Research Paper

Neural-network model for estimating leaf chlorophyll concentration in rice under stress from heavy metals using four spectral indices

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ARTICLE INFO

Article history:
Received 1 September 2009
Received in revised form 1 December 2009
Accepted 14 December 2009
Published online 15 May 2010

Heavy metal stress in soils results in subtle changes in leaf chlorophyll concentration, which are related to crop growth and crop yield. Accurate estimation of the chlorophyll concentration of a crop under heavy metal stress is essential for precision crop production. The objective of this paper is to create a back propagation (BP) neural-network model to estimate chlorophyll concentration in rice under heavy metal stress. Three experiment farms located in Changchun, Jilin Province, China with level II pollution, with level I pollution and with safe level were selected. The assessment was based on the input parameters normalised difference vegetation index (NDVI), optimized soil-adjusted vegetation index (OSAVI), modified triangle vegetation index/modified chlorophyll absorption ratio index (MTVI/MCARI), MTVI/OSAVI and the output parameters of rice leaf chlorophyll concentration. The output parameters were sensitive to heavy metal stress. The result indicated that an optimum BP neural-network prediction model has 4-10-2-1 network architecture with gradient descent learning algorithm and an activation function including the sigmoid tangent function in the input layer, a hidden layer and sigmoid logistic functions in the output layer. The correlation coefficient (R²) between the measured chlorophyll concentration and the predicted chlorophyll concentration was 0.9014, and the root mean square error (RMSE) was 2.58.

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1. Introduction

With the development of industry, some pollutants have affected farms. Heavy metals from industrial pollutants have caused stress to crops adjacent to industrial areas. Heavy metal stress is characterised by the reduction of the enzymes involved in chlorophyll biosynthesis and induced photosynthetic inhibition (De Filippis & Pallaghy, 1994), membrane disruption (Droppa & Horvath, 1990), substitution of metal ions for the chlorophyll molecule and the reduction in leaf chlorophyll concentration (Kastori et al., 1998). Heavy metal stress results in crop growth restriction and crop yield loss. It is therefore essential and urgent that measures are made to detect crop heavy metal stress.

Remote sensing is a valid alternative to traditional ground-based methods to detect plant stress, especially with the...
emergence of hyperspectral data. Some research has been conducted to establish a relationship between heavy metal content in abandoned mines and reflectance characteristics, biochemical composition, and pigment content of the plants respectively (Choe et al., 2008; Gan, Liu, & Zhou, 2004; Liu, Gan, & Wang, 2004). Studies that examined plant response to heavy metal-contaminated soil have generally focused on mines (Ellis & Eslick, 1997). Only a few studies have focused on farmland under heavy metal stress. Recently, a few researchers have demonstrated the correlation between crop spectral characteristics and crop chlorophyll content under copper or lead contamination stress (Chi, Liu, Liu, & Yang, 2006; Li, Yang, Zhang, Zhang, & Zhou, 2008; Ren, Zhuang, & Pan, 2008). However, these experiments were performed under laboratory conditions by adding copper, lead, chromium, or zinc, etc. The fact that most studies have been conducted under laboratory conditions, rather than under field conditions, is one of the primary stumbling blocks in applying hyperspectral remote sensing to precision agriculture.

The level of the pollutants found in farmlands is much lower than the level found in abandoned mines or used in laboratory-based experiments. Alterations in plant biochemistry and cellular composition imposed by heavy metal stress are subtle, and the spectral differences derived from heavy metal stress are not obvious; hence using conventional methods utilising spectral characteristic analysis has presented a challenge with respect to detecting crop heavy metal stress. Therefore, priority should be given to selecting effective methods for detecting variations in biochemical composition. It is well known that artificial neural-network models have advantages in determining the input–output relationship for complex systems based on the strength of their interconnections presented in a set of sample data (Howard & Mark, 2000). Tumbo, Wagner, and Heinemann (2002) developed a back propagation (BP) neural-network model to estimate chlorophyll content based on spectrometry readings, and verified that the estimated values from this neural-network model correlated with chlorophyll measurements reasonably. Wang and Thai (2003) created a generic algorithm model to select an optimal second-order polynomial model to assess crop nitrogen stress based on a ratio of leaf reflectance measured at 700 nm and 740 nm. Noh, Zhang, Shin, Han, and Feng (2006) used a BP neural-network model to assess crop nitrogen stress based on maize canopy reflectance in three channels (green, red, and near-infrared – NIR) of a multispectral image sensor.

