Modeling directional–hemispherical reflectance and transmittance of fresh and dry leaves from 0.4 μm to 5.7 μm with the PROSPECT-VISIR model

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ABSTRACT

Vegetation water content retrieval using passive remote sensing techniques in the 0.4–2.5 μm region (reflection of solar radiation) and the 8–14 μm region (emission of thermal radiation) has given rise to an abundant literature. The wavelength range in between, where the main water absorption bands are located, has surprisingly received very little attention because of the complexity of the radiometric signal that mixes both reflected and emitted fluxes. Nevertheless, it is now covered by the latest generation of passive optical sensors (e.g. SEBASS, AHS). This work aims at modeling leaf spectral reflectance and transmittance in the infrared, particularly between 3 μm and 5 μm, to improve the retrieval of vegetation water content using hyperspectral data. Two unique datasets containing 32 leaf samples each were acquired in 2008 at the USGS National Center, Reston (VA, USA) and the ONERA Research Center, Toulouse (France). Reflectance and transmittance were recorded using laboratory spectrometers in the spectral region from 0.4 μm to 14 μm, and the leaf water and dry matter contents were determined. It turns out that these spectra are strongly linked to water content up to 5.7 μm. This dependence is much weaker further into the infrared, where spectral features seem to be mainly associated with the biochemical composition of the leaf surface. The measurements show that leaves transmit light in this wavelength domain and that the transmittance of dry samples can reach 0.35 of incoming light around 5 μm, and 0.05 around 11 μm. This work extends the PROSPECT leaf optical properties model by taking into account the high absorption levels of leaf constituents (by the insertion of the complex Fresnel coefficients) and surface phenomena (by the addition of a top layer). The new model, PROSPECT-VISIR (Visible to InfraRed), simulates leaf reflectance and transmittance between 0.4 μm and 5.7 μm (at 1 nm spectral resolution) with a root mean square error (RMSE) of 0.017 and 0.018, respectively. Model inversion also allows the prediction of water (RMSE = 0.0011 g/cm²) and dry matter (RMSE = 0.0013 g/cm²) contents.

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1. Introduction

The characterization of natural surfaces by remote sensing usually takes advantage of their optical properties in the atmospheric windows of the solar emission spectrum (0.4 μm to 2.5 μm, visible-near infrared to shortwave infrared, VNIR–SWIR) and the terrestrial emission spectrum (8 μm to 14 μm, thermal infrared, TIR). The 3–5 μm range (middle wave infrared, MWIR) where the radiance mixes fluxes both reflected and emitted by the surface has been little investigated, in some degree because of the complexity of the signal. Despite the development of multispectral and hyperspectral sensors covering all these wave-length domains in recent years, and their relevance to environmental studies, physical models for interpreting the 3–5 μm spectral radiance of Earth’s surfaces are lacking (Boyd & Petitcolin, 2004). With several hundreds of narrow spectral bands in the infrared, the current generation of space sounders such as AIRS (Atmospheric Infrared Sounder, Chahine et al., 2006) and IASI (Infrared Atmospheric Sounding Interferometer, Siméoni et al, 1999), mainly dedicated to the study of the Earth’s atmosphere, have unequalled spectral resolution. Airborne sensors like AHI (Airborne Hyperspectral Imager, Lucey et al, 1998), SEBASS (Spatially Enhanced Broadband Array Spectrograph System, Kirkland et al, 2002), AHS (Airborne Hyperspectral Scanner, Sbrinno et al, 2006) or FIRST (Allard et al, 2008) can also acquire hyperspectral images with a spatial resolution of a few meters. Both for surface and atmospheric studies, the interpretation of these measurements is

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difficult because vegetation covers about 65% of terrestrial surfaces and we know very little about the spectral optical properties of plant canopies in the infrared domain. In order to exploit properly such information, it is necessary to improve our understanding of these properties at different scales in this wavelength range.

It is interesting to note that one of the earliest papers on leaf optical properties, published by Brown & Escombe (1905), addresses the question of radiative energy exchanges between plant leaves and their surrounding environment. Nevertheless, the first reflectance spectra of plant leaves in the infrared are published long after by Gates & Tantraporn (1952) who noticed that adult leaves reflect more light between 3 μm and 25 μm than juvenile leaves, which are very different in terms of phenology, morphology and anatomy. However, Wong & Blevin (1967) and Salisbury (1986) found relatively little spectral variation with senescence in the 8–14 μm domain. Salisbury & Milton (1988) and Elvidge (1988), who respectively measured leaf directional–hemispherical reflectance in the 2.5–13.5 μm and 2.5–20 μm regions, point out that the main effects occur at wavelengths shorter than 6 μm when a leaf is thoroughly dried, and that there is no significant influence of drying in the 8–14 μm region, where reflectance is more species dependent. Narayanan et al. (1991) confirmed that leaf reflectance does not vary with water content to a noticeable degree in the 9–11 μm wavelength region. They also showed that reflectance starts to increase at water contents far greater than the wilting point. The foregoing works suggest that the 3–5 μm atmospheric window may be a useful wavelength range to study vegetation water content, in contrast to the 8–14 μm window that may be more relevant to differentiating plant species. In addition, Salisbury et al. (1994) mention that Kirchoff’s law applies to most opaque materials, i.e., that emissivity ε(λ) is related to directional–hemispherical reflectance ρ(λ) by the relation ε(λ) = 1 − ρ(λ). Thus, Salisbury and Elvidge’s datasets form the first and, to date, the only open libraries of leaf emissivity. In most publications, the range from 0.95 to 0.98 is considered as an accepted order of magnitude for leaf emissivity in the 8–14 μm region. Ribeiro da Luz (2006) and Ribeiro da Luz & Crowley (2007, 2010) recently investigated leaf optical properties in the thermal infrared by completing a comprehensive work between 8 μm and 14 μm. They show that reflectance is linked to leaf surface properties and that plant species identification can be achieved using leaf spectral signatures. Leaf transmittance τ(λ) in the thermal infrared is generally supposed to be negligible. The only measurements of leaf reflectance and transmittance spectra between 0.3 μm and 25 μm that we know of were published by Gruninger et al. (1992). They state that a leaf cannot be regarded as an opaque medium between 4 μm and 5 μm, i.e., a leaf transmits part of the incoming radiation. In accordance with Kirchoff’s law the emissivity should then be calculated by the relation ε(λ) = 1 − ρ(λ) = 1 − τ(λ) (DeWitt & Nutter, 1988). For instance the emissivity of a leaf whose reflectance and transmittance equal 0.134 and 0.179 at 5 μm should be 0.687 = 1 − 0.134 − 0.179 and not 0.866 = 1 − 0.134. Olioso et al. (2007) who analyzed integrated emissivities acquired on drying plant canopies or drawn from the ASTER spectral library (http://speclib.jpl.nasa.gov/), emphasize the need for better knowledge of leaf optical properties in the infrared as a function of water content. The dataset of Fabre et al. (in press) containing reflectance spectra of cherry, sorghum, and sunflower leaves at different stages of drying is one of the first that directly link leaf optical properties to leaf water content in the 2.5–15 μm wavelength domain. However to date, the scarcity of experimental measurements and the complexity of the phenomena involved discouraged the development of a leaf optical properties model over this wavelength range.

