Inversion of CDOM and COD in water using HJ-1/CCD data

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Abstract. With the in-situ measurement data including the absorption coefficient of the CDOM, apparent optical properties and the COD, a regression model was established for retrieving ag(440) based on the remote sensing reflectance of the first and the third band of the environment satellite HJ-1/CCD. The measurement data were obtained at the regions of Panjin, Liaoning province in May 2008 and August 2009. Secondly, the remote sensing regression model was created based on the correlation of the CDOM optical properties and the COD. Finally, using the HJ-1/CCD data from 2009 to 2011 in Liaodong bay, the thematic snapshots of water environmental parameters in coastal waters, such as the CDOM and the COD, were calculated and analyzed. The results showed that: (1) the distribution of the CDOM tends to decrease from offshore areas to distant sea with some zonated character; (2) Most of the retrieved CDOM values vary between 0.2-1.7m-1, which is consistent with the measured value in 2009 and 2010 years; (3) the spatial distribution of the COD has good consistency with the CDOM, also shows a certain zonated distribution in coastal-offshore areas; (4) in September 2009 and September 2011, the values of the COD was basically below 40 mg/L while the values of the COD in September 2010 are relatively higher, mostly above 55 mg/L; (5) in June 2011 and May 2010, the COD values are nearly all larger than 55 mg/L.

1. Introduction
Chromophoric dissolved organic matters (CDOM) are dissolved substances in the water which can pass through the filter of 0.2 μm pore diameter. They are important light absorption materials that exist in all kinds of water. Water organic pollutants belong to chemical pollutants including natural and synthetic organic matters. Most of the organic pollutants can be decomposed and utilized by microbes, which consumes the dissolved oxygen in the water. Therefore, organic pollutants are also named as the oxygen consumption organic matters, the concentration of which is generally measured with chemical oxygen demand (COD). COD represents the amount of oxygen required to oxidize the organic pollutants in the water by chemical oxidants. The more organic pollutants exist in the water, the more oxidants are required. Therefore, COD is an important proxy for reflecting the level of water pollution by organic matters.

At present, the application of remote sensing data in extracting the information of COD has been studied by several authors, the involved satellites include Ocean Color Satellites(SeaWiFs) and land satellites (Landsat), etc. These studies have made certain progresses and been serving the society.[1-3] After detailed analysis of a large number of field observation data from Shuangtaizi River and Liaodong Bay, we found that the COD has an influence on the spectrum of the absorption coefficient.
of the chromophoric dissolved organic matter (CDOM). CDOM is one of the three main water color ingredients, whose optical properties can be detected; the others are chlorophyll a (Chl a) and suspended matters (SPM). The studies on CDOM mainly focus on establishing the absorption spectrum models of the yellow substances and retrieving the concentration of the yellow substances by using the ratio of the wave-bands \[4-5\]; and retrieving the other environmental elements by using these optical properties, such as DOC, TOC, etc \[6-8\].

The ocean remote sensing model of the CDOM has been regularly operated successfully, mainly applying the color sensors of MODIS and MERIS. Based on these studies, we determined the slope of the CDOM index spectrum of the organically polluted water in our reach areas. Using this, we established a remote sensing mode with the first band (blue band) and third band (red band) of HJ - 1/CCD to retrieve the CDOM with an absorption coefficient in 440 nm wavelength. We, therefore, proposed a remote sensing model based on the absorption properties of the CDOM, with which the COD of the water can be retrieved \[9\]. This model has been applied to the water COD monitoring system of the Liaohoe oilfield.

The environment satellites, HJ-1A and HJ-1B, were launched successfully in September 2008. Their primary mission is to collect the information of the ground environment and natural disasters. The equipped 4-band CCD cameras have broad coverage, and have been widely applied on monitoring coastal water environment \[10\].

In this paper, we establish the CDOM and the COD regression model in offshore water by using the HJ-1/CCD image data, then apply this model in the Liaodong Bay to the spatial distribution map of CDOM and COD.

