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Rapid inversion of heavy metal concentration in karst grain producing areas based on hyperspectral bands associated with soil components

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ABSTRACT

Heavy metal pollution in soil has become a prominent problem affecting agricultural security and ecological health. Hyperspectral remote sensing is used as a rapid method to predict soil heavy metal concentrations. The processing of spectral data and the variables of the estimated model has an important impact on the predictive model of soil heavy metal elements. In this paper, smoothed and resampled spectral reflections are preprocessed by using three preprocessing methods, namely, standard normal variate (SNV), multiplication scatter correlation (MSC) and normalization (NOR). Then, first and second order differential (FD and SD, respectively) and absorbance transformation (AT) are performed. Based on the adsorption and retention of heavy metals by various soil components, the relevant spectral bands are extracted as modeling variables. An extreme learning machine algorithm (ELM) is used to establish the model, and the effects of different factors on the model are compared. Results show that the combination of the three preprocessing methods (SNV, MSC and NOR) with spectral transformation can enhance the stability and predictive ability of the resulting model. The combination of SNV and FD can predict the contents of Cr, Ni and Pb. The R^2 of the model is 0.85, 0.87 and 0.80 respectively. The optimal model of Cu is derived from the combination of NOR and SD (R^2 = 0.84), and the spectral responses of soil Cr, Ni, Cu and Pb, are closely related to clay mineral-related and organic matter-related bands. The model established by the clay-related bands enhances the stability of the prediction of Ni content, and the RPD value was increased from 2.46 to 2.72 compared with the full-band model. The combination of bands associated with organic matter and clay minerals can accurately predict the content of Cr and Cu in soil; indeed, the predict model R^2 for these elements reaches 0.88. Accurate prediction of soil Pb by the full-band model indicates that the Pb concentration in the study area is related to a various of soil chemical components. The prediction effects of the four heavy metal elements show the order Cr > Cu > Ni > Pb. The results of the current study complement the theoretical basis for estimating the heavy metal content of soil by hyperspectral spectroscopy, and provide important insights into the application of hyperspectral remote sensing to monitor other heavy metals.

1. Introduction

Heavy metal pollution is a major factor affecting the soil environment. The migration of heavy metals to farmland soil is slow, and these metals are difficult to decompose, possibly resulting in deterioration of soil quality and the ecological environment. When accumulated over a long period of time, heavy metals can threaten food security and human health ([1,2]). Therefore, rapid investigation of the distribution of heavy metals in soil and effective control and prevention of heavy metal hazards are crucial to prevent and control of soil pollution in primary grain-producing areas and food security.

Compared with traditional analytical methods, hyperspectral technology is simpler, faster, more efficient, and lower cost [3]. The accuracy of soil estimation models built using hyperspectral data is influenced by many factors. In most cases, the preprocessing of modeling variables (spectral reflectance) can effectively eliminate and reduce the

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multicollinearity and randomness among bands, as well as improve the accuracy and stability of the estimated model [4]. To improve the practicability of the model, the current research focuses on the effects of external factors, such as spectral pretreatment method, regression modeling method, and soil composition, on the accuracy of heavy metal concentration estimation model. Wavelet analysis and other methods can effectively eliminate and reduce multicollinearity and randomness among bands [5]. The influences of different soil spectral pretreatment methods on the accuracy of soil nitrogen estimation model have been compared and analyzed by some researchers. The results show that the proper preprocessing method can effectively best eliminate the noise and background information of the original spectral data [6]. The goal of all preprocessing techniques is to reduce the unmodeled variability in the data and enhance the features required in the spectrum. Soil spectral features can be highlighted by using appropriate preprocessing techniques. However, applying false types or severe preprocessing methods will delete valuable information.

Another important factor affecting the prediction ability of a model is the choice of modeling variables (bands). Although soil spectroscopy is an external reflection of the physical and chemical properties of various soils, it is not necessarily the best indicator of a particular soil component. Modeling the entire hyperspectral band tends to increase the complexity of the model [7]. The retention of heavy metals by spectral active components varies with soil conditions, such as soil organic matter, soil properties, soil types, and clay minerals. Most heavy metals are adsorbed by soil components, such as clay minerals or organic matter [8]. Therefore, using the entire band in the prediction is unnecessary [9]. Analysis of the adsorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn confirms that adsorption of Pb and Cu is related to the content of organic matter. The kaolin of clay composition has strong adsorption on the heavy metal Ni element in soil [10]. Estimations of heavy metal contents by hyperspectral technology are not only affected by the spectral band but also by the noise of the original spectrum. Therefore, specific processing methods and modeling variables should be selected based on the spectral properties of the soil.

The current study proposes a method for rapidly estimating heavy metal content based on hyperspectral correlation with soil components. The effects of different pretreatments on the prediction model are also compared. On the basis of the band depth of the hyperspectral, a spectral absorption band associated with clay minerals and organic matter is extracted. Models are established using these bands and extreme learning machine algorithms. The factors influencing the prediction model are comprehensively evaluated. This study can provide theoretical and technical support for the high-spectral fast inversion of heavy metals in grain-producing areas.

