Estimating foliage nitrogen concentration from HYMAP data using continuum removal analysis

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Abstract

The concentrations of various foliar chemicals can be estimated by analyzing the spectral reflectance of dried ground leaves. The continuum-removal analysis of Kokaly and Clark [*Remote Sens. Environ.* 67 (1999) 267] has been an improvement on the standard derivative analysis in such applications. Continuum-removal analysis enables the isolation of absorption features of interest, thus increasing the coefficients of determination and facilitating the identification of more sensible absorption features. The purpose of this study was to test Kokaly and Clark's methodology with aircraft-acquired hyperspectral data of eucalypt tree canopies, which are more complex than are spectra from many coniferous canopies and much more complex than the spectra from dried ground leaves. The results of the continuum-removal analysis were most encouraging. It identified, in one experiment or another, almost all of the known nitrogen absorption features. The coefficient of determination in one case increased from 0.65, using the standard derivative analysis, to 0.85 with the continuum-removal analysis. It is recommended that continuum-removal analysis become at least a supplement to standard derivative analysis in estimating foliar biochemical concentrations from remote sensing data. This study also reports several other findings: (1) the neural network method generally achieved higher coefficients of determination and lower errors of estimation [root mean square error (RMSE) and standard error of cross validation (SECV)] than did the modified partial least squares (PLS) or stepwise regression methods, probably indicating nonlinear relationships between biochemical concentrations and canopy reflectance; (2) modified partial least squares (MPLS) proved a better statistical method than conventional stepwise regression analysis in many cases in terms of both coefficient of determination and RMSE; and (3) the maximum spectrum of a cluster of tree pixels represents canopy reflectance at least as well as the mean spectrum of the cluster, especially when used in conjunction with the modified partial least squares method.
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1. Introduction

Chemical concentrations of foliage are important indicators of ecosystem processes. Research in the past decades has shown that remote sensing technology offers the only practical alternative to the complicated, slow and expensive chemical methods for estimating foliar chemical concentrations over large geographic areas (Curran, 1989). Studies have focused on using data collected by spectrometers that

can provide hundreds or thousands of bands within the visible to near-infrared wavelengths to aid the identification of the many subtle absorption features attributable to a wide range of chemicals. For example, Curran (1989) has listed 42 of these absorption features.

Among the many foliar chemicals, nitrogen is an important indicator of photosynthetic rate and overall nutritional status (Curran, 1989; Field & Mooney, 1986) and thus has been the subject of many spectrometric studies. These have been extended from measures on dried, ground leaves (e.g., Card et al., 1988; Dury et al., 2000; Dury & Turner, 2001; Grossman et al., 1996; Martin & Aber, 1990; McLellan et al., 1991; Peterson et al., 1988; Wessman et al., 1988a), to whole fresh leaves (e.g., Curran et al., 1992; Dury et al., 2000; Dury & Turner, 2001; Grossman et al., 1996; Johnson & Billow, 1996; Martin & Aber, 1990; Peterson et al., 1988;

Tsay et al., 1982; Yoder & Pettigrew-Crosby, 1995) and, most recently, studies of entire canopies (Curran et al., 1997; Dury & Jia, 2001; Dury et al., 2000; Johnson et al., 1994; LaCapra et al., 1996; Martin & Aber, 1997; Matson et al., 1994; Peterson et al., 1988; Wessman et al., 1988b; Yoder & Pettigrew-Crosby, 1995). It should be noted that except for our previous studies (Dury & Jia, 2001; Dury et al., 2000), all these studies depended on extracting reflectance spectra not from individual trees but either from averaging pixels of study plots (Johnson et al., 1994; Martin & Aber, 1997; Matson et al., 1994; Wessman et al., 1988b) or from measuring reflectance over homogeneous areas (Curran et al., 1997; LaCapra et al., 1996; Yoder & Pettigrew-Crosby, 1995; Zagolski et al., 1996). This is inappropriate for those interested in the chemical concentrations of individual trees. For example, eucalypts show considerable within-species variation in their concentrations of certain chemicals, which may in turn determine whether or not the foliage of an individual tree is eaten by different folivorous marsupials and invertebrate species (e.g., Wallis et al., 2002).

There are many complicating factors to consider when extending reflectance measurements from dried ground leaves to whole fresh leaves and to entire canopies. These include the masking effect of leaf water absorption bands in the infrared wavelengths, the complexity of canopy characteristics, variation in leaf internal structure, and atmospheric and background effects (e.g., Matson et al., 1994; Yoder & Pettigrew-Crosby, 1995). The canopy reflectance is thought to be a function of the optical properties of tissue (leaf, woody stem and standing litter), canopy biophysical attributes (e.g., leaf and stem area, leaf and stem orientation and foliage clumping), soil reflectance, illumination conditions and viewing geometry (Asner, 1998). Among these many factors, foliar chemicals contribute only a little to the leaf optical properties.

The signal received by a remote sensor above a tree is a complicated combination of the interactions between photons and atmosphere, canopy and background. Although we have limited control over canopy characteristics, we can still extract useful information from canopy reflectance by developing methods that reduce atmospheric and background effects. After trying a number of alternatives, we achieved satisfactory atmospheric correction using the Hycorr program, essentially the ATREM model (CSES, 1992; Gao & Goetz, 1990) modified to accept data collected by the HYMAP instrument. Several methods have been suggested to reduce background effects, including band ratios or difference indices, high order derivative analysis and statistical methods like partial and modified partial least squares (MPLS). Band ratios or vegetation indices, such as NDVI, are often used to estimate leaf chlorophyll concentration, because they can use the "red edge" effect to minimize background reflectance (e.g., Chappelle et al., 1992; Curran et al., 1990, 1991, 1995; Datt, 1998; Daughtry et al., 2000; Jago et al., 1999). These methods use only the red and near-infrared bands and so

are sensitive only to leaf pigments that have strong absorption differences at the two sides of the red edge. This limits the values of the technique for estimating the concentrations of many other chemicals, like those containing nitrogen, which has many absorption bands lying outside this region. Derivative analysis, according to some researchers (Dixit & Ram, 1985; Shah et al., 1990; Tsai & Philpot, 1998; Wessman, 1989), is less sensitive to illumination intensity and background effects and thus can be used to enhance subtle absorption features of foliar biochemicals and to resolve overlaying features. The first and the second derivatives and their approximations are usually combined with different smoothing transformations to estimate foliar chemical concentrations. The WinISI package (Infrasoft International, 2000) we used has a variety of "math treatment" functions to chose from. For example, a math treatment of "1,2,2,2" refers to using the first derivative, leaving a gap of two wavebands between calculated values, doing a first smoothing over two wavebands and then a second smoothing over two wavebands.

