

THE RETRIEVAL MODEL FOR ORGANIC CONTAMINATION IN WATERS USING OPTICAL ABSORPTION PROPERTIES OF CDOM

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Abstract: Yellow Substances (also chromophoric dissolved organic matter: CDOM) is the pool of absorbing substance in water. In the fields of water colour remote sensing, its optical absorption properties are mainly described with absorption coefficient and spectral slope. It has showed by present research that the influence of organic contamination in water including petroleum pollutant and COD (Chemical Oxygen Demand) on spectral absorption coefficient is mainly represented on absorption spectral features of yellow substance. The experimental data in-situ is obtained at the regions of Panjin city, Liaoning province of China in May 2008, August 2009 and June 2010. With the measurement data, first, the exponential spectral slope (S) was determined; Secondly, the model of retrieval $a_g(440)$ based on the HJ-1 satellite was created; Thirdly, the remote sensing model to retrieve organic contamination in water including petroleum pollutant and COD were established, then the validation was done; Finally, the models of retrieving organic contamination from HJ-1 satellite were applied in the region of Liaodong bay.

Keywords: CDOM; absorption coefficient; spectral slope; petroleum concentration; COD; retrieval models.

1. INTRODUCTION

Organic contaminations belong to chemical contamination and include natural organic compounds and synthesized organic compounds. Natural organic compounds exist in the form of carbohydrate, protein, amino acid and fat. Most organic contaminations can be degradable and available by microorganism, and be called oxygen consumption organic matter because in the course dissolved oxygen will be consumed. The concentration of organic contaminations is measured by COD (Chemical Oxygen Demand), which is the oxygen demand when organic contaminations are oxygenated by oxidant. Potassium permanganate and potassium dichromate are common oxidant. Potassium permanganate method (abbreviated to CODMn) works to measure sea water. Potassium dichromate method (abbreviated to CODcr or COD) works to measure water samples which are polluted very much. The chemical oxygen demand (COD) is a very important parameter to reflect the polluted degree of organic contamination on water. The organic contamination is a general problem in the region of oil-field development, industrial production and citizen life. The traditional determination of COD in water is not only time-consuming and strenuous but also expensive. Moreover it is difficult to sample in the river which result in the difficulty to reflect synchronously the whole region status. Remote sensing has the advantage of large area, speediness, dynamic and low-cost in the obtaining regional information, so at present there are some scholars to devote themselves to extract information of COD using satellite data (Zhou et al., 2009; Twardowski et al., 2004; Bricaud et al., 1981; Yacobi et al., 2003).

Petroleum substances belong to hydrocarbon and its main components is constituted of alkane, naphthenic hydrocarbon, olefin and aromatic hydrocarbon. Floating oil, dispersed oil, emulsified oil and decomposition oil are the four forms of

petroleum pollution in water. The emulsified oil or decomposition oil or adsorbed on the surface of particulate matter will be oxy-generated and decomposed by microorganism, so petroleum pollution can be classified into organic contamination.

The two oil spills occurring in Mexico Bay and Dalian Bay in 2010 have been disasters to the marine environment, which needs decades to be removed and costs billions of dollars. Due to the fluidity of water, how much will the spread of petroleum substance and the duration of its existence influence on the oceanic environment and economy? The assessment needs urgently data of time and spatial continuity. Although the present ordinary observations of ocean and land water include the pollution of petroleum, they are all point observation and lack spatial observation points and observing times, which can hardly implement a continuous observation of spatial and time variation (Huang et al., 2007). At present, monitoring of petroleum pollution by using remote sensing mainly focuses on oil spill, whose remote sensing mechanism and models have been significantly improved (Król et al., 2006; Otremba et al., 2002). However, researches on the components of petroleum substance in water are rarely reported. So researched on its remote sensing mechanism and identify model are of great significance and application value (Huang et al., 2009).

In the water color remote sensing, $a_g(440)$ is usually used to represent the concentration of CDOM in water, spectral slope S to represent the degree of attenuation of CDOM absorption coefficient. The current researches show that spectral slope S has no relation with CDOM concentration, but is related to its component, the simulation band range by establishing a model and reference wave length (Wang et al., 2007). Petroleum substances are mainly hydrocarbons, including alkanes, cycloalkanes and aromatic. Huang et al. (2010) found in experiments that in the water polluted by petroleum, the amplitude of CDOM absorption coefficient increases with the concentration of petroleum, the shape of spectra doesn't change, obeying exponential decay law, but the spectral slope S changes, which means the petroleum substances are closely related to CDOM concentration (represented by the absorption coefficient $a_g(440)$) and spectral slope S, so it is available to retrieve the petroleum concentration in water by using the coefficients of CDOM optical characteristics.

