6136$). In each model, five spectra of varying canopy structure, containing noise, were used for each sample.

2.6. General model development

To determine how many samples are needed to build the most general and accurate PLSR model that is insensitive to potential local influences of site, lifeform, and taxonomy, we built PLSR models using an increasing number of samples randomly drawn from the spectranomics database, in increments of 250 up to 5500 samples. At each increment, we tested the model at one arbitrarily selected site, Betampona in Madagascar (Fig. 1), which contains a large number of samples ($n=330$). This site was not included in the model creation step. We repeated this entire process 10 times, each repetition created with randomly selected spectra and chemistry, increasing in volume from 250 to 5500 samples. The best model was selected based on minimum regression r^2 -values (precision) and %RMSE (accuracy) among the 10 runs. These analyses were carried out using both VSWIR and VNIR spectral configurations.

We carried out additional analyses to create the most general PLSR models for VSWIR and VNIR configurations. Twenty-five different calibration models were created using a random selection of samples from the global database, with the number of samples in each model determined from previous analyses on the Betampona site. Each of these 25 models was then used to predict 500 new, randomly-selected test samples (not used in model calibration) from the spectranomics database. This approach avoided possible biases incurred by using samples from any one site or taxonomy.

3. Results and discussion

3.1. Leaf optical properties

We found extremely broad variation in leaf reflectance and transmittance spectra among the 6136 humid tropical forest canopies (Fig. 2). This spectral variation in fully formed leaves, consistently taken from full-sunlight, top-of-canopy positions and measured using identical instrumentation and methods, exceeds most of the variation reported within and among other vegetation types, ecosystems or biomes (Asner, 1998; Curran et al., 1992; Feret et al., 2008; Gitelson and Merzlyak, 1997; Poorter et al., 2000; Roberts et al., 1998, 2004; Sims and Gamon, 2002; Weiser et al., 1986; Williams, 1991). Although the widest reflectance range was observed in the near-infrared (NIR; 750–1300 nm), the largest coefficients of variation were found in the shortwave-infrared (SWIR; 1500–2500 nm), followed by the visible spectral region (VIS; 400–750 nm) (Fig. 2). This confirms previous findings indicating that, although the reflectance range is lowest in the VIS and SWIR, the variation among canopies is proportionally greater in these spectral regions (Asner and Martin, 2008). This wide variation is requisite to developing the

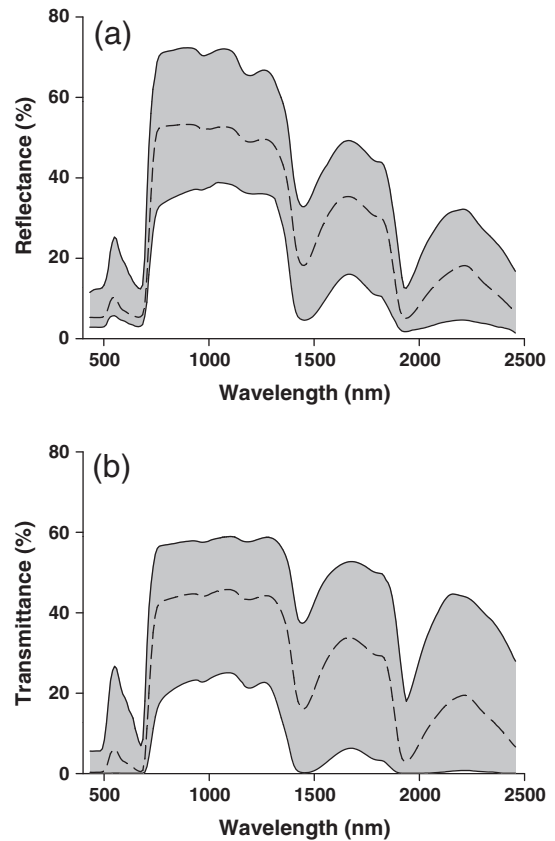


Fig. 2. Median and range of leaf hemispherical reflectance and transmittance collected from 6136 individual canopies comprised 2419 species from 61 tropical forest sites.

most general chemometric models, here at leaf and then at canopy scales.

3.2. Modeled canopy reflectance

High leaf reflectance and transmittance variability reported in Fig. 2, combined with known canopy structural variation in each plant habit (Table 3), led to highly diverse canopy reflectance spectra (Fig. 3). These results include the random and systematic sensor noise expressed in AVIRIS (Fig. 3a) and Carnegie Airborne Observatory (CAO)-Alpha system data (Fig. 3b), the latter of which incorporates a customized CASI instrument (Asner et al., 2007). The structure of the noise differs by sensor type, owing to differences in instrument performance and effects of spectral range on atmospheric correction (Green et al., 2003). Similar to leaf-level findings, the largest spectral coefficients of variation at the canopy level were observed in the VIS and SWIR regions.