The PROSPECT model (Jacquemoud & Baret, 1990; Féret et al., 2008) currently simulates the reflectance and transmittance spectra of plant leaves in the reflected solar energy domain as a function of their biochemical content (photosynthetic pigments, water, and dry matter) and a structure parameter that controls multiple scattering within the mesophyll. The model extension to longer wavelengths, beyond 2.5 μm, requires measurements of continuous spectra of leaves that display a wide range of anatomy and water content. As mentioned above, there is a lack of such data. The first part of this paper provides the background needed to understand leaf optical properties and presents a dataset of leaf reflectance and transmittance spectra acquired over the 0.4–14 μm wavelength region along with associated water and dry matter contents. Next, the physical bases of the extended version of PROSPECT, named PROSPECT-VISIR, are detailed and discussed. PROSPECT-VISIR consists of the introduction of the Fresnel complex coefficients and the addition of a top layer. The last section develops the calibration and verification of the model using this dataset.

2. Background

2.1. Leaf structure

Angiosperm leaves are made of one to several mesophyll layers sandwiched between the upper and lower epidermis. The epidermis is covered by a cuticle and an epicuticular wax layer of varying thickness, which tends to modify the surface roughness (Riederer & Müller, 2006; Ribeiro da Luz & Crowley, 2007). While most of the cells of the epidermis and mesophyll are ~20 μm in diameter, the wax particles are 1 μm (Ribeiro da Luz, 2005). Fig. 1 shows the anatomical structure of a typical dicot leaf, the mesophyll of which is specialized in two distinct tissues, the palisade and spongy mesophyll. This structure plays a major role in leaf optical properties as explained below.

2.2. Reflectance spectroscopy

The interpretation and modeling of VNIR–SWIR, MWIR and TIR reflectance spectra need a quick review of some physical processes. It is critical to list the main parameters that determine the spectral variation of reflectance: the complex refractive index n(λ) = n(λ) + iκ(λ), where n(λ) is the refractive index and κ(λ) is related to the absorption coefficient at wavelength λ, the cell or particle size D and cell/particle arrangement in the mesophyll. Considering typical values of 20 μm for D in plant leaves, the laws of geometric optics apply in the whole 0.4–14 μm domain. Then, the total scattered light corresponds to the sum of the surface reflected light and the light that is first refracted and then transmitted out of the particles (Appendix A). Fig. 2 illustrates the interactions between incident light and spherical particles. Pathways (1) and (2) stand for rays that undergo only surface reflection, i.e., that never penetrate the particles. Due to surface roughness, they may be reflected in any direction, regardless of the direction of incident radiation. They are called specular rays in contrast with volume rays that are transmitted through one or more particles. Pathways (3) and (4) show that volume rays may also exit the mat surface at any angle. According to the absorption properties of the medium, the total reflectance displays a predominant surface scattering or volume scattering, which produce spectral features that have symmetric shapes. Vincent & Hunt (1968) explain that a strong absorption (opaque region) induces a maximum of specular reflectance and a minimum of volume reflectance (Appendix B). The prevalence of one behavior over the other actually depends both on the absorption level and on the size and arrangement of the particles. The cavity effect, which results from multiple reflections between surface asperities, reduces the fraction of specular reflectance compared to volume reflectance. Although the laws of physics apply in the whole optical domain, these effects change from the VNIR–SWIR to the MWIR, and from the MWIR to the TIR, due to fluctuations of the absorption coefficient and the size parameter X = πD/λ. Some of these effects that do not occur or have little apparent influence on VNIR–SWIR reflectance cannot be neglected in the MWIR and TIR (e.g.
specular reflectance, cavity effect), which is illustrated in Section 3. The modeling of these has led to two major changes in the PROSPECT model, the use of the Fresnel complex coefficients to take into account specular scattering at the interface and the addition of a new layer to simulate surface effects.

