

VERTICAL VARIATION CHARACTERISTICS OF PETROLEUM CONCENTRATION AND BACKSCATTER COEFFICIENT IN PETROLEUM- POLLUTED WATER BODY

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ABSTRACT: August 25th to 27th, 2018, in-situ data which was used to analyze the vertical variations characteristics of petroleum concentration and backscattering coefficient, was collected at Dalian port which is located in Liaoning province, China. The analytical results of these data drew three conclusions. First of all, the regime of vertical variation of petroleum concentration is complicated, and the concentration does not decrease or increase gradually with depth increasing, due to the fact that ebb and flow of different time and stations could influence current in different way. Secondly, the minimum and second minimum of backscattering coefficient of each station are at 700nm and 590nm respectively. By the way, magnitude of backscattering coefficient is similar at 420nm, 442nm, 470nm and 510nm, and backscattering coefficients of these stations vary with depth consistently. Finally, there are three kinds of vertical variations of total backscattering coefficient in this study area, they are abrupt growth, steady growth and single hump. Abrupt growth backscattering coefficient varies less in the water column but growth quickly near 11.5m below the sea surface. Steady growth backscattering coefficient growth gradually with depth increasing. While single hump backscattering coefficient still has three subtypes: peak value at sea surface, peak value at middle-level of water column and peak value at bottom of water column. The maximum of backscattering coefficient of peak value at sea surface type lie in 0.5~2.5m below the sea surface, and the maximum of backscattering coefficient of peak value at middle-level of water column is located in 7~10m below the sea surface, and the maximum of backscattering coefficient of peak value at bottom of water column always occurs in the region of 10~12.5m.

1. INTRODUCTION

In general, vertical variations of petroleum concentration and backscattering coefficient need to be investigated in detail to describe radiative transfer in natural waters. Petroleum contaminated water body has different radiative transfer characteristics, compared with natural water body, sequentially aquatic ecological environment can be influenced by petroleum pollutants. By radiative transfer equation, the regime that the absorption coefficient and scattering coefficient varies with depth and wavelength plays an important role to understand the optical properties in petroleum contaminated water body.

Relative studies on vertical variations of water constituents have been carried out in recent years. Specifically, Pang, et al. (2009) developed a regression model for vertical distribution of suspended sediment concentration in the Yellow Sea and East China Sea, using 5000 groups of suspended sediment concentration data over 24 surveying from 1959 to 2006. He, et al. (2014) found that chlorophyll a concentration increases and then decreases with depth increasing in Qiandao lake among spring, summer and autumn. Xiu, et al. (2008) validated that the optical properties of nonuniform chlorophyll profiles in CaseIwater differ with those of homogeneous ocean whose chlorophyll concentrations are identical to the surface chlorophyll concentrations in the inhomogeneous ocean. Stramska, et al. (2005) suggested that strong effects of the subsurface chlorophyll maximum on reflectance at low surface chlorophyll concentration can lead to a severalfold overestimation in the current algorithm derived surface chlorophyll. Liang, et al. (2017) developed a BP neural network which was trained and verified by 3200 datasets simulated by Hydrolight-a radiative transfer model, to estimate the vertical distribution structure effectively. Ma,et al. (2014) analyzed the vertical distribution of water constituents based on the in-situ data in Lake ChaoHu, and studied their influence on diffuse attenuation coefficients of downwelling irradiance K_d via Hydrolight simulation. Xu, et al. (2018) studied the spatiotemporal variability of chlorophyll a and its influencing mechanism using profile data with high depth resolution, and provided more insights for understanding marine environmental dynamics in the South China Sea. Yin et al. (2019) studied vertical variations of nitrogen-related functional genes in urban eutrophic lakes. Xing et al. (2019) analyzed the vertical variations of particulate and dissolved optical properties, using data collected by two Bio-Argo floats in the northern and central basins of the South China Sea for over two years. Nevertheless, previous studies all focused on various water constituents and optical properties, while

