Spectral invariants and scattering across multiple scales from within-leaf to canopy

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Abstract

Spectral invariants can be considered fundamental descriptors of the impact of canopy structure on canopy scattering where the scattering objects are large compared with the wavelength of radiation. The paper uses the concept of canopy spectral invariants to explore scaling relationships within canopy scattering. A new approximation to the leaf-level PROSPECT scattering model of Jacquemoud and Baret [Jacquemoud, S., & Baret, F. (1990). PROSPECT: A model of leaf optical properties spectra. Remote Sensing of Environment, 34, 75–91.] is developed by applying the spectral invariant approach to leaf internal scattering, in a similar manner to that which has been used to describe canopy-level scattering. We show that it is possible to express both the canopy- and leaf-level single scattering albedo as a function of canopy spectral invariants. This approach provides a framework through which structural information can be maintained in a self-consistent manner across multiple scales from leaf- to canopy-level scattering, at least for the simple canopy architectures considered. It is demonstrated that the nesting of scales described in these relationships implies limits to the retrieval of absolute concentrations of any biochemical constituents or absolute quantities of the amount of scattering material from hyperspectral observations of total scattering. The implication is that in general it may not be possible to separate the components of structural and biochemical influences on measured total scattering signals.

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1. Introduction

Measurements of reflectance obtained by ground, airborne or satellite remote sensing instruments at optical wavelengths are a complex function of the various scattering and absorption events that photons undergo in travelling from the illumination source to the sensor. In this paper, we use the concept of spectral invariants (Huang et al., 2007; Knyazikhin et al., 1998; Panferov et al., 2001) to provide a framework for considering the scaling of radiation scattering and absorption from the leaf to the canopy.

Ignoring diffraction and re-emission effects, electromagnetic radiation incident on an object can be considered to undergo one of two particular interactions with the material: it will either be scattered (with a probability \( K_s \)) via reflectance or transmittance; or it will be absorbed (with a probability \( K_a \)). These scattering and absorption probabilities depend on the material properties of the object and will generally vary as a function of wavelength. The single scattering albedo, \( \omega \), of an object (also then a function of wavelength), is defined:

\[
\omega = \frac{K_s}{K_s + K_a}
\]  

(1)

For objects that are large compared with the wavelength of the radiation (such as leaves at optical wavelengths) we can use geometric optics theory to describe the bulk scattering (and absorption) of an ensemble of such objects (Ross, 1981). The total scattering can be subdivided for planar objects (leaves) into radiation which escapes from the upper surface relative to the incident radiation (the leaf reflectance, \( \rho_l \)) and that which is scattered through the object and escapes through the lower surface (the leaf transmittance, \( \tau_l \)).

Assuming object scattering to be bi-Lambertian (which may not be valid for individual scattering objects, but may be...
assumed for the ensemble where any angular preference for scattering will tend to average out), we can phrase the total scattering, \( W \), from a medium consisting of a single ‘type’ of object as a power series in terms of the single scattering albedo \( \omega \) of that object:

\[
W = \sum_{i=1}^{\infty} s_i \omega^i
\]  

(2)

where it follows from geometric optics theory that the terms \( s_i \) in Eq. (2) are spectrally invariant i.e. independent of the wavelength \( \lambda \) of radiation. The \( s_i \) terms are simply a function of the geometry of the scattering objects, their arrangement in the ensemble and the directions of incident and scattered radiation. In this sense, \( W \) is effectively the ‘single scattering albedo’ at another scale — the canopy scale here, assuming \( \omega \) to be the scattering by leaves within the canopy. As with the object (leaf) single scattering albedo \( \omega \), we can split \( W \) into its component parts of reflectance (\( R \)) and transmittance (\( T \)):

\[
R = \sum_{i=1}^{\infty} r_i \omega^i
\]  

(3a)

\[
T = \sum_{i=1}^{\infty} t_i \omega^i
\]  

(3b)

where \( r_i \) and \( t_i \) are the portions of scattered radiation at scattering level \( i \) that exit the canopy on the same and opposite sides as the incident radiation respectively (i.e. the reflected and transmitted portions), and:

\[
r_i + t_i = s_i
\]  

(3c)

In this paper, we explore this representation of scattering through the spectral invariant approach and discuss the implications for the scaling of scattering behaviour. We demonstrate the consistency of scattering behaviour at both leaf and canopy scale if considered in this way, and investigate the coupling implied between leaf biochemical concentrations and canopy Leaf Area Index (LAI).

