Supporting Information

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SI Text 1. Comments on Equations for Nitrogen Concentration and Broadleaf Fraction of Leaf Dry Mass

Broadleaf fraction of leaf dry mass (BfM) data can be accurately approximated by the equation for BfM (*Materials and Methods*) with $\theta = 0.30$. Approximated vs. measured BfM values on the 1:1 plane are related as $y = 0.98x - 0.01$ with $R^2 = 0.99$ and relative root mean square error (RRMSE) = 18%. The estimates are for the Bartlett Experimental Forest for which in situ canopy foliar dry mass fractions by species were available.

Values of $\%n_N$ and $\%n_L$ were specified by fitting the equation for nitrogen concentration (%N) (*Materials and Methods*) and %N data, using a Tikhonov regularization technique (1):

$$\alpha\|\mathbf{n}-\mathbf{n_0}\|^2+\|\mathbf{A}(\mathbf{n}-\mathbf{n_0})+(\mathbf{An_0}-\mathbf{N})\|^2\rightarrow\min.$$

Here α is a regularization parameter accounting for errors in the equation for %N and data; $\mathbf{n}$ and $\mathbf{n}_0$ are vectors representing unknown $\%n_N$, $\%n_L$ and their mean values over the Bartlett Forest (*Materials and Methods*); $\mathbf{A}$ is an $N \times 2$ matrix with rows (1 − BfM) and BfM; and vector $\mathbf{N}$ contains measured %N. $\alpha = -1.13$ provides best agreement between measured and simulated %N, resulting in $\%n_L = 2.33$ and $\%n_N = 1.03$. Values of %N approximated with the equation for %N vs. in situ %N on the 1:1 plane are related as $y = 0.997x + 0.001$ with $R^2 = 0.89$ and RRMSE = 10%. The retrieved $\%n_L$ equation for BfM and $\%BN = \%n_L$. BfM data were used to estimate broadleaf function of leaf area (BfLAI) for the remaining sites.

SI Text 2. Canopy Bidirectional Reflectance Factor and Directional Area Scattering Factor

If the impact of canopy background on canopy reflectance is negligible, the spectral bidirectional reflectance factor (BRF) can be approximated in terms of the leaf albedo, ω_λ, interceptance, i_0, directional gap density, $\rho(\Omega)$, and recollision probability, p, as (2, 3)

$$\mathrm{BRF}_\lambda(\Omega)=\frac{\rho(\Omega)i_0}{1-\omega_\lambda p}\omega_\lambda. \qquad \text{[S2.1]}$$

Note that we suppress the dependency of the BRF on the direction of incident beam in our notations. Accuracy of this equation is discussed in *SI Text 7*. This spectrally invariant relationship is also applicable to the bidirectional transmittance factor (BTF) formulated for radiation diffusely transmitted through the vegetation, that is, radiance of diffusely transmitted radiation normalized by F/π, where F is the incident irradiance. A detailed analysis of the spectrally invariant relationships can be found in ref. 3. Their validity for cloudy atmospheres is discussed in ref. 4.

In a nonabsorbing canopy ($\omega_\lambda \equiv 1$), the angular variation of BRF(Ω) and BTF(Ω) takes the form $\rho(\Omega)i_0/(1-p)$. The BRF coincides with the directional area scattering factor (DASF). In nonabsorbing vegetation all intercepted photons will exit the canopy via either the upper or the lower boundary. Hemispherical integrations of the BRF and BTF over up- ($2\pi^+$) and downward ($2\pi^-$) directions, respectively, should therefore result in the canopy interceptance i_0; i.e.,

$$\frac{1}{\pi}\int_{2\pi+}\mathrm{BRF}(\Omega)|\mu|d\Omega+\frac{1}{\pi}\int_{2\pi-}\mathrm{BTF}(\Omega)|\mu|d\Omega=\frac{1}{\pi}\frac{i_0}{1-p}\int_{4\pi}\rho(\Omega)|\mu|d\Omega=i_0. \qquad \text{[S2.2]}$$

