SPECTRAL AND SPATIAL DISTRIBUTION CHARACTERISTICS OF SPECIFIC ABSORPTION COEFFICIENT OF PETROLEUM-POLLUTED WATER

Miaofen Huang (1), Yang Liu(2), Xufeng Xing(1), Weijian Luo (1), Junjie Yang (1)

[1] Guangdong Ocean University, No. 1 Haida Road, Mazhang District, Zhanjiang, 524088, China
[2] PetroChina Exploration & Development Research Institute, No. 20 Xueyuan Road, Haidian District, Beijing, 100083, China
Email: hmf808@163.com; liuyang_rs@petrochina.com.cn; 4918585@qq.com; lwjluo@sina.com; junjie_y@foxmail.com

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ABSTRACT: Specific absorption coefficient is a physical quantity representing the absorption capacity of a component, which can be defined as the ratio of the absorption coefficient of a component to its concentration. It is an important inherent optical parameter of water in water color remote sensing. Data measured in the Dalian Port in Liaoning province of China on August 25-26, 2018 and May 15-16, 2019 are used. The data include remote sensing reflectance measured at different site and different time, and absorption coefficient and concentration of petroleum at different depths. The spectral variation of specific absorption coefficient of petroleum substances in water and the vertical distribution of specific absorption coefficient in characteristic bands are analyzed. The inversion model of CDOM absorption coefficient and petroleum concentration of water body based on remote sensing reflectance, was applied to Landsat 8 remote sensing data. The thematic map of specific absorption coefficient of petroleum substances in the reference band (440 nm) is obtained and analyzed the horizontal distribution characteristics. The results show that: (1) the spectral distribution characteristics of specific absorption coefficients of petroleum substances at different site and different time in the same sea area is still a natural exponential attenuation function. Due to the influence of tides, the concentration of petroleum substances is different at different time, and the spectral slopes corresponding to specific absorption coefficient are different. (2) The specific absorption coefficient of petroleum substances in the reference band has no obvious variation pattern in the vertical direction. This is mainly due to the fact that the flow directions at different depths were different at different moments, resulting in different variations at different depths. (3) There is an obvious pattern for the horizontal variation of specific absorption coefficient of petroleum substances in the reference band. The spatial distribution maps of petroleum concentration and specific absorption coefficient obtained by remote sensing are compared. The results show that in the areas with high petroleum concentration, the specific absorption coefficient of petroleum substances in the reference band (440 nm) is high, while in the areas with low petroleum concentration, the specific absorption coefficient of petroleum substances in the reference band (440 nm) is low.

1. INTRODUCTION

Specific absorption coefficient is a physical quantity representing the absorption capacity of a component, which can be defined as the ratio of the absorption coefficient of a component to its concentration. Generally, Hydorlight is one of the most popular radiative transfer models to simulate underwater light field with various water constituents in water color remote sensing. The simulation using Hydrolight needs input of absorption coefficient, scattering coefficient and scattering phase function of each water constituent. One common method to get absorption coefficient of a component is using the product of the component's given specific absorption coefficient and concentration, the prerequisite condition of the method is the hypothesis that specific absorption coefficient is a known constant (Huang et al., 2014; Wang et al., 2005; Wang et al., 2013). There are specifications for the measurement of absorption coefficient and concentration of phytoplankton and inorganic particulates, so most studies focused on absorption coefficient of these two water constituents (Wang et al., 2005; Wang et al., 2013). However, lots of research found that the specific absorption coefficient of phytoplankton is a bio-variable, and their spectral distribution and shape varies clearly. Moreover, the specific absorption coefficient of phytoplankton $a^*_{ph}(\lambda)$ always decreases with chlorophyll a concentration increasing. Several researches of lakes showed that the specific absorption coefficient of non-pigment particles reaches the maximum in autumn, and the specific absorption coefficient of non-algae particles is less affected by seasons (Huang et al., 2009; Li et al., 2009; Ma et al., 2009; Robinson et al., 2017; Sun et al., 2009; Wang et al., 2005). Thus, it can be seen that specific absorption coefficient is an important parameter in inherent optical properties, and it is essential to understanding its spectral and spatiotemporal variation characteristics.