2. Canopy scattering

Fig. 1 shows spectral invariant terms \( s_i \) in Eqs. (3a)–(3c), as a function of scattering order \( i \) for canopy directional–spherical scattering (the sum of directional-hemispherical reflectance and transmittance) for an illumination angle of 0° for LAI ranging from 1 to 10, for a canopy constructed of randomly located, non-overlapping disks, with a spherical leaf angle distribution (LAD). The reflectance of the disks in the canopy was set equal to transmittance in the simulations and their scattering properties were assumed bi-Lambertian. The spectral invariant terms were calculated from simulations of canopy scattering using a Monte Carlo ray tracing model (Lewis, 1999, modified as described in Disney et al. (2006) and tested against other models in Pinty et al. (2004a) and

![Fig. 1. Plot of s_i at i-th scattering order for canopies of LAI 1, 5, and 10. Canopies are composed of randomly located non-overlapping disks with a spherical leaf angle distribution.](image)

Widlowski et al. (in press). Several important features of canopy scattering are apparent from Fig. 1:

1. canopy scattering contributions decrease with scattering order;
2. the rate of decrease reduces until some threshold scattering order is reached;
3. the threshold scattering order increases with increasing LAI, being of the order of the LAI value;

The mechanisms behind this behaviour are relatively straightforward to understand: the radiation intensity is initially distributed (\( i = 1 \)) according to Beer’s Law in the canopy, with a peak at the top of the canopy. However this peak descends into the canopy as radiation penetrates further at higher interaction orders. The closer this peak is to the top of the canopy, the higher the probability of escape in the upward direction and the higher the reflectance contribution (the lower the transmittance contribution). The change in the vertical distribution of intensity becomes less and less with each interaction order, eventually converging down to a level that is essentially maintained for all further interactions (the threshold scattering order).

Smolander and Stenberg (2005) define a canopy recollision probability, \( p \), as the probability that a photon that intercepts a canopy object will recollide with other canopy elements rather than escaping the space of the canopy. Such a definition can be considered to apply either to an effective value (\( p_{\text{eff}} \)), averaged over all scattering orders, or separately for each order of interaction (\( p_{\text{actual}} \)). Fig. 2a illustrates \( p_{\text{actual}} \) as a function of scattering order calculated from the data in Fig. 1, which more clearly shows the settling down of this term when the radiation distributions becomes ‘well-mixed’ at approximately the LAI value.

Panferov et al. (2001) note that this constant (‘well-mixed’) recollision probability (which we shall denote \( p_{\text{rad}} \)) is the principal eigenvalue of the radiative transfer equation, and
consider it a fundamental property describing the scattering and absorption in a 3D medium of large (compared to the wavelength of the radiation) objects. Whilst it is clear from above that the recollision probability is not a single number but rather a function of scattering order, it has been shown that the total scattering (and canopy reflectance (Lewis et al., 2003) can in fact be accurately modelled by assuming $p$ to be constant for second order scattering and higher terms with the error not too great if $p$ is assumed constant for all scattering orders (Huang et al., 2007).

If $p$ is assumed constant for all scattering orders, a Neumann series follows:

$$W = a \sum_{i=1}^{\infty} \left( \frac{ap}{1-p} \right)^i$$

where $ap$ is the first-order scattering for a single scattering albedo of 1.0. From consideration of energy conservation, $W = 1$ when $\omega = 1$, so that:

$$W = \frac{(1-p)\omega}{1-p\omega}$$

(4b)

One caveat to applying this approximation (i.e. assuming $p$ constant for all scattering orders) is that the recollision probability $p$ becomes an effective value ($p_{\text{eff}}$), which is not equivalent to the principal eigenvalue of the radiative transfer equation except for low LAI (pace Panferov et al., 2001).

Fig. 2b shows $p_{\text{inf}}$ and $p_{\text{eff}}$ as a function of LAI for the structurally homogeneous canopies described above. Comparing these two probabilities, we find a strong linear relationship:

$$p_{\text{eff}} = 0.0173 + 0.9526p_{\text{inf}}$$

(5)

with a Root Mean Squared Error (RMSE) of 0.015 ($r^2=0.999$).

