Chapter 8

Estimate of Heavy Metals in Soil Using Combined Geochemistry and Field Spectroscopy in Miyi Mining Area

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Additional information is available at the end of the chapter

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Abstract

Heavy metal-contaminated soil and water is a major environmental issue in the mining areas. However, as the heavy metals migrate frequently, the traditional method of estimating the soil's heavy metal content by field sampling and laboratory chemical analysis followed by interpolation is time-consuming and expensive. This chapter intends to use field hyperspectra to estimate the heavy metals in the soil in Bai-ma, De-sheng and YuanBaoshan mining areas, Miyi County, Sichuan Province. By analyzing the spectra of soil, the spectral features derived from the spectra of the soils can be found to build the models between these features and the contents of Mn and Co in the soil by using the linear regression method. The spectral features of Mn are 2142 and 2296 nm. The spectral features of Co are 1918, 1922 and 2205 nm. With these feature spectra, the best models to estimate the heavy metals in the study area can be built according to the maximal determination coefficients (R^2). The determination coefficients (R^2) of the models of retrieving Mn and Co in the soil are 0.645 and 0.8, respectively. The model significant indexes of Mn and Co are 2.04507E-05 and 7.73E-06. These results show that it is feasible to predict contaminated heavy metals in the soils during mining activities for soil remediation and ecological restoration by using the rapid and cost-effective field spectroscopy.

Keywords: contaminated heavy metals in the soils, spectral measured, spectral analysis

1. Introduction

Due to the development of industries in recent decades, the demand for mineral resources is also growing. However, the mining and post-processing of mineral resources will increase the heavy metals that permeate and accumulate in the soil. These heavy metals are in abundance, in terms of persistence and toxicity, which can inhibit soil functions and increase the soil pollution [1–3]. And when accumulated to harmful levels, the heavy metals in soil may pose an environmental risk and threaten human health through contaminating the food chain, water and air [4–6]. Thus, the pollution of soil by heavy metals is considered as one of the major environmental problems, and the monitoring of heavy metal content is very important for environment management in mining areas.

The traditional method for estimating the heavy metal contents involves the field data measure and laboratory analysis of soil samples. Although direct sampling can provide an accurate measurement of both the intensity and diversity of soil contaminants at specific sites, however, these procedures are often time-consuming and costly, and it can only analyze the point samples [7–9]. So rapid, periodic monitoring of heavy metals in the areas vulnerable to pollution is important. The development of remote-sensing technology, especially hyperspectral, provides a possibility for the rapid and large-scale distribution of heavy metals, which can acquire the continuous spectrum of the target. Many studies have shown that the spectral curves of heavy metal-contaminated soil and the spectral curves of uncontaminated soil have a difference [10, 11]. Although soil heavy metals are spectrally inactive, their relationships with spectrally active soil properties, such as clay and Fe oxides, may allow for their visible and near-infrared diffuse reflectance spectroscopy (VNIRS) prediction [12]. Thus, the relationship between heavy metal content and soil spectrum was used to establish heavy metal retrieval model to predict and map the heavy metal content in the relevant areas [11, 13–15].

In this chapter, the spectral sampling of soil samples was obtained by ASD Fieldspec III spectroradiometer and the contents of Mn and Co were measured by chemical analysis. Then, the feature spectra can be obtained from the results of spectroscopic analysis to establish the heavy metals' retrieval models. Then, the parameters of these models can used to explore the feasibility of using hyperspectral data to retrieve soil heavy metals for soil remediation and ecological restoration.

2. Materials and methods

2.1. Study area

Miyi Country (26°42´–27°10´ N, 101°44´–102°15´ E) is located in the north of Panzhihua City, the southwest of Sichuan Province. The terrain is high in the south and low in the north. In this chapter, the Bai-ma, De-sheng and Yuan Bao-shan mining areas in Miyi County are selected as the study areas, as shown in **Figure 1**. The study area is located in the east of the Yalong River and northwest of the Anning River. The environment in the mining area and surroundings have been contaminated by heavy metals which can enter into the soil through discharge and infiltration and which exist in the waste residue and waste liquor generated in the mining process, especially Mn and Co.