Local-scale variation in the shape and brightness of the spectra was also assessed, with a typical example shown from a site at Betampona, Madagascar (Fig. 3c–d; $n=330$). Maximal variation was again observed in the VIS and SWIR from 2000 to 2500 nm. High site-level variation is important because chemometric methods, such as PLSR and others like principal components analysis (PCA), operate on relative variation among the spectra analyzed. By comparing spectra from the Betampona site to the global data set, it is apparent that shape of spectrum was similar; however, the range in spectral variation is smaller at Betampona. The median values were also similar.

3.3. Noise-free leaf and canopy PLSR

PLSR modeling results using “noise-free” VSWIR reflectance and transmittance spectra indicated that chl-a, carotenoids, LMA, water,

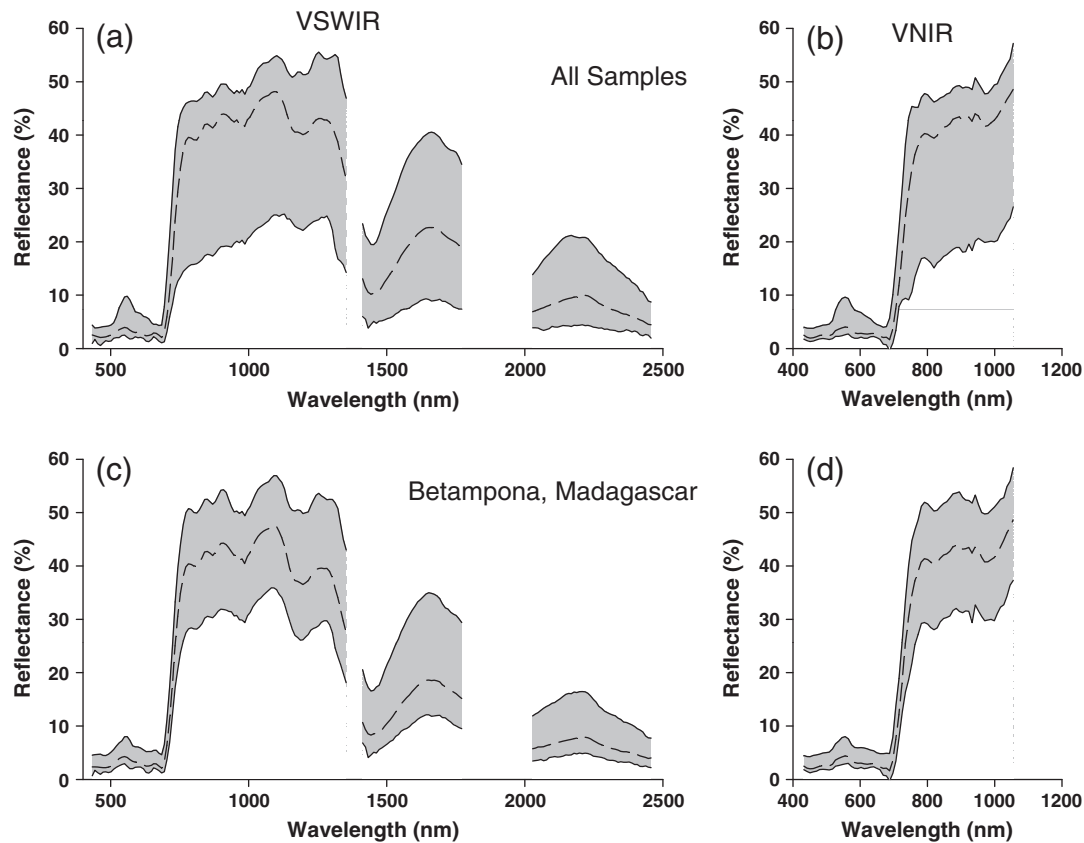


Fig. 3. Range of canopy reflectance with AVIRIS (VSWIR) sensor noise for (a) all specimens and (b) a site in Madagascar containing 330 samples. Panels (b) through (d) are similar but with CAO-Alpha (VNIR) sensor noise added to the simulations.

N, C, cellulose and phenols can be estimated with the highest accuracies at the leaf level (Table 4). For these leaf properties, regression r^2 -values and RMSE ranged from 0.69 to 0.89 and 4.5–8.5%, respectively.

Table 4

Noise-free PLSR prediction results using leaf reflectance and transmittance spectra in the VSWIR or VNIR wavelength ranges. Regression coefficient is the r^2 -value of the validation, and %RMSE is normalized as a percentage of the data range.