3. Experimental data

Two independent series of laboratory measurements were set up in June 2008 at the USGS (United States Geological Survey) National Center in Reston, VA, USA and in July 2008 at the ONERA (Office National d’Etudes et de Recherches Aérospatiales) Research Center in Toulouse, France. Each dataset contains 32 leaf samples for which the National d’Etudes et de Recherches Aérospatiales (ONERA) Research Center in Reston, VA, USA and in July 2008 at the ONERA (Office National d’Etudes et de Recherches Aérospatiales) Research Center in Toulouse, France. Each dataset contains 32 leaf samples for which the

3.1. Biophysical measurements

64 leaves were collected in the neighborhood of the laboratories. They encompass 26 broadleaf species: maple (Acer negundo L., Acer platanoides L., Acer rubrum L.), birch (Betula sp.), catalpa (Catalpa sp.), eastern redbud (Cercis canadensis L.), citrus (Citrus sp.), dogwood (Cornus sp.), beech (Fagus sp.), edible fig (Ficus carica L.), Jerusalem artichoke (Helianthus tuberosus L.), sweetgum (Liquidambar styraciflua L.), tuliptree (Liriodendron tulipifera L.), mulberry (Morus bombycis Koidz.), sour cherry (Prunus cerasus L.), cherry laurel (Prunus laurocerasus L.), pear tree (Pyrus sp.), oak (Quercus sp.), Quercus alba L.), sassafras (Sassafras albidum (Nutt.) Nees), sorghum (Sorghum bicolor (L.) Moench), basswood (Tilia sp.), common lilac (Syringa vulgaris L.), stinging nettle (Urtica dioica L.), wine grape (Vitis vinifera L.) and corn (Zea mays L.). Eight of the species are of agricultural interest. Leaf discs 3 cm in diameter were prepared using cork borers. We measured the fresh sample weight with a precision weighing balance, placed the samples in a drying oven at 60 °C for 24 h, and then reweighed them. The water (C_w expressed in g/cm^2) and dry matter (C_m expressed in g/cm^2) contents have been determined as

\[ C_w = \frac{FW - DW}{S}, \]

\[ C_m = \frac{DW}{S}, \]

where S is the surface area of the fresh leaf disc, FW and DW are the corresponding fresh and dry weights. In total, the two datasets contain 16 fresh leaves, 19 dry leaves, and 29 leaves having intermediate water contents. The latter were naturally dried in the laboratory over two or three days, or in the oven for a short time (between 20 and 90 min). The dataset displays a wide range in water content similar to that found in nature.

3.2. Radiometric measurements

Directional–hemispherical reflectance (DHR) and transmittance (DHT) spectra of the adaxial (upper) face of the leaves were recorded using laboratory spectrometers coupled with integrating spheres (Schaepman-Strub et al., 2006). Due to technological constraints that prevent most commercial spectrometers from measuring continuous spectra from 0.4 μm to 14 μm, two instruments were used in each experiment: one from 0.4 μm to 2.5 μm and the other one from 2 μm to 14 μm. Thus, the spectral domain between 2 μm and 2.5 μm was covered by the two spectrometers. The integrating spheres are coated with materials that are nearly Lambertian diffusers, and at the coated with materials that are nearly Lambertian diffusers, and at the same time have high diffuse reflectances: Spectralon® in the VNIR–SWIR domain and Infragold® in the MWIR–TIR domain. Table 1 summarizes the main characteristics of the datasets.

To correct the spectra, in particular to ensure that the VNIR–SWIR and MWIR–TIR spectra join, we refer to four Zenith® diffusers made of...
a PTFE (PolyTetraFluoroEthylene) based polymer. They are available in thicknesses of 100 µm, 250 µm, 500 µm and 1 mm with transmission ranging from approximately 0.05 to 0.55 over the wavelength region covering 250 nm to 2500 nm. Their VNIR–SWIR diffuse reflectance and transmittance were calibrated by SphereOptics (http://www.sphereoptics.com/) using a high performance UV/VIS/NIR Spectrometer Lambda 19 from PerkinElmer and independently measured using the four ONERA and USGS spectrometers. The DHR is corrected from the black backgrounds placed under the leaf sample, applying the relationship (Miller et al., 1992)

\[
R_{\text{meas}} = R_{\text{corr}} + \frac{T_{\text{meas}}}{1 - R_{\text{corr}}} R_b
\]

where \( R_{\text{meas}} \) and \( T_{\text{meas}} \) are the measured DHR and DHT, respectively, \( R_b \) is the DHR of the black background, and \( R_{\text{corr}} \) is the corrected DHR. Inferring \( R_{\text{corr}} \) from Eq. 3 is then straightforward. Due to various spectral sampling of the spectrometers, spectra are interpolated to obtain a 1 nm spectral resolution.

### 3.3. Data interpretation

All leaves display similar major spectral features over the 0.4–14 µm wavelength region. As an example, the reflectance and transmittance spectra of fresh and dry Catalpa leaves are plotted in Fig. 3. DHR and DHT vary as a function of leaf anatomy, photosynthetic pigments (chlorophylls and carotenoids), water and dry matter contents. These relationships are detailed below. The figure also shows that the transmittance of the dry leaf is not negligible above 10 µm with a maximum transmission of about 0.05 around 11 µm. The same trend is noted with most of the dry samples of the dataset. This may be an important issue for the Earth’s energy budget in arid or semi-arid regions.

Leaf optical properties depend on both absorption and scattering. In the VIS, pigment absorption dominates and is effective up to 0.8 µm while scattering prevails in the NIR. Scattering mainly depends on leaf anatomy and tends to increase the reflectance and to decrease the transmittance. Briefly, in the high absorption spectral region, absorption dominates scattering and occurs first in the palisade mesophyll when, in the low absorption spectral region, radiation is able to penetrate down to the spongy mesophyll, where it is highly scattered (Terashima et al., 2009). As seen in Fig. 3, this is pronounced when leaves dry because there are significant changes in cell compactness that modify the amount of intercellular air spaces (Gausman et al., 1970). In the SWIR and MWIR, leaf optical properties are driven by water and dry matter absorption, which is not the case in the TIR. Fig. 4 illustrates better the effect of water content and species character on leaf reflectance spectra in the MWIR and TIR with eastern redbud and sassafras leaves having different water contents.

