The Correlation Analysis between Colored Dissolved Organic Matter's Fluorescence and Absorption Characteristic in the Liaodong Bay

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ABSTRACT: CDOM (Colored Dissolved Organic Matter) is defined as the optical measurable matter dissolved in water which mainly produced by the natural process of releasing tannic acid when matter decaying. The change of CDOM is the main result of natural process, but human activities, such as logging, agriculture, pollution discharge, wetland irrigation, etc. will also affect the content of CDOM in freshwater and estuarine water. The fluorescence characteristics will be changed because of different CDOM as the different source which provides reference for tracing the source of CDOM. Liaoning Bay is located in the northeast of Bohai China, a semi closed form from northeast to southwest, particularly affected by land, and the various kinds of sewage of peripheral mariculture region, chemical plant, river discharge, oil sewage discharge, city sewage discharge, etc will also affect it which lead to it is a good research base for multi type CDOM sources. From April 14, 2015 to May 3, 2015, 33 sites which were setting while taking into account the various kinds of pollution into the region were navigate sampled in Liaodong Bay. Immediately, filter the sample with a polycarbonate filter with the aperture of 0.22 μm and the diameter of 25mm on the site, get the CDOM sample and measure immediately with fluorescence spectrometer, avoid the fluorescence decay of the active substances, and in accordance with the standard of NASA ocean optical measurement to measure the absorption coefficients of the corresponding sample. The research shows that the four fluorescence characteristics in the whole Liaodong Bay: a) the CDOM fluorescence peak positions of samples are different obviously in mariculture region, chemical plant, river discharge, oil sewage discharge, city sewage discharge; b) CDOM fluorescence intensity of fluorescence peak on the west bank is larger than seaward extension, and decreasing to the east bank; c) it is obviously that a positive correlation property between spectral slope of the absorption coefficient and the fluorescence intensity, which provides the support basic for the use of fluorescence remote sensing and visual light remote sensing congenerously invert the spectral slope of the absorption coefficient of CDOM.

1. INTRODUCTION

CDOM, also called Yellow Substance or Gelbstoff, is an important part of the dissolved organic matter which exists in all water bodies. In the natural environment, there are two main source of CDOM: one is the product of phytoplankton degradation, and the other is terrigenous dissolved organic matter that mainly including humic acid, fulvic acid, aromatic polymer and a series of material (Zhang,2010; Liu, 2009).

The research of CDOM is mainly concentrated in the following three aspects: a) using the absorption spectrum with the characteristic of the index decreasing along with the wavelength from ultraviolet to visible light to study the optical absorption properties (Lei,2013; Zhao, 2013; Hu, 2013); b) using the characteristic of fluorescent components of CDOM absorbing ultraviolet and launching fluorescence of which wavelength longer than absorbing to study the composition of the distinction and the source trace (KOWALCZUK,2005; Zhong, 2008; Del 1999); c) using remote sensing to establish the CDOM inversion model and extraction algorithm of other components of the water basic on CDOM (Feng,2011; Fan, 2013).

Due to different sources of CDOM in water and complex ingredient, it is difficult to determine the concentration which often represents its concentration by means of the absorption coefficient and other optical properties. For example often used the absorption coefficient of 355nm and 375nm and 440nm to represent the concentration, unit is m-1, but this method can't reflect the actual CDOM concentration in water. The development of fluorescence measurement technology lays the foundation for the determination of CDOM concentration. Many scholars have analyzed the absorption coefficient and fluorescence characteristics of CDOM in Chinese estuary, large lakes, and reservoir etc (Lee, 1996). The research on Liaodong Bay provides a reference frame of the CDOM source tracing, which using the ag(440) to represent the concentration of CDOM in water, in water color remote sensing area, and using spectrum slope S to represent the attenuation degree of CDOM absorption spectrum(Huang, 2011;Huang,2010). Previous researches have indicated that the spectral slope S is not related to the concentration of CDOM but the components, determination of the simulating wavelength range and the reference wavelength of spectrum index model establishment. CDOM in the different substances with a significant difference in the peak can be used to distinguish CDOM components and sources (Jerry, 2003). According to the researches of different sources of CDOM with different fluorophores, the position of fluorescence peaks and the intensity fluorescence, if link the S value with the peaks, will solve the problem of target S relies solely on the field observation data in water color remote sensing (Bowers, 2004).

