A reflectance spectra model of heavy metal stressed leaves: advances in the PROSPECT model adding specific absorption coefficients of heavy metal ion

A reflectance spectra model of heavy metal stressed leaves: advances in the PROSPECT model adding specific absorption coefficients of heavy metal ion

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Abstract This article aims to investigate the reflectance model of heavy metal copper stressed crop. Forty-six groups of copper-treated leaves were measured during a laboratory experiment in order to obtain the leaf biochemical component information and its corresponding scanning electron microscopy image. Then a new reflectance spectral model was developed on the basis of the classical broadleaf radiative transfer model-PROSPECT. Comparing with the PROSPECT model, new models mainly consider adding specific absorption coefficient of copper ion. The scattering process is described by a refractive index (n) and a leaf structure parameter (N). Absorption is modeled using pigment concentration, water content, dry matter content, copper ion contamination and the corresponding specific spectral absorption coefficients (K_{ab} , K_{w} , K_{d} , K_{Cu}). Thus, reflectance spectral modeling is an inversion procedure to calculate the above 6 parameters accurately. To validate the model 16 leaves were tested in laboratory experiment. This experiment showed that the inversion values of K_{Cu} had very strong agreement with the published absorption spectra of Cupric Chloride. The linear regression analysis between simulated and measured reflectance provides a correlation coefficient of 0.93 and a root mean squares of 0.067.

1. Introduction

Heavy metal stressed crop will present the change in the internal structure and spectra properties of the leaves. At present, the models in studying heavy metal stressed leaf spectral were mainly established by the use of empirical and semi-empirical statistical methods. Although this type of models is simple and flexible, it can't become a general model because it needs to redefine model parameters for different data sources [1]. The study presented in this paper developed a new reflectance spectral model with reflectance spectra data of the copper-treated leaves. It considers the physical interaction mechanism between the light and leaves as well as leaf internal structure. So it has clear physical significance and can be widely used as a general model.

2. Materials and methods

2.1. Modeling datasets

Wheat and lettuce are selected as experimental subjects in the copper-treated laboratory experiment. Ten treatments were designed and each had three parallel tests. Through these measurements, we obtained leaf spectral information, biochemical component information as well as corresponding scanning electron microscopy images. Forty-six groups of copper-treated leaves were measured in 4 regular periods. 30 groups of them were used to build the new model and the rest of the 16 groups for validation of the model. Reflectance spectra was collected using an ASD Fieldspec FR Spectroradiometer (Analytical Spectral Devices, Boulder, CO, USA) with a wavelength range of 350-2500nm, a spectral resolution of 1 nm. The spectrometer is equipped with a blade clamping device. The biochemical component information was measured using chemical methods.

Moreover, we downloaded LOPEX 93 datasets from internet [2]. We fit the model parameters based on laboratory experiment datasets together with the LOPEX 93 datasets.

2.2. Theory of PROSPECT model

The new reflectance spectral model is based on PROSPECT which is a leaf optical model developed from 'plate model'. A leaf is assumed to be composed of a pile of N homogeneous layers separated by N-1 air space. The final equation of the PROSPECT model needs four parameters: α, N, n and θ. θ is related to the absorption coefficient k through the following equation:

$$\theta-(1-k)e^{-k}-k^{2}\int_{k}^{\infty}x^{-1}e^{-x}dx=0 \tag{1}$$

The spectral absorption coefficient $k(\lambda)$ can be written in the form:

$$k(\lambda)=\sum k_{i}(\lambda)C_{i}+k_{e}(\lambda) \tag{2}$$

Where λ is the wavelength, $k_{i}(\lambda)$ is the spectral specific absorption coefficient relative to the leaf component i, and C_{i} is the leaf component i content per unit leaf area, and $k_{e}(\lambda)$ is the spectral specific absorption coefficient of elementary albino and dry flat leaves [3].

2.3. Determination of model parameters

The reflectance spectral model of copper-treated leaves needs following parameters: maximum incidence angle α, structure parameters N, refractive index n, specific absorption spectra of pigments, water, dry matter and copper ion.