Significant progress has been made in this field. However, there has been little research on the variations in leaf chlorophyll concentration under various levels of heavy metal stress, especially for crops growing in field situations rather than under laboratory conditions. In this paper, we propose a neural-network model to retrieve leaf chlorophyll concentration accurately from a rice crop grown under heavy metal stress using performance spectral indices from hyperspectral data.

2. Materials and methods

2.1. Field experiment design

The city of Changchun, Jilin Province in China is an important industrial district and agricultural district. Some areas have been contaminated by industrial pollutants; among the most important of these are heavy metals. Suburban farms have soils with copper and cadmium at concentrations above those...
considered to be normal for the area. Three experimental sites (43°51′34.8″N–43°51′37.0″N, 125°09′07.2″E–125°10′25.3″E) adjacent to the China First Automobile Factory (i.e., the contamination source) in Changchun were selected (Fig. 1). Heavy metal contamination stress levels in the soil of the three field experiments (labelled A, B, and C) varied. The soil and the stress rates were determined as safe level, level I pollution and level II pollution according to a soil sample analysis (Table 1). The site is within the temperate continental climate zone with a mean annual rainfall of 522–615 mm, where soils are dominated by black soils with sufficient organic matter (2–4%). The crop selected in this site was rice which is one of the most important crops in China.

2.2 Data preparation

2.2.1 Spectral data measurement

The data collection was carried out during four days during a typical rice growth season: 8 July, 4 August, 29 August and 18 September 2008, which corresponded to the seeding, tillering, booting and mature growth stages of rice. All spectral measurements were taken under cloudless or near cloudless conditions between 10:00 and 14:00, using an ASD FieldSpec Pro spectrometer (Analytical Spectral Devices, Boulder, CO, USA). The spectrometer was fitted with 10° field of view fibre optics, operated in the 350–2500 nm spectral region with sampling intervals of 2 nm. A BaSO4 calibration panel was used for determining the black and baseline reflectance. A panel radiance measurement was taken before and after rice measurement using two scans each time. Rice radiance measurements were made at 20 sites in each plot and each site was scanned 10 times. These measurements were then averaged for the particular plot. The average reflectance curves for the three field experiments are shown in Fig. 2.

2.2.2 Metal content and leaf chlorophyll measurement

The spectral measurements were correlated with measurements of the chlorophyll content of the rice and heavy metal concentrations. The metal content in the soil was analysed by the Chinese Academy of Agricultural Sciences, Beijing, China. The soils samples were firstly digested by reverse aqua-regia (HNO3: HCl = 3:1) (Stevens, 2002), then Cu was measured using a flame atomic absorption spectrophotometer (AAS) (Spectr AA 110/220, Varian, USA) and Cd with a graphite furnace AAS. Soil samples were also analysed for diethylene-triaminepentaacetic acid (DTPA) extractable heavy metals using the method of Lindsay and Norvell (1969) and the metal concentrations were determined by AAS.

A simple method of determining the chlorophyll content is the portable Chlorophyll Meter SPAD-502 (Minolta Corporation, NJ, USA). The chlorophyll content in rice leaves was measured at six randomly chosen times and the average value for each sample was calculated. The chlorophyll concentration was calculated from the SPAD-502 chlorophyll readings (Wood, Reeves, & Himelrick, 1993), using the following equation:

\[ y = 0.996x - 1.52 \]

where \( y \) is the chlorophyll concentration and \( x \) is the SPAD-502 chlorophyll readings (\( \mu g \text{ cm}^{-2} \)).

2.3 The effect of Cu and Cd contamination on rice

Cd is a non-essential element that can be easily absorbed by plants. While Cu is an essential element, high doses can adversely affect plant growth (Pahlsson, 1989). The interaction between Cu and Cd is complex and has an effect on their individual functions. Huang, Hu, and Liu (2009) demonstrated that soil application of Cu greatly enhanced Cd accumulation, but the application of Cd had a negligible effect on Cu uptake by rice plants. Biochemical, physiological, and structural aspects affected by excess Cu and Cd in rice included following: (1) Cd and Cu can inhibit the activities of several antioxidative enzymes including superoxide dismutase (SOD), ascorbate peroxidase (APOD), and glutathione reductase (GR) (Fernandes & Henriques, 1991); (2) they can inhibit the stomatal opening (Barcelo & Poschenrieder, 1990); (3) they damage the photosynthetic apparatus (Chien & Kao, 2000; Krupa, 1988; Sideleka & Baszynsky, 1993); (4) they are substituted for magnesium (Mg), the central atom of chlorophyll, and then reduce the chlorophyll content (Chien, Wang,

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**Table 1 – The information of the experiment sites.**