Here μ is the cosine of the polar angle of Ω and 4π denotes the unit sphere. Thus, the directional gap density, $\rho(\Omega)$, and the recollision probability, p, are related as

$$\frac{1}{\pi}\int_{4\pi}\rho(\Omega)|\mu|d\Omega=1-p. \qquad \text{[S2.3]}$$

The quantity $\rho(\Omega)/(1-p)$ defines the average directional escape probability density; i.e., $\pi^{-1}\rho(\Omega)|\mu|d\Omega/(1-p)$ is the probability that a photon scattered by a leaf surface element in the canopy will escape the canopy through a gap in the direction Ω about solid angle Ω. Here we adapted Stenberg's (5) definition of a gap, which is a free line of sight through the canopy from a point on the foliage surface element ds in the direction Ω. The directional gap density specifies the leaf area covered by such lines per unit total leaf area per unit solid angle. Note that here we apply a standard normalization used in remote sensing to make angular-dependent variables dimensionless.

The term $i_0/(1-p)$ is the mean number of interactions with nonabsorbing foliage that a photon undergoes before exiting the vegetation canopy (2, 3). An intuitive understanding of how the mean number of interactions is related to the foliage area follows from results (5) on the physics of relationships between interceptance, i_0, recollision probability, p, and leaf area index (LAI) for simple canopies illuminated by a diffuse radiation field. In this case i_0 gives the probability that photons entering the vegetation through gaps will be intercepted by the foliage. This quantity can also be evaluated as the probability that photons from isotropic sources distributed uniformly over the total foliage surface areas will escape the vegetation canopy. Thus, $i_0 = \mathrm{LAI}(1-p)$ (5). It follows from this relationship that $i_0/(1-p) = i_0 + pi_0 + p^2i_0 + \ldots = \mathrm{LAI}$; thus the mean number of interactions with nonabsorbing foliage can be interpreted as the foliage area per unit ground area that an average photon trajectory accumulates over successive orders of scattering (the increasing powers of p representing each successive scattering order).

Theoretical understanding of such a relationship in the general case follows from the expansion of the solution of the radiative transfer equation in the successive orders of scattering, or Neumann series (3). In a nonabsorbing canopy the contribution from high-order scattered photons to radiation reflected by the vegetation strongly dominates that from photons having undergone few interactions. High-order scattered photons can accurately be approximated by a positive eigenvector and corresponding positive eigenvalue of the radiative transfer equation (2, 3). The eigenvalue coincides with the recollision probability. This property allows us to approximate the Neumann series by a geometrical progression (3) to which the above argument regarding the average photon trajectory is applicable. It should be noted the Neumann series is sensitive to low-order scattering terms. Their impact on the solution of the radiative transfer equation depends on variation in the recollision probability with the scattering order: The smaller the variation in p with scattering order is, the larger the range of foliage area that is sampled and

consequently the more accurate the relationship between the mean number of interactions and LAI. Model calculations suggest that the recollision probability increases with scattering order and reaches a plateau after one to two scattering events for LAI up to 10 (3). The monodirectional (nondiffuse) illumination condition is another factor that can impact the accuracy of the relationship between the mean number of interactions and leaf area. Theoretical estimates of the convergence of the recollision probability and the directional gap density with the scattering order are documented in ref. 3. Techniques for estimating various mean quantities by averaging photon trajectories can be found in ref. 6.

It follows from Eq. **S2.1** that the recollision probability, p, and $\rho(\Omega)i_0$ can be obtained from spectral BRF if leaf albedo at two or more wavelengths is known, but such information is not available when interpreting satellite data. An analysis of how radiation interacts with individual leaves is needed to understand the applicability range of the spectral invariant approach.

