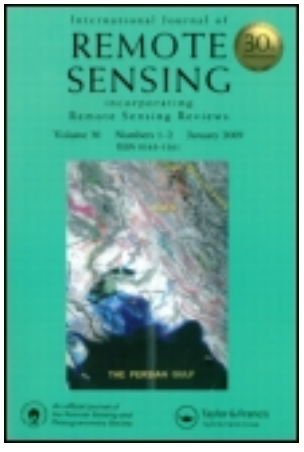

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A reflectance spectra model for copper-stressed leaves: advances in the PROSPECT model through addition of the specific absorption coefficients of the copper ion

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A reflectance spectra model for copper-stressed leaves: advances in the PROSPECT model through addition of the specific absorption coefficients of the copper ion

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This study intended to investigate the reflectance model for a crop stressed by the heavy metal copper. Forty-six groups of copper-treated leaves were measured in a laboratory experiment. Through these measurements, we obtained leaf reflectance spectra from 400 to 2500 nm, information on the biochemical components of leaves, and their corresponding scanning electron microscopy images. We then developed a new reflectance spectral model based on the classic broadleaf radiative transfer model – PROSPECT. Compared with the PROSPECT model, the new model primarily considers the addition of the specific absorption coefficient of the copper ion. The scattering process is described by a refractive index (n) and a leaf structure parameter (N). The absorption is modelled with pigment concentration, water content, dry matter content, copper ion contamination, and the corresponding specific spectral absorption coefficients (K_{ab}, K_w, K_d, and K_{cu}). Thus, reflectance spectral modelling is an inversion procedure to calculate the above six parameters accurately. For model validation, 16 leaves from the laboratory experiment were used. The validation showed that the inversion values for K_{cu} agree very well with the published absorption spectra of cupric chloride solutions. The linear regression analysis between the simulated and measured reflectance values provides a correlation coefficient of approximately 0.9441, and the root-mean-square error was less than 0.1 from 400 to 2500 nm.

1. Introduction

Currently, monitoring of heavy metal pollution primarily adopts traditional geochemical methods. Practice proves that this method is time consuming, has low efficiency, and is unsuitable for large-scale monitoring. Meanwhile, vegetation monitoring methods based on remote-sensing techniques have become powerful tools for monitoring heavy metal pollution; these methods have the advantages of wide vision, large capacity for information, and rapid dynamic monitoring (Li 2007). This remote monitoring method selects plants growing in heavy metal-contaminated environments as the primary research objects. This choice is because the status of plant growth and development is an important index of ecosystem pollution and heavy metal-stressed vegetation will present changes in the internal structure and spectral properties of the leaves (Liu, Gan, and Wang 2004). Research shows that the foliar structural changes of Zn-treated plants include a significant

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reduction in the number of chloroplasts, decreases in the cellular size and intercellular spaces, an irregular outline of epidermal cells, and gradual changes in the leaf structure with increases in metal concentration (Sridhar et al. 2007). Through the spectral variation index and correlation coefficient, Qu Ying described the relationship between spectral changes of copper-stressed leaves and metal concentration (Qu, Liu, and Li 2012). Current spectral models for heavy metal-stressed leaves were mainly established with empirical and semi-empirical statistical methods. These methods use multiple linear stepwise regression analysis to select characterized bands that are closely related to heavy metal content; then, the methods establish regression equations to assess the heavy metal content (Ding, Li, and Qian 2004). Although the method is simple and flexible, it cannot be used to develop a general model because the model parameters need to be redefined for different data sources (Ding, Li, and Qian 2004).

This study initiates a discussion regarding the physiological, biochemical, and structural properties of copper-stressed leaves. The focus of our research is to develop a new reflectance spectral model with data from reflectance spectra of copper-treated leaves. This radiative transfer model is used to forward-simulate the reflectance spectra of copper-stressed leaves from 400 to 2500 nm and to determine the concentrations of biochemical components and heavy metals in leaves. The model considers the physical interaction mechanism between the light and leaves as well as leaf internal structure. Thus, the model has clear physical significance and can be widely used as a general model.

2. Data sets

Wheat and lettuce were selected to be the experimental subjects in the laboratory experiments on copper treatment. The seeds were sown in impermeable plastic pots, which each contained approximately 10 kg of potting mix. The plants were kept outdoors in an enclosed area. Distilled water was supplied to the plants daily. To simulate heavy metal copper contamination in the soil, the soil was treated with copper sulphate solutions. Ten treatments were designed, and each treatment was tested three times in parallel. The copper treatments included a control group and 25, 50, 100, 200, 400, 800, 1600, 3200, and 4800 mg kg^{-1}.

Forty-six groups of copper-treated leaves were measured at four regular periods. Thirty groups of the leaves were used to build the new model, and the remaining 16 groups were used to conduct preliminary validation of the model. Through these measurements, we obtained information on the spectral and biochemical components of the leaves and the corresponding scanning electron microscopy (SEM) images. The reflectance spectra were collected with an ASD Fieldspec FR spectroradiometer (Analytical Spectral Devices, Boulder, CO, USA) with a wavelength range of 350–2500 nm and a spectral resolution of 1 nm. The spectrometer is equipped with a blade clamping device. Information on the biochemical components was measured with chemical methods. Through chemical analysis we obtained the chlorophyll, water, dry matter, and copper ion content. Chlorophyll is not soluble in water but is soluble in organic solvent. Therefore, chlorophyll was extracted from the copper-treated leaves with 80% acetone. To measure the dry matter and water content, the harvested leaves were heated at 105°C for 30 min and were then dried at 70°C in an oven to achieve a constant weight. The leaf samples (approximately 0.5 g) were digested with concentrated nitric acid and hydrochloric acid. The digested solution was filtered, and the copper concentration was then analysed by atomic absorption spectrophotometry. Leaf samples from plants grown in the control soil were collected and prepared for SEM. The samples were frozen and then

immediately fixed in 2% glutaraldehyde in a 0.1 M potassium phosphate buffer (pH 7.2). All of the materials were maintained at 4°C and were observed with a scanning electron microscope. The model is KYKY-EM 3200, which has a resolution better than 6 nm. All observations were completed in 2 weeks.

Moreover, we downloaded the LOPEX 93 data set from the Internet (Hosgood et al. 1995). The data set consists of approximately 70 leaf samples representing 50 plant species. A wide range of variations in leaf internal structure, pigments, and water and biochemical content was available; this range led to a wide range of variation in the optical properties of the leaves. The spectral measurements were performed with the best equipment available and can be considered to be very precise. We fit the model parameters based on the data set from the laboratory experiments together with the LOPEX 93 data sets.

3. Theory

Plant reflectance is governed by the surface properties and internal structure of the leaves and by the concentration and distribution of foliar pigments and biochemical components. The leaf structure and biochemical content change under copper stress. These changes result in changes in the spectral reflectance of the leaf. Additionally, the copper ion shows significant absorption characteristics from 400 to 2500 nm. We therefore use the absorption properties of the copper ion to describe changes caused by copper stress in the spectral reflectance of the leaf. Based on the above theoretical basis, our research develops a new radiative transfer model for copper-treated leaves.