<table>
<thead>
<tr>
<th>Geographical location</th>
<th>Copper content (mg kg(^{-1}))</th>
<th>Cadmium content (mg kg(^{-1}))</th>
<th>Pollution level</th>
<th>Soil quality standard(^{a}) (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>43°52′2″N, 125°10′2″E</td>
<td>68.2</td>
<td>0.465</td>
<td>II</td>
<td>II (50 &lt; Cu &lt; 400; 0.3 &lt; Cd &lt; 0.6)</td>
</tr>
<tr>
<td>43°54′6″N, 125°10′4″E</td>
<td>45.5</td>
<td>0.182</td>
<td>I</td>
<td>I (35 &lt; Cu &lt; 50; 0.2 &lt; Cd &lt; 0.3)</td>
</tr>
<tr>
<td>44°06′3″N, 125°10′2″E</td>
<td>20.4</td>
<td>0.093</td>
<td>Safe</td>
<td>Safe (Cu &lt; 20; Cd &lt; 0.09)</td>
</tr>
</tbody>
</table>

\(^{a}\) Soil quality standard according to the Environment Monitoring Centre of China.
In summary, the main toxic effect of Cu and Cd is oxidative stress. Heavy metal toxicity in rice leaves was assessed by the decrease in chlorophyll and protein contents (Huang et al., 2009). An average value of chlorophyll concentration was obtained from four critical growth stages of rice. The result showed that Cd and Cu induced stress in rice had a close correlation with chlorophyll concentration in rice at different growth stages (Fig. 3). From Fig. 3, within seeding, tillering, booting and mature growth stages, the chlorophyll concentration of rice with safe level was higher than those with level I pollution, and higher than level II pollution. In addition, the greatest difference in chlorophyll concentration in rice with different pollution levels occurred at the mature growth stage. Therefore, the difference in chlorophyll concentration of rice proved credible and feasible method for estimating Cu and Cd contamination levels. Low values in the chlorophyll concentrations indicated that the rice was suffering from very serious contamination.

The reduction of chlorophyll concentration in rice is caused by Cd and Cu preferentially accumulating in the chloroplasts as the rice grows. Cd and Cu levels in rice leaves with different growth stages are displayed in Fig. 4. As seen in Fig. 4, the highest values of Cd and Cu always occurred in rice with level II pollution, followed by level I pollution, and then safe level. A distinction was found between the uptakes of Cd and Cu at different growth stages of rice. The highest values of Cd and Cu uptake occurred in the tillering and mature growth stages respectively.

### 2.4. Spectral indices used in the model

As illustrated in Fig. 2, in the NIR region, the leaf reflectance of rice under heavy metal stress is somewhat lower than that of the safe level. A number of studies have demonstrated that the shifts in vegetation spectra of plant under heavy metal stress occur in both the visible and the NIR part of the spectrum (Kooistra et al., 2004). With the previous analysis results, the primary effect of Cu and Cd metal-induced stress on rice is the corresponding reduction in chlorophyll. Therefore, our goal was to select spectral indices sensitive to leaf chlorophyll concentration in rice. Strong relationships exist between chlorophyll concentrations and spectral indices formulated with some specific narrow spectral bands including 550 nm, 670 nm, 700 nm, 800 nm (Haboudane et al., 2002; Zarco-Tejada, Miller, Noland, Mohammed, & Sampson, 2001). Therefore, several spectral indices formulated with the above values were selected in this study.

#### 2.4.1. Normalised difference vegetation index (NDVI)

The most well known and widely used vegetation index is the normalised difference vegetation index (NDVI) developed by Rouse, Haas, Schell, Deering, and Harlan (1974). It is based on the contrast between the maximum absorbance in the red due to chlorophyll pigments and the maximum reflection in the infrared caused by leaf cellular structure. Using hyperspectral narrow wavebands, this index is quantified by the following equation:

$$\text{NDVI} = \frac{R_{800} - R_{670}}{R_{800} + R_{670}}$$

where $R_x$ is the reflectance at the given wavelength (nm).