Parameter	Reflectance				Transmittance			
	VSWIR ^a		VNIR ^b		VSWIR		VNIR	
	r^2	%RMSE	r^2	%RMSE	r^2	%RMSE	r^2	%RMSE
Chlorophyll a	0.80	6.8	0.76	7.9	0.83	6.2	0.72	7.0
Chlorophyll b	0.79	6.7	0.76	8.0	0.82	6.2	0.72	6.8
Carotenoids	0.76	8.0	0.69	9.6	0.79	8.1	0.66	9.4
LMA	0.86	5.9	0.82	6.6	0.89	4.7	0.77	5.7
Water	0.88	5.2	0.76	5.0	0.90	4.3	0.72	5.5
N	0.77	7.9	0.59	10.1	0.81	7.1	0.55	9.9
C	0.71	8.2	0.43	10.7	0.74	8.8	0.43	11.3
Soluble C	0.63	10.6	0.30	17.4	0.67	10.3	0.27	19.7
Hemi-cellulose	0.60	9.6	0.32	11.2	0.62	8.7	0.36	12.4
Cellulose	0.77	6.4	0.27	16.4	0.82	7.1	0.23	18.1
Lignin	0.62	10.0	0.32	13.2	0.65	9.9	0.31	13.1
Phenols	0.74	9.3	0.36	12.7	0.76	8.7	0.41	16.0
Tannins	0.62	11.4	0.28	14.3	0.63	10.6	0.32	17.5
P	0.63	11.6	0.51	13.4	0.68	11.7	0.47	12.5
K	0.51	13.5	0.38	14.6	0.55	13.5	0.37	16.1
Ca	0.65	9.6	0.32	14.7	0.69	8.6	0.35	16.7
Mg	0.57	12.0	0.33	15.6	0.61	9.9	0.33	16.1
Zn	0.26	21.2	0.19	19.7	0.27	20.5	0.18	20.0
Mn	0.24	17.9	0.12	23.5	0.29	19.3	0.14	24.2
B	0.39	17.9	0.22	16.7	0.43	15.9	0.26	20.2
Fe	0.46	7.2	0.26	9.4	0.48	9.6	0.33	14.2

^a VSWIR = visible to shortwave-infrared (400–2500 nm).

^b VNIR = visible to near-infrared (400–1050 nm).

Other well-predicted chemicals included soluble C, hemi-cellulose, lignin, tannins, P, K, Ca and Mg ($r^2=0.48$ –0.65; RMSE = 8.9–13.8%). Surprisingly, even the remaining four metals (Zn, Mn, B, and Fe) displayed weaker yet significant signal, with r^2 -values ranging from 0.19 for Mn to 0.40 for Fe, and %RMSE remains below 22% in all cases. Latent vector analysis indicated that all regions of the spectrum were important to the predictions, and while we do not show the spectral weightings here since there were a large number of chemicals tested, they were generally similar in shape and magnitude to those reported by Asner and Martin (2008).

Accuracy was reduced when predicting leaf chemical traits with data limited to the VNIR spectral range (Table 4). Chemical trait estimates most negatively affected by the reduced VNIR sampling included total C, carbon fractions, phenols and tannins, with prediction accuracy dropping by 40–75%. N, P, and K showed a decrease in accuracy by less than 28%. In contrast, leaf chemical traits showing the greatest absorption and scattering in the 400–1050 nm wavelength range, including photosynthetic pigments, LMA and water content (Curran, 1989; Jacquemoud et al., 1995), had r^2 -values that decreased by less than 20% when switching from VSWIR to VNIR sampling (Table 4).

When projecting leaf spectra to the canopy level while including canopy structural variation, but without incorporating noise, most chemical traits were well estimated when using the VSWIR spectrum (Fig. 4). Best predicted traits were LMA and water ($r^2=0.89$; RMSE < 6%). Photosynthetic pigments, N, cellulose and phenols were also estimated with relatively high precision and accuracy ($r^2 > 0.75$; RMSE < 8%). Other chemistries predicted with greater than 50% accuracy (RMSE < 12%) were C, the remaining carbon constituents (soluble-C, hemi-cellulose, lignin, tannins), P, and base cations (K, Ca, and Mg). Other micronutrients were less well predicted, but still retrievable with a range in r^2 -values of 0.25–0.44 and RMSE = 9–21%.