While conventional stepwise regression analysis is widely used in regressing reflectance measures against biochemical concentrations, its drawbacks are also well known (e.g., Curran, 1989; Grossman et al., 1996). In contrast, the partial least squares (PLS) regression method (Wold, 1982) works in a manner similar to principal components analysis. It combines the most useful information from hundreds of bands into the first several factors, while the less important factors may likely include background effects as suggested by Bolster et al. (1996). In this way, the PLS method reduces the effects of background and avoids the potential overfitting problem typically associated with stepwise regression analysis. Furthermore, different scattering effects due to the intersample differences, such as the additive offsets (baseline shifts) and the multiplicative effects (Datt, 1998) can be accounted for and corrected before any statistical models are used. This helps also to reduce the background effects. The WinISI package has "scatter correction" functions such as Standard Normal Variation (SNV), which reduces scattering effects caused by variable particle sizes, "detrending", which accounts for the variation in baseline shift and Multiplicative Scatter Correction (MSC), which attempts to remove the effect of scattering by linearising each spectrum to some "ideal" spectrum of the sample.

The above methods usually reduce background effects, but even after deriving a rather pure leaf spectrum, leaf water absorption and the overlapping of other chemical absorption features tend to mask subtle nitrogen absorption features. Clark and Roush (1984) suggested using continuum-removal analysis to remove those absorption features of no interest and thus to isolate individual absorption features of interest. The continuum is a convex "hull" of straight-line segments fitted over the top of a spectrum that connect local spectral maxima and represents the "background absorption" onto which other absorption features are super-

imposed (e.g., see Fig. 1). The local spectral maxima are determined according to each specific application. The continuum shown in Fig. 1 is only one of several possible continuums for the reflectance spectrum and is shown here for illustrative purpose. The continuum is removed by dividing the reflectance value for each point in the absorption feature by the reflectance level of the continuum line (convex hull) at the corresponding wavelength. Removing the continuum standardises isolated absorption features for comparison (Clark, 1999). For example, Fig. 2 is the continuum-removed spectrum derived from Fig. 1 using the ENVI image processing package (Research Systems Inc, 2000). This method was first used for mineral mapping (e.g., Clark, 1999; Clark et al., 1990; Clark & Swayze, 1995), and was then extended to vegetation mapping (Clark et al., 1995; Kokaly et al., 2003) and recently to the estimation of chemical concentrations in dried ground leaves (Curran et al., 2001; Kokaly, 2001; Kokaly & Clark, 1999).

Kokaly and Clark (1999) were the first to use the method in vegetation studies when they estimated nitrogen, lignin and cellulose concentrations in dried ground leaves from seven sites using stepwise regression analysis. For example, the R^2 values for nitrogen varied from 0.90 to 0.97 (numbers of samples varied from 31 to 193). In order to look at the influence of site, the data set was then calibrated with one site and validated with the others. Again, the results were very encouraging, which may indicate a potential for establishing an equation applicable to all sites. Kokaly (2001) further explored the physical basis of this kind of general equation for estimating nitrogen concentrations using continuum-removal analysis. Two absorption features centred at 2054 and 2172 nm were shown to be closely associated with nitrogen concentration. Later, the methodology was again tested by Curran et al. (2001), who compared standard derivative analysis and continuum-removal analysis. They found that the two transformations derived from continuum-removal analysis produced higher R^2 values than did standard derivative analysis on both a training set and a test set.
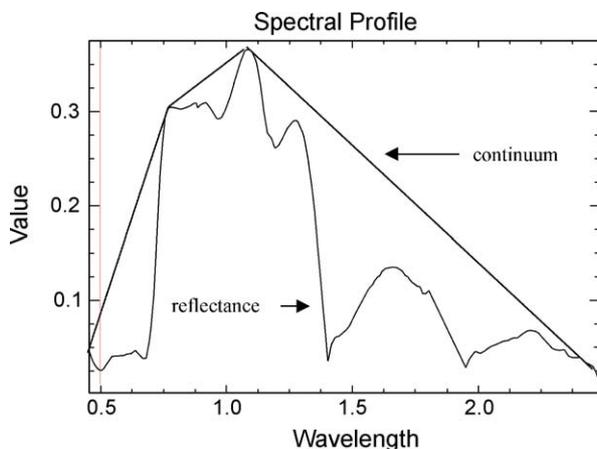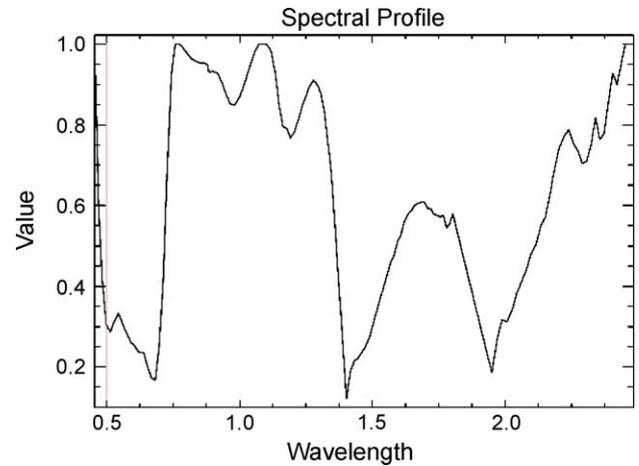

Fig. 2. A continuum removed tree reflectance spectrum.