Our results showed that NDVI has a strong non-linear relationship with chlorophyll concentration (Fig. 5), the correlation coefficient ($R^2$) being 0.6986. Gallagher, Pechmann, Bogden, Grabosky, and Weis (2008) demonstrated that NDVI can predict heavy metal stress and that it had a curvilinear relationship with total heavy metal load ($R^2 = 0.85$).
2.4.2. Modified triangle vegetation index (MTVI)

The MTVI belongs to the triangle vegetation index family (Broge & Leblance, 2000). The general principle behind this index is to describe the radiative energy absorbed by the pigments as a function of the relative difference between red and NIR reflectance in conjunction with the magnitude of reflectance in the green region, where the light absorption by chlorophylls is relatively insignificant. The index is calculated as the area of the triangle defined by the green peak, the chlorophyll absorption minimum, and the NIR shoulder in spectral space. It based on the fact that chlorophyll absorption causes a decrease in red reflectance. Some researchers have tried to modify the triangle vegetation index by adjusting the coefficient and the waveband of equation. Guang and Liu (2009) developed the MTVI by as the followed equation:

\[
MTVI = 1.5\left[1.2\left(R_{712} - R_{550}\right) - 2.1\left(R_{670} - R_{550}\right)\right]
\]

(2)

The results showed that MTVI was insensitive to chlorophyll concentration of rice under heavy metal stress. This was attributed to the insignificant difference in the area of the triangle derived from green peak and the chlorophyll absorption maximum, especially in rice with level I pollution.

2.4.3. Modified chlorophyll absorption ratio index (MCARI)

To reduce non-photosynthetic factors, Kim, Daughtry, Chapelle, McMurtrey, and Walthal (1994) developed the chlorophyll absorption ratio index (CARI) which measures the depth of chlorophyll absorption at 670 nm relative to the green reflectance peak at 550 nm and the reflectance at 700 nm. It uses bands corresponding to the minimum absorption of the photosynthetic pigments, centred at 550 nm and 700 nm, in conjunction with the chlorophyll a maximum absorption band, around 670 nm. Daughtry et al. (2000) developed the MCARI which can be simplified as the following equation:

\[
MCARI = \frac{R_{670}}{R_{550}} - \frac{R_{700}}{R_{550}}
\]

Fig. 5 – Relationship between different vegetation indices and chlorophyll concentration.
Our results showed that MCARI was also insensitive to chlorophyll concentration of rice under heavy metal stress; while other researchers have reported that MCARI was sensitive to chlorophyll concentration (Wu, Niu, Tang, & Huang, 2008). The reason is that the green peak position moved towards longer wavelengths as the heavy metal content increased. Daughtry et al. (2000) have pointed out that MCARI was still sensitive to non-photosynthetic element effects, mainly at low chlorophyll concentrations.

### 2.4.4. Optimized soil-adjusted vegetation index (OSAVI)

Daughtry et al. (2000) proved that when MCARI is combined with a soil line vegetation index like OSAVI (Rondeaux, Steven, & Baret, 1996), the sensitivity to the underlying soil reflectance properties can be reduced. OSAVI belongs to the soil-adjusted vegetation index (SAVI; Huete, 1988) family and is defined by the following equation:

\[
\text{OSAVI} = \frac{(R_{670} - R_{800})}{(R_{670} + R_{800} + 0.5)}
\]  

(4)

As shown in Fig. 5, rice leaf chlorophyll concentration was strongly correlated with OSAVI ($R^2 = 0.6990$). This agrees well with the results of Haboudane et al. (2002).

### 2.4.5. Integrating two vegetation indices

Research has indicated that an integrated index modelling is more sensitive to chlorophyll content variations and more resistant to the variations of leaf area index (LAI) and solar zenith angle than a single vegetation index (Haboudane et al., 2002). Wu et al. (2008) proved that integrated indices transformed chlorophyll absorption ratio index (TCARI/OSAVI) [705,750] and MCARI/OSAVI [705,750] have better linearity with chlorophyll content together with high correlation: $R^2$ of 0.8808 and 0.9406 respectively. To improve sensitivity of the vegetation index to subtle variations in rice leaf chlorophyll concentration under heavy metal stress, in this paper, two integrated indices are proposed. They be defined by the following equations:

\[
\text{MTVI/MCARI} = \frac{1.5[1.2(R_{712} - R_{550}) - 2.1(R_{670} - R_{550})]}{[0.5(R_{712} - R_{550}) - 0.2(R_{670} - R_{550})]} 
\]  

(5)

\[
\text{MTVI/OSAVI} = \frac{1.5[1.2(R_{712} - R_{550}) - 2.1(R_{670} - R_{550})]}{(1 + 0.5)(R_{800} - R_{670})/(R_{800} + R_{670} + 0.5)} 
\]  

(6)

Our results indicated that the two integrated indices MTVI/MCARI, MTVI/OSAVI and leaf chlorophyll content were highly correlated with $R^2$ of 0.7280 and 0.7198 respectively (Fig. 5).

