

# Spectra assessment for the soil Hg contamination

Yunzhao Wu, Jun Chen, Xinmin Wu, Qingjiu Tian, Junfeng Ji  
Department of Earth Sciences, Nanjing University, Nanjing 210093, China  
njuessi@hotmail.com

**Abstract:** Conventional methods investigating soil Hg contamination are time-consuming and expensive. A quicker method is developed to predict soil Hg content with convolved HyMap, ASTER, and TM spectra. The prediction accuracy for each sensor is satisfactory and similar. It suggests that low spectral resolution is not a limitation for predicting soil Hg content. Correlation analysis reveals that Hg-sorption by iron oxides is the mechanism by which to predict spectrally featureless Hg with reflectance spectra. Future study with field measurements and remote sensing data is recommended.

**Key words:** remote sensing, spectra, soil contamination, mercury

## 1. Introduction

In the last few decades, large amounts of Hg have been deposited in the periurban soils of Nanjing area. High concentrations of Hg are very toxic to biological lives. Now there is an increasing need to investigate soil Hg contamination. Conventional methods investigating Hg contamination based on raster sampling and chemistry analysis are time-consuming and expensive.

The remote-sensing approach, which can allow for synoptic and repetitive coverage of large areas in a cost-effective way, has become an attractive tool for assessing and mapping soil physical and biogeochemical properties for environmental purposes. Optical remote sensing techniques measure soil reflectance spectra within the VNIR-SWIR region (0.38-2.5  $\mu\text{m}$ ) to characterize soils and monitor their changes. Laboratory studies have shown successful application of soil reflectance for predicting soil constituents which have spectral features like iron oxides<sup>[1]</sup>, organic matter<sup>[2]</sup> and clays<sup>[3]</sup>. Moreover, recent studies showed that, though soil heavy metals at low concentration levels do not have spectral features, the elevated heavy metals input by anthropogenic activities are absorbed by iron oxides, organic matter and clays<sup>[4]</sup>, and via inter-correlation with these soil constituents that are spectrally active, heavy metal concentrations can be predicted<sup>[5,6]</sup>.

An important requirement for a successful application of remote sensing in mapping contaminated land is a detailed spatial and spectral resolution of the images<sup>[7]</sup>. Imaging spectrometers fulfill these requirements. Until now examples of the use of imaging spectroscopy are available for the mapping of contaminated soils in abandoned mines<sup>[8]</sup>. To the authors' knowledge, research

on investigating Hg contamination for agricultural soils with image spectrometers has not been reported.

Comparing with hyperspectral images, the data from spaceborne multispectral sensors are cost-effective and convenient to acquire. Initially laboratory reflectance spectra of 120 soil samples from Nanjing periurban area are spectrally simulated into the HyMap, ASTER, and TM bands allocated within the VNIR-SWIR region. The objectives of this study are: 1) to predict soil Hg content by simulated spectra with statistical methods and 2) to explore the influence of spectra resolution on the prediction accuracy. A successful prediction based on reflectance spectra can open the possibilities for a rapid remote mapping of soil Hg contamination levels.

## 2. Materials and methods

### 2.1 Soil Sampling and Chemical Analyses

One hundred and twenty soil samples were collected from surface soil along the designated locations in Nanjing periurban area. The samples were air-dried and sieved through a 2 mm- polyethylene sieve. They were then ground until fine particles (<200  $\mu\text{m}$ ) were obtained. Each sample was split into two subsamples. One was used for spectral measurements, the other analyzed for Hg content. Hg was determined using an acid digestion method<sup>[9]</sup> and measured by Atomic Absorption Spectrometry (AAS).

### 2.2 Spectral Measurements and Simulation

Reflectance spectra were measured in a Lambda 900 spectrophotometer with 2nm sampling intervals between 3.78 and 2.498  $\mu\text{m}$ . The sample preparation followed the procedure from Balsam<sup>[10]</sup>.

