Diffuse reflectance spectroscopy study of heavy metals in agricultural soils of the Changjiang River Delta, China

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Abstract
Heavy metal contamination of soil is becoming an increasingly serious problem in the Changjiang River Delta (China) as a result of rapid economic development. Conventional methods for investigating the contamination based on raster sampling and laboratory analysis are time-consuming and relatively expensive. Diffuse reflectance spectroscopy (DRS) within the visible-near-infrared (VNIR) region (400-2500 nm) has been widely used to identify spectrally active constituents in soils. Correlations between heavy metals (Cd, Cr, Pb, Cu, Zn, Hg and As) and DRS spectra of agricultural soils from Changjiang River Delta were studied to assess their binding forms. The results show that Cr, Cu, Zn and As have stronger negative correlation coefficients with the spectral bands attributed to the absorption features of iron oxides, clays and organic matter, suggesting they are strongly bound to these soil constituents. However, Cd, Pb and Hg only display a significant correlation with the spectral region related to organic carbon, indicating that binding with organic matter is important for these metals. This finding is consistent with the fact that Cr, Cu, Zn and As have significant correlations with Fe_2O_3, Al_2O_3 and TOC, but Cd, Pb and Hg only display a significant correlation with TOC.

Key Words
Soil contamination; Heavy metals; Diffuse reflectance spectroscopy.

Introduction
Heavy metal contamination of soil results from anthropogenic activity and influences the physical and chemical characteristics of soil ecosystems. Enrichment of heavy metals in soil and their accumulations in agricultural products presents a risk to human health. Potentially toxic elements could be involved in physico-chemical reactions as well as interaction with soil components like minerals, humic matter, metal oxides, microorganisms and/ or ligands. Conventional methods of heavy metal identification such as inductively coupled plasma (ICP), atomic absorption spectrometry (AAS) or operationally defined sequential extraction can measure physico-chemical data directly, but are time-consuming and relatively expensive. Diffuse reflectance spectroscopy (DRS) in visible-near infrared (VNIR) region (400-2500 nm) has been used to rapidly analyse and monitor soil constituents both conveniently and accurately. Through VNIR DRS, soil constituents such as iron oxides (Ji *et al.* 2002; Madeira *et al.* 1997), organic matter (Fidencio *et al.* 2002), carbonate (Ben-Dor and Banin 1990), and clay minerals (Rossel *et al.* 2009) can be quantitatively determined. Heavy metals in soil are often absorbed or bounded by spectrally active constituents, which make it possible to study the characteristics of metals in soil using VNIR DRS. Previous research has emphasized the prediction and monitoring of heavy metal in soil and sediment (Wu *et al.* 2005; Xia *et al.* 2007; Moros *et al.* 2009). This study aims to investigate the binding forms of heavy metals in agriculture soils from a fast developing area, the Changjiang River Delta of China, using the DRS approach.

Methods
Soil Sampling
A total of 122 samples of paddy rhizosphere and non-rhizosphere soils were collected from 61 locations in the Changjiang River Delta (Figure 1); 61 rhizosphere soils were sampled around the paddy root (depth < 20 cm), and 61 non-rhizosphere soils collected from areas without paddy plants (< 20 cm). The soil samples were air-dried at 25□ for 2 weeks and sieved with a 2 mm sieve to remove large debris, stones, and pebbles before analysis.

Chemical analysis
As and Hg were measured by using AFS 230E Cold Vapor Atmospheric Fluorescence Spectrometry. Cd was analyzed with graphite-furnace atomic absorption spectrometry by AAS ZEEnit60. Cr, Cu, Pb, Zn, Al_2O_3,

1 – 6 August 2010, Brisbane, Australia. Published on DVD.

and Fe_2O_3 were determined using ICP-MS by Thermo ICP-MS X SERIES. Data were evaluated for accuracy and precision using quality assurance and quality control (QA/QC) programs. Total organic carbon (TOC) was analyzed using a vario-MACRO CHN analyzer with the combustion temperature of 950 °C.