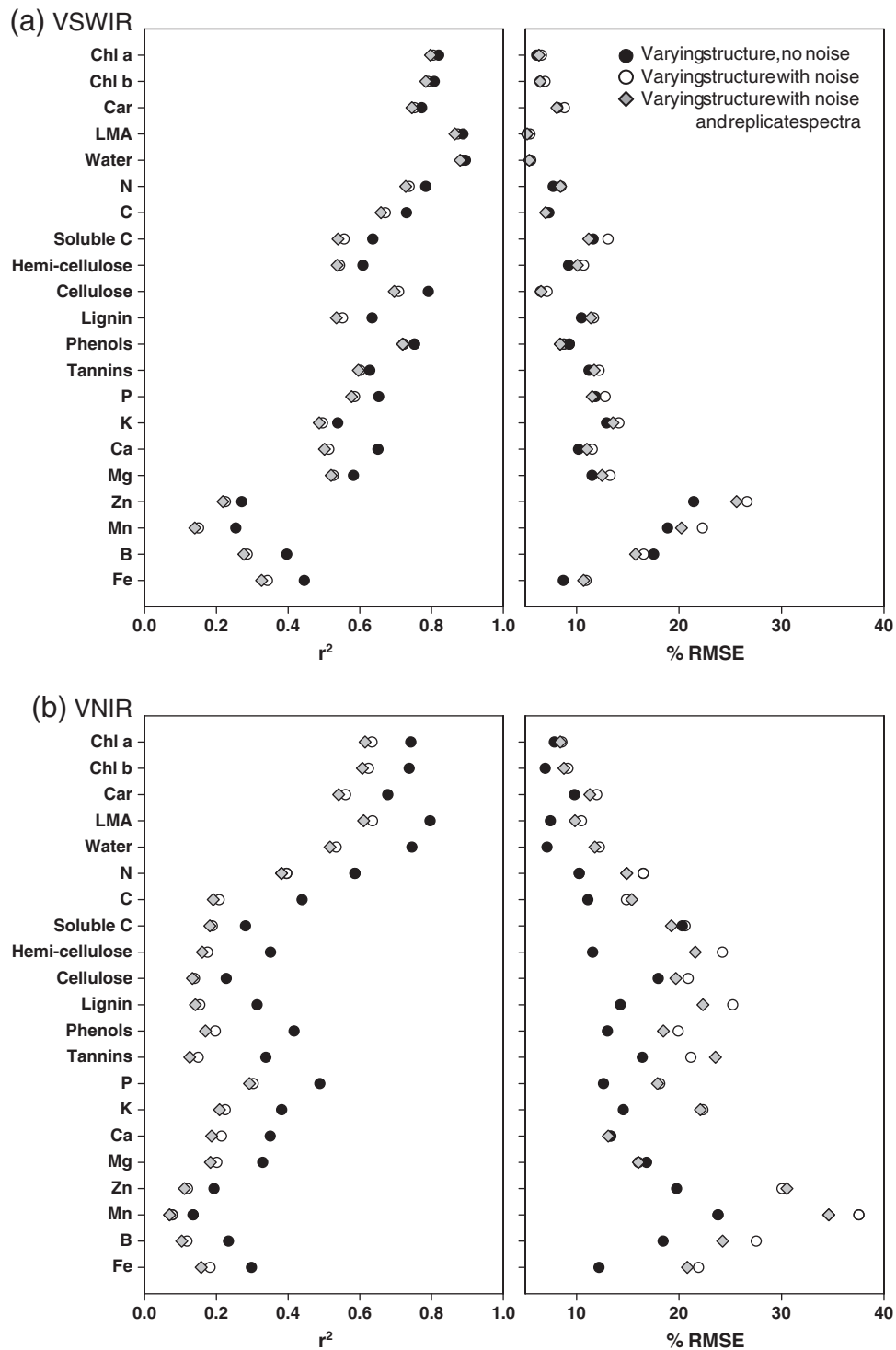


Fig. 4. Comparison of global canopy calibration models utilizing the (a) VSWIR and (b) VNIR spectral regions with varying canopy structural parameters (black circles); varying canopy structural parameters with the addition of sensor noise (white circles); and varying canopy structural parameters with the addition of sensor noise and spectral variation (gray diamonds).

Using VSWIR spectra and no added noise, the strength of the PLSR results increased by ~2.5% following up-scaling to the canopy level (Table 4, Fig. 4a). Asner and Martin (2008) observed this in a past study, highlighting the role that light scattering and absorption play in enhancing spectroscopic differences among canopies under conditions of relatively high LAI or leaf volume. However, similar to the leaf level, when restricted to the VNIR range (400–1050 nm), the ability to predict canopy chemical traits was reduced in many cases.

Photosynthetic pigments, water, LMA, and N remained relatively precise and accurate, with $r^2 = 0.58$ – 0.79 and $RMSE < 11\%$. However, predictions of other chemical properties decreased by 50–75% (Fig. 4b). In particular, estimates of soluble C, cellulose, lignin, phenols and tannins were very negatively impacted by using VNIR spectra. These results confirm, and further provide quantitative detail on, the value in using VSWIR (400–2500 nm) measurements for canopy chemical studies (Ebberts et al., 2002; Kokaly et al., 2009; Skidmore et al., 2010).

