Vis/NIR spectroscopic study for heavy metals in seasonal suspended solid of Changjiang River

Yinxian Song[12], **Junfeng Ji**[1], **Changping Mao**[1], **Ray L. Frost**[2] **and Godwin Ayoko**[2]

[1] School of Earth Sciences and Engineering, Nanjing University, Jiangsu Province, 210093China.
alex.charlton@adelaide.edu.au
[2] Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia

Heavy metals pollution in suspended solid of great rivers is due to the great rivers passing through heavily populated areas with intense anthropogenic activity (Artaxo, de Campos *et al.* 2000). Heavy metals in river are often absorbed and enrich in suspended solid, so suspended solid can become the first material for monitoring pollution in river system. Diffuse reflectance spectroscopy in visible-near infrared (Vis/NIR) region (400-2500 nm) has been used to observe and monitor the constituents of soil rapidly, conveniently and accurately (Cozzolino and Moron 2003), which should also be useful for suspended solid with similar components.

Concentration of heavy metals in flood season samples showed negative correlations with reflectance spectra of suspended solids. For reducing impact of grain size, the spectra were transformed with first derivative (FD). And the correlation coefficients between metals and reflectance, FD were compared to obtain the optimal wavelength to build a univariate regression models (Table 1). For flood season samples, only Cu and Hg can be explained by reflectivity using univariate models, and other elements were explained using spectra with FD transformation. It is clearly shown that heavy metals in suspension are related to the spectrally active constituents. As has a high correlation at 932nm due to Fe^{3+}. Cd has the highest correlation at 2422nm arose from CO_3^{2-} and C-H absorption (Ben-Dor and Banin 1990; Fidencio, Poppi *et al.* 2002). Co and Ni have a strongest correlation at the wavelength of around 2180, which is related to Fe(Al)-OH due to clay (Rossel, Cattle *et al.* 2009). Cr, Pb and Zn show high correlation at around 1830nm, which is relation the H_2O absorbed by clay mineral or iron oxides (Moros, de Vallejuelo *et al.* 2009). Cu and Hg display maximum correlation at 1546nm and 1414nm respectively, relating with O-H band (Wu, Chen *et al.* 2005).

In dry season samples, all metals can be explained by spectra with FD transformation. As, Cd, Pb and Zn have highest correlation with spectra at wavelength of around 1750nm which should be related to the first overtone of C-H stretch from organic matters. Co, Cu, Hg and Ni show high correlation at around 450nm and 550nm due to Fe^{3+} absorption. And for Cr, a high correlation shows at 992nm, suggesting a relation with iron oxides in suspended solid.

Comparison characteristics of spectra of different season suspended solid, it can be seen that spectra with FD transformation could explain heavy metals in samples. And these metals often bind to iron oxides, clay minerals and organic matter, which makes it possible to monitor heavy metals using Vis/NIR spectroscopy.

Table 1. Univariate regression of variable (y) heavy metals and variable (x) reflectivity (Ref) or first derivative (FD) of Vis/NIR spectroscopy at wavelength with the highest correlationship.

		transformation	wavelength (nm)	equation	r	Sig.
As	flood season	FD	932	$y=90.314-6639.318x+141993.143x^2$	0.735	0.000
Cd		FD	2422	$y=1.891+23.475x+130.349x^2$	0.464	0.016
Co		FD	2180	$y=5.922-1.656/x$	0.567	0.000
Cr		FD	1832	$y=116.143+2074.867x$	0.499	0.002
Cu		Ref	1546	$y=20.753+6.264x-0.110x^2$	0.448	0.022
Hg		Ref	1414	$y=9.884-0.418x+0.004x^2$	0.758	0.000
Ni		FD	2178	$y=15.012-3.679/x$	0.554	0.000
Pb		FD	1836	$y=63.142+3100.521x+490132.606x^2$	0.596	0.001
Zn		FD	1836	$y=166.133+5762.025x+552698.495x^2$	0.530	0.004
As	dry season	FD	1776	$y=44.832+700.572x$	0.560	0.001
Cd		FD	1736	$y=1.449+51.837x+6258.263x^2$	0.901	0.000
Co		FD	550	$y=246.522-2203.791x+5337.702x^x$	0.803	0.000
Cr		FD	992	$y=462-13380.202x$	0.567	0.001
Cu		FD	454	$y=1.009x^{-4.494}$	0.795	0.000
Hg		FD	550	$y=41.578-425.135x+1083.253x^2$	0.797	0.000
Ni		FD	540	$y=705.610-7193.842x+19730.124x^2$	0.711	0.000
Pb		FD	1736	$y=66.244+1528.018x+296119.478x^2$	0.837	0.000
Zn		FD	1758	$y=364.875+8564.891x$	0.548	0.001

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