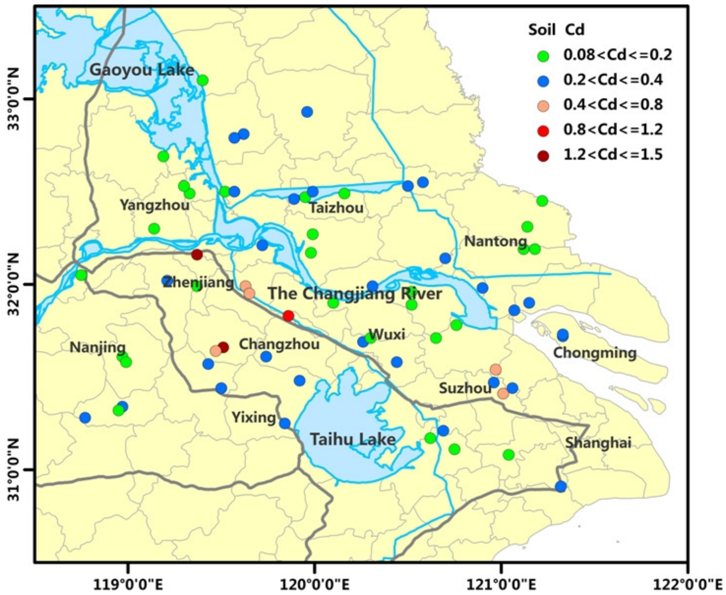

Figure 1. Soil sampling map of the Changjiang River Delta (China) with soil Cd levels indicated.

Spectral measurement

Soil samples were ground and made into a slurry on a glass microslide with distilled water, and then smoothed and dried slowly at room temperature. Diffuse reflectance spectra were recorded in a Perkin-Elmer Lambda 900 spectrophotometer at 2 nm increments between 400 nm and 2500 nm relative to a white Spectralon standard.

Results

Heavy metal concentrations of rhizosphere and non-rhizosphere soil samples from the Changjiang River Delta are shown in Table 1. Results suggest that in each location at least one metal had concentrations exceeding the environmental quality standard for soils of Ministry of Environmental Protection (MEP), China. However, among the seven heavy metals, only Cd has an average content higher than the MEP standard. Concentrations of Cd ranged from 0.08 to 1.44 mg/kg for rhizosphere soil with an average of 0.28 mg/kg, and 0.10 to 1.06 mg/kg for non-rhizosphere soil with the same average (0.28 mg/kg).

Table 1. Statistics of heavy metals in rhizosphere and non rhizosphere agricultural soils of Changjiang River Delta.

		Hg	As	Cd	Cr	Pb	Cu	Zn
Minimum	rhizosphere soil n=61	0.04	4.00	0.08	30.99	11.12	9.90	47.60
Maximum		0.27	16.60	1.44	108.90	89.68	55.50	196.40
Mean		0.11	8.06	0.28	73.96	28.17	31.95	92.38
Std. D		0.06	2.54	0.26	15.16	10.65	8.64	27.65
CV (%)		52.59	31.53	91.25	20.50	37.81	27.04	29.93
Minimum	non-rhizosphere soil n=61	0.03	3.80	0.10	11.07	12.30	9.10	47.90
Maximum		0.33	33.40	1.06	113.90	40.95	115.90	142.60
Mean		0.12	8.47	0.28	67.23	26.70	33.50	91.67
Std. D		0.06	3.72	0.16	19.74	6.62	13.58	23.26
CV (%)		50.12	43.87	58.28	29.36	24.80	40.55	25.37
MEP*		0.15	15.00	0.20	90.00	35.00	35.00	100.00

*. Environmental quality standard for soils of Ministry of Environmental Protection (MEP) China (Ministry of Environmental Protection 1995)

Concentrations of heavy metals in the rhizosphere soil samples are negatively correlated with the reflectance of soil DRS spectra. They display different correlation features (Table 2) and can be divided into two groups. Group I consists of Cr, Cu, Zn and As. These metals all have strong negative correlation coefficients with DRS spectra through most of the VNIR region, but, the strongest correlated bands differ and are indicative of their binding information. For example, Cr shows high spectral correlations at the 2300 nm spectral bands related to Fe (Mg, Al) –OH from iron oxides and clays, and C-H absorption from organic matter, reflecting its binding feature to all these fine soil constitutes. Cu and As have strong correlations with bands resulting from Fe^{3+} absorption at 538 nm and 428 nm, respectively. This suggest that binding to iron oxides is the most important form of Cu and As. Zn displays high correlations with spectral regions at around 1700 nm, which is related to the first overtone of C-H stretch from organic matter; thus binding with organic matter is the dominant form of Zn. Group II consists of Cd, Pb and Hg. They only exhibit good correlation with DRS reflectance of the spectral regions between 500 and 700 nm, which are strongly related to the total carbon contents of the soils, suggesting that Cd, Pb and Hg are only strongly associated with organic matters, not with iron oxides or clays.

