Using second-derivative spectrum to estimate Chlorophyll-*a* concentration in turbid estuarine waters

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ABSTRACT

Hyperspectral technique is considered as one promising tool to solve the problems in monitoring optically-complex waters, which can be applied in optical sensors on board bouy, plane and satellite. In order to apply the technique in the in-situ chlorophyll monitoring of estuarine turbid waters, two cruises were carried out in May, 2004 and August, 2006, respectively, in Pearl River Estuary, China. In the cruises, water samples were collected at each sample station, a portable field spectroradiometer was used simultaneously to measure the downwelling sky radiance, and upwelling radiance of water and reference plaque, and the reflectance was calculated out. Further, the original reflectance spectra with 0.38 nm spectral resolution were resampled to 10 nm resolution, and then derivative spectra were processed. The results of correlation analysis between the chlorophyll-*a* concentrations and derivative spectra indicate that the second derivative spectra especially at 670 nm can be used to estimate chlorophyll-*a* concentration of turbid estuarine waters, which suggests a new way for the in-situ chlorophyll measurement in the optically-complex waters.

Keywords: Hyperspectral, derivative spectra, chlorophyll-*a*, turbid estuarine waters

1. INTRODUCTION

Chlorophyll concentration is one of the key parameters for water quality assessment, and quantifying chlorophyll concentration effectively has been one of the major applications of remote sensing of coastal waters. Usually, due to the high content of suspending particles, yellow substance, etc, the coastal waters are highly turbid, especially for estuarine waters, and this makes it hard to estimate the chlorophyll concentration using the operational algorithms of chlorophyll retrieval in Case I waters [1].

Hyperspectral remote sensing technique has been considered as a promising tool to measure chlorophyll concentration and other water quality parameters [2,3], and hyperspectral sensors can be installed on bouy, plane and satellite for various research need. Hyperspectrum usually has consecutive narrow bands, which allows researchers to quantify chlorophyll concentration accurately by identifying and measuring its spectral response characteristics. In-situ measurement of water reflectance spectrum by field spectrometer is a fundamental way to study the characteristics of spectral response to chlorophyll concentration and to establish the relevant retrieval model. Gitelson (1992) [4] studied the behavior of the reflectance peak near 700 nm of water with content of algae, and found that the peak position shifted towards the end of longer wavelength and the peak magnitude increased when chlorophyll concentration increased. Later, Gitelson et al. (1993) [5] pointed out that it was a feasible way to estimate chlorophyll in turbid inland waters using a ratio of reflectance at 700 nm and 675 nm. Shu et al. (2000) [6] also found that the reflectance ratio of R705nm/R675nm was significantly correlated with chlorophyll concentration.

Consecutive hyperspectral bands allow further derivative analysis. The first-order derivative spectra indicate the rate of change of reflectance with wavelength, which is the slope of the reflectance curve at the wavelength, and the second-

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order derivative indicate the rate of change of reflectance curve slope, and it is the curvature. Many researchers applied derivative analysis in remote sensing studies [7, 8-13]. Several key findings on derivative analysis in chlorophyll remote sensing were concluded by Han (2005) [14]: (1) the first-order derivative can remove pure water effects, and the second-order derivative can get rid of the suspended sediments effects [15]; (2) the first derivative at 690 nm can be used to estimate chlorophyll concentration while other constituents exist [10]; and (3) derivative spectrum is a useful tool in identifying the absorption feature of phytoplankton [12].

The purpose of this study is to test the feasibility of derivative analysis techniques in estimating chlorophyll-*a* concentration of turbid estuarine waters at Pearl River Estuary, China.

2. METHODOLOGY

2.1 Study area

This research was conducted in the upper part of Pearl River estuary, which is located at the highly-developed Pearl River delta, China. Due to anthropogenic influences around the estuary, such as industry, agriculture, aquaculture, transportation, the water pollution load exceeds its self-purification capacity, the water environment is deteriorated; Because of the input of nitrogen and phosphorus, the water body is eutrophicated, and red tide occurs frequently. In order to monitor the trend of water quality changes, Guangzhou Monitoring Center of Marine Resources and Environment conducts seasonally water sampling at 17 locations (S1-S17) every year.