The spectral signature of water is obvious in fresh leaves in Figs. 3 and 4, with fundamental absorption bands at 2.9 µm and 6.08 µm and overtones at 0.97 µm, 1.2 µm, 1.47 µm, 1.94 µm and 4.8 µm. The specific absorption coefficient of water ranges from 0.45 cm⁻¹ at 0.97 µm to 12.000 cm⁻¹ at 2.95 µm, i.e., a factor of about 27,000 (Fig. 5). In the SWIR and MWIR domains, the drier the leaf, the higher the reflectance and transmittance. As seen in Figs. 3 and 4, this is no longer true around 2.9 µm and after 5.7 µm. At 2.9 µm, the signal is saturated no matter the leaf water content. This is explained by the strong absorption band of the water molecule (O–H stretching vibration) as well as the other major leaf biochemical compounds like cellulose, lignin, pigments, etc. At this wavelength, the transition from specular to volume reflection due to a decrease of absorption is well illustrated by Fig. 4. The reflectance spectrum of the fresh Sassafras leaf displays a local maximum (specular reflection) contrary to that of the driest leaf that has a local minimum (volume reflection). The importance of specular reflection in the MWIR is confirmed by the presence of narrow peaks near 3.4 µm that are due to carbon–hydrogen fundamental stretching vibrations (Salisbury & Milton, 1988). Surface effects are not observable in the VNIR–SWIR because scattered (Terashima et al., 2009).
the spectral emissivity of the fresh and dry Catalpa leaves and Table 2 provides average values in two atmospheric windows (3–5 μm and 8–14 μm) and in the 3.5–5.7 μm spectral range where the water signature is near maximum. The statistics differentiate between fresh leaves (water content greater than 0.003 g/cm², 40 samples) and dry leaves (water content less than 0.003 g/cm², 18 samples). For instance, dry leaf emissivity can be as low as 0.89 in the 8–14 μm atmospheric window. Such a low value is quite different from the 0.95 commonly used in SVAT (soil–vegetation–atmosphere transfer) models, regardless of the plant water stress, but it confirms the work of Olioso et al. (2007) who determined low emissivity in dry barley canopies. When measuring the radiant exitance on a surface using a passive infrared sensor, such a mistake in emissivity may lead to radiative temperature errors up to 5 K (Olioso, 1995). In the 3–5 μm wavelength region, leaf emissivity is more variable and ranges from 0.75 to 0.97.

These data provide crucial information about the variability of leaf emissivity in the infrared. They also show that large variation in emissivity (or reflectance and transmittance) may occur in the 3–5 μm atmospheric window as a function of leaf water content. This confirms earlier studies (e.g., Elvidge, 1988; Salisbury & Milton, 1988) and highlights a potential use of this band to study vegetation water content. In the following, as a first step to retrieve vegetation water content by remote sensing techniques in this domain, a radiative transfer model is developed that simulates leaf optical properties.

4. Modeling leaf DHR and DHT

The current version of PROSPECT, which calculates leaf DHR and DHT in the VNIR–SWIR domain, does not differentiate between species and does not treat leaf compounds separately. Cellulose, cutin, lignin, etc. are grouped together into a single variable called dry matter. This definition will be kept in the following model. The other compounds involved in PROSPECT are pigments and water. As seen before, leaf reflectance above 5.7 μm strongly depends on surface chemical composition: cutin, cellulose, trichomes, waxes, etc. These constituents are species dependent and cannot be accounted for in PROSPECT at present because information on their optical constants and effective content in each leaf is missing. Because of this we decided to extend PROSPECT up to 5.7 μm only. Compared to the present version of the model, two major changes are introduced: the use of the complex refractive index in order to take into account specular reflection at the interface and the addition of a top layer that compensates for surface effects.

4.1. A short review of PROSPECT

PROSPECT is a radiative transfer model that calculates leaf reflectance and transmittance as a function of its biochemistry and anatomical structure (Table 3). It is based on the generalized plate model (Allen et al., 1969, 1970) that considers N elementary plane parallel layers (medium 2) separated by N − 1 air spaces (medium 1). This multilayer representation is equivalent to a single layer that

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Statistics about leaf emissivity in three spectral domains.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral range</td>
<td>Minimum</td>
</tr>
<tr>
<td>Fresh leaves</td>
<td>3.5–5.7 μm</td>
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<td></td>
<td>3–5 μm</td>
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<td>8–14 μm</td>
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<tr>
<td>Dry leaves</td>
<td>3.5–5.7 μm</td>
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<td>3–5 μm</td>
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<td>8–14 μm</td>
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scatters and absorbs light following the Kubelka–Munk theory (Kubelka & Munk, 1931). N characterizes the internal structure of the leaf. The total reflectance \( R_L \) and transmittance \( T_L \) of an elementary layer at a given wavelength are given by

\[
R_L = r_{12} + \frac{r_{12}t_{21}r_{21}}{1 - r_{21}^2} t_{21}^2, \tag{4}
\]

\[
T_L = \frac{t_{12}t_{21}}{1 - r_{21}^2} t_{21}^2, \tag{5}
\]

where \( r \) and \( t \) are the reflectivity and transmissivity at the interface between media \( i \) and \( j \) and \( \tau \) is the fraction of light transmitted through the plate. \( \tau \) is related to the absorption coefficient of the plate \( A \) which sums the contribution of all individual leaf constituents:

\[
A(\lambda) = \sum_i \frac{C_i}{N} \alpha_i(\lambda), \tag{6}
\]

where \( C_i \) is the total content of constituent \( i \) (g/cm²) and \( \alpha_i(\lambda) \) its specific absorption coefficient (cm²/g). The leaf structure parameter \( N \) (real number of elementary layers in the model ranging from 1 to 3) characterizes leaf anatomy and controls volume scattering within the mesophyll. For instance, \( N \) is higher in a dry leaf than in a fresh leaf because, as above-mentioned, NIR reflectance is higher.

The update of PROSPECT up to 5.7 \( \mu \)m consists of determining the inherent leaf optical properties (specific absorption coefficients and refractive index) at all wavelengths of the extended domain. A first attempt using the present version of the model was unsuccessful, with a poor fit between the measured vs. modeled reflectance and transmittance between 3.5 \( \mu \)m and 5.7 \( \mu \)m. This problem is overcome by the model update.