2.3.1. Determination of α and N

The α has been adjusted to the lowest value of elementary reflectance and it has been set to 40 degree in this study. The assessment of N requires the knowledge of the value of refractive index first. Refractive index was set to 1.45 in this step, and it is shown that increasing or decreasing the value can't change the results. For LOPEX 93 dataset, we used three wavelengths to get the inversion value of N: corresponding to the maximum reflectance λ_{1}, maximum transmittance λ_{2} and minimum absorptance λ_{3}. We obtained the value of four parameters by minimizing the optimized equation :

$$J\left(N,k(\lambda_{1}),k(\lambda_{2}),k(\lambda_{3})\right)=\sum_{i=1}^{3}\left(R_{mes}(\lambda_{i})-R_{\mathrm{mod}}\left(N,k(\lambda_{i})\right)\right)^{2}+\left(T_{mes}(\lambda_{i})-T_{\mathrm{mod}}\left(N,k(\lambda_{i})\right)\right)^{2} \tag{3}$$

Where $R_{mes}(\lambda_i)$ and $T_{mes}(\lambda_i)$ are measured reflectance and transmittance at λ_i, $R_{mod}(\lambda_i)$ and $T_{mod}(\lambda_i)$ are simulated reflectance and transmittance at λ_i. For copper-treated dataset, we choose three wavelengths in accordance with three maximum reflectance values during 800-1200 nm to get the inversion value of N_{Cu}. The cost function is defined by the following equation:

$$J\left(N,k\left(\lambda_{\max 1}\right),k\left(\lambda_{\max 2}\right),k\left(\lambda_{\max 3}\right)\right)=\sum_{i=1}^{3}\left(R_{mes}\left(\lambda_{\max i}\right)-R_{\mathrm{mod}}\left(\lambda_{\max i}\right)\right)^2 \quad (4)$$

2.3.2. The specific absorption coefficients

The specific absorption coefficient of elementary albino leaves was directly adopted from the inversion results of PROSPECT-2. First, we use 43 groups of dry leaves in LOPEX 93 dataset to compute the specific absorption coefficients of dry matter during the wavelength from 400 to 2500 nm. We assume that the absorption between 400 nm and 800 nm is attributed to dry matter and chlorophyll. From 400 nm to 1200 nm, we set it as a constant and equal to its minimum value between 1000 nm and 1200 nm. The error function is defined in the following equation:

$$J\left(N,n,k_d\left(\lambda_j\right)\right)=\sum_{i=1}^{43}\left(R_{mes_i}\left(\lambda_j\right)-R_{\mathrm{mod}_i}\left(N,n,kd\left(\lambda_j\right)\right)\right)^2+\left(T_{mes_i}\left(\lambda_j\right)-T_{\mathrm{mod}_i}\left(N,n,kd\left(\lambda_j\right)\right)\right)^2 \quad (5)$$

And then refractive index n and specific absorption coefficient of chlorophyll are retrieved from the dataset's 64 groups of fresh leaves. We calculate the specific absorption coefficients of water and copper ion from 30 groups of copper-treated leaves. The error function is as follows:

$$J\left(k_w\left(\lambda_j\right),k_{Cu}\left(\lambda_j\right)\right)=\sum_{i=1}^{30}\left(R_{mes_i}\left(\lambda_j\right)-R_{\mathrm{mod}_i}\left(k_w\left(\lambda_j\right),k_{Cu}\left(\lambda_j\right)\right)\right)^2 \quad (6)$$

3. Results and validation

3.1. Inversion values of model parameters

The results of structure parameters are shown in Figure 1. The structure parameters of copper stressed leaves N_{Cu} are significantly larger than that of healthy leaves N_{fresh}. Jauquemoud's research showed that a larger N value indicates a more disorganized internal structure [3]. Therefore the conclusion can be induced from our inversion results that copper stressed leaves have a more disorganized internal structure than unstressed leaves which coincides with the results of scanning electron microscopy images (See Figure2).