In sensitivity analysis, bands at 550 nm, 670 nm, 700 nm, 712 nm and 800 nm were selected. Therefore, reflectance in these bands was selected to formulate vegetation indices which may have potential in estimating chlorophyll concentration. Six indices (Table 2) were tested in this study; the result indicated that NDVI, OSAVI, MTVI/MCARI and MTVI/OSAVI were sensitive to chlorophyll content variations of rice under heavy metal stress.

### 2.5. Neural-network model development

#### 2.5.1. Data pre-processing phase

In this study, to avoid data saturation, the input variables in this model were normalised, based on their possible ranges using the following equation:

\[
x_{\text{norm}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \tag{7}
\]

where $x$, $x_{\text{min}}$, $x_{\text{max}}$ and $x_{\text{norm}}$ are the real-valued input variable, the minimum input variable, maximum input variable and its normalised value respectively. The output from a neural-network model is an indexed value that corresponds to the input variable. To get the real-valued output, the indexed output value needs to be de-normalised according to the following equation:

\[
y = y_{\text{min}} + y_{\text{norm}}(y_{\text{max}} - y_{\text{min}}) \tag{8}
\]

Where $y$, $y_{\text{min}}$, $y_{\text{max}}$ and $y_{\text{norm}}$ are the real-valued output variable, the minimum and maximum values of the real-valued output, and the indexed output value from the neural-network model, respectively.

#### 2.5.2. Model building phase

Artificial neural network (ANN) models have found wide applications, including prediction, classification, system modelling, signal processing, noise filtering (Pachepsky, Timlin, & Varallyay, 1996; Pal, Pal, Das, & Majumdar, 2003; Plate, Bert, Grace, & Band, 2000; Tumbo et al., 2002). BP neural networks are popular neutral network architectures (Bishop, 1995; Cichocki & Unbehauen, 1993; Foody, 1995; Pachepsky et al., 1996; Pal et al., 2003; Plate et al., 2000; Tumbo et al., 2002). In this paper, a BP neural-network model was established to estimate the leaf chlorophyll concentration, which in turn, indicates the stress levels of rice growing under heavy metal stress. The input variables for the BP neural-network model were NDVI, OSAVI, MTVI/OSAVI and MTVI/MCARI, while the output variable of this model was chlorophyll concentration.

### Table 2 – Hyperspectral vegetation indices used in the sensitivity analysis.

<table>
<thead>
<tr>
<th>Indices</th>
<th>Wavebands (nm)</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDVI[670,800]</td>
<td>670,800</td>
<td>$\frac{R_{800} - R_{670}}{R_{800} + R_{670}}$</td>
<td>Rouse et al. 1974</td>
</tr>
<tr>
<td>OSAVI[670,800]</td>
<td>670,800</td>
<td>$\text{OSAVI} = \frac{(1 + 0.5)(R_{800} - R_{550})}{(R_{800} + R_{550} + 0.5)}$</td>
<td>Huete, 1988</td>
</tr>
<tr>
<td>MCARI[670,700]</td>
<td>550,670,700</td>
<td>$\text{MCARI} = \frac{[R_{712} - R_{550}] - 0.2(R_{670} - R_{550})}{[R_{712} + R_{550}] - 2.1(R_{670} - R_{550})}$</td>
<td>Daughtry et al. 2000</td>
</tr>
<tr>
<td>MTVI[550,712]</td>
<td>550,670,712</td>
<td>$\text{MTVI} = 1.5[1.2(R_{712} - R_{550}) - 2.1(R_{670} - R_{550})]$</td>
<td>Guang &amp; Liu, 2009</td>
</tr>
<tr>
<td>MTVI/MCARI[550,712]</td>
<td>550,670,700,712</td>
<td>$\text{MTVI/MCARI} = \frac{1.5[1.2(R_{712} - R_{550}) - 2.1(R_{670} - R_{550})]}{[0.5(R_{712} - R_{550}) - 0.2(R_{670} - R_{550})]}$</td>
<td>-</td>
</tr>
<tr>
<td>MTVI/OSAVI[550,800]</td>
<td>550,670,712,800</td>
<td>$\text{MTVI/OSAVI} = \frac{1.5[1.2(R_{712} - R_{550}) - 2.1(R_{670} - R_{550})]}{(1 + 0.5)(R_{800} - R_{670})/(R_{800} + R_{670} + 0.5)}$</td>
<td>-</td>
</tr>
</tbody>
</table>
The topological structure of this BP neural-network model consisted of four input neurons in the input layer, one output neuron in the output layer and one or two hidden layers. The flow chart of the 4-6-1 structure as an example is shown in Fig. 6.