2. EXPERIMENT AND DATA ACQUISITION

2.1 Test Description

The test area is located in Liaodong bay, which is located in the northeast of Bohai China, a semi closed form from northeast to southwest, particularly affected by land, and the various kinds of sewage of peripheral mariculture region, chemical plant, river discharge, oil sewage discharge, city sewage discharge, etc will also affect it which lead to it is a good research base for multi type CDOM sources. Figure 1 shows the sites of the test and Table 1 list the latitude and longitude that corresponding to the sites which were setting with the considerations of a variety of types of emissions and relatively clean.

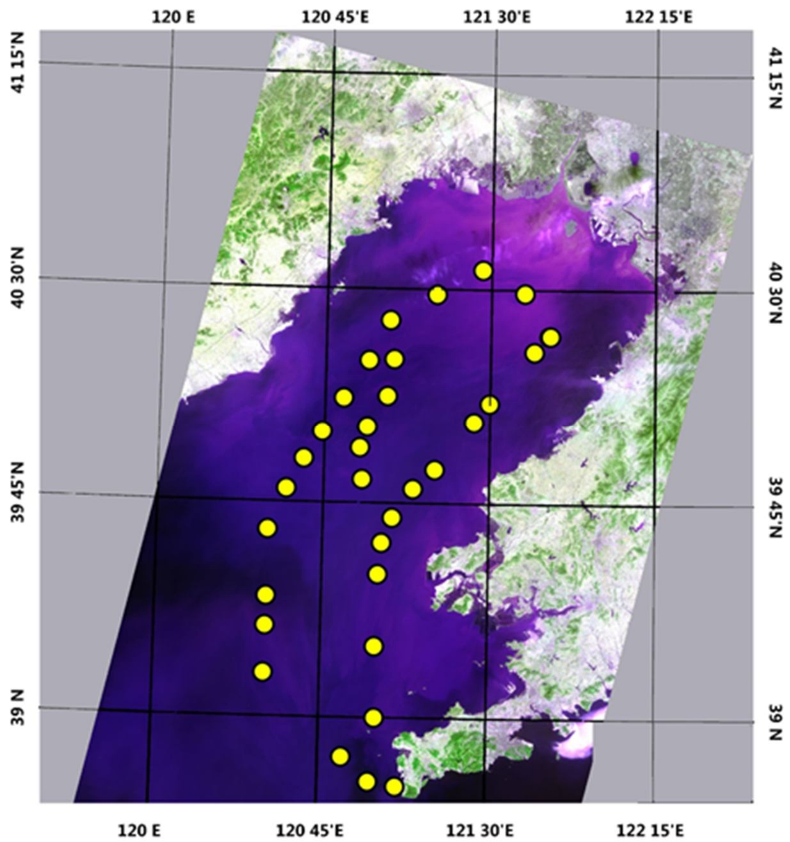


Figure 1. Sites distribution (April 8, 2014 passing, Landsat 8/OLI 4, 5, 3 band synthesis)

In the test area, setting a sampling site every 7 nautical miles or so, and observing in navigation ignore the reflection from sea floor, for a total of 33 sites. Sampling rules: if the water depth is less than 10m, the measurement levels are 0 and 5m; if the water is deeper than 15m, the measurement levels are 0, 5m, 10m, using the water sampler with the material of PMMA (polymethyl methacrylate).

