SPECTRAL SIMULATION ON REMOTE SENSING REFLECTANCE OF OIL SAND ALGAE MIXED WATER USING HYDROLIGHT

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ABSTRACT: Remote sensing technology is one of the important means to monitor marine petroleum pollution. Its core physical quantity, remote sensing reflectance $(R_{\rm rs})$, is the comprehensive embodiment of the optical characteristics of water components. Clarifying the influence of oil substance, suspended sediments and chlorophyll on remote sensing reflectance is of great significance for constructing and improving the accuracy of remote sensing inversion model for oil pollution concentration. Based on the apparent and inherent optical data of oilcontaminated water bodies measured in the sea area of Dalian Port in Liaoning in August 2018, we use the radiation transfer model Hydrolight to simulate the R_{rs} of the single component and mixed water of different components by the proportioning method. The results show that: (1) In the water body containing only oil, the shape of the spectral curve of R_{rs} decreases with the increase of wavelength, and its value decreases with the increase of oil concentration in the wavelength range of 400-480 nm, but increases with the increase of oil concentration in the range of 480-700 nm; (2) In the oil-sand mixed water, the R_{rs} value will decrease with the increase of the concentration of oil substances, but the spectral shape will not change with the wavelength; with the increase of suspended sediment concentration, the value of R_{rs} will increase, and the shape of the spectrum will change significantly with the wavelength; (3) In the oil-algae mixed water, the $R_{\rm rs}$ of chlorophyll will increase with the increase of oil concentration; (4) For the oil, sand and algae mixed water body, the R_{rs} spectrum shape is mainly affected by chlorophyll, and secondly by suspended sediment, and the oil substance has little effect on it; (5) The influence of oil on the $R_{\rm rs}$ of the water body should consider the relationship between the concentration of algae and suspended sediment. When the concentration of these two is large, the effect of oil concentration will be masked; (6) The presence of chlorophyll limits the "red shift" phenomenon of suspended sediment; (7) The combined effect of suspended sediment and oil can affect the fluorescence peak of chlorophyll. The research on the R_{rs} of oil-contaminated water by Hydrolight is helpful to enrich the basic research of ocean color remote sensing, and has important theoretical significance for improving the bio-optical model of various water bodies.

1. MANUSCRIPT

Remote sensing reflectance (R_{rs}) is a basic physical quantity of ocean color remote sensing, which contains the optical properties of water layer in a certain depth. R_{rs} is one of the important parameters of remote sensing inversion model of water component concentration. To improve the inversion accuracy of the corresponding model, the contribution of each component to the R_{rs} should be determined. In petroleum polluted water, oil substances as a kind of water color factor affects R_{rs} . At present, great progress has been made in the extraction of petroleum pollution information by remote sensing technology, mainly focusing on the inherent optical properties (IOPs), apparent optical properties (AOPs) and fluorescence characteristics of oil substances in water (Huang *et al.*, 2014, 2017; Krol, 2006). Remote sensing inversion models for oil content in water body were established based on these characteristics (Huang *et al.*, 2016). It is helpful to improve the accuracy of remote sensing inversion of oil concentration model to master the influence of oil substances on R_{rs} in oil sand algae mixed water. And understanding the "role" of oil in water plays an important role in building a bio-optical model with high accuracy for

retrieving the components of oil-bearing water body and promoting the related research of this field. Huang *et al.* (2017) studied the contribution about each component of oil and quartz sand mixed water body to the backscatter coefficient based on the proportioning experimental data, and proposed a separation algorithm to provide technical support for the separation of oil and particle backscattering coefficients. There are many studies on the effects of suspended sediment and chlorophyll on the spectral characteristics of $R_{\rm rs}$. For example, Gitelson (1994) showed that the most significant spectral characteristics of $R_{\rm rs}$ in algae bearing water body was the reflection peak at the wavelength of 685-715 nm, and the secondary peak of chlorophyll appeared near 700 nm, and its position began at 680 nm, and the peak reached the highest near 700 nm, which was closely related to chlorophyll concentration; Han (1994) shows that in the visible and near-infrared band, with the increase of suspended sediment content, the reflectivity of water body increases, and the position of reflection peak moves to the long wave direction. So far there are few reports on the influence and contribution of oil substances to the $R_{\rm rs}$ in the mixed water of oil substances and water components (such as chlorophyll, suspended sediment, etc.).