2. Experiment and data

2.1. Experiment description

The experiment is carried out in PanJin city, Liaoning province, where the third largest oil field of China (Liaohe Oilfield) and the largest reed wetland of Asia are located. In November each year, the harvested reed will be sent to the local paper mill for paper manufacture. Both the oil field and the production of paper bring inevitably organic pollutants to the local water system. The experiments lasted from May 21 to 26 2008 and from August 2 to 10 2009, respectively.

2.2. The measurement of the apparent optical properties

The purpose of the water spectrum measurement is to build a regression mode for retrieving CDOM by using the remote sensing reflection ratio. ASD FieldSpec3 spectroradiometer (Wavelength range is 350-2500nm) and the standard plate of 30% reflectivity were used to measure the water spectrum. Also, the above-water method is applied \[11\].

2.3. The measurement of CDOM absorption coefficient

The water samples were first filtrated by the GF/F membranes of 0.45μm pore diameter, then filtrated by the polycarbonate microporous membranes of 0.22μm pore diameter. Finally, the optical density of the filtered samples and pure water were measured in 10cm cuvettes with the spectrometer (HITACHI, JAPAN), the pure water here is used as a reference.

2.4. The measurement of COD value

The microwave sealed digestion method is used to measure the COD (GB11914-89). The principle of the measurement is the digestion system of the Walkley-Black acid. The water samples are digested after being heated by microwave; then the ferroin solution is taken as indicator for the excess potassium dichromate; after the titration of the ammonium ferrous sulfate, the value of CODcr is calculated.
3. Result and discussion

3.1. Establishment of the remote sensing regression model of CDOM

According to the CDOM absorption coefficient and water apparent spectral data obtained from Shuangtaizi River and its estuary in Panjin city of Liaoning province in May 2008 and August 2009, we established a regression model in respect to the CCD sensors of HJ-1. It is given by

$$a_g(440) = 2.47 \times (R_3/R_1) - 0.27$$

where \(a_g(440)\) is the CDOM optical absorption coefficient in 440 nm wavelength in \(m^{-1}\); \(R_1\) and \(R_3\) are the corresponding remote sensing reflectance (sr\(^{-1}\)) of HJ-1/CCD at B1 and B3 waveband.

There are four CCD sensors with the same waveband setting in HJ-1A and HJ-1B satellites. Figure 2 shows the remote sensing reflectance that is simulated based on the accurate measurement of the spectral data, combined with the response function at the corresponding waveband of the sensors. The results show that the difference of the remote sensing reflectance between four CCDs at band 1 (B1:430~490 nm) and band 3 (B3:630~690 nm) is very small. As a result, formula (1) is compatible for four HJ-1/CCD sensor.

3.2. The thematic map of the CDOM spatial distribution in the offshore waters

According to formula (1), the offshore water CDOM spatial distributions at different time are shown in figure 1 (a) ~ (f). They are made from eight snapshots of the HJ-1 / CCD data from 2009 to 2011.

The main source of CDOM in natural environment mainly has two ways: one is the production of water phytoplankton self-degradation; the other is the terrestrial dissolved organic matters. The discharge of life sewage and factory waste water leads to an increase in the CDOM concentration in the water. As shown in figure 1, the distribution of the CDOM tends to decrease from coastal areas to offshore areas. In other words, the high concentration of the CDOM in the coastal area is due to the terrestrial influence plus the effect of the sewage discharge. Overall, most of the retrieved CDOM values vary between 0.2-1.7m\(^{-1}\), which is consistent with the in-situ measured values in 2009 and 2010 years. Moreover, the spatial distribution of the CDOM shows zonated character.
Comparing the three images from the same month in different years, namely, September 15, 2009, September 28, 2010 and September 6, 2011, we see that in 2009, the values of the CDOM are mostly between 0.68 and 0.80 m$^{-1}$, with no value exceeding 1.8 m$^{-1}$, indicating the lower CDOM concentration; in 2010, the zonated distribution is obvious; in 2011, most of the values are between 0.52 and 1.00 m$^{-1}$, only a few values exceed 1.8 m$^{-1}$. However, the interannual variability is large. In June 2010 and May 2011, the values of the CDOM are all larger than 1.3 m$^{-1}$, indicating the higher CDOM concentration in the water.

