Reflectance Spectroscopy Study of Cd Contamination in the Sediments of the Changjiang River, China

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Sediments of the Changjiang River have been found in recent studies to be enriched in cadmium (Cd). The possibility and mechanisms for evaluating total Cd concentration and its binding form using reflectance spectroscopy within the visible-near-infrared (VNIR) region (400–2500 nm) have been investigated. Bottom sediments (69 samples) in the lower reaches of the river were collected for chemical analyses and spectral measurements. Total Cd concentration in the sediments was found to be exponentially related to the spectral proxies for organic matter (spectral reflectance at 400–530 nm), clay minerals (first derivative (FD) values at the shoulders related to absorption bands near 1400, 1900, and 2200 nm), and Fe oxides (FD values at 560–760 nm). The results indicated that the spectrally featureless Cd was mostly bound to these spectrally active materials, which made it possible for Cd concentration to be determined from reflectance spectra. This conclusion was also confirmed by the results of chemically sequential extraction of Cd. This study has demonstrated the usage and theoretical basis of reflectance spectroscopy, which is a rapid and inexpensive analytical method, for evaluating contamination by heavy metals and their binding forms in sediments.

Introduction

The Changjiang River, draining into the East China Sea, is the largest river in China and the fourth largest river in the world after the Amazon, Zaire, and Orinoco. A cadmium (Cd) anomaly spreading along the whole Changjiang River basin was reported by a recent multi-purpose geochemical map program (1). Sediments of the Changjiang have Cd concentrations several times higher than the background value. The Cd anomaly along the river spreads from the economically undeveloped western regions to the developed eastern regions. In addition, Cd is concentrated not only in the surficial sediments but also in the deep (no less than ~1.5 m) ones (2). A study by Bi et al. (3) showed that the average Cd concentration in the Changjiang bottom sediment is 0.70 mg/kg in the middle reaches. The Cd concentration in suspended sediment in the estuarine of the Changjiang varies from 0.33 to 0.73 mg/kg (4). Our measurements (unpublished) between 2004 and 2005 showed that Cd concentration in suspended sediments in the lower reaches near Nanjing is 0.75–1.2 mg/kg.

Geochemical mapping of heavy metals in sediments and soils is of much environmental concern. However, the conventional method of geochemical mapping is by a raster sampling and laboratory analysis, which is time-consuming and expensive. Accordingly, efforts have been made (5–9) to predict heavy metal concentrations in soils or sediments by reflectance spectroscopy within the visible-near-infrared (VNIR) region (400–2500 nm) because the method is rapid, inexpensive, and there is no need to destroy samples. Previous studies (5–9) emphasized the possibility of the prediction of heavy metal concentrations using multivariate statistical methods such as partial least-squares regression (PLSR), principal component regression (PCR), multiple linear regression (MLR), or artificial neural networks (ANN). However, heavy metals in soil or sediment in field conditions are spectrally featureless because of their low concentrations in field conditions. The mechanism for heavy metal prediction was assumed to be the correlation between increased input heavy metals and some spectrally active soil constituents, such as organic matter, clay minerals, and Fe oxides. The former studies used empirical statistical approaches to predict heavy metal concentrations from spectral data directly. There is a lack of a theoretically based calibration (5–9).

Chemical speciation of heavy metals, i.e., the partitioning among the various forms in which they might exist, determines their bioavailability and toxicity. However, the determination of specific chemical species or binding forms, usually by operationally defined sequential extraction procedures, is difficult. Cd does not absorb radiation in the VNIR region but it may be detectable because it is bound to some constituents in sediments. Most chemically active materials in sediments have spectral features and can be detected directly by reflectance spectra. Hence, investigation of the relationship between Cd contamination and the reflectance spectrum, which contains information about the chemically active materials, may afford information for Cd binding.

Enrichment of Cd in the Changjiang sediments offers a unique opportunity to study Cd contamination using reflectance spectroscopy. This paper aims to pursue the theoretical basis for the prediction of Cd concentration and the possibility of evaluating its binding forms based on spectral data. First, spectral proxies for the chemically active materials were identified based on chemical experiments and mathematical statistics; and then, Cd concentration and its binding form were evaluated based on its wavelength loadings on these spectral proxies.

