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Variations in Spectral Signals of Heavy Metal Contamination in Mine Soils Controlled by Mineral Assemblages

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Received: 8 September 2020; Accepted: 5 October 2020; Published: 9 October 2020



Abstract: This paper illustrates a spectroscopic analysis of heavy metal concentration in mine soils with the consideration of mineral assemblages originated by weathering and mineralization processes. The mine soils were classified into two groups based on the mineral composition: silicate clay mineral group (Group A) and silicate–carbonate–skarn–clay mineral group (Group B). Both soil groups are contaminated with Cu, Zn, As, and Pb, while the contamination level was higher for Group A. The two groups exhibit different geochemical behaviors with different heavy metal contamination. The spectral variation associated with heavy metal was highly correlated with absorption features of clay and iron oxide minerals for Group A, and the absorption features of skarn minerals, iron oxides, and clay minerals for Group B. It indicates that the geochemical adsorption of heavy metal elements mainly occurs with clay minerals and iron oxides from weathering, and of skarn minerals, iron oxides, and clay minerals from mineralization. Therefore, soils from different secondary mineral production processes should be analyzed with different spectral models. We constructed spectral models for predicting Cu, Zn, As, and Pb in soil group A and Zn and Pb in soil group B using corresponding absorptions. Both models were statistically significant with sufficient accuracy.

Keywords: heavy metal contamination; weathering; mineralization; mineral composition; regression analysis; spectroscopy; mine soil

1. Introduction

Soils play an important role in the earth system as a boundary between lithosphere and atmosphere and the settlement basement for biosphere. Soils are generated from the weathering process of lithosphere by physicochemical reactions and, thus, composed of minerals, organic matters, water, and air. Soils are often contaminated with heavy metal elements from both natural and anthropological process. Notably, mining is one of the major human activities that contaminate soils, and the contamination was transported in the drainage system and has caused serious problems in eco-systems [1–6].

Due to the threats to food safety and ecosystem sustainability, most countries have regulated soil heavy metal contamination survey protocol by requiring field sampling, preprocessing, chemical analysis, and interpretation [7–10]. Although the soil survey protocol provides highly precise and

accurate measurements of heavy metal concentration, it is costly, and labor and time intensive. Moreover, the representative area of each point-based sampling is only about several meters wide, which leaves vast vacant areas with no samples of heavy metal contamination. As a less precise but more effective alternative to traditional soil survey methods, non-destructive spectroscopic analyses have been applied to estimation of heavy metal concentration [9–12]. In addition, spectroscopic approaches assist development in remote sensing for synoptic soil contamination survey [13,14].

In a heavy metal contaminated soil, the spectral signal is not manifested by single metal element, but by the physicochemical reaction between metal elements and adsorption agents in the soil. Spectral signals of heavy metal elements in soils must be studied by considering the geochemical reaction agents, such as clay minerals, organic matters, and iron/manganese oxides [11,13,15–18]. Previous studies on visible-near infrared-shortwave infrared (VNIR-SWIR hereafter) spectroscopy applied to heavy metal concentration in soils have identified spectral regions associated with chemical compounds participating physicochemical reactions in soils [5,13,14,18–21]. For example, Choe et al. [13] identified OH and FeO compounds association with heavy metal concentration for stream sediments, and Song et al. [14] detected wide range of VNIR-SWIR spectrum show spectral signals associated with Al, Cu, and Cr concentrations in mining soils. Wang et al. [18] reviewed possible application of spectroscopic approaches for detection of heavy metal contamination in soils and emphasized that the approaches were very site-specific and hard to be utilized universally.

To overcome the site-specific issues of spectroscopic analysis, recent studies considered mineral composition and interpreted the spectral signals of heavy metal concentration with reaction agents between heavy metal cations and bonding minerals [4,5,21,22]. Jeong et al. [5] reported hydrothermal alteration minerals were the major reaction agents for tailing soils of a hydrothermal deposit where major spectral signals are located at SWIR region. Shin et al. [21] found clay minerals and carbonate minerals as main producers of spectral signals to indicate heavy metal concentration in mining soils of a hydrothermal ore deposit. Lim et al. [4] identified secondary minerals as major association with heavy metal contamination in white precipitates induced by acid mine drainage. Shin et al. [22] identified spectral interference between spectral signals of moisture content and heavy metal concentration.

However, the soils distributed near mining areas may be impacted by surface geology and excavated materials from the mine. Indeed, many mines have different geological distribution between surface material and excavated materials where the mining often occurs underground. However, the association between spectral signals with heavy metal contamination controlled by different combinations of mineralogy, with respect to geological processes in mine soils, has rarely been reported before. In consideration of heterogeneity of mineral composition, this study used samples from heavy metal contaminated soils in the mining area to analyze by mineral composition, heavy metal concentration, and associated spectral characteristics. The soil samples are grouped by mineral composition, among which the spectral signals associated with heavy metal concentration were analyzed. Finally, the spectral signals of heavy metal concentration controlled by mineral assemblage and associated geochemical agents are discussed.

2. Materials and Methods

2.1. Study Area

The study area, Gagok Mine, is located in Samcheok city, Gangwon province (37°7'3"N and 129°6'41"E), 195 km east from Seoul of South Korea (Figure 1). The mine is a Skarn type Pb-Zn ore deposit developed in the Taebaek mineralized zone. The geology of the mine is composed of Precambrian granitic gneiss as basement, Cambrian/Ordovician sedimentary rock alternating sequence of shale/slate and limestone, and Cretaceous quartz monzonite intrusions [23–25]. The ore body is developed along the contact between Paleozoic limestone and Cretaceous quartz monzonite dipping towards underground as a vein type. The surface area of the mine is mainly covered by Cretaceous quartz monzonite, and a small section of sedimentary rocks and ore bodies are exposed. The ore had

been mined via underground mining methods following ore bodies from 1971 to 1987. The major ore minerals are sphalerite, galena, chalcopyrite, and pyrrhotite, and the gangue minerals are pyroxene, quartz, calcite, fluorite, and sericite [23–25]. Pyroxene, garnet, wollastonite, amphibole, epidote, phlogopite, and chlorite were reported as skarn minerals [23,25]. During the operating period, the mine produced about 600,000 metric tons of ore per year [23]. After the mining operation was finished, the mine area was abandoned without major reclamation for future operation. Notably, a great amount of mine waste was released to the stream and contaminated the drainage basin with severe storms in 2002 and 2003 [26,27].

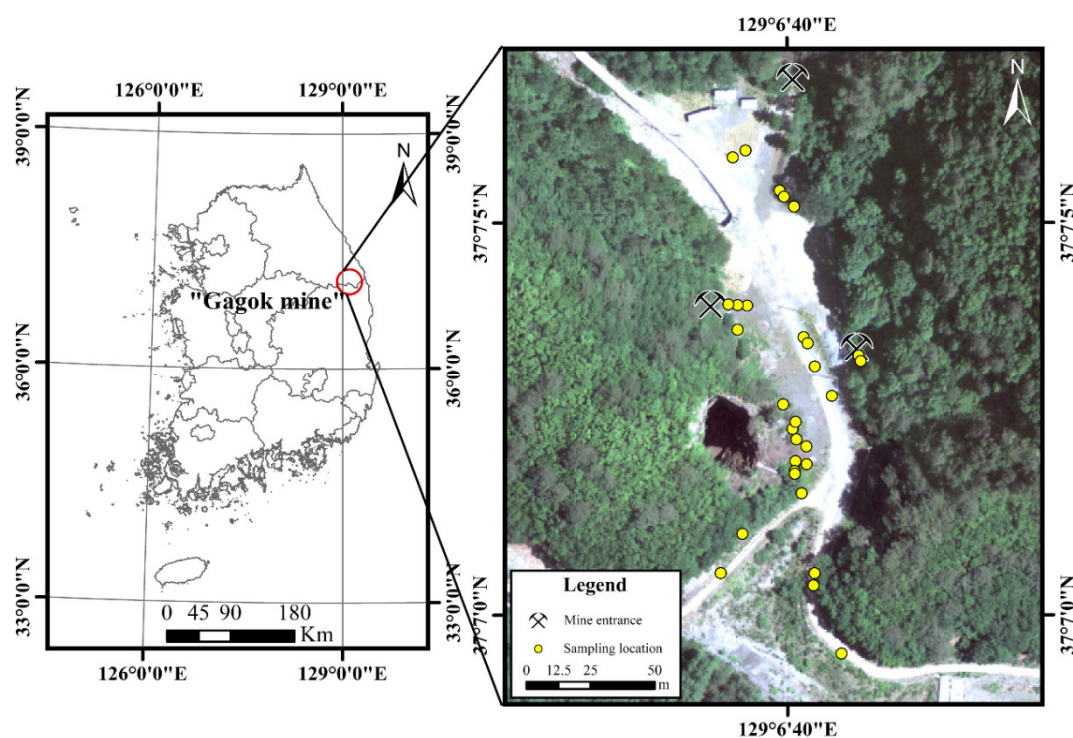


Figure 1. Location map and sampling location of Gagok mine, South Korea.