By using the experiment data obtained in Liaohe oil field of Panjin city, Liaoning province of CHINA in May 2008, August 2009 and June 2010, the remote sensing modes of retrieving water petroleum pollution and COD based on CDOM optical characteristics are established, which can provide technical support for detecting organic contamination by remote sensing data.

2. EXPERIMENT AND DATA ACQUISITION

2.1 Experimental Description

The experimental field work was conducted in Panjin city, Liaoning province of China. In the region there are Liaohe oil field which is the third largest oil field in China and reed wetland which is largest in Asia. In November each year reed is processed in the paper mills after harvested. The activity of

field's producing and paper-making is inevitably to bring about organic contamination.

The experimental time is in May 2008, August 2009 and June 2010. The experimental data in-situ included the absorption coefficient of CDOM, apparent optical properties, COD and petroleum pollutants concentration. The measuring method is showed in table A and seventy samples were obtained

Table A the measuring data and methods

Items	Contents	Method	Reference standard
apparent optical properties inherent optical properties water quality parameter	remote sensing reflectance absorption coefficient of CDOM	spectrometry (ASD) UV-3900, 350-900nm (HITACHI)	NASA standard
water quality parameter	petroleum	JK-951	GB11914-89
water quality parameter	COD	dichromic acid	GB11914-89

2.2 Measurements of CDOM absorption coefficients

The measurement of CDOM absorption coefficients is using GF / F membrane to filter water samples and then measuring their absorbance by spectrophotometer. Firstly, soaked the polycarbonate membrane of 0.22 μ m aperture with 10% hydrochloric acid, and then filtered water samples with vacuum pump to obtain CDOM samples, used sample pools of 10cm length and made reference by Milli-Q water (pure water), the spectrophotometer is U-3010 of Hitachi, put the 10cm cuvette filled with water and sample cuvette into the two optical paths of spectrophotometer, measuring the optical density $OD_{bs}(\lambda)$ of the reference water (dimensionless); removed the sample cuvette, discarded the water, filled with samples, measuring the optical density of CDOM related to water $OD_s(\lambda)$ (dimensionless). In accordance with the specification of marine optical measurements (Mitchell et al., 2000) given by NASA, CDOM absorption coefficient is calculated as,

$$a_g(\lambda) = 2.303/L * [(OD_s(\lambda) - OD_{bs}(\lambda)) - OD_{null}] \quad (1)$$

Where: L is the optical path of cuvette (typically 0.1m); $OD_s(\lambda)$ is the optical density related to the reference water samples (dimensionless); $OD_{bs}(\lambda)$ is the optical density of blank pure water processed by the sample handling procedure related to the reference pure water (dimensionless); OD_{null} is the apparent residual optical density at the long wavelength band of visible light or at the bands of near-infrared where the absorption of dissolved substances can be assumed to be zero (dimensionless), which is the residual absorption of long wavelength visible light or near infrared band. In the specification of marine optical measurements given by NASA it is recommended that OD_{null} takes the average of 590-600nm, due to the turbid water body case II, taking the recommended 590 ~ 600nm band as a residual correction band will result in a "too low" estimate of CDOM absorption coefficients, mainly because the absorption of the dissolved substances of high turbidity in water case II at 590 ~ 600nm band is strong and small particles in filtered clear liquid may cause scattering, so in this paper, the residual correction method using 750nm wavelength band made for turbid water bodies by Bricaud et al. (1981) is applied, which is calculating the absorption coefficients of each wavelength λ (nm) by formula (2), and then correcting scattering by formula (3).

$$a_g(\lambda') = 2.303/L * [OD_s(\lambda) - OD_{bs}(\lambda)] \quad (2)$$

$$a_g(\lambda) = a_g(\lambda') - a_g(750) \cdot \lambda / 750 \quad (3)$$

Where, $a_g(\lambda)$ is the absorption coefficient of CDOM (m^{-1}) at wavelength λ ; $a_g(\lambda')$ is the uncorrected absorption coefficient of CDOM (m^{-1}) at wavelength λ ; $a_g(750)$ is the absorption coefficient of CDOM (m^{-1}) at wavelength 750nm; the meaning of λ , $OD_s(\lambda)$, $OD_{bs}(\lambda)$ and L is the same as formula (1).

2.3 The measurement of petroleum substance concentration

The methods of determining petroleum pollution include Gravimetric method, ultraviolet spectrophotometry, fluorescence and infrared method. Infrared methods including non-dispersive infrared method and infrared spectroscopy use absorption characteristics at about 3-4 μ m, but non-dispersive infrared method does not consider aromatics, thus non-dispersive infrared method will reduce the measured value of petroleum pollution, especially those containing aromatic hydrocarbon oils. So this study used infrared spectrophotometry (GB16488-96) to determine oil pollution. The used device is the JK-951 Multi-function infrared oil content analyzer.

