

# OBSERVATION OF SPECTRAL CHARACTERISTICS FOR SOIL CONTAMINANTS

Eun-Young Choe<sup>1</sup>, Kyoung-Woong Kim<sup>1\*</sup>, Sung-Soon Lee<sup>2</sup> and Kwang-Hoon Chi<sup>2</sup>

1) Advanced Environmental Monitoring Research Center (ADEMRC), Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST)

2) Geoscience Information Center, Korea Institute of Geoscience and Mineral Resources (KIGAM)

\*e-mail: kwkim@gist.ac.kr, phone: +82-62-970-2450, Fax: +82-62-970-2434

## ABSTRACT:

Spectral characteristics depending on soil constituents and their proportion in a soil were firstly studied for monitoring of soil contamination using hyperspectral remote sensing. The reflectance spectra of heavy metals in soils were investigated in the VIS-NIR-SWIR regions (400-2500 nm) to observe spectral variation as a function of constituents and concentrations. Commercial kaolinite soils mixed with lead, copper, arsenic, and cadmium were used as synthetic soil samples for spectral measurement. In case of copper, relatively spectrally active regions was observed with some band shift whereas other heavy metals had only simple spectral variations expected to be related to the sorption phase and the amount of metal onto kaolinite. The reflectance spectrum of each metal on kaolinite could be identified in VIS-NIR region.

**KEY WORDS:** Hyperspectral, Reflectance Spectroscopy, Spectral Characteristics, Heavy Metals, Kaolinite

## 1. INTRODUCTION

The hyperspectral remote sensing is applying to the field of environmental sciences as a complementary tool. This field has shown a potential for observing soil status, soil properties, and some soil environment interactions in the soil environmental science. Soil spectral information can predict soil contaminations. For monitoring and estimating soil contamination using hyperspectral remote sensing, spectral characteristics have to be firstly studied depending on soil constituents and their portion in soils.

Moreover, it has been demonstrated that reflectance spectroscopy within the visible-near-infrared region is able to provide non-destructive rapid prediction for soil physical, chemical, and biological properties in the laboratory (Ben-Dor and Banin, 1995). The discrimination of major soil types from satellite multi-spectral and aircraft hyperspectral data was successfully performed with reflectance spectroscopy (Coleman *et al.*, 1993; Palacios-Orueta *et al.*, 1999).

### 1.1 Reflectance Spectroscopy

Fundamental features in reflectance spectra occur at energy levels that allow molecules to rise to higher vibrational states. Spectral characteristics of most minerals in the visible to near-infrared region reflect the presence of transition elements in their crystal structures. Such optical spectra originate from electromagnetic radiation exciting electrons between incompletely filled d or f orbital energy levels of transition metal cations located in specific coordination sites in the crystal

structures. The energies, intensities, and widths of these spectral features are often sufficiently diagnostic to enable individual transition metal cations and their host minerals to be identified in remote-sensed reflectance spectra of sunlit planetary surfaces when measured in the 350-2500 nm region of the electromagnetic spectrum (Pieters, 1993).

Empirical approaches are required to derive chemical-physical information from the soil spectra because the complexity of soil and soil spectra prevent a straight forward prediction of reflectance properties by physical theories or models, (Ben-Dor, 2002). Earlier studies (Kemper and Sommer, 2002; Wu *et al.*, 2005) in this field have shown feasibility to estimate heavy metal in field soil samples with relationship between spectrally featureless heavy metal and spectrally active materials in NIR region such as clay, iron oxide mineral, and organic matter. In this study, the reflectance spectra of artificially contaminated kaolinite soils with arsenic, copper, cadmium, and lead as a series of concentration gradients are measured to explore the possibility of spectral identification of heavy metal and to directional spectral relationship between heavy metals and spectrally active matrix.

## 2. MATERIALS AND METHODS

### 2.1 Synthetic Soil Samples

Soils used in this measurement were commercial kaolinite soils contaminated with As, Cd, Cu, and Pb

artificially. For artificial contamination, 0.75, 7.5, 75, 750, and 7500 mg/L of arsenic(V) solutions and lead solutions, 0.75, 7.5, 37.5, and 75 mg/L of cadmium solutions, and 0.75, 75, 375, and 750 mg/L of copper solutions were prepared. The pH of each solution was adjusted to 5-6 with HCl and NaOH for a favourable sorption condition. Fifteen ml of 23 solutions were added to 20 mg of oven-dried kaolinite soils. These mixtures were allowed to settle down for 48 h at a room temperature to attain the uniform distribution of contaminants and to complete sorption in kaolinite soils. After aging time, each sample was ground and packed in 55 mm diam. polystyrene petri-dishes for spectral measurements.