### 4.2. PROSPECT-VISIR

As mentioned earlier, the infrared domain is characterized by very high absorption levels of leaf constituents compared to the visible–near infrared. Kortüm & Vogel (1958) argue that deviations from the Kubelka–Munk theory in high absorbing materials are entirely attributable to an increased proportion of specular reflection. Moreover, the surface of waxy leaves may affect the spectral contrast by the cavity effect. PROSPECT was modified in two ways accordingly: Fresnel complex coefficients were first introduced to model specular reflection, then a top layer was added to take into account surface effects. A constant volumetric scattering parameter \( N \) is considered to be acceptable up to 5.7 \( \mu \)m: according to Kortüm & Oelkrug (1964), the scattering coefficient in the Kubelka–Munk equations (\(-N\) in PROSPECT) does not depend much on the wavelength (\( \lambda^{-1} \) to \( \lambda \)) when the particle size is equal to or greater than the wavelength (\( \lambda \geq 1 \)), like it is for the interior leaf particles in the 0.4–5.7 \( \mu \)m domain. The influence of small surface particles (\( \lambda \leq 1 \)) will also be accounted for in the additional layer. Since pigment absorption is negligible in the 0.8–5.7 \( \mu \)m domain (Gates & Tantrarom, 1952; Holt & Jacobs, 1955; Schlüchter et al., 2003), the only components involved hereafter are water and dry matter, which includes cellulose, cutin, lignin, etc.

#### 4.2.1. Fresnel complex coefficients

Consider the reflection and transmission of a wave by a plane boundary that separates a medium with refractive index \( n_1(\lambda) = n_1(\lambda) + i\kappa_1(\lambda) \) from one with \( n_2(\lambda) = n_2(\lambda) + i\kappa_2(\lambda) \). The real part of \( n \) is just called the refractive index and the imaginary part is the absorption coefficient. The relative refractive index of the interface is given by (Hapke, 1993):

\[
\hat{n}(\lambda) = \frac{n_2(\lambda)}{n_1(\lambda)} = n(\lambda) + i\kappa(\lambda) \tag{7}
\]

so that

\[
n = \frac{n_1n_2 + \kappa_1\kappa_2}{n_1^2 + \kappa_1^2} \tag{8}
\]

and

\[
\kappa = \frac{n_1\kappa_2 - n_2\kappa_1}{n_1^2 + \kappa_1^2} \tag{9}
\]

The imaginary part of the refractive index \( \kappa(\lambda) \) can be expressed in terms of the absorption coefficient \( \alpha(\lambda) \) and the wavelength of the light \( \lambda \) according to

\[
\kappa(\lambda) = \frac{\lambda}{4\pi} \alpha(\lambda). \tag{10}
\]

In the VNIR–SWIR, \( \kappa(\lambda) \) is generally ignored in Fresnel equations because it is much lower than \( n(\lambda) \). This is not the case beyond the SWIR for many materials. Assuming that the leaf is made of several constituents, the effective refractive index \( \hat{n} \) can be modeled as a weighted linear combination of the individual refractive indexes of all leaf compounds. Therefore, Eq. (10) becomes

\[
\kappa(\lambda) = \frac{\lambda}{4\pi} \sum_i C_i \alpha_i(\lambda) / \sum_i C_i. \tag{11}
\]

The variability of the real part of the refractive index \( n \) as a function of \( C_i \) is supposed to be weaker and, because determining it for each leaf compound is impractical in the present state of our knowledge, we decided to use only an average spectrum. If the incident light is unpolarized, the Fresnel reflection coefficient is defined by

\[
r = \frac{1}{2} \left( r_{\perp} + r_{\|} \right) \tag{12}
\]

where \( r_{\perp} \) and \( r_{\|} \) are the reflection coefficients for perpendicular and parallel polarization, respectively. The corresponding transmission coefficient is simply deduced by \( t = 1 - r \). In the case of complex \( \hat{n} \), for any incidence angle \( \theta \) and refractive index \( n \), they can be written as

\[
r_{\perp} = \frac{\left( (n^2 - \kappa^2) \cos \theta - \psi_1 \right)^2 + (2\kappa \cos \theta - \psi_2)^2}{\left( (n^2 - \kappa^2) \cos \theta + \psi_1 \right)^2 + (2\kappa \cos \theta + \psi_2)^2} \tag{13}
\]

and

\[
r_{\|} = \frac{(\cos \theta - \psi_1)^2 + \psi_2^2}{(\cos \theta + \psi_1)^2 + \psi_2^2} \tag{14}
\]

where

\[
\psi_1^2 = \frac{1}{2} \left( (n^2 - \kappa^2 - \sin^2 \theta) + \left( (n^2 - \kappa^2 - \sin^2 \theta)^2 + 4\kappa^2 \right)^{1/2} \right) \tag{15}
\]

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**Table 3**

PROSPECT input parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific absorption coefficient of leaf constituent ( i )</td>
<td>( \alpha_i(\lambda) )</td>
</tr>
<tr>
<td>Real refractive index</td>
<td>( n(\lambda) )</td>
</tr>
<tr>
<td>Chlorophyll, carotenoids, water, and dry matter content</td>
<td>( C_i )</td>
</tr>
<tr>
<td>Leaf structure parameter</td>
<td>( N )</td>
</tr>
</tbody>
</table>
and

$$\psi_2^2 = \frac{1}{2} \left( -\left( n^2 - \kappa^2 \sin^2 \theta \right) + \left( \left( n^2 - \kappa^2 \sin^2 \theta \right)^2 + 4n^2 \kappa \right)^{1/2} \right).$$  \hspace{1cm} (16)

A detailed explanation of these equations can be found in Hapke (1993). For normal incidence and \( n > 1 \), the Fresnel reflection coefficient simplifies to:

$$r = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \hspace{1cm} (17)$$

These relations are valid in the whole wavelength region from 0.4 \( \mu \)m to 5.7 \( \mu \)m because Eqs. (8) and (9) simplify when \( \kappa \ll 1 \), which occurs for wavelengths lower than 2.5 \( \mu \)m. The expressions of the former version of PROSPECT are then restored.