3.1. *Theory of the PROSPECT model*

The new reflectance spectral model is based on the PROSPECT model. Thus, this study first introduces the basic principles of the PROSPECT model.

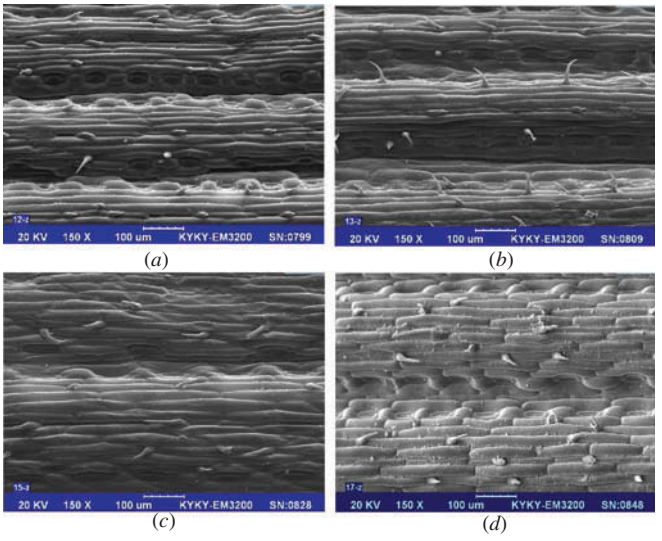
PROSPECT is an optical model for leaves developed from the 'plate model'. PROSPECT is a generalization of the 'plate model'. Based on the radiative transfer theory, PROSPECT describes the optical properties of a leaf from 400 to 2500 nm with a minimum number of parameters in order to facilitate its inversion.

A leaf is assumed to be composed of a pile of N homogeneous layers separated by $N-1$ air spaces. The non-diffuse character of the incident beam concerns only the top of the pile. Inside the leaf, the light flux is assumed to be isotropic. The final equation of the PROSPECT model requires four parameters: α, N, n, and $k(\lambda)$.

The PROSPECT model uses the refractive index n and leaf structure parameter N to describe the scattering process and uses the spectral absorption coefficient $k(\lambda)$ to describe the absorption process. $k(\lambda)$ can be written in the form

$$k(\lambda) = \frac{\sum_i k_i(\lambda) \times C_i}{N} + k_e(\lambda), \tag{1}$$

where λ is the wavelength, $k_i(\lambda)$ is the specific spectral absorption coefficient for leaf component i, C_i is the content of leaf component i per unit area of the leaf, and $k_e(\lambda)$ is the specific spectral absorption coefficient of elementary albino, dry, and flat leaves (Jacquemoud and Baret 1990).



(*a*) (*b*) (*c*) (*d*)

Figure 1. Scanning electronic micrographs showing the upper epidermis of wheat in the jointing stage. The copper ion content of the leaves is 9.6614, 10.7155, 14.5455, and 18.2780 μg g^{-1} in panels (*a*), (*b*), (*c*), and (*d*), respectively.

3.2. *Structural characteristics of copper-treated leaves*

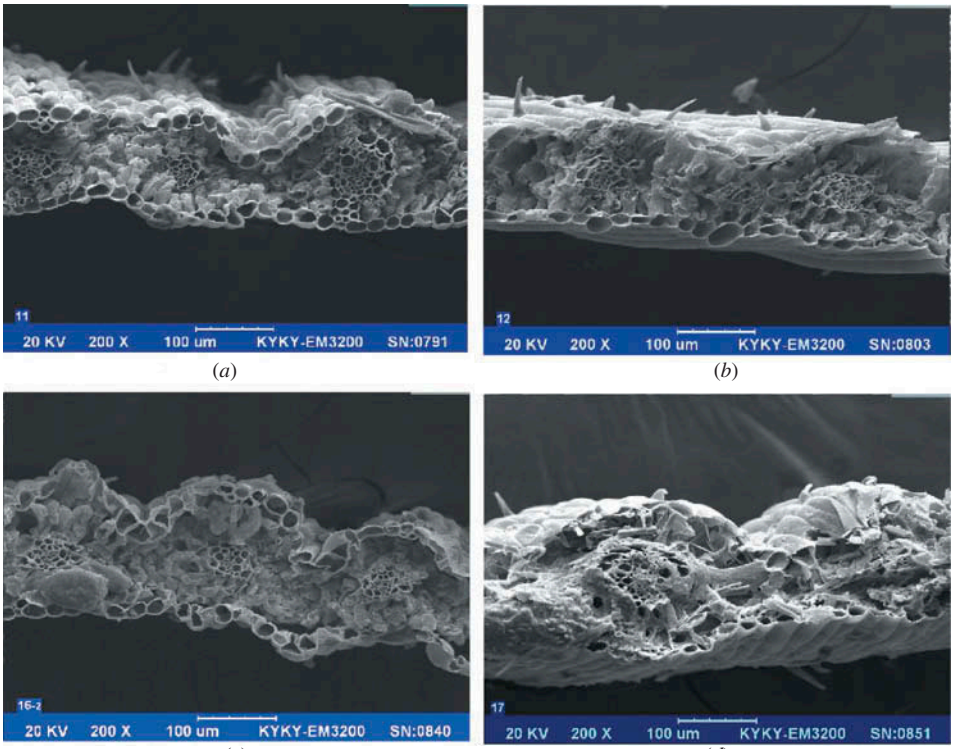
When heavy metal content in soil exceeds the target value, heavy metal ions accumulate in plant tissues as the plant grows. This accumulation leads to changes in the internal structure of the leaf; thus, this accumulation causes spectral changes (Su et al. 2007).

Figure 1 shows scanning electronic micrographs of the upper epidermis of wheat during the jointing stage. As shown in Figure 1, the stomata density and the number of glandular hairs clearly increased as the copper concentration increased. The degree of fluctuation in the leaf surface changes significantly from copper stress. Because there is no quantitative method to assess the degree of fluctuation in the leaf surface, we evaluated the degree of fluctuation through visual inspection. The degree of fluctuation in the leaf surface gradually diminished as the copper concentration in the leaf increased. That is, a higher copper content in the leaf indicates a flatter leaf surface. The PROSPECT model was constructed by separating the first layer from the $N - 1$ other layers. Therefore, when the first layer receives an incident beam within a solid angle, the leaf with a higher copper content has a relatively high reflectance value.

Figure 2 shows scanning electronic micrographs of the transverse section of wheat during the jointing stage. As shown in Figure 2, the internal structure of the leaf becomes more disordered as the copper concentration of the leaf increases. In detail, as the metal concentration increases, the cellular changes consist of the following aspects: the upper epidermal cells decompose, the mesophyll cells shrink, and the vascular bundle disintegrates.

3.3. *Absorption characteristics of copper ion*

There are two basic forms of the copper ion in plants: univalent and bivalent. The transformation between these forms constitutes an important redox system in living



(*a*) (*b*) (*c*) (*d*)

Figure 2. Scanning electronic micrographs of the transverse section of wheat in the jointing stage The copper ion content in the leaves is 7.2072, 9.6614, 14.0649, and 18.2780 μg g^{-1} in panels (*a*), (*b*), (*c*), and (*d*), respectively.

cells (Wu 2003). Cu^{+}/Cu^{2+} is an important cofactor for many oxidoreductases and is a major component of plastocyanin. Copper ions play an important role in photosynthetic electron transmission. That is, copper ions usually exist in compounds and form coordinate bonds with hydrogen or sulphur ions. The ions participate in many intracellular physiological and biochemical processes that are accompanied by electron gain or loss.