2. Materials and methods

2.1. Study area and sample collection

In this study, the Houzhai River Basin in Puding County, Guizhou Province was used as the sampling area. The Houzhai River Basin is a typical plateau karst basin. The geographical position is 105°40′ to 105°49′ E and 26°12′ to 26°18′N, in the central part of the Pearl River Basin and the Yangtze River Basin, with a total area of about 81 km2. The terrain in the area that is high in the southeast and low in the northwest. It is open and flat, with an altitude of 1100–1400 m. The climate type belongs to the subtropical plateau monsoon humid climate in China, and the mountainous hills are the main topography. The land use type is mainly agricultural land, and it is the main grain producing area in Puding County. Fig. 1 is the location map of the study area.

Set the sample points according to the geographical conditions such as the topographical features of the study area, the type of land cover, and the corresponding area of the type of landscape. The sampling depth is 20 cm, which is divided into 4 layers. Each layer collects 100 g of soil, and 4 layers of soil samples are mixed to be the soil samples corresponding to the sample points. The total number of samples is 100, numbered according to the coordinates.

2.2. Measurement of elemental content and hyperspectral reflectance

The collected soil samples were air dried and sieved to remove stones and large debris. They were then passed through a 2 mm sieve. The screened soil samples were divided into three parts, two of which were used for chemical element determination and spectral collection in the soil laboratory; the third part was sealed for future reference to prevent cross contamination.

The soil samples were subjected to microwave digestion (using the HNO_3-HCL-$HClO_4$-HF solution). Inductively coupled plasma mass spectrometry (ICP-MS, Thcrmo Electron, USA) was used to measure the contents of four heavy metal elements such as lead, copper, nickel and chromium. The hyperspectral data of the raw soil samples were measured by an ultraviolet-visible-near-infrared spectrophotometer. The detection range is 500–2500 nm, with a total of 2000 bands and an interval of 1 nm. Each sample was tested 10 times.

2.3. Data processing

Errors are affected by random factors during the spectrometry. Spectral preprocessing can reduce the error caused by random factors in the spectrum. The anomaly of the spectral data was detected by the Mahalanobis distance, and the average value of the remaining spectral data was used as the final reflectance spectrum. Sample outliers were detected by The Unscrambler 10.4 software, and the four outliers detected were removed from 100 sample points.

Savitzky–Golay convolution with a window length of 9 was used to smooth out the noise, and the breakpoint of the spectral curve at 800 nm repaired by the splicing correlation method was used (Fig. 2). To reduce noise and computational cost, resampling at 10 nm intervals to reduce redundancy was performed based on previous research [11]. The band reflectivity described below is the band reflectance obtained after resampling. The resampled spectral data were preprocessed by standard normal variate (SNV), normalized processing (NOR), and multiplicative scattering correlation (MSC). Finally, the processed data were separately differential and reciprocal logarithmically transformed.

2.4. Spectral bands related to soil components were extracted

Soil and its components have a great influence on the adsorption and analytical equilibrium of heavy metal elements. Studies have shown that some soil components (clay minerals, organic matter) have a strong adsorption capacity for individual metal elements [10]. Adsorption of metal elements by soil components provides a mechanism for estimating the concentration of heavy metals in soils using spectral reflectance. Considering the adsorption and retention of soil organic matter and clay minerals for Cr, Cu, Ni, and Pb, these four metals are taken as examples in this work.

In the reflection curve of soil the samples, three water absorption peaks near 1413, 1922, and 2200 nm are evident; these peaks are primarily caused by H_2O molecules and −OH groups and metal −OH in clay minerals [12]. The primary characteristics of the kaolinite spectrum are an absorption band at 2200 nm and a weak absorption band at 1900 nm [13]. When using the spectrum to predict the clay content, the absorption bands at 1400, 1900, and 2200 nm are selected [14]. The sensitive bands of soil organic carbon in different regions were analyzed, and results showed that most of the spectral response bands are concentrated at 600–800 nm [15]. Referring to previous studies, this study selected absorption characteristics based on band depth (Fig. 3). The absorption characteristics in the band 600–800 nm are believed to be related to organic matter, and the absorption peaks are related to clay minerals at 1400, 1900, and 2200 nm.