Reflectance values of HyMap, ASTER, and TM spectral bands were simulated using the full width half maximum (FWHM) values for their respective filter functions.

### 2.3 Model Construction and Validation

Firstly an exploratory analysis is carried out for all 120 samples to detect outliers. The samples which decrease the prediction accuracy can be defined as outliers and hence will be left out. Then the remaining samples are split into a calibration set and a test set. In order to obtain the optimum performance, several models are tried using the calibration set, such as Linear, Exponential, Quadratic, and Logarithmic. The model that gives the highest regression coefficient (R) is chosen as

Table 1. The optimal equations of the calibration sets for the three sensors for predicting Hg

	R	F	Sigf	$E_0$	$E_1$
HyMap51	-0.661**	64.37	0.000	20.044	-0.120
ASTER3	-0.645**	59.20	0.000	11.115	-0.119
TM4	-0.645**	59.11	0.000	12.049	-0.120

Note: The optimal regression models for all the three sensors are Exponential equations

\*\* : Correlation is significant at the 0.01 level

final model, and to validate the model, F-test is added.

Moreover, in order to explore further the mechanism by which to predict Hg, the relationship between Hg content and spectral absorption depth at  $0.49 \mu\text{m}$ , which is attributable to ferric electronic transition of goethite, is examined. Goethite has much higher surface areas and thus can adsorb Hg. The absorption depth is measured on continuum-removed spectra<sup>[11]</sup>.

### 3. Results

Fig. 1 presents the continuum-removed spectra of sample JNX-1 and goethite. The presence of iron results in absorption at wavelengths in the  $0.4$  to  $1.3 \mu\text{m}$  region, While the absorption features are broad and weak. By continuum removal, the small absorption features are enhanced. Doublet absorption feature near  $0.49 \mu\text{m}$  is weaker and broader than pure goethite because of the soil matrix effect.

Variations of the reflectance are negatively correlated with Hg content. However, the samples with low Hg content have large deviation. In order to obtain optimal prediction, fifteen samples with Hg concentrations lower than  $0.05\text{ppm}$  are left out. The remaining dataset of 105 samples is split into a calibration set consisting of 85 samples and a test set consisting of 20 samples.

Table 1 shows the optimal equations for predicting Hg. HyMap51, ASTER3 and TM4 are the optimal bands for each sensor respectively, and exponential models are the optimal regression models for all sensors. The R value for HyMap51 is the highest. However, it is not much different from that of ASTER3 and TM4. It suggests that spectral resolution is not necessarily a limitation for predicting soil Hg content with empirical methods.

The final models are validated using the test sets. Table 2 presents the regression line ( $C_{\text{predicted}} = a + b C_{\text{measured}}$ ) parameters of the validation stage along with their statistical significance. The low  $b$  values are due to sample JNX-129, which has the highest Hg content (15

Table 2. The regression line parameters of the test sets for the three sensors in the validation stage

	R	F	Sigf	$a$	$b$
HyMap51	0.641**	12.52	0.002	0.256	0.333
ASTER3	0.629**	11.78	0.003	0.259	0.311
TM4	0.628**	11.71	0.003	0.260	0.313

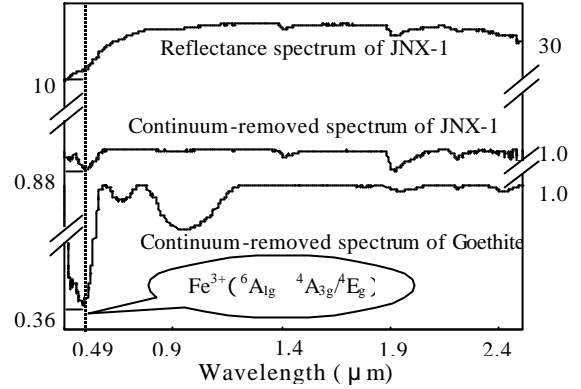


Fig. 1. The original and continuum-removed spectra of sample JNX-1, also presents the continuum-removed spectrum of Goethite

times higher than background value) and shows an underestimation of the predicted value. An explanation for this sample is that it originates from point source pollution instead of diffuse pollution. Also, it can be seen that the R values for all sensors are similar, which strengthens the finding that the prediction abilities for all sensors are similar. So considering the cost, multispectral spaceborne images (e.g. TM) can be good choices to investigate soil Hg contamination levels.