Figures 3 and 4 represent the reflectance and *K–M* absorption spectra of crystalline $CuCl_2$. At 550 nm, the copper ion gives a strong response, which corresponds to an absorption valley. The copper ion also has low reflectivity and high absorptivity in the near-infrared region. Above 1200 nm, the absorption characteristics of the copper ion are similar to those of the hydroxide radical. Based on the above analysis, we conclude that the copper ion has obvious absorption properties from 400 to 2500 nm.

3.4. Reflectance characteristics of copper-treated leaves

Spectral measurements acquired for each sample of copper-treated leaves were compared to those of the control samples to determine whether significant spectral changes occurred for the stressed leaves. To determine the spectral significance of each sample, we calculated the spectral angle between the mean reflectance spectra for the given sample and the mean reflectance spectra for the control plants. The spectral angle was calculated

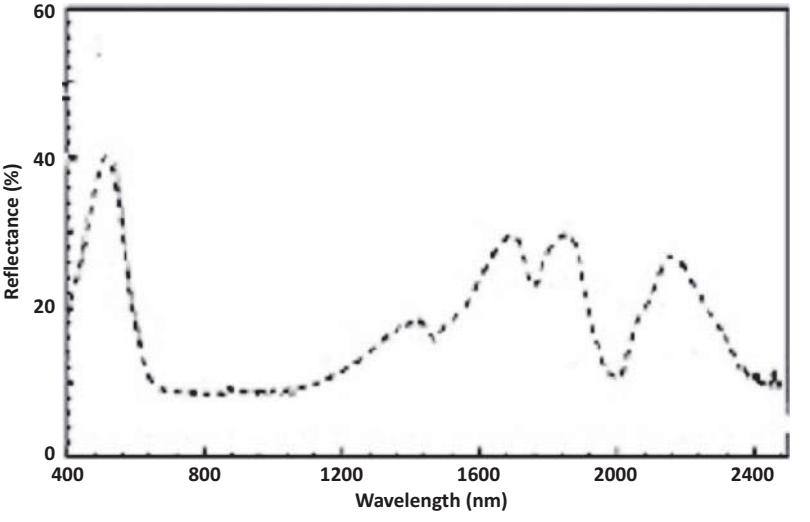


Figure 3. Reflectance spectra of crystalline copper chloride.

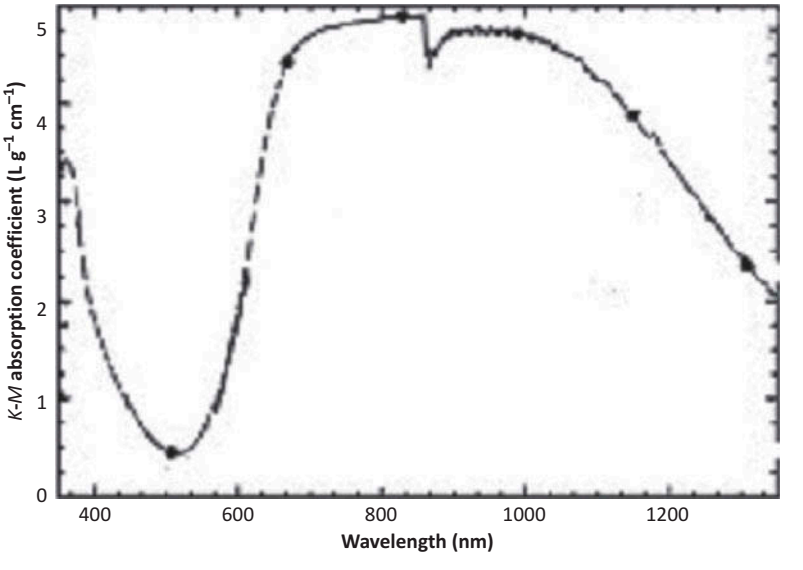


Figure 4. *K–M* absorption coefficient of crystalline copper chloride.

for six spectral regions, including the full spectral range (400–2500 nm) and specific regions. These regions included the visible region, which focused on pigments, (400–716 nm) at 4 nm intervals, a region focusing on the red edge (717–975 nm) at 3 nm intervals, three regions primarily associated with water content (976–1265 nm at 17 nm intervals, and 1266–1770 nm and 1771–2500 nm both at 3 nm intervals), and lastly, the full spectral range (400–2500 nm) at 5 nm intervals.

We calculated the spectral angle through the following equation:

$$\theta = \arccos\left[\frac{\sum\left(R_{\text{control}}(i) \times R_{\text{stress}}(i)\right)}{\left|R_{\text{contro;}}(i)\right| \times \left|R_{\text{stress}}(i)\right|}\right](i = 1, 2, 3, \ldots, n), \tag{2}$$

where θ is the spectral angle, $R_{\text{control}}(i)$ is the reflectance value of the control leaves at wavelength i, and $R_{\text{stress}}(i)$ is the reflectance value of the copper-stressed leaves at wavelength i.

$|R_{\text{control}}(i)|$ and $|R_{\text{stress}}(i)|$ can be calculated through the following equations:

$$\left|R_{\text{control}}(i)\right| = \sqrt{\left(\sum\left(R_{\text{control}}(i) \times R_{\text{control}}(i)\right)\right)}, \tag{3}$$

$$\left|R_{\text{stress}}(i)\right| = \sqrt{\left(\sum R_{\text{stress}}(i) \times R_{\text{stress}}(i)\right)}. \tag{4}$$

Additionally, n can be calculated by the following equation:

$$n = \frac{\lambda_{\max} - \lambda_{\min}}{\delta}, \tag{5}$$

where $\lambda_{\max}$ is the upper bond of the spectral bands, $\lambda_{\min}$ is the lower bond of the spectral bands, and δ is the band interval (Dennison, Halligan, and Roberts 2004).

If the angle exceeded a threshold for any spectral range, the spectrum was considered to contain significant spectral changes. The threshold was computed through the following equations:

$$\varepsilon_x = \arccos\left[\frac{\sum\left(R_{\text{control}-x}(i) \times \overline{R(i)}\right)}{\left|R_{\text{control}-x}(i)\right| \times \left|\overline{R(i)}\right|}\right], \tag{6}$$

$$\varepsilon = \frac{\sum_{x=1}^{q} \varepsilon_x}{q}, \tag{7}$$

where $R_{\text{control}-x}(i)$ is the reflectance value for measurement x of the control group leaves, $\overline{R(i)}$ is the mean reflectance value of the control group leaves at wavelength i, and q is the total number of measurements. In conclusion, the threshold values for each spectral range were determined by calculating the difference between the reflectance value for a single measurement and the mean reflectance value of the control sets for each species.