In addition, the wavelengths selected by the stepwise regression methods were closely related to the known absorption features. Therefore, they concluded that estimating chemical concentrations by stepwise regression was more accurate when used with continuum-removed, band-normalized spectra, rather than standard First Derivative Spectra (FDS). Although continuum-removal analysis appears superior to standard derivative analysis in estimating chemical concentrations in dried leaves, Kokaly and Clark (1999) point out that interference from leaf water shall present the greatest challenge to extending the method to the analysis of fresh whole leaves and canopies. Curran et al. (2001) recommended that the Kokaly and Clark methodology be investigated for estimation of foliar biochemical concentration from airborne and spaceborne spectra, i.e., at the canopy level. Recently, Mutanga et al. (2003) showed that continuum-removal analysis could be used to better discriminate differences in foliar nitrogen concentrations in grass grown in the greenhouse with different fertilization treatments.

The aim of this study was to apply Kokaly and Clark's (1999) method to spectral data of the canopies of individual eucalypt trees and to compare the results with those obtained by applying standard derivative analysis to the same data set.

2. Methods

2.1. Data preparation

Leaf samples from the upper canopy of 60 *Eucalyptus melliodora* trees were collected in April 1999 in open woodland, approximately 20 km east of Canberra, Australia. Trees were selected to be on the flightline of the HYMAP mission and reasonably accessible for collecting foliage. All samples were of fully expanded adult foliage from the mid to upper canopy. Nitrogen concentrations were determined on freeze-dried leaves using the semimicro Kjeldahl technique. They ranged from 9.8 to 17.8 mg/g dry matter (DM)

Fig. 1. A tree reflectance spectrum and its continuum.

with a mean and standard deviation of 14.35 and 1.52 mg/g dry matter, respectively.

Airborne HYMAP data of the study area was obtained in April 1999, 1 or 2 days before the foliage was sampled. The HYMAP data originally comprises 128 wavebands (three corrupted bands were excluded later) in the wavelength range from 450 to 2500 nm. The spatial resolution of the HYMAP data was about 3 m, which is adequate to identify individual trees as most of the trees occupy several pixels on the image. Data processing occurred in several steps. The first of these was to convert the original Digital Number (DN) to radiance using the DN-to-radiance conversion factors that accompanied the HYMAP data (Integrated Spectronics, http://www.intspec.com). The next step of preprocessing was the atmospheric correction to convert the radiance to surface reflectance. In earlier work on the same data set, Dury et al. (2000) applied a flat field atmospheric correction method. The drawback of this method is that the apparent radiance cannot be converted to the real reflectance of canopy as it uses only data from the image itself. We tried to overcome this problem first by using a physical atmospheric model, 6S (Second Simulation of the Satellite Signal in the Solar Spectrum) (Vermote et al., 1997), to calibrate the atmospheric effects of the HYMAP data. However, derived vegetation spectra were of a different magnitude to that expected and were very noisy. This may be due to the difficulty of converting radiance to apparent reflectance or to the different canopy structures of eucalypts compared with Northern Hemisphere forest types at which the 6S model is aimed. We discarded the 6S model in preference for Hycorr, which is a version of ATREM (CSES, 1992; Gao & Goetz, 1990) for HYMAP data combined with an Empirical Flat Field Optimal Reflectance Transformation (EFFORT) procedure (Boardman, 1998). The resulting vegetation spectra were acceptable overall and the atmospheric effects, such as the atmospheric water vapor absorption, were largely removed. A typical mean reflectance spectrum (i.e., averaged spectrum of several tree pixels of a single tree, as detailed in the next section) for an *E. melliodora* tree canopy is compared with its corresponding laboratory reflectance in Fig. 3. The shape of the canopy spectrum is similar to that of the whole fresh leaf spectrum for most of the wavelengths. One apparent anomaly of the canopy spectrum is in the 750–950 nm region. This may be due to some peculiarity of eucalypt crown spectra or structure or to some idiosyncrasy of the correction procedure. We believe this should not affect the results much, as only one known nitrogen absorption feature falls in that spectral range (910 nm).

2.2. Extraction of tree spectra

With the 3-m spatial resolution of HYMAP data, a mature eucalypt tree usually occupies several pixels in the image. The HYMAP sensor receives reflectance from the vertical mixture of foreground canopy and the background.
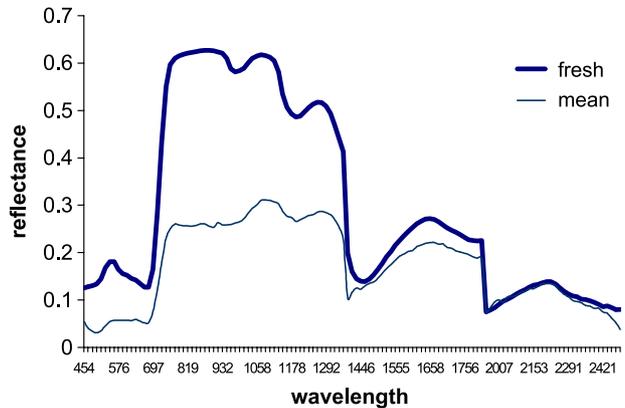

Fig. 3. Mean canopy spectrum and whole fresh leaf spectrum.

These background effects come from soil, understorey and shadow. We used the following procedure to minimize these effects and to extract the relatively pure tree spectra (canopy spectra) from the image. First, the 60 tree samples were individually located on the false color HYMAP image through a field inspection. Then tree pixels of each sample tree were carefully identified by separating them from the surrounding pixels. This is reasonably easy because the tree pixels are a different colour to the background in the false colour image. At least four tree pixels were extracted for each tree. Subsequently, we obtained both the mean and maximum spectrum of each tree by either averaging or deriving the maximum spectra of the chosen tree pixels.

2.3. Spectral transformation methods

In this comparative study, two spectral transformation methods were applied: standard derivatives and continuum removal. For the standard derivative analysis, which is widely used by researchers, the first or second derivatives of the reflectances are used in the analysis rather than the reflectances themselves.