4.2.2. Addition of a surface layer

As mentioned in Section 3.4, the leaf surface plays an important role in the distribution of volume vs. specular reflection and may increase volume scattering and/or the cavity effect, according to anatomical structure and biochemical composition. One of the simplest ways to introduce such an effect in PROSPECT is to add a non-absorbing layer on top of the \( N \) layers, which is characterized by its own refractive index \( n_{\text{surf}}(\lambda) \). As Fresnel coefficients depend on the effective refractive index of the interface \( n \), the smaller the difference between the two refractive indexes, the smaller the specular reflection. Moreover, the difference between \( n_{\text{surf}}(\lambda) \) and \( n(\lambda) \) induces multiple reflections between the air and the first elementary plate of the leaf that absorbs light. This additional layer should not be considered as a true representation of the cuticle but as an equivalent layer compensating surface effects. It is bound to the first layer of the leaf model without any interspace filled by air (Fig. 7).

The light incident on this non-absorbing layer is assumed to be inscribed in a right cone having an opening angle of 40° as in PROSPECT (Féret et al., 2008). It becomes isotropic when transmitted through this layer. The reflectance \( R_{t_1} \) and the transmittance \( T_{t_0} \) of the first grouped layer (top layer + first leaf layer) are now defined by

$$R_{t_1} = R_{t_0} + \frac{t_{10} r_{01} r_{021}}{1 - t_{01} r_{021}}, \hspace{1cm} (18)$$

and

$$T_{t_1} = \frac{t_{10} r_{01} r_{021}}{1 - t_{01} r_{021}}. \hspace{1cm} (19)$$

with \( r_{021} = r_{02} + \frac{t_{02} r_{21}^2}{1 - r_{02} r_{21}^2} \) and \( t_{021} = \frac{t_{02} r_{21}^2}{1 - r_{02} r_{21}^2} \) (Hagmann & Hummel, 1996; Windt, 1998). The subscript 0 corresponds to the top layer, 1 to the air, and 2 to the leaf interior. The reflectance \( R_t \) and transmittance \( T_t \) of the other plates continue to follow Eqs. (4) and (5).

4.3. Calibration of the model

The calibration of the model aims to assess the specific absorption coefficients \( \alpha(\lambda) \) of water and dry matter, the surface equivalent refractive index \( n_{\text{surf}}(\lambda) \) and the leaf interior refractive index \( n(\lambda) \). Since leaves cannot be compared to compact layers, the structure parameter \( N \) representing leaf anatomy must also be known. It changes from leaf to leaf, is assumed to be wavelength independent, but it cannot be directly measured. Ideally, it should be obtained for each leaf together with the refractive indexes and the specific absorption coefficients. Nevertheless, with spectrometric measurements at \( N \) wavelengths, such a method would require fitting \( 2N + 1 \) parameters. The computation of such a large number of unknowns is unrealistic so that the calibration was split into two steps. First, we assessed \( N \) for each leaf using leaf reflectance and transmittance in the 0.8–1 \( \mu \)m plateau where its effect is maximum because of very little absorption. In this stage, the refractive index is assumed to be constant and equal to 1.45 (Féret et al., 2008). Second, the two refractive indexes \( n_{\text{surf}}(\lambda) \) and \( n(\lambda) \) and specific absorption coefficient of dry matter \( \alpha_{\text{dry matter}}(\lambda) \) are determined all together considering the whole leaf dataset. Because pigments are beyond the scope of this paper, the wavelength domain from 0.4 \( \mu \)m to 1.2 \( \mu \)m is not considered. The calibration is then done at each wavelength in the 1.2–5.7 \( \mu \)m. The specific absorption coefficient of water \( \alpha_{\text{water}}(\lambda) \) is taken from the literature since previous calibrations of PROSPECT showed close similarities with that of pure liquid water (Fig. 4). The three unknown parameters \( \Theta = (n_{\text{surf}}(\lambda), n(\lambda), \alpha_{\text{dry matter}}(\lambda)) \) are determined by inversion of PROSPECT-VISIR at each wavelength minimizing the merit function

$$J(\Theta) = \sum_\lambda \left( \frac{R_{\text{meas}}(\lambda) - R_{\text{mod}}(\lambda, \Theta)}{T_{\text{meas}}(\lambda) - T_{\text{mod}}(\lambda, \Theta)} \right)^2, \hspace{1cm} (20)$$

where \( R_{\text{meas}}(\lambda) \) and \( T_{\text{meas}}(\lambda) \) are the measured reflectance and transmittance at wavelength \( \lambda \), and \( R_{\text{mod}}(\lambda, \Theta) \) and \( T_{\text{mod}}(\lambda, \Theta) \) stand for the modeled values.

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4.4. Verification of the model

Two tests are carried out on the whole dataset in the 1.2–5.7 μm and the 3–5 μm spectral ranges to check if predictions are consistent with observational data. A first test, called direct mode, consists of simulating leaf reflectance and transmittance spectra using experimental values of $C_w$ and $C_m$ and then comparing them with measured spectra. This stage requires a preliminary fit of the best $N$ values using the calibrated specific absorption coefficients and refractive indexes as detailed in Féret et al. (2008). The second test, called inverse mode, retrieves leaf water and dry matter content by model inversion. Note that the limited number of experimental data drove us to perform the calibration and verification on the same dataset.