SI Text 3. Leaf Albedo

The fraction of radiation, ω_λ, reflected or transmitted by a leaf/needle surface element (leaf albedo) results from photon interactions with leaf surface and its interior,

$$\omega_\lambda = i_L \varpi_\lambda + s_L. \quad \textbf{[S3.1]}$$

Here i_L is the leaf interceptance defined as the fraction of radiation incident on the leaf that enters the leaf interior. The fraction of surface reflected radiation, $s_L = 1 - i_L$, is assumed to be a wavelength-independent function of leaf surface properties and varies with the direction of incident radiation. The transformed leaf albedo, ϖ_λ, is defined as the fraction of radiation scattered from the leaf interior given that it interacts with internal leaf constituents (7). This variable is assumed to be independent of leaf surface properties and varies with leaf anatomical structure and leaf absorbing constituents.

Consider two different leaves, e.g., hazelnut leaf and coniferous needle. The difference, $\Delta\omega_\lambda = \omega_{1\lambda} - \omega_{2\lambda}$ between their albedo spectra is

$$\Delta\omega_\lambda = -a_{2\lambda} i_{1L}\left(\frac{\Delta i_L}{i_{1L}} + \frac{\Delta a_\lambda}{a_{2\lambda}}\right). \quad \textbf{[S3.2]}$$

Here $a_\lambda = 1 - \varpi_\lambda$ is the leaf absorptance, i.e., the probability that a photon will be absorbed by a leaf given that it interacts with internal leaf constituents. Thus, the variation, $\Delta\omega_\lambda$, in leaf scattered radiation is due to differences in leaf surface properties, $\Delta i_L = i_{1L} - i_{2L}$, and leaf interior, $\Delta a_\lambda = -(\varpi_{1\lambda} - \varpi_{2\lambda}) = -\Delta\varpi_\lambda$. The former can vary greatly between species (8), whereas the latter is independent of leaf surface characteristics and is a function of the leaf interior tissue only. At wavelengths where $\Delta a_\lambda / a_{2\lambda} \sim 0$, it can be seen from Eq. **S3.2** that the leaf albedo will become sensitive to differences in leaf surface features rather than its interior. This can occur at strongly absorbing wavelengths, e.g., 445 nm, where the leaf absorptance, a_λ, saturates and becomes weakly sensitive to variation in the concentrations of leaf biochemical constituents. In the near infrared (NIR), where pigments do not absorb and the wavelength is still shorter than regions of strong absorption by water, variation between species in the radiation absorbed by the leaf interior, $|\Delta a_\lambda / a_{2\lambda}|$, can be comparable to or smaller than that of the leaf surface reflected radiation; i.e., $|\Delta a_\lambda / a_{2\lambda}| < |\Delta i_L / i_{1L}|$. This acts to weaken the sensitivity of the total leaf albedo, ω_λ, to the amount of leaf constituents.

SI Text 4. Reference Spectrum

Analyses of leaf albedo spectra from the Boreal Ecosystem Atmosphere Study (BOREAS) campaign (9) and the Spectra Barrax Campaign (SPARC) of 2004 (10) suggest that, in the spectral interval [710, 790 nm], transformed albedos of all spectra samples are related to a fixed spectrum, $\varpi_{0\lambda}$, from the BOREAS set via the spectral invariant relationship (10, 11); i.e.,

$$\varpi_\lambda = \frac{1 - p_L}{1 - p_L \varpi_{0\lambda}} \varpi_{0\lambda}. \quad \textbf{[S4.1]}$$

The wavelength-independent within-leaf recollision probability, p_L, varies with samples. In this interval the empirically derived $\varpi_{0\lambda}$ can be obtained from Lewis and Disney's (7) approximation of the PROSPECT model (12) with the following parameters: chlorophyll content of 16 $\mu g \cdot cm^{-2}$, equivalent water thickness of 0.005 cm^{-1}, and dry matter content of 0.002 $g \cdot cm^{-2}$. This spectrum is used as a reference albedo, $\varpi_{0\lambda}$, in all our calculations.

