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Monitoring stress levels on rice with heavy metal pollution from hyperspectral reflectance data using wavelet-fractal analysis

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ABSTRACT

Remote sensing allows monitoring heavy metal pollution in crops for agricultural production and food security. This paper presents an approach to wavelet-fractal analysis for exploring a set of sensitive spectral parameters to monitor the heavy metal pollution levels in rice crops from hyperspectral reflectance data. Hyperspectral and biochemical data were collected from three study farms in Changchun, Jilin Province, China. Our study explored the fractal dimension of reflectance with wavelet transform (FDWT) that demonstrated a better performance than other existing methods. Our results obtained in this study show that the red edge position (REP) was the most sensitive indicator for monitoring the heavy metal pollution levels in rice crops among common indices. As compared with REP, the FDWT is more sensitive to biochemical composition, namely with respect to chlorophyll concentrations, N, Cu and Cd. The established linear models showed a correlation coefficient (R^2) above 0.70, model efficiency (ME) above 0.65 and a root mean square error (RMSE) below 3.5. Minimum FDWT values occurred in rice with Level II pollution followed by Level I pollution, and finally the safe level. This study suggests that wavelet transform is well suited as a spectral analysis method to eliminate noise and amplify the stress information from heavy metals. The wavelet transform in conjunction with fractal analysis is promising for detecting heavy metal-induced stress in rice crops.

1. Introduction

One of the major environmental problems resulting from rapid industrial development in today's China is the heavy metal contamination of soils. High levels of heavy metal concentrations may influence plant growth in a negative way and, if these heavy metals end up in agricultural crops or in grazing lands, they pose a serious health threat. As is well-known, rice, which is a staple food crop in China, uses 24% of all agricultural land to provide about 40% of the overall yield, suggesting that the heavy metal pollution levels in rice crops may be a critical problem for food safety in China (Hu et al., 2002). Therefore, timely and accurate detection of heavy metal pollution levels in rice is an essential issue. Traditionally, soil testing, plant tissue analysis, and long-term field trials have been used to assess the heavy metal pollution levels in rice crops (Hang et al., 2009). These methods, however, are very labor-intensive and time-consuming. Hyperspectral remote sensing data have been an alternative to conventional ground-based methods to detect plant stress and play a valuable role in providing time-specific and time-critical information for precision farming, due to the ability to measure biophysical indicators and detect spatial variability. The existing studies demonstrated that metal stress related to spectral features can be discriminated from field data by using high-spectral resolution instrumentation and analysis techniques (Collins et al., 1983; Clevers et al., 2004). Some researchers have applied original hyperspectral reflectance to detect the heavy metal pollution levels in crops under controlled laboratory conditions by adding copper, lead, chromium, or zinc, etc. (Kemper and Sommer, 2002; Chi et al., 2006). However, the pollution level in the real world ecosystems is relatively low, which means that no visible symptoms exist in leaf reflectance spectra. Other researchers have developed spectral analysis methods, such as derivative transform (Gitelson et al., 1996; Ren et al., 2008), continuum removal (van der Meer, 2006; Liu et al., 2010c), in order to enhance the vegetative stress signals through minimizing the effects of background materials. Several studies using hyperspectral data of vegetation have already demonstrated the benefits of wavelet transform for spectral smoothing and noise removal (Bruce and Li, 2001; Schmidt and Skidmore, 2004). Recent studies have demonstrated the potential of fractal analysis for analyzing the vegetation health status (Du et al., 2009) from remotely sensed images and leaf or canopy reflectance spectra. Few papers, however, were found to apply wavelet transform in conjunction with fractal techniques to extract spectral parameters for monitoring metal-induced stress on plants. Compared with

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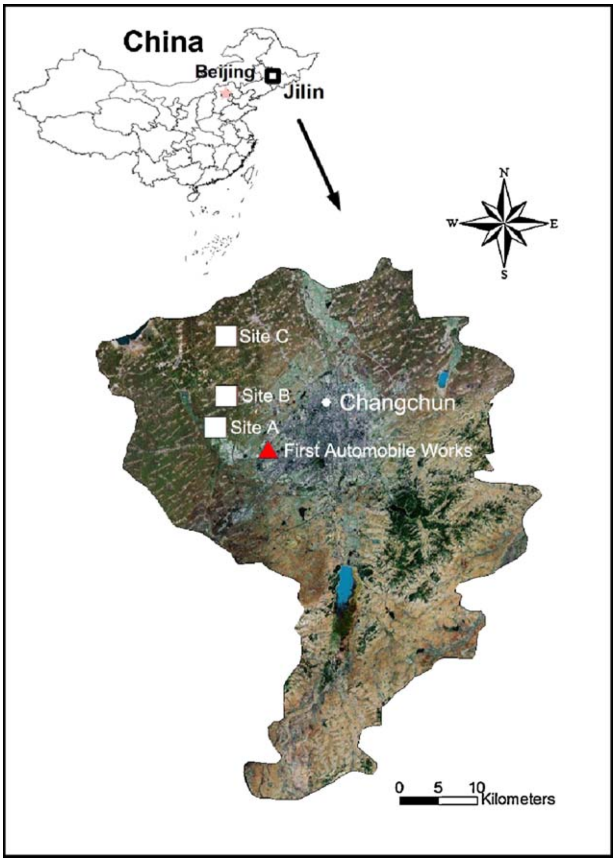

Fig. 1. Location map for experimental sites in Changchun, Jilin Province, China.

derivative analysis, wavelet transform is equally sensitive but has the added advantage of being an excellent frequency filter and an intensity filter. Therefore, using it for field spectral data analysis in the frequency domain can be shown to be more sensitive in detecting stress and most effective in filtering out background noise in the spectral data (Chang and Collins, 1983). In addition, fractal dimensions can be used to explain the comprehensive variation of spectrum curves as a 'global parameter'. So, it has the advantage of capturing much more information provided by reflectance spectra than previous analytical approaches such as red edge parameters and some spectral vegetation indices for investigating changes in plant stress. This paper aims at detecting the heavy metal pollution levels in rice crops through improving the sensitivity of spectral parameters by applying wavelet analysis and fractal techniques to leaf reflectance spectra.

2. Study area and data

2.1. Field experiment design

The City of Changchun, Jilin Province is an important industrial and agricultural region in China. Some areas have been contaminated by industrial pollutants, particularly by heavy metals. Suburban farms have soils with copper (Cu) and cadmium (Cd) at higher concentrations than what is considered to be normal for the area. Three field plots (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 plots (labeled A, B, and C) varied. The soil and the stress rates were determined according to a soil sample analysis (Table 1) to be at the safe level, Level I pollution and Level II pollution, respectively. The site is within the temperate continental climate zone with a mean annual rainfall of 522–615 mm, where land is predominantly of the black soil variety, with a pH of 7.0–7.3 and 2–4% of sufficient organic matter. The crop selected in this site was rice, which is one of the most important crops in China.