Table 1. Latitude and longitude of sites

sample number	site number	longitude	latitude
1	LDW01_1	121°05.944′E	38°45.637′N
2	LDW01	121°0.0′E	39°0.0′N
3	LDW02	120°59.664′E	39°14.920′N
4	LDW03	121°00.186′E	39°30.058′N
5	LDW04_1	121°01.007′E	39°36.654′N
6	LDW04_2	121°03.773′E	39°41.914′N
7	LDW05_1	121°09.312′E	39°47.987′N
8	LDW06_1	121°15.110′E	39°52.054′N
9	LDW07_1	121°25.602′E	40°02.079′N
10	LDW08_1	121°29.832′E	40°06.081′N
11	LDW10	121°41.905′E	40°17.000′N
12	LDW11_1	121°45.924′E	40°20.288′N
13	LDW11_2	121°46.256′E	40°29.237′N
14	LDW12	121°39.122′E	40°29.237′N
15	LDW13	121°27.492′E	40°34.077′N
16	LDW14	121°14.997′E	40°28.903′N
17	LDW16	121°02.408′E	40°23.371′N
18	LDW17_1	121°03.634′E	40°15.257′N
19	LDW18	120°56.808′E	40°14.911′N
20	LDW19	121°01.934′E	40°07.506′N
21	LDW20	120°50.025′E	40°06.976′N
22	LDW21_1	120°56.563′E	40°00.983′N
23	LDW22_1	120°44.332′E	39°59.844′N
24	LDW23	120°39.510′E	39°54.096′N
25	LDW24_1	120°34.933′E	39°47.739′N
26	LDW25	120°30.165′E	39°39.122′N
27	LDW26_1	120°30.121′E	39°25.177′N
28	LDW27	120°30.016′E	39°18.999′N
29	LDW28	120°29.884′E	39°09.081′N
30	LDW29_1	120°58.592′E	38°46.545′N
31	LDW29_2	120°51.346′E	38°51.687′N
32	LDW_p1	120°54.710′E	39°56.568′N
33	LDW_p2	120°55.425′E	39°49.909′N

2.2 CDOM Absorption Coefficient Measurement

Absorption coefficients were measured by using a UV visible spectrophotometer (model UV-3900, Hitachi, Japan). The output value will be deviated to the expected if the instrument got external factors interference (such as moving). As a result, before the formal test, the spectrophotometer calibration should be done firstly for checking whether the optical properties meet the requirements or not, reducing the system error and determining whether the characteristic index measuring instrument system error is within the controllable range or not. Filter the sample with a polycarbonate filter with the aperture of 0.22 μm as the CDOM sample and measure with a 10cm long sample quartzose pool and the reference sample - Milli.Q water. The wavelength should be set from 220-900nm when measuring.

2.3 Fluorescence Measurement

Using SHIMADZU RF-5301 fluorescence spectrophotometer to fluorescence analyze with the 1cm long sample quartzose pool and the reference sample - Milli.Q water. The width of the excitation and emission monochromator slit was set to 10 nm, scanning speed is 1300nm•min-1, excitation wavelength is from 220-450nm and emission wavelength is from 220-800nm. Because of Rayleigh scattering and Raman scattering, the scattering peaks where the proportion of excitation wavelength and emission wavelength is 1:1 and 1:2 cover the CDOM fluorescence peaks with the Milli.Q water reference sample. As a result, it is necessary to correct the fluorescence measurement data, and this test using the method of Delaunay triangle interpolation algorithm (MORTEZA, 2004; RICHARD, 2007)

3. CONCLUSION AND ANALYSIS

3.1 Characteristic Analysis of CDOM of Liaodong Bay

A large number of researches have indicated that the different CDOM sources having different fluorophores will result in various position of the fluorescence peak and diverse fluorescence intensity. Generally speaking, there are four kinds of main components of CDOM in the natural environment of which the excitation / emission (Ex / Em) fluorescence peak positions are shown in Table 2 (Zepp, 2004).

Table 2. Fluorescence peak positions of four main components of CDOM

CDOM components	Ex（nm）	Em（nm）	Source
humic acid	320-340 370-390	410-430 460-480	terrigenous
fulvic acid	237-260	400-500	terrigenous
Tyrosine	275 225-237	310 310-320	Phytoplankton degradation
Tryptophan	270 225-237	340 340-381	Phytoplankton degradation

After analyzing, the fluorescence spectrums of the surface level (0m) samples of all the 33 sites on the design route can be divided into three types: single peak type, double peaks and triple peaks. The range of single peaks are mainly distributing on Ex/ Em: 225-235nm/325-350 nm as is shown in Figure 2 that corresponding sites are basically offshore to a certain distance lead to the less terrigenous influence and of which main component is tryptophan that shown in Figure 2. Double peaks are divided into two kinds, one is the marine type both of the two peaks that distributed in Ex/ Em: 225-235nm/325-350 nm Ex/ Em: and 275-285nm/325-355 nm, as is shown in Figure 3, and of which main component is tryptophan of phytoplankton degradation that shown in Figure 2. The sites of which main components of tryptophan have two peaks are basically offshore to a certain distance without large river discharging. The other type – marine and land type, is distributing on Ex/ Em: 225-235nm/325-350nm and Ex/ Em: 230-240nm/410-450nm, as is shown in Figure 4, and of which main component is tryptophan of phytoplankton degradation and fulvic acid of terrigenous that shown in Table 2. This type of sites are locating near the Shuang Tai Zi River estuary which leads to the large influence of terrigenous. Peaks of triple peaks are distributing on the Ex/ Em: 225-235nm/325-350nm, Ex/ Em: 235-245nm/410-440nm and Ex/ Em: 270-290nm/320-355nm, as is shown in Figure 5 and of which main component is tryptophan with two fluorescence peaks of phytoplankton degradation and fulvic acid with one fluorescence peak of terrigenous that shown in Table 2.