The radiation transfer model Hydrolight is an internationally recognized effective tool for the study of radiation transfer process in water bodies, and is widely used in the field of international ocean color remote sensing, focusing on the simulation of R_{rs} and underwater light field, as well as the evaluation of remote sensing inversion algorithm (Pahlevan *et al.*, 2017; Sundarabalan *et al.*, 2016). The existing analysis shows that Hydrolight is an effective model for the study of radiative transfer characteristics of petroleum polluted water bodies (Huang *et al.*, 2019). However, in order to apply Hydrolight to the study of radiation transfer characteristics of petroleum polluted water bodies, it is necessary to know the parametric models of IOPs of water components with wavelength and depth, such as absorption coefficient, scattering coefficient and scattering phase function, as well as external environmental parameters (such as wind speed, bottom medium, etc.). Nowadays, the research about the distribution, absorption coefficient and backscattering coefficient of water color factors (chlorophyll, suspended sediment, yellow matter and so on) of class II water body is relatively mature, and many parametric models have been formed (Martin *et al.*, 2017; Charles *et al.*, 2002; Song *et al.*, 2006), which lays a foundation for the simulation of the influence and contribution of oil bearing water components on the R_{rs} .

In this paper, based on the measured data of oil content and absorption coefficient measured in Dalian port, Liaoning Province, combined with some parameters provided by Hydrolight, the R_{rs} spectral simulation of the single and mixed components of oil, suspended sediment and chlorophyll is carried out. It can theoretically explore the influence of oil-bearing water on the variation of R_{rs} spectrum, and provides a reference for improving the accuracy of remote sensing inversion of oil concentration model and developing the characteristics of underwater light field variation of petroleum polluted water.

2. METHOD

2.1 Test Area and Observation Time

The experimental area is located in the sea area of Dalian port, Liaoning Province, where oil pipeline explosion has occurred and crude oil remains. In addition, this area brings certain oil pollution to crude oil terminals, production activities and shipping channels. It is an ideal area for the study of apparent optical properties and inherent optical properties of petroleum water. The measurement time is from August 25th to 27th, 2018, starting at 8:00 and ending at 16:00 every day, with observations every 2 hours.

2.2 Field Data Collection

Oil concentration measurement

The measurement of oil concentration adopts the TD-500D fluorescent oil test of American Turner, and the measuring principle of the equipment is the same as that of molecular fluorescence spectrometry (SL366-2006 Water quality - Determination of petroleum oil – molecular fluorescence spectrometric method). Firstly, the petroleum in the sample is extracted with n-hexane, and then the extracted petroleum is irradiated by ultraviolet light of specific wavelength to release fluorescence. Finally, the concentration of petroleum is calculated according to the close linear relationship between fluorescence intensity and petroleum concentration in a certain range.

Measurement of oil absorption coefficient

The absorption coefficient of oil is determined by the Japanese Hitachi UV-3900 ultraviolet-visible spectrophotometer, and the wavelength is set to 400-700 nm during the measurement. In addition, the sample preparation, measurement and analysis process all follow the NASA water color observation specification. The absorption coefficient of oil-free water sample and oil-bearing water sample are measured respectively, and then the oil-free water sample is taken as the background value, and the absorption coefficient of oil-bearing water sample is subtracted from the absorption coefficient of oil-free water sample to obtain the absorption coefficient of oil substances.