Petroleum-polluted water body has different optical properties than natural water, owing to the petroleum substances can change the specific absorption coefficient characteristics. Hydrolight can be used for the study of radiative transfer property in petroleum-polluted water body. When radiative transfer simulated by Hydrolight, absorption coefficient can be calculated by the given specific absorption coefficient and concentration of petroleum substance. Huang et al., (2010), and Huang et al., (2016) indicated that petroleum substances can influence the absorption coefficient of CDOM, according to the characteristics of petroleum substances in water, and absorption coefficient of colored scraps can be retrieved by quasi-analytical algorithm (QAA). Furthermore, they also developed an algorithm to separate the absorption coefficient of petroleum substances and CDOM, to extract petroleum substances absorption coefficient at last.

Field data which were used to analyze absorption coefficient spectra and vertical distribution of petroleum substances in petroleum-polluted water body, were collected between August 25 to 27, 2018, and May 15 to 16 2019, in Dalian Port and Yuan island which is located in the southeast of Dalian Port, in order to extend the study of inherent optical properties in water color remote sensing and to provide primary input data for the simulation of radiative transfer of petroleum-polluted water body using Hydrolight.

2. SURVEYING DESCRIPTION AND DATA PROCESSING

2.1 Surveying Area and Time

There are a group of petrochemical enterprises distributed in Dagushan peninsula which is located in Dalian Port, China. Hence, the petrochemical production and ship traffic inevitably bring about petroleum pollution in this area.

Survey was conducted per hour from 7:00 to 17:00 o 'clock at each site from August 25 to 27, 2018, and May 15 to 16, 2019. And then we numbered them in site and time sequence, such as A1 refers to the data was collected at 7:00 o 'clock at site A, and B4 refers to the data was gathered at 10:00 o 'clock at site B.

2.2 Data Measurement Method

2.2.1 Absorption Coefficient: Due to petroleum substances can influence absorption coefficient of CDOM and there is no given specification to measure petroleum substances absorption coefficient, the study measured CDOM absorption coefficient instead of petroleum substances absorption coefficient according to *The specification for marine monitoring*. So the absorption coefficient includes the contribution of CDOM and petroleum substances together, which is denoted as $a_{g/oil}(\lambda)$. In the following, the paper denotes absorption coefficient and specific absorption coefficient contributed by CDOM and petroleum substances together as mixed absorption coefficient and mixed specific absorption coefficient respectively.

2.2.2 Remote Sensing Reflectance Measurement: The study adopts above-water measurement method to measure remote sensing reflectance, and water spectra measured by instrument of visible-near infrared spectrometer (ASD FieldSpec3; 350~2500 nm) made by ASD, USA, and reference board is a standard board with 30% reflectivity.

2.2.3 Petroleum Substances Concentration Measurement: In this study, portable TD-500D (Turner Designs, USA) which is applicable in *The specification for marine monitoring*, (*GB 17378.3-1998)* is used for the measurement of petroleum concentration. Before using the instrument for measurement, standard oil samples need to be produced by n-hexane and petroleum reference substance first, to calibrate the solid samples of the instrument, which is used for instrument calibration before field measurement. Particularly, standard oil samples are provided by National Marine Environmental Monitoring Center.

2.3 Calculation of Specific Absorption Coefficient for Petroleum Substances

2.2.1 has mentioned that in-situ absorption coefficient includes the contribution of CDOM and petroleum substances together, denoted as mixed absorption coefficient $a_{g/oil}(\lambda)$. It is essential to separate them first in order to get petroleum substances absorption coefficient. Huang et al., (2010) indicated that the parameterized model of absorption coefficient of CDOM and petroleum substances can be expressed as Equation (1).

$$a_{g/oil}(\lambda) = a_{g/oil}(\lambda_0)\exp[-S_{g/oil}(\lambda-\lambda_0)] \tag{1}$$