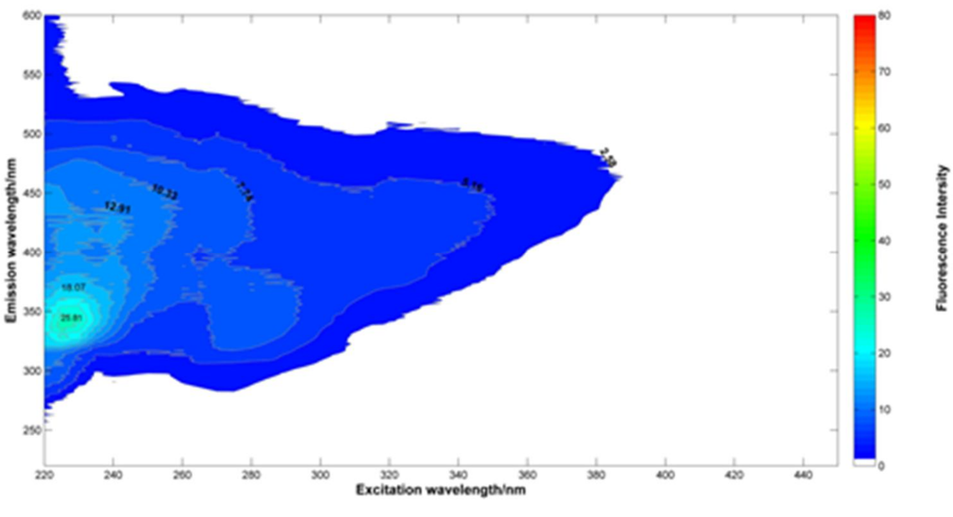


Figure 2. Single peak

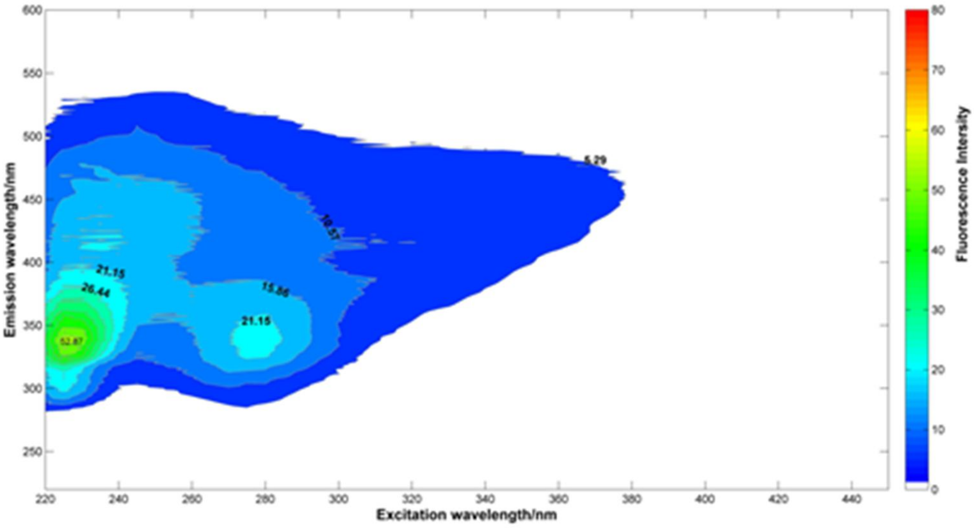


Figure 3. Marine double peaks

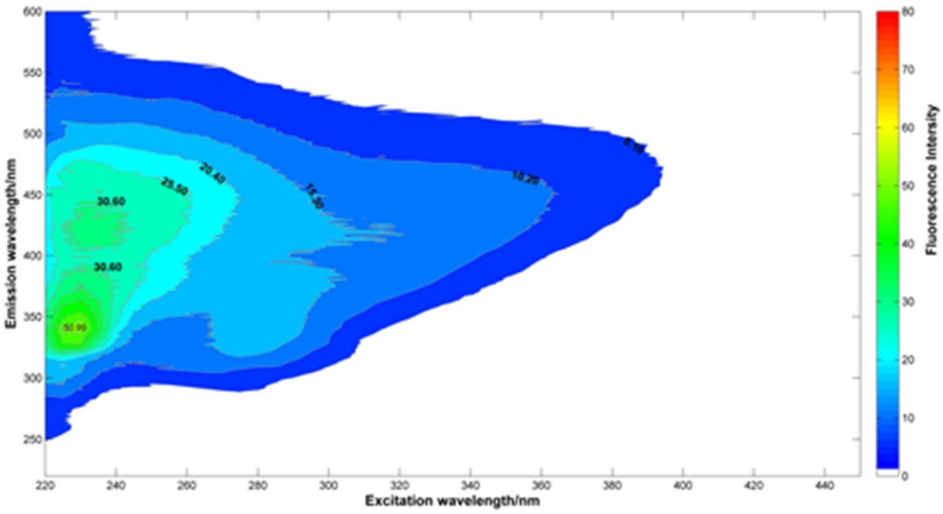