2.4 The measurement of chemical oxygen demand COD

The method of applying microwave to sealing and dissipating was introduced to measure the value of COD (GB11914-89). The basic principles of this method are to calculate the value CODcr after water sample was heated by microwave and it titrates with ferrous ammonium sulfate, using the ferrousulfatesolution as a catalyst and with H_2SO_4 and $K_2Cr_2O_7$ digestion.

2.5 Water spectrometry measurement

The aim of water spectrometry measurement is to reverse CDOM by using remote sensing reflectance. For water spectrometry measurement we applied visible near infrared spectroradiometer (ASD FieldSpec3 350-2500nm) produced by ASD company of the USA, the reference board is the 30% reflectance standard board. The measurement method was above the water surface, using (40°, 135°) relative observation geometry, where observation nadir angle was 40°, the angle between equipment observation azimuth and solar was 135°. At each observation point, measured in the order of the gray board, water, sky, gray board, gray shading board, each group measured 15 spectra, each spectral interval was 1 second.

2.6 HJ-1A/1B CCD

The satellites environment A & B (HJ-1A/1B) was successfully launched on September 6, 2008, each HJ-1A and HJ-1B were loaded with two CCD cameras of exactly the same designed principle, which are 4-band wide-cover multi-spectral visible light camera CCD. Table B shows the technical parameters of the CCD on HJ-1A and 1B. HJ-1A and HJ-1B are not color satellite, but the CCD cameras still has some information of water, which may serve as a water color remote sensing device of environment (Huang etc, 2010).

Table B the technical parameters of HJ-1A/1B CCD

Item	Performance	
Nadir ground pixel resolution(m)	30	
Band set(μ m)	B1	0.43~0.52
	B2	0.52~0.60
	B3	0.63~0.69
	B4	0.76~0.90
Quantified value(bit)	8	

3 . THE INVERSION MODEL OF ORGANIC CONTAMINATION

3.1 Analysis of CDOM optical absorption characteristics

Previous studies (Bricaud et al, 1981) showed that , CDOM absorption spectrum decreased exponentially with wavelength from UV to visible light, under normal circumstances, using the formula (4) to describe the CDOM absorption coefficient changes with wavelength,

$$a_g(\lambda) = a_g(\lambda_0) \exp[-S(\lambda - \lambda_0)] \quad (4)$$

Where $a_g(\lambda)$ is the CDOM absorption coefficient(m^{-1})at wavelength λ , λ_0 is the reference wavelength (nm), S is the spectrum slope coefficient(nm^{-1}). In the study of CDOM optical coefficient properties, the absorption coefficient at 440nm ($a_g(440)$) and spectral slope S are two important parameters. About 28 samples was used of mix proportion text in August 2009 and June 2010, took 440nm as reference band λ_0 , substituting into formula (4) fitting out spectral slope S in water with organic contamination. It is showed that in this experiment the spectral slope S are between $0.0086 \text{ nm}^{-1} \sim 0.014 \text{ nm}^{-1}$, the average is 0.010892 nm^{-1} .

3.2 The retrieval model of CDOM concentration

Currently, the CDOM concentration retrieval models established for water color sensors are mostly used the band ratio method (Shen, etc., 2006). Bowers et al (2004) proposed the remote sensing model for the estuary region to use the reflectance ratio at 670nm and 490nm estimating CDOM absorption coefficient at 440nm, that is,

$$a_g(440) = 1.45 * (R(670)/R(490)) - 0.488 \quad (5)$$

Where $a_g(440)$ is CDOM absorption coefficient at wavelength 440nm(m^{-1}); R(670) and R(490) are remote sensing reflectance at wavelength 670nm and 490nm respectively.

Taking into account that HJ-1/CCD band set includes 670nm (B3) and 490nm (B1), the study area is located in estuaries, so based on the Bower's model, we used the test data in August 2009, combining with HJ-1/CCD band response function to simulate the remote sensing model of retrieving CDOM water by using the two wide-bands (B1: 430~490nm and B3: 630~690nm) of non-water-color satellite HJ-1/CCD, that is

$$a_g(440) = 2.47 * (R_3/R_1) - 0.27 \quad (6)$$

Where $a_g(440)$ is the same as in Formula (5); R_1 and R_3 are the remote sensing reflectance corresponding to band B1 and B3 of HJ-1/CCD (dimensionless).

3.3 Correlation analysis

$a_g(440)$ usually represents the concentration of CDOM, while the variation of S mainly depends on the composition of yellow substances, so these two factors should be both considered by establishing organic contamination remote sensing retrieval model based on CDOM optical absorption properties to improve the retrieval accuracy. The correlation coefficient between organic contamination and the various combinations of S and $a_g(440)$ are showed in table C and table D (S averaged 0.010892).