2.2 Water sampling

Water sampling and spectral data collection were conducted simultaneously on board the boat of China Ocean Monitoring for 17 stations over the one-day period on two occasions: May 18, 2004 and August 21, 2006. The depths of the 17 sampling sites range from 1.2 m to 9.4 m. At each station, water surface reflectance was measured, and water sample was collected at 0.5 m below the water surface. The temperature, salinity were measured by the instrument of YSI (YSI Inc.), and the water samples were taken to the lab for turbidity, chlorophyll-*a* and other water quality parameters analyses. Fig. 1 and Fig. 2 illustrate the measured chlorophyll-*a* concentrations and turbidity, respectively. For the two cruises, the chlorophyll-*a* concentrations showed a large spatial variation ranging from 0.76-48.38 μg/L on August 21, 2006, and 3.20-49.97 μg/L on May 18, 2004. The turbidity ranged from 13.6-101.1 NTU on August 21, 2006, 15.5-128.9 NTU on May 18, 2004, and the high turbidity status at the study area was supposed to be caused by the high content of suspending matter in water.

2.3 Measurement of reflectance and derivative spectra processing

During water sampling, a portable field spectroradiometer (SD2000 by Ocean Optics Inc.) was used to measure the upwelling radiance of the water (Lw), the sky light radiance (Ls), and the upwelling radiance of the reference plaque (Lp) at each sampling station. The spectroradiometer has two channels, and the main channel records a continuous spectrum in 2048 bands, ranging from 188.98 nm to 869.39 nm with 0.38 nm spectral resolution. The calibrated reflectance (ρ_p) of the reference plaque ranges from 23.4% to 25.5% with the change of wavelength. When measuring, the probe of fibre optic cable was hold at 0.5 m above the water surface, Lw, Ls and Lp were measured in turn. For the details of observation geometry, please refer to Muller et al. (2003)[16]. At each sampling station, the protocols of measurement were repeated by 3~5 times, and the averaged reflectance was adopted. The water reflectance (Rrs) was calculated using the following equation:

$$Rrs = \frac{L_u - L_s \times \rho_f}{L_p \times \pi / \rho_p}, \tag{1}$$

where ρ_f is the fresnel reflectance of sky light at water surface, empirically, it is 0.022 [17].

The work of resampling original spectral resolution to be coarser, was useful to remove the noises caused by fresnel effects of sky light at water surface when derivative analysis applied [18]. So, original reflectance spectra with 0.38 nm

resolution were resampled to 10 nm resolution. And then, as Eq. (2) and Eq. (3) [13], the spectrum was processed to derivative spectrum:

$$Rrs^{1st} = \frac{Rrs_{n+1} - Rrs_n}{\lambda_{n+1} - \lambda_n} \tag{2}$$

and

$$Rrs^{2nd} = \frac{Rrs_{n+1}^{1st} - Rrs_n^{1st}}{0.5(\lambda_{n+2} - \lambda_n)}, \tag{3}$$

where Rrs^{1st} and Rrs^{2nd} are the first derivative and second derivative spectrum, respectively, n is the band number, and λ is the wavelength, nm.