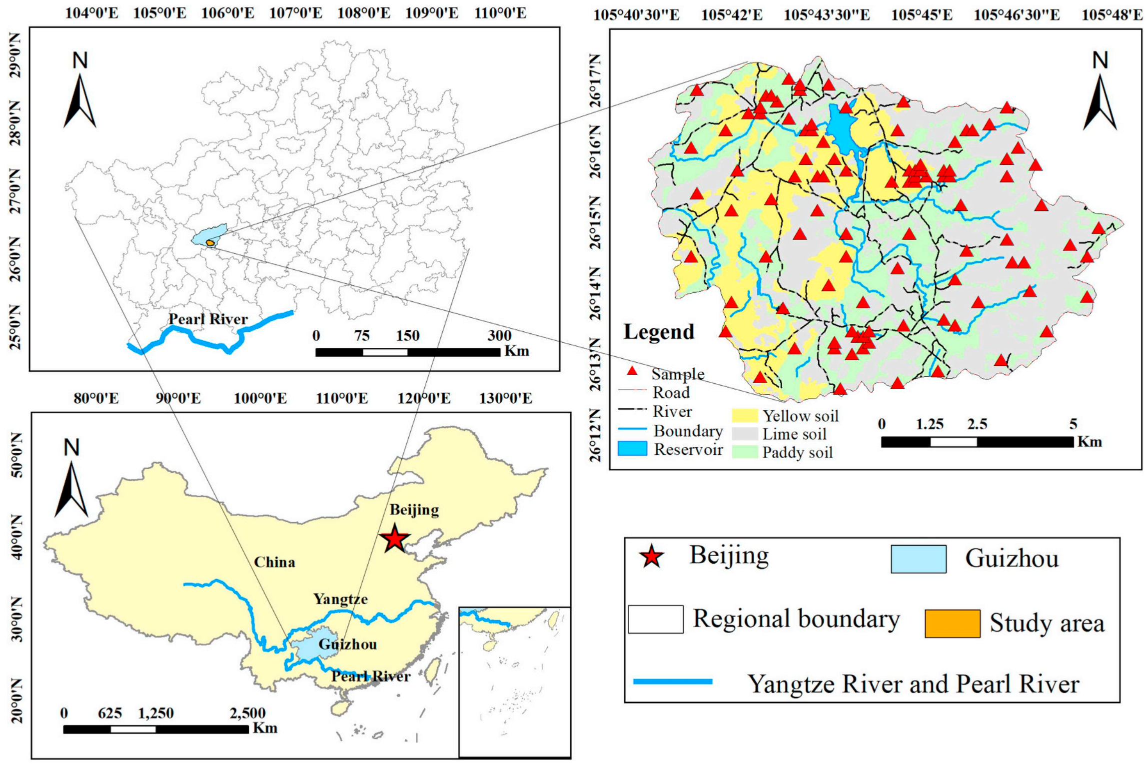

Fig. 1. Study area and the distribution of soil samples.

2.5. Modeling approach

The Extreme Learning Machine (ELM) is a new and efficient learning algorithm that not only achieves better accuracy than traditional models, but also maintains faster training speeds [16]. ELM with high generalization capabilities avoids many problems of the faced by gradient learning. In this paper, the excitation function of ELM is the "sig" function, and the number of hidden layer nodes is selected based on the minimum average value of the iterative results, and the test is repeated for 600 times. The final prediction model is determined when the RMSE value in the model structure is the lowest. The ELM model was built in Matlab R2010a software.

Three statistical methods were used to evaluate the fitted model: coefficient of determination (R^2), residual prediction deviation (RPD) and root mean square error (RMSEp). The coefficient of determination provides the percentage of variance explained by the model and is the most widely used measure of fitness. Robust models typically have lower RMSEP, higher R^2 and RPD. Model accuracy is usually evaluated using R^2 and RPD because RMSEP is susceptible to measurement range. The prediction results were evaluated using the following criteria: the RPD and R^2 values were better than 2.00 and 0.80, and the prediction results were good; the RPD values were between 1.5 and 2.00, and the R^2 values were between 0.51 and 0.80, and the approximate prediction was determined [17].

3. Results

3.1. Description of soils samples

The Kennard–Stone algorithm is used to select the most suitable modeling and prediction samples. One-third of the entire data set was selected as the training sample (n = 64), and the rest of the data were used as test samples (n = 32). Statistical information of the contents of Cr, Ni, Cu, and Pb is shown in Table 1. The average contents of Cr, Ni,