Figure 5 compares the spectral angles and threshold values for wheat and *Brassica chinensis* in six specific spectral regions. The horizontal axis represents the growth period of the experimental samples, and the vertical axis is the corresponding spectral angle. As shown in Figure 5, more than 90% of the copper-treated leaves exhibit significant spectral changes compared to the control samples over the full spectral range (400–2500 nm), 77% of the copper-stressed leaves show significant spectral changes in the visible region

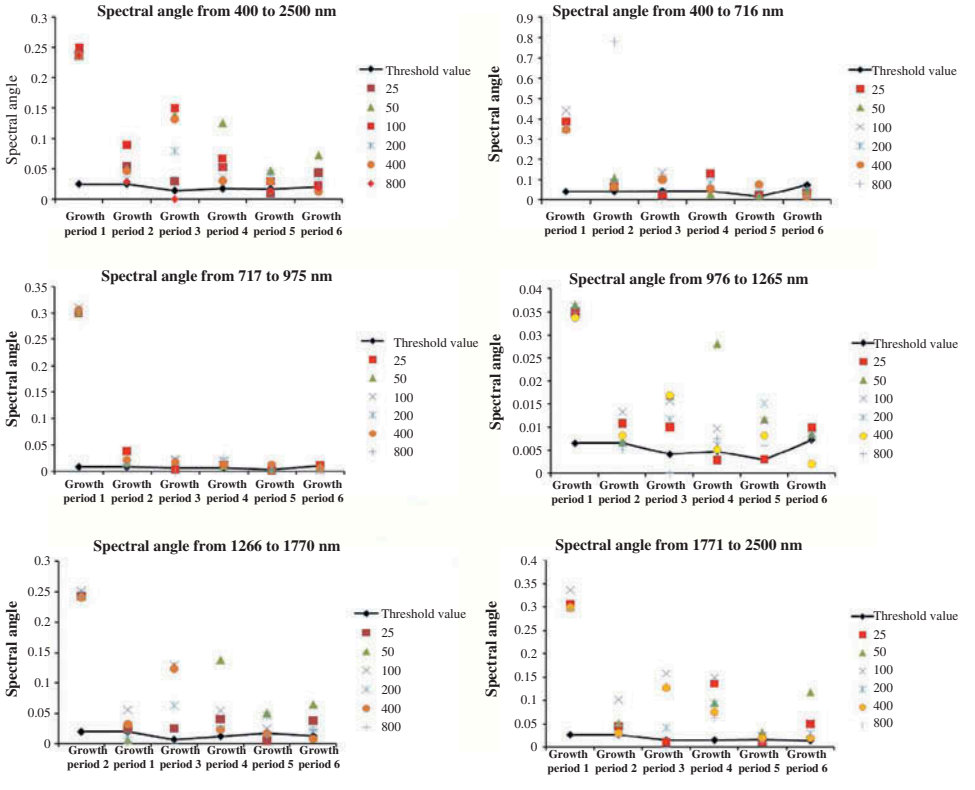


Figure 5. Spectral angles calculated for six spectral regions.

focusing on pigments (400–716 nm), 76% of the copper-treated leaves exhibit obvious spectral changes in the region focusing on the red edge (717–975 nm), and 87% of copper-treated leaves show significant spectral changes in the three regions associated with water content. The statistical results for the spectral angles in the above six band regions show that more than 84% of the copper-stressed leaves have a spectral angle greater than the threshold value. These results indicate that more than 84% of the copper-treated leaves demonstrated significant spectral differences. That is, copper stress leads to evident spectral changes.

4. Determination of model parameters

The new reflectance spectral model is based on the PROSPECT model. Compared with the PROSPECT model, the new model primarily adds the specific absorption coefficient of copper ion. Reflectance spectral modelling is an inversion procedure to accurately calculate the model parameters. The final equation of the new reflectance spectral model requires the following model parameters: the maximum incidence angle, α; the structure parameter, N; the refractive index, n; and the specific absorption spectra of the pigments, water, dry matter, and copper ion (K_{a+b}, K_w, K_d, K_{cu}). The specific modelling process is shown in Figure 6.

4.1. *Determination of* α

The α has been adjusted to the lowest value of the elementary reflectance and is set to 59° in the PROSPECT model (Jacquemoud and Baret 1990). However, in PROSPECT-4 and

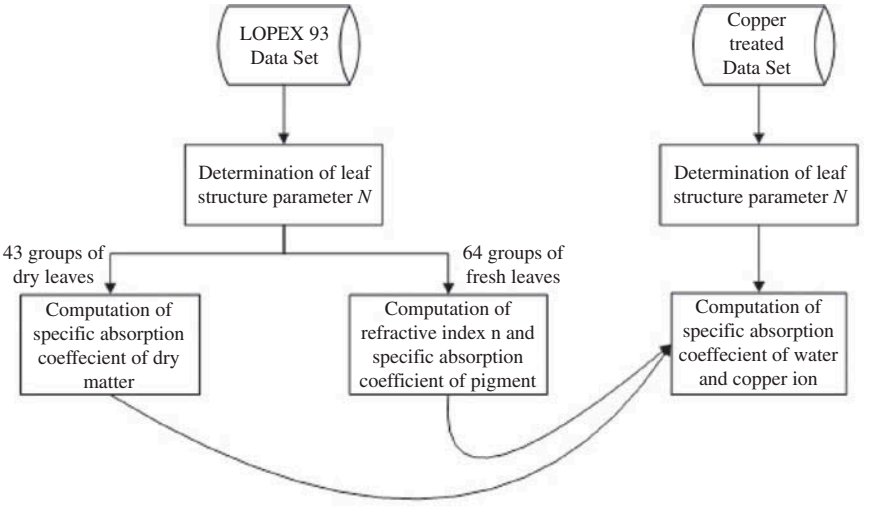


Figure 6. Diagram of the calibration process.

PROSPECT-5, the probability density function of the facet orientations $D(\alpha, \sigma)$ was physically linked to the surface roughness parameter σ and the angle α. These models indicate that 40° is a more realistic value (Feret et al. 2008). Thus, we fixed $\alpha = 40°$ in this study.

4.2. *Determination of the structure parameter* N

Determination of N requires the refractive index. The refractive index was set to 1.45 in this step, and it was shown that increasing or decreasing the value of the refractive index does not change the results. For the LOPEX 93 data set, we used three wavelengths to obtain the inversion value of N; these wavelengths corresponded to the maximum reflectance at λ_1, the maximum transmittance at λ_2, and the minimum absorbance at λ_3. We obtained the value of four parameters by minimizing the following optimized equation:

$$J(N, k(\lambda_1), k(\lambda_2), k(\lambda_3)) = \sum_{i=1}^{3} (R_{\text{mes}}(\lambda_i) - R_{\text{mod}}(\lambda_i))^2 + (T_{\text{mes}}(\lambda_i) - T_{\text{mod}}(\lambda_i))^2. \quad (8)$$

$R_{\text{mes}}(\lambda_i)$ and $T_{\text{mes}}(\lambda_i)$ are the measured reflectance and transmittance at λ_i, and $R_{\text{mod}}(\lambda_i)$ and $T_{\text{mod}}(\lambda_i)$ are the simulated reflectance and transmittance at λ_i.