The results of other model parameters are shown in Figure 3. It shows that the inversion values of n, K_{ab}, K_w, K_d are consistent with other literatures and K_{Cu} agrees very well with the published absorption spectra of Cupric Chloride solution [4].

3.2. Validation of the new model

The validation has been carried out with 16 groups of copper treated data. The results of the comparison between simulated and measured reflectance values are shown in Figure 4. The linear regression analysis between simulated and measured reflectance value provides a correlation coefficient of 0.93 and root mean squares of 0.067. Moreover, we calculate correlation coefficients and root mean squares for each group of samples. It shows that the value of Pearson correlation coefficients ranging from 0.909 to 0.999. Prediction of the spectral optical properties by the model does not vary significantly with wavelength in terms of accuracy.

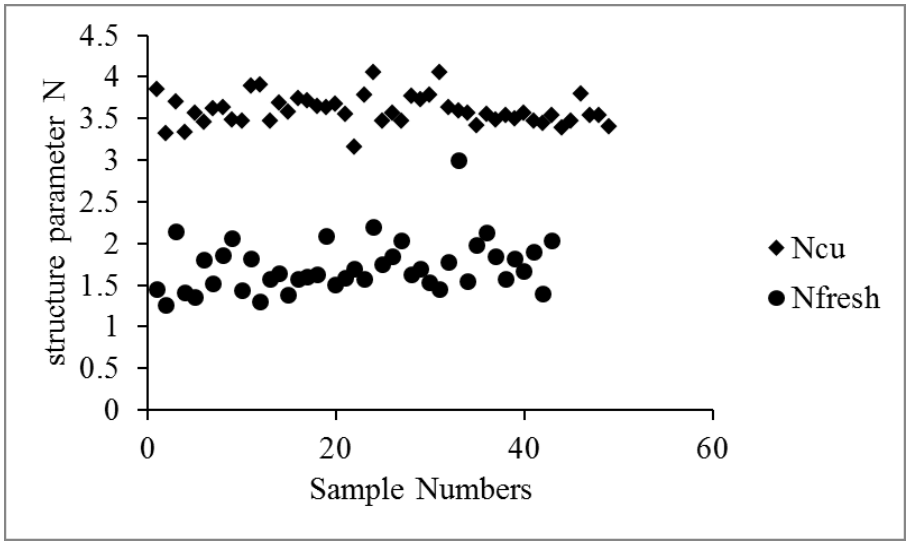
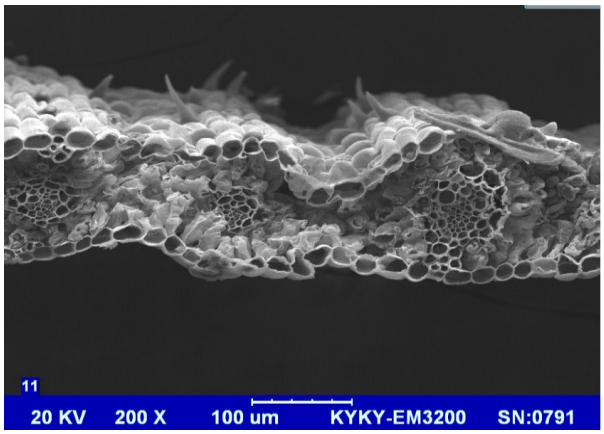
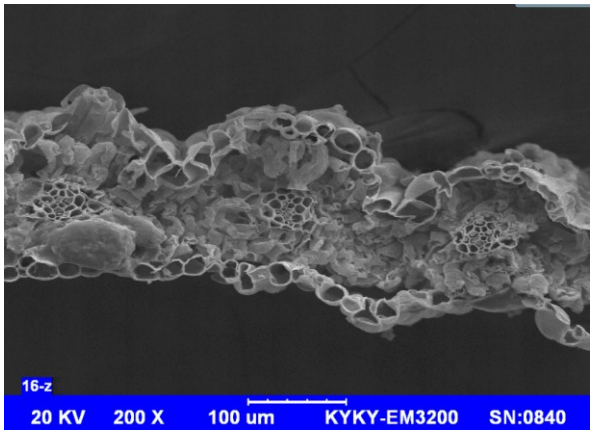