The continuum removal employed in this study was calculated as the band depth normalized to the band depth at the centre of the absorption feature (BNC),

$$\text{BNC} = \frac{1 - (R/R_i)}{1 - (R_c/R_{ic})} \tag{1}$$

where R is the reflectance of the sample at the waveband of interest, R_i is the reflectance of the continuum line at the waveband of interest, R_c is the reflectance of the sample at the absorption feature centre and R_{ic} is the reflectance of the continuum line at the absorption feature centre. We used two approaches to extract continuum-removed spectra. The first was to select several wavelength ranges according to the known nitrogen absorption features, just as Kokaly and Clark (1999) and Curran et al. (2001) did. The five such wavelength ranges and known nitrogen absorption features in the band-ranges are shown in Table 1. They were determined by taking account of the locations of the local spectral maxima of a tree

spectrum and the known nitrogen absorption features so that most of the known nitrogen absorption features were included. Wavelengths considered to be known nitrogen absorption features are: 460, 640, 660, 910, 1020, 1510, 1980, 2060, 2130–2180, 2240, 2300 and 2350 nm (derived from Curran, 1989), and 1645 nm (from Murray & Williams, 1987). Among these nitrogen absorption features, 460, 640 and 660 nm are actually chlorophyll absorption features that are closely related to those of nitrogen; all others except 1645 nm are protein absorption features that are closely related to those of nitrogen. None of these absorption features is close to a known water absorption feature; thus, we believe we have avoided potential overlay problems. Because there are large differences in the canopy spectra of individual trees, the locations of band depth centres are not necessarily consistent for all trees (e.g., see Fig. 4). Therefore, we simply chose the location of the largest band depth as the band centre of each absorption feature (e.g., 1418 nm for tree 13 and 1460 nm for tree 3 in Fig. 4).

The second approach to extract continuum-removed spectra assumes that we do not know where the relevant nitrogen absorption features are located across the whole wavelength range. Thus, we applied continuum-removal analysis to the whole spectrum (i.e., from 454 to 2500 nm) of each sample. For example, Figs. 1 and 2 show an example of a tree reflectance spectrum and its continuum and the same spectrum with the continuum removed using the ENVI image processing package.

2.4. Statistical analysis

This study employed three statistical methods for developing models for estimating nitrogen concentrations from the tree spectra, namely the stepwise regression, the modified partial least squares (MPLS), and the artificial neural network methods. All three were implemented through the WinISI package. Since there are limited samples, we did not use independent test samples to measure the effectiveness of the models but used a cross-validation method, which is performed by dividing each sample population into groups. For example, if the population is divided into four groups, prediction occurs on every fourth sample with the calibration developed from the remaining three (Infrasoft International, 2000). The method, sometimes known as "leaving one out" (Duda & Hart, 1973), has been used in similar
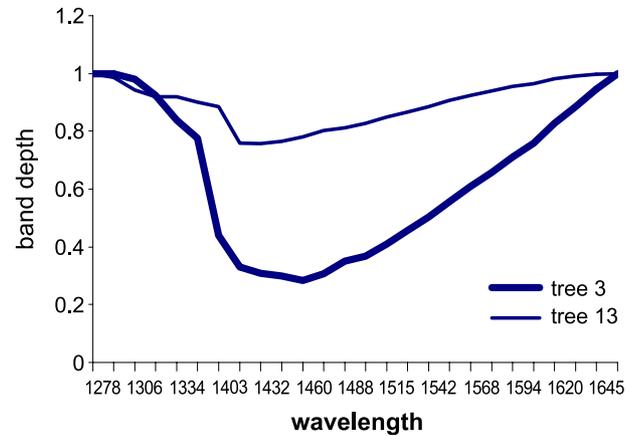

Fig. 4. An example of intertree difference of the continuum-removed spectra.

studies (e.g., LaCapra et al., 1996; Martin & Aber, 1997). The statistical results were assessed in terms of coefficient of determination (R^2), Standard Error of Cross-Validation (SECV), Root Mean Square Error (RMSE) and the agreement between wavelengths identified as important by statistical analysis and known nitrogen absorption features. For all of the three statistical methods, the coefficient of determination (R^2) was calculated on the whole 60 samples using equations selected by the WinISI package. The best MPLS equation was chosen on the basis of the lowest SECV; the best neural network equation was chosen on the basis of the lowest Standard Error of Validation (SEV); the best stepwise regression equation was chosen on the basis of the parameters of maximum number of bands and F-value.

Stepwise regression analysis has been widely used to regress leaf chemistry against some transformations of leaf reflectance. For example, most of the studies mentioned above used this approach. But it is also well recognized that the stepwise regression method suffers from the potential of overfitting and the selection of bands that fail to correspond with known absorption bands (e.g., Curran, 1989). Furthermore, Grossman et al. (1996) also found that the R^2 values from stepwise linear regression were not significantly different from those obtained from a randomized baseline.

The MPLS method that we used previously (Dury & Jia, 2001; Dury et al., 2000; Dury & Turner, 2001) and which has been used in several other studies (e.g., Bolster et al., 1996; Zagolski et al., 1996) overcomes some of the difficulties found with stepwise regression. It does this by combining the most useful information from hundreds of bands into a limited numbers of components, similar to the principal components approach. This process largely avoids the potential overfitting problem while using as much information as possible. One problem with MPLS is that identifying predictive bands is not straightforward and one must use correlograms of reflectance and chemical concentration to help identify optimal bands.

Both the stepwise regression and MPLS methods are based on the assumption that linear relationships exist be-

Table 1
Preselected wavelength ranges and their associated absorption features for nitrogen

Selected wavelength ranges (nm)	Known nitrogen absorption features (nm)
583–750	640, 660
910–1081	910, 1020
1270–1666	1510, 1645
1796–2214	1980, 2060, 2130–2180
2230–2415	2240, 2300, 2350

tween biochemical concentrations and some transformation of leaf reflectance. Since nonlinear relationships probably occur too, especially in canopy measurements, it seems appropriate to use nonlinear statistical models such as Artificial Neural Networks (ANNs). In this study, we applied a modified back-propagation neural network (Rumelhart et al., 1986). Instead of starting from randomized initial weights, the neural network uses a partial least squares (PLS) method to calculate the initial weights. This accelerates the running of the network and minimizes the instability problem, typical of neural networks. However, it is still a slow process to identify the best combinations of network parameters. To avoid overtraining, which may happen when there are too few test samples, at least 10 out of the 60 samples were set aside as a test set for each run.