2.2. Sample Collection and Preparation

A total number of 200 soil samples were collected from 30 different locations around the mine areas including mine waste, unpaved road, and mine audit (Figure 1). All samples were from the top soil layer at the depth of 0 to 15 cm excluding organic materials. The samples were contained in the polyethylene sample bags and transported to the lab and air dried at a room temperature to remove moisture. The samples were then sieved at 10 mesh and 100 mesh to remove granule effect. The preprocessed samples were chemically analyzed to figure out concentration levels of heavy metal elements and spectrally analyzed to identify spectral signals associated with the heavy metal concentration. The same samples were powered for mineralogical analysis to assess mineral effects in the spectral characteristics.

2.3. Mineralogical and Chemical Analysis

The samples were grouped by spectral patterns with similar spectral signatures, and a total of 18 samples representing each type of spectral pattern from 30 sample locations were selected for mineralogical analysis. The mineral analysis was conducted by an X-ray diffraction (XRD hereafter) analysis. We used a Rigaku Ultima IV X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The X-ray tube voltage and current were set to 40 kV and 30 mA, and the diffraction pattern was acquired with a 2θ range of 3° to 90° at a scan step of 0.02° and a scan speed of $20^\circ/\text{min}$.

The heavy metal concentration of the soil samples was analyzed by a portable X-ray fluorescence spectrometry (PXRF hereafter). The PXRF method is one of the chemical analysis methods used by United States Environmental Protection Agency (USEPA) and National Institute for Occupational Safety and Health (NIOSH) [28,29]. The method is a non-destructive and cost-effective analytical method with prompt result acquisition. Due to the convenience of the method, this method is widely used in the field and laboratory despite the relative limitation in the limit of detection and accuracy compared to Inductively Coupled Plasma (ICP) analysis [21]. The method provides sufficient levels of accuracy for the most of elements except light elements and cobalt [30–34]. Indeed, many previous studies used this method for heavy metal contamination analyses [4,5,21,35–37]. Furthermore, the method enables the rigorous correlation analysis between the chemical concentration and spectral characteristics of samples because the instruments can read from the same spot of a sample [4,5,21,22].

This study used an Innov-X delta professional portable XRF (Olympus, Waltham, MA, USA) for concentration of heavy metal elements in soil samples including Cu, As, Hg, Pb, Cr, Zn, Ni and Fe. The beam condition of the instrument is 50 kV with a resolution of <168 eV. The detection limit is 8–15 ppm for Cd, 3–7 ppm for Cu, 1–3 ppm for As, 2–4 ppm for Hg, 2–4 ppm for Pb, 3–10 ppm for Cr, 2–5 ppm for Zn, 4–10 ppm for Ni, and 7–20 ppm for Fe. The instrument was calibrated with a 316 stainless steel alloy clip attached at the docking station at the beginning of measurements for each use. The chemical data was measured 3 times for 60 s at each sample, and the measured readings were averaged for further use.

To further understand how the heavy metal contamination levels could alter the spectral characteristics of soil samples, we used the pollution index (PI hereafter) of the soil samples to separate heavy contamination levels [26]. PI values larger than 1.0 indicate the sample is contaminated over a tolerable level [26].

$$PI = \frac{\sum \frac{(\text{Concentration of Heavy Metal})}{(\text{Tolerable Level of each Heavy Metal})}}{\text{Number of Heavy Metal Elements}} \quad (1)$$

Specifically, we used the worrisome level of soil contamination of Ministry of Environment by Korean government as the tolerable level [8].

2.4. Spectral Analysis

The spectral characteristics of heavy metal contaminated soils were measured with a LabSpec 5100 portable spectrometer (Analytical Spectral Devices Inc., Boulder, CO, USA) covering the spectral range of 350–2500 nm at a 3–6 nm resolution. The reflectance spectra of soil samples were measured with the contact probe mode and a halogen light source [5,13,21]. The spectrometer was calibrated with a Spectralon panel (Labsphere, Inc., North Sutton, NH, USA) coated by barium sulfate with a reflectance of >96–98% for each use. The measurement was made at the exact spot and with the identical diameter that was used by the PXRF measurement for one-on-one correlation. The diameter of the aperture was set to 2 cm [5]. The reflectance readings were acquired three times for each measurement and averaged.

The reflectance spectra were smoothed with the Savitzky–Golay filter to remove random noise and then processed with the hull quotient correction algorithm [10,38]. The hull quotient correction technique maximizes and characterizes absorption features. The correction helps detect the position and depth of absorption features. The absorption depth was calculated from the hull quotient reflectance spectra and used for spectral variations associated with heavy metal concentration in soils [10,39]. A first derivative transformation was used to enhance spectral features [10,38]. The first derivative transformation can minimize the background interference and baseline drift of raw reflectance spectra [10]. The first derivative transformation was processed by the Savitzky–Golay first derivative filter. All Savitzky–Golay filters were based on the second-order polynomial method with a window size of 25 nm for smoothing and 3 nm for first derivative filters. The spectral analysis was carried out by The Spectral Geologist (TSG) 7.5 and ENVI 4.8. The spectral libraries of United State Geological

Survey (USGS) spectral library version 6 and 7 [40,41] and Jet Propulsion Laboratory (JPL) Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) spectral library version 2.0 [42] were used for spectral analysis associated with mineral composition.

2.5. Model Development and Evaluation

In order to select the most sensitive wavelengths to the heavy metal concentration based on the correlation analysis between spectral variables and heavy metal concentration, the Pearson correlation coefficients (r) were calculated for each spectral band to develop a correlogram for visualization. The candidate wavelengths for the model were selected with the cutoff value of $r > |0.7|$.

The prediction models were constructed using the spectral variables at the selected wavelengths for each mineral group. Moreover, 70% of the samples were used to construct the model, and the rest (30%) of the soil samples were used for model validation. The prediction models were developed using the stepwise multiple linear regression (SMLR hereafter) method. The SMLR method selects the best fit variables by iterations of different variable combinations based on the F-test [43]. This study selected the prediction models with p -value < 0.05 and variance inflation factor (VIF) < 10 to avoid the multi-collinearity problem [44]. The final model was selected as the one with the highest coefficient of determination (R^2 hereafter) for an independent variable, the highest adjusted coefficient of determination ($\text{Adj-}R^2$ hereafter) for multi independent variables, and the minimum root-mean-square error (RMSE). The coefficients (β_n) and the constant (β_0) of the regression equations were derived for model prediction. The models were also tested with normalized RMSE (NRMSE), p -values and standard error (SE).

The prediction models were validated with 30% of soil samples as the validation set. R^2 , RMSE, NRMSE, and the slope of the regression line with a 95% confidence interval were calculated between predicted and observed values. In addition, the residual prediction deviation (RPD) was calculated based on the standard deviation and RMSE of the validation set [43,45–47]. The statistical analysis was carried out using the Statistical Package for the Social Sciences (SPSS), Inc., Chicago, IL, USA.