Figure 4. Two peaks of marine and land

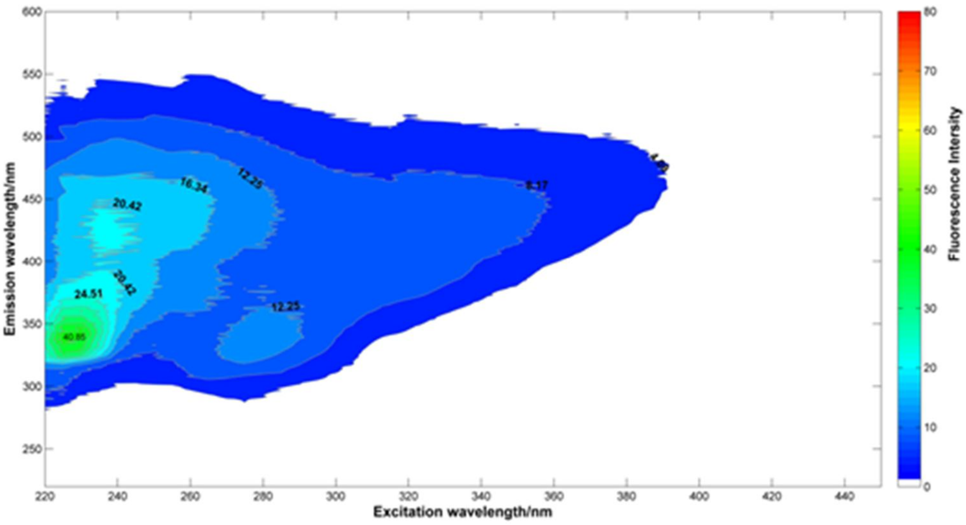
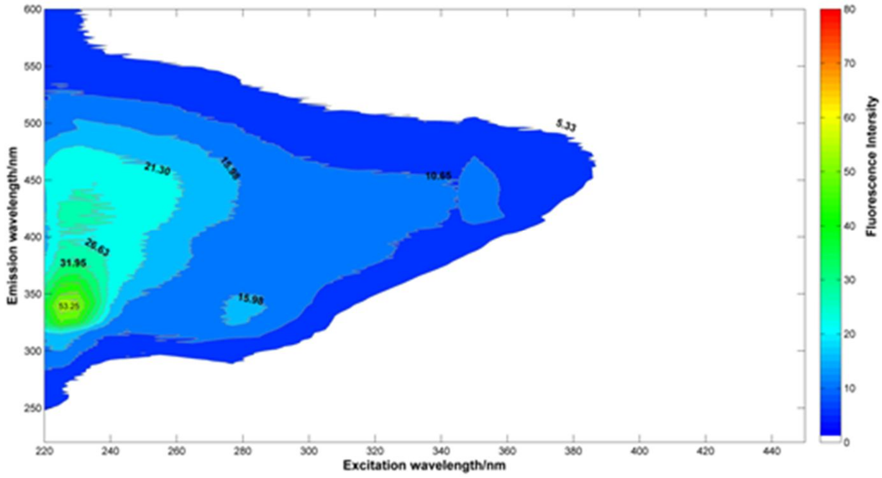
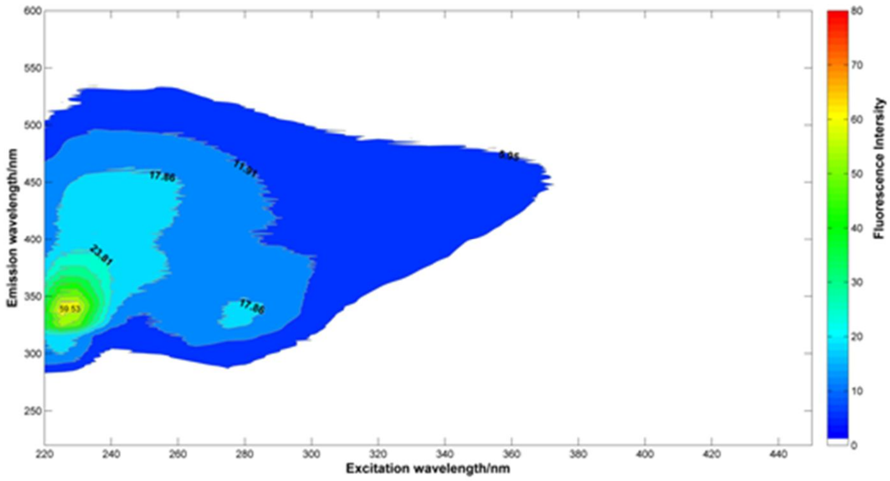