Measurement of backscattering coefficient

The backscattering coefficient was measured by Hydroscat-6 (HS-6) of HOBI labs. The measurement method was carried out according to the technical specification for marine optical survey. In order to reduce the influence of sea water temperature and air bubbles on the measurement results of the instrument, the instrument was immersed in water and placed at rest for 2 min before deploying it. The data measured by HS-6 is taken as the average value of the surface layer (0-0.5m) as the backscattering coefficient.

Calculation of specific absorption coefficient and specific scattering coefficient of oil

The absorption coefficient (a) of oil can be calculated by the specific absorption coefficient (a^*) and the oil concentration (C) (Bricaud et al., 1995), and the relationship is as follows:

$$a = a^* * C \tag{1}$$

Where a is the absorption coefficient (m⁻¹), a^* is the Specific absorption coefficient (m²•mg⁻¹), and C is the concentration (mg/m³).

The backscattering coefficient obtained by HS-6 includes the contributions of oil substances and suspended sediments. The oil sands mixed separation algorithm proposed by Huang *et al.* (2017) is used to obtain the backscattering coefficient of pure oil substances, followed:

$$b_{b,o} = 0.0282 \ln(b_{b,os}) + 0.1703$$
 (2)

Where $b_{b,os}$ are the backscattering coefficients (m⁻¹) of oil and sand mixed water samples, and $b_{b,o}$ are the backscattering coefficients (m⁻¹) of pure oil water bodies.

For the fitting relationship between the mass specific backscattering coefficient and the concentration of petroleum substances proposed by song *et al.* (2010), see formula (3):

$$b_{b,o}^* = A * C^B \tag{3}$$

Among them, A and B are the fitting coefficients, and the specific values are shown in Table 1; $b_{b,o}^*$ is the specific backscattering coefficient of oil substances (m²•mg⁻¹).

Table 1 Petroleum mass-specific backscattering coefficient of different band (song et al., 2010)

Wavelength/nm	442	488	532	589	676	852
A	0.6269	0.5382	0.4566	0.4301	0.3388	0.2381
В	-1.3085	-1.2962	-1.3135	-1.3247	-1.2882	-1.301
\mathbb{R}^2	0.773	0.7646	0.8191	0.8044	0.82	0.8198

Hydrolight simulation parameter setting

In this paper, the function of "a user defined model" provided by Hydrolight 5.3 is selected to simulate the R_{rs} of single water component and mixed water body. Water components include pure water, oil, chlorophyll and suspended sediment. Considering that most orders of magnitude changes in nature are in accordance with the exponential law, the concentrations of oil substances, suspended sediment and chlorophyll are set as 0.1, 0.2, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, and 10.0 mg/L respectively; The specific absorption coefficient and specific scattering coefficient of oil are 0.019 and 0.1472 (m²•mg⁻¹), respectively. The IOPs setting of chlorophyll and suspended sediment is in reference Li et al. (2010). But the difference is that the depth is set as infinite depth; as for the selection of phase function, the typical particle phase function provided by Hydrolight is selected, which is suitable for most radiative transfer operations. Based on petzold (1972) data, Mobley (1993) proposed a method of taking $b_b/b = 0.0183$ and substituting it into Fournier and Ford (FF) volume scattering function is solved to obtain the particle scattering function which varies with wavelength and depth.

3. RESULTS AND DISCUSSION

3.1 Single Component Simulation Results

Changes of R_{rs} spectra of oil

Previous studies have shown that the oil in water before the formation of oil film can be regarded as a water color factor (Huang *et al.*, 2009), so Hydrolight can be used to simulate the $R_{\rm rs}$ of oily water, as shown in Figure 1. It can be seen that according to the spectral characteristics of pure oil water, it can be roughly divided into two characteristic sections: 400-480 nm and 480-700 nm. In the wavelength range of 400-480nm, the $R_{\rm rs}$ decreases with the increase of wavelength λ and also decreases with the increase of oil concentration $C_{\rm oil}$, and the difference of $R_{\rm rs}$ gradually decreases. This is due to the low $C_{\rm oil}$ mainly affected by pure water. With the increase of $C_{\rm oil}$, the characteristics of oil gradually reflect, making the $R_{\rm rs}$ of this band gradually decrease; In the 480-700 nm range, the $R_{\rm rs}$ decreases with the increase of λ , but increases with the increase of $C_{\rm oil}$. Pure water has strong absorption in this band. In addition, the reflection characteristics of oil substances increase with the increase of λ .