In the 710- to 790-nm spectral interval the diffuse leaf albedo dominates; i.e.,

$$\omega_\lambda \approx i_L \varpi_\lambda = \frac{1 - p_L}{1 - p_L \varpi_{0\lambda}} i_L \varpi_{0\lambda}. \quad \textbf{[S4.2]}$$

In this spectral interval, the reference albedo $\varpi_{0\lambda}$ is determined by absorption spectra of chlorophyll, dry matter and water (Fig. 4). Impact of water absorption can be neglected.

SI Text 5. Retrieving DASF from Hyperspectral Data

Consider the 710- to 790-nm spectral interval. By substituting Eq. **S4.2** into Eq. **S2.1** one obtains

$$\mathrm{BRF}_\lambda(\Omega) = \frac{i_L \rho(\Omega)(1 - p_L) i_0}{1 - \varpi_{0\lambda} p_1} \varpi_{0\lambda}, \quad \textbf{[S5.1]}$$

where $p_1 = p_L + i_L p(1 - p_L)$. The spectral BRF can be standardized to a single known albedo, $\varpi_{0\lambda}$. Standardization accuracy is discussed in *SI Text 7* and illustrated in Fig. S1.

Eq. **S5.1** can be rearranged to

$$\frac{\mathrm{BRF}_\lambda(\Omega)}{\varpi_{0\lambda}} = p_1 \mathrm{BRF}_\lambda(\Omega) + i_L \rho(\Omega)(1 - p_L) i_0. \quad \textbf{[S5.2]}$$

By plotting the ratio $\mathrm{BRF}_\lambda(\Omega)/\varpi_{0\lambda}$ vs. $\mathrm{BRF}_\lambda(\Omega)$, a linear relationship is obtained (Fig. S1*A*), where the intercept and slope give $i_L \rho(\Omega)(1 - p_L) i_0$ and p_1. The ratio between the intercept and $(1 - p_1)$ becomes independent of p_L and gives the DASF in the following form:

$$\mathrm{DASF} = \rho(\Omega) \frac{i_L i_0}{1 - p i_L}. \quad \textbf{[S5.3]}$$

For vegetation canopies with a dark background, or sufficiently dense vegetation where the impact of canopy background is negligible, this parameter therefore can be derived from the BRF spectrum in [710 nm, 790 nm] without prior knowledge/ancillary information of the leaf albedo, using the following simple algorithm:

Step 0. Calculate the reference leaf albedo, $\varpi_{0\lambda}$, in the 710- to 790-nm spectral interval using, e.g., the PROSPECT model with input specified in *SI Text 4.* This is a fixed spectrum used by the algorithm.

Step 1. Given the measured $\mathrm{BRF}_\lambda(\Omega)$ spectrum in the 710- to 790-nm spectral interval, plot values of the ratio $\mathrm{BRF}_\lambda(\Omega)/\varpi_{0\lambda}$ vs. values of $\mathrm{BRF}_\lambda(\Omega)$. A linear relationship will be obtained (Fig. S1*A*).

Step 2. Find slope, k, intercept, b, and R^2 of the $\mathrm{BRF}_\lambda(\Omega)/\varpi_{0\lambda}$ vs. $\mathrm{BRF}_\lambda(\Omega)$ relationship.

Step 3. The ratio $b/(1 - k)$ is an estimate of the DASF whereas the R^2 coefficient is an indicator of the retrieval quality. A low

R^2 value suggests that conditions for the applicability of the algorithm are not met; e.g., impact of canopy background is not negligible.

Step 4. Take the next $\mathrm{BRF}_\lambda(\Omega)$ spectrum and go to step 1.

SI Text 6. Canopy Scattering Coefficient

Eq. **S2.1** can be rearranged as

$$\mathrm{BRF}_\lambda(\Omega) = \frac{\rho(\Omega) i_0}{1-\omega_\lambda p}\omega_\lambda = \frac{\rho(\Omega) i_0 i_\mathrm{L}}{1-p i_\mathrm{L}}\left(\frac{1-p i_\mathrm{L}}{1-\hat{\omega}_\lambda p i_\mathrm{L}}\hat{\omega}_\lambda\right) = \mathrm{DASF}\cdot W_\lambda, \quad \textbf{[S6.1]}$$