Figure 5. Triple peaks

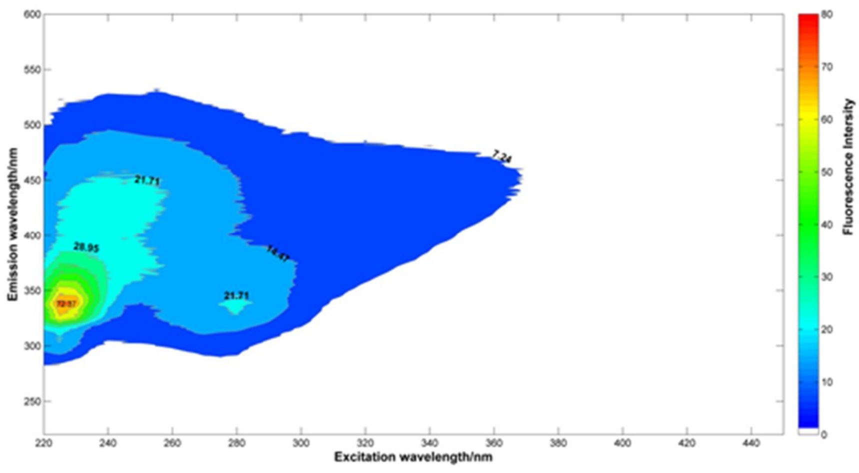
Analyzing from the east bank to the west, as is shown in Figure 6, part (a) is corresponding to east bank of which fluorescence intensity, part (b) meaning the middle and part (c) corresponding to west. It can draw a conclusion of the change that the fluorescence intensity increase when closing to bank, the fluorescence intensity of fluorescence peak on the west bank is larger than seaward extension, and decreasing to the east bank. Both of the east bank and west bank are influenced terrigenously, but the flow is slower on west which cause a weak water exchange and eliminate the influence of land will be slower causing the western fluorescence intensity larger than east obviously.