2.2. Field data

The data were collected during four days of typical rice growing season: 8 July, 4 August, 29 August and 18 September 2008, which corresponded to the seeding, tillering, booting and mature growth stages of rice. 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). This spectrometer was fitted with fiber optics having a 10° field of view, and was operated in the 350–2500 nm spectral regions with the sampling interval of 2 nm. Reflectance spectra were measured through calibration with a standardized white Spectralon panel. A panel radiance measurement was taken before and after the crop measurement with 2 scans each time. The measurements were carried out from a height of 1.0 m above the rice canopy. Crop radiance measurements were taken at 30–40 sample sites over each plot and each site was scanned 10 times. These measurements were then averaged for the particular site.

A simple method of determining the chlorophyll content is the portable Chlorophyll Meter SPAD-502 (Minolta Corporation, NJ, USA). Within rice canopy of the spectral measurement for each sample site, four rice plants were selected, and the chlorophyll content in rice leaves was measured at six chosen leaves per individual rice plant, namely random two leaves from the top, middle and bottom, respectively, and the average value (the total of chlorophyll meter reading/24) for each sample site was calculated. The chlorophyll concentration was calculated from the SPAD-502 chlorophyll readings (Wood et al., 1993) by

$$y = 0.996x - 1.52 \quad (1)$$

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

Crop and soil samples were taken almost synchronously with canopy spectral reflectance measurements. Both the leaves per rice (used as chlorophyll measurement) and the soil per sample site were collected and placed into respective sealed plastic bags to obtain biochemical composition, such as nutrient elements and heavy metal concentrations. Heavy metal concentration (Cu, Zn, Pb, Cd, Cr, and As) in the soil and crop samples were determined by flame atomic absorption spectrometry (AAS), after nitric–perchloric acid (2:1) digestion. Soil extractable metals were separated with 5 mM diethylenetriaminepentaacetic acid (DTPA)/10 mM $CaCl_2$/100 mM triethanolamine at pH 7.3 (Lindsay and Norvell, 1978). Nitrogen in rice leaves was measured by elemental analyzer (Leco, USA) at the Chinese Academy of Agricultural Sciences (Bao, 2005).

3. Method

3.1. Hyperspectral data analysis

3.1.1. Discrete wavelet transform

Wavelets are mathematical functions that are used to dissect data into different frequency components, each of which is characterized with a resolution appropriate to its scale (Strang, 1993). Wavelet transform has an excellent time and frequency property. It can make the components of interest that are submerged in an original signal become distinct with certain scales (Blackburn, 2007). In this study, hyperspectral reflectance was performed by

Table 1
The information of the three field plots.

Geographical location	Copper content (mg kg^{-1})	Cadmium content (mg kg^{-1})	Pollution level	Soil quality standard[a] (mg kg^{-1})
43°52.2′ N, 125°10.2′ E	68.2	0.465	II	II ($50 \leq Cu \leq 400$; $0.3 \leq Cd \leq 1.0$)
43°54.6′ N, 125°10.4′ E	45.5	0.182	I	I ($35 \leq Cu < 50$; $0.2 \leq Cd < 0.3$)
44°06.3′ N, 125°10.2′ E	20.4	0.093	Safe	Safe ($Cu < 20.8$; $Cd < 0.097$)

[a] Soil quality standard according to the Environment Monitoring Centre of China.

discrete wavelet transform to amplify the stress information associated with heavy metal pollution. The original spectral signal can be expressed by

$$f(\lambda) = a_j(\lambda) + \sum_{i=1}^{j} d_i(\lambda) \quad (2)$$

where $f(\lambda)$ is the original signal, a is the low-frequency component and d is the high-frequency component.

Here, rice reflectance spectra between 350 and 1300 nm was taken into account. The primary reason is that heavy metal-induced stress occurred in both the visible and near infrared parts of the spectrum. Also this is because absorption by atmospheric water vapor occurred in the regions around 1400 and 1900 nm, and the relative high noise level occurred in the spectra between 1900 and 2500 nm. In this study, Daubechies db5 as mother wave and five decomposition levels were considered on the basis of our previous study (Liu et al., 2010a). Firstly, 'db5' wavelet function provides a good balance between wavebands and frequency localization. Secondly, 'db5' wavelet function has proved to be successful in eliminating noise and amplifying the stress information from heavy metals through selection of the proper decomposition level of signal. The reflectance curve was filtered using a discrete wavelet transform implemented in Matlab. In this way, the curve was decomposed into a low-frequency component (a5) and high-frequency components (d1, d2, d3, d4, and d5) and the general flow for decomposition spectral reflectance curve is shown in Fig. 2(3). High-frequency components are suitable for analyzing subtle changes in the reflectance of adjacent wavebands. The results showed that the fifth high-frequency components (d5) had a good capacity for detecting stress information in a satisfactory way by reducing the impact of atmospheric scattering, absorption, background and equipment noise on the spectral signal of rice (Liu et al., 2010a).

3.1.2. Fractal dimension calculation

Fractals, here referring to broken or irregular fragments, were first introduced by Mandelbrot (1967) to describe complex and irregular natural objects. They can be generally defined as geometric shapes that have two properties: self-similarity and fractional dimensionality. A number of studies demonstrated that remotely sensed images and hyperspectral reflectance proved to have fractal characteristics (Qiu et al., 1999; Du et al., 2009). Similarly, d5, which belongs to the fraction of original reflectance, has fractal properties. Since there is a noticeable difference occurring in 480–850 nm region of the d5 curve for different stress levels of rice with heavy metals (Liu et al., 2010a), fractal dimensions of original spectral reflectance and d5 in the 480–850 nm and 350–1300 nm regions were both calculated to quantitatively and comprehensively analyze stress levels of rice with heavy metals. In this study, fractal dimensions were calculated by the box-counting method, which is based on the division of an area into regular boxes with the same box edge length (Borodich, 1997).

$$D = \lim_{n \to \infty} \frac{\log M(n)}{n \log 2} \quad (3)$$

where D is the fractal dimension, $M(n)$ and n is the count of boxes in the grid divided curve and scales, respectively. Fractal dimension (D) is a quantitative measure of complexity in the shape of the spectral signal. Its value ranges from 1.0 to 2.0. In this study, FD and FDWT in the following text of this paper denote fractal dimensions of original reflectance and fractal dimensions of reflectance with wavelet transform (namely fractal dimension of d5), respectively. We delineate the fractal dimensions of the 480–850 nm and 350–1300 nm regions, in order to facilitate interpretation and discussion, with subscripts indicating the range of the wavelength used. $FD_{480–850}$ or $FDWT_{480–850}$ represents FD or FDWT involving bands 480–850 nm and $FD_{350–1300}$ or $FDWT_{350–1300}$ denotes FD or FDWT involving bands 350–1300 nm.