The model building phase aims to produce a robust ANN model that can accurately map outputs from inputs. A good ANN model mainly relies on the choice of an optimum neural network architecture and network internal parameters (i.e., the number of hidden layers, number of neurons, type of scaling and activation functions, learning and momentum rates, and stopping criterion), and the selection of the training algorithm (Gautam, Panigrahi, & Franzen, 2006).

In this study, different network architectures, activation functions and training algorithms were tested. The ideal activation function develops models using a sigmoid tangent function that scales the input data in the open interval of \( -1 \rightarrow 1 \), a hidden layer utilising the sigmoid tangent function, and an output layer utilising sigmoid logistic functions which scales the input data to lie within the open interval of \( 0 \rightarrow 1 \). The typical gradient descent BP algorithm in learning algorithms proved to be suitable for this study. Maier and Dandy (2000) and Zealand, Burn, and Simonovic (1999) reported that over 80% of previous neural-network models used a gradient descent BP training algorithm, which is a supervised learning paradigm. By supervising learning, a desired response is available to guide the learning process. In a BP algorithm, the weights are initially assigned arbitrary small values. As training progresses, the root mean square error (RMSE) between the target output and the network output is calculated. If the network output does not produce the expected criterion, the training transfers to the BP. The error signal carries through a reverse calculation by a connecting pathway. The gradient descent BP algorithm utilises a learning rate and momentum coefficient to adjust weight values and to move towards a global minimum in the error surface. Fig. 7 shows the gradient descent BP learning algorithm in the neural-network architecture.

By trying different numbers of hidden layers and different numbers of neurons in each hidden layer, the optimum model architectures were 4-6-1, 4-8-1, 4-10-2-1 and 4-10-3-1. Compared with one hidden layer, two hidden layers had higher accuracy in estimating chlorophyll concentration. Table 3 summarised the optimum model architecture and internal parameters utilising in the different models developed in this study.

2.5.3. Model evaluation phase

Generally, RMSE and average accuracy have been used to measure the performance of neural-network models (Gautam...
et al., 2006). In this study, the parameters were: (i) RMSE; (ii) average accuracy ($P_{av}$); (iii) $R^2$. The three parameters were computed by:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (y_{ai} - y_{mi})^2}{N - 1}}$$

(9)

Where $y_{ai}$, $y_{mi}$, RMSE are the real-valued output variable, measured output variable, RMSE between real-valued output variable and measured output variable respectively, $N$ is the sample number. The lower RMSE, the better the performance of the model.

$$P_{av} = \frac{\sum_{i=1}^{N} P_i}{N}$$ and $$P_i = \left[1 - \frac{y_{ai} - y_{mi}}{y_{ai}}\right]$$

(10)

Where $P_{av}$ and $P_i$ are the average accuracy and the accuracy of the $i^{th}$ result. $P_{av}$ provides information on the accuracy that the model can yield using a given data set. The nearer the value approaches 1; the better is the performance of the model.

$$R^2 = \frac{\left[\sum_{i=1}^{N}(y_{ai} - \bar{y}_a)\sum_{i=1}^{N}(y_{mi} - \bar{y}_m)\right]^2}{\sum_{i=1}^{N}(y_{ai} - \bar{y}_a)^2 \sum_{i=1}^{N}(y_{mi} - \bar{y}_m)^2}$$

(11)

Where $R^2$, $\bar{y}_a$ and $\bar{y}_m$ are the correlation coefficient, average measured output variable and average real-valued output variable respectively. The $R^2$ represents the correlation between predicted and measured variables. It is assumed that the predicted and measured variables follow a normal distribution. Its value ranges from 0 to 1. The higher the value of the correlation, the stronger is the indication of existing linear relations between the actual and predicted variables.

3. Result and discussion

Due to the large variation of chlorophyll concentration in rice with different levels of pollution that occur in the mature growth stage, the best stage for monitoring heavy metal stress is at the mature growth stage of rice. Therefore, in this research, 138 training data sets and 69 test data sets from the mature growth stage of rice were obtained for different levels of heavy metal pollution. By trying different neutral network architectures, network internal parameters and training algorithms, satisfactory neural-network models were developed (Table 3); namely, the BP neural-network architectures were 4-6-1, 4-8-1, 4-10-2-1 and 4-10-3-1; the learning algorithm was a gradient descent BP algorithm.

Table 3 – Summary table showing optimum ANN model’ architecture and internal parameters.