### 3.3. The establishment of regression modes of COD

Tab. 1 shows the correlation between the COD and the slope of the absorption spectrum S of the CDOM, the CDOM optical absorption coefficient in 440 nm wavelength $a_g(440)$, ln($a_g(440)$) and ln($a_g(440)\times S$) (70 samples). In Tab. 1, except for the correlation between the COD and spectral slope S, the correlation coefficients are all larger than 0.9.

| spectral slopes S | $a_g(440)$ | ln($a_g(440)$) | ln($a_g(440)\times S$) |
|------------------|-----------|----------------|----------------------|
| 0.0464           | 0.9083    | 0.925          | 0.9279               |

Based on the correlation of the CDOM’s optical properties and the COD, a new model of the COD and $a_g(440)$ of the CDOM was created as follows,

$$y = 2.583936X^2 + 9.5481X + 0.52127 \quad (R^2=0.868) \quad (2)$$

where $y$ is COD (mg/L), $X$ is CDOM’S concentration obtained from Eq.1 (the absorption coefficient in 440nm wavelength, m$^{-1}$).

### 3.4. COD’s spatial and temporal distribution in offshore waters

Eq. 2 was applied to eight scene of HJ-1/CCD data from the year 2009 to 2011, and the thematic snapshots of the temporal and spatial distribution of the COD in the offshore waters were made, as shown in figure 2 (a) ~ (f). The snapshots shows that (1) The spatial distribution of the COD is in a good agreement with the CDOM; (2) The COD presents spatially a certain zonated distribution in coastal-offshore areas; (3) In September 2009 and September 2011, the values of the COD was basically below 40 mg/L while the values of the COD in September 2010 are relatively higher, mostly above 55 mg/L; (4) In June 2011 and May 2010, the COD values are nearly all larger than 55 mg/L.
Chemical oxygen demand (COD) reflects primarily to what extent the water is polluted by organic matters. The influence of the COD on the water absorption coefficient mainly manifests on the absorption coefficient of the chromophoric dissolved organic matter (CDOM); therefore, it is feasible to use CDOM’s optical properties to obtain the COD by a regression model. With the analysis of a large number of field observation data, the averaged spectral slope of the CDOM in the study area is determined as 0.011378(nm^-1). According to the first band (blue) and the third band (red) of HJ-1/CCD, a remote sensing regression model of the CDOM’s absorption coefficient in 440nm is established, and the remote sensing regression model of the COD based on the CDOM absorption spectral characteristics is further established.

Figure 2. Spatial distribution of COD in Liaodong Bay

4. Conclusion
Chemical oxygen demand (COD) reflects primarily to what extent the water is polluted by organic matters. The influence of the COD on the water absorption coefficient mainly manifests on the absorption coefficient of the chromophoric dissolved organic matter (CDOM); therefore, it is feasible to use CDOM’s optical properties to obtain the COD by a regression model. With the analysis of a large number of field observation data, the averaged spectral slope of the CDOM in the study area is determined as 0.011378(nm^-1). According to the first band (blue) and the third band (red) of HJ-1/CCD, a remote sensing regression model of the CDOM’s absorption coefficient in 440nm is established, and the remote sensing regression model of the COD based on the CDOM absorption spectral characteristics is further established.
The regression model is simple and easy to operate, and also more suitable as a regular operation model. The COD values of water can be computed if \( a_g \) (440) of the CDOM is calculated using remote sensing reflectance and spectral slope \( S \) in the study area. The establishment of the model can promote the application of color remote sensing in monitoring the water environment pollution components and provide a new remote sensing method in monitoring organic pollution in the water.

A linear regression model that uses the CDOM optical characteristics to calculate the COD information in the water was preliminary established. However, several questions, for example, which type of the models (linear or nonlinear) can more accurately extract the COD information of the organic pollution from the optical characteristics of the CDOM, and how to build the remote sensing models that use broadband and non-water-color landsat sensors (such as HJ - 1 satellite) to obtain the absorption coefficient of the CDOM in 440 nm wavelength, still needs to be addressed with more observational data and further research.

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