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Analysis of petroleum-polluted water absorption spectral properties

HUANG Miao-fen[1], **TANG Jun-wu**[2], **SONG Qing-jun**[2]

1. *Dalian Fisheries University, Liaoning Dalian* 116023, *China*;
2. *National Satellite Ocean Application Service, Beijing* 100081, *China*

Abstract: Petroleum pollutions exist in waters in various forms, which impacts its apparent optical properties and inherent optical properties. Field works has been carried out in the rivers in Panjin city, Liaoning province of China in May 2008 in order to understand this impact. The absorption coefficient data of yellow substance, De-pigment particles and phytoplankton pigments and the corresponding water samples for laboratory measurements of chlorophyll, petroleum pollutions, and suspended material were collected. Firstly, absorption spectral features of yellow substance, De-pigment particles and phytoplankton pigments in Case II water were analyzed. Secondly, the absorption spectral properties of yellow substance and phytoplankton pigments with petroleum pollutions were discussed. Finally, the impact of petroleum pollutions on water absorption properties was analyzed using the method of algebraic difference. The results showed that (1) whether there is petroleum substance or not in water body, the absorption spectra of yellow substance and de-pigment particles all follow e-exponential attenuation trend in the research region; (2) with the presence of petroleum pollution, the absorption coefficients of yellow substance and phytoplankton pigments are both increased; (3) the absorption spectral feature of petroleum pollution appears similar to those of the yellow substance and de-pigment particles by following an e-exponential attenuation trend. However, it is feasible to distinguish them because their spectral exponential slopes have obvious difference.

Key words: petroleum pollutions, yellow substance, absorption properties, e-exponential slope

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1 INTRODUCTION

Facing the increasingly serious problems of environmental pollution, all the countries in the world are making greater effort at environmental improvement and instituting laws and regulations. Among the various pollution problems, the impact of water pollution is the most serious. Water pollutions, caused by human activities related to petroleum, such as oil field exploration, oil field accidents, oil spills and discharge of channel oil sewage, are becoming prominently obvious. It is imperative to have the information about the spatial distribution of the petroleum polluted water body due to the outburst of petroleum pollutions in a timely manner in order to better monitor it. The remote sensing technology can be used as one of these measurement methods because it has the advantages of large scale, dynamic and low-cost access to regional information, which are not comparable for those traditional observation methods. Currently, the remote sensing technology is mainly applied to oil spill detection in the field of oil-contaminated waters. The researches on mechanisms and models of remote sensing have made a great progress, and the operational monitor system of marine oil spill has been established in China, Canada, America, Germany and some other countries (Liu, 2005; Otremba, 2000; Otremba & Piskozub, 2003; Zielinski, 2003). However, the related research reports about the case of petroleum-polluted water without forming a visible or detectable film have not yet been seen domestically or internationally. The researches on the detection mechanism and identification models by using remote sensing technology are of great scientific significance and application value (Huang *et al.*, 2007).

Ocean color remote sensing is an important branch of remote sensing technology. In the monitoring of ocean color factor and chlorophyll in Case I water, the application of remote sensing technology has already been in operational stage of business. In the monitoring of chlorophyll, yellow substances and suspended particles of ocean color factor in Case II water, the researches on mechanisms and models of remote sensing are very comprehensive, and the research results are serving the society. The primary composition of the petroleum substances is hydrocarbon, including the alkane, the cycloalkanes and the aromatic hydrocarbon. In water, they exist in the forms of suspended oil, dispersion oil, emulsified oil and decomposition oil,

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First author biography: HUANG Miao-fen (1963—), female, professor, graduated from Beijing Normal University, major in cartology and GIS, primarily interesting on the research of ocean color and infrared remote sensing. She has published more than 40 papers. E-mail: hmf808@163.com and they become a source of the water pollutions, posing direct influence on ocean color. So in the situation where detected obvious oil film has not been formed, they can be considered as one of the factors of ocean color. As regards the main factors of ocean color in Case II water, such as the monitoring of pigments (chlorophyll), de-pigment particles (inorganic suspended solids), yellow substance and the inherent optical properties (absorption and backscattering coefficient) of pure water, scholars around the world have done a lot of researches on different types of water bodies and have established parametric models (Pope & Fry, 1997; Smith & Baker, 1981; Gallegos & Neale, 2002; Gallie & Murtha, 1992; Yu *et al.*, 2003; Song & Tang, 2006; Zhou *et al.*, 2005; Wang *et al.*, 2004). To apply remote sensing semi-analytical models to quantitatively inverse the concentration of petroleum pollution in water, we must firstly ascertain the inherent optical properties of petroleum substance (Otremba & Krol, 2002). This paper focuses on absorption coefficient properties of petroleum-polluted water in order to provide reference to the establishment of quantitative inversion of the petroleum-polluted concentration in water based on the model of remote sensing semi-analysis.

The experimental field work was conducted in Shuangtaizi River and Raoyang River in Panjin city (the area of Liaohe oil field), Liaoning province of China. Liaohe oil field is the third largest oil field in China, whose products are mainly crude oil and natural gas. The oil exploration activities will inevitably have side effects on the water environment. It becomes a typical experimental field of inherent and apparent optical properties in the petroleum-polluted water (Huang *et al.*, 2007).

2 THE MEASUREMENTS OF ABSORPTION COEFFICIENT

2.1 Field samples collection

Field samples collection consisted of two parts, which were experiment of mixing-ratio in water tank and collecting water samples in situ. All samples of the water were divided into two portions, one was directly poured into the sample bottle, which was kept in liquid nitrogen. It was then filtered in laboratory in order to get prepared for the measurement of yellow substance's absorption coefficient; the other portion was transferred into a clean container to make it particles with filtration. The particle samples were used for the measurement of absorption coefficient of particle substance.

2.1.1 Experiment with water tank

The water tank for the experiment is self-made U-PVC plastic container with the diameter of 50cm and the height of 30cm. The inner walls of the water tank should be blackened with Ethyl polypropylene. The refined Thin Oil and Thick Oil from Liaohe oilfield were taken as standard samples for the mixing test. In addition, the used sewage in Facultative pond at the sewage treatment plants is also taken in the experiment. For getting water samples polluted by petroleum product with different concentration, the samples were gotten onsite from Raoyang River during the experiment, totally producing 10 results of different water samples.

2.1.2 Collecting water samples in the field

All of 24 water samples were collected per 1000m along Shuangtaizi River and Raoyang River within the testing area. In addition, three water samples were collected separately at drain outlet of three different sewage treatment plants at Liaohe oilfield.

2.2 Measurement in laboratory

Measurement of absorption coefficient in laboratory covers testing of 3 components of ocean color, namely yellow substance, de-pigment particles and pigment.

2.2.1 Measurement of absorption coefficient of yellow substance

Firstly we used 0.45μm GF/F filter to filter 75mL water sample, secondly filtered the filtered sample from first step with polycarbonate membrane with 0.22μm filter, the resultant sample was the yellow substance for experiment. Put 10cm long reference cuvette and sample cuvette in spectrophotometer, both full filled with pure water, into two different light paths of spectrophotometer (model: U-3010, made in Hitachi Japan), for measuring $\mathrm{OD_{bs}}(\lambda)$ of reference water. Pull the sample cuvette out of spectrophotometer and empty it, again full filled cuvette with sample to measure $\mathrm{OD_s}(\lambda)$ of yellow substance relative to pure water.

According to NASA's specification of marine optics measurement (Mitchell *et al.*, 2000), the calculating formula of absorption coefficient of yellow substance is:

$$a_g(\lambda)=\frac{2.303}{l}[[\mathrm{OD_s}(\lambda)-\mathrm{OD_{bs}}(\lambda)]-\mathrm{OD_{null}}] \tag{1}$$

where, l is the optical path of photometer cuvette (normally 0.1m); $\mathrm{OD_s}(\lambda)$ is the optical density of sample relative to reference pure water (dimensionless); $\mathrm{OD_{bs}}(\lambda)$ is the optical density of blank pure water (dimensionless), which is after being processed through sample processing program, relative to reference pure water; $\mathrm{OD_{null}}$ is apparent remained optical density in condition of supposing no dissolved substances absorption within long wave band or close infrared wave band of visible light, which refers to remained absorption in long wave band visible light or close infrared wave band (dimensionless). During the procedure of measuring absorption coefficient of yellow substance with spectrophotometer, the datum must be inspected in order to find out appropriate range of wavelength to be as null point for rectifying, for the reason that big differences exist in absorbing spectrum of pure water according to different temperatures, especially at 650—750nm. While Case I water is comparative "clean", the absorption coefficient of yellow substance follows an e-exponential attenuation, and normally spectrum value approaches to null at 600nm, therefore NASA's specification of marine optics measurement recommends to take average value between 590nm and 600nm for $\mathrm{OD_{null}}$. The

Series 1 in Fig. 1 is the absorption spectrum of yellow substance which had not been calibrated in the research region, i.e., without considering the result of $\mathrm{OD_{null}}$ when using Eq. (1). Accordingly it is obvious that the absorption coefficient of yellow substance still follows an e-exponential attenuation, but after 600nm it does not obviously approaches to zero. The Series 2 in Fig. 1 shows the absorption coefficient curve of yellow substance while taking 590—600nm as remnants calibration following Eq. (1). It is obvious that when use 590—600nm as remnants calibration wave band for measuring muddy Case II water following NASA's specification of marine optics measurement recommendation, it "underestimate"s the absorption coefficient of yellow substance mainly because the strong absorption of dissolved materials in heavy muddy Case II water still exists in 590—600nm wave band.