3. Results and Discussion

3.1. Mineral Composition and Heavy Metal Concentration

The mineralogical analysis was carried out for representative samples from 18 sampling sites. The results revealed that the mineral composition of heavy metal contaminated soil samples showed distinctive differences in mineral composition depending on the geographic distribution and geology. This study classified the soil samples into two groups based on the mineral assemblage. Group A samples are classified as silicate clay mineral combination, including silicate minerals, such as quartz and feldspar, and clay minerals including illite, kaolinite, and montmorillonite (Table 1). Group B samples have mineral combination of silicate–carbonate–skarn–clay minerals, where carbonate mineral (calcite) coexist with silicate and skarn minerals, such as quartz, pyroxene, epidote, and chlorite (Table 1). In addition, occasional occurrence of clay minerals such as illite, kaolinite, and montmorillonite was observed. The major difference between the two groups is occurrence of clay mineral (Group A) and carbonate/skarn mineral (Group B).

Table 1. Mineral composition of the samples derived from XRD analysis.

Site No.	Primary Minerals	Accessory Minerals	Group
G01	Quartz, Plagioclase	Illite, Kaolinite, Biotite, Montmorillonite	A
G03	Calcite, Quartz, Pyroxene	Epidote, Kaolinite	B
G04	Calcite, Quartz	Illite, Chlorite, Kaolinite	B

Table 1. Cont.

Site No.	Primary Minerals	Accessory Minerals	Group
G05	Calcite, Quartz, Epidote	Pyroxene	B
G08	Quartz, Pyroxene, Calcite	Epidote, Kaolinite, Montmorillonite	B
G09	Quartz, Plagioclase, Illite	Kaolinite	A
G11	Quartz, Plagioclase	Kaolinite, Montmorillonite	A
G12	Quartz, Plagioclase	Kaolinite, Montmorillonite	A
G14	Epidote, Pyroxene, Quartz	Calcite, Kaolinite, Illite	B
G15	Epidote, Chlorite	Quartz	B
G16	Calcite, Pyroxene	-	B
G18	Plagioclase, Quartz, K-Feldspar	Illite, Calcite	A
G19	Calcite	Plagioclase, Quartz, Kaolinite	B
G20	Quartz, Plagioclase	Kaolinite, Phlogopite	A
G22	Quartz, Plagioclase	Chlorite, Kaolinite, Biotite	A
G23	Plagioclase, Quartz, Illite	Kaolinite, Biotite	A
G25	Pyroxene, Epidote	Quartz	B
G30	Quartz, Plagioclase	Illite, Calcite	A

The silicate major minerals of the Group A are main rock-forming minerals of quartz monzonite, and the clay minerals are common weathering products in soils [1]. It indicates that the soil samples of the Group A are originated from the surface geology and experienced long period of weathering. Indeed, the geographic distribution of Group A samples shows that the samples are mainly located on the unpaved road and the area of quartz monzonite as surface geology (Figure 2). On the other hand, the mineral composition of Group B samples includes calcite, pyroxene, and epidote. Those minerals are representative gangue minerals found in the skarn ore deposit [23,25]. It infers that these samples are originated from the excavated materials representing subsurface geology of skarn ores and carbonate rocks. Actually, the Group B samples are located at the mine entrance and waste dumps (Figure 2). Moreover, the occasional occurrence of clay minerals in Group B samples infers that the soils were only shortly exposed to the surface for weathering to occur. The results confirm that the soil composition is controlled by mineral composition representing the geology of the area, and the mine soils could have different mineral composition due to excavation and waste dumping. The spectral characteristics of all soil samples were compared with that of the samples belonging to each mineral group. The samples with similar spectral patterns were assigned to each mineral group based on the absorption features manifested by mineral composition.

The chemical composition of soil samples was analyzed with PXRF, and the outliers were excluded for further analysis based on interquartile range box plot [48]. As a result, 99 soil samples for Group A and 84 samples for Group B were used for further analysis. The PXRF analysis detected seven heavy metal elements of Cu, Zn, As, Pb, Ni, Cd, and Cr in the soil samples among the eight pollutive heavy metal elements excluding Hg. Only 4 elements (Cu, Zn, As, and Pb) out of the 7 elements showed a concentration over the limit of quantification, and, thus, we excluded Ni, Cd, and Cr for further analysis. The Group A samples are extremely polluted with Zn, As, and Pb with 1.4 to 9.3 times of average concentration compared to the soil pollution standard [8] (Table 2). The Group B samples showed a significant pollution level for average Zn and As concentration with 1.3 to 1.7 times of the pollution standard [8] (Table 2). Comparing the two groups, Group A samples showed higher pollution in heavy metal elements. This is mainly caused by geochemical reactions where clay minerals actively participate in adsorption with heavy metal cations [5,11,13,49] while carbonate minerals are geochemically non-reactive with heavy metal cations as they maintain pH level towards alkali [50].

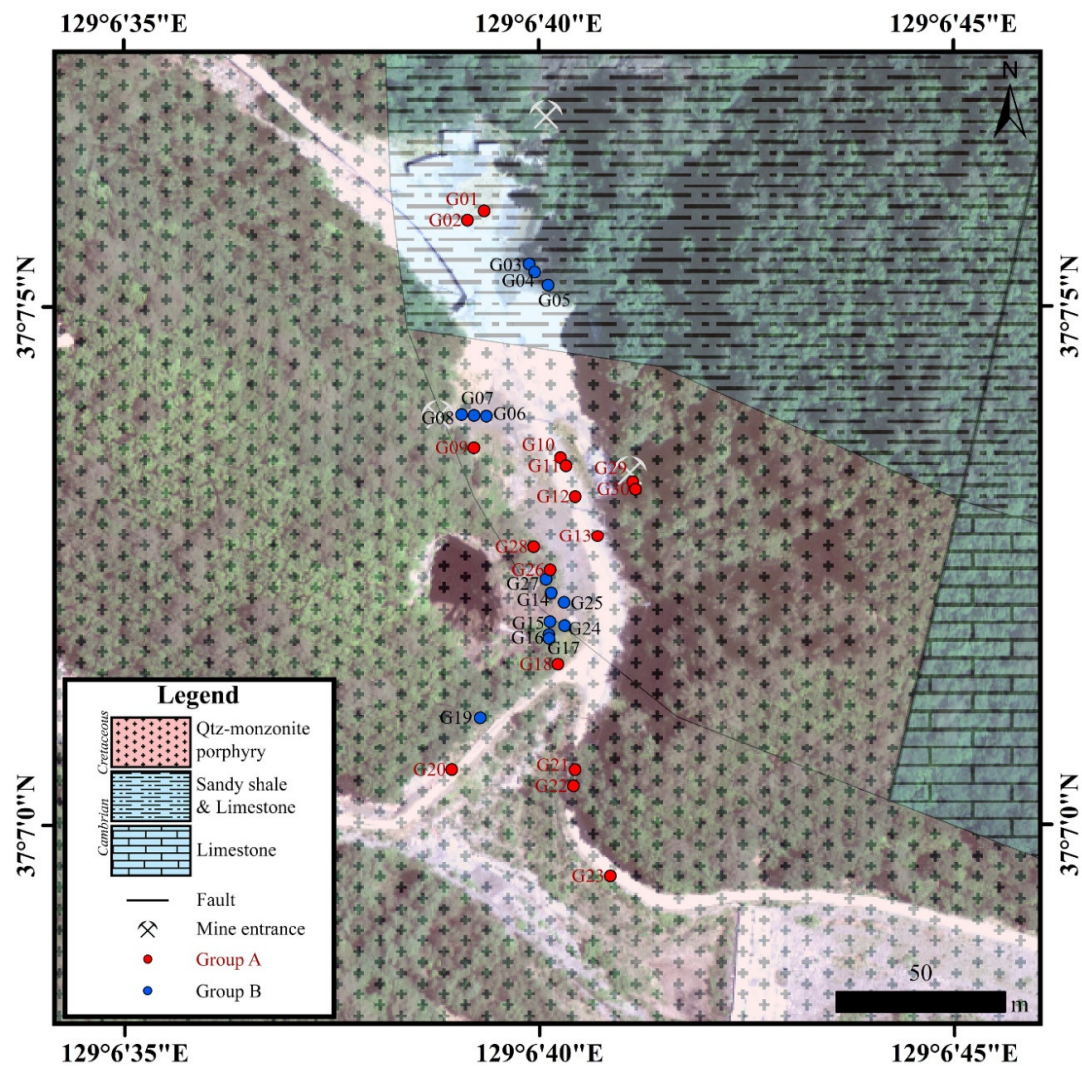


Figure 2. Sample location of each group and geologic map in Gagok mine, South Korea.