where

$$W_\lambda = \frac{1-p i_\mathrm{L}}{1-\hat{\omega}_\lambda p i_\mathrm{L}}\hat{\omega}_\lambda \quad \textbf{[S6.2]}$$

is the canopy scattering coefficient and $\hat{\omega}_\lambda = \omega_\lambda / i_\mathrm{L} = \varpi_\lambda + s_\mathrm{L}/i_\mathrm{L}$. Smolander and Stenberg (13) introduced this coefficient under an assumption of $i_\mathrm{L} = 1$. In this case W_λ is insensitive to surface properties. It depends on the transformed leaf albedo and the factor $(1-p)/(1-\varpi_\lambda p)$ that accounts for the absorption due to within-canopy photon multiple interactions. In our analyses we allow for variation in leaf surface properties by relaxing the assumption $i_\mathrm{L} = 1$. It should be noted that the normalization of the BRF by DASF gives an approximation of the canopy scattering coefficient. An integration of Eq. **S2.1** over directions should precede the normalization to obtain its value accurately.

Fig. S2 shows correlations of BRF_λ and W_λ with canopy foliar %N at NIR (800–850 nm), red (645 nm), and green (557 nm) wavelengths. One can see that BRF exhibits either positive or no relation with the canopy %N, whereas the canopy scattering coefficient is negatively related to %N. Similar relationships are valid for broadband photosynthetically active radiation (PAR) (400–700 nm) BRF and W; that is, there is no correlation between BRF and canopy foliar %N ($y = 0.001x + 0.024$, $R^2 = 0.006$), whereas the W is negatively correlated with foliar nitrogen ($y = -0.042x + 0.141$, $R^2 = 0.428$). We found that the scattering coefficient is negatively correlated with foliar %N at all wavelengths in the interval between 423 and 855 nm. This is summarized in Fig. 7*B*.

SI Text 7. Accuracy in the Standardization of the Spectral BRF to a Single Reference Spectrum

Accuracy of Eq. **S5.1** was assessed as follows. First, we used the reference albedo $\varpi_{0\lambda}$ and the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) BRF in the 710- to 790-nm spectral interval to derive slope (k) and intercept (b) from the $\mathrm{BRF}_\lambda/\varpi_{0\lambda}$ vs. BRF_λ relationship (Fig. S1*A*). Second, $\varpi_{0\lambda}$, k, and b were used to simulate BRF spectra (Fig. S1*B*). Finally, the RRMSE between measured and simulated BRFs was taken as a measure of the standardization accuracy.

A very high accuracy within the 710- to 790-nm spectral interval has been achieved. All plots passed the accuracy test RRMSE $\leq$ 4.8% (*Materials and Methods*). An overall RRMSE is 1.86%. Eq. **S6.1** was used to calculate mean NIR BRF over the spectral interval [800, 850 nm] (weighted by a normalized solar radiance spectrum). An overall RRMSE between measured and simulated NIR BRF is 1.63%. Note that a high accuracy can be achieved only if the impact of the canopy background on canopy reflectance is negligible.