For the unclean or muddy water, Bricaud *et al.* (1981) gave out another formula to do scatter calibration by using absorption coefficient of the yellow substance at 750nm. In details, use Eq. (2) to calculate absorption coefficient of each wavelength, and use Eq. (3) to make scatter correction.

$$a(\lambda') = 2.303D(\lambda)/r \qquad (2)$$

$$a(\lambda) = a(\lambda') - a(750)\lambda/750 \qquad (3)$$

where, $D(\lambda)$ is the absorbance, equal to $[\mathrm{OD_s}(\lambda) - \mathrm{OD_{bs}}(\lambda)]$, r is optical path(m), $a(\lambda')$ is the uncorrected absorption coefficient of wavelength λ ($\mathrm{m^{-1}}$), $a(\lambda)$ is absorption coefficient of wavelength λ ($\mathrm{m^{-1}}$). The Series 3 in Fig. 1 shows the absorption coefficient curve of yellow substance, by using Eq. (2) and Eq. (3). It appears reasonable to choose 750nm as the scatter correction. Therefore 750±10nm was used in this paper to be the method of scatter calibration for the absorption coefficient of yellow substance.

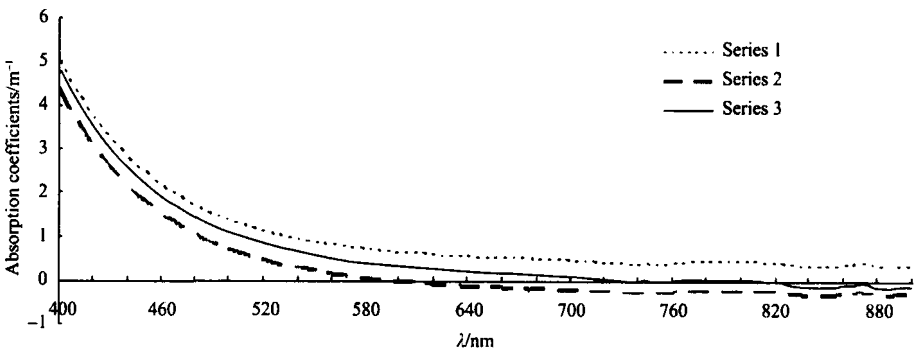

Fig. 1 Comparion of two remnants calibration methods to yellow substance absorption coefficients

2.2.2 *Measurement of absorption coefficient of total particles*

Filtered enough water through GF/F filter paper with 0.7μm aperture at low light level and low vacuum degree (approximate to 125mm mercury), and record the datum about diameter of effective area with numerous particles and filtered volume. Then respectively put filter paper covered with numerous particles and fully soaked blank filter paper of the same specification, into two optical paths in spectrophotometer, to measure the $\mathrm{OD_{fp}}(\lambda)$ of total absorption coefficient. Afterwards, calculated $a_p(\lambda)$ of particles.

After acquired the optical density, the absorption coefficients of particles were calculated with the following Eq. (4):

$$a_p(\lambda) = \frac{2.303A_f}{\beta V_f}[\mathrm{OD_{fp}}(\lambda) - \mathrm{OD_{null}}] \qquad (4)$$

where, A_f is the actual area which was covered by samples on sample membrane; V_f is the corresponding filtered volume of samples; β is the coefficient of optical path scale effect due to numerous particles on sample membrane(dimensionless); and $\mathrm{OD_{null}}$ is the mean of optical density within 790—800nm range of waveband. "β", the correction factor of optical path scale effect in this study introduced the result of Mitcehll (1990):

$$\beta = [0.392 + 0.655(\mathrm{OD_{fp}}(\lambda) - \mathrm{OD_{null}})]^{-1} \qquad (5)$$

2.2.3 *Measurement of absorption coefficient of de-pigment particles*

To remove the pigment through extraction with methanol on the filter paper used for measuring the absorption coefficient of particles. After that, to measure $\mathrm{OD_{fd}}(\lambda)$ of de-pigment particles using the same method as what's used for measuring the absorption coefficient of particles, namely calculated de-pigment absorption coefficient, $a_d(\lambda)$. Use Eq. (4) and (5) to do thecalculation with replacement of, $\mathrm{OD_{fp}}(\lambda)$ by and $\mathrm{OD_{fd}}(\lambda)$, and $a_p(\lambda)$ by $a_d(\lambda)$.

2.2.4 *Calculation of pigment particles absorption coefficient*

Total particles contains pigment and de-pigment particles, therefore the absorption coefficient of pigment particles equals to the difference between the one for the total particles and the one for de-pigment particles which can be expressed in Eq. (6) as following,

$$a_{ph}(\lambda) = a_p(\lambda) - a_d(\lambda) \qquad (6)$$

where $a_{ph}(\lambda)$ is the absorption coefficient of pigment particles.

2.2.5 *Absorption coefficient of petroleum substance*

Petroleum substance exists in the water in the form of float oil, decomposed oil, dispersed oil or emulsified oil. The float oil shows as oil film, the decomposed and dispersed oil appear as yellow substances, while the emulsified oil in particle mainly attaches on the suspended particles in water. Thus the measurement of yellow substance involved petroleum optics properties. In the total particle's absorption coefficient measurement, it also contains effect of petroleum substance. After removing the pigment with methanol in the total particle samples, the absorption coefficient of de-pigment particles is determined because the petroleum substance can be dissolved in methanol, during pigment removing they were taken away at the same time. The way of getting the absorption coefficient of pigment particles is to deduct the total particles' absorption coefficient by the de-pigment particles' absorption coefficient. Obviously in the water with petroleum pollution, the pigment particles' absorption coefficient includes the properties of petroleum absorption coefficient. Here the crucial question becomes how to separate the petroleum absorption coefficient from the absorption coefficients of yellow substance and pigment.

3 ANALYSIS AND DISCUSSION

3.1 Absorption properties of the three-component factors in testing Area

Fig. 2 (a) and (b) are two representative absorption spectrum diagrams of three-component factors extracted out of natural water from all observing sites in the experimental area. Table 1 tells the concentration of three corresponding factors and petroleum pollution of which concentration of yellow substance is expressed by concentration parameter a_g(440nm).

According to Fig. 2, the following conclusions about the general characteristics of absorption coefficient of three factors in the water of the experimental area can be drawn. (1) Within the range from 400nm to 800nm, absorbing of water in study area was effected together with pigment particles, de-pigment particles and yellow substance. (2) The absorption coefficients of de-pigment particles and yellow substance are following an e-exponential attenuation law. (3) On the absorption spectrum of pigment particles of the water in study area, there were typical pigment absorbing peaks at 440nm and 675nm because mainly of chlorophyll, and there was absorption peak of carotenoid at 490nm. There are a few Chinese scholars who have already studied about water absorption coefficient for offshore area such as Huanghai and Donghai seas, as well as Taihu and Qinghaihu Lakes. Because of the complexity of Case II water and flexible regional character of absorption coefficient, the general distribution trend of the three factors in this study is basically consistent with those of Case II water in the zones mentioned above.

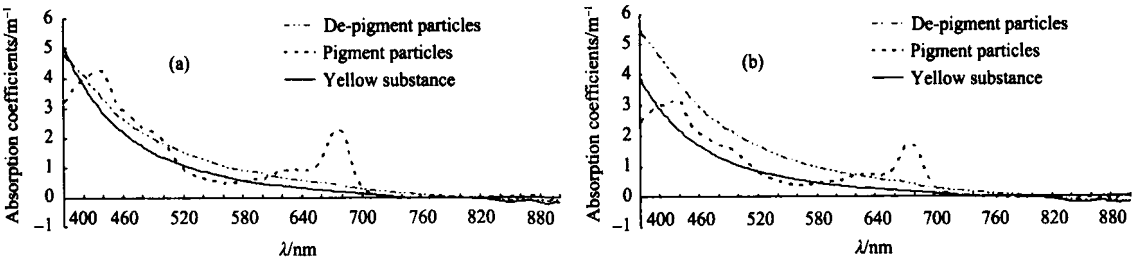

Fig. 2 Natural water absorption sperctal curves of three-component in the experiment fields

Table 1 Analysis result of optical active constituents in the water samples listed in Fig. 2

Concentration of water constituents	(a)	(b)
Pigment particles/(g/m^3)	68.67902	74.83208
De-pigment particles/(g/m^3)	18	10.66667
Yellow substance/(1/ m)	2.820446	2.167398
Petroleum substance/(mg/L)	0.38	0.66

3.2 Analysis of absorption properties of petroleum substance

3.2.1 The influences of petroleum substance on absorption feature of yellow substance

From the analysis about the properties of petroleum substance, it is known that in petroleum-polluted water, the absorption coefficients of yellow substance are the ones affected by the petroleum substance. To prove it, the mixture ratio experiment in water tank were conducted. Fig. 3 reveals the absorption coefficient spectrum of yellow substance of four samples which were acquired from sink mixture ratio test of the same aquatic system (to assure consistency of other constituents' value in other aquatic system) by using sewage from the water treatment plants. The graphic symbol in the spectrum is concentration of petroleum substance.