Materials and Methods

Sediment Sampling. Samples were collected around Baoguazhou Island, one of the largest alluvial islands (area ~50 km²) in the lower reaches of the Changjiang near Nanjing in Jiangsu Province, in October 2004, when the river was at low water level and bottom sediments were exposed. A total of 43 samples of bottom sediments (AC section) were collected from two channels around the island by a light boat with sampling intervals 0.5–1.5 km. Two vertical sediment profiles (A and C), one at the northwest bank (profile A) and the other (profile C) at the southeast bank of the island, were sampled at an interval of 5 cm (21 samples were from profile A and 5 samples were from profile C).

The collected samples (~500 g each) were air-dried (25 °C, 2 weeks) in the laboratory, and sieved at 2 mm to remove large debris, stones, and pebbles for analysis.
Chemical Analysis. Grain-size distribution of the samples was determined by a microphotosize analyzer and the content of the <2 μm fraction was defined as the content of total clay minerals. The carbonate and total organic carbon (TOC) were analyzed using a method modified from Wang (10) by combusting sample at 950 °C in a vario MACRO CHN analyzer. TOC was measured by combusting residues digested with 1 N HCl to remove carbonates. The difference between total carbon, measured before carbonate removal, and TOC is converted to carbonate content assuming all inorganic carbon is present as calcite or aragonite.

A small portion of each sample (~1 g) was ground to 80-mesh size with a mortar and digested following the method of McGrath and Cumilhlo (11). Cd concentrations in the digest solutions were determined by graphite-furnace atomic absorption spectrometry (GFAAS). Concentrations of Fe2O3, Al2O3, and Mn were determined by ICP-AES.

Analyzed data were assessed for accuracy and precision using a quality control program which included reagent blanks, duplicate samples, and certified reference materials.

Spectral Measurements and Transformations. Sample preparation for spectral measurement followed procedures given by Wu et al. (9). Samples were first ground to <38 μm with a mortar and pestle, made into a thick slurry on a glass microslide with distilled water, smoothed, and dried slowly at low temperature (~40 °C). Reflectance spectra of the samples were then collected using a Perkin-Elmer Lambda 900 spectrophotometer at 2 nm from 400 to 2500 nm, that is, from visible (VIS, 400–700 nm), to the near-infrared (NIR, 700–2500 nm). A total of 1051 numbers in % were collected to form a spectrum for each sample.

Three spectral preprocessing techniques were applied to the original reflectance spectra (Ref). Derivative transformation is known to minimize additive baseline effects (8). The original reflectance values were transformed with first derivative (FD) processing using Savitzky-Golay smoothing with a second-order polynomial fit with a window width of 20 nm using the Unscrambler software package version 8.0.5 (CAMO ASA, Trondheim, Norway; 12).

Second, the Ref data in the VIS (400–700 nm) region were processed to obtain normalized reflectance (nRefVIS). An nRefVIS spectrum was calculated by dividing the reflectance in each band by the brightness, which is calculated by averaging the sample’s reflectance values within 400–700 nm.

Third, reflectance signals from TM/ETM, the most widely used multi-spectral remote sensor, were simulated following the method described by Ji et al. (13). Then, the simulated TM/ETM (STM) bands were normalized as calculation of nRefVIS. Normalized STM values (nSTM) were calculated by dividing STM values by the brightness, which was calculated by averaging the STM values in visible region, i.e., STM1, STM2, and STM3.

Correlation and Regression. Not all spectral regions were sensitive to Cd concentration. Pearson correlation coefficients between Cd concentration and spectral variables (Ref, FD, nRefVIS, and nSTM) were calculated to determine the sensitive wavelengths for Cd concentration. This procedure not only explored which spectral variables were the most relevant to determine Cd concentration, but also probed the possibility to unravel the mechanism.

Prior to regression, the dataset was split into a calibration set and a validation set. The 69 samples were sorted from the lowest to the highest Cd concentration. Odd-numbered samples were used as the calibration set and even-numbered ones were used as the test set.

Univariate regressions were first used to establish the models for Cd concentration prediction. The bands that had the highest correlations with Cd concentration for each spectral transformation were tested. A total of four univariate regression models (linear, logarithmic, power, exponential regression models) were attempted using the calibration set. The models were validated using the test set. Root-mean-square errors (RMSE) were used to evaluate the quality of the models.

