Absorption coefficient of yellow substance in the Pearl River estuary

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ABSTRACT

The Pearl River system is mainly located in the Guangdong Province in southern China, with the length of 2214 km and total area of 453,690 km². The Pearl River estuary is the largest estuary in the South China Sea (SCS), with a mean annual discharge of 326 billion m³, of which are about 30 million tons of dissolved matters annually discharged into the estuary. The high concentration of suspended sediments and dissolved matters makes the optical properties of the coastal waters very complex.

The spectral absorption coefficient of yellow substance ($A_y(\lambda)$) is one of the inherent optical properties that influence the reflectance (or water-leaving radiance) of the water body. It is essential to measure $A_y(\lambda)$ and to quantify its contributions to the total absorption of the water body. In this study, the Gelbstoff Optical Analyse Laboratory System (GOALS), with spectral range from 200 to 850 nm and with spectral resolution of 0.37 nm per pixel, was used to measure $A_y(\lambda)$ in the Pearl River estuary and in the adjacent coastal waters in July 2002. $A_y(400)$ was around 1.5 m⁻¹ near the river mouth (zero salinity). It decreases with increasing salinity following an apparent non-linear mixing line. There is no apparent relationship between $A_y(400)$ and dissolved organic carbon (DOC) concentration, indicating that the estuary is a complex, non-point source environment. This presents a great challenge to remote sensing study in this area.

Keywords: yellow substance, absorption coefficient, Pearl River estuary, GOALS, remote sensing.

1. INTRODUCTION

Dissolved organic matter (DOM) in natural waters is one of the largest organic carbon pools on earth. It plays a significant role in the biogeochemistry of a variety of elements in estuarine, coastal, and oceanic environments (Farrington, 1992). The composition of DOM is complex, usually with hundreds of compounds of a large range of molecular weights, which are collectively called yellow substance (YS) or Gelbstoff. This collection of compounds falls into several distinct chemical groups. In marine waters, the most important groups are humic and fulvic acids of low molecular weight (Carder et al., 1989), which are usually abundant in inland (lakes and ponds) and coastal waters. Yellow substance in coastal waters is mostly from the breakdown of organic matters in terrestrial soils, and it is transported to the marine environment by river discharges. Yellow substance in open oceans without the influence of river discharges is from the decomposition of local marine organisms and is chemically different from coastal end

members (McKnight et al., 1994).

Accurate estimates of yellow substance in the ocean are critical to many biogeochemical studies, for example, to better understanding of the carbon cycle and trace metal scavenging in the ocean (e.g., Guo et al., 1994, 1995). Yet its determination is extremely difficult even at the laboratory level (Guo et al., 1995), not to mention the need for higher temporal and spatial estimates. On the other hand, because Yellow substance also absorbs light, particularly in the UV (<400 nm) and short visible wavelengths, it is possible, at least in principle, to estimate its abundance and spatial distribution from remote sensing. Recent advances in both engineering and algorithm development show promises of such estimates (McClain et al., 1998; Carder et al., 1999; Hu et al., in press). Because of the similarities between the absorption of yellow substance and absorption of phytoplankton pigment (they both strongly absorb blue light), the presence of yellow substance is often an important error source in the determination of biological components (e.g., Chlorophyll concentration) in seawater by remotely-sensed ocean colour data (Ferrari and Tassan, 1992). In-situ measurement of the absorption properties of yellow substance is of great importance in both algorithm development and satellite data validation.

Yellow substance absorption can typically be described with an exponential formulation (Bricaud et al., 1981): $a_y(\lambda) = a_y(\lambda_0) \exp[-s(\lambda - \lambda_0)]$, where a_y is the absorption coefficient (in units of m^{-1}) of YS, s is the slope (in units of nm^{-1}) of the exponential function, and λ_0 is the reference wavelength. Note that there is demonstrable ambiguity between absorbance and absorption coefficient in many studies (Hu et al., 2002). The measurement of a_y is typically with a double beam spectrometer to compare the light attenuation through a water sample and through a pure water (usually MilliQ or distilled water) reference.