The following conclusions can be drawn according to the curves of absorption coefficient of yellow substance from Fig. 3: (1) with the increase of petroleum substance concentration (from curve "*a*" to "*b*", the concentration is increased from 0.31mg/L up to 4.09mg/L), the numerical value of yellow substance absorption coefficient is increased accordingly. It is proved that in petroleum-polluted water, the yellow substance measurement contains the influence from petroleum optics properties. (2) With the increase of the concentration of petroleum substance in the polluted water, the absorption spectrum of the yellow substance is kept the same shape in terms of following the e exponential attenuation while the slopes of their exponential functions were diversified obviously. The analysis about the slope of exponential functions will be discussed later on.

To further confirm the impact of petroleum substance on the absorption coefficient of the yellow substance, the analysis was also carried out for the absorption coefficient of yellow substances using different waters at different observing sites. With the 0.2mg/L testing limitation of the infrared spectrophotometer, basically it could be said there is no petroleum substance if the measured value is lower than the testing limitation. Taking the half of the testing limitation as the benchmark, the samples with concentration of petroleum pollution lower than 0.1mg/L were classified into petroleum-unpolluted water, those with concentration more than 0.1mg/L, petroleum polluted water. Fig. 4 illustrates the absorption coefficient of the yellow substances in the petroleum-unpolluted water samples from different aquatic systems. Table 2 lists the constituents concentrations in the water samples corresponding to Fig. 4.

Table 2 Analysis result of optical active constituents in the water samples listed in Fig. 4

Concentration of water constituents	Series 1	Series 2	Series 3
Petroleum substance/(mg/L)	0.1	0.1	0.1
D2-pigment particles/(g/m^3)	48	101.33	34.67
Chlorophyll-a/(mg/m^3)	12.17	58.84	13.45
Yellow substance/(1/ m)	0.74	1.01	1.02

As illustrated in Table 2, the concentrations of the yellow substance in the water samples represented by a_g (440nm) were respectively 0.74, 1.01, 1.02 and the concentrations of petroleum substancec were all under 0.1mg/L. According to Fig. 4 and Table 2, it showed that there was little difference among the concentrations of yellow substance in the petroleum-unpolluted water.

Fig. 5 describes the yellow substance's absorption coeffi-

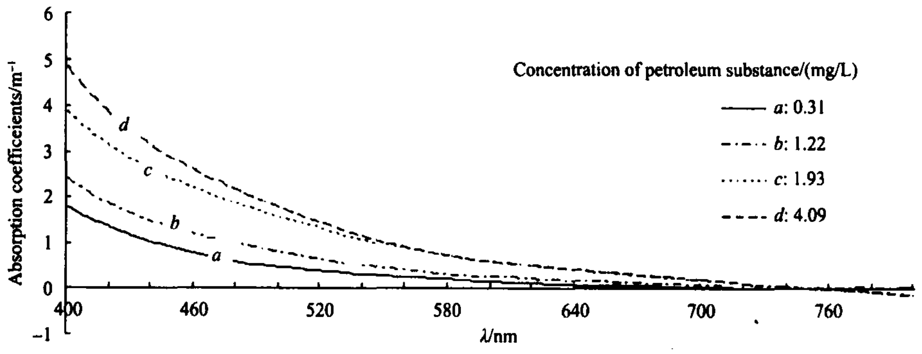

Fig. 3 Yellow substance absorption spectra in the same water with difference petroleum concentration

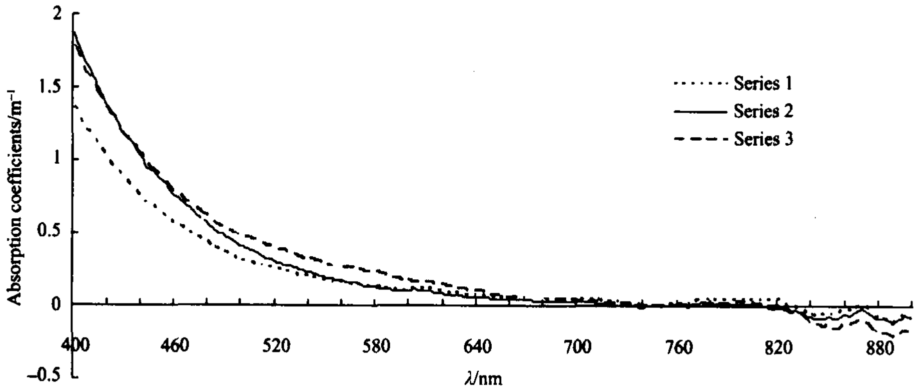

Fig. 4 Yellow substance absorption spectra in the same petroleum-polluted water

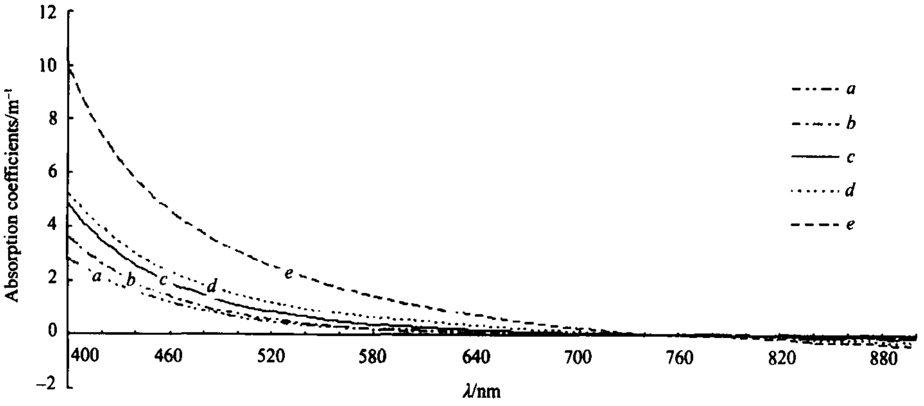

Fig. 5 Yellow substance absorption spectra in the same water with petroleum pollution

cients of the petroleum-polluted water samples from different aquatic systems. The corresponding compositions' concentration of each water sample was captured in Table 3. According to Table 3 and Fig. 5, the same result as what implied by Fig. 3 can be acquired, i.e., with the increase of the concentration of petroleum substance (from curve "*a*" to "*e*", the concentration was increased from 0.6mg/L up to 125.3mg/L), the value of the yellow substance's absorption coefficient was increased accordingly and the yellow substance's absorption spectrum was holding the same shape by following the exponential attenuation while the slopes of the exponential functions were obviously varied.

Table 3 Analysis result of optical active constituents in the water samples listed in Fig. 5

Concentration of water constituents	*a*	*b*	*c*	*d*	*e*
Petroleum substance/(mg/L)	0.6	0.82	1.39	2.1	125.3
De-pigment particles/(g/m^3)	174.67	56.00	49.33	21.33	26.67
Chlorophyll-a/(mg/m^3)	40.04	38.25	121.75	72.12	191.56
Yellow substance/(1/ m)	1.54	1.87	2.55	2.96	5.71

Taking the yellow substance's absorption coefficient at 440nm as the concentration of the yellow substance, the correlation coefficient between the concentration aforementioned and the concentration of the petroleum pollution was calculated with the result of 0.8263 (with 37 samples). It also indicated that the measured absorption coefficients of yellow substance were directly bound up with the concentration of petroleum substance.

3.2.2 The influence of petroleum substance on absorb properties of pigment

The petroleum substance in the water would be attached to suspended particles in the form of emulsified oil, so when it was being measured, the absorption coefficient of the total particles actually contained that of the de-pigment particles, the pigment and the petroleum substance. Because it is very easy for the petroleum substance to be dissolved in benzene, carbon tetrachloride, chloroform, petroleum ether, alcohol and other organic solvents, during the measurement of de-pigment particles, petroleum substance would be taken away while we removed pigment particles with methanol. This made it possible that the measurement of the absorption coefficient of de-pigment particles did not contain the petroleum substance. However if we obtained the absorption coefficient of pigment particles using the difference method, the absorption coefficient of pigment particles would contain the impact of the petroleum substances.

The absorption spectrum of pigment particles has the feature that at 440nm and 675nm there are both typical pigment absorption peaks of chlorophyll and there is the absorption peak of carotenoid at 490nm. The analysis aforementioned showed that, the absorption coefficient of petroleum substances followed the e exponential attenuation. So in theory, if the absorption coefficient of pigment particles was affected by the petroleum substance, with the same concentration of chlorophyll and pheophytin, the overlay of these three peaks should be the absorption coefficient of petroleum substance. In other words, at these three peaks, there was an increment in the situation of petroleum substance existence. Especially, that the absorption of the blue band was increased obviously would lead to a more apparent increment at the peak of 440nm.

Fig. 6 shows a curve of pigment particles' absorption coefficient which changes with the increase of the concentration of chlorophylls. Table 4 gives the corresponding concentration value of the water components, from which it can be seen that from Curve *a* to Curve *d*, the concentration of chlorophyll is gradually decreased. Therefore the absorption peak at 440nm, 490nm and 675nm should be showing as *a* > *b*> *c* > *d*, but curves *c* and *d* do not follow the rule, which in contract, appears as *d* > *c*. From Table 4, the petroleum pollution concentration of *d* is 1.39mg/L, one time larger than curve *c*, 0.66 mg/L. It can be inferred that this increase is due to the existence of the petroleum substance, and this also indicated that the petroleum absorption follows the e exponential decay equations.