Where $a_{g/oil}(\lambda)$ is the mixed absorption coefficient at wavelength λ (m^{-1}), $a_{g/oil}(\lambda_0)$ is the mixed absorption coefficient at reference wavelength λ_0 (m^{-1}), λ_0 equals to 440nm generally, and $S_{g/oil}$ is the slope of absorption spectra. Equation (1) shows that $a_{g/oil}(\lambda)$ can be calculated out only if $a_{g/oil}(440)$ and $S_{g/oil}$ are known in advance. Huang et al., (2015b) developed Equation (2) to compute $a_g(440)$ using remote sensing reflectance of blue band (430~490nm) and red band (630~690nm).

$$a_g\ (440) = 2.47*(R3/R1)-0.27 \tag{2}$$

Where a_g (440) is the absorption coefficient of CDOM at reference wavelength 440 (m^{-1}), and R1 and R3 are remote sensing reflectance of blue band (430~490nm) and red band (630~690nm) respectively (sr^{-1}). The results computed by Equation (2) is slightly large, so the equation need to be corrected before using in Dalian Port waters. Remote sensing reflectance and absorption coefficient of CDOM which was measured around Yuan island, located in the southeast of Dalian Port, from May 15 to 16, 2019, are used for the correction of Equation (2), to get Equation (3).

$$a_g(440) = 1.72*(R3/R1)-0.41 \tag{3}$$

Bring the measured remote sensing reflectance into the Equation (3) to calculate $a_g(440)$, and with the help of measured $a_{g/oil}(440)$ and Equation (4), $a_{oil}(440)$ can be calculated out

$$a_{oil}\ (440) = a_{g/oil}(440) - a_g(440) \tag{4}$$

Huang et al. (2010) also pointed out that the value of S_{oil} is 0.023 (m^{-1}). a_{oil} (λ) can be calculated out by Equation (1) naturally. Followed by the definition of specific absorption coefficient shown in Equation (5),

$$a_{oil}{}^*(\lambda) = a_{oil}\ (\lambda)/Coil \tag{5}$$

where $a_{oil}{}^*(\lambda)$ is specific absorption coefficient of petroleum substances [L/(mg·m)], Coil is petroleum substances concentration, and $a_{oil}(\lambda)$ is absorption coefficient of petroleum substances (m^{-1}), the petroleum substances specific absorption coefficient can be calculated out logically.

2.4 Remote Sensing Data Preprocessing and Processing

Operational Land Imager (OLI), which is one of two main sensors loaded in Landsat 8, will collect images using 8 spectral bands at different wavelengths of visible near-infrared and shortwave light to observe a 185 kilometer wide swath of the Earth in 15-30 meter resolution covering wide areas of the Earth's landscape while providing sufficient resolution to distinguish features like urban centers, farms, forests and other land uses. The sensor's information is listed in Table 1. Band 9 are designed for atmospheric correction and revisiting period is 16 days (USGS, 2013).

Table 1. LANDSAT 8 Satellite Sensor Specifications

Band # and Type	Bandwidth (nm)	Resolution (m)
Band 1 Coastal	433 - 453	30
Band 2 Blue	450 - 515	30
Band 3 Green	525 - 600	30
Band 4 Red	630 - 680	30
Band 5 NIR	845 - 885	30
Band 6 SWIR 1	1570 - 1650	30
Band 7 SWIR 2	2110 - 2290	30
Band 9 Cirrus	1360 - 1380	30

The remote sensing data of Dalian Port in August 25, 2018 that the paper used is sensed by Landsat8/OLI, and are downloaded from official website: https://earthexplorer.usgs.gov/.The data are level 1 production, need to be calibrated radiometrically and corrected by FLAASH module provided by ENVI, to get remote sensing reflectance. Sequentially, normalize the remote sensing reflectance according to Equation (6), to get normalized remote sensing reflectance R'_{rs} (dimensionless).