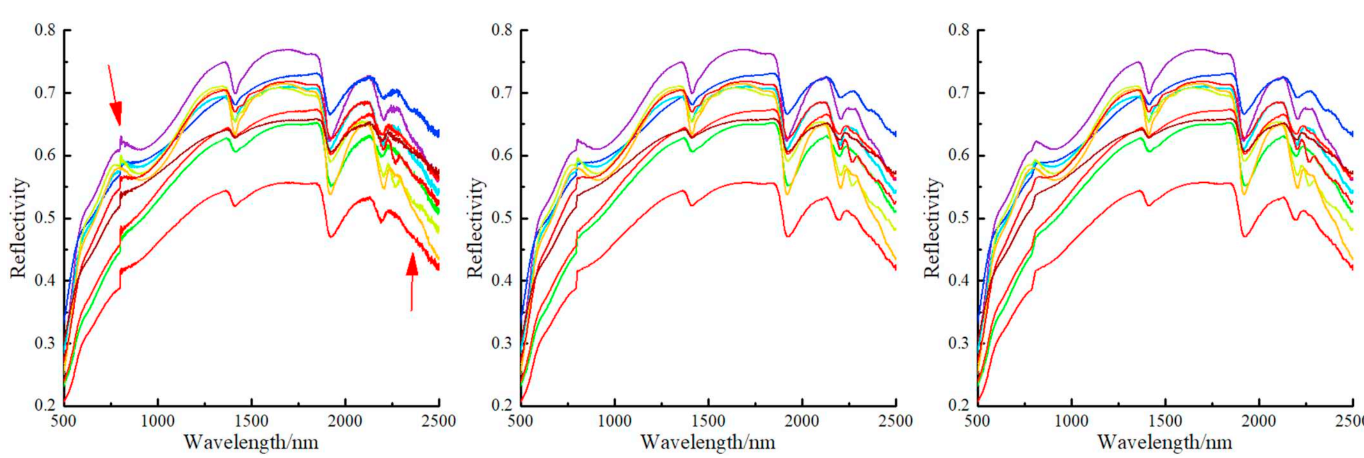

Fig. 2. Pretreatment of spectral data: (a) original spectrum, (b) smoothing, (c) removing the break point at 800 nm.

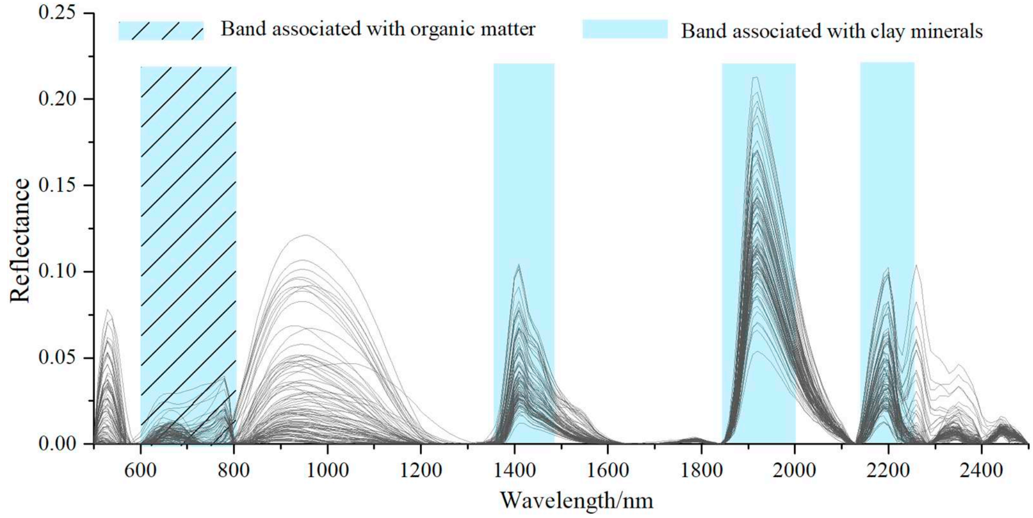

Fig. 3. Selection of bands related to soil properties based on band depth.

Cu, and Pb do not exceed the national environmental quality standard for secondary pollution (GB 15618-1995). However, they all exceed the background values of soil heavy metals in Guizhou Province. The over-standard rates of Ni and Cu were 27.55% and 7.14%, respectively. The contamination factor (CF) of three heavy metals, namely, Cr, Ni, and Cu, was between 1 and 2, and a slight pollution hazard is observed. The pollution factor of Pb is > 2, which indicates moderate pollution. As an important major grain-producing area, the study area should strengthen efforts to investigate and dynamically monitor soil quality to discover and control soil heavy metal pollution in a timely manner.

3.2. Model construction and evaluation

3.2.1. Prediction model based on different preprocessing methods

The spectral data processed by MSC, SNV, NOR, first-order differential (FD), second-order differential (SD), and absorbance transformation (AT) were used as model variables, and heavy metal estimation models were established by the ELM method. The models were evaluated by R^2 and RPD. The larger the R^2 and RPD of the test sample, the stronger the model prediction ability. Fig. 4 shows the model effects of the four heavy metals under different pretreatment combinations. Spectral data modeling after SNV-AT pretreatment failed, and no statistics are given for this process. The results of the four pretreatments indicate that differential transformation of the spectrum is beneficial to the effect of the model. Peaks are observed in the four sets of differential transformations. The transformation of the SNV group in the three pretreatments has a great influence on the prediction ability of the model. The best modeling accuracy of the elements Cr, Ni, and Pb is obtained by the SNV group. Furthermore, the SNV–FD combination showed the best prediction effect (model parameters are: $R^2 = 0.85$, RPD = 2.59; $R^2 = 0.87$, RPD = 2.46; $R^2 = 0.80$, RPD = 2.10). The best predictive model for Cu is based on a combination of NOR-SD preprocessing, with an R^2 of 0.84 and RPD of 2.53. For the elemental Cr, Ni, and Cu prediction models, R^2 is concentrated around 0.80, and the RPD value is within 2.00–3.00; thus, the contents of these elements can be predicted well. The contents of elemental Pb can be approximated. The model prediction results of these four elements show the order Cr > Cu > Ni > Pb.