Smolander and Stenberg (2005) describe an empirical relationship between $p_{\text{eff}}$ and LAI for a spherical leaf angle distribution for a homogeneous canopy:

$$p_{\text{canopy}} = p_{\text{max}}(1-\exp(-k\text{LAI}^p))$$

(6)

with $p_{\text{max}}=0.88$, $k=0.7$, $b=0.75$. For the simulations performed here, we find that this is an appropriate representation for the dependency but that for $p_{\text{inf}}$, $p_{\text{max}}=0.96$, $k=0.61$, $b=0.71$, and for $p_{\text{eff}}$, $p_{\text{max}}=0.92$, $k=0.63$, $b=0.73$.

If we define $\delta p$ as the recollision probability for some small LAI $\delta L$, we can calculate the total scattering according to Eq. (4b) for $2\delta L$ from:

$$W(2\delta L) = \frac{(1-p)(\delta L)}{1-p(\delta L)} = \left(1-p(2\delta L)\right)^{\omega}$$

(7a)

where

$$p(2\delta L) = 2\delta p - \delta p^2$$

(7b)

By examining the behaviour $P(n\delta L)$ for further multiples $n$ of $\delta L$ we find:

$$\frac{\delta p(L)}{\delta L} = \left(\frac{\delta p}{\delta L}\right)(1-\delta L)^{1/\delta L}$$

(7c)

which in the limit $\delta L \rightarrow 0$ gives:

$$p(L) = 1-\exp(-kL)$$

(7d)

where $k$ is $\delta p/\delta L$. This is a theoretical expression for the dependence of recollision probability on LAI, derived from nesting recollision probabilities. We see from the simulations above (Fig. 2) that $p_{\text{inf}}$ and $p_{\text{eff}}$ have somewhat similar behaviour as a function of LAI. However, the form of the dependency is slightly different to an exponential (Eq. (6) and Fig. 2b) and neither $p_{\text{inf}}$ nor $p_{\text{eff}}$ tend quite to 1.0, even for high LAI.

As well as recognising that recollision probability varies as a function of scattering order, the observation that multiple nesting of the scattering Eq. (4b) gives a slightly different dependency on LAI to that observed in reality shows the scattering equation to be only an approximation of true canopy scattering behaviour. However, there is growing evidence that this is a useful description of overall scattering in a canopy and that it can provide insights into the information that can be retrieved from remote sensing data (Huang et al., 2007).
3. Shoot scattering

Smolander and Stenberg (2005) consider the case of scattering from the shoot to the canopy scale in conifers. They demonstrate in their Eqs. (3a)–(3c) that an equivalent expression to that of Eq. (4b) can be used to describe the scattering relative to radiation that intercepts the shoot, \( W_{sh} \), through the use of a shoot recollision probability, \( p_{sh} \):

\[
W_{sh} = \frac{(1-p_{sh})\omega}{1-p_{sh}\omega}
\]

(8)

where \( \omega \) is taken to represent the scattering at the needle scale.

The nesting of shoot scattering within a canopy can then be given through:

\[
W = \frac{(1-p_{cc})\omega}{1-p_{cc}\omega}
\]

(9a)

where \( p_{cc} \) is the recollision probability of the clumped shoot canopy:

\[
p_{cc} = p_{sh} + (1-p_{sh})p_{canopy}
\]

(9b)

and \( p_{canopy} \) is the recollision probability of an equivalent canopy comprising planar leaves (\( p_{eff} \) in Fig. 2) in place of shoots. \( p_{sh} \) is calculated from the ratio of mean projected silhouette to total area (STAR), being of the order of 0.47 for Scots pine shoots (Smolander & Stenberg, 2005).

If successive scales of geometric organisation can be represented by the Neumann series of the form of Eqs. (4a) and (4b), then Eqs. (9a) and (9b) gives us information on how radiation scattering and absorption translate across these scales. Shoot clumping is seen to reduce the apparent LAI (i.e. the LAI that would be inferred from \( p_{cc} \)) as might be expected (Pinty et al., 2004b; Rochdi et al., 2004).

4. Leaf scattering

The discussion above has demonstrated how a consideration of canopy scattering in terms of spectral invariants can describe fundamental scaling properties in canopy scattering (and therefore absorption) from the leaf to canopy scale, at least for the cases considered above (a single type of scattering object in a structurally homogeneous medium). In this section, we will consider the application of these concepts to within-leaf scattering, i.e. relating leaf biochemical constituents to leaf single scattering albedo (hence canopy scattering).