petroleum contaminated water body are seldom paid attention to our knowledge. Over the past half century, the theories of ocean color remote sensing have already been developed maturely, and also applied to actual project in various industries, especially the study of ocean three-components. These mature theories have been transplanted into the study of petroleum pollutants in petroleum contaminated water pretty successfully, which consider emulsions, suspensions and dissolved phases petroleum pollutions that oil layer has not developed as a new water constituent, to study apparent optical properties, inherent optical properties (absorption coefficient and scattering coefficient) and fluorescence characteristic of petroleum contaminated water body (Huang, et al., 2014a; Huang, et al., 2014b; Huang, et al., 2015; Huang, et al., 2016; Huang, et al., 2016). Huang, et al. (2017) also developed a new separation algorithm successfully to separate the contribution to backscattering coefficient between petroleum and sand from mixed water. However recent studies about absorption coefficient and scattering coefficient are independent on depth, the input variables of absorption coefficient and scattering coefficient in Hydrolight, both are dependent upon depth and wavelength to study the radiative transfer in petroleum contaminated water body. Hence, this study focuses on the backscattering coefficient in petroleum contaminated water body, to discuss its vertical variation regime, and to lay the foundation for the study of field light underwater in petroleum contaminated water body.

2. METHOD

2.1 Test Station Description

Located in Dalian city, the south of Liaotung peninsula, Dalian port which was built in 1899 with a hundred years of history, is an important petrochemistry base in China. Petrochemistry production and tanker can bring about petroleum pollution, while it makes Dalian port a natural laboratory to study optical properties of petroleum contaminated water body and variation of petroleum concentration. Three stations used to collect data were set separately in this area from August 25th to 27th. The first station which collected data at August 25th lies in an accident area where oil pipeline exploded in 2010, and the station's water depth is 21.5m. August 26th, the second station was installed on the shipping lane of Dalian port on which the shipping traffic could influence the petroleum concentration in the water obviously, and the station's water depth is 24.8m. In the east side of waters between Dashan island and Xiaoshan island, the third station which has lesser disturbance by ship due to the low frequency of shipping traffic than the first two stations, was used to collect data at August 27th. The water depth of the station is 33.0m.

Data were collected from 7:00~17:00 at each station from August 25th to 27th, 2018, and the total effective surveying number is 30 in three days. In each station, we measured data at depth of 0, 3, 5, 10 and 15 meters below the sea surface, so 150 effective data were collected during this period. And then we numbered them in stations and time sequence, that is A1、 A2、 A4-A11 for A station, B1-B8、 B10-B11 for B station and C1-C10 for C station.

2.2 Measurement Methods

2.2.1 Petroleum Concentration Measurement: In this study, portable TD-500D (Turner Designs, USA), which is applicable in GB 17378.4-2007—the specification for marine monitoring – Part 4: Seawater analysis, is used for the measurement of petroleum concentration, whose parameters are listed in Table 1. Its measurement principle is identical to SL 366-200 — Water quality – Determination of petroleum oil – molecular fluorescence spectrometer method, that is: firstly, the petroleum in the water is extracted by n-hexane, and then the ultraviolet light at specific wavelength is used as the incident light to radiate the petroleum molecule, and the electrons in the petroleum molecule absorb the energy of the incident light and then transition occur; sequentially, when the electron returns from the excited state to the ground state, fluorescence at specific wavelength is emitted; furthermore, owing to the link between the fluorescence intensity and the petroleum concentration are close to a linear relationship, thereby the petroleum concentration can be calculated out with the relationship.

Table 1. Technical parameters of TD-500D

Measurement range	Accuracy	Applicable range	Suitable solvent
0.01-1000ppm	0.1ppm	Oil organics such as crude oil, condensate, diesel and lubricating oil	n-hexane, vertrel, AK-225, xylene, freon, horiba

The instrument needs to be calibrated by standard oil samples with concentration of 10ppm which is produced by

n-hexane and petroleum reference substance (reference substance used for monitoring and analysis of petroleum composition in marine environment) before operating it. And then solid samples of the instrument need to be calibrated by the standard oil samples, in case of need for in-situ calibration. When we operating the instrument, we should extract petroleum by n-hexane first, subsequently keep the supernatant liquid into special cuvette, and then use the instrument to measure the liquid for 4 times and record them at last.

Next, we should average these 4 records to get petroleum concentration at each water level and each station for different time. After that, the study interpolates these data of each station with same depth interval as backscattering coefficient, and average them of the same station at the same time to get the mean value curve of petroleum concentration of each station varies with time.