3.2. Spectral parameters

3.2.1. Common spectral parameters

Generally speaking, spectral indices for detecting heavy metal pollution levels have been primarily classified into three categories (Table 2). (i) Derivative spectral indices, such as blue edge, chlorophyll absorption edge and red edge. The shift of red edge position (REP) was the most well known and widely applied spectral index as a sensitive indicator for detecting heavy metal pollution levels in rice crops (Gitelson et al., 1996; Ren et al., 2008). (ii) Normalized spectral absorption depth, which is the standard transform in spectroscopy through continuum removal to enhance the spectral absorption features based on metal binding mechanisms. It includes variations in absorption features, such as the peak depth and peak area at specific wavebands (van der Meer, 2006; Liu et al., 2010c). (iii) Integrated spectral indices, which combine two or more spectral bands to enhance the vegetative signal while minimizing background effects and are commonly used to measure the sensitivity of vegetation to heavy metal stress (Kooistra et al., 2004; Gallagher et al., 2008).

3.2.2. FDWT spectral parameters

In this study, we propose a novel procedure using wavelet transform in combination with fractal analysis to estimate spectral parameters to be used in the FDWT to detect the heavy metal pollution levels in rice crops. The procedure for the calculation of the FDWT spectral parameters can be summarized as follows (see Fig. 2):

1) Hyperspectral reflectance was performed by wavelet transform to reduce the impact of noise and amplify the stress information associated with heavy metal pollution.
2) Fractal dimension of d5 was calculated by the method of box dimension. In this study, $FDWT_{480–850}$ and $FDWT_{350–1300}$ were explored as the new proposed spectral parameters based on the above analysis. According to the tillering growth stage as the best-detected phase of rice with heavy metal pollution (Ren et al., 2008), hyperspectral reflectance of rice from the tillering growth stage were selected to obtain spectral parameters.

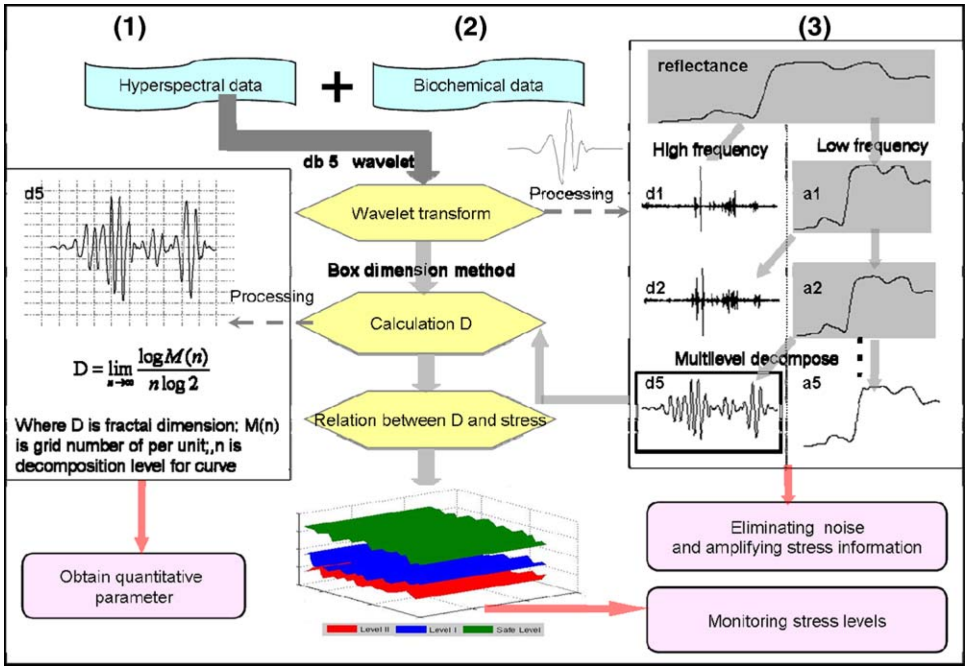

Fig. 2. The general flow chart of monitoring the stress levels of rice under different heavy metal pollution.

3.3. Analysis and testing of estimation model

3.3.1. Sensitivity analysis

The variations of biochemical composition occur, when rice is affected by heavy metal in soils. The important variation of biochemical composition in rice is the increase of heavy metal content, which results in the change of nutrient elements and pigment concentrations in rice (Chien et al., 2001; Chi et al., 2006). In this study, chlorophyll, N, Cu, and Cd in rice leaves were selected as sensitive biochemical composition to stress levels according to previous studies where the concentration of Cu and Cd in plants serve as direct and useful indicators of Cu and Cd contaminations in soil (Pugh et al., 2002) and the chlorophyll concentration and nitrogen content of plant were both affected by excessive Cu and Cd concentrations in plants (Fernandes and Henriques, 1991; Lagriffoul et al., 1998; Chien et al., 2001; Liu et al., 2010b). In addition, the above four biochemical compositions correlate to each other. The interaction between Cu and Cd is complex and has an effect on their individual functions. Huang et al. (2009) demonstrated that Cu greatly enhanced Cd accumulation, but the application of Cd had a negligible effect on Cu uptake by rice plants. Cu and Cd in rice are substituted for magnesium (Mg), the central atom of chlorophyll, and then reduce the chlorophyll content (Lagriffoul et al., 1998; Chien et al., 2001). Some researchers demonstrated that crop N content is positively correlated to leaf chlorophyll content (Jongschaap and Booij, 2004; Botha et al., 2007). That is to say, Cu and Cd in rice have indirect influence on N content in rice. A number of field studies have demonstrated that the general shape of the spectrum and the distinctive absorption features in the spectrum can change due to variations of biochemical composition in crops with heavy metal stress (Chang and Collins, 1983; Kooistra et al., 2004). Therefore, hyperspectral reflectance is feasible to estimate changes in biochemical composition.