1. Tikhonov AN, Goncharsky AV, Stepanov VV, Yagola AG (1995) *Numerical Methods for Solving Ill-Posed Problems*, trans Hoksbergen RAM (Kluwer, Boston).
2. Knyazikhin Y, Schull MA, Xu L, Myneni RB, Samanta A (2011) Canopy spectral invariants. Part 1: A new concept in remote sensing of vegetation. *J Quant Spectrosc Radiat Transf* 112(4):727–735.
3. Huang D, et al. (2007) Canopy spectral invariants for remote sensing and model applications. *Remote Sens Environ* 106(1):106–122.
4. Marshak A, Knyazikhin Y, Chiu JC, Wiscombe WJ (2011) Spectrally invariant approximation within atmospheric radiative transfer. *J Atmos Sci* 68(12):3094–3111.
5. Stenberg P (2007) Simple analytical formula for calculating average photon recollision probability in vegetation canopies. *Remote Sens Environ* 109(2):221–224.
6. Marchuk GI, et al. (1980) *The Monte Carlo Methods in Atmospheric Optics* (Springer, Berlin).
7. Lewis P, Disney M (2007) Spectral invariants and scattering across multiple scales from within-leaf to canopy. *Remote Sens Environ* 109(2):196–206.
8. Grant L (1987) Diffuse and specular characteristics of leaf reflectance. *Remote Sens Environ* 22(2):309–322.
9. Middleton E, Sullivan J (2000) *BOREAS TE-10 Leaf Optical Properties for SSA Species. Data set* (Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN). Available at http://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=531. Accessed May 16, 2008.
10. Latorre Carmona P, Schull M, Knyazikhin Y, Pla F (2010) The application of spectral invariants for discrimination of crops using CHRIS-PROBA data. *Hyperspectral Image and Signal Processing: Evolution in Remote Sensing (WHISPERS), 2010 2nd Workshop*, eds Benediktsson JA, Chanussot J, Waske B (Institute of Electrical and Electronic Engineers, Piscataway, NJ), pp 1–4.
11. Schull MA, et al. (2011) Canopy spectral invariants, Part 2: Application to classification of forest types from hyperspectral data. *J Quant Spectrosc Radiat Transf* 112(4): 736–750.
12. Jacquemoud S, Baret F (1990) PROSPECT: A model of leaf optical-properties spectra. *Remote Sens Environ* 34(2):75–91.
13. Smolander S, Stenberg P (2005) Simple parameterizations of the radiation budget of uniform broadleaved and coniferous canopies. *Remote Sens Environ* 94(3): 355–363.