2.2.2 Backscattering coefficient Measurement: Backscattering coefficient was measured by HydroScat-6 Spectral Backscattering Sensor (HS-6, 140°, Hobilabs, USA), the corresponding wavelengths of the six channels of HS-6 are 420, 442, 470, 510, 590 and 700nm. The measurement of backscattering coefficient refers to Technical specification for Marine optical survey. The measurement was conducted once an hour from 7:00 to 17:00, and the maximum measurement depth need to be adjusted every day in case of lens hit the water bottom. For the consistency of temperature between the instrument and water body and the reduction of influence by bubble, the instrument should be immersed into water totally at least two minutes before the measurement.

The backscattering coefficient measured by HS-6 should be corrected by sigma method (Song, Tang and Ma, 2008), the correction formula is

$$b_b = i \cdot b_{bu} \quad (1)$$

Where b_b is corrected backscattering coefficient (m^{-1}), i is correction coefficient (dimensionless), and b_{bu} is the original backscattering coefficient (m^{-1}). In addition, there are two calculation methods for i shown in Equation (2) and (3).

$$i = k_0 + k_1 K_{bb} + k_2 K_{bb}^2 \quad (2)$$

$$i = k_1 \cdot e^{(k_{exp} \cdot K_{bb})} \quad (3)$$

Where, k_0, k_1, k_2 , and k_{exp} are calibration parameters (dimensionless), which could read from calibration file, and K_{bb} is the attenuation of backscattering coefficient that caused by non-water constituents that comes directly from Equation (4).

$$K_{bb} = a + 0.4b \quad (4)$$

Where a and b are absorption coefficient and scattering coefficient (m^{-1}), and a was measured by spectrophotometer and b is the ratio of backscattering coefficient and backscattering reflectance. Moreover, due to the design and optical transmission geometry of HS-6, the magnitude of attenuation when signal transmit include entire absorption (a) and 40% scattering (Boss, et al., 2004).

3. RESULTS AND DISCUSSION

3.1 Vertical variations of petroleum concentration

Figure 1 shows the vertical variation of petroleum concentration of stations A, B and C in Dalian port. X-coordinate is petroleum concentration (mg/L) and y-coordinate is depth of water (m). The petroleum concentration of Station A, B and C is within 0.7~4.1 mg/L, 1.0-9.3mg/L and 0.2-7.8mg/L respectively. And the petroleum concentration at station B stays at high value throughout the day.

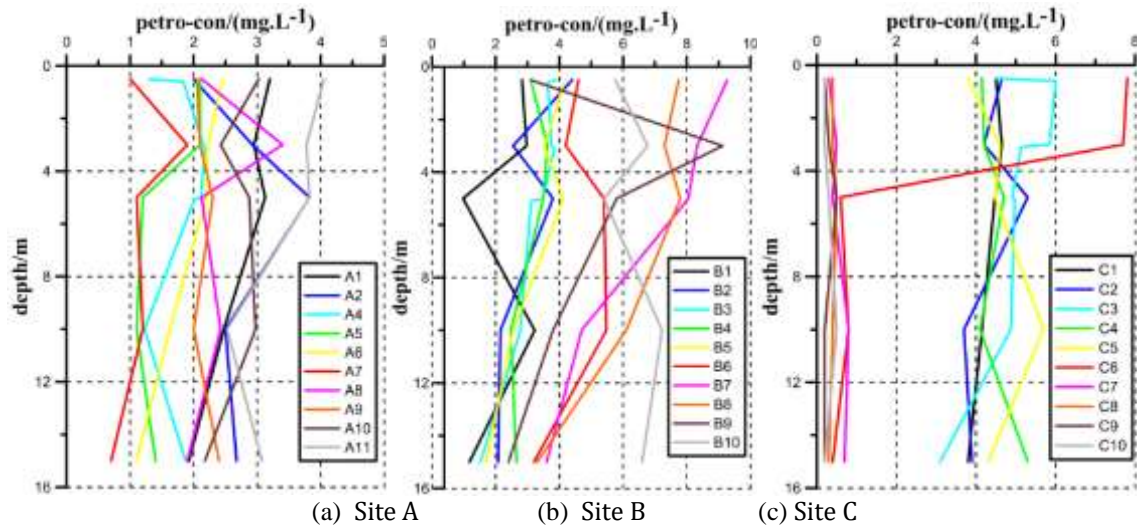


Fig. 1 Vertical variations of petroleum concentration of station A, B and C

Figure 2 shows tidal curves in different times at station A, B and C. And it also shows that the observation period of Station A, B and C is in a complete same ebb and flow process. The Climax occurs at about 10 o'clock, the maximum of tide for these stations with little differences are among 360~370cm. The height of low ebb is about 95cm which occurred at 16:30. Velocity and direction of current are not unanimous at different time and different station, because our observation corresponding to different tide period. The current directions of each station are listed in Table 2. Figure 2 and Table 2 together indicate that the tide of three stations was rising from 7:00 to 10:00, and falling between 11:00 to 15:00. Although three stations have similar ebb and flow, the current direction of them varied greatly. This illustrates that the sources of water are different and the constituents in the sea water are different either.