Affected by the petroleum substance, the value of the absorption coefficient of the pigment particles in the petroleum-polluted water will be increased. So does the absorption peak. This resulted in an over-estimation of the absorption coefficient of the pigment particles. Therefore, to obtain the true value of pigment particles' absorption coefficient, the influence of the petroleum substance must be considered. Because the

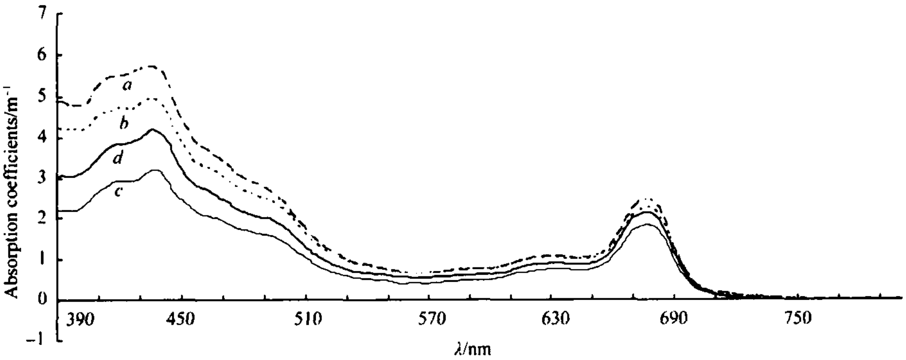

Fig. 6 Pigments absorption spectra in the same water with petroleum pollution

Table 4 Analysis result of optical active constituents in the water samples listed in Fig. 6

Concentration of water constituents	*a*	*b*	*c*	*d*
Petroleum substance /(mg/L)	2.1	0.93	0.66	1.39
De-pigment particles /(g/m^3)	49.33334	45.33333	26	21.33334
Chlorophyll-a/(mg/m^3)	121.74917	109.30731	99.08238	72.11749

petroleum substance's absorption coefficient also follows the rule of an e-exponential attenuation, it will be possible to remove the quantitative impact of the petroleum substance on the pigment particles absorption coefficient as long as the formula of petroleum substance absorption coefficient can be obtained.

3.2.3 Parametrization of petroleum substance absorption coefficient

According to the analysis above, the existence of petroleum substances in water would not change the shape of the yellow substance's absorption spectrum, yet it would change the value of absorption coefficient. This indicated that: (1) Petroleum substance's absorption spectrum should also follow the e exponential attenuation equation along the change in wavelength. (2) If a better way could be found to separate the influence of petroleum pollution from the absorption spectrum of yellow substance, then the absorption spectrum of petroleum substance can be represented quantitatively.

Similarly to Section 3.2.1, the samples of which the concentration of the petroleum substance is less than 0.1 mg/L were regarded as petroleum-unpolluted water. The average value of yellow substance absorption coefficient was calculated from all samples of which the petroleum pollution are less than 0.1mg/L as the benchmark. For those samples with the petroleum substance being great than 0.1 mg/L, then subtracting each yellow substance absorption coefficient by the benchmark, the result would be the absorption coefficient of petroleum pollution. As showed in Fig. 7, the absorption spectral properties of petroleum pollution follow e-exponential attenuation trend.

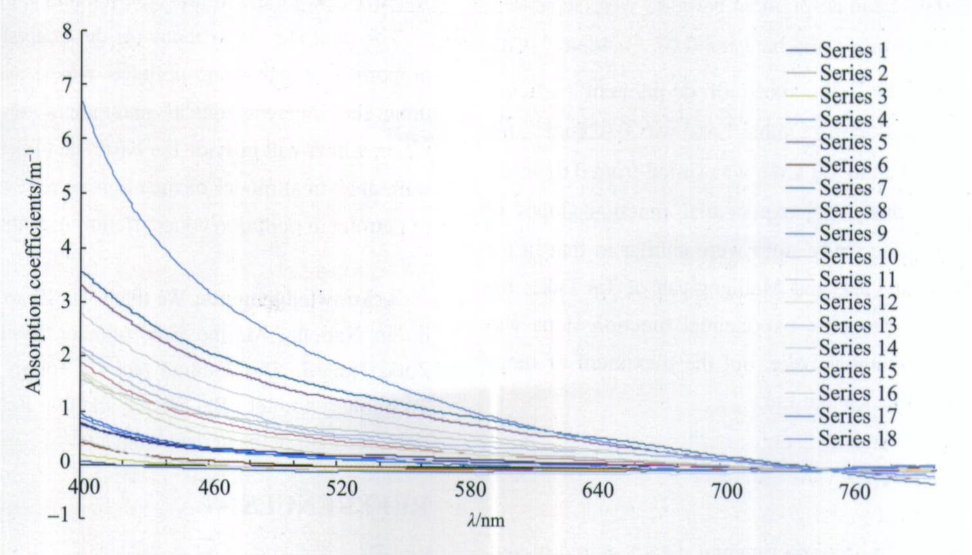

Fig. 7 Petroleum pollution absorption spectra

Now that the absorption spectral properties of petroleum pollution follow e-exponential attenuation trend, the parameterization models of the absorption spectral properties of yellow substance can be employed. The researches had showed that the relationship between the absorption spectral properties of yellow substance $a_g(\lambda)$ (m^{-1}) and the wavelength is negative exponential (Bricaud *et al.*, 1981), so

$$a_g(\lambda)=a_g(\lambda_0)\exp[-S(\lambda-\lambda_0)] \tag{7}$$

where, S is the parameter of Index Spectrum Slop, which has nothing to do with wavelength and concentration of yellow substance (shown as a_g(440nm)), and represents the act of spectrum (the shape of spectral curve). If applying Eq. (7) to petroleum pollution substance, we can gain the e exponential decay equation of the absorption coefficient.

3.2.4 Analysis of exponential function slope of yellow substances, petroleum substances and de-pigment particles

Based on the preceding analysis, the absorption coefficients of yellow substance, petroleum substance and de-pigment particles follow the e exponential decay equation, which will make it difficult to distinguish those three factors. However, if these three factors have an obvious distinction in exponential function slope, it is achievable to distinguish them in an optimization way.

Taking the following three aspects into consideration: (1) Exponential function slope S characterizes that the parameter of the absorption coefficient of matters under study decreases with the increasing wavelength. (2) The slope S has nothing to do with concentration, but the composition and selection of the band. (3) Two main factors have impact on the value of the exponential function slope S: One is concerned with the band selection of fitting and the other with the material composition and molecular size, we take the reference wavelength at λ_0= 440nm, and calculate separately the exponential function slope S of the three factors at 400—600nm band. With the 21 samples, the experience value of absorption exponential function slope S of petroleum substance was worked out and illustrated in Fig. 7. It has the minimum of 0.023nm^{-1} and the maximum of 0.089nm^{-1}. With the 8 samples from petroleum-polluted water to calculation the exponential function slope S of yellow substances' e exponential attenuation equation in the study areas, the results were between 0.016—0.023nm^{-1}. With the 26 river samples to calculate the exponential function slope S of suspended sediment's e-index equation, the results were between 0.001—0.07nm^{-1}.

Usually the yellow substance's exponential function slope S of the clean water body in the ocean is between 0.014—0.019nm^{-1}, but in Qinhai Lake the exponential function slopes S of yellow substance and de-pigment particles were separately between 0.016—0.024nm^{-1} and between 0.07—0.46nm^{-1} (Curtis, 1994; Zhang, 2006), the mean of de-pigment particles' exponential function slope in Qinhai Lake was 0.028nm^{-1}, the S-value in Meiliangwan in Tai Lake was varied from 0.014nm^{-1} to 0.018nm^{-1}. Obviously, the exponential function slopes of yellow substance in the study areas were similar to that in the clean ocean, Qinghai Lake and Meiliangwan of Tai Lake; the mean of de-pigment particles' exponential function slope was bigger than that in Qinghai Lake, but the maximum of range was smaller than that in Qinhai Lake.

4 CONCLUSIONS

This paper, based on the experimental data acquired in situ, through absorption coefficient of yellow substance and pigment from petroleum-polluted water and petroleum-unpolluted water, discusses the effects of the petroleum substance on the water absorption coefficient. The results show that: (1) In the study area, no matter petroleum-polluted water or petroleum-unpolluted water, the absorption spectrum of de-pigment particles and yellow substance would always follow the e exponential attenuation. In pigment's absorption spectrum there were two typical pigment absorption peaks of chlorophyll at 440nm and 675nm, and an absorption peak of Carotenoid at 490nm. (2) In terms of petroleum polluted water bodies, when the absorption coefficient of yellow substance and pigment particles were measured, the absorption coefficient of which would be enlarged, for it contained the influence of petroleum substance. (3) Petroleum absorption spectrum curve appeared the same as that of de-pigment particles and yellow substance, both followed the e exponential attenuation. But the slope of the three exponential functions had significant differences, which would provide feasibility for distinguishing them.