We take as the basis of this work the PROSPECT leaf scattering model of Jacquemoud and Baret (1990), modified in the work of Jacquemoud et al. (1996). PROSPECT is a solar spectrum plate model of radiative transfer within a leaf. Leaf single scattering albedo is calculated as a function of leaf cell–air interface refractive index (\( n \)), the number of leaf layers, \( N \), and absorption coefficient \( A \). \( A \) is related to the concentration \( C_i \) (units of mass per unit leaf area) of \( m \) biochemical constituents through:

\[
A = \sum_{i=1}^{m} C_i k_i(\lambda)
\]

(10)

where \( k_i(\lambda) \) is the specific absorption coefficient of the \( i \)th constituent, a function of wavelength \( \lambda \). Fig. 3 shows \( k_i(\lambda) \) as a function of wavelength for chlorophyll, water and leaf dry matter. These specific absorption coefficients are used for later PROSPECT simulations. Fig. 4 shows the impact on leaf single scattering albedo of varying \( n \) and \( N \) over the ranges 1.27 to 1.52 and 1.0 to 2.5 respectively, the typical range of variation of these parameters. The impact of \( N \) on leaf single scattering albedo is seen to be rather small, this term being mostly responsible for affecting the ratio of leaf reflectance to transmittance. The impact of refractive index \( n \) is somewhat higher, particularly for low absorption coefficients.

A portion of the scattering from a leaf, as modelled by PROSPECT, comes from an interaction with the leaf surface only (i.e. it does not interact with internal leaf biochemical constituents). We term this quantity \( \omega_{ss} \), since it can be considered as the scattering for infinite (internal leaf) absorption. We can define a transformed leaf single scattering...
albedo, $\omega'$ which is the probability of being scattered from the leaf given that it interacts with internal leaf constituents:

$$\omega' = \frac{\omega - \omega_\infty}{1 - \omega_\infty} \quad (11)$$

Fig. 5a shows the variation of $\omega_\infty$ with leaf refractive index, $n$. This can be very accurately modelled (RMSE $2.37 \times 10^{-3}$, $r^2=0.998$) through the quadratic (shown as symbols in Fig. 5a):

$$\omega_\infty = -0.0492 - 0.00618 n + 0.04836 n^2 \quad (12)$$

An examination of the PROSPECT model behaviour (and consideration of the form of Eqs. (4a), (4b) and (11)) suggests that it can be very closely approximated by the equation:

$$\frac{(\omega - \omega_\infty)}{(1 - \omega_\infty)} = \frac{(1 - p_{\text{leaf}}) W_{\text{leaf}}}{1 - p_{\text{leaf}} W_{\text{leaf}}} \quad (13a)$$

where:

$$W_{\text{leaf}} = \exp(-aA) \quad (13b)$$

$A$ is given by Eq. (10) and $a$ has a dependency on refractive index (Fig. 5b) that can be modelled by the quadratic (RMSE $5.06 \times 10^{-5}$, $r^2=0.9999$):

$$a = 1.3168 - 0.02294 n + 0.01299 n^2 \quad (13c)$$

Since $n$ is a function of wavelength, we can define new specific absorption coefficients $k'(\lambda) = a(\lambda) k(\lambda)$, so that:

$$A' = \sum_{i=m}^{i=m} \frac{C_i k'_i(\lambda)}{1 - A'} \quad (14a)$$

$$W_{\text{leaf}} = \exp(-A') \quad (14b)$$

Fig. 5c shows the variation in $p_{\text{leaf}}$ (Eq. (13a), given in the figure as $p$) with $n$. This can be described by (RMSE $8.95 \times 10^{-4}$, $r^2=0.9999$):

$$p_{\text{leaf}} = -1.2523 + 2.2307 n - 0.6094 n^2 \quad (15)$$

The term $p_{\text{leaf}}$ term plays the role of an ‘equivalent’ recollision probability within the leaf. This is analogous to the effective recollision probability $p_{\text{canopy}}$ defined by Smolander and Stenberg (2005) at the canopy level. Whilst the $p_{\text{leaf}}$ term varies significantly between around 0.60 and 0.73 over the refractive index range of interest across the solar spectrum (Fig. 5c), the impact of assuming it to be constant is seen to be relatively small. Fig. 6 demonstrates the impact of assuming $n$ to be constant in the approximation to PROSPECT developed here: $n$ is set to 1.39, the refractive index of a mid-range solar spectrum wavelength and the value that gives a minimum error for simulations at other refractive indices. This gives $p_{\text{leaf}}=0.6708$ and $\omega_\infty=0.03566$ from Eqs. (15) and (12) respectively. The RMSE introduced into leaf single scattering albedo by assuming $n$ to be any particular fixed value in the range of interest rather than being a function of wavelength ranges from 0.010 if $n$ is...
fixed to a value of 1.39 to 0.021 for $n$ fixed to 1.27 (0.020 for $n=1.52$). In line with Fig. 4, the maximum error occurs at low values of absorptance, being up to 0.045 in magnitude, but generally much less than 0.02.