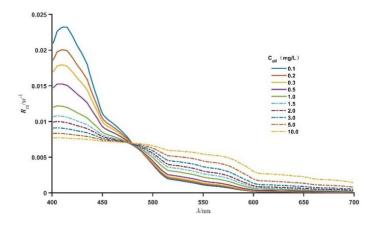


Figure 1 The R_{rs} of oil substances

Changes of R_{rs} spectra of suspended sediment

Figure 2 shows the simulation results of R_{rs} under various suspended sediment concentrations C_{spm} . It can be seen from Figure 2 that: (1) the R_{rs} intersection point of different concentration values is about at 440 nm. Before 440 nm, the shape of R_{rs} spectrum corresponding to each concentration value increases linearly with λ , and the difference of magnitude is not obvious. (2) when the concentration of suspended sediment is higher than 2.0 mg/L, the spectral change of R_{rs} appears obvious peak, and the peak position gradually moves to the long wave direction with the increase of C_{spm} , which is called "red shift" phenomenon; (3) in the range of 560-700 nm, with the increase of λ , the R_{rs} decreases gradually, and the difference of R_{rs} decreasing trend between different C_{spm} becomes larger, which is consistent with the research results of Han *et al.*(1994).

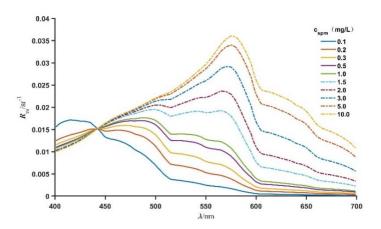


Figure 2 The $R_{\rm rs}$ of suspended sediment

The change of R_{rs} spectrum of chlorophyll

Figure 3 shows the simulation results of $R_{\rm rs}$ at each chlorophyll concentration $C_{\rm chl}$. Figure 3 (a) and (b) are the $R_{\rm rs}$ spectra in the case of low $C_{\rm chl}$ and high $C_{\rm chl}$ respectively. Figure 3 (a) shows that the $R_{\rm rs}$ of low $C_{\rm chl}$ reflects the spectral characteristics of pure water; and figure 3 (b) shows that, under high $C_{\rm chl}$, due to the strong absorption of chlorophyll in violet blue band, there are valley values at 440 nm and 675 nm; and there is a reflection peak at the wavelength range of 510-610 nm, which are caused by the weak absorption of chlorophyll, and the peak gradually decreases as the concentration increases. Additionally, a second reflection peak caused by the fluorescence characteristics of chlorophyll is at the wavelength of 675-700 nm. This is consistent with the results of Gitelson *et al.*(1994).

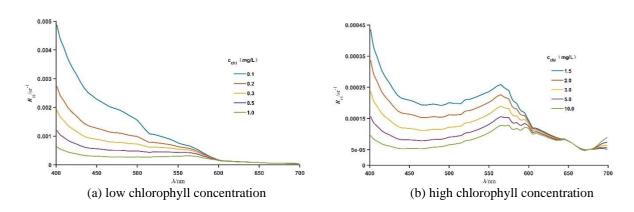


Figure 3 The R_{rs} of suspended sediment

3.2 Mixed Component Simulation Experiment

Variation of R_{rs} spectra in oil sand mixed water

Figure 4 shows the curve of R_{rs} versus C_{spm} when oil concentration C_{oil} is 1.0 and 10.0 mg/L. The results show that: (1) in the oil sand mixed water, with the increase of C_{oil} , the value of R_{rs} will decrease, but the spectral shape with wavelength λ does not change; (2) with the increase of suspended sediment concentration C_{spm} , the peak value of R_{rs} gradually increases and moves to the long wave direction, that is, "red shift", which mainly reflects the characteristics of suspended sediment; (3) with the increase of C_{spm} , the spectral shape is similar to that of suspended sediment, that is, the R_{rs} curve of pure oil changes due to the influence of suspended sediment.