On the other hand, when we calculated the remnants calibration of yellow substance, it was found that using NASA specifications recommended 590—600nm as a yellow substance absorption coefficient of the remnants calibration was obviously unreasonable for a highly turbid Case II water body, but the use of 750nm scatter correction methods was more appropriate.

Because of the specificity of the petroleum pollutants, the sample collection of petroleum-polluted water in the field need to be extracted with carbon tetrachloride. The carbon tetrachloride is easy to volatile, which is not conducive to the preservation of samples. In addition, the carbon tetrachloride belongs to organic solvents, it could not be achieved in laboratory to place a normal water body and petroleum polluted water into two different light paths of spectrophotometer, to measure the optical density of the petroleum substances, and then to calculate the absorption coefficient of petroleum substance in polluted water. These are the future experimental studies.

The next step is to focus on the analysis of the absorption properties of petroleum-polluted water, and ultimately determine the inherent optical parameters of petroleum-polluted water, which will provide the basic data for the establishment of semi-analytical model of quantitative remote sensing inversion of petroleum pollution concentration in water body.

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石油类污染水体吸收特性分析

黄妙芬[1], 唐军武[2], 宋庆君[2]

1. 大连水产学院, 辽宁 大连 116023;
2. 国家卫星海洋应用中心, 北京 100081

摘 要: 石油类污染物主要以漂浮油、分散油、乳化油和分解油等形式存在于水体中, 影响着水体的表观和固有光学特性。利用2008年5月在辽宁省盘锦市辽河油田境内双台子河和绕阳河所测定的水色三要素吸收系数以及对应的水体组分数据, 分析了研究区域内 II 类水体水色三要素的吸收光谱特性; 探讨了水体中由于石油类污染物的存在, 黄色物质和色素吸收光谱的变化特征; 采用差值法确定了水体中石油类污染物的吸收系数。研究结果表明: (1) 研究区域内, 无论是石油类污染水体还是非石油类污染水体, 非色素颗粒物和黄色物质的吸收光谱都遵循 e 指数衰减规律, 色素吸收光谱在 440nm 和 675nm 处有以叶绿素为主的典型的色素吸收峰, 在 490nm 处有类胡萝卜素的吸收峰; (2) 对于石油类污染水体, 在测定黄色物质和色素吸收系数时, 由于包含了石油类污染物的作用, 会增大黄色物质和色素的吸收系数; (3) 石油类物质的吸收光谱曲线和非色素颗粒物、黄色物质一样遵循 e 指数衰减规律, 但三者的指数函数斜率有明显的差别, 这为将三者区分开来提供了可行性。

关键词: 石油类污染, 黄色物质, 吸收特性, 指数函数斜率

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1 引 言

面对日趋严重的环境污染问题, 世界各国在加大治理力度, 制定相应的法律法规政策。在众多污染问题中, 水体污染的影响最为严重, 其中油田开采、油田事故、油轮泄漏、航道油污水排放等人类活动对水体(河流、湖泊、海洋)造成的油污染等引发的环境问题日益凸显。面对突发性和缓发性的水体石油类污染事件, 加大监测力度, 及时掌握水体石油类污染的空间分布和时间变化信息势在必行, 遥感技术可作为重要的监测手段之一。遥感具有大面积、动态、低成本获取区域信息的优势, 这是传统点观测方法无法比拟的。目前利用遥感技术监测水体石油类污染集中在溢油探测方面, 其遥感机理与模型研究已取得长足的进展, 在中国、加拿大、美国、德国等国家已经初步形成了海上溢油的业务化运行监测系统(刘良明, 2005; Otremba, 2000; Otremba & Piskozub, 2003; Zielinski, 2003)。对于水体中石油类污染已经存在, 但未形成明显可探测油膜的情况, 进行此情况下的遥感探测机理和识别模型研究具有重要的科学意义和应用价值(黄妙芬等, 2007)。

水色遥感是遥感技术的重要分支。在 I 类水体中, 应用遥感技术对水色因子叶绿素的监测已进入业务化运行阶段。在 II 类水体叶绿素、黄色物质、悬浮物等水色因子的监测中, 遥感机理和遥感模型的研究也较为全面, 取得了不少的研究成果, 并服务于社会。石油类物质主要由烷烃、环烷烃和芳香烃等烃类组成, 在水中, 以飘浮油、分散油、乳化油和分解油等形式存在, 成为水体污染物之一, 直接影响着水色, 因此对于未形成明显成片的可探测油膜的情况, 可以把它看成是水色因子的一种。对于 II 类水体中主要的水色因子, 例如色素(叶绿素)、非

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第一作者简介: 黄妙芬(1963—), 女, 教授, 博士, 2005 年毕业于北京师范大学地理学与遥感科学学院, 目前主要从事水色遥感和热红外遥感研究, 已发表论文 40 余篇。E-mail: hmf808@163.com。

色素颗粒物(无机悬浮物)和黄色物质，以及纯水的固有光学特性(吸收系数和后向散射)的测定，针对不同类型的水体，已做了大量工作，建立了参数化模型(Pope and Fry, 1997; Smith and Baker, 1981; Gallegos and Neale, 2002; Gallie and Murtha, 1992; 俞宏等, 2003; 宋庆君 & 唐军武, 2006; 周虹丽等, 2005; 汪小勇等, 2004)。要用遥感半分析模型定量反演水体石油类污染浓度，必须先确定石油类物质的固有光学特性(Otremba & Krol, 2002)。本文侧重探讨石油类污染水体吸收系数特征，为进一步建立遥感半分析模式定量反演水体石油类物质浓度提供参考。

研究区位于辽河平原的辽宁省盘锦市(辽河油田区域)，境内有双台子河和绕阳河，辽河油田是中国第三大油田，主要产品为原油和天然气。油田开采活动不可避免地对水环境产生一定影响，成为石油类污染水体固有和表观光学特性的一个较为典型的实验研究区域(黄妙芬等, 2007)。

2　吸收系数的测量

2.1　现场样品采集

现场样品采集包括水槽配比实验和现场采集水样两种方式。所有采集的水样被分成两部分，一部分直接注入样品瓶，并将样品瓶保存在液氮中带回到实验室进行过滤，做黄色物质吸收系数测量使用；另一部分直接转移到干净的容器中，进行过滤处理，制作颗粒物样品，做颗粒物吸收系数测量使用。

2.1.1　水槽配比实验

水槽配比实验中所使用的水槽为自制的U-PVC塑料容器，内壁用聚丙稀酸乙酯涂黑，其直径50cm，高度30cm。

利用取自辽河油田的稠油和稀油标样，以及污水处理厂的自然污水，在绕阳河边上现场取河水，进行水槽配比试验，获取不同浓度下石油类污染水体样本。利用稀油、稠油和污水处理厂兼性池中的自然污水进行配比实验，分别获取样本数为3, 3, 4个。

2.1.2　现场采集水样

沿着辽河油田区域内的绕阳河和双台子河，约每1000m采集一个样点河水，一共采集24个样本；另外在辽河油田3个污水处理厂的外排口采样，获取3个样本。

2.2　实验室测定

吸收系数的实验室测定主要包括黄色物质、非色素颗粒物和色素的吸收系数。

2.2.1　黄色物质吸收系数测定

先利用孔径为0.45μm的GF/F滤膜过滤75mL的水样，再使用孔径0.22μm的聚碳酸酯滤膜过滤上面已经过滤过的水样，作为黄色物质样品。将10cm的盛满纯水的参比比色皿和样品比色皿放入分光光度计(型号U-3010，日本日立)的两个光路，测量参比纯水的光学密度$\mathrm{OD_{bs}}(\lambda)$(无量纲)；取出样品比色皿，倒掉纯水空白，盛满样品，测量黄色物质相对于纯水的光学密度$\mathrm{OD_s}(\lambda)$(无量纲)。

按照NASA给定的海洋光学测量规范(Mitchell等, 2000)，黄色物质吸收系数的计算公式为，

$$a_g(\lambda)=\frac{2.303}{l}[[\mathrm{OD_s}(\lambda)-\mathrm{OD_{bs}}(\lambda)]-\mathrm{OD_{null}}] \quad (1)$$

式中，l是比色皿的光程(通常是0.1m)；$\mathrm{OD_s}(\lambda)$是样品相对于参比纯水的光学密度(无量纲)；$\mathrm{OD_{bs}}(\lambda)$是经过样品处理程序处理的空白纯水相对于参比纯水的光学密度(无量纲)；$\mathrm{OD_{null}}(\lambda)$是在可见光长波段或近红外波段溶解物质吸收可以假定为零波段的表观残余光学密度(无量纲)，即在长波段可见光或近红外波段的残余吸收。在利用分光光度计测量黄色物质吸收系数过程中，由于纯水的吸收光谱随温度变化很大，特别是在650—750nm，因此必须检查数据找出合适的波长范围作为零点进行校正。由于I类水体比较“清洁”，黄色物质吸收系数呈e指数衰减，一般光谱在600nm波段趋近零值，因此NASA给定的海洋光学测量规范推荐$\mathrm{OD_{null}}(\lambda)$采用取590—600nm的平均值。图1中的系列1为本研究区域未进行任何校正的黄色物质吸收光谱，即用公式(1)不考虑$\mathrm{OD_{null}}(\lambda)$的计算结果，很显然虽然黄色物质的吸收系数依然呈e指数衰减，但在600nm后没有明显的趋近零值。图1中的系列2为根据公式(1)采用590—600nm作为残余校正获取的黄色物质吸收系数曲线，显然在浑浊II类水体按照用NASA海洋光学测量规范推荐的590—600nm波段作为残余校正波段，会导致黄色物质吸收系数的“过低”估计，这主要由于II类高浑浊水体溶解物质在590—600nm波段有强烈的吸收存在。