3.4. Canopy PLSR with sensor noise and structural variation

Incorporation of sensor noise is essential to a more realistic use of PLSR approaches for chemical analysis of airborne or space-based imaging spectrometer data. Overall, we found that noise negatively affects PLSR results, but it does so to varying degrees depending on wavelength range and chemical constituent (Fig. 4). Chemicals that had previously been well predicted using VSWIR models without noise – photosynthetic pigments, water, LMA, N, phenols and tannins – were minimally affected when noise was added (Fig. 4a). For these leaf properties, r^2 -values decreased by 0.01–0.04, while associated RMSE values increased by less than 2%. Other less well predicted chemicals displayed larger decreases in r^2 -value (0.03–0.13) and/or increases in RMSE (1–5%), but not always both. When only the VNIR was used, noise had a proportionally larger negative effect on the prediction of all chemicals (Fig. 4b), with r^2 -values decreasing 0.11–0.22 and RMSE increasing by up to 8% for the well predicted canopy traits. Changes were less pronounced for other chemistries where r^2 -values were already low prior to adding noise.

Brightness normalization of either VNIR or VSWIR data had a negligible effect on the accuracy of chemical estimates using PLSR on the modeled canopy spectra. When the VSWIR wavelength range was used, brightness normalization decreased RMSE values by less than

2% for a quarter of all chemical traits (data not shown). With the VNIR model, 10 chemical traits exhibited a 1–3% improvement based on RMSE values. In both cases, r^2 -values changed by only 0.01. These results do not discount the work of Feilhauer et al. (2010), but instead show that incorporating noise and canopy structural uncertainty via radiative transfer modeling, prior to using PLSR for chemometric analysis, is another way to accommodate the inherent brightness variation in canopy spectra when applying PLSR methods. Specifically, PLSR includes an internal normalization step (Martens, 2001), so including brightness variation due to canopy structural variability, a priori, is one way to accommodate it when up-scaling leaf spectral measurements for use in creating PLSR models for actual airborne or satellite imaging spectrometers.

3.5. General model stabilization

The number of samples required to develop a stable global model was determined by building calibration models of increasing sample size (incrementing by 250) and then predicting one arbitrarily selected site, Betampona, Madagascar, which contained many samples ($n = 330$). With the VSWIR spectra, the precision of calibration, averaged over 10 different model runs incorporating randomly-selected calibration samples (see Materials and methods), initially decreased

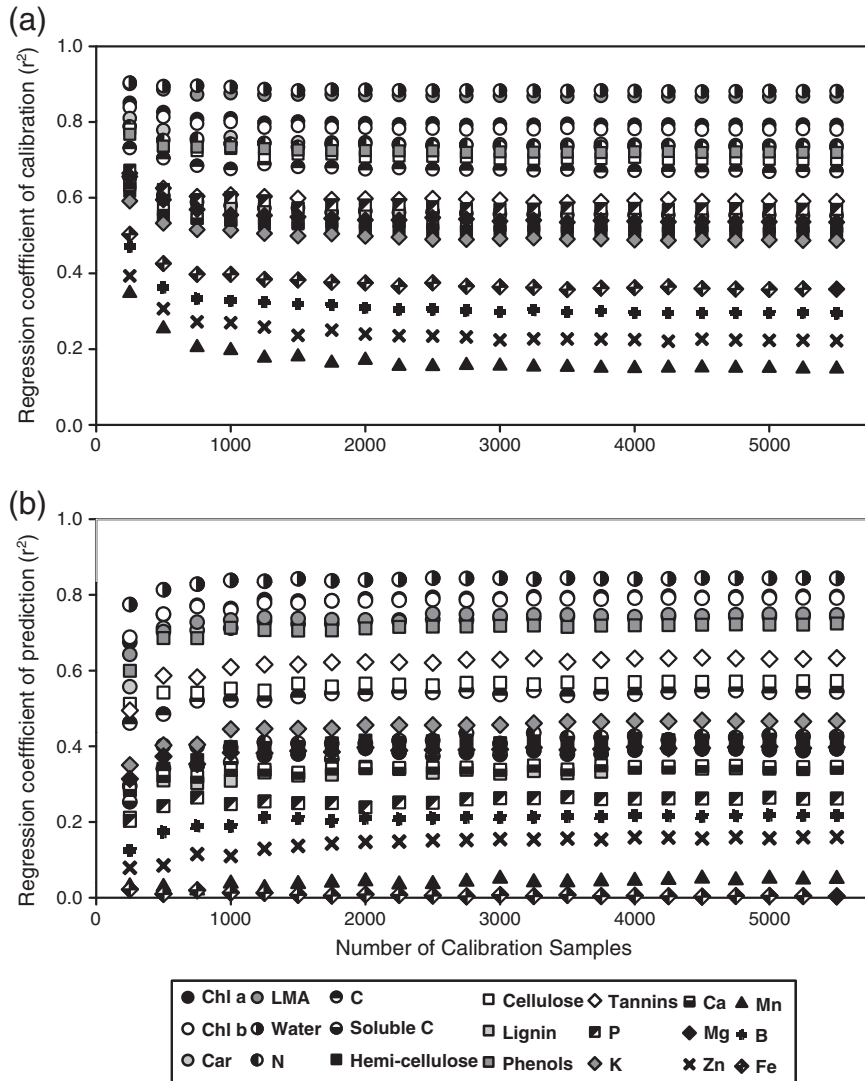


Fig. 5. Calibration and prediction statistics for PLSR models of increasing sample size using the VSWIR spectrum. The different symbols represent 21 different leaf traits that were estimated.