3.2.2. Prediction model based on different modeling variables

The bands related to clay minerals and organic matter are obtained on the basis of the previous analysis. The two bands and their combination are used as modeling variables to establish models to estimate the contents of heavy metals in four soils. Fig. 5 compares the model effects of the entire visible near-infrared spectral reflectance (VS), organic matter-related bands (OM), clay mineral-related bands (CM), and their combination (OC). Table 2 shows the prediction effect for each heavy metal element based on different model variables.

As shown in Fig. 5, the prediction models of Cr and Ni are sensitive to the clay mineral-related bands. The model R^2 established by the clay-related bands is stably above 0.80, and the RPD values are in the range of 2.00–3.00. The prediction ability of the model for this element is excellent. By contrast, the accuracy of predictions using organic matter-related spectral bands is very low. The predictions of Cu and Pb are related to the organic matter-related bands. The prediction model R^2 of Cu is above 0.80, while that of Pb is above 0.70. It can be seen from the Fig. 5 that the accuracy of the model is in equilibrium under different preprocessing methods. In Table 2, the best predictive effect on the soil heavy metal element Ni is the model established by the clay mineral related zone, here, R^2 is 0.86, and RPD is 2.72. The best model for predicting Cr and Cu is established in the combined band; in this case, the model R^2 values are 0.88, and the RPDs are 2.89 and 2.73, respectively. The model established by the complete VNIR–SR can predict Pb the best; the R^2 of this model is 0.80, and its RPD is 2.10. The results of the Pb prediction model of the organic matter-related and clay mineral-related bands are similar.

Table 1
Descriptive statistics of the elements concentrations.

Element	Number	Min	Max	Mean	SD	CV	CF	BV	GradeII
Cr	96	53.29	184.00	105.90	29.14	0.27	1.25	84.4	250
Ni	96	23.14	160.00	52.93	26.61	0.50	1.61	32.9	60
Cu	96	23.45	141.00	52.50	23.69	0.16	1.95	26.9	100
Pb	96	19.88	221.27	63.94	39.71	0.62	2.04	31.3	350

SD: standard deviation; C.V.: coefficient of variation; CF: Contamination factor; BV: Background value for soils in Guizhou; Grade II: National soil environmental quality standard (GradeII) (pH > 7.5).