$$R'_{rs} = \frac{R_{rs,i}}{\sum_{i=1}^{n} R_{rs,i}} \tag{6}$$

Where $R'_{rs,i}$ is remote sensing reflectance at *i* band. The remote sensing data are sensed by OLI, so n equals to 5. Equation (6) expresses that remote sensing reflectance at each band divided by the sum of remote sensing reflectance of all bands. It not only can zoom the original remote sensing reflectance into the range of 0 ~ 1, but also can present remote sensing reflectance as a dimensionless variable. Huang et al., (2015a) proposed Normalized Difference Petroleum Remote Sensing Reflectance Index (NDPRI) which is the ratio of the difference to the sum of normalized remote sensing reflectance at green band and near infrared band (Equation (7)), to determine whether the water is contaminated by petroleum.

$$NDPRI = (R_{rs,G}' - R_{rs,NIR}')/(R_{rs,G}' + R_{rs,NIR}') \tag{7}$$

Where $R_{rs,G}'$ is normalized remote sensing reflectance at green (G) band (dimensionless), that is normalized remote sensing reflectance of Band 3 for Landsat 8/OLI data, and $R_{rs,NIR}'$ is normalized remote sensing reflectance at near infrared (NIR) band (dimensionless), that is normalized remote sensing reflectance of Band 5 for Landsat 8/OLI data. The research indicated that water body had been contaminated by petroleum, if *NDPRI* of corresponding pixel less than 0.49.

Huang et al., (2015a) also developed a remote sensing model (Equation (8)) to inverse the petroleum concentration using *NDPRI.*

$$Petr\_con = -7.4629\ln(x) - 4.6031 \tag{8}$$

Where *Petr_con* is petroleum concentration (mg/L), *x* is *NDPRI* (dimensionless). Petroleum concentration of sea surface at Dalian Port can be inversed by the model, in which *NDPRI* is calculated by the remote sensing data in Dalian Port on August 25, 2018. However, the results inversed by the model is slightly high, due to the parameters of Equation (8) was determined by petroleum concentration of water body sampled from sewage treatment plant of Liaohe oilfield in Panjin, China and corresponding matching experiments, in which petroleum concentration is high generally. So, before using the model to this study area, it needs to be corrected first. In-situ spectra data can be used for band simulation of Landsat 8/OLI, in order to correct parameter of Equation (8) and get appropriate inverse model of Dalian Port (Equation (9)).

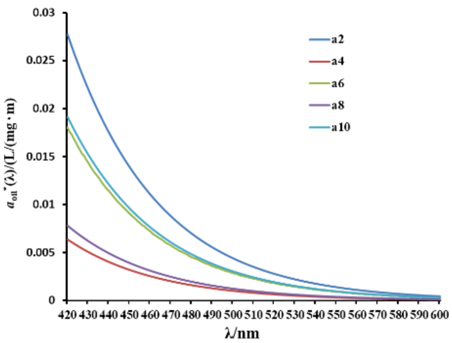
$$Petr\_con = -6.019\ln(x) - 9.89 \tag{9}$$

So far, the petroleum concentration and absorption coefficient both can be inversed by remote sensing model, then Equation (5) also can be used for the calculation of specific absorption coefficient at reference band, to make the thematic map of absorption coefficient at reference band at sea surface.