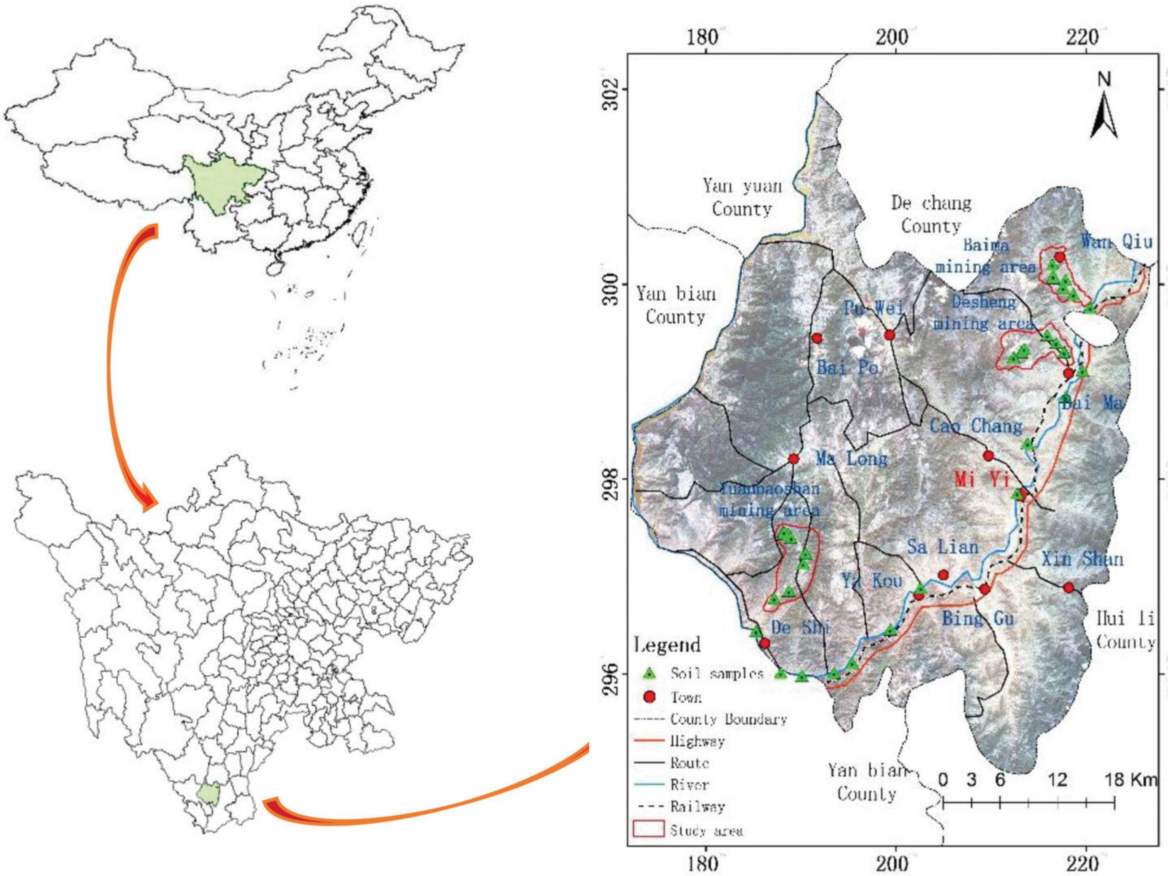


Figure 1. The study area locations of sampling points.

2.2. Data collection

The spectra of 55 soil samples were collected in June 2015; the locations of the sample points are shown in **Figure 1**. Meanwhile, 32 out of the 55 soil samples had been chemically analyzed for the Mn and Co contents by conventional digestion methods using inductively coupled plasma mass spectrometer (ICP-MS). The ICP-MS is the most popular ion source in analytical chemistry for elemental mass spectrometry. In ICP-MS, a mass spectrometer is coupled to an ICP torch by an interface including sampler and skimmer cones so that representative samples of the plasma can be transmitted through its orifices to the mass analyzer [16].

The soil sample's spectrum was obtained from a high spectral resolution ASD Fieldspec III spectroradiometer, which covers the visible and near-infrared (350–2500 nm) region and offers a spectral resolution between 3 and 10 nm, interpolated to 1 nm. Illumination was provided by an ASD high-reflectance probe when collecting soil spectra in the field, while a halogen bulb was used as the light source while collecting water spectra in the laboratory. Each sample was measured three times and the average value was calculated afterwards [11].