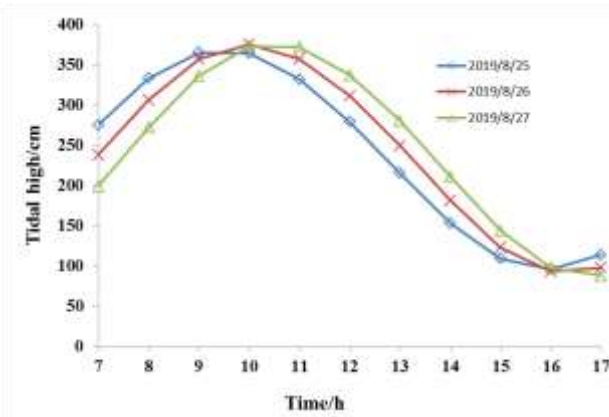


Fig. 2 Tidal table in Dalian port

Table 2 details of current direction of Station A, B and C

Time	A	B	C
7:00	SW	SE	SE
8:00	SW	SE	SE
9:00	SW	S	SW
10:00	W	S	W
11:00	W	S	W
12:00	SE	SW	W
13:00	SE	SW	W
14:00	E	W	W
15:00	NE	N	N
16:00	NE	N	NE

Figure 1 still shows that the regime of vertical variation of petroleum concentration is complicated, without obvious linear decrease or linear increase relations with depth, due to that the ebb and flow of different time for each station could influence current in different way. Furthermore, although the relation between petroleum concentration and depth of water is complicated, we still found that there is a maximum of petroleum concentration at the depth of 3m below the sea surface, and then the petroleum concentration decreases as depth increasing. The last point shown in Figure 1 is the minimum of petroleum concentration is at 15m below the sea surface in general.

3.2 Vertical variations of backscattering coefficient

Previous studies indicated that petroleum substance could influence backscattering coefficient together with suspended matter in petroleum contaminated water body (Huang, Song and Tang, 2009; Song, Huang, Tang and Wang, 2010). The measurement of backscattering coefficient by using HS-6 includes the backscattering coefficient caused by petroleum and suspended matter. So, this part analysis on vertical variations of backscattering coefficient contains those caused by petroleum and suspended matter together. Figure 3 shows suspended matter concentration at depths in different time for each station. And it also indicates that suspended matter concentration of each station at different time and depth are unlike clearly, and suspended matter concentration of station A is bigger than that of the station B and C mostly, but the magnitude of concentration at station B and C are similar.