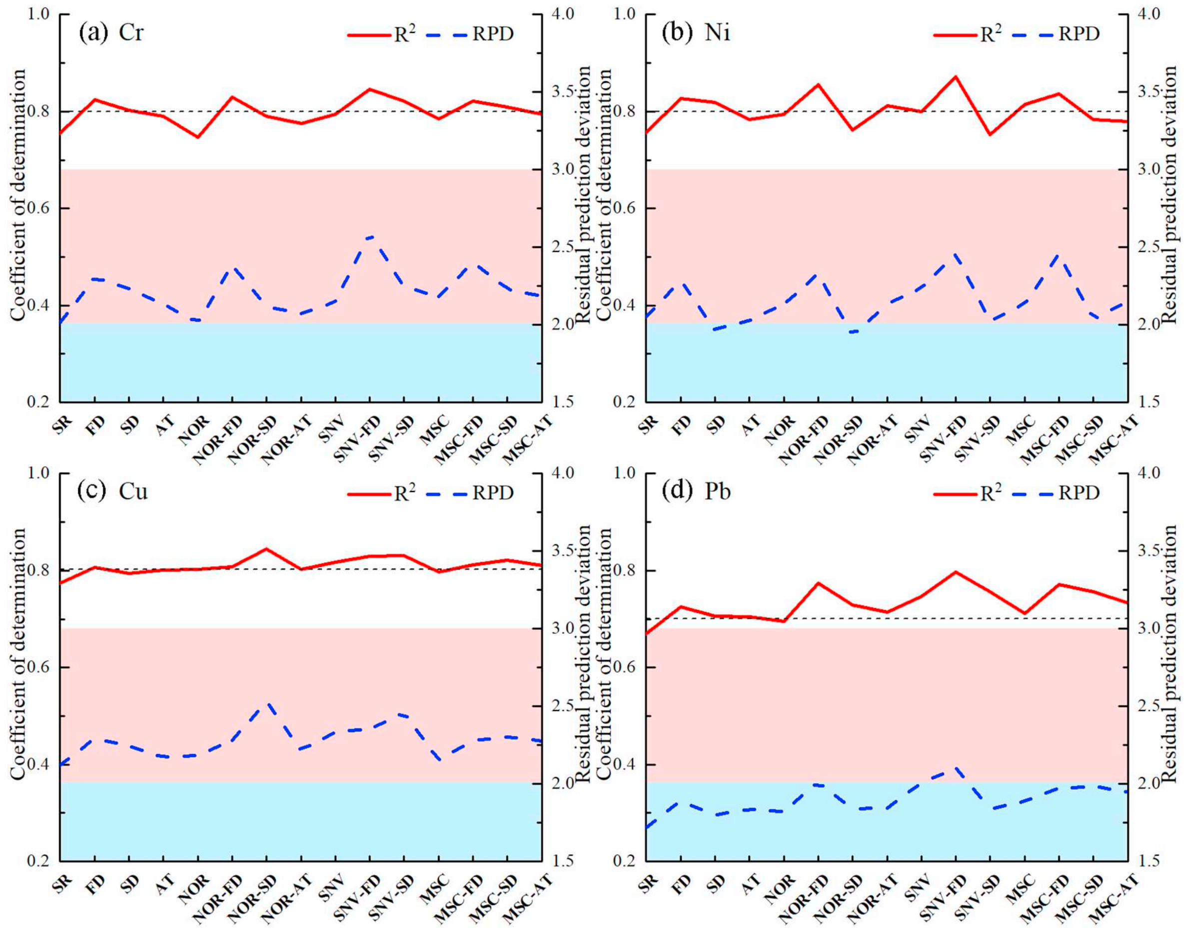

Fig. 4. Prediction effect of four elements under different pretreatment technologies.

Fig. 6 shows a scatter plot of the predicted and measured values of each element. Each sample point is concentrated near the 1:1 line. The ELM algorithm exhibits good stability for the elements Ni and Cu, and the predicted value is close to the measured value over the entire concentration range studied. Elemental Cr and Pb samples at concentrations between 80 and 130 and 20–140 mg/kg, respectively, are accurately predicted. As shown in Table 2, prediction of Cr, Ni, and Cu by the ELM model can achieve good results; here, R^2 and RMSE are approximately 0.80 and 10.00, respectively, and the model performs well. However, the prediction results of Pb are relatively poor, indicating that the ELM method has poor applicability when the sample range is very large.

4. Discussion

4.1. Influence of different preprocessing techniques on the accuracy of the models

The pretreatment techniques mainly include scattering correction and spectral derivative. The data preprocessing methods include MSC, SNV, and NOR, followed by spectral derivative transformation. The modeling effects of the different spectral preprocessing methods shown in Fig. 4 reveal that the spectral modeling effects are improved after SNV, NOR, and MSC processing. The performance of the model obtained by MSC and SNV pretreatment is better than that of the control group. The performance of MSC preprocessing fluctuates among the models with R^2 values ranging from 0.70 to 0.84 and RPD values ranging from 1.80 to 2.50. Spectral derivative preprocessing removes additive and multiplicative effects in the spectrum, and models built by differential and absorption conversion show improved predictive power [18]. The combination of SNV and FD or SD performs better than other methods and is advantageous for predicting Cr, Ni, and Pb. To predict Cu, the combination of NOR and SD is the best pretreatment. The SNV preprocessing method can eliminate the multiplicative interference of granularity [19]. As shown in Fig. 4, the three pretreatments of SNV, MSC, and NOR reveal different reflectance scales, and the trends of model performance have obvious similarities. These results represent a powerful spectral preprocessing technique that separates and removes complex effects from physical phenomena, leaving accurate soil spectral information that is conducive to modeling.

4.2. Influence of soil composition related variables on the accuracy of the models

Adsorption of heavy metals in soil is an important factor in controlling the concentration of metal in soil. The content of heavy metals is affected by of pH, soil organic matter, and clay mineral content [20]. Adsorption and desorption experiments of soil heavy metal show that kaolinite has a marked retention effect on Cr, Ni, and vermiculite. Organic matter and Fe–manganese oxide have strong adsorption and retention effects on Pb. Clay minerals also have a certain influence on this element [21]. Fig. 5 shows that clay mineral-related bands can stably predict Cr and Ni. Furthermore, organic matter-related bands can stably predict Cu and Pb, which can be affected as little as possible by the pretreatment method. These results confirm the retention of soil components. Selection of bands associated with soil components can improve the accuracy of the prediction models for Ni, Cr, and Cu. To some extent, the complete spectral bands associated with these three elements are preserved, which reduces dimensional and accuracy errors of the model variables. The prediction ability of the complete VNIR–SR