Fig. 7 shows the impact of the approximations in the model developed here (Eqs. (10)–(15)) compared to the full PROSPECT model for a range of concentrations of different absorbing constituents. Goodness of fit metrics for Fig. 7 are shown in Table 1. A very high degree of correlation is seen between the PROSPECT-modelled spectra and those arrived at by the approximation ($r^2 > 0.9997$ in all cases). The RMSE due to the approximate representation is always less than 0.0042 (and in most cases is much smaller than this), with a maximum error of 0.013. The additional assumption of constant $n$ (i.e. constant $p_{\text{leaf}}$ and $\omega_{\infty}$) results in RMSE values of up to 0.016 ($r^2 > 0.995$ in all cases), with a maximum error of 0.049. Whilst these latter errors are somewhat higher than for the case of varying $n$, they are only significantly so for low absorptance values. Consequently, even the approximation of fixing $n$ is seen to produce very good representations of leaf single scattering albedo.

5. Nesting of leaf scattering in a canopy

We have seen that a good approximation to the scattering of radiation at optical wavelengths can be achieved through the use of a constant canopy spectral invariant, the recollision probability, at least for the canopy structures considered here. Such a parameter can be used to express the major impacts of multiple scattering at a variety of spatial scales (shoot to canopy), via a compound recollision probability, again, at least for the cases considered in this paper. We have shown here

<table>
<thead>
<tr>
<th>Relative constituent concentration</th>
<th>RMSE</th>
<th>Max. error</th>
<th>$\lambda_{\text{max error}}$ (nm)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed $n$ 0.5</td>
<td>0.001463</td>
<td>0.0125</td>
<td>685</td>
<td>0.99996</td>
</tr>
<tr>
<td></td>
<td>0.016370</td>
<td>0.0485</td>
<td>2400</td>
<td>0.99455</td>
</tr>
<tr>
<td>Fixed $n$ 1.0</td>
<td>0.002578</td>
<td>0.0132</td>
<td>2400</td>
<td>0.99991</td>
</tr>
<tr>
<td></td>
<td>0.015596</td>
<td>0.0468</td>
<td>2338</td>
<td>0.99686</td>
</tr>
<tr>
<td>Fixed $n$ 2.0</td>
<td>0.003676</td>
<td>0.0134</td>
<td>2274</td>
<td>0.99886</td>
</tr>
<tr>
<td></td>
<td>0.012027</td>
<td>0.0413</td>
<td>2234</td>
<td>0.99850</td>
</tr>
<tr>
<td>Fixed $n$ 10.0</td>
<td>0.004151</td>
<td>0.0127</td>
<td>1378</td>
<td>0.99974</td>
</tr>
<tr>
<td></td>
<td>0.010059</td>
<td>0.0208</td>
<td>1664</td>
<td>0.99852</td>
</tr>
</tbody>
</table>

* Relative to the values shown in the upper right panel of Fig. 7.
through an approximation to the PROSPECT model that leaf
scattering that interacts with internal biochemical constituents
can also be represented in the same way by a Neumann series.

Whilst the terms in this series are seen to vary as a function of
wavelength, a reasonable approximation can be found by setting
\( p_{\text{leaf}} \) and \( \omega_{sc} \) constant in Eq. (13a). If we ignore the impact of
radiation that interacts only with the leaf surface for the present
(i.e. assume \( \omega_{sc} \) to be zero), we can see that the scaling Eqs. (9a)
and (9b) applies to all scales from internal scattering within the
leaf through to the canopy. The overall recollision probability is
then given by:

\[
 p' = (p_{\text{sh}} + (1-p_{\text{sh}})p_{\text{canopy}})(1-p_{\text{leaf}}) + p_{\text{leaf}} \tag{16a}
\]

and total canopy scattering \( W \) is represented by:

\[
 W = \frac{(1-p')\exp\left(\sum_{i=1}^{m} C_i k_i'(\lambda)\right)}{1-p'\exp\left(\sum_{i=1}^{m} C_i k_i'(\lambda)\right)} \tag{16b}
\]

This equation can be rearranged to give:

\[
 \sum_{i=1}^{m} C_i k_i'(\lambda) = -\ln\left[\frac{W}{1-p'(1-W)}\right] \tag{16c}
\]

which provides a transformation between a measurable spectral
canopy property \( W \) and a linear summation of leaf bio-
chemical constituents. The effective ‘scaling’ parameter be-
tween leaf and canopy is \( p' \), with the nesting of the various
spatial scales of organisation given by Eq. (16a).