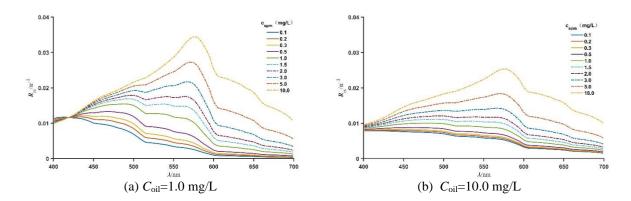


Figure 4 Variation of R_{rs} of oil-sand mixed water with suspended sediment concentration when the oil concentration is fixed

Figure 5 shows the curve of R_{rs} with oil concentration C_{oil} when the suspended sediment concentration C_{spm} is 1.0 and 10.0 mg/L. It can be seen from Figure 5 (a) - (b) that with the increase of C_{oil} , the R_{rs} decreases. This may be because the suspended sediment adsorbs oil substances, which makes the particle size of suspended sediment larger, resulting in the increase of forward scattering and the decrease of backward scattering, thus reducing the R_{rs} . However, the change trend of spectrum with wavelength λ is little affected by C_{oil} , which indicates that the presence of oil only changes the value of R_{rs} , but does not change the variation trend of spectrum.

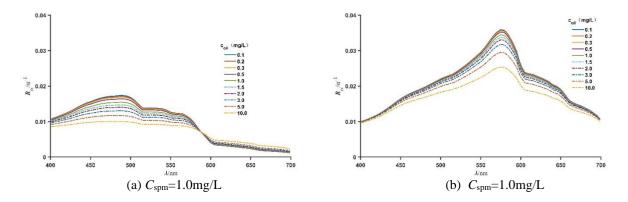


Figure 5 Variation of R_{rs} of oil-sand mixed water with oil concentration when the suspended sediment concentration is fixed

Variation of R_{rs} spectra in oil algae mixed water

The spectral characteristics of oil algae mixed water are mainly reflected in the characteristics of chlorophyll, even at low chlorophyll concentration or high oil concentration. Figure 6 shows the change of R_{rs} with oil concentration C_{oil} when the chlorophyll concentration C_{chl} is constant and not less than 1.0 mg/L. The results show that with the increase of C_{oil} , the R_{rs} gradually increases,

which may be adsorbed on the algal substances with oil substances, making the absorption of algal substances weaken and the reflection enhanced. The existence of oil affected the fluorescence peak of chlorophyll at 670-700 nm. Due to the "blocking" effect of oil substances, the fluorescence peak of chlorophyll decreased with the increase of $C_{\rm chl}$, but the spectral characteristics of chlorophyll were not affected. In conclusion, the spectrum of mixed water is mainly the spectral characteristics of chlorophyll, and the presence of oil increases the $R_{\rm rs}$ of chlorophyll, but does not change the spectral shape.

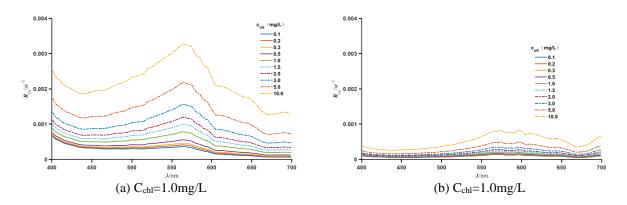
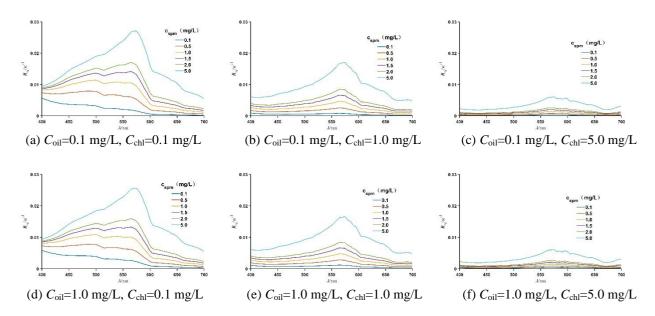