3. Results

3.1. Results of the standard derivative analysis

Nitrogen concentration was estimated using the first and second derivative transformation of the $\log(1/R)$ spectra data. Almost all possible combinations of "math treatments", scatter correction methods and neural network parameters were tried to find optimal combinations for both the maximum and mean spectra. For the MPLS method, using the maximum spectra gave higher R^2 and lower SECV and RMSE (Table 2) than with the mean spectra. Fig. 5 is a correlogram for the nitrogen concentration from the maximum spectra using the same "math treatment" as the MPLS method (e.g., "1,2,2,2"), and many of the absorption features are known nitrogen absorption features (see Table 2). For example, 667 nm corresponds to a chlorophyll absorption feature that is closely related to nitrogen and 1501 nm is a typical protein and nitrogen absorption band corresponding to the N–H stretch, 1st overtone. The band at 1633 nm corresponds to the 1st overtone of N–H absorption and the 3rd overtone of $NH_3 + NH$ deformation (Murray & Williams, 1987), while that at 1988 nm is a protein
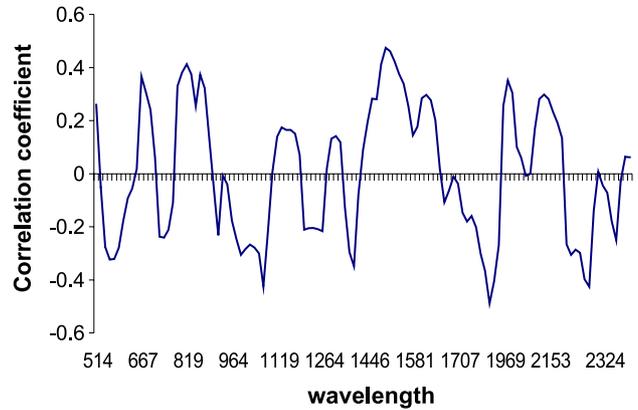

Fig. 5. Correlogram on the maximum spectra using the standard derivative analysis.

absorption band corresponding to N–H asymmetry. The area of 2135–2187 nm covers another typical protein and nitrogen absorption area, which corresponds to N–H stretch, and to N–H bend, 2nd overtone. Curran (1989) suggests that 2307 nm could be contributing to protein and nitrogen absorption also. Fig. 6 is the correlogram for the nitrogen concentration from the mean spectra (e.g., the math treatment is "2,1,1,1"). Among those absorption features identified in Table 2, 483 nm may be related to chlorophyll absorption, while 2170 nm falls in the absorption region mentioned previously for nitrogen.

We set the maximum number of independent variables (bands) in the models to six (default value recommended by WinISI), to prevent the stepwise regression method from potentially overfitting a model, and set the F-value for accepting a variable to seven for the same purpose. Five bands were selected from the mean spectra, which gave a model with a slightly higher R^2 and lower SECV and RMSE than did the six bands selected from the maximum spectra (Table 2). None of the wavelengths selected by using either the maximum or the mean spectra corresponds to the known nitrogen absorption features derived from Curran (1989). However, the 1645 nm wavelength selected by using the mean spectra does correspond to a nitrogen

Table 2
Results of the standard derivative analysis

Spectra applied	Statistical methods	Math treatment	Scatter correction	R^2	SECV	RMSE	Wavelengths selected (nm) using correlograms
Mean spectra	MPLS	2,1,1,1	Standard MSC	0.51	1.46	1.052	483[c], 529, 576, 682[c], 697, 774, 849, 879, 1043[c], 1058, 1264, 1320, 1334, 1803, 1950, 2170[a], 2223
	Stepwise regression	1,1,1,1	None	0.65	1.0	0.892	948, 1645[a], 1278, 880, 2223[b]
	Neural network	2,1,1,1	Inverse MSC	0.90	0.36	0.483	N/A
Maximum spectra	MPLS	1,2,2,2	SNV only	0.65	1.35	0.896	513, 560, 667[a], 819, 865, 1073, 1403, 1501[a], 1607–1633[a], 1791, 1988[a], 2135[a]–2187[a], 2307[a]
	Stepwise regression	1,2,1,2	SNV only	0.64	1.02	0.906	1163, 499, 865, 1670[c], 932[c], 2204[c]
	Neural network	1,1,2,2	Detrend only	0.94	0.46	0.387	N/A

[a] Within 12 nm of known absorption features.
[b] Within 20 nm of known absorption features.
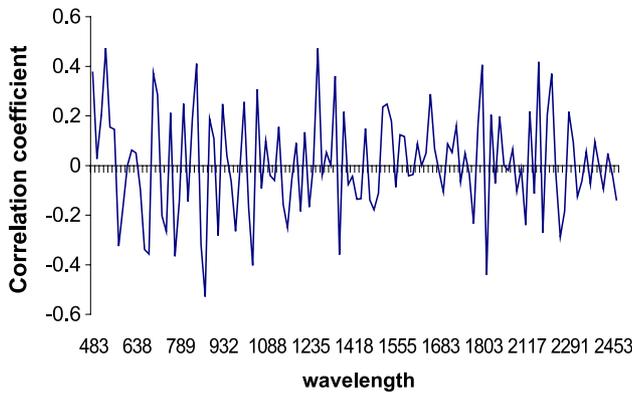[c] Within 25 nm of known absorption features.