and then remained nearly constant once about 2500 samples were incorporated into the model (Fig. 5a). However, the number of required samples did noticeably vary by chemical trait. Well-predicted leaf properties, such as LMA and water content, were also relatively stable throughout the experiment. Other chemicals including photosynthetic pigments, C, N, phenols and cellulose stabilized after about 1250 samples, reaching stable calibration r^2 -values of 0.67–0.79. Still other, less accurately predicted constituents (P, carbon fractions and cations) stabilized after including 2250 samples, with resulting r^2 -values 0.49–0.59.

In contrast to the calibration results (Fig. 5a), the precision (r^2) of leaf chemical predictions from canopy spectra at the Madagascar test site initially increased for many chemical traits as the number of calibration samples increased (Fig. 5b). The r^2 -values usually reached an asymptote when ~2500 samples were used, but the overall prediction precision among leaf properties did not always follow the same order as observed during calibration. These differences could be due to the particular canopy chemical distributions found at the Betampona test site, or due to the combination of the site's chemical distribution relative to the distribution of chemicals in the calibration samples. Irrespective of the final prediction accuracy, the reversed pattern of rising to a maximum at 2500 samples indicates that, although increasing the sample size lowers the calibration precision slightly due to the

incorporation of additional canopy variation, this variation is largely accommodated at the chemical prediction step.

The VNIR spectra proved less sensitive to the number of samples used to build the PLSR calibration and prediction models, reaching stable values when 1000 samples were included (Fig. 6). The lower sensitivity and faster stabilization of the VNIR dataset results from the fact that 400–1050 nm spectra have fewer degrees of freedom in the spectra as compared to full-range VSWIR spectra. However, overall VNIR performance was much lower in comparison to the same analyses using VSWIR data. Well-estimated leaf properties (LMA, water and photosynthetic pigments) had calibration accuracies of 0.52–0.61. Below this, N and P had r^2 -values of 0.36 and 0.26, respectively, while the precision of the remaining chemical estimates was less than 0.20.

3.6. Creating a global model

Because model stabilization was achieved when 2500 samples were incorporated into the calibration, we used this data volume threshold to test model repeatability at a global scale. Twenty-five different calibration models were built incorporating 2500 randomly-selected samples from around the world. Each model was then used to predict 500 new test samples that were also randomly selected