Figure 6 Variation of R_{rs} with oil concentration under fixed chlorophyll concentration

Interaction of oil substances, suspended sediment and chlorophyll

Figure 7 shows the spectral curve of the variation of R_{rs} with C_{spm} under the condition of fixed oil concentration C_{oil} and chlorophyll concentration C_{chl} . C_{oil} is 0.1mg/L in figure 7 (a) - (c), belonging to low concentration. Analysis of them shows that with the increase of C_{chl} , the value of R_{rs} decreases under different C_{spm} , the peak value of 550-600nm always exists, and the shape of R_{rs} spectrum does not change; C_{oil} is 1.0 mg/L in figure 7 (d) - (f), belonging to medium concentration. On the whole, the influence of oil substances on R_{rs} has not been shown, and the shape and value of R_{rs} with the increase of C_{chl} is similar to figure 7 (a) - (c); C_{oil} is 5.0 mg/L in figure 7 (g) - (I), belonging to high concentration. At this time, the shape change of R_{rs} is not affected by C_{oil} , which is consistent with the change curve of low and medium oil concentration, but the influence on the value of R_{rs} is obvious, which all reduces the R_{rs} . This shows that the effect of C_{oil} on R_{rs} appears when the concentration is greater than 1.0 mg/L.



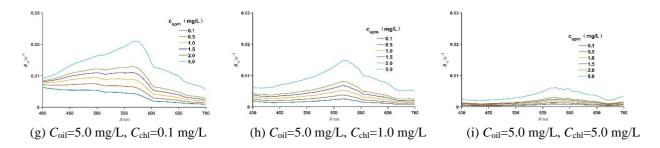


Figure 7 Spectral curve of R_{rs} with suspended sediment concentration under fixed oil and chlorophyll concentration

Figure 8 shows the spectral curve of $R_{\rm rs}$ with the change of chlorophyll concentration $C_{\rm chl}$ under the conditions of fixed oil concentration $C_{\rm oil}$ and suspended sediment concentration $C_{\rm spm}$. Analysis of figure 8 (a) - (c) shows that in the oil sand algae mixed water body, with the increase of $C_{\rm chl}$, the spectral characteristics of the influence of chlorophyll on $R_{\rm rs}$ gradually become prominent, but the value of $R_{\rm rs}$ gradually decreases. In addition, due to the influence of oil and suspended sediment, the characteristics of chlorophyll fluorescence peak change, which may be due to the increase of $C_{\rm chl}$, the absorption of chlorophyll in the visible light band is strengthened, the absorption of oil and the scattering of suspended sediment are weak, resulting in the decrease of $R_{\rm rs}$ with the increase of concentration. It also shows that the contribution of chlorophyll absorption to the $R_{\rm rs}$ is greater than that of the scattering of suspended sediment and oil in the 400-700 nm band.