In this study a Gelbstoff Optical Analyse Laboratory System (GOALS) was used to study the absorption properties of Gelbstoff in the Pearl River estuary. The experiment was conducted in the Pearl River estuary and its adjacent coastal waters from 26 to 30 July 2002. Below we briefly describe the study area, then describe the experimental method and present the results.

2. STUDY AREA

The Pearl River is 2214 km long and 453,690 km^2 in area (Zhao, 1990). It is the largest river in southern China, and has a mean annual runoff of 326 billion m^3 , only second after the Yangtze River. The annual discharge variation is significant and depends on the amount of rainfall received in the catchment. From October to April the weather is dominated by the northeast monsoon, and the mean rainfall is relatively low with about 30–40 mm/month (Justesen et al., 1996; Zhao, 1990). During the period of May to September the monsoon comes from the southwest and warm, humid air is brought up from lower latitudes causing considerably larger amounts of rainfall (300–400 mm/month). The discharge into the Pearl River estuary during the dry season is typically around 1,500 m^3/s , whereas the flow could increase up to 20,000 m^3/s during the wet season. The annual discharge of suspended sediments is about 87.451 million tons, of which more than 90% are discharged in the wet season (May to September). The warm-humid climate results in strong chemical weathering, and about 30 million tons of dissolved matters are discharged per year (Zhao, 1990). The river water is discharged to the South China Sea through eight discharge

mouths, forming a complex delta. There are several major cities in the delta, including Guangzhou, Foshan, Shenzhen, and Zhuhai. The whole delta area has increased through rapid industrialization and urbanization. This rapid economic expansion has adversely impacted the water quality in the downstream areas of the Pearl River system because of an increase in the discharge of industrial and domestic wastewater (Jayawardena and Lai, 1989). Water quality in the estuary has been getting worse in the last 20 years. Many serious red tide or harmful algal blooms have occurred in the estuary or its adjacent coastal waters since the 1980s and caused huge economic loss. The water environment of the area is widely concerned in local societies.

3. METHOD

Water samples were collected along five transects in the Pearl River estuary and its adjacent waters between 26 - 30 July 2002 (Fig. 1. Station A1 was cancelled because the water is too shallow, and data file of station B3 was lost). At

Figure 1. Map of the station positions.

each station the surface water was sampled and then filtered through Whatman glass-fiber GF/F filter (25mm in diameter with poresize of 0.2 μ m). The filtered water samples were analyzed with GOALS onboard the cruise. GOALS is composed of an Ocean Optics SD2000 spectrometer (200 to 850 nm with a spectral resolution of 0.37 nm/pixel), a Miniature Tungsten Halogen light source, and a 1-m liquid waveguide (D'Sa et al., 1999). Double-distilled water was used as the reference, and absorbance of yellow substance was determined based on the

comparison to the reference water. The absorbance data were converted to absorption coefficients by least-square fitting with an exponential function. The equation is of the form: $a_y(\lambda) = a_y(\lambda_0) \exp[-s(\lambda - \lambda_0)]$ (Bricaud et al., 1981), where a_y is the absorption coefficient (in units of m^{-1}) of YS, s is the slope (in units of nm^{-1}) of the exponential function, and λ_0 is the reference wavelength. Note that there is demonstrable ambiguity between absorbance and absorption coefficient in many studies (Hu et al., 2002). We used 400 nm as the reference wavelength, and used an offset to remove the effects of baseline drift due to small particles or bubbles in the water sample. A non-linear least-square fitting was used to determine $a_y(400)$ and s . The filtered water samples were frozen onboard for dissolved organic carbon (DOC) analysis later in the lab. DOC was determined with the instrument TOC-5000A. Salinity was determined with a YSI-6600 Multi-parameter water quality monitor instrument.