Table 2. Descriptive statistics of heavy metal concentration (unit: ppm (mg/kg)) in soils derived from XRF analysis and soil pollution standard [8].

Element	Group A (n = 99)				Group B (n = 84)				Soil Pollution Standard
	Min	Max	Mean	SD	Min	Max	Mean	SD	
Cu	0	363	144	124	0	172	106	41	500
Zn	82	15,167	5477	4466	143	3014	1004	682	600
As	0	349	95	91	27	116	63	63	50
Pb	27	1268	541	375	30	327	103	79	400

Note: Soil Pollution Standard indicates remediation standards of non-residential areas including forest and barren lands (unit: ppm (mg/kg)).

We analyzed correlations between the heavy metal elements to figure out geochemical behaviors in the soil samples (Table 3). Group A samples showed high correlations between the three elements excluding As ranging from 0.82 to 0.84, and Group B samples showed high correlation only for Pb and Zn (0.86) (Table 3). The results showed that geochemical behavior of heavy metal elements in soil samples is different between the two groups, where mineral composition and associated geochemical reactions may be related to the differences in heavy metal concentration.

Table 3. Coefficient (r) between concentrations of heavy metal elements in soil samples.

	Group A (n = 99)					Group B (n = 84)			
	Cu	Zn	As	Pb		Cu	Zn	As	Pb
Cu	1.00				Cu	1.00			
Zn	0.84	1.00			Zn	0.41	1.00		
As	0.55	0.57	1.00		As	0.06	0.05	1.00	
Pb	0.85	0.85	0.26	1.00	Pb	0.33	0.86	0.01	1.00

3.2. Spectral Characteristics

Spectral analysis of the heavy metal contaminated samples excluding outlier samples revealed distinctive spectral characteristics between Group A and B. The averaged hull quotient reflectance spectra of Group A showed absorption features around 420, 470, 900, 1400, 1900, 2200, and 2350 nm associated with chemical components of ferric ion(Fe^{3+}), hydroxyl(OH), water, AlOH , MgOH , and/or CO_3 , respectively (Figure 3). On the other hand, the averaged reflectance spectra of Group B samples showed additional absorption features at 1100 and 2250 nm manifested by ferrous ion(Fe^{2+}) and FeOH (Figure 3).

Considering the mineral composition of Group A samples, the absorption features at 1400, 1900, and 2200 nm are manifested by plagioclase and clay minerals, and that of 2350 nm is associated with illite (Table 1, Figure 3). The absorption features associated with ferric ion near 420, 470, and 900 nm are manifested by iron oxides. The iron oxides in soils generally occur as a mineral form such as goethite or amorphous iron oxides [1]. The XRD analysis of the soil samples did not detect any iron oxide minerals. Indeed, the XRD analysis has a limitation in detection of iron oxide minerals due to strong absorbance of $\text{Cu-K}\alpha$ radiation by Fe used for the XRD analysis [51,52]. We think the ferric ion absorption features of Group A samples are manifested by the combined effect of iron oxide minerals and amorphous iron oxides. Indeed, the Fe concentration of Group A samples showed an average concentration of 5.17%.

On the other hand, the absorption features of Group B samples were manifested by skarn minerals in addition to clay minerals, while those of group A samples were mainly associated with clay minerals. Different from Group A samples, the absorption features of Group B samples were associated with pyroxene/chlorite for ferrous ion absorption (near 1000–1200 nm), and epidote/chlorite for FeOH (near 2250 nm), MgOH and/or CO_3 (near 2300–2350 nm) absorptions [53]. The Group B samples showed the same type of absorptions of ferric ions as Group A samples, where those are associated with iron oxide minerals or amorphous iron oxide. The Group B samples showed an average Fe concentration of 7.24%.

Group A and Group B samples showed distinctive spectral absorption features (Figure 4). Group B samples showed higher average reflectance at visible and near infrared (350–1000 nm) and short wave infrared (>1300 nm) regions (Figure 4). The two groups are most separable by the absorption features in their hull quotient corrected reflectance spectra (Figure 4). In general, the absorption depth indicates the quantity of chemical components absorbing the incident electromagnetic energy [5,21]. Group A samples showed stronger absorption features manifested by ferric ion (420 and 470 nm), water ion (1400 and 1900 nm), and AlOH component (near 2200 nm), while Group B spectra have strong absorption features associated with ferrous ion (1000–1200 nm), FeOH (2250 nm), MgOH and/or CO_3 (2300–2370 nm). It indicates that the spectral characteristics of Group A samples is controlled by iron oxides and clay minerals, and Group B sample spectra are manifested by skarn minerals. However, it should be noted that the absorption features associated with ferric iron was exaggerated by the hull quotient transformation (Figure 4). The results confirm that the spectral characteristics soil samples are controlled by mineral composition even within the same region.

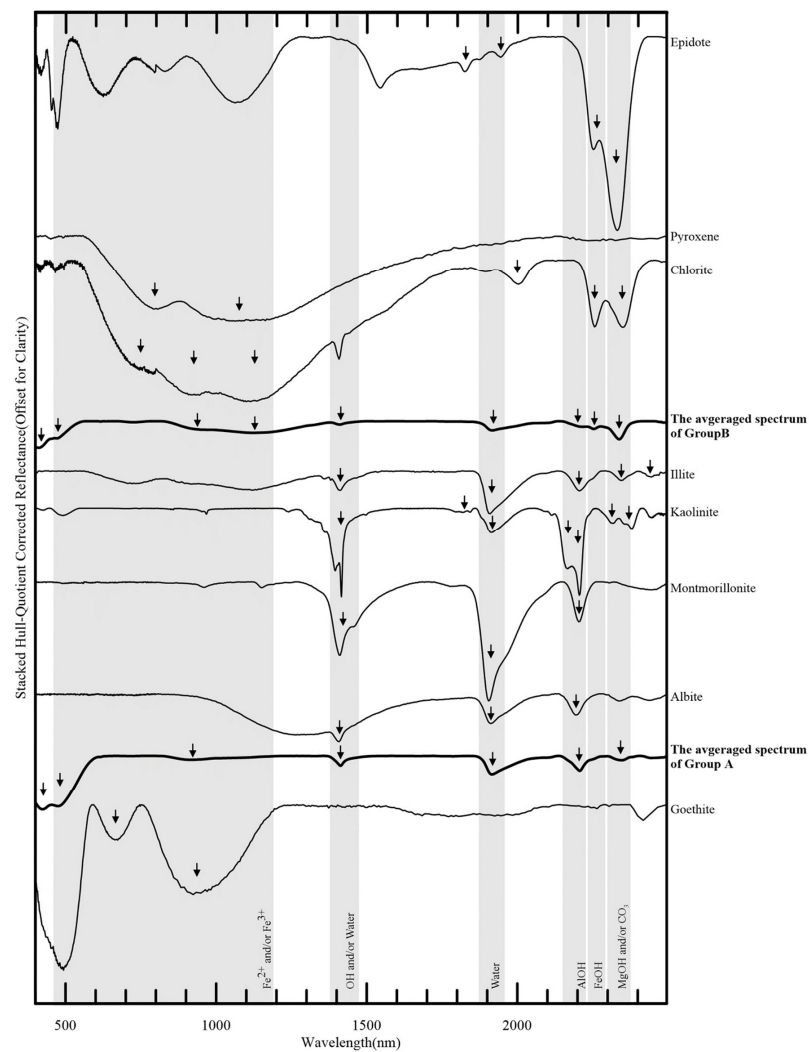


Figure 3. The average hull quotient spectra of Group A and B matched with epidote, pyroxene, chlorite, illite, kaolinite, montmorillonite, albite, and goethite.