## 2.2 Measurements of Spectral Reflectance

Reflectance spectra of the soil samples were measured using GER 3700 (Spectra Vista Corp.) had the spectral range from 350 to 2500 nm with a spectral resolution 10 nm in a black lab. Samples were illuminated with a tungsten quartz halogen lamp and a infrared lamp for each visible and near-infrared region. Before reading each sample, white reference spectra were recorded using calibrated with white barium spectralon and the average of two spectra of each sample was recorded.

## 2.3 Processing of Spectrum

The raw spectral reflectance data measured under two kinds of illumination was resampled by selecting value at 350-1000 nm with a tungsten quartz halogen lamp and spectral region from 1000 to 2500 nm with an infrared lamp. A halogen lamp illuminates stably in 350-1000 nm region and IR lamp gives continuous and stable light in 1000-2500 nm regions. The reflectance values were then transformed to second- and forth-order derivatives using the Savitzky-Golay smoothing method. It is known that derivative transformation is able to minimize variation among samples caused by variation in surface grain size and optical set-up (Shepherd and Walsh, 2002).

Variation in spectral shape among samples was explored. Absorptions in a spectrum have two components; individual features and continuum which is the background absorption onto which other absorption features are superimposed (Clark, 1999). Continuum removed spectra were plotted to help detect subtle differences in spectral absorption features among soils. Continuum removal is used to normalize reflectance spectra so that individual absorption features can be compared from a common baseline. (RSI, 1999).

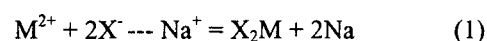
## 3. RESULTS AND DISCUSSIONS

According to Figures 1 and 2, it is observed that there are changes in the spectral features (position and intensity) in the VIS-NIR-SWIR region, which, are difficult to assess in many case. The spectral features in the NIR-SWIR region are the result of overtones and combination modes of functional groups' fundamentals (Ben-Dor *et al.*, 1997). Because the chemistry of soil

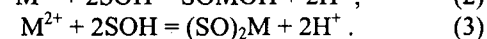
constituents is thought to be very complex, and adsorption reaction of each heavy metal onto kaolinite is variable, the corresponding spectrum is rather complex as well.

### 3.1 Synthetic Soil Chromophores

Pure metals are spectrally featureless in NIR region whereas pure metals complexed with clay minerals, oxide minerals, or organic matter can be detectable because clay minerals, oxide minerals, and organic matter can absorb light and are spectrally active in wavelength range (Malley, 1997). Therefore, spectral measurement for heavy metals on kaolinite soils was performed. Each metal can be sorbed onto kaolinite in various forms. Earlier modelling studies of the adsorption suggested that transition of metals were adsorbed at permanent- and variable-charge sites. Reaction 1 was suggested to adsorption of all metals on kaolinite for permanent charge sites.



Where  $M^{2+}$  represented Cd(II), Cu(II), or Pb(II),  $X^-$  is a permanent charge site and  $X_2M$  is an outer-sphere complex in the model. For variable charge site, inner-sphere complexes of the form SOMOH were required to give adequate fit to potentiometric titration, adsorption edge, and isotherm experiment involving Cu and Pb (reaction 2). Bidentate inner sphere complexes of the Stoichiometry  $(SO)_2M$  were required for Cd (reaction 3) (Srivastava *et al.*, 2005),



Hydrogen and hydroxides bonding group in clay mineral have common spectral characteristics. Overtones and combination tones of the O-H stretching and H-O-H and M-O-H bending fundamentals, where M is the metal to which the OH- is bound, occur at near 1400 nm. Spectral of minerals containing OH- alone lack 1200 and 1900 nm features, but have absorption features in the range of 2.0-2.4  $\mu$ m due to a combination of the O-H stretch and the M-O-H bend (Pieters, 1993).