3.3.2. Relationship between FDWT spectral parameters and stress levels

Due to chlorophyll, N, Cu, and Cd as sensitive biochemical composition to stress levels based on the above discussion, the regression model was created to establish the relationship between the spectral parameters and chlorophyll, N, Cu, and Cd. Whether the function was linear or power or exponential depends on R^2 between the spectral parameter and the biochemical composition. To quantify performance of model established for assessing stress level, three evaluation parameters between the measured values and the predicted values were calculated: model efficiency (ME), the correlation coefficient (R^2), and the root mean square error (RMSE). The three parameters were computed by:

$$\mathrm{ME} = 1 - \frac{\sum_{i}^{n}(y_{pi} - y_{mi})^2}{\sum_{i=1}^{n}(y_{mi} - \overline{y_m})^2} \quad (4)$$

where y_{pi}, y_{mi}, $\overline{y_m}$ are the predicated value, measured value and average measured value, respectively; n is the sample number. ME values range from 0 to 1. The higher ME values indicate the better

Table 2
Summary of the common spectral indices for assessing of plant under heavy metal stress.

Spectral indices	Formula/meaning	Spectral analysis method	Reference
Blue edge	Maximum slope of reflectance in blue regions	Derivative analysis	Chang and Collins (1983)
Chlorophyll absorption position	Maximum value in chlorophyll absorption	Derivative analysis	Chang and Collins (1983)
Red edge	Maximum slope of reflectance spectra between the red and NIR	Derivative analysis	Chang and Collins (1983)
D_n	Normalized spectral absorption depth at specified bands	Continuum removal	Liu et al. (2010c)
DVI	DVI = $R_{nir} - R_r$	Bands integrated	Kooistra et al. (2004)
NDVI	NDVI = $\frac{R_{nir}-R_r}{R_{nir}+R_r}$	Bands integrated	Gallagher et al. (2008)

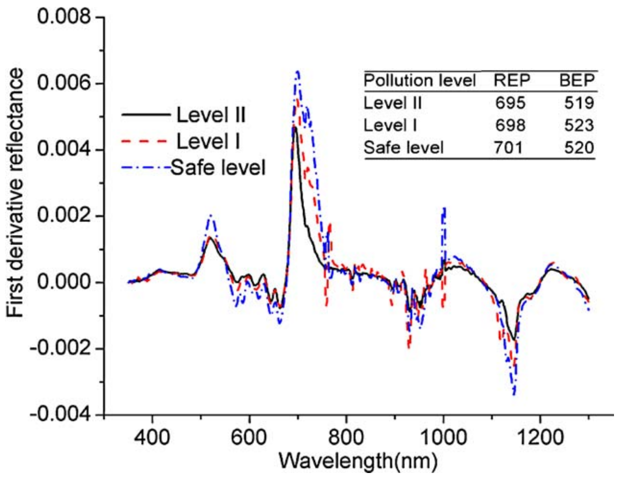

Fig. 3. The first derivative reflectance of rice under different heavy metal pollution. REP and BEP denote red edge position and blue edge position measured in nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

prediction model's efficiency:

$$R^2 = \frac{\left[\sum_{i=1}^{n}(y_{pi} - \overline{y_p})\sum_{i=1}^{m}(y_{mi} - \overline{y_m})\right]^2}{\sum_{i=1}^{n}(y_{pi} - \overline{y_p})^2\sum_{i=1}^{n}(y_{mi} - \overline{y_m})^2} \quad (5)$$

where $\overline{y_m}$ and $\overline{y_p}$ are the average measured value and the average predicated value, respectively. R^2 is the correlation coefficient, which represents the correlation between the predicted and measured value. The higher the R^2 value is, the stronger the indication of an existing linear relationship between the measured and predicted values.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(y_{pi} - y_{mi})^2}{n-1}} \quad (6)$$

where RMSE is the root mean square error between the predicted and measured value. The lower RMSE, the better the performance of the model.

In this study, three-dimensional (3D) models were established to visually describe the relationship between spectral parameters and stress levels, in which the *x* and *y* coordinates are used as the sample grids and the *z* coordinate represents the FDWT (fractal dimension of d5) or FD (fractal dimension of original reflectance) corresponding to the sample grids of cultivated rice. *z* values are simulated by the famous Delaunay, which is used to create a triangular grid for scattered data points (Weatherill and Hassan, 1994). The 3D models were conducted using a routine written in Matlab. Intervals of the different curved surfaces can suggest that spectral parameters matching with *z* can distinguish the heavy metal stress levels in rice crops effectively. The intersection of the different curved surfaces indicates that spectral parameters matching with *z* is poor at differentiating the heavy metal stress levels in rice crops.

4. Results

4.1. Comparison of spectral indices

In order to ascertain the sensitivity of the common spectral indices to heavy metal stress levels in our field experiment, Fig. 3 shows the first derivative reflectance curves from different heavy metal stress levels. As shown in Fig. 3, there is no significant difference in the REP of rice from different heavy metal pollutions. Compared with the REP of rice at the safe level, the REP of rice under the Level II and Level I pollutions shifted 6 nm and 3 nm towards the short wavelength, respectively; while the shift of the blue edge position had nearly no variation. Furthermore, R^2 between biochemical composition and the three types of indices, derivative spectral indices, normalized chlorophyll absorption depth (Dn_{680}), Difference vegetation index (DVI) and normalized difference vegetation index (NDVI) as representative of the integrated indices that are calculated and listed in Table 3. Cu and Cd had relatively low R^2 with all spectral indices. This indicated that the spectral indices failed to estimate changes in the concentration of Cu and Cd in rice leaves. REP, Dn_{680}, DVI and NDVI had a better relationship with chlorophyll concentration, with R^2 equaling 0.6233, 0.6833, 0.6334 and 0.6203, respectively. Furthermore, REP and DVI were well correlated to N with somewhat higher R^2 values of 0.7413 and 0.5017, respectively. However, none of spectral indices examined was simultaneously sensitive to all four biochemical compositions. Compared with other spectral indices (Table 3), REP was sensitive to heavy metal stress levels in rice crops with relatively higher R^2 values, with chlorophyll concentration and N. The result agrees well with previous studies (Mutanga and Skidmore, 2007).

Table 3
The correlation relationship (R^2) between spectral indices and chlorophyll, N, Cu, and Cd.

Spectral indices	Chlorophyll	N	Cu	Cd
BEP	0.0001	0.0659	0.0001	0.0041
REP	0.6233	0.7413	0.1618	0.2742
CAP	0.1543	0.0319	0.2046	0.1650
Dn (680 nm)	0.6833	0.3201	0.3332	0.3659
DVI (734, 682 nm)	0.6334	0.5017	0.3576	0.3519
NDVI (734, 682 nm)	0.6203	0.3527	0.3309	0.3838

Note: The parentheses contain specific wavebands. BEP, REP, CAP stand for blue edge position, red edge position, chlorophyll absorption position, respectively.