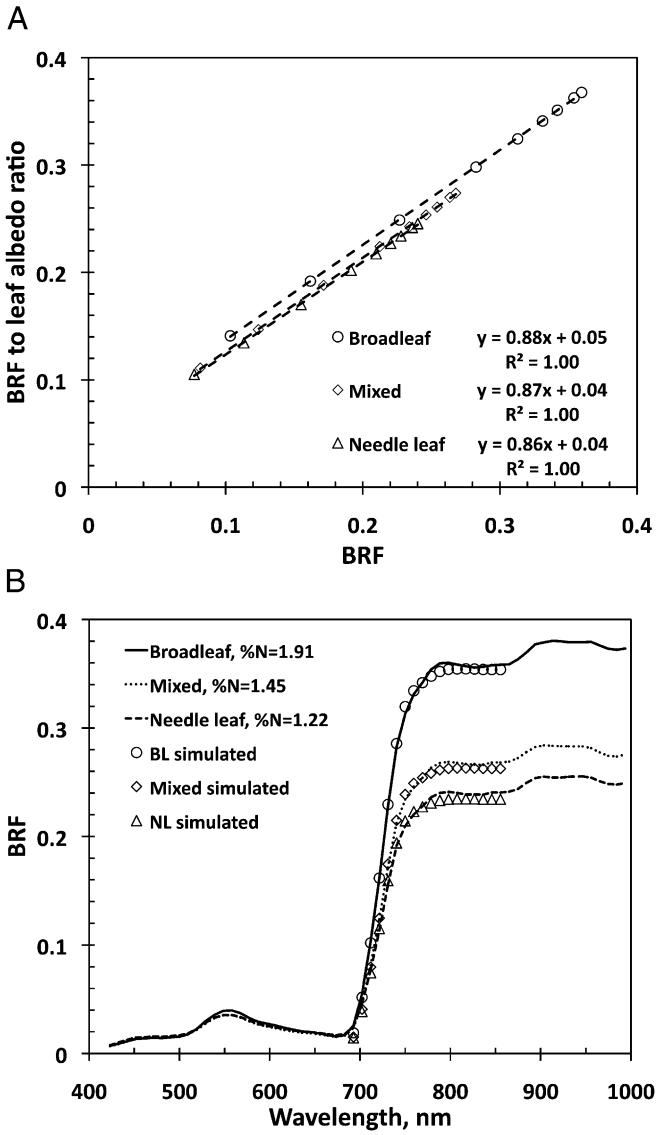

Fig. S1. (*A*) Linear relationship between the ratio $BRF_\lambda/\varpi_{0\lambda}$ and BRF_λ for three plots at Bartlett Forest representing broadleaf, mixed, and needle-leaf forests for the 710- to 790-nm spectral interval. The directional area scattering factor (DASF) is just the ratio between the intercept and $(1 - k)$, where k is the slope. (*B*) Observed (lines) and simulated (symbols) spectral BRFs for the same plots as in Locant *A*. Simulated BRFs are for the spectral interval between 690 and 855 nm. This spectral interval includes the transition of the reflectance spectrum to a plateau. The simulated BRF captures this feature with a very high accuracy.

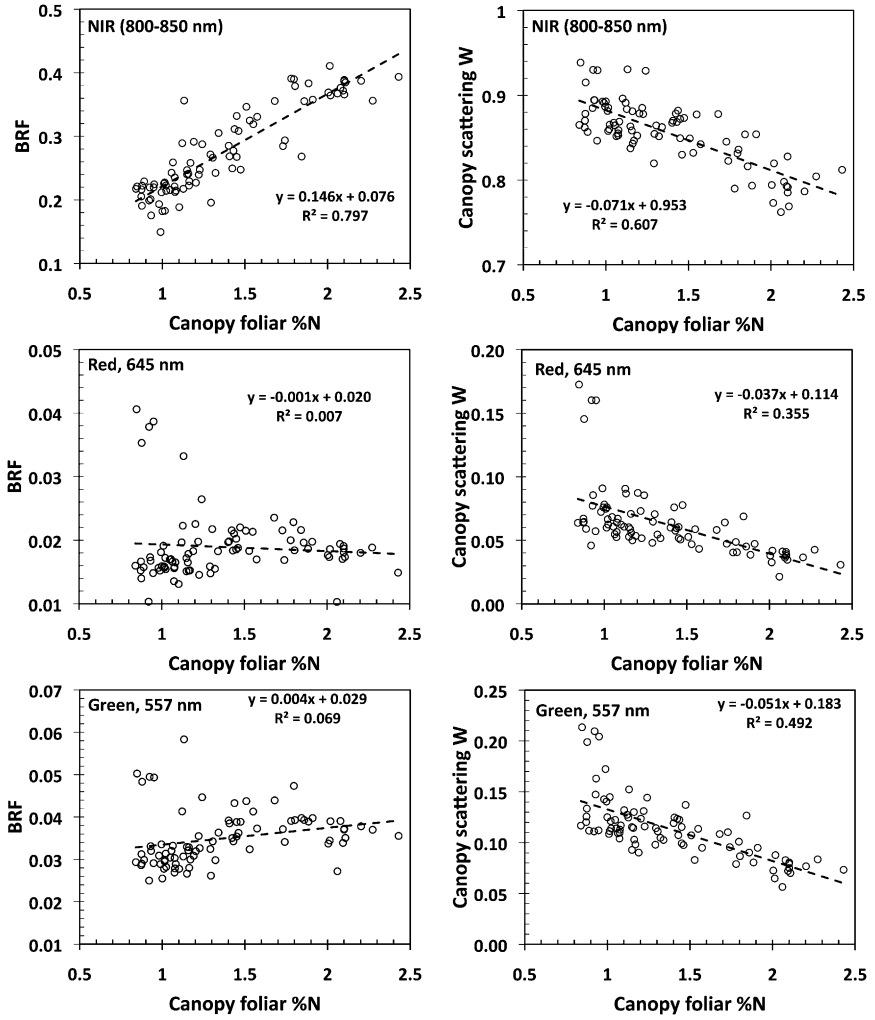

Fig. S2. Canopy BRF vs. canopy foliar %N (*Left*) and canopy scattering coefficient *W* vs. canopy foliar %N (*Right*) in the NIR, red, and green spectral wavelengths.