Table C correlation between petroleum concentration and yellow substance absorption spectral parameters (n=70)

S+ $a_g(440)$	S* $a_g(440)$	S/ $a_g(440)$	$a_g(440)/ S$
0.817764	0.835172	0.732592	-0.767891

Table D correlation between petroleum concentration and yellow substance absorption spectral parameters (n=70)

S	$a_g(440)$	$\ln(a_g(440))$	$\ln(a_g(440))*S$
0.0464	0.9083	0.925	0.9279

It can be seen from table C, the concentration of petroleum pollution has the highest correlation with S* $a_g(440)$, their

correlation coefficient is 0.835132. It can also be seen from table D, the value of COD has the highest correlation with S* $\ln(a_g(440))$, their correlation coefficient is 0.927975. So we used these combinations as independent variables to establish the model of retrieving organic contamination in water.

3.4 The establishment of retrieving models

In table E they are the established relationships models of S * $a_g(440)$ and the concentration of petroleum substances. It can be seen from the table, in the relational model of petroleum content and $a_g(440) * S$, the R^2 of power is maximum, up to 0.7418, the R^2 of linear, logarithmic and exponential relationship are all less than 0.7, so we chose power as the model of retrieving water petroleum pollution based on CDOM optical absorption spectra, that is,

$$y = 127.566x^{1.3288} \quad (7)$$

Where y is the concentration of petroleum pollution in water (mg/L), x is $a_g(440))*S$, the meanings of $a_g(440)$ and S are the same as before; $a_g(440)$ is calculated in formula (6).

Table E correlation models between petroleum concentration and yellow substance absorption spectral parameters (n=70)

Type of models	Power	Linear	Logarithmic	Exponential
Formula	$y = 127.566x^{1.3288}$	$y = 240.64x - 0.5815$	$y = 5.7608\ln(x) + 27.858$	$y = 1.4527e^{40.796x}$
R^2	0.7418	0.6974	0.618	0.6989

*where,y is the concentration of petroleum pollution in water; x is $a_g(440))*S$.

According to the correlation of CDOM and COD, the relational model of retrieving COD was established based on the parameters of $\ln(a_g(400))*S$, that is,

$$y = 0.583936X^2 - 9.5481X + 0.52127 \quad (R^2 = 0.876) \quad (8)$$

Where y is the value of COD in water (mg/L), x is $\ln(a_g(400))*S$, the meanings of $a_g(440)$ and S are the same as before..

4. THE VERIFICATION AND APPLICATION OF THE MODEL

4.1 The verification of the model

Substituted the value of COD and petroleum contamination determined in a natural river in May 2008 and August 2009, and the absorption coefficient value at $a_g(440)$ of yellow substances in water into formula (7) and (8) to estimate the values (31 Samples). The results showed that estimated values are very close to measured values, the relative errors are 6.8847% and 7.6695, respectively. This indicates that formula (7) and (8) as the model of remote sensing retrieving organic contamination concentration, the retrieval results are relative accurate, which provides a new way to estimate organic contamination concentration in water with remote sensing.

4.2 The application of the model

Applying the model of Remote sensing retrieving petroleum substances established in this paper to the two HJ-1 transit images on September 22, 2009, as shown in Fig. 1 below. Fig. 1 showed that the concentration of petroleum substances from the offshore to the high sea maintains a high-to-low tendency.

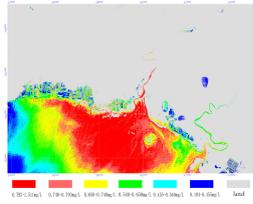


Fig. 1 The spatial distribution of the petroleum concentration in Liaodong bay on September 22, 2009

Applying the model of Remote sensing retrieving petroleum substances established in this paper to the two HJ-1 transit images on September 22, 2009, as shown in Fig. 2 below. Fig. 2 showed that the value of COD is among 52.1-168.2mg/L and from the offshore to the high sea maintains a low-to-high tendency.

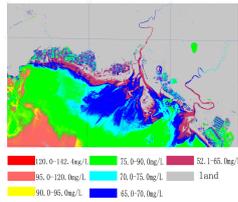


Fig. 2 The spatial distribution of the value of COD in Liaodong bay on September 22, 2009

5. CONCLUSIONS

COD reflects the degree of organic contamination on water and its influence on water absorption coefficient mainly reflect on that of CDOM. Petroleum contamination belongs to the one of organic contamination. Thus it is feasible that using optical absorption properties of CDOM retrieve organic contamination in water. Through the mix proportion test in field, the remote sensing models of retrieving organic contamination in water based on the CDOM absorption spectral is proposed. The models are not only simple and easy to operate, but also suitable as a business running. As long as the CDOM concentration $a_g(440)$ is calculated with remote sensing reflectance to determine a regional exponential slope S , the value of organic contamination in water can be figured out. The establishment of and provide a way to monitor water organic contamination with remote sensing technology. The models can promote the application of water color remote sensing in monitoring components of environmental pollution.

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