2.3. Spectral pre-processing

The soil spectra may contain noise or error that was introduced by operating in situ measurement instruments improperly or using an in situ measurement instrument that is not calibrated properly [17]. And, heavy metals are spectrally featureless in the visible and near-infrared parts of the electromagnetic spectrum. Thus, a serious predicament is observed while dealing with the analysis of overlapping bands of the analytes and interferences which make the extraction of qualitative and quantitative data difficult [18]. Pre-processing of the spectrum is often required to reduce the effect of noise and enhance the spectral signature. Meanwhile, Savitzky–Golay differentiation is a commonly used spectral pre-treatment method, and in practice the first and second derivatives eliminate the interference of the baseline or background, improve sensitivity and detect and enhance minor or subtle spectral features [18, 19]. Obtained spectra were continuum removed and normalized to enhance the spectral absorption features. The continuum that is a convex hull of straight-line segments is fitted over a reflectance spectrum and subsequently removed by division or ratioing relative to the complete reflectance spectrum [8].

2.4. Spectral analysis and model development

In view of the weak relationship between soil spectroscopy and heavy metals, the logarithmic treatment of feature bands can be used to enhance their relationship [8]. In this chapter, the reflectivity of all bands is extracted to create a single-band reflectivity matrix. The band reflectivity from the second band to the last band was selected as the outer loop and the first band to the penultimate band was selected as the inner loop. Then, the band ratio matrix can be obtained when the outer loop is divided by the inner loop, and the band normalization matrix can be obtained by the difference of reflectivity divided by the summation between the outer loop band reflectance and the inner loop, and the multivariate analysis matrix of two bands and three bands can be obtained by combining two or three output feature bands randomly. Then, these matrices were used for Pearson correlation analysis with the soil heavy metal content matrices. The Pearson correlation coefficient is a measure of the linear dependence (correlation) between two variables X and Y, the greater the absolute value of the correlation coefficient, the greater the correlation between the two variables [20, 21]. Thus, it is possible to predict heavy metal contents in the soil with the high correlation between heavy metal content and soil spectrum [22].

In this chapter, the methods of smoothed, the first derivative, the second derivative and the continuum removal of the spectral data were performed by the View Spec Pro and ENVI to eliminate background noise and enhance the spectral feature. The methods of ratio, normalization and multivariate analysis are used to enhance the correlation between heavy metal content and feature spectra. Finally, the IBM SPSS software was used to establish retrieval model.

3. Results

3.1. Geochemical analysis

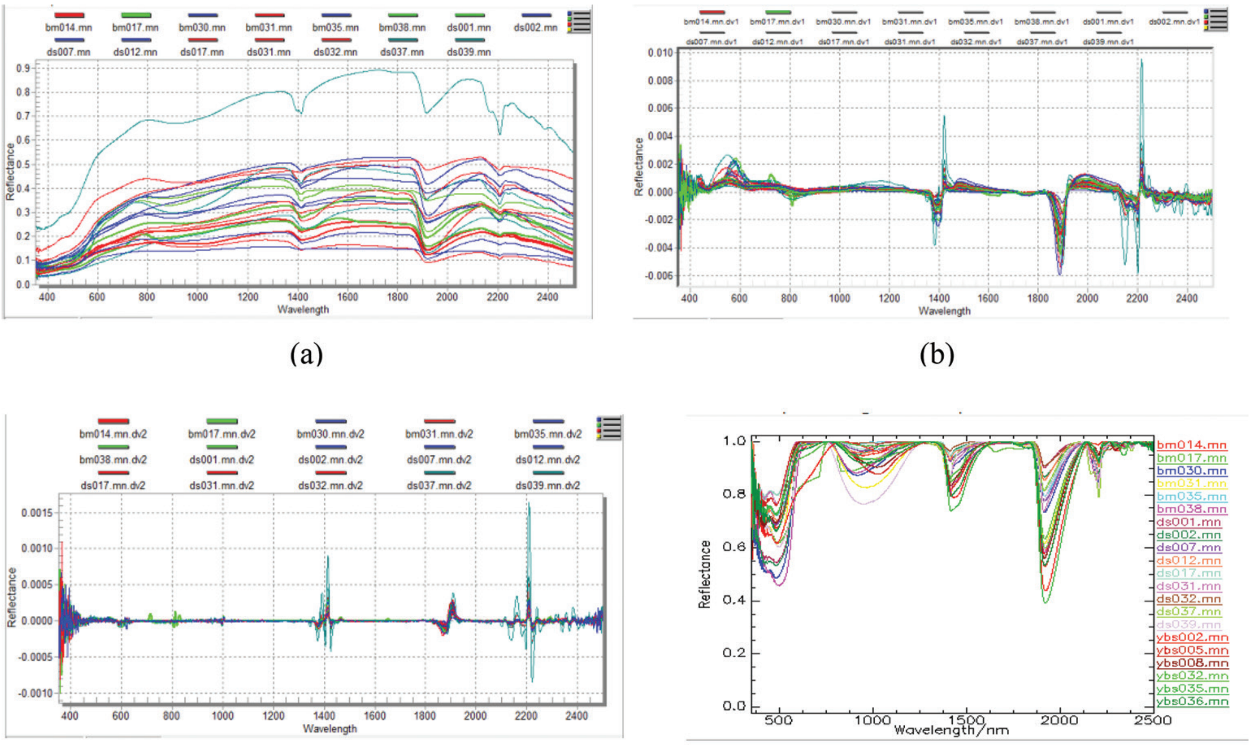
Mn and Co are the predominant heavy metals in mining waste in the study area, so they were selected as indicators of the environmental impacts from mining activity. The chemical analysis results of soil samples are shown in **Table 1**. From **Table 1**, we can see that the contents of Mn made a great difference with the contents of Co in soil. The standard deviation (SD) of Mn in the soil was relatively high (773.6), which indicates that its concentrations are of little great difference, while the contents of Co in the soil is of small difference.