Bricaud等(1981)针对浑浊水体，提出了一种利用750nm黄色物质吸收系数进行散射校正的计算公式，即利用式(2)计算各波长λ(nm)的吸收系数，再利用式(3)进行散射校正。

$$a(\lambda')=2.303D(\lambda)/r \quad (2)$$

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

式中，$D(\lambda)$为吸光度(无量纲)，相当于$[\mathrm{OD_s}(\lambda)-$

$OD_{bs}(\lambda)]$，r 为光程路经(m)，$a(\lambda')$为波长λ未校正的吸收系数(m^{-1})，$a(\lambda)$为波长λ的吸收系数(m^{-1})。图 1 中的系列 3 为利用式(2)和式(3)计算出来的黄色物质的吸收系数曲线，显然选择 750nm 做为散射校正比较合理，故本文采用 750 ± 10nm 对黄色物质吸收系数进行散射校正的方法。

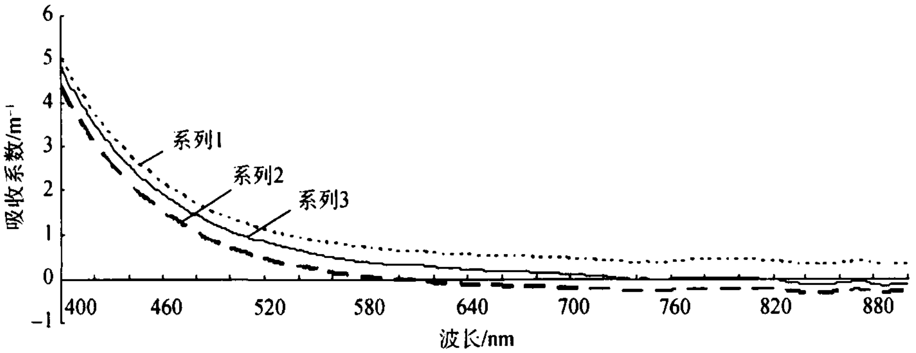

图 1 黄色物质吸收系数两种长波段残余校正方法对比

2.2.2 总颗粒物吸收系数测定

在微光和低真空度(约 125mm 汞柱)下，过滤足够体积的水样到 0.7μm 孔径 GF/F 滤纸上，记录滤膜上富含颗粒物的有效面积直径及过滤体积；将分光光度计的两条光路分别放置富集了颗粒物的滤纸和同样规格被充分润湿的空白滤纸，测量总颗粒物的光密度 $OD_{fp}(\lambda)$，然后计算颗粒物的吸收系数 $a_p(\lambda)(m^{-1})$。

在获取样品的光密度值之后，通过式(4)计算颗粒物吸收系数 $a_p(\lambda)$

$$a_p(\lambda)=\frac{2.303A_f}{\beta V_f}[OD_{fp}(\lambda)-OD_{null}] \qquad (4)$$

式中，A_f是样品膜中样品所占的真实面积(cm^2)，V_f是样品对应的过滤体积(ml)，β为滤膜富集颗粒导致的光路扩大效应系数(无量纲)，$OD_{null}(\lambda)$取 790—800nm 波段范围光密度的平均值。本研究中光路扩大校正系数 β 采用 Mitcehll(2000)的结果，

$$\beta=[0.392+0.655(OD_{fp}(\lambda)-OD_{null})]^{-1} \qquad (5)$$

2.2.3 非色素颗粒物吸收系数测定

将颗粒物吸收系数测量的滤纸，采用甲醇萃取的方法去掉色素；然后同颗粒物吸收系数光学密度方法相同，测量非色素颗粒物光学密度 $OD_{fd}(\lambda)$，计算非色素颗粒物吸收系数 $a_d(\lambda)(m^{-1})$。用式(4)和式(5)计算，只是把式中的 $OD_{fp}(\lambda)$改为 $OD_{fd}(\lambda)$，$a_p(\lambda)$改为 $a_d(\lambda)$即可。

2.2.4 计算色素吸收系数

总颗粒物中含有色素和非色素颗粒物，因此色素吸收系数为颗粒物和非色素颗粒物吸收系数的差，即色素吸收系数 $a_{ph}(\lambda)(m^{-1})$为，

$$a_{ph}(\lambda)=a_p(\lambda)-a_d(\lambda) \qquad (6)$$

2.2.5 石油类物质的吸收系数

石油类物质主要以漂浮油、分解油、分散油和乳化油的形式存在于水体中，漂浮油以油膜形式存在，分解油和分散油主要以黄色物质的形式存在，乳化油主要以颗粒物的形式附者于水体的悬浮颗粒物上。因而黄色物质测量中含有石油光学特性，在总颗粒物吸收系数测量中，也包含石油类物质的影响。在总颗粒物样本中，利用甲醇去除色素后测定非色素颗粒物的吸收系数，由于石油类物质溶解于甲醇，因而去除色素时就把石油类物质带走了。色素的吸收系数的获取是由总颗粒物吸收系数减去非色素颗粒物的吸收系数得到的，受石油污染的水体中，色素的吸收系数含有石油吸收系数特征，要解决的关键问题是从黄色物质和色素的吸收系数中分离出石油类物质的吸收系数。

3 分析和讨论

3.1 研究区域内三要素的吸收特性

图 2(a)和(b)是研究区内选取的 2 个具有代表性观测点三要素吸收光谱曲线图，表 1 为对应观测点三要素以及石油类污染浓度值，其中黄色物质浓度以吸收系数 a_g(440nm)表示。

分析图 2，对研究区域三要素吸收系数的总体特征，可得出如下结论：(1)在 400—800nm 范围内，水体的吸收特性受色素、非色素颗粒物和黄色物质三者共同作用；(2)非色素颗粒物和黄色物质的吸收系数遵循 e 指数衰减规律；(3)水体色素吸收光谱在 440nm 和 675nm 有以叶绿素为主的典型的色素吸收峰，在 490nm 处有类胡萝卜素的吸收峰。这些特征，与中国其他学者针对黄东海近海区域、太湖和青海湖等 II 类水体区域的研究所得出的水体吸收系数分布趋势基本一致。

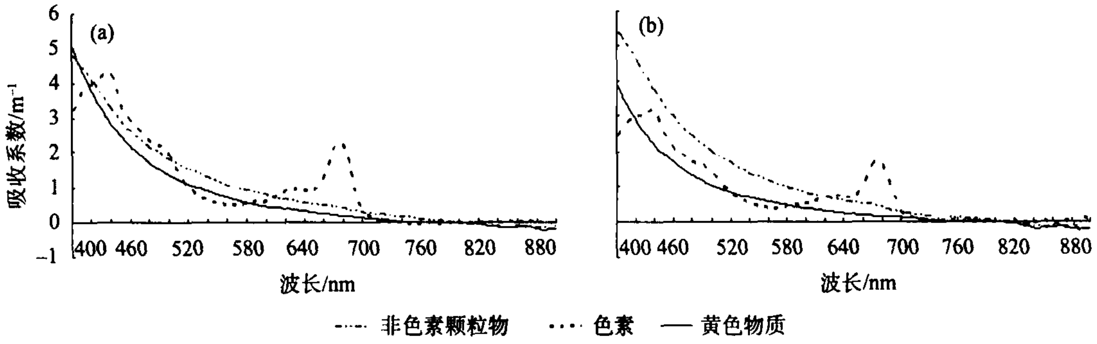

图 2 实验区自然水体三要素吸收光谱曲线

表 1 图 2 中水样(a)和(b)对应的水体组分浓度值

水体组分项目	(a)	(b)
色素浓度/(g/m^3)	68.67902	74.83208
非色素颗粒物浓度/(mg/m^3)	18	10.66667
黄色物质/(1/m)	2.820446	2.167398
石油类污染浓度/(mg/L)	0.38	0.66

3.2 石油类物质的吸收特性分析

3.2.1 石油类物质对黄色物质吸收特性的影响

根据石油类物质在水中存在的特性可知，在有石油类污染的水体中，石油类物质的影响主要体现在黄色物质的吸收系数上，利用水槽进行配比实验，研究在不同石油类物质浓度下黄色物质吸收系数所呈现的光谱变化特征。取污水处理厂的污水，对同一水体(以保证水体其他组分值一致)进行配比，图 3 为实验获取的 4 个样本。

从图 3 所示的黄色物质吸收光谱曲线，可得出如下结论：(1)随着石油类物质浓度的增加(曲线 *a* 到 *d*，石油类物质浓度由 0.31mg/L 增加到 4.09mg/L)，黄色物质吸收系数的量值随着增大，这说明在有石油污染的水体，黄色物质吸收系数的测定含有石油物质光学特性的影响；(2)在有石油类物质存在的水体中，随着石油类物质浓度的增大，黄色物质吸收光谱形状不变，依然遵循指数衰减规律，但指数函数斜率明显改变，关于指数函数斜率的变化程度在后面部分单独进行讨论。