Fig. 6. Correlogram on the mean spectra using the standard derivative analysis.
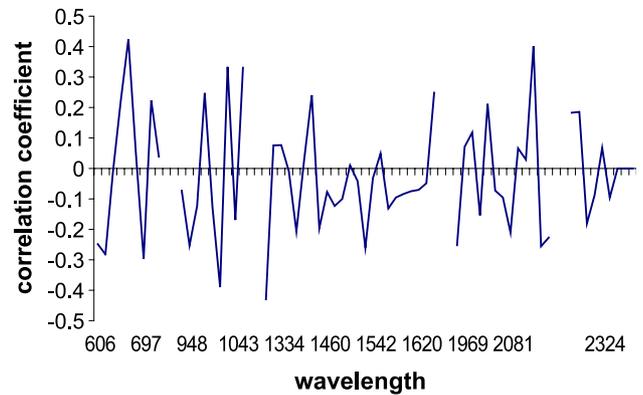

Fig. 7. Correlogram on the mean spectra of the preselected wavelength ranges using the continuum removal analysis of BNC.

absorption feature identified by Murray and Williams (1987).

Results from the back-propagation neural network produced much higher R^2 values and much lower SECVs and RMSEs than those from both the stepwise regression analysis and the MPLS method (Table 2). Similar results were obtained with both maximum and mean spectra.

3.2. Results of continuum removal analysis

3.2.1. Correlations between nitrogen concentrations and continuum-removed spectra from the five selected wavelength ranges

The correlations between the continuum-removed maximum spectra and nitrogen concentrations for either BNC or log(1/BNC) are very low and are not reported in this paper. The results for the continuum-removed mean spectra are listed in Table 3. Generally, using BNC yields higher R^2 values and a larger number of sensible bands selected than using log(1/BNC). Among the three different statistical methods, the neural network achieved the highest R^2 values, followed by the MPLS and then the stepwise regression. Both the correlogram and the stepwise regression method

identified some known nitrogen absorption features. For example, for the regression between BNC and nitrogen using MPLS, six out of 19 wavebands selected using the correlogram (Fig. 7) are within 12 nm of known nitrogen absorption features, another two are within 20 nm, while two others are within 25 nm. Moreover, the wavebands selected by stepwise regression for both BNC and log(1/BNC) were all from the last three wavelength ranges (i.e., short and medium wave infrared, see Table 1).

The neural network methods gave the lowest values of SECVs followed by the stepwise regression methods, and the MPLS methods produced the highest SECV values. In terms of RMSE, the neural network methods were superior to the MPLS methods which in turn were superior to the stepwise regression methods.

3.2.2. Correlations between continuum-removed spectra from the whole wavelength range and nitrogen concentrations

The results from analyses of both the continuum-removed mean and maximum spectra are shown in Table 4. In most cases for the continuum-removed mean spectra, untransformed BNC yielded higher R^2, lower SECVs and lower

Table 3

Results of correlations between continuum-removed mean spectra from the five selected wavelength ranges and nitrogen concentrations

Spectra applied	Spectral transformation	Statistical methods	Math treatment	Scatter correction	R^2	SECV	RMSE	Wavelengths selected (nm) using correlograms
Mean spectra	Band-normalized to centre (BNC)	MPLS	2,1,1,1	Detrend only	0.751	1.416	0.75	652[a], 697, 728, 932[c], 981, 1011[a], 1043[c], 1058, 1320, 1334, 1432, 1460, 1555, 1969[a], 1988[a], 2063[a], 2117[b], 2170[a], 2257[b] (Fig. 7)
		Stepwise regression	1,1,1,1	Standard MSC	0.603	1.087	0.948	1528[b], 1555, 1988[a], 2026, 2153[a], 2170[a]
		Neural network	1,1,1,1	Inverse MSC	0.839	0.6596	0.616	N/A
	log(1/BNC)	MPLS	2,1,1,1	Inverse MSC	0.667	1.453	0.869	932[c], 981–996[c], 1043[c], 1058, 1320, 1334, 1346, 1460, 1988[a], 2170[a], 2257[b], 2291[a]
		Stepwise regression	2,1,1,2	Standard MSC	0.606	1.074	0.948	1446, 1460, 1542, 1645[a], 2007, 2153[a]
		Neural network	1,1,1,1	Standard MSC	0.821	0.5674	0.616	N/A

[a] Within 12 nm of known absorption features.
[b] Within 20 nm of known absorption features.
[c] Within 25 nm of known absorption features.

Table 4
Results of correlations between continuum-removed spectra from the whole wavelength range and nitrogen concentrations

Spectra applied	Spectral transformation	Statistical methods	Math treatment	Scatter correction	R^2	SECV	RMSE	Wavelengths selected (nm) using correlograms
Mean spectra	Band-normalized to centre (BNC)	MPLS	2,1,1,1	None	0.505	1.355	1.059	529, 576, 652[a], 697, 728, 849, 880, 996[c], 1148, 1221, 1235, 1306, 1334, 1988[c], 2170[a], 2187[a], 2307[a]
		Stepwise regression	1,1,1,1	SNV and Detrend	0.663	0.991	0.873	545, 880, 918[a], 1607, 1645[a], 1950
		Neural network	1,1,1,1	Detrend only	0.851	0.5047	0.584	N/A
	log(1/BNC)	MPLS	2,1,1,1	Weighted MSC	0.487	1.488	1.078	529, 576, 697, 743, 849, 996[c], 1043[c], 1221, 1264, 1306, 1320, 1501[a], 1744, 1756, 1969[a], 1988[a], 2063[a], 2170[a], 2307[a]
		Stepwise regression	1,1,2,2	Standard MSC	0.627	1.023	0.919	1043[c], 1732, 1988[a], 2187[a], 2291[a], 2324[c]
		Neural network	1,1,1,1	SNV only	0.877	0.6701	0.587	N/A
Maximum spectra	Band-normalized to centre (BNC)	MPLS	2,1,1,1	Weighted MSC	0.677	1.524	0.856	529, 591, 667[a], 743, 834, 996[c], 1148, 1192, 1221, 1235, 1346, 1403, 1418, 1432, 1460, 1474, 1515[a], 1581, 1950, 2324[c]
		Stepwise regression	2,1,2,2	Inverse MSC	0.6	1.076	0.952	529, 682[c], 1306, 1515[a], 2044[b], 2324[c]
		Neural network	1,1,1,2	Standard MSC	0.856	0.6842	0.576	N/A
	log(1/BNC)	MPLS	2,1,1,1	Standard MSC	0.853	1.376	0.577	529, 591, 728, 898[a], 1043[c], 1221, 1306, 1320, 1346, 1403, 1418, 1432, 1474, 1515[a], 1645[a]
		Stepwise regression	2,1,1,1	Detrend only	0.624	1.044	0.922	1043[c], 1306, 1460, 1645[a], 1683, 1988[a]
		Neural network	2,1,1,1	Inverse MSC	0.863	0.5361	0.56	N/A

[a] Within 12 nm of known absorption features.
[b] Within 20 nm of known absorption features.
[c] Within 25 nm of known absorption features.