3.2. Spectral analysis

The visual inspection of the measured soil spectra with different pre-treatment methods showed a significant difference. The original spectral curve and the curves pre-processed by the first derivative, the second derivative and the continuum removal method of soil samplings in the study area are shown in **Figure 2**. The feature spectra can be obtained from these spectrum curves, as shown in **Table 2**. From **Figure 2**, we can see that only 12 feature spectra can be selected as the feature bands from the original soil spectral curve at 473, 791, 1395, 1413, 1926 nm and so on; however, more feature spectra can be selected as feature bands from the soil spectral curves after pre-processing at 584, 1382, 1396, 1403, 1421, 1452, 1890, 1906 nm and so on.

	Max	Min	Mean	SD
Mn	4114.0	531.3	1536.1	773.6
Co	111.9	6.00	43.5	25.87

Table 1. Content of heavy metals in soil statistics (unit: mg/kg).



(a)

(b)

(c)

(d)

Figure 2. Reflectance spectra of soil samples. (a) Raw reflectance spectral, (b) first-derivative reflectance spectral, (c) second-derivative reflectance spectral, (d) continuum removed reflectance spectral.

	Original spectra	1st spectra	2nd spectra	Continuum removed spectra
Feature spectra	473, 791, 1395, 1413, 1854, 1926, 2136, 2170, 2208, 2243, 2259, 2320,	439, 465, 549, 584, 1382, 1396, 1403, 1421, 1452, 1482, 1766, 1890, 1926, 1993, 2121, 2151, 2172, 2200, 2215, 2234, 2280, 2361, 2375, 2398	550, 590, 625, 995, 1006, 1374, 1393, 1403, 1411, 1425, 1466, 1883, 1906, 2138, 2163, 2196, 2209, 2220, 2240, 2291, 2368, 2387	452, 486, 627, 765, 810, 962, 1029, 1285, 1414, 1698, 1786, 1835, 1918, 1922, 2142, 2205, 2236, 2267, 2296, 2342, 2371, 2386, 2411

Table 2. Feature spectra of four kinds of curves (unit: nm).

3.3. Model development

The spectral features selected from the reflectance spectra are used for spectral analysis and the band combination with the maximum Pearson correlation coefficient (R) is selected as the feature band to build the inversion models of heavy metals. And the regression equations of heavy metals' concentrations in the soil are presented in **Table 3**. For the heavy metal in the soil, the determination coefficients (R^2) of the regression equations are Mn: 0.645 and Co: 0.8. And the determination coefficient (R^2) of the regression equations indicates that the measured heavy metals have a strong relationship with spectral features. Specifically, the ratio of bands at 2124 and 2296 nm has a strong relationship with the contents of Mn, and the bands at 1918, 1922 and 2205 nm have strong relationships with the contents of Co. And the significance indexes of these regression equations are less than 0.05.