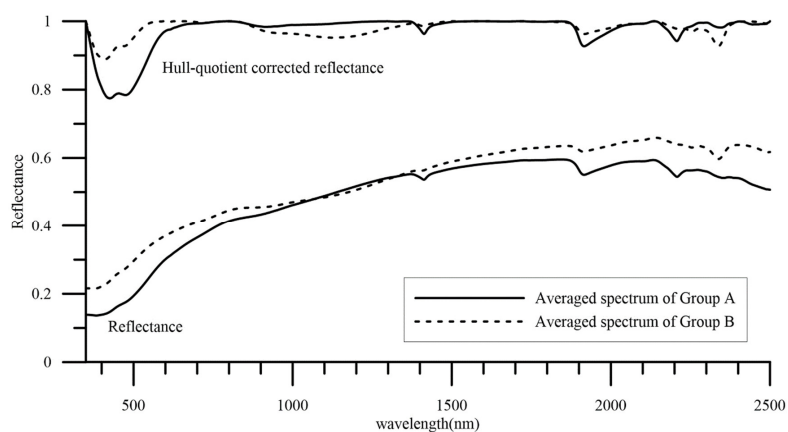


Figure 4. The averaged reflectance and averaged hull quotient corrected spectra of Group A and Group B.

The hull quotient corrected spectra with the highest and lowest PIs for each group were analyzed to figure out spectral variations caused by heavy metal contamination (Figure 5). The two soil sample groups are discussed separately because their major manifestation elements are different (Figure 5).

Group A spectra showed with increased contamination level there was a decrease in absorption depth for absorption features related to ferric ion, water, and AlOH components. This spectral variation indicates geochemical agents participating in the chemical bonding with heavy metal cations [5,21,22]. The decrease in absorption depth indicates that the iron oxides and clay minerals participated in the chemical bonding with heavy metal ions may decrease the available corresponding chemical components. In Group B, the decrease in absorption depth was observed at the absorption features associated with ferric ions, ferrous ions, AlOH, and MgOH components. The mineral agents for possible participants in geochemical bonding with heavy metal cations for Group B may include iron oxides for ferric ion, pyroxene/chlorite for ferrous ion, clay mineral for AlOH, and chlorite/epidote for MgOH. Given the fact that the geochemical agents for heavy metal bonding include clay minerals, iron oxides, manganese oxides, and organic materials [11,13,15–18], the geochemical agents for the reactions in Group B samples can be narrowed down to iron oxides, skarn mineral (chlorite), and clay minerals.

In general, geochemical reaction agents with heavy metal cations, such as clay minerals and iron oxides, adsorb the heavy metal cations elements (M^{2+}) at hydroxylated lattice of ROH minerals in soils [11,13].



The geochemical bonding between mineral agents and heavy metal cations reduces chemical components corresponding to specific absorptions resulting a decrease in absorption, depth such as AlOH and FeOH absorptions [5,11,13,21]. Previous studies listed clay minerals and hydrothermal alteration minerals for heavy metal contaminated soils of a hydrothermal ore deposit [21] and hydrothermal minerals for a tailing soils of a vein type ore deposit [5]. The geochemical agents in this study showed distinctive variations associated geological history of soils depends on weathering and mineralization processes. The geochemical reaction of the weathering process is controlled by clay minerals, and that of mineralization processes is associated with skarn minerals. The results confirm the major controls in geological process in spectral variations associated with heavy metal contamination in soils as suggested by previous studies [5,21].

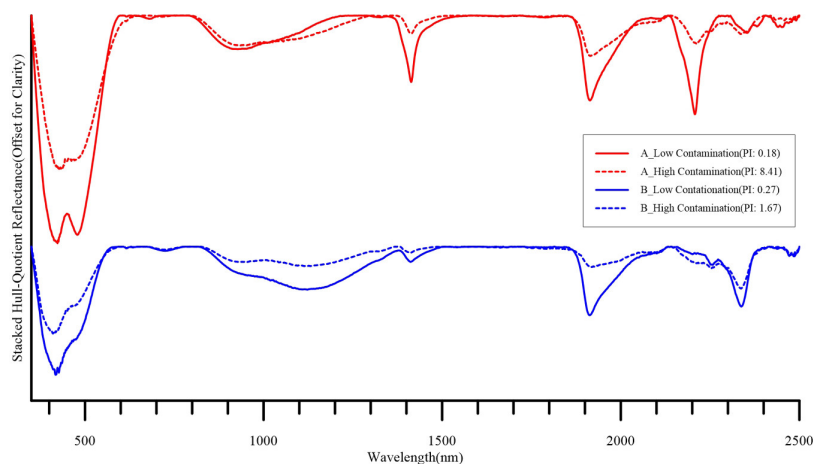


Figure 5. The hull quotient corrected reflectance spectra of highest and lowest pollution index by each group.

3.3. Model Development

3.3.1. Band Selection

The correlograms show the correlation between heavy metal concentration and spectral variables including reflectance, absorption depth, and first derivative spectra for each group were developed to figure out spectral bands sensitive to heavy metal concentration for soil samples of Group A and B (Figures 6 and 7). The correlation pattern of the heavy metal concentration in Group A is more

consistent than that in Group B (Figures 6 and 7). These correlation patterns are consistent with the correlations between the concentration of heavy metal elements where Group A sample had high correlations for Cu, Zn, and Pb and Group B sample had high correlation for only Zn and Pb (Table 3). It confirms that spectral variations associated with heavy metal concentration are closely related to the geochemical behavior of heavy metal cations in soil controlled by mineral composition.

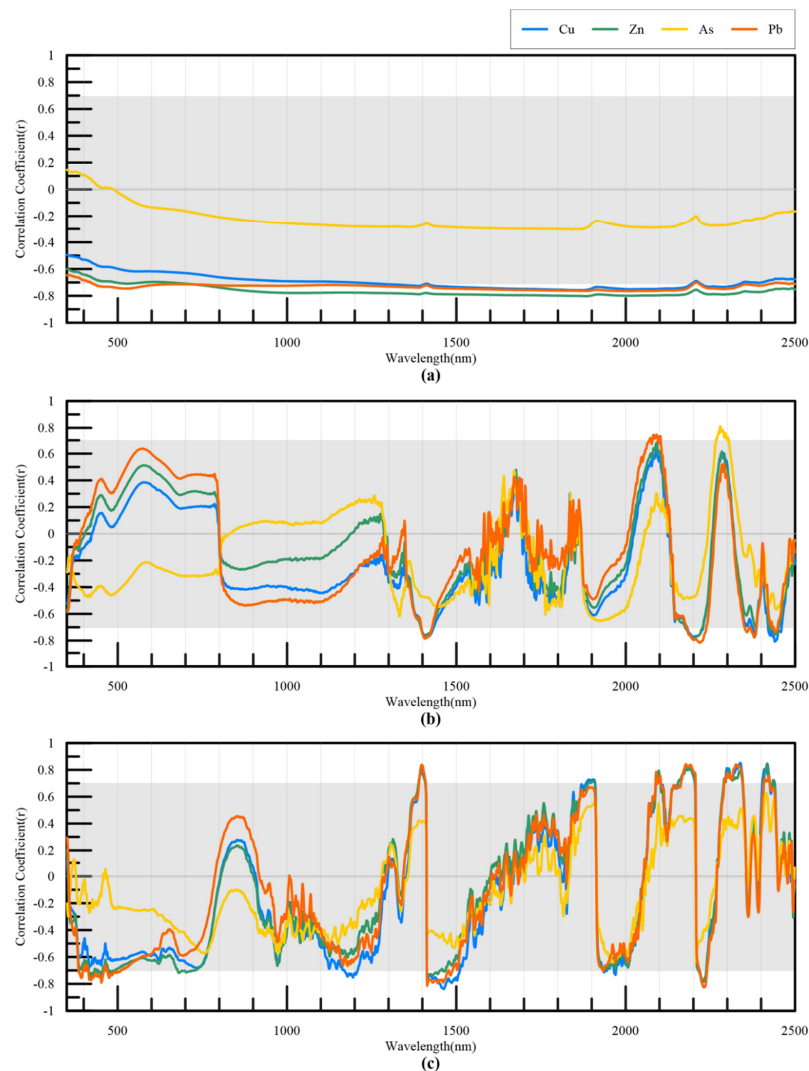


Figure 6. Correlograms between heavy metal concentration and (a) reflectance, (b) absorption depth, and (c) first derivatives of Group A.