Partial least-square regression (PLSR) was often used in spectral analysis (6, 8). PLSR models for Cd prediction have been calculated using the different data transformations (Ref, nRefVIS, FD) for comparison with the univariate prediction models. The one-out cross-validation was used when establishing the PLSR models using the calibration set. The root-mean-square error of cross-validation (RMSECV) was used to evaluate the quality of the results (8). This RMSECV was also used to determine the number of components retained in the regression model. The optimal number of PLS-components was determined by using a small number of components that gives a minimal RMSECV. The final models were validated using the root-mean-square error of prediction (RMSEP) for the test dataset. PLSR were performed with the Unscrambler.

Results and Discussion

Cd Concentration. The average value of Cd concentrations is 0.669 mg/kg, ranging from 0.17 to 1.57 mg/kg. Cd concentration in bottom sediments collected by Bi et al. (3) in the middle reaches of the river ranged from 0.51 to 0.94 mg/kg with the average of 0.70 mg/kg, which is comparable to our data. The average Cd content of the lithosphere is estimated at 0.2 mg/kg and the background concentration of soil Cd in Nanjing determined by Nanjing Agricultural University is 0.16 mg/kg. This demonstrates that Cd is significantly concentrated in sediments of the Changjiang, at least from the middle reaches to the lower reaches. The wide range (0.17–1.57 mg/kg) of Cd concentrations in our samples benefits statistics and model construction.

Sediment Spectra. The measured sediment spectra (Figure 1) followed the same basic shapes as soil samples described by Ben-Dor et al. (14). They are characterized by distinct absorption bands at near 1400, 1900, and 2200 nm associated with clay minerals. Additional weak absorption bands are centered near 900 nm due to Fe3+. In the visible region, there is a significant decrease in reflectance intensity toward the blue wavelengths mainly caused by charge transfer absorption of iron (15).

Spectral Proxy for Organic Matter. Previous studies (14) of soil reflectance spectra showed that organic matter is broadly related to differences in albedo. To evaluate the contribution of organic matter to the spectrum, we first measured the spectrum of commercial humic acid, the dominant component in organic matter. The humic acid has a black color showing very low reflectance intensity in...
the VIS region. In NIR region, broad and overlapped absorption bands from overtones and combinations of various chemical bonds also result in low reflectance intensity with few unique absorption features except a weak absorption at about 1414 nm and a shallow wide absorption at 2200–2300 nm (Figure S2 in the Supporting Information).

The contribution of organic matter to reflectance spectrum was further evaluated by removing it from samples using chemical methods. Organic matter was removed from 1 g of a selected sample by oxidation in 30% H₂O₂ for 1 h at room temperature and 1 h under 75 °C. The residual was washed with distilled water. The analysis of reflectance spectrum for the residual followed the same methods as their precursors, the samples before the organic matter removal. The results showed that the removal of organic matter increased the reflectance intensity at all through the NVIR region, bringing in neither the absence of absorption features nor the presence of new ones (Figure S2 in the Supporting Information).

As the dominant feature of organic matter in sediments is to decrease reflectance intensity, the correlation coefficients between TOC and Ref for each wavelength were calculated (Figure 2). The highest correlation coefficients (r < −0.79) appeared at the region 400–530 nm. So, reflectance at this spectral region is regarded as the spectral proxy of organic matter.

**Spectral Proxy for Clay Minerals.** OH (hydroxyl) in free water and lattice OH in clay minerals produce the prominent absorption features around 1400, 1900, and 2200 nm. FD curves of the reflectance spectra indicate their slopes at each wavelength. Peaks on FD curves occur on the shoulders of absorption bands. Deeper absorption results in higher absolute values in the FD curves at the left and right shoulders of that absorption. As a result, the FD values at the absorption shoulders of clay minerals at about 1410, 1910, and 2300 nm are highly correlated with Al₂O₃ and clay content (Figure 3).

**Spectral Proxy for Iron Oxides.** In the visible region, the significant decrease in reflectance toward the blue wavelengths is mainly caused by charge transfer absorption of iron. Goethite and hematite are dominant iron oxides in sediments. Because of the complexity of absorption features caused by charge transfer absorption of iron, FD curves are the most suitable transformation for investigating spectral features of iron oxides. Balsam and Deaton (16) suggested that the dominant FD peak for hematite is at about 565 nm and that for goethite is at 335 nm with a secondary peak at 435 nm.