5. Result and discussion

5.1. Calibration

Fig. 8 shows that the specific absorption coefficient of dry matter is consistent with our knowledge of leaf constituent (e.g., cellulose, lignin, waxes) optical properties (Reeves et al., 2008). Below 2.5 μm the spectrum matches the one published in Féret et al. (2008). According to Ribeiro da Luz (2006), the peaks at 3.4 μm and 3.5 μm, also reported by Salisbury & Milton (1988), are typical from long chain aliphatic compounds like methylene. Around 2.94 μm, we observe a minimum, although lignin and cellulose display a maximum due to O–H bond stretching (Kondo, 1997; Dalimova & Kristallovich, 1999). Besides very low reflectance and transmittance, this disagreement could also be explained by high values of the specific absorption coefficient of pure liquid water around 2.94 μm, which may lead to an underestimation of the specific absorption coefficient of dry matter.

The retrieved refractive indexes are difficult to interpret (Fig. 9). Their overall decrease as a function of wavelength is consistent with our fundamental knowledge of such optical constants. The major variation around 3.5 μm also agrees with the maximum absorption of methylene, according to the Kramers–Kronig relations. A similar behavior was expected around 2.9 μm but, as seen before, there is an uncertainty in the specific absorption coefficient of dry matter that may lead to inaccurate refractive indexes. Fig. 9 shows that $n(\lambda)$ and $n_{surf}(\lambda)$ split in the MWIR domain after 2 μm, which justifies the addition of a top layer that permits a better fit of the data. The impact of the top layer on reflectance and transmittance from 1 μm to 2.5 μm is actually very limited, compared to the former version of PROSPECT. Thus, use of $n_{surf}(\lambda)$ still makes sense in this region of the spectrum. The calibration of PROSPECT-VISIR would be improved if we had access to a larger dataset.

5.2. Evaluation of model consistency and performance

Fig. 10 compares the measured and modeled reflectance and transmittance spectra of two fresh leaves (Catalpa and Tilia) and two dry leaves (Catalpa and Acer platanoides). The shape and amplitude of both $R$ and $T$ are well reproduced in each sample. The results of model consistency in direct mode are summarized in Table 4 in terms of root mean square error of prediction (RMSEP), bias (BIAS), and standard error of prediction corrected from the bias (SEP). They are very satisfactory regardless of the leaf water content and comparable to those obtained by Féret et al. (2008) who found a mean RMSEP of 0.025 and 0.021 for the reflectance and transmittance in the 0.4–2.5 μm range.

Table 5 and Fig. 11 summarize the results of the inversions obtained for water and dry matter contents. They confirm that model inversion in the VNIR–MWIR permits accurate retrieval of water and dry matter content. As water absorption dominates in the infrared, the estimation of leaf biochemical content is better for $C_w$ than $C_m$. The 3–5 μm range also provides very satisfactory results, although these are less accurate than those obtained using the full wavelength range.

5.3. General discussion

Despite the fact that there is a good agreement between model outputs and experimental data, this study emphasizes the limits of such physically based models. During the calibration phase, a strong sensitivity to initial variables may be encountered while computing the leaf inherent optical properties. For instance, as mentioned by Allen et al. (1970), the refractive index $n(\lambda)$ and the structure parameter $N$ are complexly linked so that one variable cannot be determined independent of the other. An initial value of $n(\lambda)$ is needed to determine $N$, which in turn is used to estimate the refractive index and the specific absorption coefficient. The calibration is quite sensitive to that first guess. Moreover in the Kubelka–Munk theory, the refractive index is linked to the scattering parameter and Hapke (1993) demonstrated that the latter was actually absorption dependent. Thus $n$, $N$ and $k$ are not independent variables and their estimation may have been distorted by compensation errors. Such spectral artifacts are typically suspected to affect the refractive index because of its strong link to the absorption coefficient. Although these features occur both in the VNIR–SWIR and MWIR, the major limits actually concern the infrared domain because of high absorption levels. Kortüm & Vogel (1958) and Hapke (1993) show that a divergence from the Kubelka–Munk theory is observed in strong absorption conditions and can be theoretically predicted. Like the Kubelka–Munk model, the plate model of Allen et al. (1969) is valid in weak absorption conditions. Despite this structural weakness of the model, PROSPECT has provided the scientific community with very useful and accurate quantitative information on leaf optical properties for about 20 years (Jacquemoud et al., 2009).
6. Conclusion

This paper presents the first continuous leaf directional–hemi-spherical reflectance and transmittance spectra from 0.4 μm to 14 μm associated with variations in leaf water and dry matter content. These measurements confirm the effective variability of leaf optical properties as a function of water content up to 5.7 μm and highlight the potential of the 3–5 μm band to study vegetation water content. In contrast, TIR spectra closely depend on leaf surface optical properties. Furthermore, our measurements show that the transmittance of the driest leaves is non-zero, leading to a notable change in leaf emissivity, for instance, 0.89 instead of 0.95 in the 8–14 μm band.

PROSPECT-VISIR is the first model that simulates leaf optical properties between 1.2 μm and 5.7 μm and that allows retrieval of leaf water and dry matter contents by inversion in this wavelength range. Compared to the former version of the model, two major changes have been introduced: high absorption levels (use of the Fresnel complex coefficients) and some surface effects (addition of a top layer). However, these changes do not fully represent the complexity of reflectance spectroscopy in the MWIR domain, between the VNIR–SWIR domain where physical phenomena are well modeled (e.g., Kubelka–Munk theory) and the TIR domain where the complexity of the phenomena involved have not been, up to now, modeled. PROSPECT-VISIR gives satisfactory results insofar as the RMSE between the model and the measurements are small in both direct and inverse testing modes. In the 3–5 μm range, leaf reflectance is calculated with a RMSE of 0.013 and leaf water content is retrieved with a RMSE of 0.0021 g/cm².