Overall, there is a negative correlation between the heavy metal concentration and the spectral reflectance in Group A (Figure 6a). Excluding As, the heavy metal elements with high elemental correlations (Cu, Zn, and Pb) have high correlations ($r > |0.7|$) for most of the VNIR and SWIR bands. The high correlations between absorption depth and concentration of heavy metal elements were observed from spectral bands at 1400, 2200, 2300, and 2450 nm with negative correlations, which confirm the decrease in absorption depth was caused by geochemical adsorption between heavy metal cations and clay minerals in Group A samples (Figure 6b). However, the correlation for the absorption features of iron oxides was not as high as clay minerals, which infers that the iron oxides are not as active as clay minerals as geochemical agents to bond with heavy metal elements. The highly correlated spectral bands between the concentration of heavy metal elements and first derivative spectra were similar to that of absorption depth (Figure 6c), because the first derivative spectra are more sensitive to the absorption features. Different from the absorption depth, the spectral band associated with iron oxide

was detected as a highly correlated band while the correlation coefficient was lower than the bands of clay minerals.

Compared to the Group A samples, the spectral variables of Group B samples showed relatively weaker correlations with heavy metal elements (Figure 7). The correlation between reflectance and heavy metal concentration was not statistically significant for most of the spectral bands except for the spectral region of 1900 nm and >2400 nm with positive correlation with As concentration (Figure 7a). The correlation between absorption depth and heavy metal concentration was statistically significant for 420 nm (As) and 900–1400 nm (Zn and Pb) with negative correlation (Figure 7b). It indicates that heavy metal cations of As, Zn, and Pb are geochemically adsorbed to iron oxides and chlorite and/or clay minerals resulting decrease in available ions corresponding to the absorption features (Figure 7b). On the other hand, As concentration has high positive correlation with the absorption depth at 2245 nm and 2380 nm. The highest correlation between first derivative sample spectra and heavy metal concentration were observed at 1508 nm for Zn, 2381 nm for As, and 1385 nm for Pb, which are associated with chlorite, epidote, and clay minerals (Figure 7c).

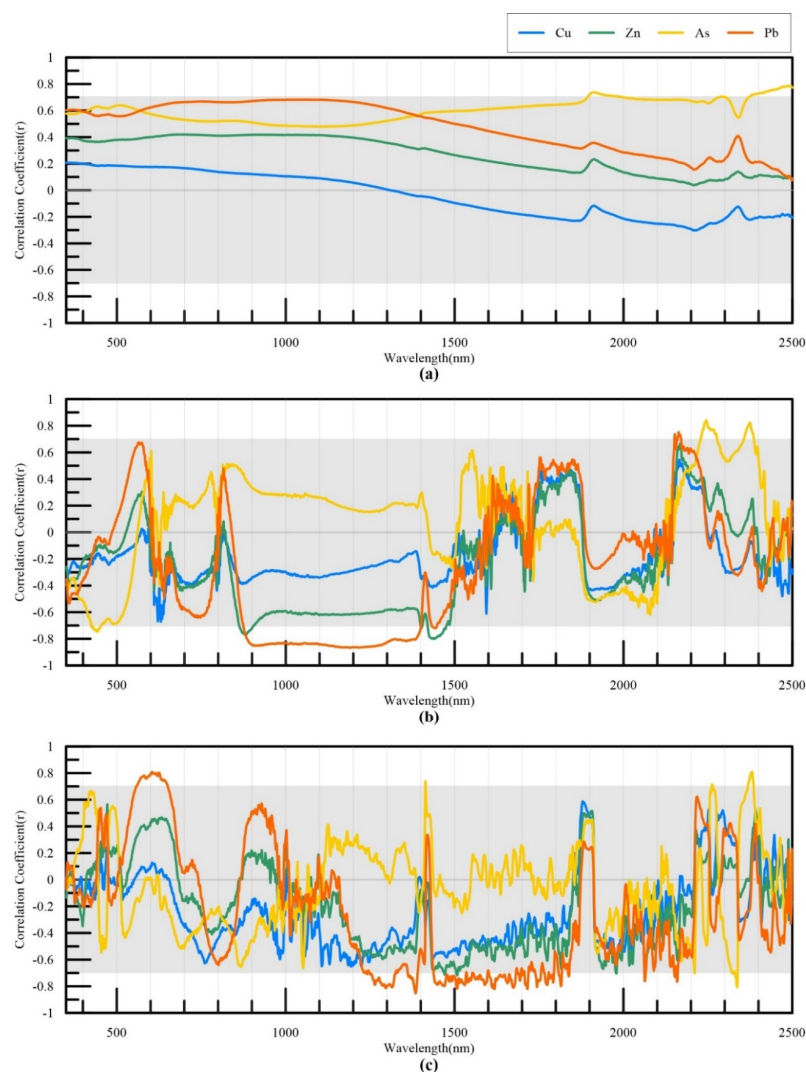


Figure 7. Correlograms between Heavy metal concentration and (a) reflectance, (b) absorption depth, and (c) first derivative of Group B.

These results confirm that the Group A and B samples have distinctive differences in mineral components geochemically adsorbing with heavy metal elements. Group A has stronger reactions with heavy metal elements where clay minerals originated from the weathering process are the main

geochemical agents, whereas Group B has relatively weaker reaction of iron oxides, skarn, and clay minerals from mineralization. The spectral variation controlled by mineral assemblage at one study site has never been reported, and the results confirm that geochemical reactions control spectral characteristics of heavy metal contaminated soils.

3.3.2. Regression Model Development

The prediction models estimating heavy metal concentration in soils using spectral variables were developed for each mineral group based on SMLR model (Tables 4 and 5). The SMLR models were constructed with heavy metal concentration of Cu, Zn, As, and Pb as dependent variables and spectral parameters of the best candidate spectral bands selected from correlation analysis as independent variables. As a result, 8 and 3 regression models were derived for Group A and B, respectively.

The prediction models for Group A samples were constructed based on reflectance for Zn, absorption depth for Cu, Zn, As, and Pb, and first derivatives for Cu, Zn, and Pb (Table 4). The R^2 or Adj- R^2 of the models range from 0.618 to 0.831 with NRMSEs ranging from 12.6% to 19%. The best prediction model of Zn concentration was the one using first derivatives at 2419 nm, 1890, 2410 nm with Adj- R^2 of 0.831 and NRMSE of 12.6% (Table 4). The variables used for the model coincide with absorption features of clay minerals, which indicates the geochemical reaction between clay minerals with heavy metal elements is manifested as the spectral variations of Group A samples.

In soil sample Group B, the prediction models for Zn and Pb used absorption depth at 1440 nm and 1190 nm, respectively, and that for Pb used the first derivatives at 1773 nm and 2065 nm (Table 5). The coefficients of determination for Group B models range from 0.621 to 0.818 with NRMSEs ranging from 11.2% to 15.1%. The best prediction model for Pb concentration had an Adj- R^2 of 0.818 and NRMSE of 11.2%. Unlike Group A, the models for Group B samples have absorption features associated with skarn minerals selected as spectral variables for model development. This difference confirms the spectral variations associated with mineral composition and geochemical reactions in heavy metal contaminated soils. Moreover, the geochemical reaction between clay minerals and heavy metal elements is stronger to affect spectral responses than that between skarn minerals and heavy metal elements.

Table 4. Parameter for fitting the reflectance, absorption depth, and first derivatives to heavy metal concentration using an empirical equation ($y = \beta_0 + \beta_1 x_1 + \dots + \beta_n x_n$) for regression model based on calibration subsets of Group A.