（a） Eastern



（b） Middle



（c） Western

Figure 6. Fluorescence intensity changing from bank to the middle of the bay

3.2 Absorption Characteristic Analysis of CDOM of Liaodong Bay

In the study of the CDOM optical coefficient, the absorption coefficient on 440nm ag(440) and the exponential slope S are two important parameters. ag (440) is usually used to characterize the concentration of CDOM in Remote sensing field. Figure 7 shows the CDOM absorption coefficient change of 33 sites which follow the e index attenuation law. Figure 8 shows the ag(440) which the largest value is 0.31/m-1 of the site that located in the Shuangtaizi River estuary leading to a large number of pollution matter which is the cause of ag(440) increasing and meaning the CDOM concentration reach the highest in the area. It also shows the ag(440) which the smallest value is 0.13/m-1 of the site that located in the middle of Liaodong Bay with little terrigenously influence. Figure 9 shows the calculated spectral slope S (400nm-600nm) of every site according to Figure 7 with the maximum value of 0.0031nm-1 and the minimum value of 0.001nm-1.

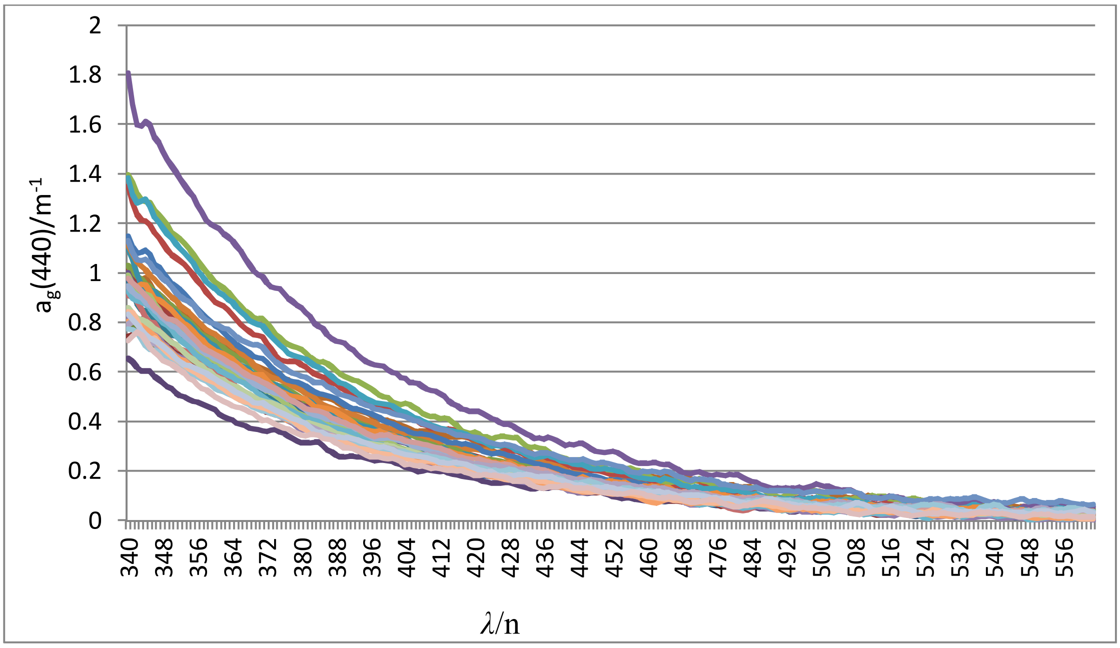


Figure 7. CDOM absorption coefficient change curve of 33 sites

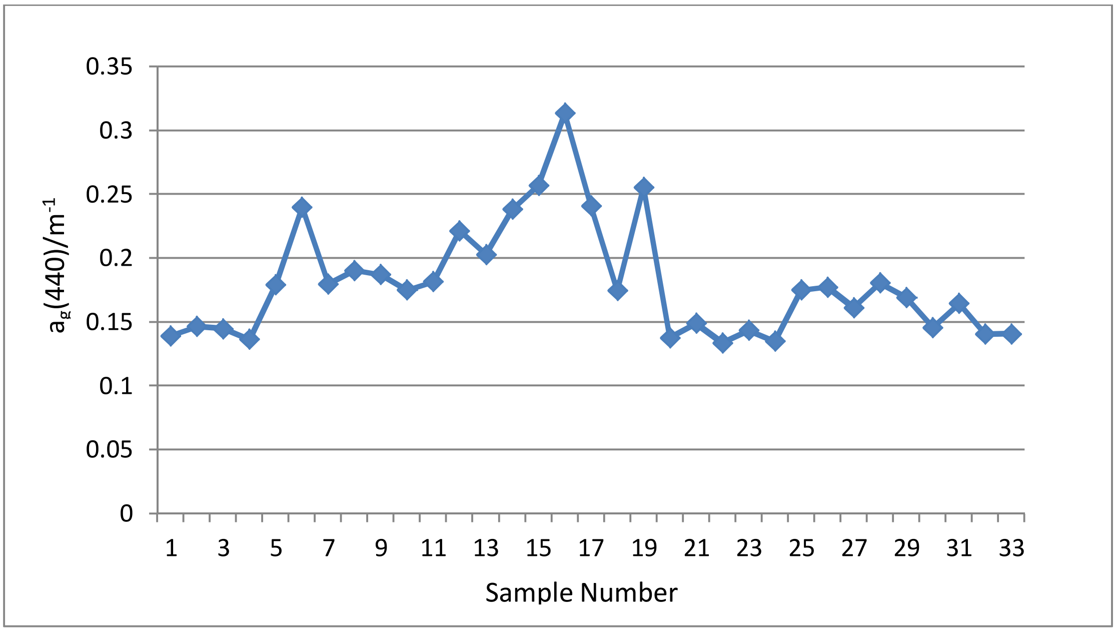