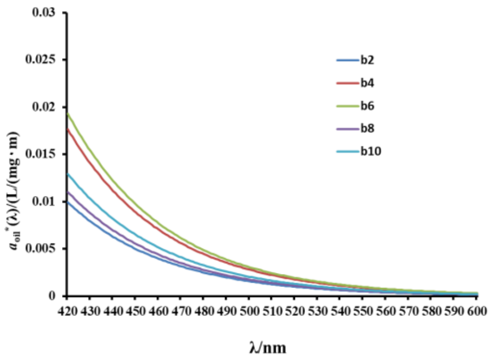
3. RESULTS AND DISCUSSION

3.1 Spectral Distribution of Specific Absorption Coefficient for Petroleum Substances

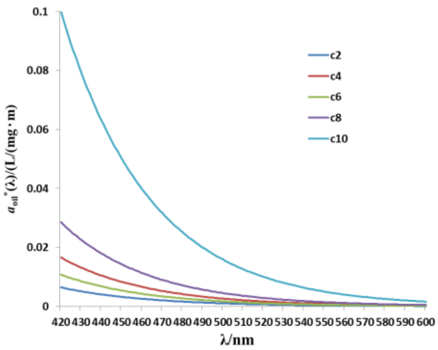
Put in-situ spectra data into Equation (3) to get $a_g(440)$, and also put in-situ $a_{g/oil}(440)$ into Equation (4) to get $a_{oil}(440)$. Set the slope of petroleum substances spectra as 0.023 (nm^{-1}), and put it into Equation (1) to get $a_{oil}(\lambda)$. At last, Specific absorption coefficient of petroleum substances $a_{oil}*(\lambda)$ can be calculated out by Equation (5) and given variables above. Figure 1 shows part of petroleum substances specific absorption coefficient of three site. Table 2 shows petroleum concentration, tide and current of each site. Figure 1 also indicates that specific absorption coefficient spectra of petroleum substances is still a natural exponential attenuation function in this sea area.



(a) Site A



(b) Site B



(c) Site C

Fig. 1 Specific absorption coefficient spectra of petroleum substances at Site A, B and C

Table 2. Petroleum concentration and tide of each site at different time

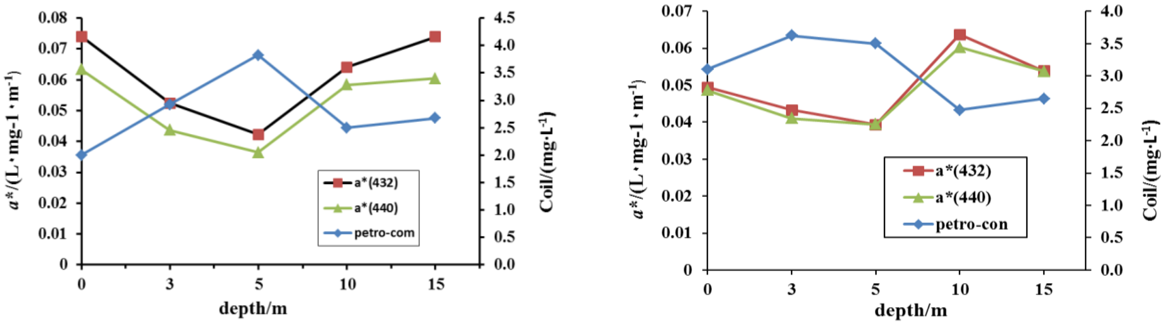
Site	Petroleum concentration(mg/L)	Height(m) (Based on sea level)	Tidal process	Direction (North is 0º)	Velocity (cm/s)
a2	2	1.42	flow	249	51
a4	1.3	1.74	ebb	279	65
a6	2.5	0.89	ebb	117	27
a8	2.1	-0.37	ebb	90	54
a10	3	-0.94	ebb	72	49
b2	4.4	1.16	flow	139	51
b4	3.1	1.85	slack	185	76
b6	4.6	1.21	ebb	200	74
b8	7.8	-0.09	ebb	253	25
b10	3.1	-0.97	ebb	29	55
c2	4.7	0.82	flow	152	28
c4	4.2	1.83	flow	256	49
c6	7.8	1.47	ebb	255	85
c8	0.4	0.21	ebb	251	53
c10	0.2	-0.92	ebb	55	24

Table 2 shows that the height, velocity and direction of tide at each site and different time are different. Different sources of water lead to various water constituents, thus petroleum concentration varied as well due to the influence of tide. Figure 1 and Table 2 together shows that the specific absorption coefficient of petroleum substances vary with petroleum concentration changing, indeed, there are even great discrepancy between these spectra. For instance, the petroleum concentration of c10 is 0.2mg/L, and its specific absorption coefficient reaches 0.1 L/(mg·m) at 420nm, which is higher than the results of Site C at any other time. In addition, petroleum concentration of c10 is less, owing to the site C is located in the east of an island and waters comes from sources around the island. In the meantime, ebb occurs, the current direction is northeast and the current runs slow.