为了进一步证实石油类物质对黄色物质吸收系数的影响，对不同水体不同观测点黄色物质吸收系

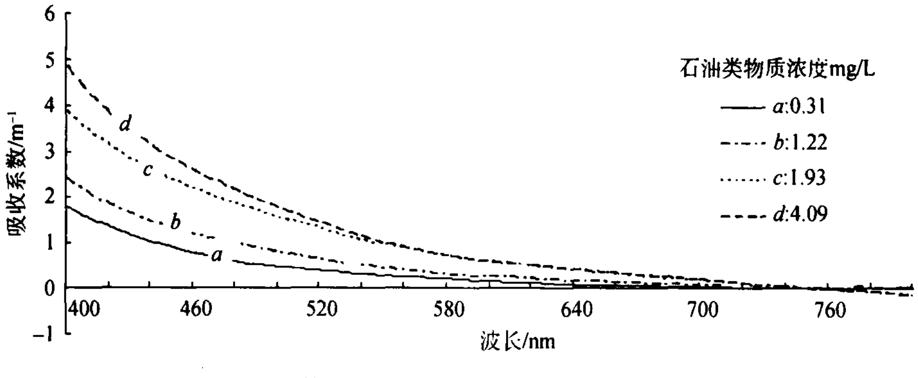

图 3 同一水体不同石油类污染浓度黄色物质吸收光谱

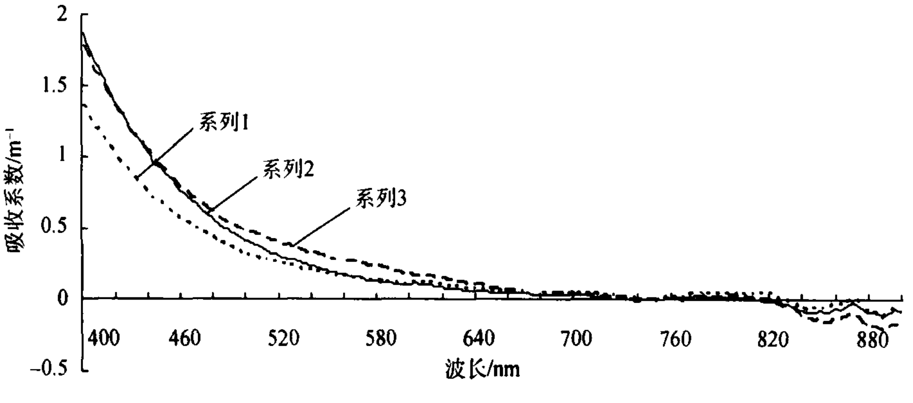

图 4 非石油类污染水体黄色物质吸收系数

数进行分析。考虑到所使用的红外测油仪检测限为0.2mg/L，当低于检测限时，说明基本无石油类物质，此时按检测限的 1/2 记录的情况，把石油类污染浓度小于 0.1mg/L 归为无石油类污染的水体，把大于0.1mg/L 归为有污染的水体。图 4 为取自不同水体，无石油类物质浓度的水体黄色物质吸收系数，表 2 为图 4 对应的水体组分浓度。

表 2 图 4 观测样点对应的水体组分浓度值

水体组分项目	系列 1	系列 2	系列 3
石油类/(mg/L)	0.1	0.1	0.1
非色素悬浮物浓度/(g/m^3)	48	101.33	34.67
叶绿素 a 浓度/(mg/m^3)	12.17	58.84	13.45
黄色物质浓度/(1/m)	0.74	1.01	1.02

表 2 中黄色物质浓度以浓度参数 a_g(440nm)表示，分别为 0.74，1.01 和 1.02，石油类物质浓度在0.1mg/L 以下。由图 4 和表 2 可见，非石油类污染水体的黄色物质浓度差别不大。

图 5 是取自不同水体，有石油类污染的水体黄色物质吸收系数，表 3 为图 5 对应的水体组分浓度。根据表 3 和图 5 可得到与图 3 相同的结论，即随着石油类物质浓度的增加(曲线 *a* 到 *e*，石油类物质浓度由 0.6mg/L 增加到 125.3mg/L)，黄色物质吸收系数的量值随之增大，而且随着石油类物质浓度的增加，黄色物质吸收光谱的形状不变，依然遵循指数衰减规律，但指数函数斜率明显改变。

进一步利用 440nm 处黄色物质吸收系数作为黄色物质浓度，计算其与石油类污染浓度相关系数，结果为 0.8263(37 个样本)，这也表明了所测定的黄色物质吸收系数与石油类物质的浓度密切相关。

表 3 图 5 观测样点对应的水体组分浓度值

水体组分项目	*a*	*b*	*c*	*d*	*e*
石油类/(mg/L)	0.6	0.82	1.39	2.1	125.3
非色素悬浮物浓度/(g/m^3)	174.67	56.00	49.33	21.33	26.67
叶绿素 a 浓度/(mg/m^3)	40.04	38.25	121.75	72.12	191.56
黄色物质浓度/(1/m)	1.54	1.87	2.55	2.96	5.71

3.2.2 石油类物质对色素吸收特性的影响

存在于水中的石油类物质，会以乳化油的形式附着于悬浮颗粒物，在总颗粒物的吸收系数测定中实际包含了非色素颗粒物、色素和石油类物质三者的吸收系数。由于石油类物质极易溶解于苯、四氯化碳、氯仿、石油醚、醇等有机溶剂，因此在测量非色素颗粒物时，用甲醇去除色素会将石油类物质带走，这使得测量的非色素颗粒物吸收系数不含石油类物质的影响。但由于色素吸收系数是由测定的总颗粒物吸收系数减去非色素颗粒物的吸收系数确定的，因此这种用差值法确定的色素吸收系数的方法包含石油类物质的影响。

色素吸收系数光谱特征是在 440nm 和 675nm 有以叶绿素为主的典型色素吸收峰，在 490nm 处有类胡萝卜素的吸收峰。由前面的分析表明，石油类物质吸收系数呈 e 指数衰减，从理论上，如果色素吸收系数中存在石油类物质，在同样的叶绿素浓度下，这 3 个峰值应该叠加了石油类物质的吸收系数，也就是说在这 3 个峰值上，有石油类物质的情况下会存在一个增量，特别是在蓝波段，其吸收明显增强，导致 440nm 峰值的增量更为明显。

图 6 为随着叶绿素浓度增大，色素吸收系数的变化曲线。表 4 是对应的水体组分浓度值。从表 4 可见，从曲线 *a* 到曲线 *d*，叶绿素浓度是逐渐降低的，在图 6 表现出来的 440nm、490nm 和 675nm 的吸收峰，应该是曲线 *a*>*b*>*c*>*d*，但是曲线 *c* 和 *d*，没有遵循这个规律，而是曲线 *d*>*c*。由表 4 可见，曲线 *d* 石油类污浓度为 1.39mg/L，比曲线 *c* 的值 0.66mg/L 大近 1 倍，由此可推断这个规律的改变是由于石油类物质引起，这也进一步证明石油类物质的吸收系数呈现 *e* 指数衰减。

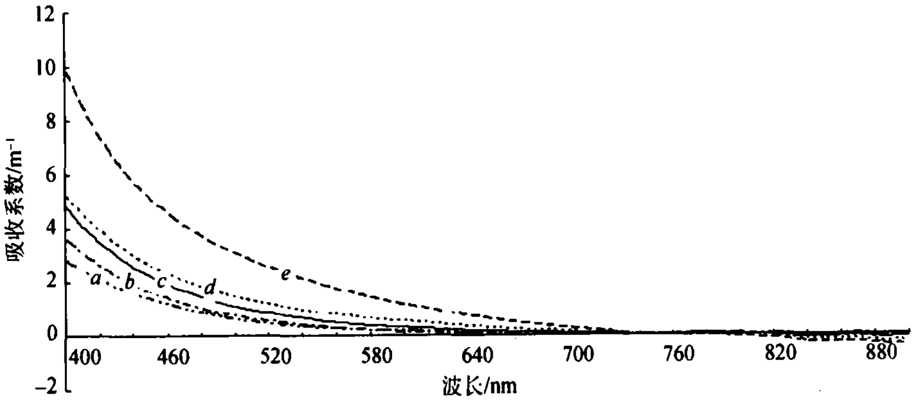

图 5 有石油类污染水体黄色物质吸收系数

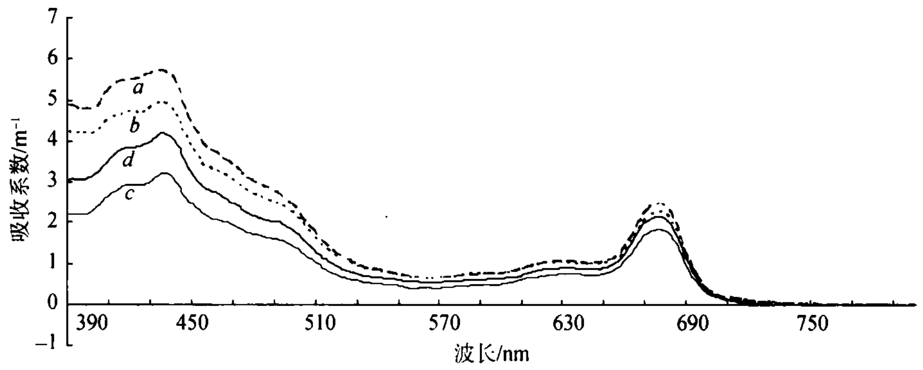

图 6　石油类污染水体色素吸收系数

表 4　图 6 观测样点对应的水体组分浓度值

水体组分项目	*a*	*b*	*c*	*d*
石油类/(mg/L)	2.1	0.93	0.66	1.39
非色素悬浮物浓度/(g/m^3)	49.33334	45.33333	26	21.33334
叶绿素 a 浓度/(mg/m^3)	121.74917	109.30731	99.08238	72.11749