Figure 8. ag (440) value of 33 sites

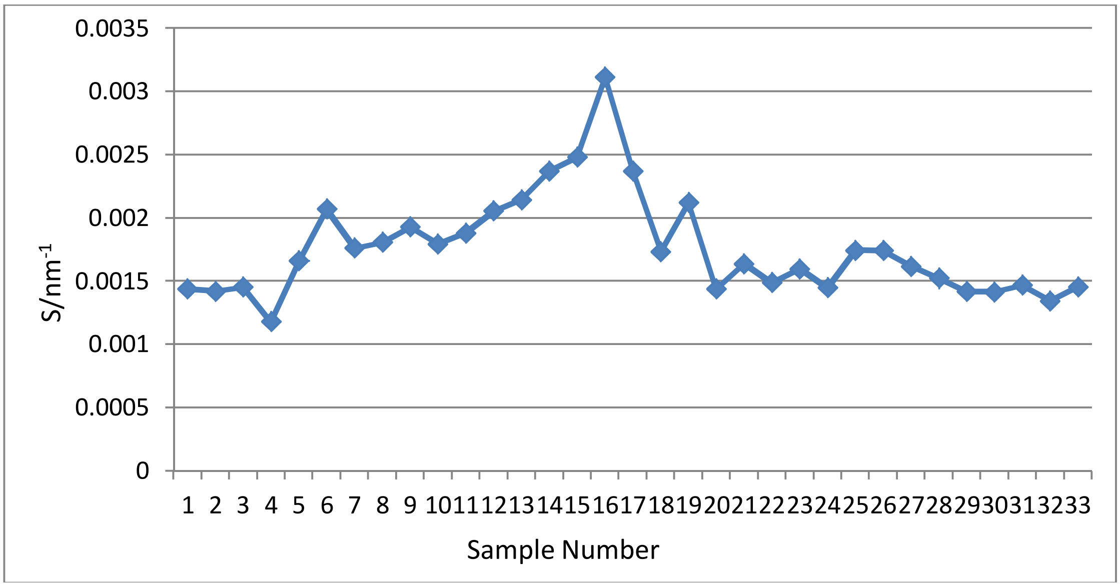


Figure 9. Spectrum slope S of 33 sites

3.3 Correlation Analysis

The spectral slope S value is related to the composition of CDOM and the composition of the band, and its value varies in different regions, so it can be used to distinguish the different CDOM components. Using the 33 obtained S, working out the 33 maximum value of the fluorescence intensity, and correlation analyzing with the S value and the fluorescence peak intensity of which the correlation coefficient is 0.78 that indicates we can using fluorescence remote sensing and visible light remote sensing congenerously inversion from a remote sensing perspective to determine the S values, so as to improve the inversion accuracy of CDOM concentration.

4. CONCLUSION

Through the CDOM fluorescence spectrum comparative analysis of Liaodong Bay, determine the Liaodong Bay waters CDOM has single peak type, double peaks type and triple peaks type, among them, double peaks can be divided into marine type and marine and land type. Tryptophan is the main component of CDOM in the whole area, and humic acid will be increased by the influence of land.

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