For the copper-treated data set, we chose three wavelengths that corresponded to three maximum reflectances from 800 to 1200 nm to obtain the inversion value for N_{Cu}. The cost function is the following equation:

$$k(N_{\text{Cu}}, k(\lambda_{\max 1}), k(\lambda_{\max 2}), k(\lambda_{\max 3})) = \sum_{i=1}^{3} (R_{\text{mes}}(\lambda_{\max i}) - R_{\text{mod}}(\lambda_{\max i}))^2. \quad (9)$$

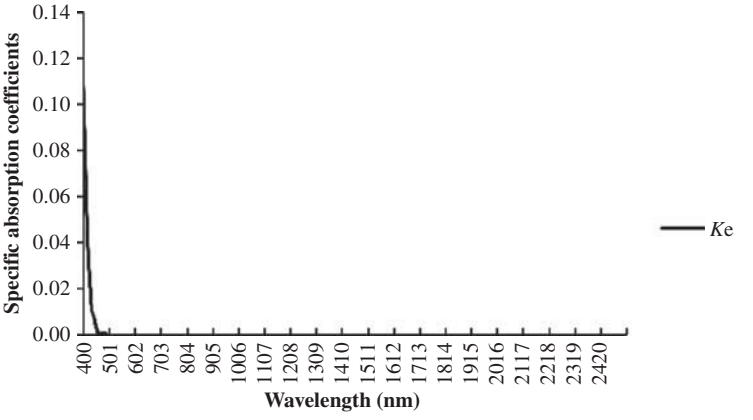


Figure 7. Spectrum of specific absorption coefficient of an albino leaf.

4.3. *Determination of specific absorption coefficients*

Because albino leaves are extraordinarily rare, the specific absorption coefficient of elementary albino leaves was directly adopted from the inversion results of PROSPECT-2 (Jacquemoud et al. 1996). The spectrum of the absorption coefficient, k_e, of an albino leaf is shown in Figure 7.

First, to avoid interference from water absorption, we used 43 groups of dry leaves in the LOPEX 93 data set to compute the specific absorption coefficients of dry matter from 400 to 2500 nm. We assumed that the absorption between 400 and 800 nm arises from dry matter and chlorophyll. From 400 to 1200 nm, we set the absorption to be constant and equal to its minimum value between 1000 and 1200 nm. Then, the refractive index n and the specific absorption coefficient of chlorophyll were retrieved from the 64 groups of fresh leaves in the data set. We calculated the specific absorption coefficients for water and copper ion from 30 groups of copper-treated leaves. Because the absorption features of copper ion were clear from 400 to 2500 nm, we studied pigments and copper ion from 400 to 800 nm and water and copper ion from 800 to 2500 nm.

We determined the absorption coefficients with the partial least square method. The error function is as follows:

$$J\left(K_{\mathrm{spec},i}(\lambda), n(\lambda)\right) = \sum_j \left(R_{\mathrm{mes},j}(\lambda) - R_{\mathrm{mod},j}(K(\lambda), n(\lambda))\right)^2, \tag{10}$$

$$K(\lambda) = \sum_i K_{\mathrm{spec},i}(\lambda) \times \frac{C_{i,j}}{N_j} + K_{\mathrm{e}}(\lambda), \tag{11}$$

where $R_{\mathrm{mes},j}(\lambda)$ is the measured reflectance of leaf j at λ, $R_{\mathrm{mod},j}(\lambda)$ is the modelled reflectance, $K(\lambda)$ is the spectral absorption coefficient at λ, $K_{\mathrm{spec},i}(\lambda)$ is the absorption coefficient of component i at λ, $C_{i,j}$ is the content of component i in leaf j, and N_j is the structure parameter of leaf j.

5. Results

5.1. *Structure parameter* N

Figure 8 compares N_{cu} and N_{fresh}. Although the LOPEX 93 data set and the copper-stressed data set are composed of different plant species, the 64 groups of fresh leaves in the LOPEX 93 data set sufficiently represent the range of variation in the structure parameters of healthy plants. Therefore, the comparison between N_{cu} and N_{fresh} can be explored. From Figure 8, we find that the structure parameters of the copper stressed leaves, N_{cu}, are significantly larger than those of healthy leaves, N_{fresh}. According to Figure 9, the results indicate that N_{cu} has a median value of 3.6 and ranges from a high of 3.9 to a low of 3.2; N_{fresh} has a median value of 1.6 and ranges from a high of 2.2 to a low of 1.2.

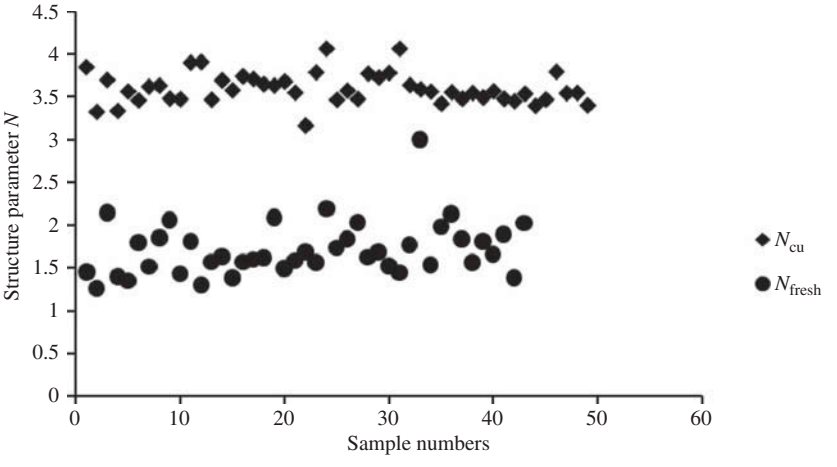


Figure 8. Comparison between leaf internal structure parameter of copper-stressed and healthy leaves.

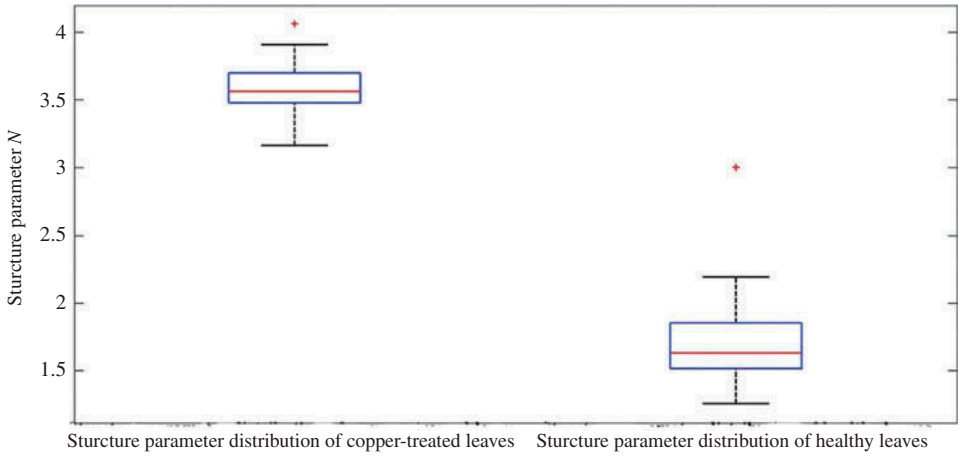


Figure 9. Box plot of leaf internal structure parameter of copper-stressed and healthy leaves.