<table>
<thead>
<tr>
<th>Model</th>
<th>Optimum network</th>
<th>Activation function</th>
<th>Training algorithm</th>
<th>Learning rate</th>
<th>Momentum coefficient</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>$P_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-6-1</td>
<td>[tansig, logsig]</td>
<td>Traindm</td>
<td>0.2</td>
<td>0.2</td>
<td>0.8040</td>
<td>4.01</td>
<td>0.8516</td>
</tr>
<tr>
<td>2</td>
<td>4-6-1</td>
<td>[tansig, linear]</td>
<td>Traindm</td>
<td>0.2</td>
<td>0.2</td>
<td>0.7412</td>
<td>5.25</td>
<td>0.8423</td>
</tr>
<tr>
<td>3</td>
<td>4-8-1</td>
<td>[tansig, logsig]</td>
<td>Traindm</td>
<td>0.2</td>
<td>0.2</td>
<td>0.8014</td>
<td>3.37</td>
<td>0.8664</td>
</tr>
<tr>
<td>4</td>
<td>4-8-1</td>
<td>[tansig, linear]</td>
<td>Traindm</td>
<td>0.2</td>
<td>0.2</td>
<td>0.7016</td>
<td>4.34</td>
<td>0.8510</td>
</tr>
<tr>
<td>5</td>
<td>4-10-3-1</td>
<td>[tansig, tansig, logsig]</td>
<td>Traindm</td>
<td>0.15</td>
<td>0.2</td>
<td>0.8483</td>
<td>3.14</td>
<td>0.8662</td>
</tr>
<tr>
<td>6</td>
<td>4-10-3-1</td>
<td>[tansig, tansig, linear]</td>
<td>Traindm</td>
<td>0.15</td>
<td>0.2</td>
<td>0.7378</td>
<td>4.03</td>
<td>0.8421</td>
</tr>
<tr>
<td>7</td>
<td>4-10-2-1</td>
<td>[tansig, tansig, logsig]</td>
<td>Traindm</td>
<td>0.15</td>
<td>0.2</td>
<td>0.9014</td>
<td>2.58</td>
<td>0.8922</td>
</tr>
<tr>
<td>8</td>
<td>4-10-2-1</td>
<td>[tansig, tansig, linear]</td>
<td>Traindm</td>
<td>0.15</td>
<td>0.2</td>
<td>0.7791</td>
<td>3.06</td>
<td>0.8737</td>
</tr>
</tbody>
</table>

Notes: Tansig denotes sigmoid tangent function; logsig denotes sigmoid logistic functions; linear denotes linear function; traindm denotes gradient descent BP algorithm.

Table 4 – Quantitative relationships of leaf chlorophyll concentration ($y$) to individual spectral index ($x$) in rice.

<table>
<thead>
<tr>
<th>Spectral index</th>
<th>Regression equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDVI</td>
<td>$y = 4.9705x - 0.7648$</td>
<td>0.6799</td>
</tr>
<tr>
<td></td>
<td>$y = 5.6535x^2 - 2.0623x + 1.3419$</td>
<td>0.6986</td>
</tr>
<tr>
<td></td>
<td>$y = 0.5746e^{2.7683x}$</td>
<td>0.6514</td>
</tr>
<tr>
<td></td>
<td>$y = 2.8959ln(x) + 3.7551$</td>
<td>0.6441</td>
</tr>
<tr>
<td></td>
<td>$y = 7.8019x - 0.7146$</td>
<td>0.6780</td>
</tr>
<tr>
<td></td>
<td>$y = 14.493x^2 - 3.5562x + 1.3885$</td>
<td>0.6990</td>
</tr>
<tr>
<td></td>
<td>$y = 0.5859e^{5.0489x}$</td>
<td>0.6521</td>
</tr>
<tr>
<td></td>
<td>$y = 2.8241ln(x) + 5.0382$</td>
<td>0.6384</td>
</tr>
<tr>
<td></td>
<td>$y = -0.6401x + 4.871$</td>
<td>0.6886</td>
</tr>
<tr>
<td></td>
<td>$y = 0.1125x^2 - 1.5414x + 6.5817$</td>
<td>0.7198</td>
</tr>
<tr>
<td></td>
<td>$y = 6.699e^{-2.7379x}$</td>
<td>0.6568</td>
</tr>
<tr>
<td></td>
<td>$y = 2.4517ln(x) + 5.6369$</td>
<td>0.7179</td>
</tr>
<tr>
<td></td>
<td>$y = -1.2729x + 4.8087$</td>
<td>0.6131</td>
</tr>
<tr>
<td></td>
<td>$y = 0.9931x^2 - 5.3069x + 8.9348$</td>
<td>0.7280</td>
</tr>
<tr>
<td></td>
<td>$y = 6.7585e^{0.5712x}$</td>
<td>0.6236</td>
</tr>
<tr>
<td></td>
<td>$y = -2.7379ln(x) + 4.0951$</td>
<td>0.6794</td>
</tr>
</tbody>
</table>