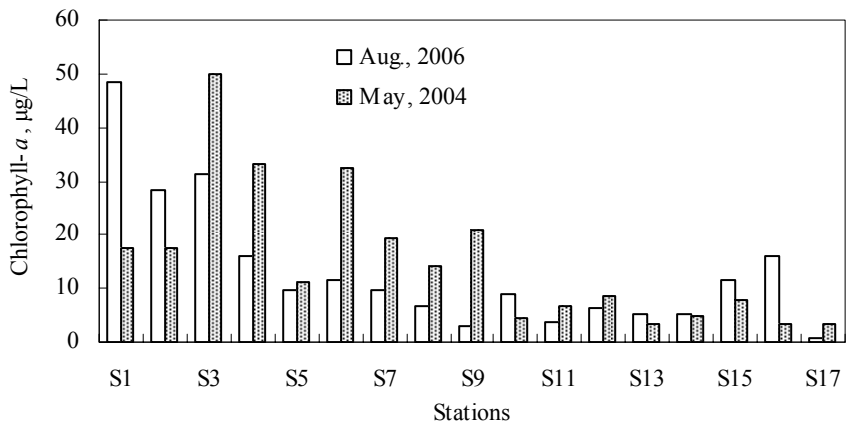

Fig. 1. Chlorophyll-*a* concentrations at 17 sampling stations for two cruises

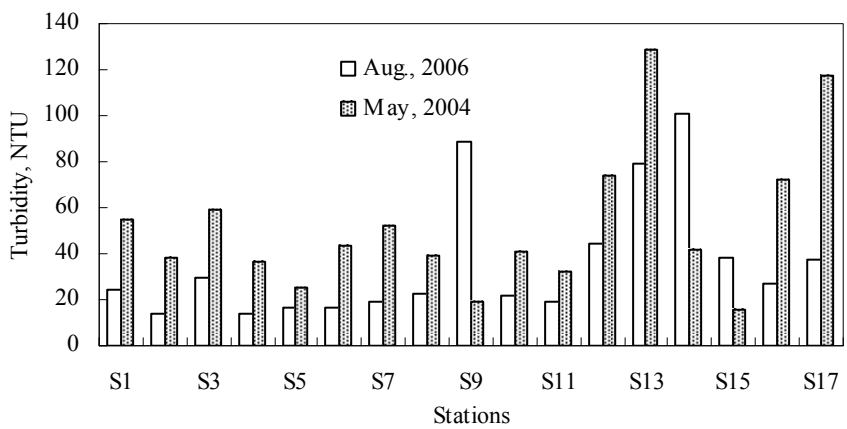

Fig. 2. Turbidity at 17 sampling stations for two cruises

3. RESULTS AND DISCUSSION

Fig. 3 shows the reflectance, the first-order and the second order derivative spectra for all 17 sampling sites at two occasions: August 21, 2006 and May 18, 2004. The highest reflectance peak is located at about 580 nm, and the reflectance at peak ranges from 0.034 to 0.057, which suggests that the sun-glints were well avoided when measuring.

Note that the waters were highly turbid at study area, and there was no need to consider bottom effects even for stations in shallow water.