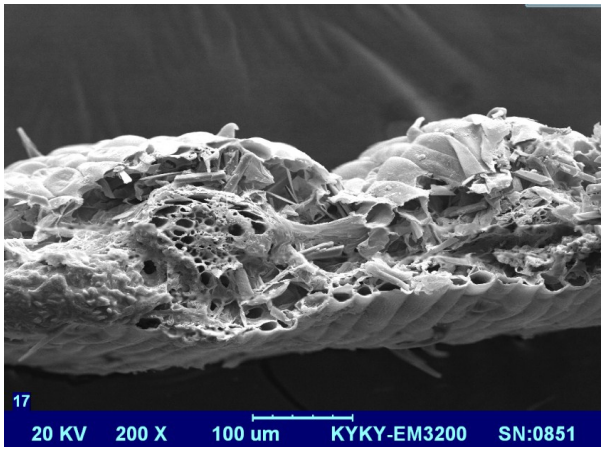
Figure 1. N_{Cu} and N_{fresh}



(a) $C_{Cu} = 7.2072\,ug/g$

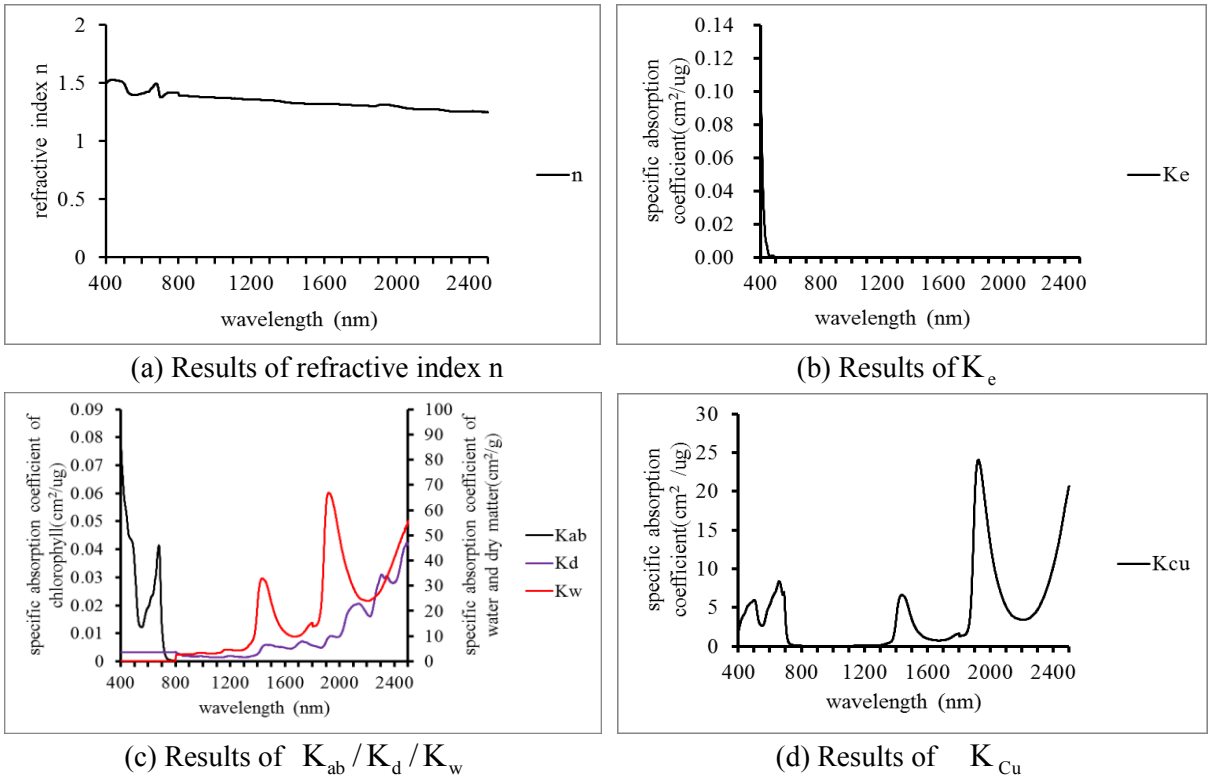


(b) $C_{Cu} = 9.6614\,ug/g$



(c) $C_{Cu} = 18.2780\,ug/g$

Figure 2. The scanning electron microscopy images of wheat.