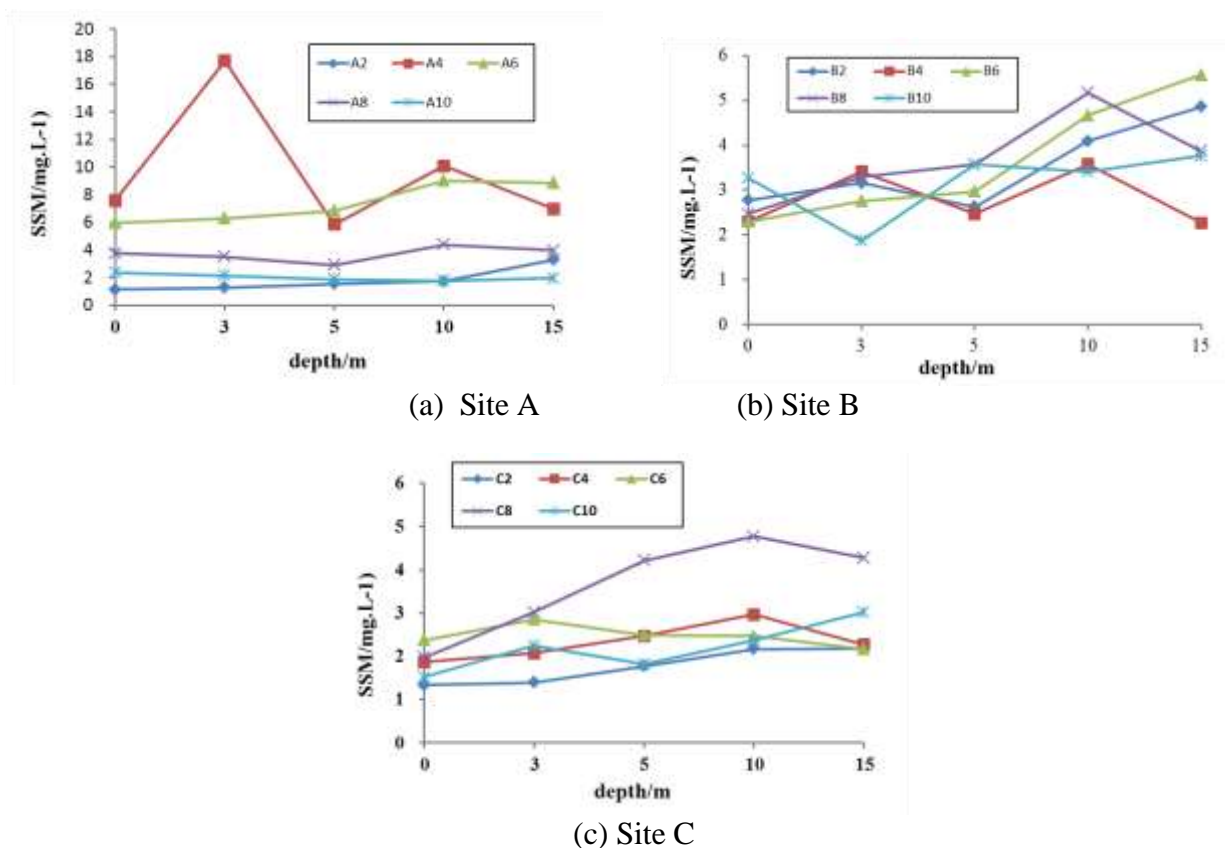


Fig. 3 Suspended matter concentration versus times and depth of station A, B and C

Petroleum and suspended matter concentration are measured at depth of 1, 3, 5, 10 and 15m separately, while the maximum depth of the instrument we used here is more than 15m (except for A4 and B10), so there are differences in depth between backscattering coefficient and concentration data. In order to eliminate the difference and increase the consistency of them, we selected backscattering coefficient from 1m to 15m below the sea surface for this study. Moreover, Song and Tang (2006) developed a parameter model for backscattering coefficient which depend on wavelength, is shown in Equation (5).

$$b_b(\lambda) = b_b(\lambda_0) \cdot \left(\frac{\lambda_0}{\lambda}\right)^n \quad (5)$$

Where, λ_0 is reference wavelength and n is the index of scattering coefficient which depends on wavelength. Song et al. (2006) pointed out that λ_0 is 555nm or the band which has the smallest differences with 555nm among the 6

bands for HS-6 and n varies in different water body with dissimilar water constituents. The study chose 590nm band of HS-6 which is the closest band to 555nm as reference band to compute backscattering coefficient at any other wavelength. Figure 4. shows the backscattering coefficient curves of each station versus depth.