3.2 Analysis of Vertical Characteristics of Mixed Specific Absorption Coefficient at Reference Band in Petroleum-Polluted Water Body

In-situ mixed absorption coefficient are measured at depth of 0, 3, 5, 10 and 15m below the sea surface at Dalian Port. CDOM absorption coefficient can be inversed by remote sensing reflectance at sea surface, use to subtract absorption coefficient of CDOM to get absorption coefficient of petroleum substances at sea surface. However, CDOM absorption coefficient at depth of 3, 5, 10 and 15m below the sea surface cannot be retrieved by remote sensing, so the petroleum substances absorption coefficient cannot be extracted at those depth. As a result, the study analyzed vertical variations of mixed absorption coefficient instead. In addition, the study chose 432nm and 440nm as reference bands which are generally used in ocean color remote sensing.

$a_g(440)$ can be used to represent CDOM concentration in remote sensing. Add $a_g(440)$ with petroleum concentration together as total concentration of CDOM and petroleum substances. With given mixed absorption coefficient at depths of 0, 3, 5, 10 and 15m, the mixed specific absorption coefficient can be calculated out by Equation (5). Figure 2 shows that mixed specific absorption coefficient at reference band (432 and 440nm) and petroleum concentration vary with depth. Figure 2 also shows that mixed specific absorption coefficient at 432nm and 440nm vary with depth similarly, in contrast to petroleum concentration. That is at the depth with high petroleum concentration, mixed specific absorption coefficient is low, while at the depth with low petroleum concentration, mixed specific absorption coefficient is high. The inhomogeneous distribution of petroleum substances in vertical profile owing to waters comes from different sources driven by changing direction and velocity of current, leads to inhomogeneous characteristics of mixed specific absorption coefficient in corresponding water column. In a word, the mixed specific absorption coefficient at the reference band has no obvious variation pattern in vertical profile.



(a) Site A2 (b) Site B4

Fig. 2 $a^*_{g/oil}(432)$, $a^*_{g/oil}(440)$ and petroleum concentration vary with depth

3.3 Horizontal distribution of petroleum substances specific absorption coefficient at reference bands

Petroleum concentration of Dalian Port can be inversed by Equation (9), using remote sensing data of Landsat 8 sensed on August 25, 2018. Figure 3 shows the spatial distribution of petroleum concentration at sea surface. There is a significant variation of petroleum concentration in spatial distribution at Dalian Port. And petroleum concentration is between 0.4~5mg/L. Moreover, petroleum concentration is low around coast, while it is high in the east and north of Sanshan island.