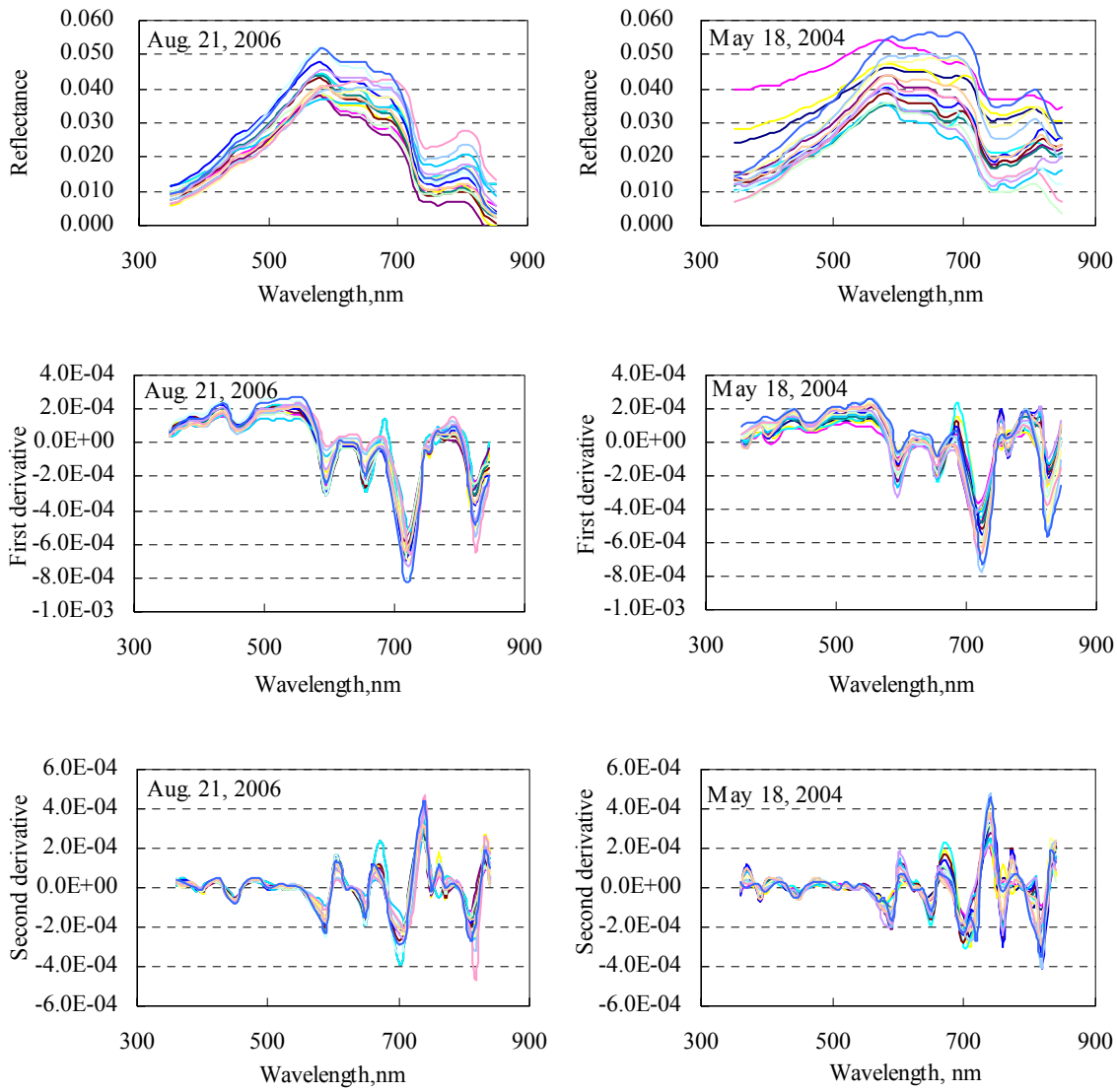

Fig. 3. Original reflectance, first derivative and second derivative spectra at the two occasions: August 21, 2006 (left) and May 18, 2004 (right)

To test if the reflectance value at a specific wavelength can be used to estimate chlorophyll-*a* concentration, correlation analysis was conducted for the 46 bands from 370 nm to 820 nm. As shown in Fig. 4a, poor coorelation is found between reflectance values and chlorophyll-*a* concentration ($|r|<0.33$), and it also implies the complexity of chlorophyll retrieval in turbid water.

The same analysis was performed with the first derivative and the second derivative. Compared with the coorelation produced with the reflectance, the first derivative has much higher correlation with chlorophyll-*a* concentration (Fig. 4b), and which is similar to the results of Han's (2005) research [14]. The highest coorelation coefficients ($|r| > 0.6$) is found at the wavelengths of 685 nm ($r = 0.69$), 665 nm ($r = -0.67$), and 695 nm ($r = 0.66$). when compared with the first derivative, higher correlation coefficients ($|r| > 0.7$) can be found between the second derivative and chlorophyll-*a* concentration, and the biggest coefficients are at 620 nm ($r = 0.74$), 670 nm ($r = 0.83$) and 680 nm ($r = 0.75$). This

suggests that the second derivative may be a better variable that can be used to estimate chlorophyll concentration, especially at 670 nm.