(a) Results of refractive index n (b) Results of K_e

(c) Results of $K_{ab}/K_d/K_w$ (d) Results of K_{Cu}

Figure 3. Results of model parameters

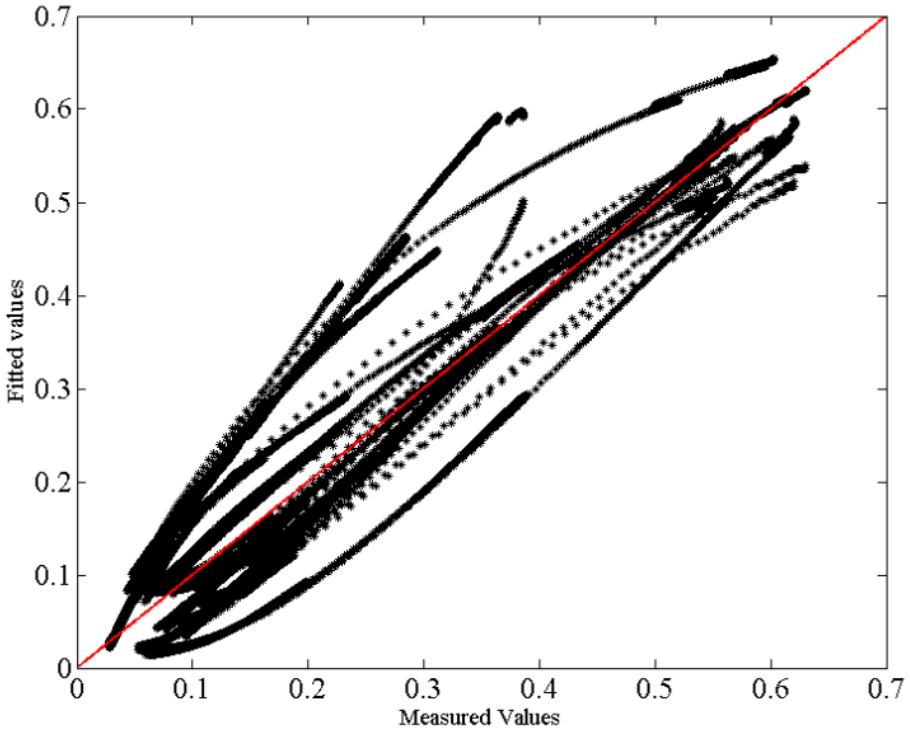


Figure 4. Model validation.

4. Discussion and conclusion

This article aims to investigate the reflectance model of heavy metal copper stressed crop. Forty-six groups of copper-treated leaves were measured during a laboratory experiment. And then a

PROSPECT based new reflectance spectral model is developed which is validated using 16 leaves of laboratory experiment. It showed that the inversion values of n, K_{ab}, K_w, K_d agrees very well with other literatures and K_{Cu} gives very good agreement with the published absorption spectra of Cupric Chloride solution. The linear regression analysis between simulated and measured reflectance value provides a correlation coefficient of 0.93 and root mean squares of 0.067.

This new reflectance spectral model has clear physical significance and can be widely used as a general model. More research can be done on how to avoid the dependence between leaf biochemistry components and copper ion. And then using the new model to retrieve copper ion content in leaves will provide technical support to heavy metal monitoring from remote sensing image.

Acknowledgement
This work was supported by the National Natural Science Foundation of China (No. 41271348) and the National Basic Research Program of China (No.2013CB733403)

5. References

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