In our study, four FD peaks (Figure 1 and Figure S3 in the Supporting Information) were observed in the shorter wavelength region: a strong peak near 565 nm (peak C), the peak for hematite by Balsam and Deaton (16); a small peak near 435 nm (peak A), which is the secondary peak for goethite; a broad peak at 500 nm (peak B) joint with peak C and a lower broad peak (peak D) between 650 and 760 nm. Experiments were done for a confirmation of the origin of the four peaks (Figure S3 in the Supporting Information). Iron oxides were removed from selected samples using the citrate–bicarbonate–dithionite (CBD) extraction procedure developed by Mehra and Jackson (17). All the four peaks (peaks A, B, C, and D) in the FD curves disappeared after the CBD treatment. This indicates that the four peaks (A, B, C, and D) are all associated with iron oxides. Heating the samples at 400 °C in a muffle furnace for 12 h makes goethite transform to hematite (18). Peaks A and B disappeared and peaks C and D remained in the FD curves for the heated samples, which indicated that peaks A and B were caused by goethite and peaks C and D were caused by hematite. Both pure goethite and hematite have sharp slopes at 600–740 nm in untransformed reflectance spectra, which caused their common FD peaks (peak D) in sediments. So, it was concluded that presence of goethite would produce peaks A, B, and D, and hematite would produce peaks C and D.

High correlation coefficients (Figure 4) between Fe₂O₃ content and FD values appeared in the spectral regions relating to these peaks. Although peak D is weaker than the other peaks, it is most strongly correlated with total Fe₂O₃, probably because it is the common peak for both goethite and hematite. Thus, FD values in 560–760 nm are considered as a spectral proxy for total Fe₂O₃ content.
Spectral Response for Cd Contamination.

To investigate the relationship between Cd concentration and the spectral variables, correlation coefficients of Cd concentration with Ref, FD, and nRefVIS values were calculated (Figure 5). Cd concentration is negatively correlated with spectral reflectance intensity. The higher values for correlation coefficient were at short wavelengths, which coincide with the spectral proxy for organic matter. Cd concentration is positively correlated with the FD values corresponding to the left shoulders of the absorptions around 1410, 1910, and 2210 nm, and negatively correlated with those corresponding to the right shoulders. FD values in these spectral regions are proxies for clay minerals. In the VIS, high correlation coefficients with FD values appeared in a broad region (530–768 nm). The highest correlation coefficient appeared near 670–760 nm, which is associated with the spectral proxy for iron oxides.

Table 1 shows a summary of the optimal univariate models and statistical parameters from variables at the most important wavelengths. The best prediction equations from all the spectral transformations (Ref, FD, and nRefVIS) are exponential. This agrees with results from Wu et al. (9) who predicted Hg contamination in soil by reflectance. These important wavelengths and spectral transformations used as independent variables for prediction were also related to the spectral proxies for those spectrally active materials. This reveals that good prediction results can be achieved through the theoretically based univariate models.

In former studies (5–6), PLSR has been frequently used for calibration with spectral variables. PLSR models have been calculated for comparison with the univariate models. Wavelength loadings for Cd concentration determined from PLSR were similar to that from correlation analysis. The RMSECV from the calibration data set and RMSEP from the independent test set for the models are listed in Table 2. It seemed that PLSR results revealed no significant improvement compared to the theoretically based univariate models. This implies that PLSR models are based on the spectral proxies of the spectrally active materials for prediction. The intercorrelation among the spectrally active materials caused intercorrelation among their spectral proxies. More spectral bands introducing correlated information do not improve prediction.

Spectral information can also be acquired by remote sensing. Reflectance signals from TM/ETM, the most widely used multi-spectral remote sensor, were simulated and used to investigate the potential possibility for Cd mapping by remote sensing. The result showed that acceptable results can be achieved by nSTM1 (Table 1). However, it should be noted that the results here were based on data acquired in laboratory conditions. More studies are required to study the feasibility of spectra in the field or with remote sensing instruments.

Binding Form: The Cd Prediction Mechanism.

It is generally accepted (19) that organic matter, hydrous oxides of Fe and Mn, and clay minerals are critical components of
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Supporting Information Available

STM simulation method (S1); sketch map of the study area (Figure S1); reflectance spectra showing spectral contribution of organic matter (Figure S2); FD curves showing spectral contributions of iron oxides (Figure S3); plots of predicted against measured Cd concentrations (mg/kg) from the univariate models (Figure S4); Cd fractions of the samples examined by sequential extractions (Figure S5); and correlation coefficients among sediment constituents (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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