Eqs. (16a)–(16c) are particularly interesting for the remote
sensing problem of estimating canopy parameters from
radiometric data, even in this limited case of considering total
scattering from a canopy. Eq. (16c) demonstrates that \( W \) contains
information on (is a function of) both the (nested) canopy structure
and the leaf biochemical concentrations. If one of these
terms is known, the other can be readily calculated, but since the
recollision probability must be considered an effective value, it
cannot be directly measured: rather, it must generally be inferred
from some radiometric measurement assuming knowledge of
leaf biochemistry or leaf single scattering albedo. There have
been several attempts at this, summarised in Huang et al. (2007),
whereby a measurement of mean leaf single scattering albedo is
used e.g. with a measurement of canopy spectral transmittance to
infer \( p \). However, leaf reflectance can vary significantly over a
canopy. For conifer canopies for example, there are variations
with leaf age (e.g. Middleton & Walter-Shea, 1995) as well as
other factors that lead to vertical gradients of leaf biochemistry
(e.g. Ford & Newbould, 1971). There is therefore some
significant difficulty in defining a (weighted) mean needle
scattering spectrum for use in such an inference, but the
dependence of the derived recollision probability on this has not
yet been investigated.

Many studies that have attempted to simultaneously infer
leaf biochemistry (e.g. leaf chlorophyll) and canopy structural
parameters (expressed here through \( p \)) have run into the
difficulty that there appears to be a relatively strong coupling
between the quantity of leaf biochemical constituents (per unit
leaf area) and vegetation amount/cover (structure) (e.g.
Jacquemoud et al., 1995). Some attempt to get around this
issue has been made e.g. by using multi-angular datasets (e.g.
Barnsley et al., 2000); by constraining the canopy LAI or other
parameters through some form of prior knowledge/ancillary
information (e.g. Combal et al., 2002); by simply fixing
parameters to assumed ‘reasonable’ values (e.g. Jacquemoud et al.,
1995); or by attempting to derive the total canopy con-
centration of biochemical constituents (i.e. the product of LAI
and concentration per unit leaf area \( \text{ibid} \)).

Given that a reasonably accurate representation of leaf-
scatter has been developed above, we can use this model to elucidate the nature of this coupling in a simple and
general form. We start by noting that according to Eqs. (14a)
and (14b), any change in the quantity of absorbing leaf
biochemical constituents by a factor \( k \) will be manifested as
simply raising \( W_{\text{leaf}} \) to the \( k \)th power, i.e.:

\[
 A'' = k A' = k \sum_{i=1}^{m} C_i k_i'(\lambda) \tag{17a}
\]

\[
 W_{\text{leaf}}'' = \exp(-A'') = \exp(-k A') = W_{\text{leaf}}^k \tag{17b}
\]

Fig. 8 shows a variable \( x \) over the range \([0,1]\) raised to the
\( k \)th power, along with approximations to this function using a
Neumann series, i.e.:

\[
 W_{\text{leaf}}^k \approx \frac{(1-p(k)) W_{\text{leaf}}}{1-p(k) W_{\text{leaf}}} \tag{18}
\]

where \( p(k) \) is found to be approximately \( 1-k^{-1.313} \). Although
this is not precise over its whole range, the functional
approximation demonstrates that a large proportion of the
variation in \( W_{\text{leaf}}^k \) due to an increase in biochemical constituent
concentration by a factor \( k \) can be explained by the same nesting
equation that was seen to operate at the leaf, shoot, and canopy
levels. If we approximate \( W_{\text{leaf}}^k \) by Eq. (18) and insert this into
the leaf-canopy scaling Eq. (16b), we can see that a modulation
of the leaf biochemical concentrations can be reasonably
approximated as a modification to the recollision probability, where the nested total recollision probability \( p''' \) becomes:

\[
p''' = (p'' + (1-p'')p(k))
\]

To examine the nature of the coupling between LAI and leaf biochemistry concentration, we consider a structurally homogeneous canopy, the recollision probability for which we assume can be expressed as a function of LAI via Eq. (6). Taking

the approximation of \( p(k) \) given above, we obtain the compound probability as:

\[
p_{\text{canopy}} = 1 - k^{-1.313} \left[ 1 - 0.88(1 - \exp(-0.7 \text{LAI}^{0.75})) \right]
\]

From this we can infer that the impact on scattering of increasing LAI by some factor \( k \) and decreasing the biochemical concentration per unit leaf area by the same factor (i.e. keeping the total canopy concentration the same) is not negligible. For
$k=1$ and LAI=1 for example, $p$ is 0.443 but for $k=2$ and LAI=0.5, $p$ is 0.72.