4.2. Feature analysis

Fig. 4 shows respective average value of spectral reflectance from rice with three different heavy metal pollution levels, namely, Level II pollution, Level I pollution, and the safe level. The subtle difference of the original spectral reflectance was observed in the red valley, the reflectance of rice under Level II pollution in the red valley was higher than Level I pollution and than that occurring at the safe level. The original reflectance of rice with heavy metal stress presented a typical spectrum with higher reflectance around 550 nm and a weak absorption peak around 680 nm. In the visible and near infrared region, the significant distinction was that the spectral curve of rice with heavy metal pollution was slightly smoother than that at the safe level. This distinction can show

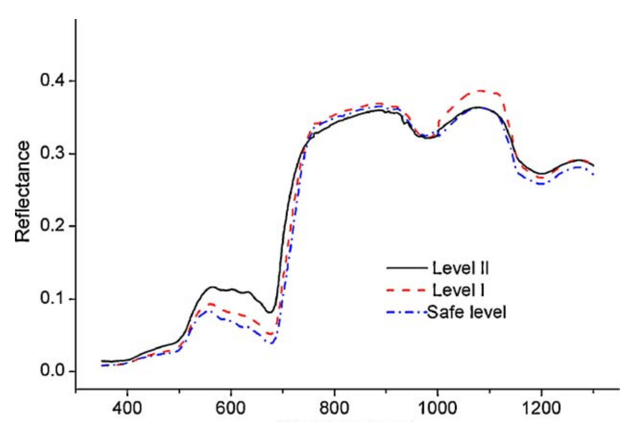

Fig. 4. The original reflectance of rice under different heavy metal pollution.

Table 4
Statistics of $FD_{480-850}$ and $FD_{350-1300}$ with different heavy metal pollution levels in rice crops.

Pollution level	$FD_{480-850}$				$FD_{350-1300}$			
	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev
Level II	1.034	1.081	1.058	0.013	1.066	1.094	1.077	0.006
Level I	1.041	1.078	1.061	0.010	1.065	1.095	1.078	0.006
Safe level	1.034	1.095	1.063	0.012	1.069	1.100	1.084	0.007

Note: FD denotes fractal dimension of original reflectance, the subscript of FD represents the wavebands' regions.

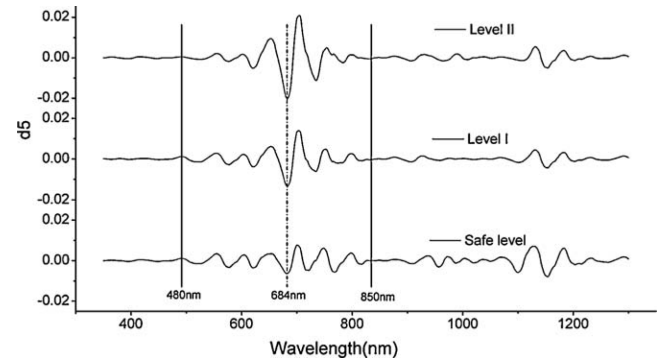

Fig. 5. The fifth high frequency reflectance (d5) of rice under different heavy metal pollution.

the values of fractal dimension in the original spectral reflectance with heavy metal pollution lower than what happens at the safe level. In order to explain the resultant overall variation of original reflectance, the fractal dimensions for all rice samples in the 480–850 nm and 350–1300 nm regions are computed and summarized (Table 4). Regardless of whether $FD_{480-850}$ or $FD_{350-1300}$ was the focus, the difference of mean values for FD with different stress levels was subtle, thus indicating that there were no visible symptoms in original leaf reflectance spectra due to spectral noise, such as background and atmospheric effects.

In order to evaluate the sensitivity of FD to stress levels, the relationships between FD and Cu, Cd, leaf chlorophyll concentrations, N concentrations were established, respectively. The results showed that $FD_{480-850}$ and $FD_{350-1300}$ had a weak relationship with four biochemical compositions in rice, the R^2 value ranged between 0.02 and 0.13. That is to say, $FD_{480-850}$ and $FD_{350-1300}$ failed to match the changes in biochemical composition levels in metal-stressed plants, and thus, $FD_{480-850}$ and $FD_{350-1300}$ were not good indicators of the heavy metal-induced plant stress.

Based on the above analysis, $FD_{480-850}$ and $FD_{350-1300}$ were less sensitive to heavy metal stress. The primary reason is that the environment-induced noise in the field spectra is generally greater by two orders of magnitude than the subtle features associated with stress (Collins et al., 1983). Therefore, it is necessary to remove noise and amplify stress information in original reflectance. Heavy metal stress information was revealed by transient changes in the reflectance of adjacent wavebands and was closely associated with singularity points, which were discontinuous (shocks) points at the x_0 waveband in the original spectrum signals or the derivatives of the spectrum signals (Peng and Chu, 2007). Whereas, wavelet transform seems to be suited for analyzing short-lived phenomena such as discontinuities (shocks) and transient structures in hyperspectral signals, the fifth level high-frequency compositions (d5) through wavelet transform have been proved successful in identifying crop heavy metal stress for the foregoing. Fig. 5 shows the average d5 values of rice with different heavy metal pollution levels. The three lines were arranged vertically with d5 of Level II pollution, Level I pollution and the safe level at the top, central and bottom of the series, respectively. By arranging the data in this way we can quite clearly interpret the changes that took place at the module maximum points of d5, which correspond well to the singularity points of original reflectance (Liu et al., 2010a). Vertical lines were drawn to locate module maximum points at 480 nm, 684 nm and 850 nm, respectively, in the d5 spectral curve. Accurate results are summarized in Table 5. As shown in Fig. 5 and Table 5, the variation of module maxima and the shift of module maximal points position for d5 led to the following observations:

(i) The module maxima around 680–700 nm with Level II pollution was larger than Level I pollution, and then the safe level. The relative deviations of module maxima of rice with heavy metals around 680–700 nm exceeded 80% as opposed to what occurs at the safe level.
(ii) There were no apparent shifts of module maximum points position in the spectral region below 680 nm, regardless of the rice's pollution level. While obvious shifts of module maximum points position occurred beyond 700 nm, especially around 701 nm, 730 nm, 748 nm, and 769 nm, respectively. These shifts of module maximum points position were associated with metal stress. The shift of module maximum points position with Level II pollution was larger than Level I pollution, and then the safe level. In addition, maximum shift of module maximum points position moved 14 nm towards the long wavelength around 770 nm. The wavelet analysis techniques have been tried on the hyperspectral data to quantify these shifts.
(iii) The fluctuation of module maxima under Level II pollution was bigger than Level I pollution and the safe level in 480–850 nm

Table 5
Statistics of absorption feature edge of rice at different heavy metal pollution levels in 480–850 nm regions.