### 3.2 Soil Spectra

Three major spectral regions were active around 1300-1400, 1900-2000, and 2200-2300 nm where clay minerals generally have absorption features. OH features of free water are found at 1456, 1910, and 1978 nm. Ben-Dor (2002) reported that the Al-OH bond was spectrally active at 2210-2240 nm and the Fe-OH was effective at 2121-2170 nm. All observed spectra had absorption features at near 2200 nm, indicating that Al-OH group was contained in synthetic soil samples. It was expected that synthetic soil samples have specific spectral variation at near 2200 nm in proportion to concentration because of metal replacement but in most case, spectral

absorption feature was similar to pure kaolinite soil at 2200 nm.

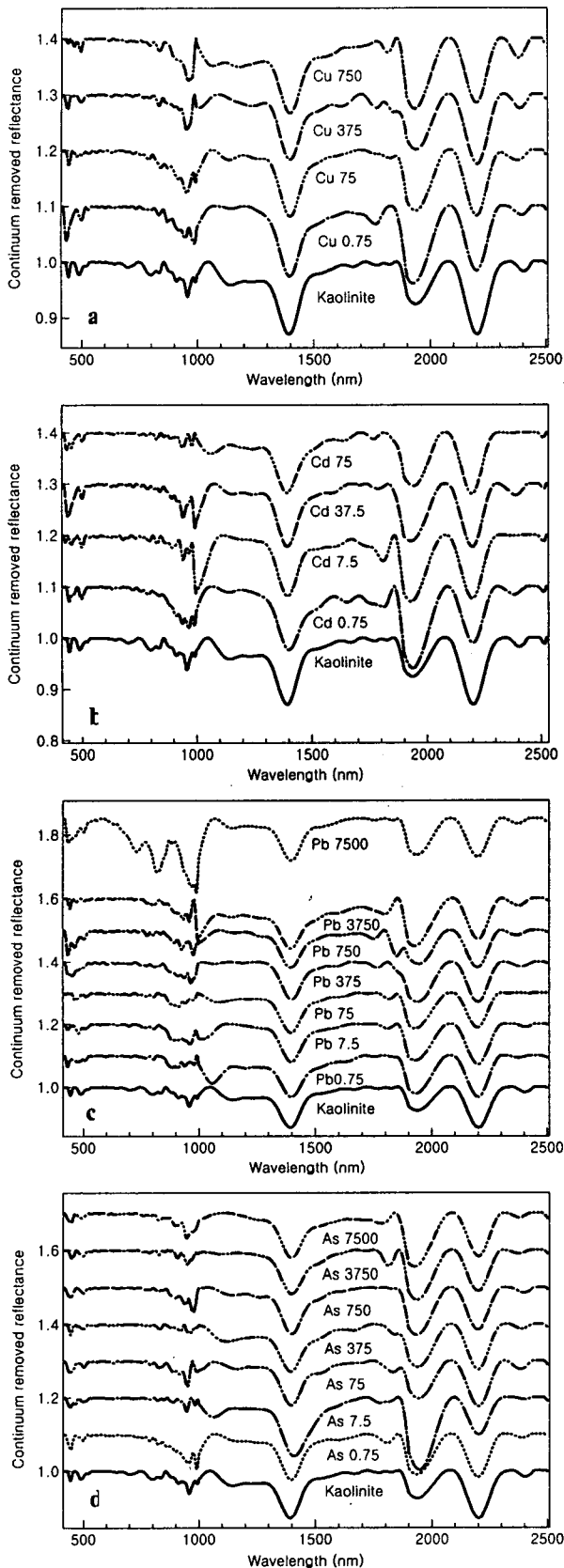


Figure 1. The continuum removed reflectance spectra of four heavy metals on kaolinite with each concentration; a.

Copper; b. Cadmium; c. Lead; d. Arsenic (Each spectrum was offset up or down so that the curves do not overlap. Original reflectances were between 0.8 and 1.).

According to each heavy metal spectrum curve in terms of concentration (Figure 1), in case of copper, there were relatively spectrally active regions from 900 to 1000 nm and from 2350 to 2450 nm though those had some band shift. Even though other heavy metals were difficult to explain spectrally specific active pattern as a function of concentrations, each heavy metal had spectral variations in 700- 1100 nm region for cadmium, in 400-1000 nm for lead, and 1000-1200 nm and 1700-1800 nm region for arsenic. It is expected that these spectral variations were related to the sorption phase and the amount of metal onto kaolinite. Figure 2 showed that each metal on kaolinite was possible to be identified in VIS-NIR region.