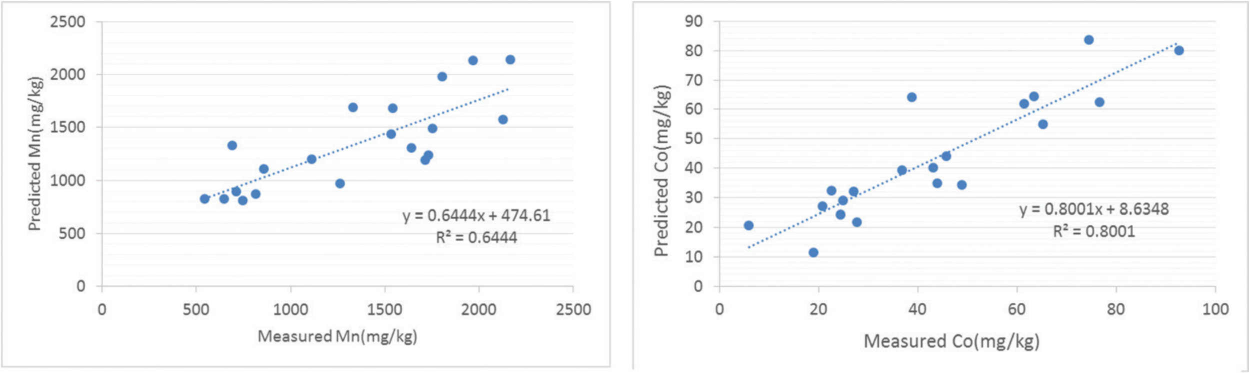
The relationship of the measured and predicted concentrations of Mn and Co in soil is shown in **Figure 3**. From the scatter diagrams, we can see that there is a good linear relationship between the measured and predicted concentrations of Mn and Co.

The contents of 12 test soil samples of Mn and Co can be calculated by these regression equations. Then the F-test was carried out to validate the feasibility of these regression models for predicting heavy metal contents, as shown in **Table 4**. From the statistics, we can see that the difference of the mean values of Mn and Co is smaller and the P-value of the F-test between measured and predicted values of Co and Mn in the soil is less than 0.05. This indicates that the models can be used to predict the heavy metal contents in the study area.

	Feature bands (nm)	R^2	Regression equations	Significance F
Mn	2142, 2296	0.645	$Y = -33749.8 + 34703.04X$	2.04507E − 05
Co	1918, 1922, 2205	0.800	$Y = -235.03 - 7507.17X1 + 7452.81X2 + 333.65X3$	7.73E − 06

Note: X corresponding to R2142/R2296; X1, X2, X3 corresponding to R2121, R2234, R2398, respectively.

Table 3. Spectra parameters and regression equation of Mn and Co.