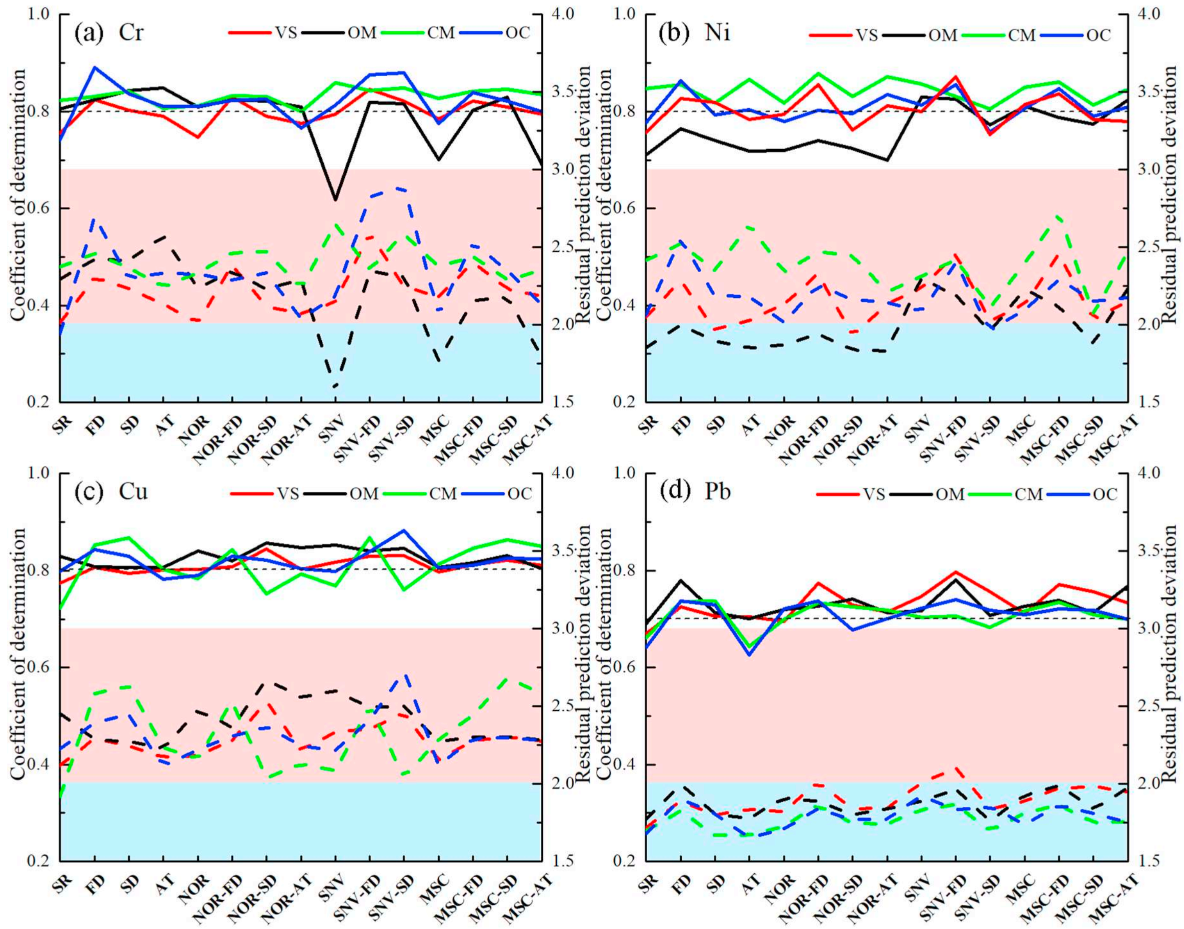

Fig. 5. Prediction results based on different model variables: (a) Cr; (b) Ni; (c) Cu; (d) Pb
OM bands: Organic matter-related spectral bands; CM bands: Clay mineral- related spectral bands; OC bands: Organic and clay mineral related spectral bands.

model is optimal for Pb, which indicates that Pb in soil is also affected by other factors, such as iron oxide. It also facilitates the prediction of the element Pb. Therefore, the band associated with soil components is the core of the overall VNIR–SR estimation of soil Pb concentration. The results of the adsorption experiments are also confirmed.

In theory, when the same band is selected, models built using the entire VNIR–SR should achieve at least the same prediction accuracy. The prediction accuracy of the entire VNIR–SR may be higher than that of the organic or clay-related bands because the former may contain more useful spectral information, although they are not as significant as the latter. For the elements Cr and Cu, the model established by using the combined bands, the model has better performance. In this model, a useful band for element concentration estimation can be extracted at a low computational cost.

4.3. Application prospect of hyperspectral remote sensing

In terms of environmental monitoring, traditional methods for investigating the spatial distribution of soil heavy metals, such as on-site sampling, indoor chemical analysis, and geostatistical interpolation, are expensive and labor-intensive [22]. Hyperspectral inversion of soil heavy metal content, the possibility of mapping heavy metal concentration maps is constantly confirmed [18,23]. At the same time, the application of hyperspectral technology faces several challenges. For example, the low signal-to-noise ratio of the sensor negatively affects the quality of the hyperspectral images obtained. Several techniques, including preprocessing techniques, stable fitting models, and variable extraction methods, have been adopted to improve the quality of hyperspectral data. Studies have also shown that the range of soil element concentrations also has a certain impact on model accuracy [24,25]. Therefore, when establishing the related estimation model, considering the influence of various factors on the prediction model is necessary. Heavy metal pollution in agricultural soils seriously threatens food security. Remote sensing images have broad application prospects in soil heavy metal pollution monitoring due to its periodicity, wide area coverage, and high efficiency.

Table 2
Prediction accuracy of the optimal model based on different model variables.