在有石油类物质的水体中，由于石油类物质的影响，增加色素的吸收系数测定值，以及增强吸收峰，相当于“高估”了色素的吸收系数，因此要获取色素吸收系数的真值，必须考虑去除石油类物质的影响。由于石油类物质吸收系数也遵循 e 指数衰减，只要把石油类物质吸收系数的方程求出来，就有可能从色素吸收系数中定量的去除石油类物质的影响。

3.2.3　石油类物质的吸收特性参数化

根据上面的分析，若水体中存在石油类物质，不会改变黄色物质吸收光谱的形状，但会改变吸收系数的数量，这给我们启示：(1)石油类物质的吸收光谱也应该是随着波长的变化呈现 e 指数衰减；(2)如果能找到一种较好的方法，从所测定黄色物质的吸收光谱中，将石油类污染物质的影响分离出来，那么就可以定量地表示石油类物质的吸收光谱特性。

与 3.2.1 节一样，把本次实验中石油类污染浓度小于 0.1mg/L 的所有样本作为无石油类污染水体，对它们的黄色物质吸收系数求算术平均值，作为本底数据，然后将每一个石油类污染大于 0.1mg/L 的水样的黄色物质吸收系数减去本底值，作为石油类污染物的吸收系数，如图 7。由图 7 可见，石油类物质的吸收系数也遵循 e 指数衰减规律。

既然石油类物质的吸收系数也遵循 e 指数衰减规律，可以借鉴黄色物质吸收系数的参数化模型实现对石油类物质系数参数化。已有的研究表明(Bricaud 等，1981)，黄色物质 $a_g(\lambda)$ (m^{-1})与波长呈负指数关系，有，

$$a_g(\lambda)=a_g(\lambda_0)\exp[-S(\lambda-\lambda_0)] \tag{7}$$

式中，S 为指数光谱斜率参数，它与波长及黄色物质浓度(以 a_g(440nm)表示)无关，代表了光谱行为(光谱曲线的形状)。把式(7)应用于石油类污染物质，可以得到其吸收系数 e 指数衰减方程。

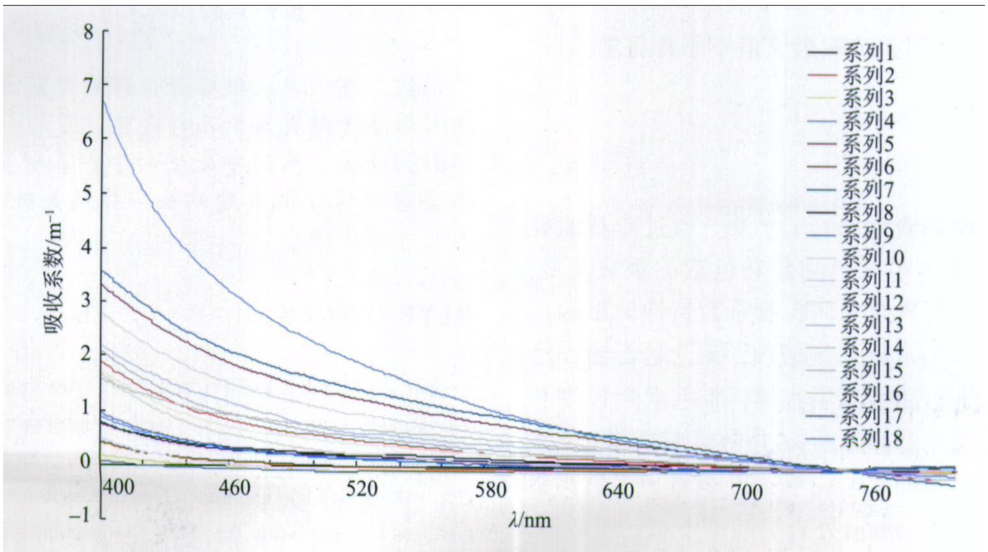

图 7　石油类物质吸收系数

3.2.4 黄色物质、石油类物质和非色素颗粒物指数函数斜率分析

由前面的分析可知，黄色物质、石油类物质和非色素颗粒物的吸收系数遵循 e 指数衰减方程，这增加了将黄色物质、石油类物质和非色素颗粒物的吸收系数区分开的难度，但如果这三者的指数函数斜率在量级上差别较大，就有可能利用优化的方法将它们区分开。

考虑到：(1)指数函数斜率 S 表征所研究物质的吸收系数随波长增加而递减的参数；(2)其与浓度无关，但与组成及波段的选择有关；(3)对指数函数斜率 S 值结果的影响主要有两个方面：一是拟合的波段选择，二是与物质的组成和分子大小有关等因素，为此，取参考波长 λ_0=440nm，在 400—600nm 波段上分别计算三者的指数函数斜率 S。利用图 7 的 18 个样本，计算得到石油类物质吸收系数指数函数斜率的经验值 S，S 最小值为 0.023nm^{-1}，最大值为 0.089nm^{-1}；利用非石油类水体 8 个样本，计算本研究区域黄色物质的 e 指数方程的指数函数斜率 S 为 0.016—0.023nm^{-1} 之间，利用河流的 26 个样本，计算得到悬浮泥沙的指数函数斜率 e 指数方程的指数函数斜率 S 为 0.001—0.07nm^{-1} 之间。根据已有的研究(Mobley, 1994；张运林, 2006)，一般情况下，大洋清洁水体黄色物质的指数函数斜率 S 在 0.014—0.019nm^{-1} 之间，青海湖黄色物质和非色素颗粒物的指数函数斜率 S 分别在 0.016—0.024nm^{-1} 和 0.07—0.46nm^{-1} 之间，青海湖非色素颗粒物指数函数斜率平均值为 0.028nm^{-1}，太湖梅梁湾 S 值的变化范围为 0.014—0.018nm^{-1} 之间。显然本研究区域水体中黄色物质的指数函数斜率与大洋清洁水体、青海湖和太湖梅梁湾相近，非色素颗粒物指数函数斜率的平均值大于青海湖，但是范围最大值小于青海湖。

4 结 论

根据野外现场获取的实验数据，通过非石油类和石油类污染水体中黄色物质和色素的吸收系数，探讨石油类污染物质对水体吸收系数特性的影响。研究结果表明：(1)本研究区域内，无论是石油类污染水体，还是非石油类污染水体，非色素颗粒物和黄色物质的吸收光谱都遵循 e 指数衰减规律，色素吸收光谱在 440nm 和 675nm 有以叶绿素为主的典型的色素吸收峰，在 490nm 处有类胡萝卜素的吸收峰；(2)对于石油类污染水体，在测定黄色物质和色素吸收系数时，由于包含了石油类污染物的作用，会增大黄色物质和色素的吸收系数；(3)石油类物质的吸收光谱曲线和非色素颗粒物、黄色物质一样皆遵循 e 指数衰减规律，但三者的指数函数斜率有明显的差别，这为将三者区分开提供了可行性。

另外对黄色物质进行残余校正计算时，发现对于高浑浊的 II 类水体，利用 NASA 规范中推荐的 590—600nm 作为黄色物质吸收系数的残余校正显然不合理，采用 750nm 散射校正方式更为合适。

由于溶解和分散在水中的石油类物质，其吸收系数的测定是和黄色物质混合在一起的，本研究采用的分离方法是：选择无石油类污染水体，作为背景值，然后用有石油类污染水体的黄色物质的吸收系数减去无污染水体的黄色物质吸收系数，得到的就是石油类物质的吸收系数，进一步针对获取的石油类物质的吸收系数，建立了指数衰减方程。实际上，如果能在实验室内，将正常水体和受石油污染水体分别置于分光光度计两条光路上，通过测定石油物质的光学密度，计算污染水体中石油物质的吸收系数，是最有效获取石油类物质吸收系数的方法。但目前对于石油类污染水体样本的获取，一般是采用野外采集水样，然后用四氯化碳萃取的方法，由于四氯化碳挥发性较强，不利于样本的长时间保存，加上四氯化碳属于有机溶剂，使得将正常水体和受石油污染水体分别置于分光光度计两条光路上直接测定石油类污染吸收系数的方式未能实现，这是今后要进行的实验研究工作。

下一步的研究重点是对石油类污染的吸收特征进行更深入的分析，最终确定水体石油类污染的固有光学特性参数，为建立遥感定量反演水体石油类污染浓度半分析模式提供基础数据。

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