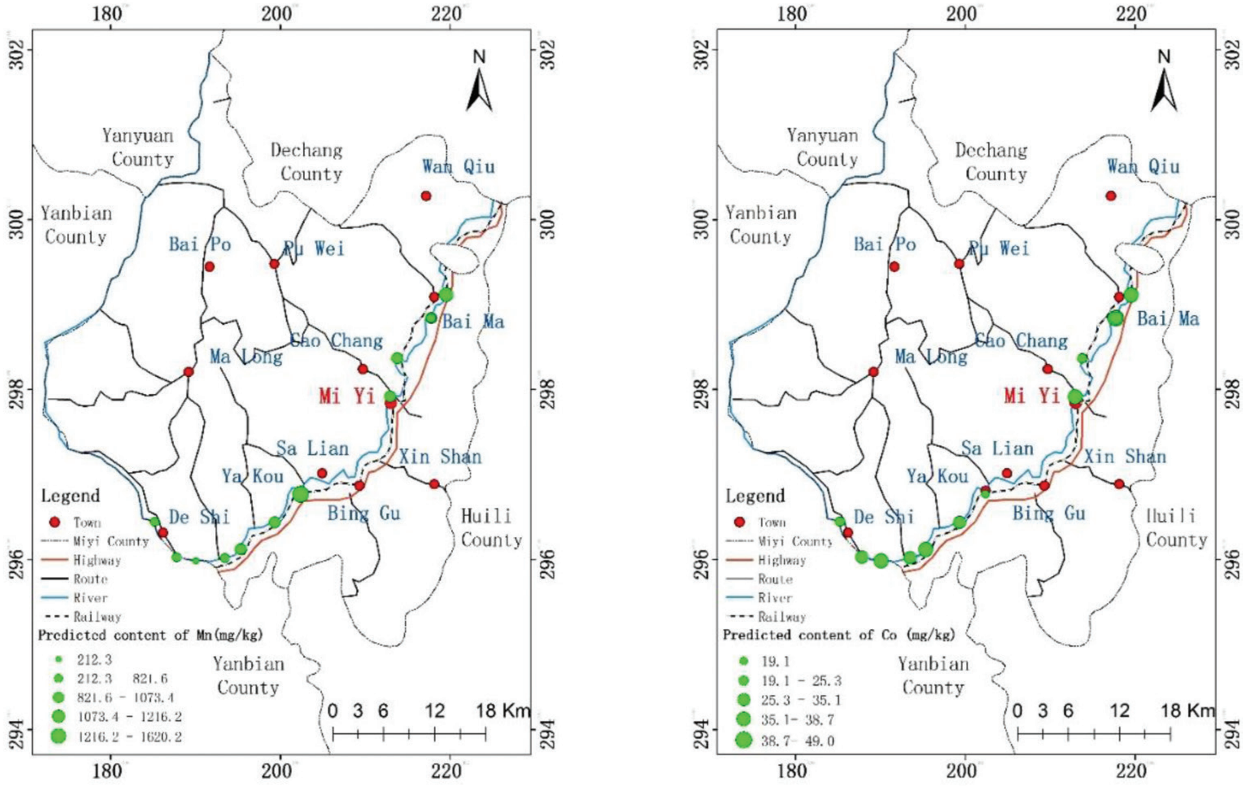


(a) (b)

Figure 3. Scatter plots of the measured values and predicted values: (a) Mn and (b) Co.

	Measurement			Prediction			P(F ≤ f)
	Max	Min	Mean	Max	Min	Mean	
Mn	4114	531.3	1871.6	2290.1	924.9	1474.7	0.003
Co	111.9	13.1	44.0	82.2	22.1	48.4	0.008

Table 4. Summary statistics of measured and predicted heavy metal concentration and F-test (concentration unit: mg/kg).



(a) (b)

Figure 4. Predicted content of Mn and Co. (a) The predicted content of Mn and (b) the predicted content of Co.

The results of the predicted content of Mn and Co in soil are shown in **Figure 4**. From the content distribution of the test samplings, we can see that the sampling sites are mainly distributed along the Anning River area. From **Figure 4(a)**, we can see that the content of Mn in the vicinity of Yakou Town is the largest, and it is decreased with the water that flows southward. This indicates that the water has a great influence on the distribution of the content of Mn. From **Figure 4(b)**, we can see that the contents of Co are high in Yuanbaoshan county and Desheng mining area. This indicates that the water has a poor influence on the distribution of the content of Co. The reasons of the high content of Co are (1) the leakage of minerals and slag during transportation and (2) the combustion of Co which is not complete.

4. Discussion

The roughness of soil surface, molecular vibration and electron transition can be changed by the particles of heavy metals adsorbed by the soil organic matter, which makes it is possible to use the soil spectrum to invert the soil heavy metals. The quantitative relationship between the spectrum and the heavy metal content was established by using spectral analysis and chemical analysis of the soil samples. Then the heavy metal content of Co and Mn can be obtained to provide prediction data for regional soil quality research and treatment. From **Figure 4**, we can see that the content distribution of each heavy metal is irregular in the study area for the influences of the river, vegetation and mineral transportation. The flow of river could help transform gradients to the location and extent of heavy metal pollution. The absorption of vegetation could reduce the heavy metal pollution in the soil and the mineral transportation could lead to the jumping change of heavy metal pollution.

Compared to traditional methods, the field of hyperspectral method has many advantages such as fast, efficient, wide coverage and nondestructive to estimate the heavy metals' contents. It can provide predictive data for mine environment monitoring to improve the efficiency of monitoring and management of mine area and protect the surrounding residents' normal life quality. But it still needs much time to collect spectral data and build models, and the monitoring area is limited, and the field sample collection and spectral measurements may contain errors. Therefore, the following research work is to (1) consider the influence of temperature, altitude, weather and other factors on the spectrum to improve the accuracy of the model, (2) obtain the spectral data at the same time when the field data collection is obtained and (3) acquire the Hyperion or AVIRIS imagery of the study area but considering the influence of vegetation, rock and atmosphere on soil spectrum.

5. Conclusions

In this chapter, a fast and convenient method to get the heavy metals' contents in the soils of the study area is described, which can provide a prediction for the eco-remediation of heavy metals in the mining area, leading to assign the human and other resources properly. So the time of remediating the heavy metals contaminated soils can be shortened and prevent the further spread of heavy metals in the soils.

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