4. RESULTS

Because the chemical components of yellow substance are very complex and some of them are unknown, it is virtually impossible to directly measure the concentration. Instead, the concentration is usually expressed with its absorption coefficient (e.g., $A_y(400)$). $A_y(400)$ measured in the five transects (Fig. 1) is presented in Table 1. Transect B has the highest mean absorption coefficient, as the stations are closer to river discharge mouths. Further offshore, Transect E has the lowest mean absorption coefficient. $A_y(400)$ varied over an order of magnitude, from 0.05997 m^{-1} at station C10, to 1.42367 m^{-1} at station B2. The isoline of 0.3 m^{-1} passes approximately through vicinity of A8, C7 and D1. This regional distribution pattern is in agreement with the known water-mass movement and with the location of sources of yellow substance: waters with higher than 0.3 m^{-1} were under the influence of freshwater discharge, and offshore waters have lower values where the South China Sea water is the main water source.

Table 1. Absorption properties of yellow substance in the Pearl River estuary ($A_y(400)$: m^{-1} ; Slope: nm^{-1})

Transect	Mean $A_y(400)$	$A_y(400)$ range	Mean Slope	Slope range
A	0.37105	0.14890-0.68311	0.01592	0.01126-0.01896
B	0.94347	0.51321-1.42367	0.01519	0.01264-0.01854
C	0.38990	0.05997-0.67987	0.02104	0.01209-0.03412
D	0.21134	0.12448-0.28492	0.01295	0.00835-0.02219
E	0.14044	0.06196-0.21910	0.01787	0.01256-0.02276
mean	0.40956		0.01695	

The mean exponential slope s is 0.01695 nm^{-1} . Of the 38 samples, 32 samples have the s values ranging from 0.011 to 0.025 nm^{-1} ; 4 samples (all in transect D) have low s values from 0.0083 to 0.0099 nm^{-1} ; while the samples from C9 and C10 have high s values of 0.0318 and 0.0341 nm^{-1} , respectively. The slope value depends on the chemical composition of yellow substance, therefore may vary with water type.

Figure 2 shows that $A_y(400)$ negatively correlates with salinity. The relationship is polynomial rather than linear, indicating a non-conservative mixing behavior. $A_y(400)$ drops quickly from salinity 0 to 5, and then slowly for salinity > 30 . This could be caused by photobleaching. The straight line in Figure 2 shows a conservative mixing line between the freshwater end-member ($A_y(400)=1.5 \text{ m}^{-1}$ at salinity 0) and pure marine end-member ($A_y(400) = 0$ at

salinity 37). The data points above the line suggest that there are some local generation of yellow substance from marine processes. There is no apparent trend (data not shown) between Ay(400) and DOC concentration.

Fig.2. The relationship between Ay(400) and salinity in the Pearl River estuary

On 4 June 2002 when red tide occurred in the vicinity of the Guishan Island (Southwest to Station C1), three water samples were taken for absorbance measurement. Ay(400) was 2.116 m⁻¹ in the red tide center and 1.206 m⁻¹ in the edge, while Ay(400) at station B8, C1 and C2 was 0.513, 0.508, and 0.419 m⁻¹, respectively. Red tide remarkably increased the concentration of yellow substance.

5. DISCUSSION AND CONCLUSION

Absorption coefficients of yellow substance in the Pearl River estuary and its adjacent coastal waters were measured during July 2002 and on 4 June 2002. Absorption coefficient at 400 nm, Ay(400), varied from 0.05 m⁻¹ for offshore waters to 1.5 m⁻¹ near river mouths. The exponential slope, *s*, also covered a large range. The slope value relates not only with the yellow substance composition, but also possibly with the concentration. We measured pond water samples with different concentrations by dilution (with double-distilled reference water) to one-half, one-fourth and one-eighth of the original concentration, respectively. We noted that the *s* value increases from 0.0125 to 0.0194 with the YS concentration decreasing from 4.378 (m⁻¹) to 0.795 (m⁻¹). The reason is unclear at this stage. It is also possible that the exponential fitting procedure, which was used to determine Ay(400) and the slope, may have some artifacts.

Ay(400) increased remarkably (~ four times) in red tide waters, as compared with nearby, non-redtide waters. The increased absorption has a direct impact on the remote sensing signal. Therefore it presents potential for red tide detection with remote sensors.

The absorption coefficient of yellow substance has a negative correlation with salinity. However, the complex rather than a linear, conservative mixing relationship suggests that the estuary is a non-point source environments and it undergoes a variety of biological and chemical processes. This presents a great challenge to remote sensing study in this area.

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