Perhaps more fundamentally, Eqs. (19) and (20) suggests that it is simply not possible to derive robust estimates of both leaf biochemical concentration and structural parameters such as LAI from (hyperspectral) data of the sort considered here, no matter how narrow the wavebands or how many wavebands there are. The ability to achieve this decoupling of structure and biochemistry (from total canopy scattering at least) relies entirely on the residuals from the approximation shown in Fig. 8, which are only a small proportion of the variation.

To demonstrate this, we use Monte Carlo ray tracing to simulate a set of canopy scattering spectra for the same range of leaf biochemical concentrations used in Fig. 7, for an idealised disk canopy of the type described above (Section 2), for a range of LAI values (1 to 10 in steps of 1). We then attempt to infer the recollision probability $p$ of the canopy through assumed knowledge of the leaf single scattering albedo via inversion of Eq. (4b). To demonstrate the structure-biochemistry coupling, the leaf spectrum is assumed to be that shown in the top right panel of Fig. 7 for all cases. The values of $p$ retrieved by fitting Eq. (4b) are then equivalent values that incorporate the canopy structural impacts (LAI variation here) and $p(k)$ from Eq. (18).

Fig. 9(a–c) presents ‘full’ simulations of canopy spectra over the range 400 to 2400 nm (i.e. those performed with the Monte Carlo modelling with the leaf scattering represented by the PROSPECT model) for canopy LAI values of 1, 5 and 10 respectively, along with spectra reconstructed assuming canopy scattering to be represented by Eq. (4b). The four sub-panels show canopy spectra simulated with each of the four leaf scattering parameterisations of Fig. 7. The reconstructed spectra are seen to be very similar to the original spectra in all cases, although the representation becomes slightly poorer for high LAI. Goodness of fit metrics for Fig. 9a–c are shown in Table 2. The RMSE is always less than 0.011, although the maximum error at a particular wavelength can be as high as 0.054.

From this, we can infer that we can reasonably account for multiplicative variations in the concentration of leaf biochemical constituents through a recollision probability. What then does this tell us about canopy and leaf biochemistry coupling in a scattering signal? If we assumed that we knew the canopy LAI (or rather $p$ here) we could find a solution for the leaf biochemistry that would give a very good spectral fit, even if this assumed LAI were very different to the actual canopy LAI. Similarly, if we assumed we knew the leaf biochemistry (per unit leaf area), we could derive a viable estimate of $p$ (thence LAI).

<table>
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<th>LAI</th>
<th>Relative constituent concentration</th>
<th>RMSE</th>
<th>Max. error</th>
<th>$\lambda_{\text{max error}}$ (nm)</th>
<th>$r^2$</th>
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<tr>
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<td>735</td>
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</tbody>
</table>

* Relative to the values shown in the upper right panel of Fig. 7.
provided the relative concentrations of biochemical constituents were correct. If we were incorrect in our assumptions of leaf biochemistry, we would still get a good fit to the data, even if the inferred LAI (or \(k\times\text{LAI}\)) were incorrect. As noted above, one attempt to circumvent such coupling is to attempt to derive an estimate of the total biochemical concentration in the canopy, but this is still prone to very large uncertainty. Fig. 10 illustrates this. It shows the recollision probability calculated from Eq. (20) for LAI values ranging between 0.5 and 10.0 (\(\text{LAI}\)) of 1.0. It also shows the recollision probability for LAI values 0.25 to 5.0 for \(k=2\), i.e. the effective recollision probabilities when the biochemical concentration is doubled. The difference between the recollision probabilities for these two scenarios, which have the same total canopy concentrations, is very large, particularly at low to moderate concentrations/LAI.