The analysis of correlation between heavy metal and soil constitutes of Fe_2O_3, Al_2O_3 and TOC (Table 2), which represented the clay minerals, iron oxides and organic matter, respectively, could support the above predicated binding forms of heavy metals. The order of the correlation coefficients from high to low between metal and wavelength is Cr > Cu > Zn > As > Pb > Hg > Cd. This is the same as the order of their correlation coefficients with Fe_2O_3, Al_2O_3 and TOC (Table 2). Cr and Cu have significant correlations with all Fe_2O_3, Al_2O_3 and TOC, whereas Pb, Cd and Hg only show significant correlation with TOC. These findings also validate a mechanism to predict trace elements that have no absorption features in reflectance spectra.

Table 2. Univariate regression of heavy metals and DRS reflectivity (R) at wavelengths with the highest correlation. Also shown are the correlations between heavy metals and Al_2O_3, Fe_2O_3 and TOC.

	Wavelength (nm)	Equation	r	Sig.	Correlation coefficient		
					Al_2O_3	Fe_2O_3	TOC
Hg	640	$Hg = -0.445+0.047R-0.001R^2$	0.392	0.008	0.108	0.164	0.346*
As	428	$As=e^{(2.814-0.061R)}$	0.552	0.000	0.474*	0.601*	0.153
Cd	630	$Cd=e^{(0.891-0.051R)}$	0.329	0.010	-0.189	-0.081	0.445*
Cr	2376	$Cr = -85.356+11.547R-0.192R^2$	0.823	0.000	0.637*	0.712*	0.496*
Pb	578	$Pb = e^{(4.365-0.044R)}$	0.512	0.000	-0.046	-0.007	0.415*
Cu	538	$Cu = -31.678+7.685R-0.217R^2$	0.676	0.000	0.565*	0.658*	0.649*
Zn	1728	$Zn = e^{(6.499-0.050R)}$	0.635	0.000	0.216	0.342*	0.540*

*. Correlation is significant at the 0.01 level (2-tailed).

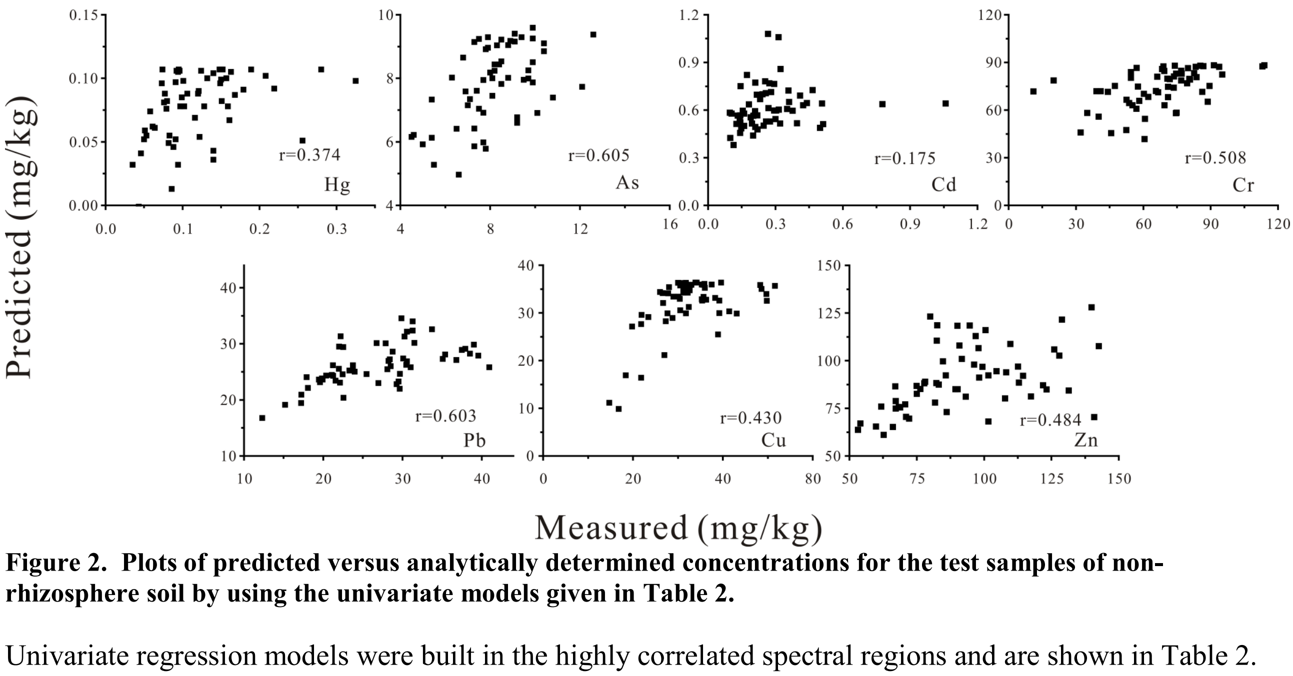

Figure 2. Plots of predicted versus analytically determined concentrations for the test samples of non-rhizosphere soil by using the univariate models given in Table 2.