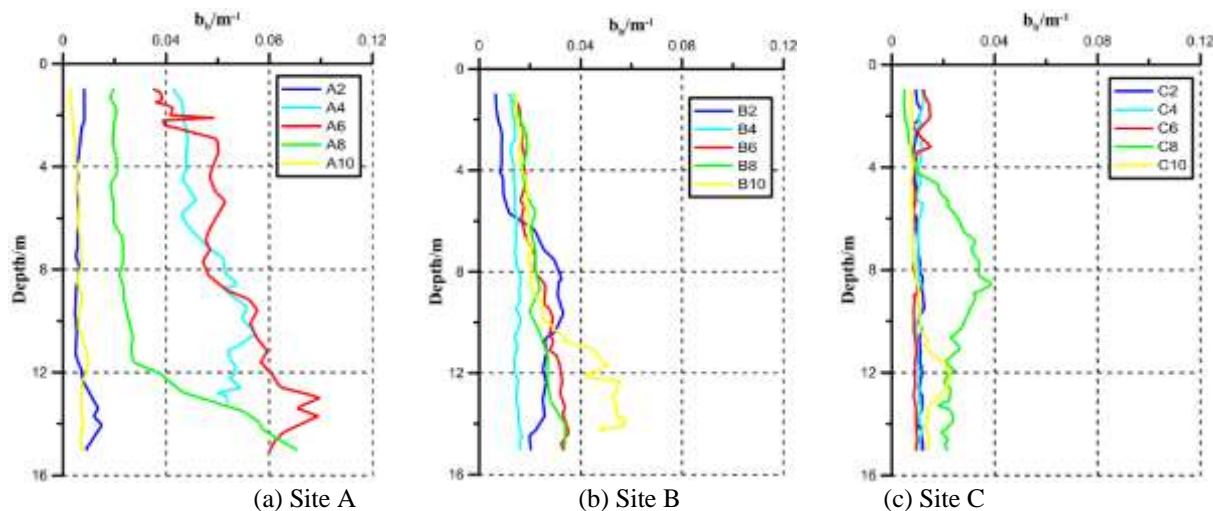


Fig. 4 Backscatter coefficient versus depth at station A, B and C

Figure 4 indicates that: 1) The resemblance between curves in Figure 4 and Figure 3 makes clear that the suspended matter concentration is the main influencing factor of backscattering coefficient, the same as the conclusion made by Le, et al (2009). 2) From the comparison of backscattering coefficient and petroleum concentration, we know that petroleum concentration is not the main influencing factor of backscattering coefficient, but it also can affect backscattering coefficient to make a discrepancy between backscattering coefficient and suspended matter concentration. For instance, backscattering coefficient and petroleum concentration of C6 is bigger than those of C8, but suspended matter concentration of C6 is less than that of C8 in the contrary from 1m to 5m below the sea surface. 3) In general, backscattering coefficient increases with depth increasing. 4) 10m is the depth that backscattering coefficient increases quickly mostly. 5) the maximum value of A4, B2, C8 and C10 located in depth of 10m, 8m, 8~10m and 12m and these depths exceed 7m, 6m, 6m and 10m separately at which backscattering coefficients are greater than the average of backscattering coefficients in corresponding water column. These facts indicate that although the backscattering coefficient decreases in deep water column, backscattering coefficient still increases overall. 6) The maximum of A2 lies in water column deeper than 12m and that of C4 and C6 lie in water column from sea surface to 5m. In addition, the magnitude of backscattering coefficients of station A2, C4 and C6 are small and the means magnitude of backscattering coefficient of these stations are only about 1×10^{-2} . Despite backscattering coefficient of station A2 increases rapidly after 12m, but the magnitude is still small compared to other stations. 7) Backscattering coefficient of A4 and A6 are greater than that of others in station A obviously, the same as C8. This means that backscattering coefficient is dependent on time. 8) Overall, the magnitude of backscattering coefficient of station A is maximal, then that of station B is less than station A, and that of station C is minimal. The range size of backscattering coefficient among each station has similar order as the magnitude of backscattering coefficient of these stations. So, it indicates that suspended matter concentration of site A is high and site A susceptible to environment.

In a whole, there are three kinds of vertical variations of backscattering coefficient in this study area, they are abrupt growth, steady growth and single hump. Abrupt growth backscattering coefficient varies less in the water column but growth quickly near 11.5m below the sea surface such as backscattering coefficient of A8, A10 and B10 (Figure 5a). Steady growth backscattering coefficient growth gradually with depth increasing (Figure 5b) including that of A4, A6, B4, B6, B8, C2 and C4. While single hump backscattering coefficient, such as A2, B2, C6, C8 and C10, still has three subtypes: peak value at sea surface, peak value at middle-level of water column and peak value at bottom of water column. The maximum of backscattering coefficient of peak value at sea surface type lies within 0.5~2.5m below the sea surface (Figure 5c), and the maximum of backscattering coefficient of peak value at middle-level of water column is located in 7~10m below the sea surface (Figure 5d), and the maximum of backscattering coefficient of peak value at bottom of water column always occurs in the region of 10~12.5 m.