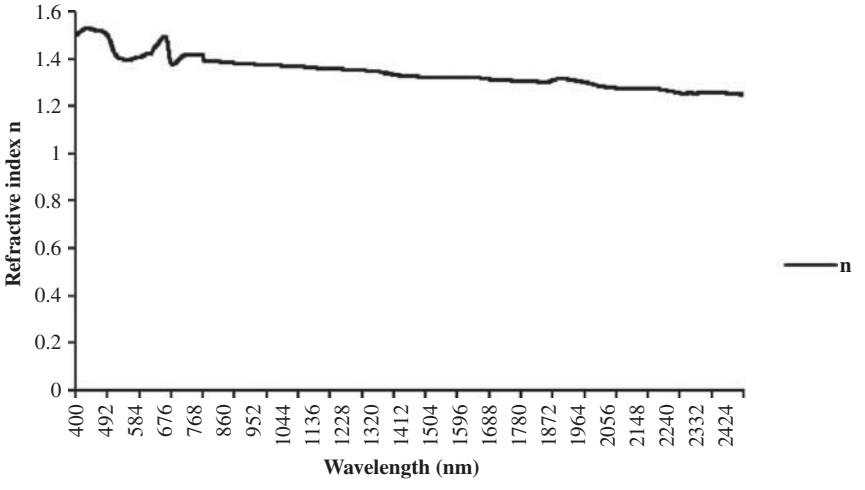


Figure 10. Refractive index of leaf material.

Studies show that a larger N value indicates a more disorganized internal structure Jacquemoud and Baret 1990). Therefore, the conclusion can be induced from our inversion results that the copper-stressed leaves have a more disorganized internal structure than the unstressed leaves; this conclusion coincides with the results of the SEM images (Figure 2). However, it is still difficult to estimate the copper content from changes in the internal structure of the leaves.

5.2. *Refractive index* n

The refractive index of leaf material calculated from the PROSPECT-5 model is shown in Figure 10 and its average value is approximately 1.4. The refractive index regularly decreases from 400 to 2500 nm. The inversion results are consistent with the results obtained in other studies (Feret et al. 2008; Jacquemoud and Baret 1990).

5.3. *Specific absorption coefficients*

The shape of the spectra for the estimated specific absorption coefficient for dry matter is not easy to interpret. According to Jacquemoud, the high absorption peak below 450 nm also observed in albino leaves and in leaves with very low pigment content is absent given that the spectra of these samples are constant from 400 to 800 nm (Jacquemoud et al. 2000). Thus, we set the absorption coefficient of dry matter from 400 to 800 nm to be constant to the minimum value in the near-infrared bands. The absorption coefficients of dry matter, chlorophyll, and water are shown in Figures 11–13. The results are consistent with other studies (Jacquemoud and Baret 1990; Feret et al. 2008; Malenovský et al. 2006).

The absorption coefficient of copper ion is shown in Figure 14. The result agrees very well with the published absorption spectra of a solution of cupric chloride (Figure 4). The absorption coefficient of copper ion has an absorption valley at approximately 550 nm and has absorption properties similar to water from 800 to 2500 nm. The similarity arises primarily because the copper ions do not exist alone but form coordinate bonds with hydroxide.

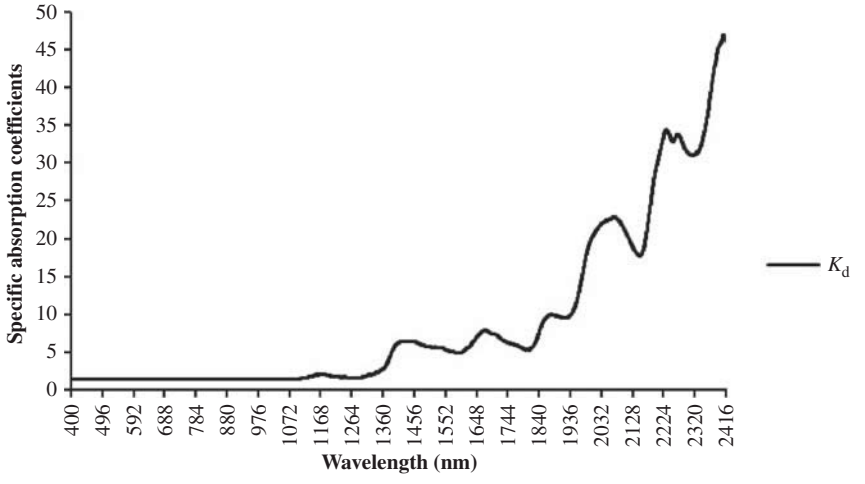


Figure 11. Specific absorption coefficient of dry matter.

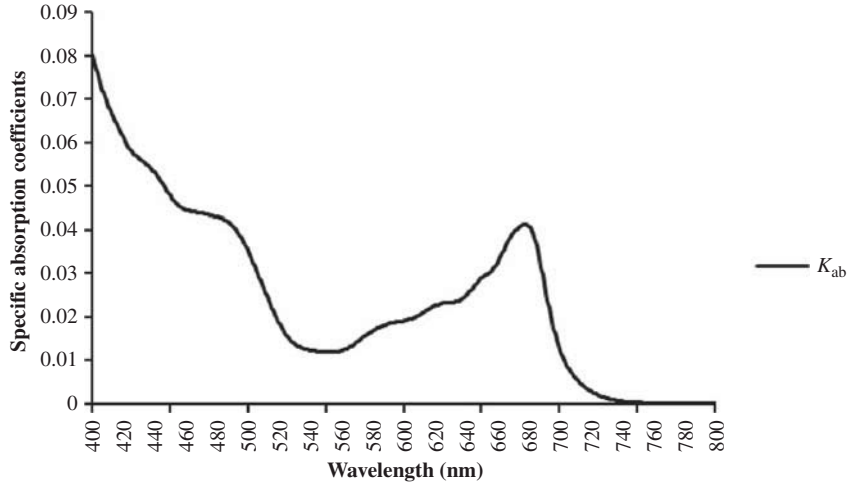


Figure 12. Specific absorption coefficient of chlorophyll.

6. Validation of the new model

Validation was performed with 16 groups of copper-treated samples. We simulated the reflectance spectra of copper-treated leaves with the new model and the PROSPECT model. Then, the simulated values and measured values are compared at the absorption peaks and valley of the copper ion at 491, 552, 665, 766, 1265, 1437, 1675, 1925, and 2500 nm. The results of the comparison are shown in Figure 15. Figure 15 clearly shows that the simulated results from the improved model are closer to the measured values and that most of the simulated values from the PROSPECT model are higher than the measured values. The determination coefficients for the simulated values obtained from the improved model and PROSPECT model are respectively 0.9442 and 0.9071. That is, the improved model, which considers the absorption of the copper ion, has higher accuracy and gives a more reasonable result.