PROSPECT-VISIR has already been incorporated into the 4SAIL vegetation canopy reflectance model (Verhoef et al., 2007; Jacque-moud et al., 2009) and coupled with the MODTRAN atmospheric radiative transfer to perform the first simulations of vegetation MWIR radiance spectra at canopy and top-of-atmosphere levels. The analysis of such spectra requires understanding of the complexity of the MWIR domain, e.g., reflected and emitted light superposition, atmospheric corrections, impact of vegetation and soil temperatures on the signal, cavity effect in the canopy, etc. With this integrated model, we expect to better understand the effect of vegetation water content on hyperspectral airborne or satellite images. A validation study using

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Comparison between simulated and measured reflectance and transmittance over two wavelength ranges. RMSEP = ( \sqrt{\frac{1}{n} \sum (x_j - y_j)^2} ), BIAS = ( \frac{1}{n} \sum (x_j - y_j) ) and SEPC = ( \sqrt{\frac{1}{n} \sum (x_j - y_j - BIAS)^2} ), where the ( x_j ) stand for the measurements and the ( y_j ) stand for the modeled values.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reflectance</strong></td>
<td>1.2–5.7 μm</td>
</tr>
<tr>
<td>RMSEP</td>
<td>0.0168</td>
</tr>
<tr>
<td>BIAS</td>
<td>0.0008</td>
</tr>
<tr>
<td>SEPC</td>
<td>0.0167</td>
</tr>
<tr>
<td><strong>Transmittance</strong></td>
<td></td>
</tr>
<tr>
<td>RMSEP</td>
<td>0.0180</td>
</tr>
<tr>
<td>BIAS</td>
<td>-0.0019</td>
</tr>
<tr>
<td>SEPC</td>
<td>0.0178</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Test of water and dry matter content retrieval using PROSPECT-VISIR.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water content Cw</strong></td>
<td></td>
</tr>
<tr>
<td>RMSEP (g/cm²)</td>
<td>0.0011</td>
</tr>
<tr>
<td>BIAS (g/cm²)</td>
<td>-0.0002</td>
</tr>
<tr>
<td>SEPC (g/cm²)</td>
<td>0.0011</td>
</tr>
<tr>
<td><strong>Dry matter content Cm</strong></td>
<td></td>
</tr>
<tr>
<td>RMSEP (g/cm²)</td>
<td>0.0013</td>
</tr>
<tr>
<td>BIAS (g/cm²)</td>
<td>0.0003</td>
</tr>
<tr>
<td>SEPC (g/cm²)</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

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AHS data acquired by the European Space Agency as part of the AGRISAR2006 and SEN2FLEX campaigns is underway. This should help to understand scaling issues and to improve vegetation water content retrieval by remote sensing techniques, particularly for the newest sensors covering the MWIR domain (e.g. AHS, SEBASS).

Acknowledgments

The datasets are available on request to the authors and the model on the web site http://teledetection.ipgp.fr/prosail/. This work has been funded by the French national remote sensing program (INSU Programme National de Télédétection Spatiale) as part of the SVETIR (Soil-Vegetation Emissivity in the Thermal Infra-Red) project. The authors are grateful to the USCS Spec Lab and ONERA DOTA teams for their welcome during the measurement campaigns. Many thanks to Susan L. Ustin (U.C. Davis) for editing this paper and to the three reviewers for their valuable comments. IPGP contribution no. 3082.

Appendix A. Scattering as a function of particle size

Scattering is a function of the size parameter \( X = nD/\lambda \) and follows different regimes. \( X < 1 \) corresponds to the Rayleigh region, \( X = 1 \) is the resonance region, and \( X > 1 \) is the geometric-optics region (Hapke, 1993). In the geometric-optics region, and for a large amount of particles close together, scattering is not caused by diffraction but corresponds to surface reflection and to the refracted rays that are transmitted out of the particles. For the leaf cells, \( X \) ranges from 150 to 4.5 in the 0.4 - 14 \( \mu \text{m} \) domain. For the wax layer, it ranges from 7.9 to 0.2. Table 6 gives some values of \( \mu_{\text{fl}} \) for inside leaf cells (\( D - 20 \mu \text{m} \) and wax particles (\( D - 1 \mu \text{m} \)). As mentioned by Hapke (1993), there is a good agreement between the Mie theory (which gives the exact solution for light scattering by spherical particles of any size) and geometric-optics for \( X \) as small as 6. Geometric-optics is then used to model leaf reflectance in the 0.4 - 2.5 \( \mu \text{m} \) region and, with a few exceptions (very glaucous leaves) scattering by the thin wax layer can be neglected due to limited effects on reflectance.

Table 6

<table>
<thead>
<tr>
<th>Wavelength (( \mu \text{m} ))</th>
<th>0.4</th>
<th>2.5</th>
<th>5</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf cells</td>
<td>150</td>
<td>25</td>
<td>12.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Wax particles</td>
<td>7.9</td>
<td>1.3</td>
<td>0.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Fig. 11.** Retrieved vs. measured water (left) and dry matter (right) contents of the whole dataset in the 1.2-5.7 \( \mu \text{m} \) range.

Appendix B. Volume vs. surface scattering

A maximum of absorption induces a maximum of specular scattering and a minimum of volume scattering. It may appear contradictory that an increase in absorption of radiation also causes an increase in reflected light. This can be explained by microscopic phenomena occurring when electromagnetic radiation interacts with the boundary between two media: the incident fields may be thought of as inducing dipoles and currents at the surface and they generate radiation that propagates in both directions from the surface. The radiation travelling backward constitutes the reflected light; that travelling forward combines coherently with the incident fields and reduces the intensity of the transmitted light. If the absorption is weak, the induced dipole moments are relatively small, so that the radiation generated by them is weak, hence the reflectance is small and the transmittance is large. Conversely, if the absorption is high, the dipoles and the radiation they generate are strong, resulting in a high reflectivity. Most of the radiation is reflected, rather than being absorbed, as a consequence of the ability of the charges on the surface to rearrange themselves in such a manner as to inhibit the fields from entering the second medium (Hapke, 1993).

References


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