Fig. 2 presents the boundary of the Hg pollution index which is calculated as the quotient between the predicted /measured Hg concentration and its background value. When the samples fall within the boundaries of a certain class depicted by the box on the diagonal then they are classified right. Prediction for the cleanliness and low contamination samples is satisfactory. Sample JNX-129 shows an underclass of the predicted value but it is not representative for the set we want to investigate.

### 4. Discussion

For a better understanding of the functioning of the prediction model, the relationship between Hg content and the spectral feature depth at  $0.49 \mu\text{m}$  is examined. Our result shows that Hg content is positively correlated with the absorption depth ( $R^* = 0.52$ ). However, from Table 1 it can be clearly seen that Hg content is negatively correlated with soil reflectance, and the highest correlation is at  $1.14 \mu\text{m}$  HyMap band (HyMap51).

These findings indicate the Hg-sorption by soil iron oxides. Soils of the research area, mainly yellow brown soil, contain large amounts of goethite. The yellowish color is attributable to the iron absorption near  $1 \mu\text{m}$  of the goethite. Goethite has strong adsorption capability<sup>[12]</sup>. For example Oliveira found that the higher levels of Hg were associated with higher Fe concentrations<sup>[13]</sup>. Hg content becomes higher as goethite content increases, and accordingly the spectral absorption depth at  $0.49 \mu\text{m}$  becomes deeper. Therefore, Hg content is positively correlated with the absorption depth. However, the soil

reflectance values decrease because of iron absorption. So Hg content is negatively correlated with soil reflectance. Other iron oxides can also adsorb Hg. The absorption feature around 1.14 $\mu\text{m}$  is caused by iron in ferric or ferrous form. It reflects the presence of all the forms of iron oxides, so at which the soil reflectance is the strongest negatively correlated with Hg content.

The increasing Hg by anthropogenic input and iron oxides are inter-correlated. However, it is notable that the levels of Hg in unpolluted soils are naturally accumulated from rocks through pedogenesis, and most of them are not absorbed by iron oxides but exist in the crystal lattice of the minerals. Therefore, the correlation between the low levels of Hg and iron oxides is weak. It explains why the prediction accuracy becomes higher by removing samples with Hg concentration far lower than background value.

Hg is hard to transfer, and tends to be concentrated in surface soils. Hence, future applications will focus on mapping Hg contamination levels through remote sensing in a cost-effective way. However, the predicting with remote sensing will be faced with several other problems, such as soil roughness, sun zenith, soil moisture, atmospheric attenuation, low signal-to-noise ratio (SNR), pixel mixing, etc. Future study will be carried out to collect spectra directly in the field or with remote sensing instruments in winter or early spring, when vegetation still hasn't burgeoned; soil moisture is low; and soil hasn't been furrowed. It should be noted that the results of this study are only valid for the soil types represented in the investigated region. Further studies are required on other soil types and heavy metals.

## 5. Conclusions

This study shows that the simulated soil reflectance for HyMap, ASTER, and TM bands is a promising method for assessing elevated Hg concentration. Comparing with expensive hyperspectral images,