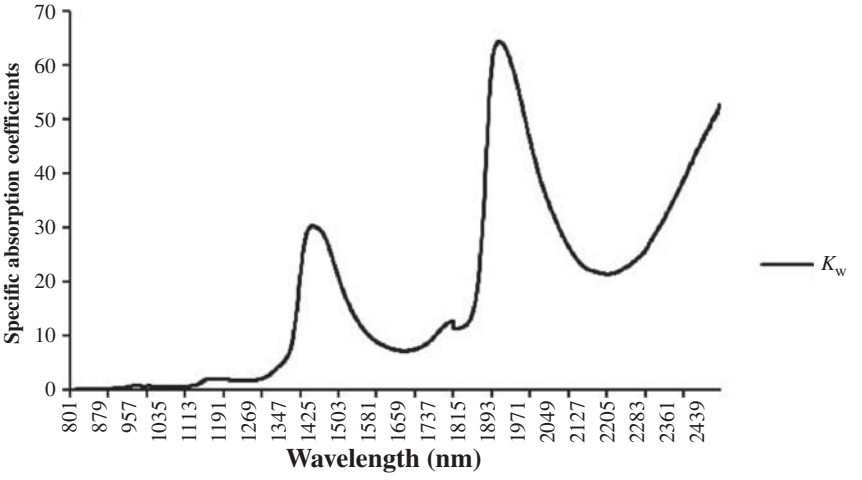


Figure 13. Specific absorption coefficient of water.

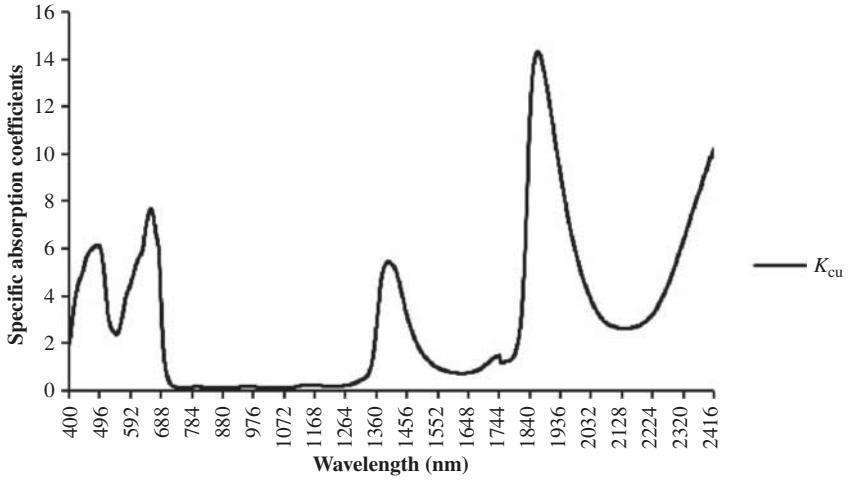


Figure 14. Specific absorption coefficient of copper ion.

Figure 16 shows the root-mean-square errors computed between the reflectance values for the 16 samples and the values simulated by PROSPECT and the improved model at each of the investigated wavelengths (400–2500 nm). The RMSE of the improved model is smaller than the RMSE of the PROSPECT model from 400 to 2500 nm. Figure 16 shows an RMSE for the improved model of less than 0.1 from 400 to 2500 nm. For the wavelengths from 400 to 800 nm and from 1300 to 2500 nm, the RMSE values of the improved model are very small whereas the RMSE values from 800 to 1300 nm are relatively above average. The results indicate acceptable performance for the improved model for copper-treated leaves.

We selected 3 representative samples from the 16 samples for further analysis of the reflectance spectra based on the copper content in the leaves. The copper content of the

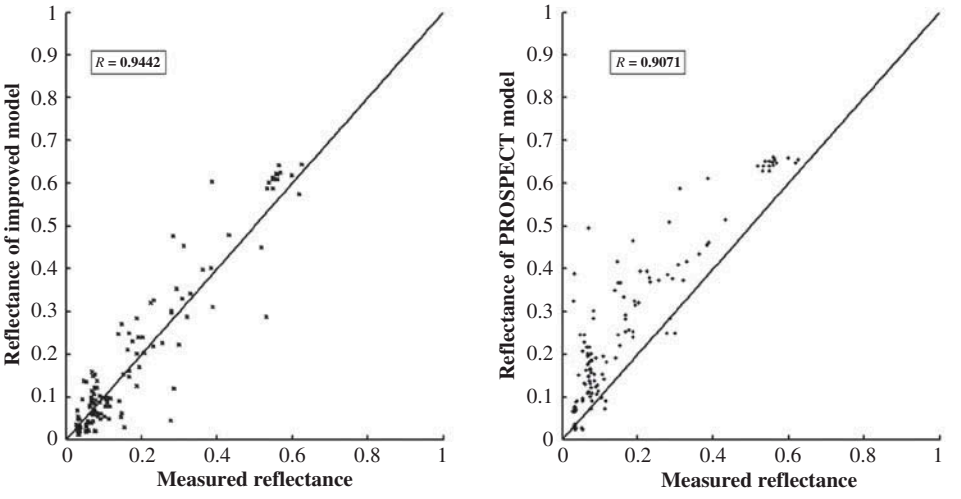


Figure 15. Comparison between simulated and measured reflectance data. (*a*) Comparison between simulated reflectance data from the improved model and measured reflectance data. (*b*) Comparison between simulated reflectance data from the PROSPECT model and measured reflectance data.

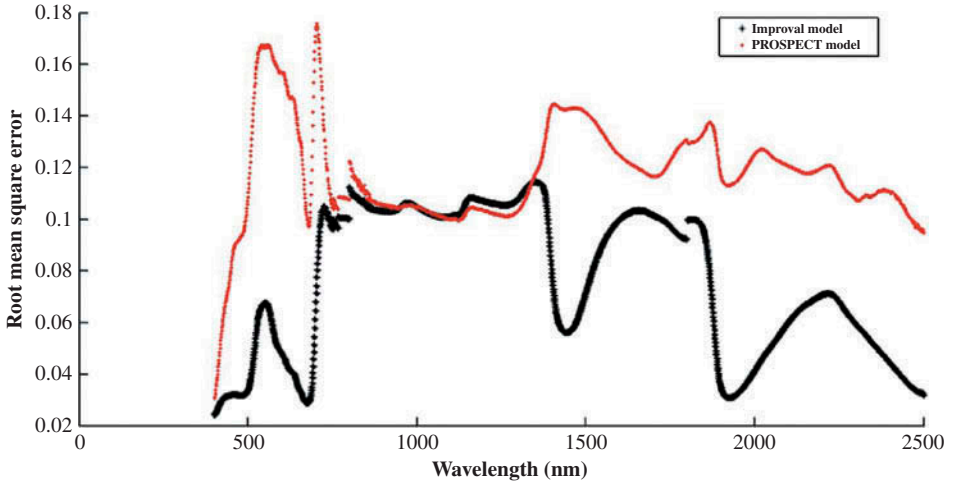


Figure 16. Root mean square errors computed between the reflectance values for the 16 samples and the values simulated by PROSPECT and the improved model for each of the investigated wavelengths (400–2500 nm).

selected samples is 0.06, 0.16, and 0.22 μg g^{-1}. Figures 17 and 18 compare the reflectance values for the three selected samples and the values simulated by PROSPECT and by the improved model. Figure 17 shows that the values of the reflectance spectra computed by the improved model are closer to the measured values. The values of the reflectance spectra simulated by the PROSPECT model are all greater than the measured values and the simulated values from the improved model. Figure 18 shows that the reflectance values simulated with the improved model are uniformly distributed on both sides of the line $y = x$. The correlation coefficients between the simulated values from the improved