Elements	Wavelength	β_0	β_1 (SE)	β_2 (SE)	β_3 (SE)	F	R^2	Adj- R^2	RMSE (mg·kg ⁻¹)	NRMSE (%)
Reflectance										
Zn	1884 nm	27,932	−37,907 (3619) ***			109.7	0.621		2880	19.1
Absorption depth										
Cu	2442 nm, 2383 nm	318	−13,099 (2649) ***	−10,422 (3808) ***		77.1		0.691	68	18.8
Zn	2441 nm, 2200 nm	13,199	−405,254 (149,575) **	−75,832 (29,849) *		56.0		0.618	2870	19.0
As	2279 nm	−26	26,251 (2225) ***			139.1	0.675		54	15.3
Pb	2220 nm, 2356 nm	1305	−11,913 (2441) ***	−16,582 (5591) ***		70.0		0.67	220	17.7
First derivatives										
Cu	2337 nm, 1510 nm, 2410 nm	488	217,583 (41,479) ***	−1,165,632 (283,556) ***	224,261 (66,445) ***	110.9		0.829	51	14.0
Zn	2419 nm, 1890 nm, 2410 nm	15,756	30,762,496 (2,912,237) ***	−7,779,064 (1,273,252) ***	13,646,303 (3,329,708) ***	112.7		0.831	1907	12.6
Pb	2178 nm, 2220 nm	1356	1,549,406 (188,336) ***	373,484 (91,923) ***		101.9		0.748	193	15.5

Note: F-test; $p < 0.05$ *, $p < 0.01$ **, $p < 0.001$ ***; VIF < 10; β_0 = regression constant; β_n = regression coefficients; SE = standard error; R^2 = coefficient of determination; Adj- R^2 = adjusted coefficient of determination; RMSE = root-mean-square error; NRMSE = normalized root-mean-square error.

Table 5. Parameter for fitting the reflectance, absorption depth, and first derivatives to heavy metal concentration using an empirical equation ($y = \beta_0 + \beta_1x_1 + \dots + \beta_nx_n$) for regression model based on calibration subsets of Group B.

Elements	Wavelength	β_0	β_1 (SE)	β_2 (SE)	F	R ²	Adj-R ²	RMSE (mg·kg ⁻¹)	NRMSE (%)
Absorption Depth									
Zn	1440 nm	2477	-2,228,796 (23,681) ***		93.4	0.621		434	15.1
Pb	1190 nm	292	-4321 (265) ***		140.4	0.711		42	14.2
First Derivatives									
Pb	1773 nm, 2065 nm	279	-1,422,971 (181,834) ***	-968,853 (156,127) ***	131.0		0.818	33	11.2

Note: F-test; $p < 0.05$ *, $p < 0.01$ **, $p < 0.001$ ***; VIF < 10.

3.3.3. Regression Model Evaluation

The scatter plots of measured and predicted heavy metal concentration were used to validate the regression models (Tables 6 and 7, Figures 8 and 9). The models for Cu, Zn, Pb, and As of Group A samples showed a R² from 0.612 to 0.794 with slope (a) from 0.567 to 0.826 (Table 6, Figure 8). The NRMSE ranges from 12.4 to 16.2%, and RPD values of 1.58 to 2.12 indicate the models are statistically acceptable. The highest RPD for Pb concentration is greater than 2.0 [43,47]. In addition, to avoid the bands located in the atmospheric absorption spectra, the models constructed for Cu and Zn concentration that used those bands (1510 nm and 1890 nm) were redeveloped by adding the constraint not to include the atmospheric absorption bands. As a result, the alternative models selected spectral bands at 2337 nm and 2410 nm for Cu concentration and 2419 nm for Zn concentration. The alternative models showed satisfactory statistical significance (Table 6).

Table 6. Parameter for fitting measured heavy metal concentration to the predicted heavy metal concentration using a linear equation ($y = ax + b$) for validation models of Group A. RPD = residual prediction deviation.

Element	Wavelength Selection	a	b	R ²	RMSE (mg·kg ⁻¹)	NRMSE (%)	RPD
Reflectance							
Zn	1884 nm	0.749	2018	0.727	1867	12.4	1.88
Absorption Depth							
Cu	2442 nm, 2383 nm	0.567	79	0.634	54	15.0	1.62
Zn	2441 nm, 2200 nm	0.799	1445	0.639	2441	16.2	1.64
As	2279 nm	0.653	37	0.612	47	13.4	1.58
Pb	2220 nm, 2356 nm	0.786	165	0.716	179	14.4	1.84
First Derivatives							
Cu	2337 nm, 1510 nm, 2410 nm	0.638	62	0.707	52	14.3	1.82
	2337 nm, 2410 nm	0.794	28	0.794	50	13.8	1.72
Zn	2419 nm, 1890 nm, 2410 nm	0.707	1609	0.632	2194	14.5	1.62
	2419 nm	0.765	1473	0.624	2417	16.0	1.60
Pb	2178 nm, 2220 nm	0.826	124	0.784	156	12.6	2.12

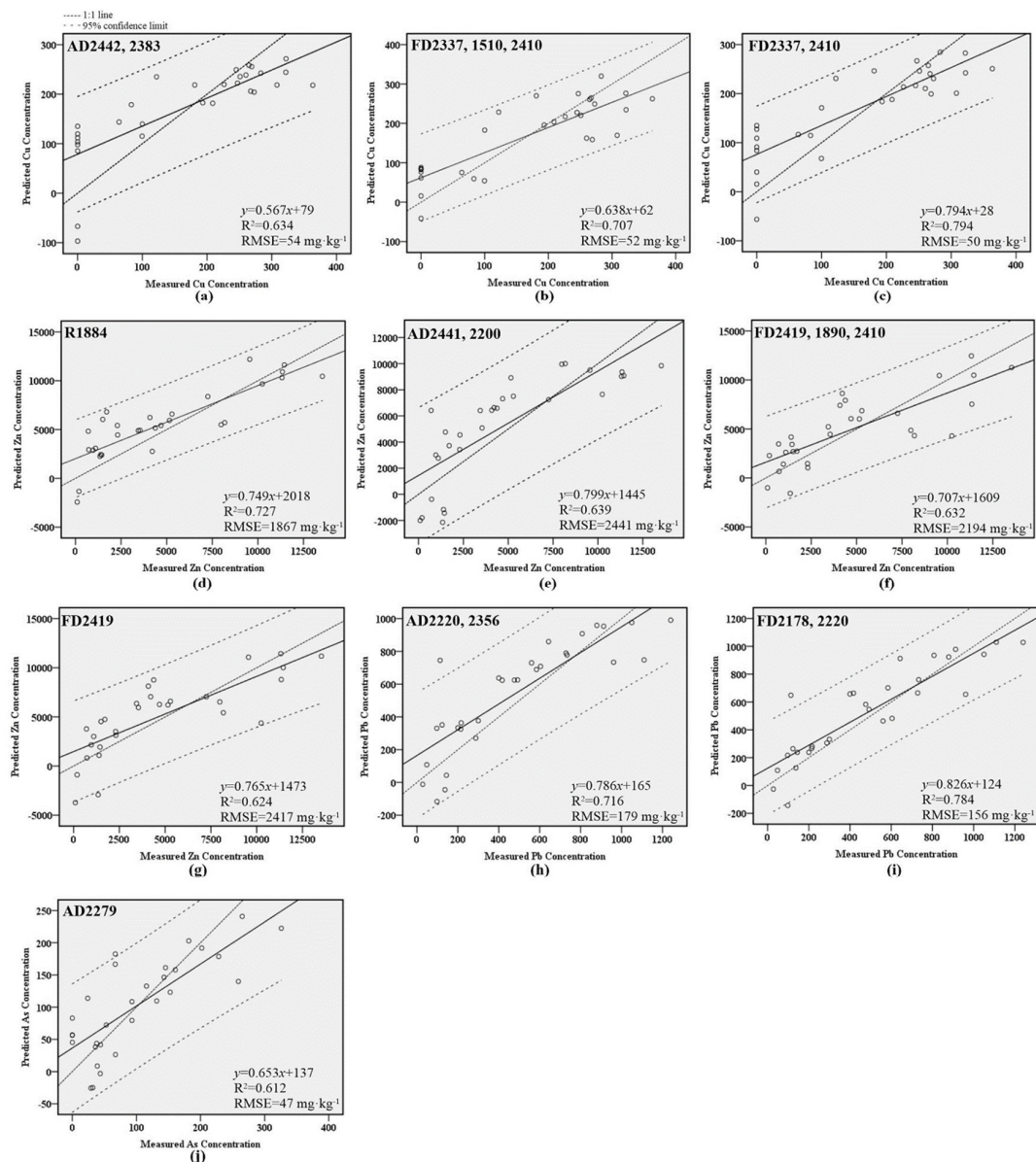
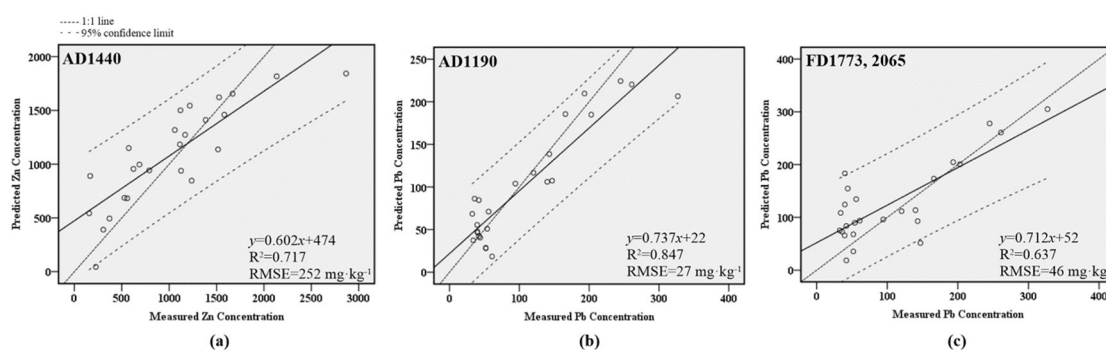