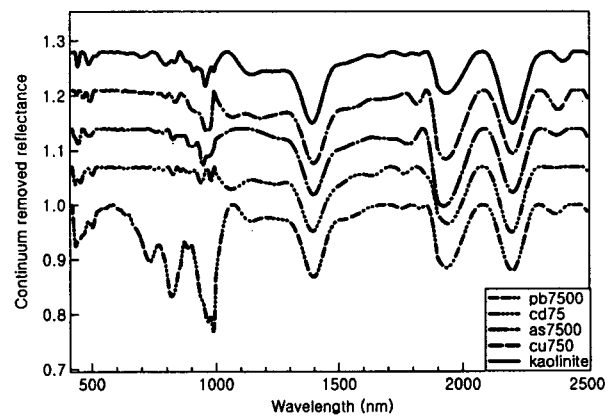


Figure 2. Comparison among reflectance spectra of the most contaminated soil samples by As, Cd, Cu, and Pb (Each spectrum was offset up or down.).

#### 4. CONCLUSIONS

The reflectance spectra of heavy metals in soils were investigated in the VIS-NIR-SWIR regions to observe spectral variation as a function of constituents and concentrations. The reflectance spectra of artificially contaminated kaolinite soils mixed with heavy metals such as As, Cu, Cd, and Pb as a series of concentration were measured to find spectral identification of heavy metals and directional spectral relationship between heavy metals and spectrally active matrix.

From heavy metal spectrum curves in terms of concentration, copper had relatively spectrally active regions with some band shift. Moreover, other heavy metals had only simple spectral variations without specific pattern which were expected to be related to the sorption phase and the amount of metal onto kaolinite. Each metal on kaolinite was possible to be identified in VIS-NIR region. In this study, the sorption phase and the amount of metal onto kaolinite were considered as an important factor to detect spectral variation. For the observation of specific metal phase sorbed onto kaolinite,

direct analysis using X-ray absorption fine structure spectroscopy (EXAFS) or X-ray diffraction (XRD) is further required .

## REFERENCES

Ben-Dor, E. 2002. Quantitative Remote Sensing of Soil Properties. *Advances in Agronomy*, 75, pp. 173-243

Ben-Dor, E. and Banin, A. 1995. Near Infrared Analysis as a Rapid Method to Simultaneously Evaluate Several Soil Properties. *Soil Sci. Soc. Am. J.*, 59, pp. 364-372.

Clark, R.N. 1999. Spectroscopy of Rocks and Minerals, and Principles of Spectroscopy., In N. Rencz (ed.) *Remote Sensing for the Earth Sciences: Manual of Remote Sensing*. John Wiley & Sons, New York, pp. 3-52.

Coleman, T.L., Agbu, P.A., and Montgomery, O.L. 1993. Spectral Differentiation of Surface Soils and Soil Properties: Is It Possible from Space Platforms? *Soil Sci.*, 155, pp. 283-293.

Kemper, T. and Sommer, S. 2002. Estimate of heavy Metal Contamination in Soils after a Mining Accident Using Reflectance Spectroscopy. *Environ. Sci. Technol.*, 36, pp. 2742-2747.

Malley, D.F. 1997. Use of Near-Infrared Reflectance Spectroscopy in Prediction of Heavy Metals in Freshwater Sediment by Their Association with Organic Matter. *Environ. Sci. & Technol.*, 31(12), pp. 3461-3467.

Palacios-Oreuta, A., Pinzon, J.E., Ustin, S.L., and Roberts, D.A. 1999. Remote Sensing of Soil in the Santa Monica Mountains: II. Hierarchical foreground and background analysis. *Remote Sens. Environ.*, 68, pp. 138-151.

Pieters, C.M. 1993. *Remote Geochemical Analysis: Elemental and Mineralogical Composition*. Cambridge University Press, New York, pp. 3-77.

Research Systems Inc. 1999. *ENVI User's Guide*. Research Systems Inc. Boulder, CO., pp. 747-748.

Srivastava, P. Singh, B., and Angove, M. 2005. Competitive Adsorption Behaviour of Heavy Metals on Kaolinite. *Journal of Colloid and Interface Science*, 290, pp. 28-38.

Shepherd, K.D. and Walsh M.G. 2002. Development of Reflectance Spectral Libraries for Characterization of Soil Properties. *Soil Sci. Soc. Am. J.*, 66, pp. 988-998.

Wu, Y.Z. *et al.* 2005. Feasibility of Reflectance Spectroscopy for the Assessment of Soil mercury Contamination. *Environ. Sci. Technol.*, 39, pp. 873-878.

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