Pollution	Number	1	2	3	4	5	6	7	8	9	10
Level II	MMPP (nm)	555	577	601	620	653	683	705	735	754	783
	Module maxima 10^{-3}	2.20	1.79	1.67	5.18	9.51	20.31	20.83	11.30	4.99	2.42
	DS (nm)	0	0	−3	−1	−1	−1	+4	+13	+6	+14
	Relative deviation (%)	34.91	46.41	40.36	44.29	175.65	224.44	169.47	132.99	17.79	57.69
Level I	MMPP (nm)	554	577	604	621	653	683	703	734	751	782
	Amplitude 10^{-3}	2.80	2.77	2.24	3.90	6.13	13.61	13.92	6.26	4.70	2.01
	DS (nm)	0	0	0	0	−1	−1	+2	+12	+3	+13
	Relative deviation (%)	17.16	17.07	20.00	8.64	77.68	117.41	80.08	29.07	22.57	64.86
Safe level	MMPP (nm)	554	577	604	621	654	684	701	722	748	769
	Module maxima 10^{-3}	3.38	3.34	2.80	3.59	3.45	6.26	7.73	4.85	6.07	5.72

Note: MMPP stands for module maximum points position. DS represents distance of shift for module maximum points position of rice under heavy metal pollution against safe level and unit is nanometer; +, towards longer wavelength; −, towards shorter wavelength. In the equation $RD = |A - B|/B$, RD is relative deviation, A is module maxima of d5 under heavy metal stress, B is module maxima of d5 under safe level.

Table 6
Statistics of FDWT in 480–850 nm and 350–1300 nm regions of rice at different heavy metal pollution levels.

Pollution level	$FDWT_{480–850}$				$FDWT_{350–1300}$			
	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev
Level II	1.157	1.183	1.165	0.006	1.179	1.209	1.194	0.008
Level II	1.174	1.204	1.189	0.008	1.203	1.257	1.223	0.015
Safe level	1.220	1.289	1.262	0.017	1.286	1.320	1.305	0.009

Note: FDWT denotes fractal dimension of reflectance with wavelet transform, the subscript of FDWT represents the wavebands' regions.

regions. In short, the larger shifts of module maximum points and the bigger fluctuation of module maxima indicated the more highly polluted rice suffering from heavy metals. The variation of module maximum points indicated that metallic elements had important influence on the molecular environment of rice and induced electron transport. By applying wavelet transform to original reflectance, the d5 curve had the ability to capture very subtle changes associated with stress responses to heavy metal pollution.

In order to explain the resultant overall variation of module maximum points, the FDWT (namely, the fractal dimension of d5) for all rice samples in 480–850 nm and 350–1300 nm regions are calculated and summarized in Table 6. The mean values of FDWT in the 480–850 nm and 350–1300 nm regions with Level II pollution were both lower than Level I pollution as well as that of the safe level. The primary reason is that the original spectral curve of rice with heavy metal pollution in the visible and near infrared region is slightly smoother than the safe level. The lower the value fractal dimension, the smoother of the original reflectance curve is. Given the fact that the d5 value is the fraction of the original reflectance, it has the fractal property coinciding with original reflectance. Moreover, mean values in $FD_{480–850}$ and $FD_{350–1300}$ of rice at the same pollution levels being identical, suggested the spectral characteristic change at wavelengths of 480–850 nm played an important role in the whole 350–1300 nm spectrum region. Thus, it further proves that the change of spectral region of the metal-induced stress occurred in the visible and near infrared region, which is in agreement with the findings from previous studies (Kooistra et al., 2004).

4.3. Sensitivity analysis

Comparing the different regression model, the quadratic models had relative high R^2 between FDWT and biochemical composition. So, a series of quadratic fit models were conducted from $FDWT_{480–850}$, $FDWT_{350–1300}$ values with chlorophyll concentrations, N concentrations, Cu and Cd (Fig. 6). In general, chlorophyll and N correlate positively to $FDWT_{480–850}$ or $FDWT_{350–1300}$, while Cu and Cd correlate negatively to $FDWT_{480–850}$ or $FDWT_{350–1300}$. Regardless of whether $FDWT_{480–850}$ or $FDWT_{350–1300}$ was the focus, both had high R^2 values with all four biochemical components. The maximum value ($R^2 = 0.89$) occurred between $FDWT_{480–850}$ and chlorophyll, while the minimum value ($R^2 = 0.62$) occurred between $FDWT_{350–1300}$ and Cu. It indicates that FDWT are sensitive to biochemical components and can well reflect the changes in biochemical composition in metal-stressed plants. In addition, FDWT values are stable parameters for identifying the difference in biochemical components of rice with heavy metal stress, because the R^2 value of $FDWT_{480–850}$ and $FDWT_{350–1300}$ were exhibited to a similar degree against the same biochemical composition. Compared with the spectral parameters described above, FDWT values were significantly correlated to chlorophyll and N as well as the concentration of heavy metal in rice leaves. Nevertheless, the common spectral indices resported in this paper such as REP and DVI were proved to be only well correlated to chlorophyll and N.

In this study, data sets consisting of 75 datasets for establishing the model and 40 datasets for verifying the model, were obtained at different heavy metal pollution levels from the tillering