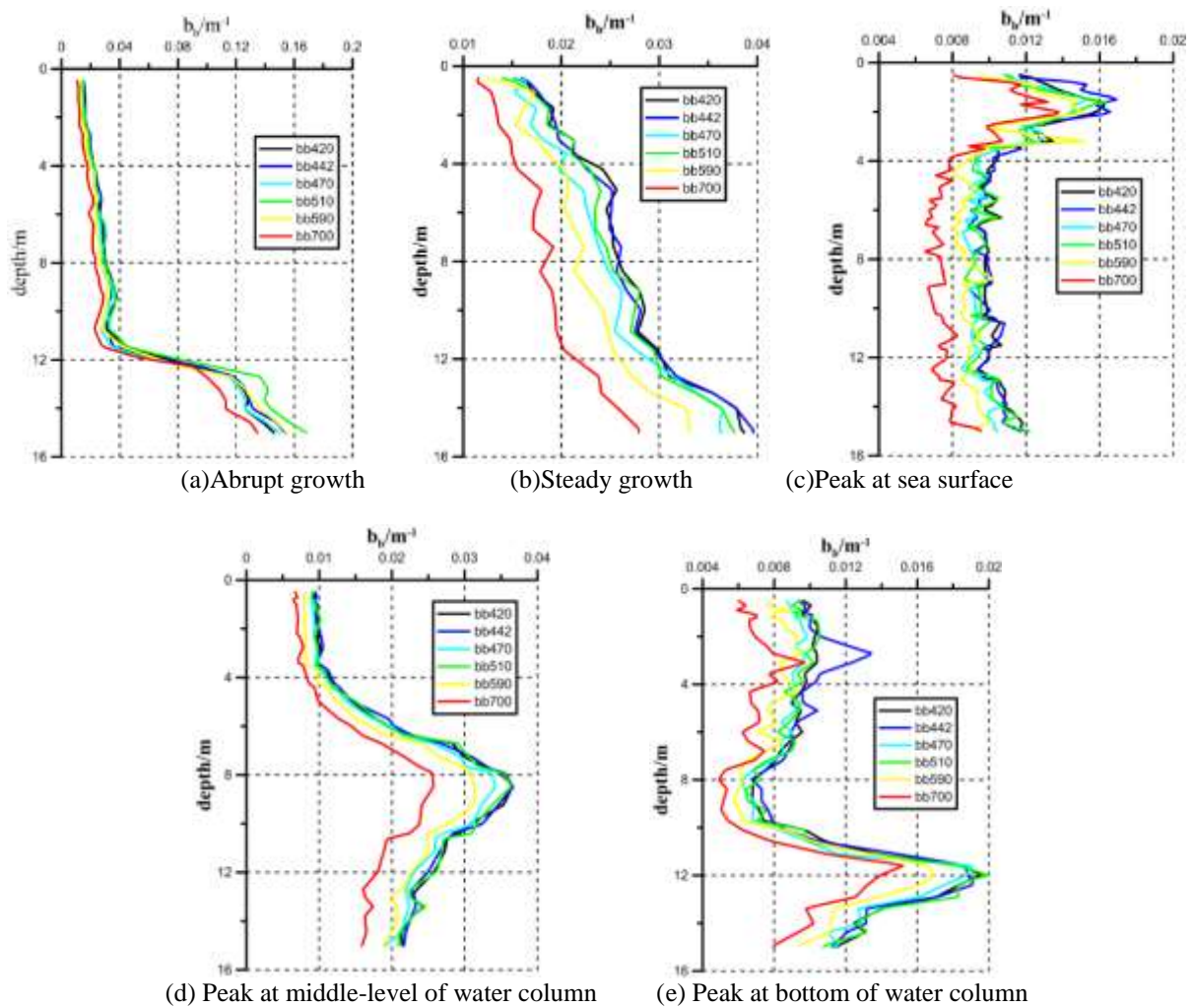


Fig. 5 Vertical variation categories of backscattering coefficient

4. CONCLUSIONS

Petroleum substance could influence water optical properties as a new water constituent of ocean color remote sensing in petroleum contaminated water body. To understand the vertical variation regime of petroleum concentration and backscattering coefficient in petroleum contaminated water body will lay foundation for understanding the water optical properties.

The study chose three kinds of stations to conduct in-situ data collection, they respectively are station nearby petroleum enterprises which could pollute water body directly, station on the shipping lane of Dalian port serving for cargo vessel carrying crude oil that could pollute water by discharge and oil spill, and station in the east of Dashan island and Xiaoshan island, which will be polluted less frequently due to the effect of ebb and flow. By the analysis of in-situ data, the study demonstrated the vertical variation of petroleum concentration is complicated and classified backscattering coefficient by depth and curve shape into three main types.

The stations of in-situ data collection are distributed near Dalian port in China, so the study need to be extended to other sea to conduct more extensive research, that will improve the accuracy and feasibility of these conclusions.

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