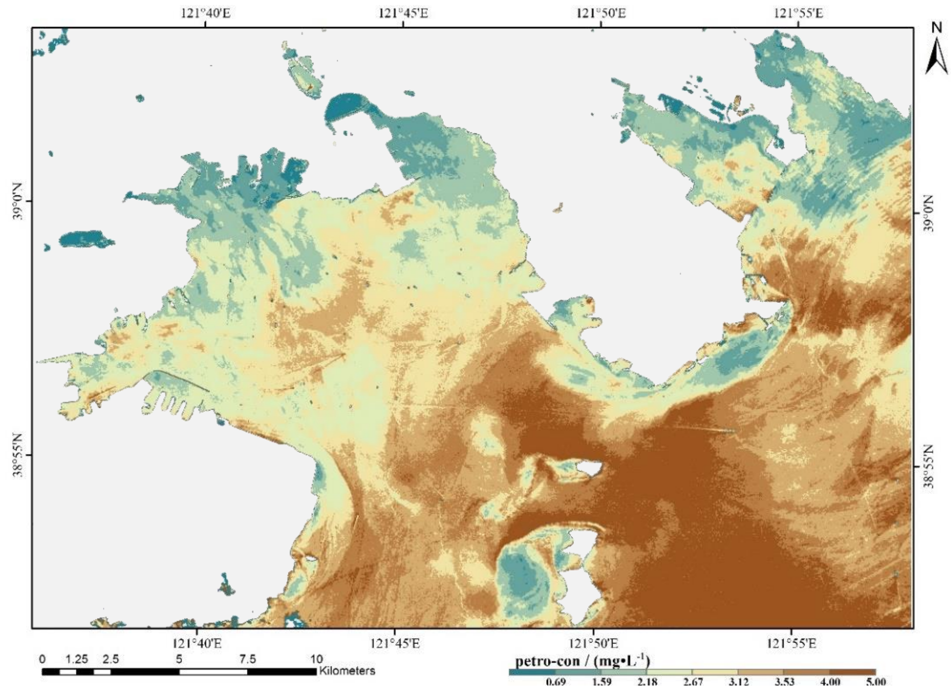


Fig. 3 Spatial distribution of petroleum concentration at Dalian Port

Huang et al. (2016) developed a new algorithm to retrieve $a_{g/oil}(\lambda)$. Firstly, retrieve r_{rs} with remote sensing data by Equation (10). Secondly, compute remote sensing reflectance just beneath water surface $u(\lambda)$ with the retrieved $r_{rs}(\lambda)$ by Equation (11). Thirdly, compute absorption coefficient of water body $a(\lambda)$ and total backscattering coefficient $b_{bp}(\lambda)$ by Equation (12) ~ (18). Lastly, Compute absorption coefficient of CDOM at reference wavelength 440nm $a_{d/g}(440)$ by Equation (19) ~ (21) subsequently. In this study, we use $a_{d/g/oil}(440)$ instead $a_{d/g}(440)$ for petroleum-polluted water body.

$$r_{rs}(\lambda)=R_{rs}(\lambda)/(0.52+1.7R_{rs}(\lambda)) \tag{10}$$

$$u(\lambda)=\{-g_0+[g_0^2+4g_1r_{rs}(\lambda)]^{(1/2)}\}/(2g_1) \tag{11}$$

$$p=\ln[r_{rs}(440)/r_{rs}(555)] \tag{12}$$

$$a(440)_i=\exp(-2.0-1.4p+0.2p^2) \tag{13}$$

$$a(555)=0.0596+0.2[a(440)_i-0.01] \tag{14}$$

$$b_{bp}(555)=\{u(555)a(555)/[1-u(555)]\}-b_{bw}(555) \tag{15}$$

$$Y=2.2\{1-1.2\exp[-0.9(r_{rs}(440)/r_{rs}(555)\} \tag{16}$$

$$b_{bp}(\lambda)=b_{bp}(555)(555/\lambda)^{Y} \tag{17}$$

$$a(\lambda)=[1-u(\lambda)][b_{bw}(\lambda)+b_{bp}(\lambda)]/\mathrm{u}(\lambda) \tag{18}$$

$$\zeta=0.71+0.06/[0.8+r_{rs}(440)/r_{rs}(555)] \tag{19}$$

$$\xi=\exp[S(440-410)] \tag{20}$$

$$a_{d/g/oil}(440)=\frac{[a(410)-\zeta a(440)]-[a_{w}(410)-\zeta a_{w}(440)]}{(\xi-\zeta)} \tag{21}$$

Where $r_{rs}(\lambda)$ is remote sensing reflectance just above water surface (sr^{-1}), $u(\lambda)$ is remote sensing reflectance just beneath water suface (sr^{-1}), u is the ratio of backscattering coefficient and the sum of absorption coefficient and backscattering coefficient (dimensionless), Y is spectral index of backscattering coefficient of suspended particulates, and the other variables has the same meaning as above.

Mixed absorption coefficient $a_{g/oil}(\lambda)$ is the result that $a_{d/g/oil}(\lambda)$ retrieved by QAA algorithm subtract $a_d(\lambda)$ retrieved by Equation (22).

$$a_{g/oil}(\lambda)=a_{d/g/oil}(\lambda)-a_{d}(\lambda) \tag{22}$$

$$a_{d}(440)=0.6771b_{bp}(555)^{2}-0.2796b_{bp}(555)+0.3126 \quad (R^{2}=0.8318, n=54) \tag{23}$$

Finally, specific absorption coefficient $a^{*}_{oil}(440)$ can be retrieved by Equation (5) using $a_{g/oil}(440)$ and petroleum concentration in Figure 3 and Figure 4 shows spatial distribution of specific absorption coefficient of petroleum substances at reference band in Dalian Port.