RMSEs than using log(1/BNC). One exception was that the neural network achieved a higher R^2 value when using log(1/BNC) than when using BNC. In terms of selecting known nitrogen absorption features, using log(1/BNC) resulted in the selection of more sensible bands than did using BNC. However, in contrast with the results of the correlations between continuum-removed mean spectra from the five preselected wavelength ranges and nitrogen concentrations (see Table 3), the MPLS method resulted in much lower R^2 values and higher RMSE values than when the stepwise regression and neural network techniques were used.

For the continuum-removed maximum spectra derived from the whole wavelength range and for all three statistical methods, using log(1/BNC) gave superior statistical results to the untransformed BNC in terms of R^2, SECV and RMSE. The high R^2 (0.85) obtained by regressing log(1/BNC) against nitrogen concentrations using the MPLS method is most encouraging. The results are superior, in terms of R^2, SECV and RMSE, to those from using continuum-removed mean spectra of the five preselected wavelength ranges. One drawback, however, is that the procedure selected fewer sensible bands than did the con-
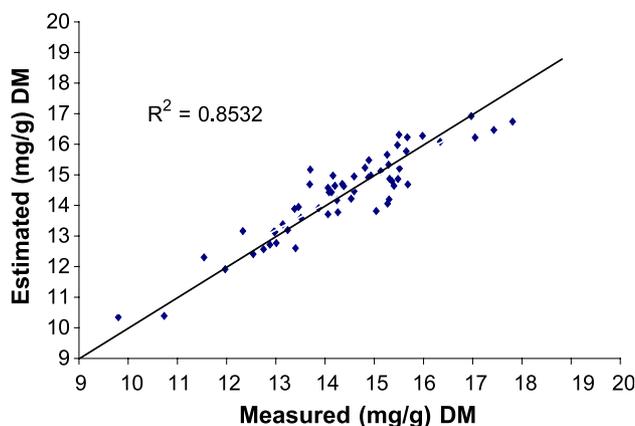

Fig. 8. Scatter plot using MPLS on the maximum spectra of the whole wavelength range using the continuum removal analysis of log(1/BNC).
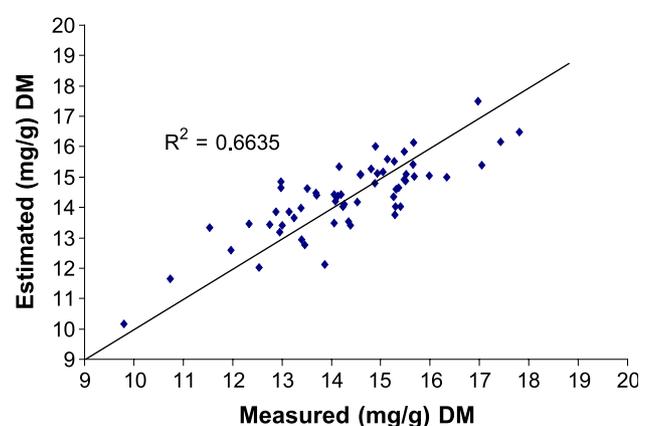

Fig. 9. Scatter plot using stepwise regression on the mean spectra of the whole wavelength range using the continuum removal analysis of BNC.
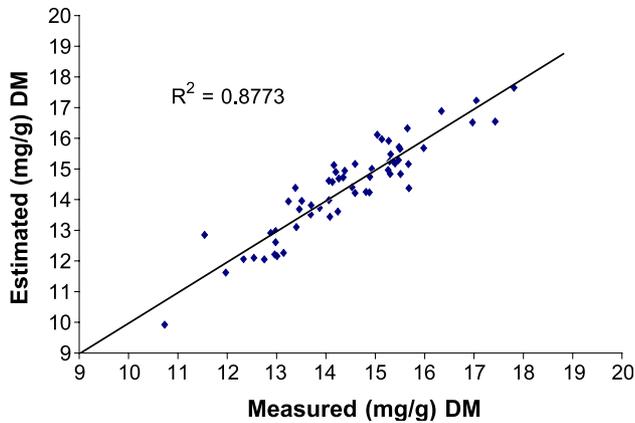
Fig. 10. Scatter plot using neural network on the mean spectra of the whole wavelength range using continuum removal analysis of log(1/BNC).

tinuum-removed mean spectra used in conjunction with the five preselected wavelength ranges.

3.2.3. Comparison of results

The three statistical methods gave maximum R^2 values and the lowest RMSEs in different circumstances. For the MPLS method, the highest R^2 (0.85) and the lowest RMSE (0.58) was obtained by using log(1/BNC) derived from the whole wavelength range of maximum spectra (see Fig. 8 for the scatter plot). For stepwise regression analysis, the highest R^2 (0.66) and the lowest RMSE (0.87) came from using BNC derived from the whole wavelength range of mean spectra (see Fig. 9 for the scatter plot). Using log(1/BNC) derived from the whole wavelength range of mean spectra gave the highest R^2 (0.88) for the neural network method (see Fig. 10 for the scatter plot), but the lowest RMSE (0.56) were obtained from using log(1/BNC) derived from the whole wavelength range of maximum spectra. In terms of selecting known nitrogen absorption features, using the continuum-removed mean spectra is better than using the continuum-removed maximum spectra for all three statistical methods.