Fig. 8 – Comparison of predicted chlorophyll concentration using an artificial neural-network model and multiple regression models.
algorithm; with a the learning rate of 0.2 or 0.15; the momentum coefficient was 0.2; the activation function was the sigmoid tangent function in the input layer and hidden layer and there were sigmoid logistic functions in the output layer. According to the three parameters for assessing the performance of the neural-network models, optimal network architecture should have the lowest RMSE, and the value of $P_{av}$ and $R^2$ close to 1. As seen in Table 3, the optimal network architecture was obtained when the neural-network model had ten neurons in the first hidden layer and two neurons in the second hidden layer. The $R^2$ for the optimal structure BP network model was 0.9014; RMSE was 2.58 and $P_{av}$ was 0.8922.

To assess the performance of the neural-network model more thoroughly, a comparison between the neural-network model and a statistical regression model was made. The baseline model was a best-fit regression model obtained from four spectral indices analysis of the rice crop and estimated values of the optimal structure BP network model. Applying two methods to the results gave the following respectively:

\[
y = 3.209 + 1.993 \times \text{NDVI} - 0.6390 \times \text{OSAVI} - 0.363 \\
   \times (\text{MTVI}/\text{OSAVI}) - 0.220 \times (\text{MTVI}/\text{MCARI})
\]

Where $R^2 = 0.713$, $y$ is predicted chlorophyll concentration from four spectral indices using multiple regression models.

\[
y_{ai} = 0.9873y_{mi} - 0.091
\]  

(13)

Where $R^2 = 0.9014$, $y_{ai}$, $y_{mi}$ are the real-valued output variable (predicted chlorophyll concentration), measured output variable (measured chlorophyll concentration) using optimal structure BP network model.

The quantitative relationships between leaf chlorophyll concentration and individual spectral indices in rice are summarised in Table 4. As shown in Fig. 8 and Table 4, the neural-network model showed stronger correlation than the statistical regression model.

Before a neural-network model can be confidently applied to predict the leaf chlorophyll concentration to determine rice heavy metal stress levels, it is necessary to validate the model by checking the degree to which the model predicted leaf chlorophyll concentration matches the measured leaf chlorophyll concentration obtained from field tests. Fig. 9 shows that the predicted leaf chlorophyll concentration matched the measured leaf chlorophyll concentration well. As well as predicting that the rice leaf chlorophyll concentration increases with decreasing heavy metal content, the highest chlorophyll concentration values were predicted for the experiment site with safe level, followed by that of level I pollution and then level II pollution.

4. Conclusion

Hyperspectral data can provide an effective means for estimating leaf chlorophyll concentration variation of crops under heavy metal stress. Because of heavy metal stress, the biochemical component of the crop changes and crop leaf cellular structure is damaged, resulting in differences in
sensory reflectance. Therefore, it is feasible to detect such variations in the biochemical composition of crops, specifically using leaf chlorophyll concentration in the crop through spectral reflectance. In this research, some spectral indices were formulated by the reflectance of two or more bands. In sensitivity analysis, it was found that NDVI, OSAVI, MTVI/MCARI and MIVI/OSAVI are more sensitive to chlorophyll concentration than the other indices, so they were selected to estimate leaf concentration. The relationship between these indices and chlorophyll concentration was developed by the BP neural-network model. The input neurons in the model were NDVI, OSAVI, MTVI/MCARI and MIVI/OSAVI, and the output neuron from this model was chlorophyll concentration which was then used to assess rice heavy metal stress levels. After testing a training set, our results showed that the neural-network model developed can accurately estimate chlorophyll concentration variation to assess heavy stress levels. When crops were contaminated by heavy metal, the leaf chlorophyll concentration in the crop decreased. The higher the level of heavy metal content, the lower the leaf chlorophyll concentration. This finding agrees with the results of Kastori et al. (1998).

This research verified that the neural-network model developed here could provide an effective and faithful estimation of leaf chlorophyll variation based on the four performance spectral indices. In trials with the BP neural-network model, the optimal model, with ten neurons in the first hidden layer and two neurons in the second hidden layer, performed better than a statistical model of multivariable regression parameters. Changes in the biochemical composition of crops, specifically using combined geochemistry, field spectroscopy, and hyperspectral remote sensing: a case study of the Rodalquilar mining area, SE Spain. Remote Sensing of Environment, 112, 3222–3233.


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