Univariate regression models were built in the highly correlated spectral regions and are shown in Table 2. Validation of non-rhizosphere soil showed the univariate models for As, Pb, Cr, Zn, Cu and Hg all have a significant prediction potential (Figure 2), suggesting the potential of using remote sensing data in the future for the rapid mapping of contaminated areas in agriculture fields of Changjiang River Delta.

Conclusion

This study suggests that analysis of DRS within the VNIR region can be used for extracting the binding forms and for prediction of heavy metal concentration in agriculture soils. The results show that heavy metals Cr, Cu, Zn and As have stronger negative correlation coefficients with the spectral bands attributable to the absorption features of iron oxides, clay, and organic matter, suggesting they are strongly bound to these soil constitutes. The metals Cd, Pb and Hg only display significant correlation with the spectral region related to TOC, indicating binding with organic matter is important for these metals. This finding was consistent with the fact that the correlation coefficients between the first group and Fe_2O_3, Al_2O_3 and TOC were higher than that of latter group. The binding of elements by the spectrally active constituents of soils is the mechanism by which we assess the spectrally featureless heavy metals. This observation suggests that remote sensing data has the potential to rapidly map contaminated areas in agriculture fields of the Changjiang River Delta.

Acknowledgements: This study was financially supported by the National Natural Science Foundation of China (Grant 40625012) and China Geological Survey(GZTR02-01).

References

Ben-Dor E, Banin A (1990) Near-infrared reflectance analysis of carbonate concentration in soils. *Applied Spectroscopy* **44**, 1064-1069.

Cozzolino D, Moron A (2003) The potential of near-infrared reflectance spectroscopy to analyse soil chemical and physical characteristics. *Journal of Agricultural Science* **140**, 65-71.

Fidencio PH, Poppi RJ, de Andrade JC (2002) Determination of organic matter in soils using radial basis function networks and near infrared spectroscopy. *Analytica Chimica Acta* **453**, 125-134.

Ji JF, Balsam W, Chen J, Liu LW (2002) Rapid and quantitative measurement of hematite and goethite in the Chinese loess-paleosol sequence by diffuse reflectance spectroscopy. *Clays and Clay Minerals* **50**, 208-216.

Madeira J, Bedidi A, Cervelle B, Pouget M, Flay N (1997) Visible spectrometric indices of hematite (Hm) and goethite (Gt) content in lateritic soils: the application of a Thematic Mapper (TM) image for soil-mapping in Brasilia, Brazil. *International Journal of Remote Sensing* **18**, 2835-2852.

Ministry of Environmental Protection P (1995) Environmental quality standard for soils (in Chinese). *Ministry of Environmental Protection of PRC, Beijing, PRC*, Available from: http://kjs.mep.gov.cn/hjbhbz/bzwb/trhj/trhjzlbz/199603/W020070313485587994018.pdf.

Moros J, de Vallejuelo SFO, Gredilla A, de Diego A, Madariaga JM, Garrigues S, de la Guardia M (2009) Use of Reflectance Infrared Spectroscopy for Monitoring the Metal Content of the Estuarine Sediments of the Nerbioi-Ibaizabal River (Metropolitan Bilbao, Bay of Biscay, Basque Country). *Environmental Science & Technology* **43**, 9314-9320.

Rossel RAV, Cattle SR, Ortega A, Fouad Y (2009) In situ measurements of soil colour, mineral composition and clay content by vis-NIR spectroscopy. *Geoderma* **150**, 253-266.

Wu YZ, Chen J, Ji JF, Tian QJ, Wu XM (2005) Feasibility of reflectance spectroscopy for the assessment of soil mercury contamination. *Environmental Science & Technology* **39**, 873-878.

Xia XQ, Mao YQ, Ji J, Ma HR, Chen J, Liao QL (2007) Reflectance spectroscopy study of Cd contamination in the sediments of the Changjiang River, China. *Environmental Science & Technology* **41**, 3449-3454.