Figure 8. Comparison between the measured heavy metal concentration in experiments and predicted heavy metal concentration derived from regression models of Group A. (a) Validation model at absorption depth of 2442, 2383 nm for Cu concentration; (b) validation model at first derivatives of 2337, 1510, 2410 nm for Cu concentration; (c) validation model at first derivatives of 2337, 2410 nm for Cu concentration; (d) validation model at reflectance of 1884 nm for Zn concentration; (e) validation model at absorption depth of 2441, 2200 nm for Zn concentration, (f) validation model at first derivatives of 2419, 1890, 2410 nm of Zn concentration; (g) validation model at first derivatives of 2419 nm for Zn concentration; (h) validation model at absorption depth of 2220, 2356 nm for Pb concentration; (i) validation model at first derivatives of 2178, 2220 nm for Pb concentration, and (j) validation model at absorption depth of 2279 nm for As concentration.

The validation models for Group B samples are statistically significant showing R^2 of 0.637 to 0.847, NRMSE of 8.8 to 15.6%, slope of 0.602 to 0.737, and RPD values 1.63 to 2.50 (Table 7, Figure 9). The highest statistical significance was observed for Pb concentration models using absorption depth at 1190 nm with the highest R^2 (0.847) and RPD (2.50) values [43,47].

Table 7. Parameter for fitting measured heavy metal concentration to the predicted heavy metal concentration using a linear equation ($y = ax + b$) for validation models of Group B.

Element	Wavelength Selection	<i>a</i>	<i>b</i>	R ²	RMSE (mg·kg ^{−1})	NRMSE (%)	RPD
Absorption Depth							
Zn	1440 nm	0.602	474	0.717	252	8.8	1.84
Pb	1190 nm	0.737	22	0.847	27	9.1	2.50
First Derivatives							
Pb	1773 nm, 2065 nm	0.712	52	0.637	46	15.6	1.63

**Figure 9.** Comparison between the measured heavy metal concentration in experiments and predicted heavy metal concentration derived from regression models of Group B. (a) Validation model at absorption depth of 1440 nm for Zn concentration; (b) validation model at absorption depth of 1190 nm for Pb concentration; (c) validation model at first derivatives of 1773, 2065 nm for Pb concentration.

4. Conclusions

This study investigated spectral characteristics associated with heavy metal concentration in mine soils with considerations in heterogeneity of mineral composition associated with geological processes that shaped the mineral composition. The samples acquired from various locations, such as mine waste, unpaved road, and mine audit, were classified into two types based on the mineral composition. The Group A samples were composed of rock-forming minerals and clay minerals originated by a weathering process named silicate clay mineral group. The Group B samples were silicate–carbonate–skarn–clay minerals consisting of rock forming minerals and skarn minerals originating from skarn mineralization as excavated materials by mining activities. It indicates that soils in mine areas can be affected by both mineralization and weathering processes.

The chemical analysis revealed that both groups of soils are severely contaminated with Cu, Zn, As, and Pb while the contamination level was higher for the silicate clay mineral group (Group A) than the silicate–carbonate–skarn–clay mineral group (Group B). This phenomenon infers that the geochemical bonding reaction with heavy metal cation is stronger with clay minerals than that with carbonate or skarn minerals because the alkaline carbonate minerals commonly increases pH levels and, thus, could reduce the chemical activity of heavy metal cations. Therefore, it indicates that the mineral composition of heavy metal contaminated soils controls geochemical bonding between heavy metal cation and reaction agents. The geochemical behavior difference between Group A and B samples is also confirmed by the correlation analysis between heavy metal elements with the spectral variables.

The spectral characteristics associated with heavy metal concentration for Group A and Group B soil samples identifies the mineral agents participating in geochemical reactions with heavy metal cations. The Group A spectra showed a decrease in absorption depth associated with clay minerals and iron oxides with an increase in heavy metal concentration, while the Group B spectra showed a decrease in absorption depth associated with skarn minerals/iron oxides/clay minerals with an increase in heavy metal concentration. It infers that chemical bonding between clay minerals/iron oxide and heavy metal

cation for Group A samples has reduce the available chemical components manifested by clay minerals and iron oxides, while that of Group B samples has reduced chemical components associated with skarn minerals, iron oxides, and clay minerals. Thus, the geological history involved with secondary mineral production, such as mineralization and the weathering process, are closely related to spectral manifestation of heavy metal elements in soils.

The correlation analysis between heavy metal concentration and spectral variables confirmed the spectral variations was controlled by geochemical adsorption between minerals and heavy metal cations. In Group A samples, high correlations was found at the absorption features of clay minerals and Cu, Zn, As, and Pb, and at the absorption feature of iron oxide and Zn and Pb concentration. On the other hand, the correlation between spectral variables and heavy metal concentration for Group B samples was relatively weaker in statistical significance, indicating high correlation at spectral bands associated with skarn minerals and Pb/Zn concentration and clay minerals and As concentration. A total of 8 prediction models using spectral variables on Cu, Zn, As, and Pb concentration for Group A samples were developed mainly at the clay mineral absorption features. Three models for Zn and Pb concentration were developed for Group B samples using spectral variables of skarn minerals. All models were statistically validated and acceptable for prediction of heavy metal concentration. This study reports on distinctive spectral variation controlled by mineral assemblages at one study site associated with heavy metal contamination in mine soils. The results confirm the hypothesis that there exist geochemical reactions controlling spectral characteristics of heavy metal contaminated soils. It suggests the importance of specifying geological parameters in heavy metal contamination detection using spectroscopy. It is expected that these models, with further adjustment to sensor specifications, can be used to map heavy metal concentration in a remote sensing setting.

Author Contributions: Conceptualization, J.Y. and H.K.; methodology, J.Y., H.K., and Y.J.; software, H.K.; validation, J.Y., J.K., and L.W.; formal analysis, H.K.; investigation, J.Y., H.K., and L.W.; resources, H.K. and Y.J.; data curation, H.K. and Y.J.; writing—original draft preparation, H.K. and J.Y.; writing—review and editing, J.Y. and L.W.; visualization, H.K. and J.K.; supervision, J.Y.; project administration, J.Y.; funding acquisition, J.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government under Grant NRF-2020R1A2C2005439 and Grant NRF-2018R1A4A1059956.

Acknowledgments: The authors deeply appreciate the anonymous academic editors and reviewers for their constructive comments.

Conflicts of Interest: The authors declare no conflict of interest.

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