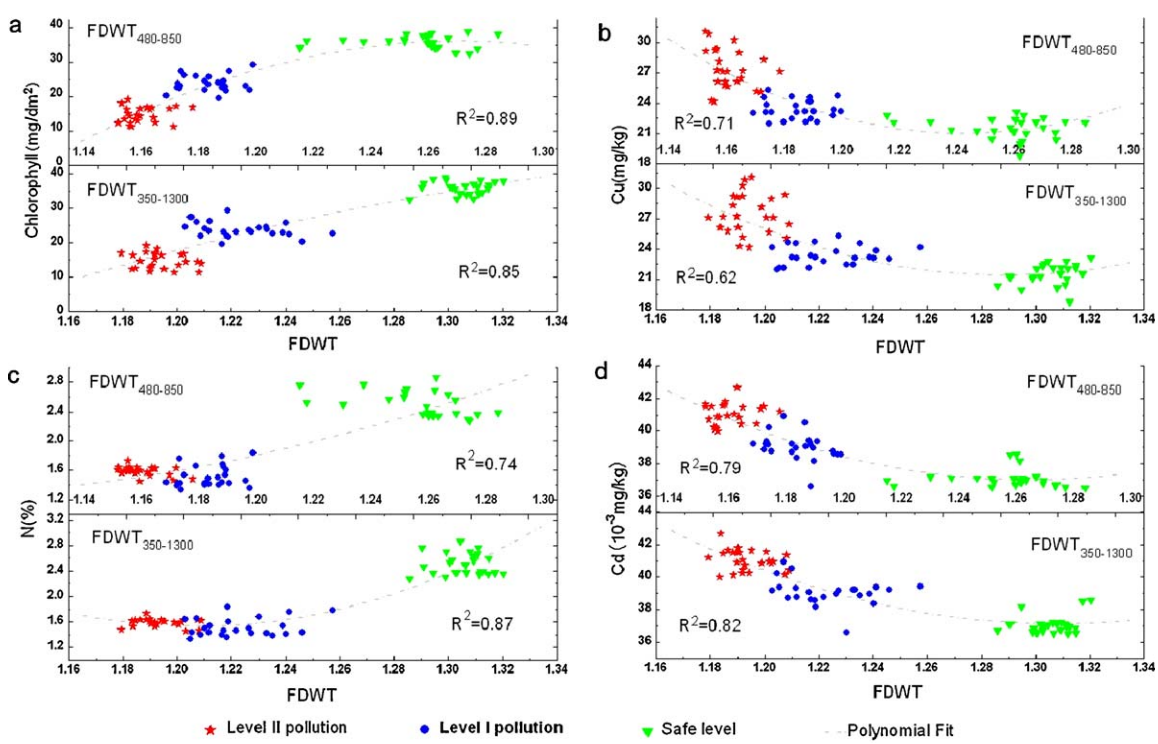

Fig. 6. The relationship between FDWT and chlorophyll concentration, N, Cu, and Cd. FDWT is fractal dimension of reflectance of with wavelet transform, the subscript of FDWT indicates the wavebands' regions.

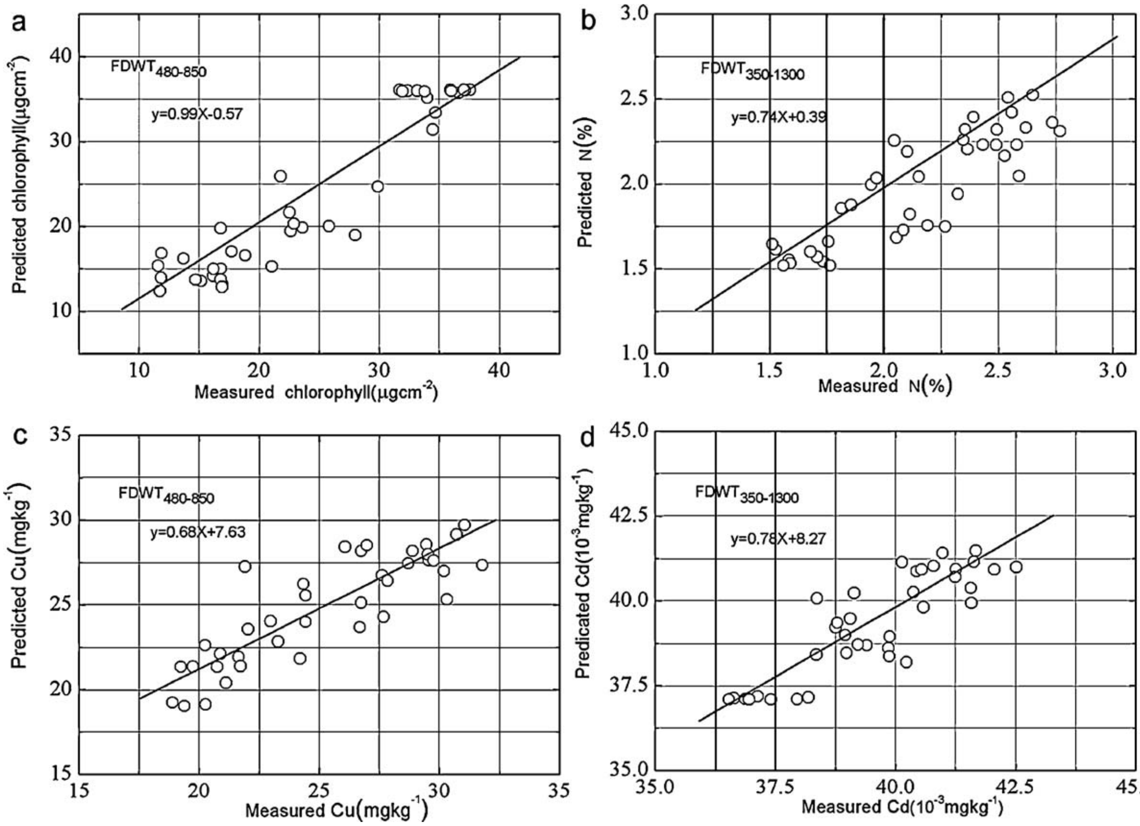

Fig. 7. The relationship between predicated and measured chlorophyll concentration, N, Cu, and Cd. FDWT is fractal dimension of reflectance of with wavelet transform, subscript of FDWT shows the wavebands' regions.

growth stage of rice. To further evaluate the performance of FDWT, the quadratic models established were verified using the validation dataset, which had the relatively high R^2 value. $FDWT_{480–850}$ and $FDWT_{350–1300}$ were selected to predict chlorophyll, N, Cu and Cd, respectively. $FDWT_{480–850}$ values can yield more accurate chlorophyll and Cu concentration predictions than that from $FDWT_{350–1300}$. When it came to the N and Cd, $FDWT_{350–1300}$ values were better than $FDWT_{480–850}$ (Fig. 6). The relationship between the predicted and measured biochemical compositions is shown in Fig. 7. Three performance parameters of the model validation for estimating chlorophyll, N, Cu and Cd concentrations of rice leaves are summarized in Table 7. The result suggests that the performance of FDWT developed in this study was good. In detail, R^2 between the measured and the predicated biochemical compositions was greater than 0.70, ME was above than 0.65 and RMSE was less than 3.5, especially for chlorophyll concentrations having higher accuracy of the predicted values than the measured values, with R^2 and ME equaling 0.88 and 0.87, respectively.