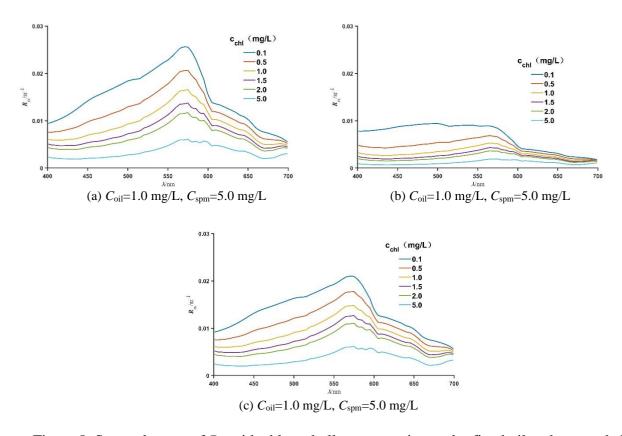


Figure 8 Spectral curve of R_{rs} with chlorophyll concentration under fixed oil and suspended sediment concentration

Figure 9 shows the spectral curve of R_{rs} versus oil concentration C_{oil} in the case of fixed chlorophyll concentration C_{chl} and suspended sediment concentration C_{spm} . Figure 9 (a) shows that the R_{rs} increases with the increase of C_{oil} when the concentration of suspended sediment is low and chlorophyll is high. Meantime, the R_{rs} spectrum reflects the effect of C_{oil} on chlorophyll; Figure 9 (b) shows that when the concentration of suspended sediment is low and the concentration of suspended sediment is high, the R_{rs} gradually decreases with the increase of C_{oil} . The spectral

characteristics reflect the influence of $C_{\rm oil}$ on suspended sediment; Figure 9 (c) shows that when the concentration of both is high, the $R_{\rm rs}$ increases with the increase of $C_{\rm oil}$. The shape of the spectrum is mainly affected by $C_{\rm chl}$. With the increase of $C_{\rm oil}$, the size and shape of the spectrum do not change significantly, that is, under the high concentration of suspended sediment and chlorophyll, the information of oil substances will be covered up. In conclusion, the relationship between $C_{\rm chl}$ and $C_{\rm spm}$ should be considered in the influence of oil on the $R_{\rm rs}$. Rudz et al. (2013) studied the oil-bearing water bodies in the Baltic Sea and found that oil droplets with different particle sizes also increased and decreased the $R_{\rm rs}$, which proves to a certain extent that the influence of oil substances on the $R_{\rm rs}$ can not only increase but also reduce.

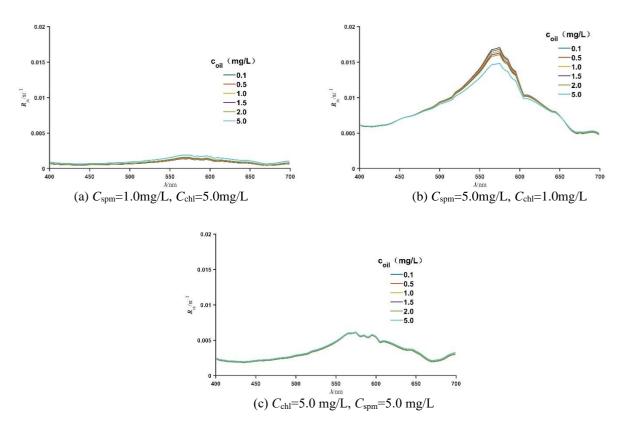


Figure. 9 Spectral curve of R_{rs} with oil concentration under fixed chlorophyll and suspended sediment concentration

4. CONCLUSION

In order to explore the effect of oil substances on $R_{\rm rs}$ of water body, the concentration and inherent optical parameters of oil substance were calculated based on the measured data of Dalian port. The results show that the relationship between the concentration of chlorophyll and suspended sediment should be considered in the influence of oil substances on the $R_{\rm rs}$ of water body. Therefore, different concentrations of chlorophyll and suspended sediment should be considered separately when establishing the model of oil concentration inversion based on $R_{\rm rs}$.

The conclusion obtained in this paper is carried out under ideal conditions and fixed parameters, which may be different from the measured spectra, mainly reflected in: (1) wind speed and tidal current may affect the measurement of inherent optics properties of oil substances; (2) For the calculation of specific absorption coefficient and specific scattering coefficient of oil substances, empirical algorithm and fixed value are used. Its applicability and accuracy need more data to verify.

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