These results illustrate the coupling between the structural and biochemical properties of the canopy, suggesting that without knowledge of either \(p\), or the leaf biochemical constituents, independent retrieval of either from total scattering measurements is not possible. It also illustrates that any attempt to estimate ‘total’ canopy biochemical concentration as a coupled measure may contain a large error. Although these results are only directly applicable to studies of total scattering from a homogeneous medium, they suggest that studies that examine relationships between canopy spectra and such quantities should pay careful attention to such errors. The work of Dash and Curran (2004) for example, develops relationships between a chlorophyll index and total canopy chlorophyll content for application to MERIS data, but assumes that total canopy concentration can be described by varying the chlorophyll per unit leaf area with a fixed LAI value of 1.0. The results presented in this paper suggest that such studies should at least further investigate the nature of such relationships for a wider range of LAI values if any relationship to total canopy concentrations is to be claimed.

6. Discussion and conclusions

The results and analyses presented in this paper apply only directly to total canopy scattering for leaves or shoots in a homogeneous canopy and we can make no direct inference about other components of canopy radiative transfer such as reflectance and transmittance. Further, we examine only the case of a canopy composed of a single ‘type’ of object. However, there is growing evidence that the approach of using spectral invariants is equally applicable to the examination of reflectance and transmittance, and that the approach lends itself to consideration of interactions between different types of elements. For example, Lewis et al. (2003) examine an approach to modelling interactions between canopy and soil in a 3D wheat canopy, and Disney et al. (2003, 2005) consider interactions between leaves, branches and ground in modelling reflectance from a 3D forest model. Although further studies are required in developing all aspects of a fuller solution directly applicable to modelling remote sensing measurements, this work indicates useful directions to explore in this regard. The reader is referred to Huang et al. (2007) for a wider synthesis of the current state of understanding in this field.

Despite these caveats, some interesting results are apparent that inform us about fundamental scaling relationships and couplings in the canopy radiation regime.

First, we provide further evidence to support the assertion that the impact of canopy structure on scattering can be accurately expressed through the use of a single recollision probability, even though Monte Carlo simulations show that the true recollision probability varies considerably as a function of scattering order. This analysis has however only investigated this for a structurally homogeneous canopy and within-leaf scattering. Further work is required to examine the generality of these findings for more structurally complex canopies. We have noted other work in this area (principally Smolander & Stenberg, 2005) that shows how these effective recollision probabilities are nested, the impact of multiple scales of scattering being expressed by a combined recollision probability. Because of this, it is not possible to decouple the recollision probabilities using a measurement of canopy scattering: only a single ‘effective’ value can be reliably retrieved.

Second, we apply the concept of canopy spectral invariance to describe scattering at the leaf-level. As an example of this approach, an approximation to the widely-used PROSPECT leaf model is developed by introducing the concept of within-leaf scattering recollision probability in the same way as that proposed at the shoot (Smolander & Stenberg, 2005) and canopy (Huang et al., 2007) scales. The resulting approximation to leaf single scattering albedo is a function of \(\omega_n\), \(p_{\text{leaf}}\) and specific absorption coefficients only, where: \(\omega_n\) is the single scattering albedo of a leaf of infinite internal absorption; and \(p_{\text{leaf}}\) is the effective leaf recollision probability. Both \(\omega_n\) and \(p_{\text{leaf}}\) are functions of wavelength through dependency on refractive index \(n\), but can be simply described by quadratic functions in \(n\). The impact of assuming \(n\) and \(p_{\text{leaf}}\) to be constant is shown to be rather small in practice. The resulting description provides a consistent framework for describing scattering from the leaf to the canopy scale, requiring the introduction of a new ‘effective’ recollision probability, \(p''\), relating \(p_{\text{leaf}}\), \(p_{\text{shoot}}\) and \(p_{\text{canopy}}\).
Third, we show that even though increasing the concentration of leaf biochemical constituents by some factor $k$ is more completely modelled by raising a fundamental scattering term to the power $k$, such a dependency is functionally similar enough to the Neumann series that the latter can be used to accurately model the former. Consequently, if canopy scattering is modelled assuming some leaf single scattering albedo that is the $k$th power of the ‘true’ leaf single scattering albedo (i.e. a leaf in which the relative concentrations of absorbing constituents is correct), this is very similar (Fig. 9) to the scattering of a canopy with different structural properties (a different $p$). The main consequence of this is that the absolute concentration (per unit leaf area or total for a canopy) of any biochemical constituents cannot be accurately derived from hyperspectral observations of total scattering, except where particular correlations between structure and biochemistry permit this.

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References