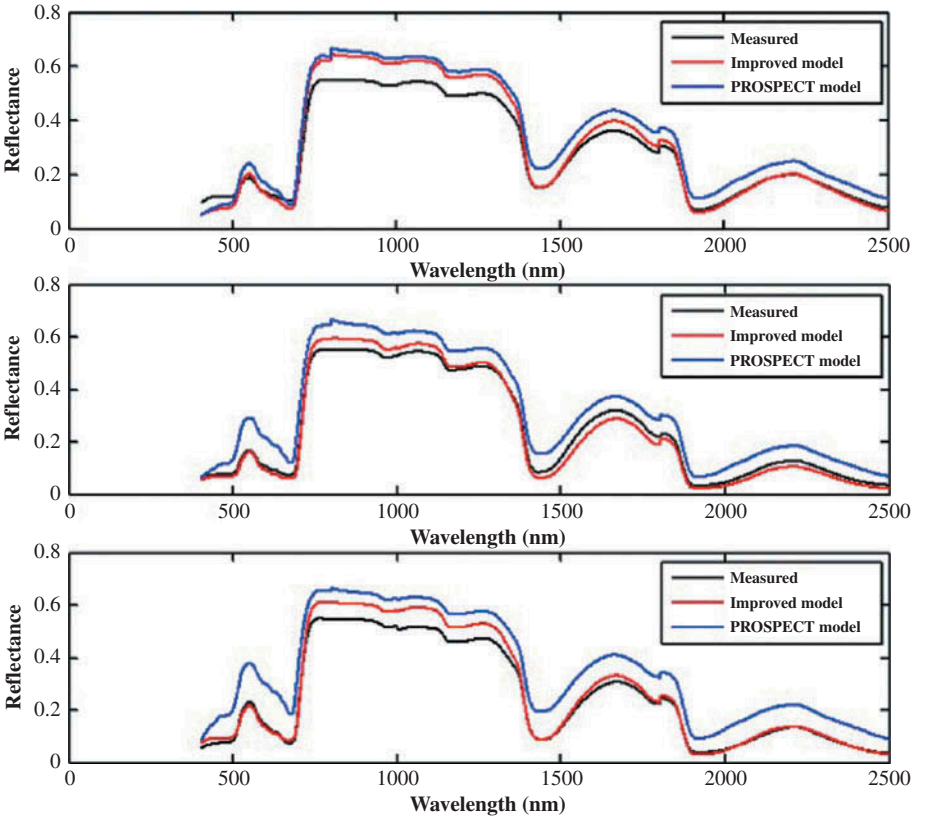


Figure 17. The reflectance spectra of three selected samples from 400 to 2500 nm.

model and the measured values of the 3 selected samples are 0.9990, 0.9973, and 0.9988; the RMSE values are 2.0892, 1.0993, and 1.5722. The correlation coefficients between values simulated with the PROSPECT model and the measured values for the three selected samples are 0.9951, 0.9946, and 0.9941; the RMSE values are 3.2000, 3.2539, and 4.7029. The results indicate that simulation of the reflectance spectra of copper-treated leaves with the improved model can yield better correlation estimates, smaller errors, and more accurate values.

7. Discussion and conclusions

This study intended to investigate a reflectance model for a crop stressed by the heavy metal copper. Forty-six groups of copper-treated leaves were measured in a laboratory experiment. Through these measurements, we obtained leaf reflectance spectra from 400 to 2500 nm, information on the biochemical components of the leaves, and corresponding SEM images. We then developed a new model for the reflectance spectra based on the classic broadleaf radiative transfer model – PROSPECT. Compared with the PROSPECT model, the new model primarily considers the addition of the specific absorption coefficient of the copper ion. Model validation used 16 leaves from the laboratory experiment. The validation showed that the inversion values for K_{cu} gave very good agreement with the published absorption spectra for cupric chloride. Linear regression analysis between

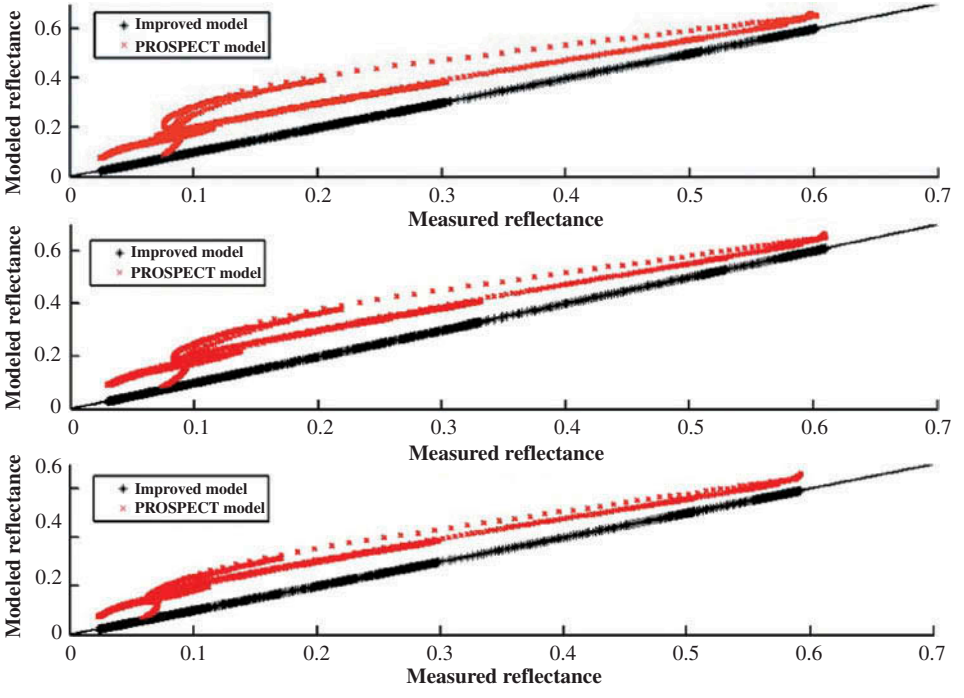


Figure 18. Comparison between the measured reflectance spectra and modelled reflectance spectra.

the simulated and measured reflectance values provides a correlation coefficient of approximately 0.9442, and the root-mean-square error was less than 0.1 from 400 to 2500 nm. That is, the improved model, which considered the absorption by the copper ion, has higher accuracy and gives a more reasonable result than the PROSPECT model. The results indicate that the improved model is better suited to simulate the reflectance spectra of copper-treated leaves.

Copper is a heavy metal environmental pollutant, and people have been concerned about detection of the concentration of copper ions. Recently, there has been gradual development of new radiative transfer models. Copper pollution monitoring primarily uses empirical and semi-empirical statistical methods. This study developed a new reflectance spectral model that has clear physical significance and can be widely used as a general model to monitor copper pollution. However, further validation of the model needs to be performed. We must perform more research into how to avoid the dependence of the biochemical component of the leaf on the copper ion. Then, use of the new model to retrieve the copper ion content in leaves will provide technical support for heavy metal monitoring from remote-sensing images.

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