Element	VNIR-SR (500-2400 nm)			OM bands			CM bands			OC bands		
	R^2	RMSEp	RPD	R^2	RMSEp	RPD	R^2	RMSEp	RPD	R^2	RMSEp	RPD
Cr	0.85	11.15	2.59	0.85	11.23	2.57	0.86	10.90	2.65	0.88	9.99	2.89
Ni	0.87	10.74	2.46	0.83	11.46	2.30	0.86	9.70	2.72	0.86	10.33	2.55
Cu	0.84	9.32	2.53	0.86	8.82	2.67	0.85	8.79	2.68	0.88	8.64	2.73
Pb	0.80	18.58	2.10	0.78	19.87	1.97	0.74	20.93	1.87	0.72	20.94	1.87

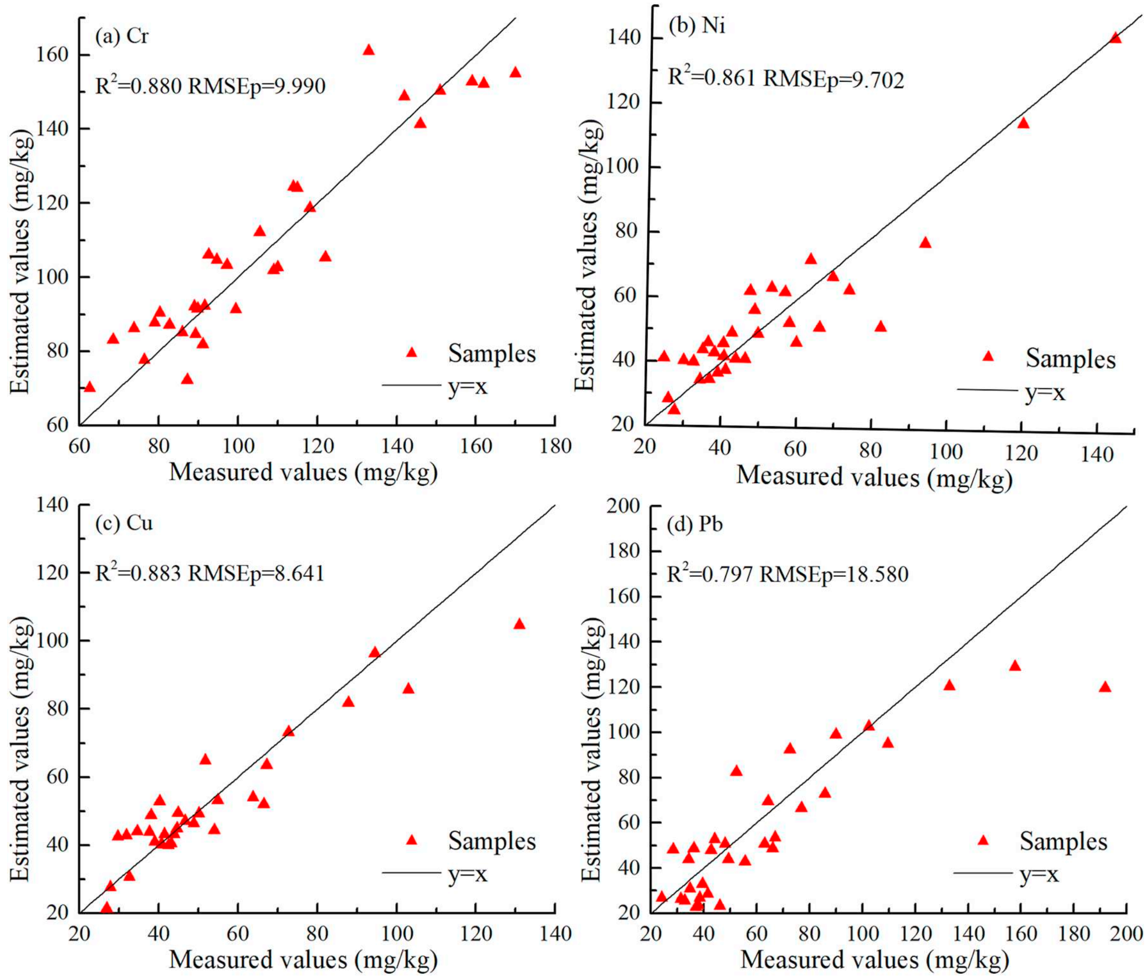

Fig. 6. Scatter plot of predicted and measured values of the model.

5. Conclusions

The combination of NOR, MSC, and SNV and differential transformation can enhance the performance and stability of heavy metal prediction model. The combination of SNV and FD can predict the contents of Cr, Ni, and Pb. Accurate prediction of Cu is achieved by the model established by the combination of NOR and SD. The bands related to soil composition can improve the accuracy and stability of the Cr, Ni, Cu, and Pb prediction models and verify the effectiveness of the proposed method. The spectral responses of soil Cr, Ni, Cu, and Pb are closely related to the relevant bands of clay minerals and organic matter. The model established by band related to clay minerals has good prediction ability for Ni content. The combination of the bands associated with the two soil components (organic matter and clay mineral) can stably predict soil Cr and Cu. Accurate prediction of soil Pb comes from the entire VNIR-SR model, which indicates that the concentration of Pb in the study area is related to a various of soil chemical components. The ELM algorithm can improve the training speed and accuracy of the model but has poor prediction results for Pb with large sample ranges. Therefore, ELM is only suitable for samples with a small magnitude. Finally, according to the prediction results of the models, the ELM models established show the order Cr > Cu > Ni > Pb.

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