4. Discussion

The high R^2 values and the large number of sensible bands selected make the results of this study most encouraging. This is especially true when using the MPLS method and its associated correlograms in conjunction with continuum-removed spectra rather than standard derivatives. For maximum spectra, continuum-removal analysis slightly increased the R^2 value from 0.65 to 0.68 using MPLS on BNC of the whole wavelength range. However, there was a noticeable increase to 0.85 when using log(1/BNC). For mean spectra, the continuum-removal analysis has increased the R^2 from 0.51 to 0.67 when using MPLS on log(1/BNC) and it is increased further to 0.75 using BNC. In addition, continuum removal enables correlograms to identify more known nitrogen absorption features using the mean spectra. The MPLS associated correlograms however, identified fewer known nitrogen absorption features using the continuum-removed maximum spectra. Moreover, although using continuum-removal analysis did not increase the resulting R^2 values for the stepwise regression method, it did identify more wavebands that are within 12 nm of the known nitrogen absorption features than the standard derivative analysis. This finding is in partial agreement with that of Curran et al. (2001).

Furthermore, although the neural network models are unable to identify sensible bands due to the nature of the method, they resulted in generally higher R^2 values than did either the MPLS or the stepwise regression methods. This implies that the relationship between chemical concentrations and reflectance measures may indeed be non-linear. The continuum-removal analysis did not improve the regression results of the neural network method. This may be explained by the fact that the resulting R^2 values are already very high, which leaves little room for further improvement.

Almost all of the known nitrogen absorption features, except the first (460 nm) and the last (2350 nm), were identified by at least one experiment of the continuum-removal analysis (Table 5). There are good explanations for the unrecognized absorption features. The 460 nm band falls on the lower limits of the HYMAP data and is effectively out of range, while the small signal to noise ratio at the tail of the MIR wavelength range probably explains why the 2350 nm absorption feature was missed. Other absorption features proved difficult to detect for a variety of reasons. For example, the difficulties in detecting the 910 and 2240 nm absorption features may be due to these bands responding strongly to the C–H stretch rather than the N–H stretch (Curran, 1989) and perhaps the anomalies between 750 and 950 nm. The analysis failed to identify the 1020 nm as a major nitrogen absorption feature but identified the 1043 nm band six times. This study detected nitrogen absorption features that other studies missed, for instance, that at 1645 nm. This was missed by Curran (1989) but the 1640

Table 5
Number of times the known nitrogen absorption features were identified using the continuum removal analysis (derived from Tables 3 and 4)

Known nitrogen absorption feature (nm)	460	640–660	910	1020	1510	1645	1980	2060	2130–2180	2240	2300	2350
Times identified in this study	0	3	2	1	4	3	10	2	9	2[a]	4	0

[a] Within 20nm of known absorption feature.

nm wavelength was described by Murray and Williams (1987) as representing both the 1st overtone of an N–H absorption and the 3rd overtone of a $NH_3 + NH$ deformation. This nitrogen absorption feature has been identified by the studies of Dury et al. (2000), Lacaze and Joffre (1994), Martin and Aber (1997) and Yoder and Pettigrew-Crosby (1995).

Another important finding in this study concerning absorption features is the prominence of two features at 1980 nm and in the range from 2130–2180 nm. This suggests that it may be possible to establish a general equation to estimate nitrogen concentrations using these two absorption features. If so, this can alleviate the over-fitting problem common to stepwise regression.

This study showed that continuum-removal analysis has the potential to improve the estimation of nitrogen concentrations in remotely sensed tree canopies. Apart from showing better modeling performance than standard derivative analysis, our study identified several other advantages of continuum-removal analysis of canopy data. First, it gives high coefficients of determination (and consequently lower RMSEs) with MPLS. Second it allows the identification of more known nitrogen absorption features using stepwise regression analysis. Third, it provides the potential for establishing a general equation for nitrogen based on the commonly identified absorption features such as the 1980 nm wavelength and the 2130–2180 nm area.

The results of this study were inconclusive as to whether the use of maximum spectra is superior to mean spectra. However, using maximum spectra did give lower RMSE results than using mean spectra when used with the MPLS method. This held true both for the standard derivative analysis and the continuum-removal analysis. We believe deriving maximum spectra may be most useful when estimating biochemical concentrations in canopies of individual trees where large illumination differences exist within a canopy because, under these conditions, the maximum spectrum better represents the canopy spectrum.

Of the three statistical methods, the neural network approach is clearly most satisfactory in terms of R^2, SECV and RMSE. Although there are theoretical advantages of using MPLS over stepwise regression, the results of this study were inconsistent. The stepwise regression approach appears to be able to give quite stable results while the results of the MPLS methods vary greatly.

The confounding factor of interference by leaf water remains a problem when remotely sensing canopies, but it is a difficulty that afflicts all methods and not just continuum-removal analysis. On the contrary, if leaf water absorption is the major source of confusion, then this study suggests that continuum-removal analysis is less sensitive to the problem than is standard derivative analysis.

This was the first attempt to measure the concentrations of foliar biochemicals of a natural stand of eucalypts with airborne hyperspectral remote sensing. The success of this research prompts further work with larger sample sets and more complex canopies, especially those containing a mixture of species.

5. Conclusion

In this study, we demonstrated the potential of using continuum-removal analysis to estimate nitrogen concentrations in the canopies of individual eucalypts trees. The method produced higher coefficients of determination and lower RMSE and identified more sensible bands than did the standard derivative analysis. These encouraging results are not unexpected, because continuum-removal analysis is able to remove irrelevant background reflectance and to isolate and enhance absorption features of interest. In summary, continuum removal based regression analysis appears able to detect more useful causal relationships between chemical absorption and leaf reflectance and to aid the interpretation of the relationship. We suggest that continuum-removal analysis is an effective method for the estimation of chemical concentrations in leaves from remote sensing data. Therefore, it should be considered at least as a supplement to standard derivative analysis at this stage. Most research, however, is needed to give a conclusive result.

Acknowledgements

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