In order to further discuss the difference in sensitivity of FDWT and FD with respect to stress levels of heavy metals, the three-dimensionality of FDWT and FD are shown in Fig. 8. From Fig. 8, $FD_{350–1300}$ and $FD_{480–850}$ were unable to distinguish the stress levels, whereas $FDWT_{350–1300}$ and $FDWT_{480–850}$ was able to discriminate three stress levels, namely the safe level, Level I pollution and Level II pollution. More particularly, curved surfaces corresponding to the safe level, Level I pollution and Level II pollution are located in the upper, medium, and lower plane of 3D space, respectively. That is to say, the minimum values of FDWT occurred in rice under Level II pollution, followed by Level I pollution, and then the safe level.

Table 7
Performance parameters of the model validation for estimating of chlorophyll, N, Cu, and Cd concentration of rice leaves.

Biochemical composition	R^2	ME	RMSE
Chlorophyll	0.88	0.87	3.29
N	0.75	0.68	0.25
Cu	0.74	0.72	2.10
Cd	0.77	0.76	0.85

5. Discussion

Four common spectral indices including REP, Dn_{680}, DVI and NDVI had better relationships (R^2 above 0.6) with the leaf chlorophyll concentration of rice (Table 3). In addition, REP is also sensitive to the nitrogen content of rice with heavy metal stress. The fractal dimension of original reflectance in this study was verified and the result showed that it performed poorly in detecting the heavy metal stress levels in rice crops. The primary reason is that environment-induced noise in the field spectra masks subtle features associated with stress. The noise, however, is to a large extent non-spectral scattered energy which can be separated by spectral analysis, using methods such as the derivative technique, continuum removal and wavelet transform. The previous studies demonstrated that wavelet transform was related to derivative spectral analysis, but when used for field spectral surveys, wavelet transform was more sensitive in the detection of stress and most effective in filtering out background noise in the spectral data. In this study, wavelet transform was used for noise removal in order to improve the sensitivity of spectral signals to the heavy metal stress levels. Furthermore, the fractal dimension of d5 through wavelet transforms were calculated as a quantitative and comprehensive indicator by capturing more information in the detection of the heavy metal stress levels. Therefore, compared with common indices and FD, the FDWT developed in this study was much

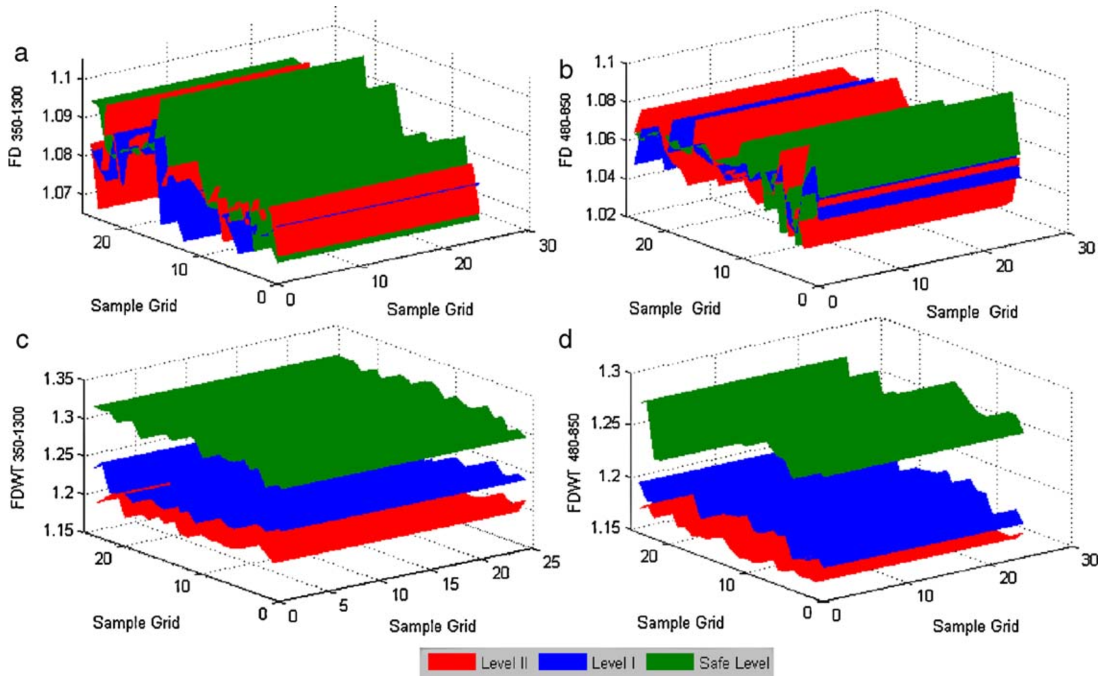

Fig. 8. The three-dimensional distribution of FD and FDWT of rice with differing heavy metal pollution. FD is the fractal dimension of original reflectance curve; FDWT is fractal dimension of reflectance of with wavelet transform, subscript of FD and FDWT denotes the wavebands' regions.

more accurate for identifying the heavy metal stress levels, since FDWT included more spectral shifts, such as green peak, chlorophyll absorption edge and REP in addition to eliminating noise.

6. Conclusions

In this paper, we have examined the spectral indices and fractal dimensions of original reflectance in monitoring the heavy metal pollution levels in rice crops. In addition, $FDWT_{480–850}$ and $FDWT_{350–1300}$ were explored as comprehensive indicators for monitoring stress levels of rice with heavy metal pollution. The most important findings and conclusions drawn from this study include:

1) REP was the most sensitive indicator for monitoring the stress levels of rice with heavy metal among common indices in this study. As compared with REP, $FDWT_{480–850}$ and $FDWT_{350–1300}$ were more sensitive to chlorophyll concentration, N, Cu and Cd. The established linear models showed that R^2 was above 0.70, ME above 0.65 and a RMSE below 3.5 between the measured data and the predicated data.
2) FDWT was proved to be successful in discriminating the heavy metal pollution levels in rice crops. The minimum values of FDWT occurred in rice under Level II pollution followed by Level I pollution, and then the safe level. The lower FDWT value, the higher heavy metal pollution level in rice crops.
3) Wavelet transform developed in this study was indeed the optimum method for eliminating noise and amplifying the stress information from heavy metals; it proved be the most effective at detecting the variation of module maximum points of spectral signal of rice with heavy metal pollution.

In summary, wavelet transform in combination with fractal technique can provide an effective and accurate method for monitoring the heavy metal pollution levels in rice crops. These techniques may offer insight into investigating crops under various environmental stresses, such as the heavy metal-induced stress.

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