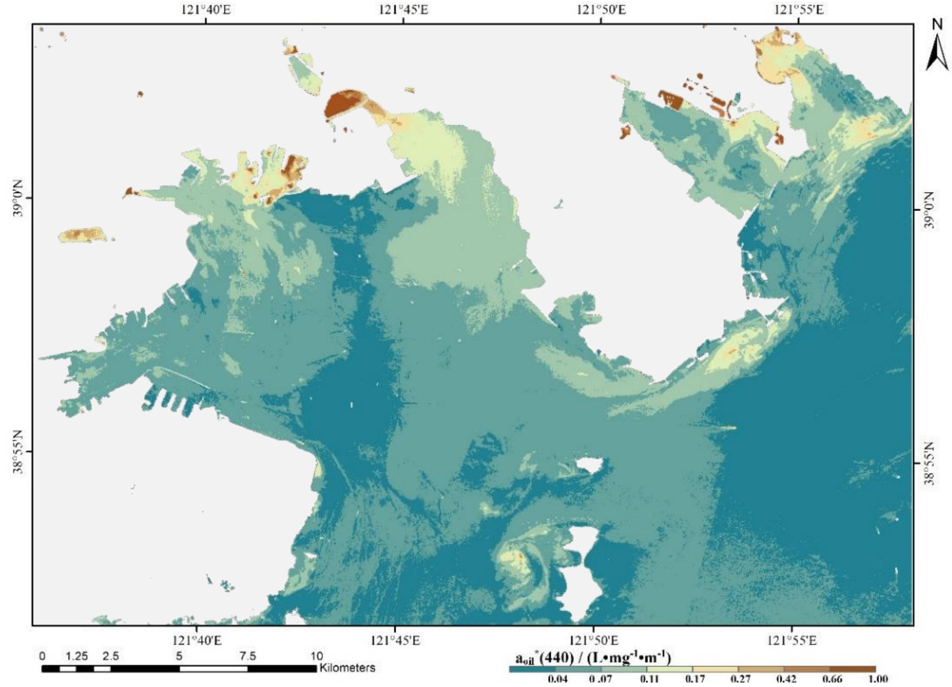


Fig. 4 Spatial distribution of specific absorption coefficient of petroleum substances at reference band in Dalian Port

Figure 3 and Figure 4 indicates that in the areas with high petroleum concentration, the specific absorption coefficient of petroleum substances at the reference band (440 nm) is low, while in the areas with low petroleum concentration, the specific absorption coefficient of petroleum substances in the reference band (440 nm) is high. There is an obvious pattern for the horizontal variation of specific absorption coefficient of petroleum substances in the reference band, and it has close relation with petroleum concentration.

4. CONCLUSIONS

Specific absorption coefficient is the primary parameter to study optical properties of water body and bio-optical model. Understanding specific absorption coefficient variation characteristics will help us improve the simulation accuracy of radiative transfer model in water body. The study used field data and remote sensing model to analyze spectra distribution characteristics and spatial variation of specific absorption coefficient in petroleum-polluted water body. The analysis shows that the specific absorption coefficient spectra of petroleum substances is still a natural exponential attenuation function in the area. The variation of current direction and velocity at depth could influence the vertical distribution of petroleum substances, and it also makes an inhomogeneous distribution of specific absorption coefficient in petroleum-polluted water body at reference band in the corresponding water column. Nevertheless, the specific absorption coefficient of petroleum substances at reference band varies with petroleum concentration obviously, specifically there is negative correlation between them at sea surface.

Owing to that absorption coefficient of CDOM at depths 3, 5, 10 and 15m at reference band cannot detected and retrieved by remote sensing technology at present, so the absorption coefficient of petroleum substances at these depths cannot retrieved either. The specific absorption coefficient used for analysis of vertical variation is contributed by CDOM and petroleum substances together, thus the results may exist deviation compared with specific absorption coefficient analysis contributed only by petroleum substances theoretically, but it also obeys natural exponential attenuation function pattern in the study spectral wavelength. Next, we will concentrate on the work to separate absorption coefficient of CDOM and petroleum substances at depths beneath water surface.

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