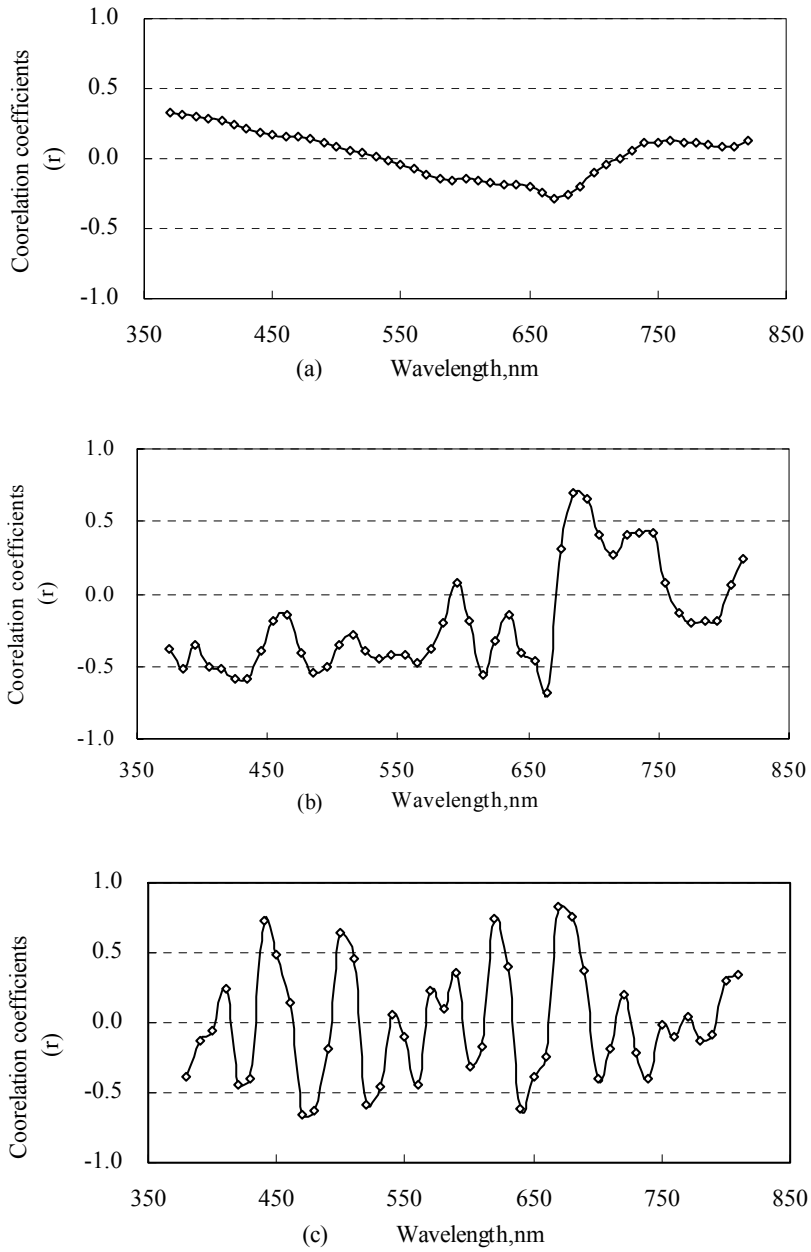

Fig. 4. Correlation coefficients (r) between the values of reflectance (a), first derivative (b) and second derivative (c) spectra and chlorophyll-*a* concentrations

It is well-know that chlorophyll has absorption peak at 670 nm, reflectance peak from 685 nm to 700 nm and fluorescence peak near 685 nm, and the magnitude increases with the increase of chlorophyll concentration. So the first derivative at 685 nm and the second derivative at 670 nm show highly positive correlation with chlorophyll-*a* concentration. Note that the fluorescence behavior is hardly to observe when chlorophyll concentration is small, especially under in situ conditions when the waters are highly turbid. The first derivative can remove not only the specular reflection effects of sky light at water surface [18], but also the pure water effects [15]; and the second

derivative can get rid of the suspended sediments effects [15]. So, when second derivative used to estimate chlorophyll concentration, the noises caused by sky light, pure water and suspended sediments can be removed.