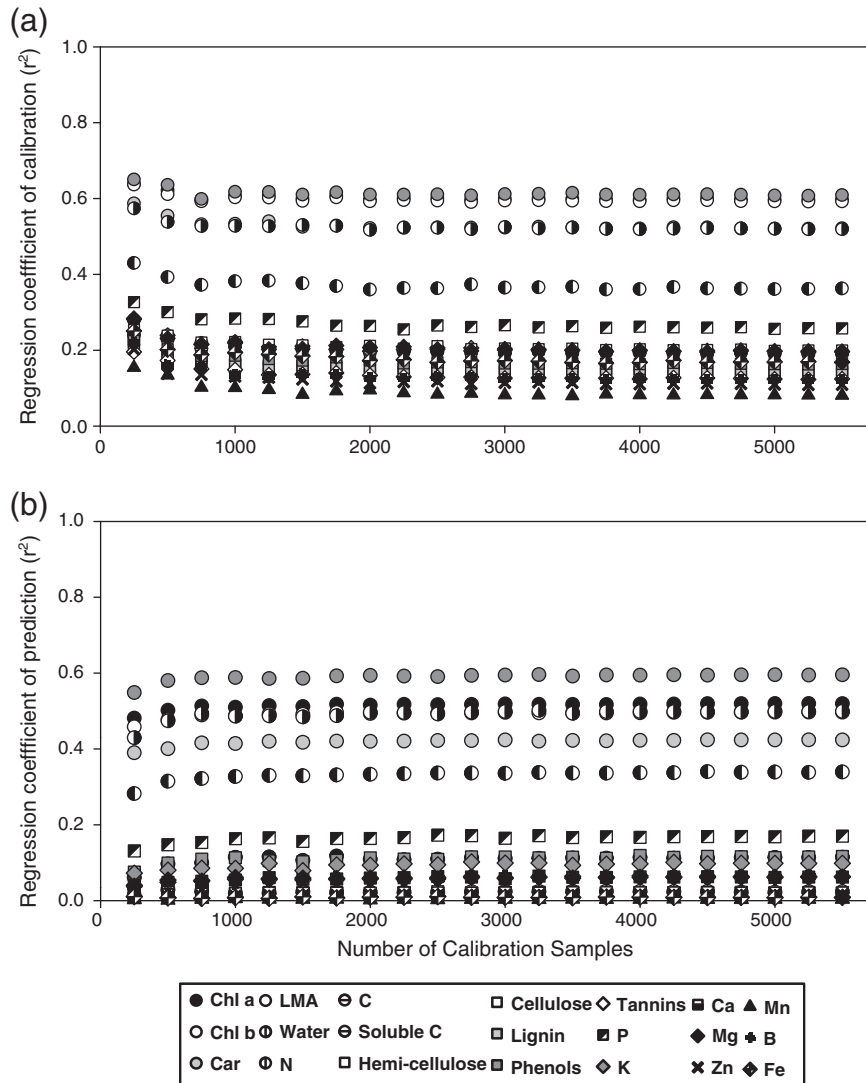


Fig. 6. Calibration and prediction statistics for PLSR models of increasing sample size using the VNIR spectrum. The different symbols represent 21 different leaf traits that were estimated.

from the spectranomics database. This was done to avoid possible bias from the suite of chemicals found at a given site. Although stabilization was reached with fewer samples during the VNIR calibration model, there was no drawback to using 2500 samples as was required for the model using the VSWIR spectrum. Therefore, we used the same number of samples for both tests.

The calibration and prediction results were very similar for all chemical properties in each of the 25 simulations, with means

deviating by a maximum r^2 -value of 0.04 for K and Mg when using VSWIR spectra (Fig. 7a, Appendix 1). The global models show that chl-a, chl-b, carotenoids, LMA, water, N, cellulose and phenols were consistently predicted with the high precision ($r^2 > 0.75$) and high accuracy (RMSE < 15%). Other leaf constituents such as total C, soluble C, lignin, hemi-cellulose, and tannins were predicted with moderate precision and high accuracy. P, K, Ca and Mg were also retrieved, albeit with lower precision. Critically, we found that variation among the