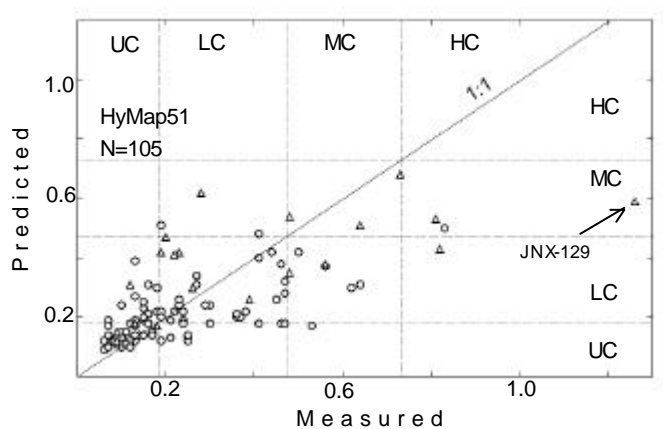


Fig. 2. The predicted by HyMap 51 versus measured values for both the calibration ( ) and test ( ) set, and also presents the boundary of the Hg pollution index (UC=uncontaminated; LC=Low contamination; MC= Moderate contamination; HC= High contamination)

spaceborne multispectral sensors which are relatively cost-effective may be good choices to investigate soil Hg contamination levels. Correlation analysis reveals that the inter-correlation between Hg and iron oxides is the mechanism by which to predict spectrally featureless Hg. Future study with real remote sensing data and field measurements is strongly recommended.

## References

- [1] Ji, J.F., Balsam, W.L., Chen J., Liu, L.W., 2002. Rapid and quantitative measurement of hematite and goethite in the Chinese Loess-Paleosol sequence by diffuse reflectance spectroscopy, *Clays and Clay Miners*, 50, 210-218.
- [2] Fidencio, P.H., Poppi, R.J., de Andrade, J.C., 2002. Determination of organic matter in soils using radial basis function networks and near infrared spectroscopy, *Analytica Chimica Acta*, 453: 125-134.
- [3] Ben-Dor, E., Banin, A., 1995. Near infrared analysis (NIRA) as a rapid method to simultaneously evaluate several soil properties, *Soil Science Society of American Journal*, 59: 364-372.
- [4] Naidu, R., Sumner, M.E., Harter, R., 1998. Sorption of heavy metals in strongly weathered soils: an overview, *Environmental Geochemistry and Health*, 20: 5-9.
- [5] Kooistra, L., Wehrens, R., Leuven, R.S.E.W., Buydens, L.M.C., 2001. Possibilities of visible near infrared spectroscopy for the assessment of soil contamination in river floodplains, *Analytica Chimica Acta*, 446: 97-105.
- [6] Kemper, T., Sommer, S., 2002. Estimate of heavy metal contamination in soils after a mining accident using reflectance spectroscopy, *Environmental science and technology*, 36: 2742-2747.
- [7] Folkard, A.M., 1998. How far can imaging spectroscopy go in identifying the cause of vegetation stress around landfill sites? *Proc. 1st EARSeL workshop on imaging spectroscopy*, Zurich, 6-8 October 1998, EARSeL Paris, pp. 447-453.
- [8] Hauff, P.L., D.C. Peters, G. Borstad, W. Peppin, E. Dillenbeck, E.G. Gloss & E.C. Prosh. 2000. Hyperspectral investigations of mine waste and abandoned mine lands - The Dragon calibration site case study, *Summaries of the Ninth Annual JPL Airborne Earth Science Workshop*, 23-25 February 2000, JPL, Pasadena.
- [9] Li, X.D., Thornton, I., 1993. Multi-element contamination in soil and plant in the old mining area. U.K. *Applied Geochemistry* S2, 51 – 56.
- [10] Balsam, W.L., Deaton, B.C., 1991. Sediment dispersal in the Atlantic Ocean: Evaluation by visible light spectra, *Reviews in Aquatic Sciences*, 4: 411- 447.
- [11] Clark, R. N., Roush, T. L., 1984. Reflectance spectroscopy: quantitative analysis techniques for remote sensing application, *Journal of Geophysical Research*, 89:6329-6340.
- [12] Sparks, D. L., 1995. *Environmental soil chemistry*, San Diego: Academic press.
- [13] Oliveira S M B D, et al. 2001. Soils as an important sink for mercury in the Amazon, *Water, Air Soil Pollution.*, 26: 321-337.