The above suggests that the second derivative at 670 nm can be used to estimate chlorophyll-*a* concentration. Based on the data collected in situ, one simple linear model was developed as Eq. (4) to estimate chlorophyll concentration (Fig. 5), and the estimated chlorophyll concentration and in situ measured values are plotted in Fig. 6.

$$[Chl\text{-}\alpha] = 194655 \times Rrs_{670nm}^{2nd} - 3.5002 \quad (R^2 = 0.7218)\,, \tag{4}$$

where Chl-*a* is the chlorophyll-*a* concentration, μg/L, and Rrs_{670}^{2nd} is the second-order derivative value at 670 nm.

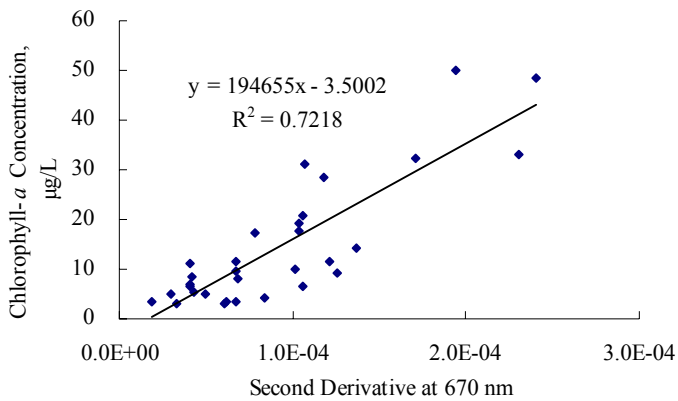

Fig. 5. Correlation between second derivative at 670 nm and chlorophyll-*a* concentration

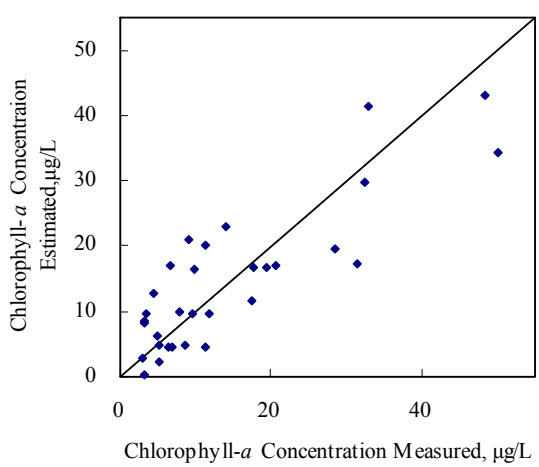

Fig. 6. Chlorophyll-*a* concentrations measured in situ vs. the estimated

4. CONCLUSIONS

Two field surveys were conducted in Pearl River Estuary, China on August 21, 2006 and May 18, 2004, to measure chlorophyll-*a* concentration and remote sensing reflectance. The measured reflectance spectra were resampled to consecutive bands with 10 nm resolution, and then processed to the first and second derivative. The results of correlation analysis between derivative and chlorophyll-*a* concentration indicate that the second derivative can be used to estimate the chlorophyll-*a* concentration of estuarine turbid waters, especially at the wavelength of 670 nm.

It should be noted that a 10 nm spectral resolution is used in this paper while other researchers used the field instrument's original resolution of 1~2 nm, the effects caused by broader bandwidths will be studied in our future work. Hyperion on board the satellite of EO-1 can record hyperpectral images with about 10 nm resolution, future work can be done to apply this derivative technique to it.

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