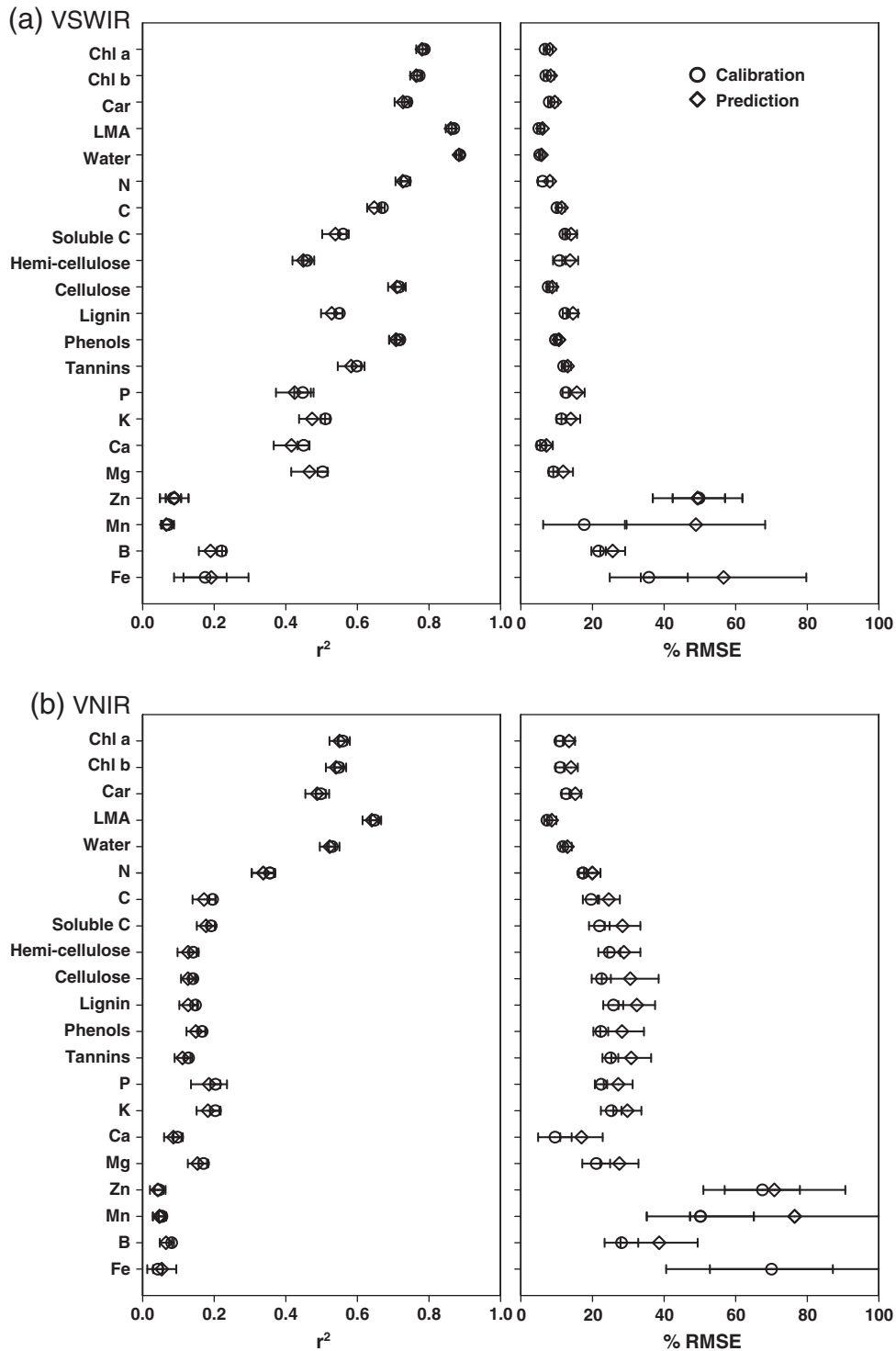


Fig. 7. Mean and standard deviation of the calibration (circles) and prediction (diamonds) statistics generated from 25 models generated from a set of 2500 randomly selected calibration samples and their prediction of 500 randomly selected test samples, both globally distributed.

25 global model runs was small, with standard deviations in calibration ($n=2500$) and prediction ($n=500$) r^2 -values ≤ 0.02 and $RMSE \leq 1.7\%$ for well-predicted chemical constituents using VSWIR spectra. Maximum variation was observed among the weakest predictions for Zn, Mn, B and Fe, with a worst-case standard deviation in r^2 -value of 0.06 for Zn and RMSE of 11% for Mn. The prediction equation coefficients are provided for reference in Appendix 2.

The differences between calibration and prediction performance, as well as variation among model runs, for the VNIR case paralleled the VSWIR results (Fig. 7b, Appendix 1). However, as found throughout this study, the accuracy and precision of the results were lower for all leaf properties when limited to the VNIR spectral range. Whereas photosynthetic pigments, LMA and water can be estimated with moderate precision and good accuracy using VNIR measurements, all other foliar elements and compounds cannot be reliably estimated using the approach developed here.

4. Conclusions

Remote sensing of canopy chemistry is essential to understanding changes in the functional and biological diversity of tropical forests. A major step toward reaching the goal of accurate canopy chemical mapping rests in the development of a general, transportable and scalable approach using high-fidelity spectroscopy. Here we found that a number of chemical traits can be universally estimated using a combination of globally-distributed, consistently measured leaf spectral and chemical databases, PLSR analysis, and radiative transfer modeling that incorporates canopy structural variability as well as sensor noise and atmospheric correction errors. Even with these steps carefully coordinated, our ability to do multi-chemical remote sensing in tropical forests varies by chemical constituent and by wavelength region. Under conditions of varying canopy structure and spectral noise, we are best able to estimate photosynthetic pigments, water, LMA, N, several carbon fractions such as cellulose and lignin, and phenols using full-range VSWIR measurements. Foliar P and base cations are somewhat less well retrieved globally, but they do remain measurable with relatively low RMSE. We found this to be a general and repeatable result, independent of site conditions, taxonomic composition or phylogenetic history, and thus we believe this is an approach that will be broadly applicable to multi-chemical mapping of humid tropical forest canopies.

Finally, we found that leaf chemical properties are estimated far more consistently, and with much greater precision and accuracy, using the VSWIR (400–2500 nm) spectrum rather than with VNIR (400–1050 nm) observations. Differences in performance varied by chemical trait, and VNIR remote sensing performed well for three photosynthetic pigments, LMA, and water concentrations. However, using the full-range VSWIR spectrum provided a far more stable solution for three times the number of canopy chemical traits (and LMA) than could be achieved with VNIR measurements. Whereas VNIR imaging sensors have become quite common, a relatively few high-fidelity VSWIR spectrometers are currently available onboard aircraft, and none are available from space. AVIRIS is somewhat unique, proving its high fidelity following a major upgrade in 2005. Other sensors including EO-1 Hyperion have proven difficult to use for canopy chemistry applications due to issues of sensor fidelity (Asner et al., 2004; Kokaly et al., 2009). A next generation of airborne, very high fidelity imaging spectrometers has just been launched, with the CAO-AToMS flying now (<http://cao.ciw.edu>) to utilize techniques such as the spectranomics approach presented here for humid tropical forests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at [doi:10.1016/j.rse.2011.08.020](https://doi.org/10.1016/j.rse.2011.08.020).

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