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Absorption properties of chromophoric dissolved organic matter in highly-polluted Yundang Lagoon, China

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Abstract

Optical properties of chromophoric dissolved organic matter (CDOM) from highly polluted Yundang Lagoon, China were investigated from April 2008 to June 2009. The absorption spectra of DOM from this polluted saline lake resembled that of DOM from other natural environments. The spatial distribution of absorption coefficients at 280 nm (a_{280}) indicated that sewage discharge was the main source of CDOM in this lagoon. A notable seasonal variation of a_{280} was observed from spring of 2008 to spring of 2009, indicating the reduction in sewage discharge from municipal works. Most values of spectral slope ratio (SR) of CDOM absorption were >1 , implying that sewage-derived DOM has a low molecular weight. There was a significant linear correlation between a_{280} and the DOC concentration, demonstrating the feasibility to use optical properties of DOM to assess the degree of organic pollution in highly-polluted aquatic environments.

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Keywords: chromophoric dissolved organic matter (CDOM), absorption, spatio-temporal variation, Yundang lagoon

Introduction

Sewage and wastewater discharge has resulted in serious organic pollution issues in many aquatic environments [1-3]. Since the dissolved organic matter (DOM) composition in these aquatic systems is highly heterogeneous, it is essential to characterize the properties of DOM to evaluate the environmental and ecological effects of organic pollution. The commonly-used index such as chemical oxygen demand (COD), biological oxygen demand (BOD) or total organic carbon (TOC) can only provide a quantitative indication for the organic content [4]. The analytic methods to study the composition of dissolved organic matter (DOM) like chromatography, mass spectrometry need complicated sample pretreatment procedures and are not suitable for simple and quick determination [2].

In recent years, spectroscopic techniques have become an important approach to characterize the properties of DOM including its sources, transformation and reactivity [5-10]. UV-Visible absorption spectroscopy is

one of such techniques which can simultaneously provide both quantitative and qualitative information for the colored fraction of DOM, i.e. chromophoric dissolved organic matter (CDOM) [5-7]. Absorption coefficient at certain wavelength (e.g., 280 nm, 350nm or 440nm) can be used as an indicator for the DOM concentration [11], while absorption ratio at 250 to 365 nm (called E2:E3) or molar absorptivity at 280nm can be used to trace the changes in the molecular size and aromaticity of DOM [12, 13]. The spectral slope ratio of 275-295nm and 350-400nm (called S_R) has been suggested to be a good proxy for DOM molecular weight [14].

Yundang Lagoon is a small shallow lake located in the central Xiamen Island, China (Fig. 1). The water quality is highly polluted in recent three decades due to the fast economic development of Xiamen City. Although relatively clean seawater from outer bay is drawn into the lagoon at high tide for many years, the degree of pollution is still quite high. In this study, water samples were collected from this lagoon from April 2008 to June 2009. The main objective was to study the spatial and temporal variability of optical properties of CDOM, and to illustrate the potential of absorption spectroscopy as a monitoring tool for organic pollution in such highly-polluted coastal waters.

Materials and Methods

Sample collection and pretreatment

Water samples were collected from 13 stations in Yundang Lagoon (Fig. 1). Sampling were carried out every half month from April to December 2008, and every month from January to June 2009. Subsamples filtered through precombusted (500 °C for 5 h) 0.7 μm glass fiber filters (Whatman GF/F) were collected for DOC analysis, while subsamples filtered with 0.2 μm Millipore polycarbonate filters were collected for absorption spectroscopic measurements.

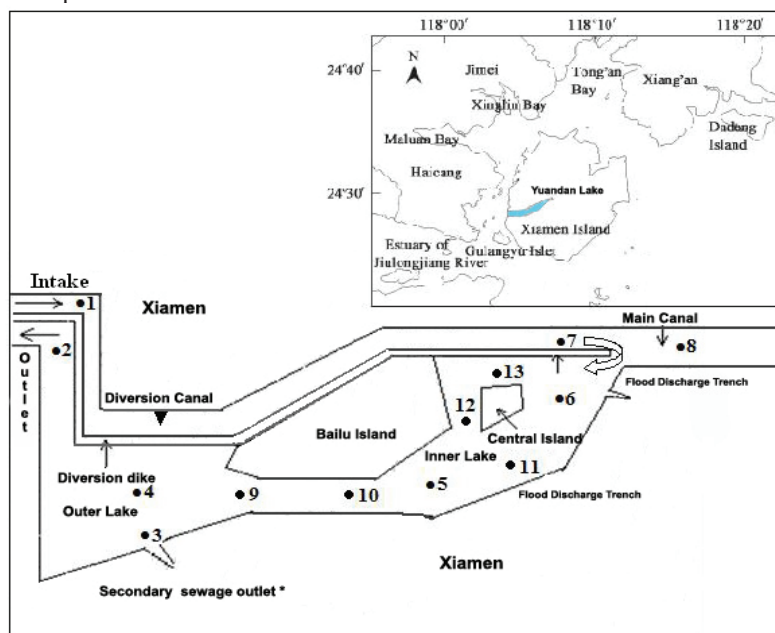


Fig. 1 Map of sampling sites in Yundang Lagoon

Absorption measurements

CDOM absorption measurements were carried out using a Techcomp UV-2300 dual-beam UV-Vis spectrophotometer with a 10 cm quartz cell, in the scanning wavelength range of 240-800 nm at 1 nm intervals. Milli-Q water was used as the reference. Absorbance (A) was converted into absorption coefficient (m^{-1}) using the expression $a(\lambda) = 2.303 A(\lambda)/L$, where λ is the wavelength and L is the cuvette length in meters. Absorption coefficient at wavelength of 280 nm (a_{280}) was chosen as an index of DOM concentration. The spectral slope ratio (S_R) was calculated following Helms et al. (2008) [14].

DOC measurements DOC concentrations were determined using a Multi N/C 3100 TOC-TN analyzer (Analytik Jena, Germany). Measurements were performed in triplicate with a fixed instrumental variance <2%. The accuracy of measurements was daily verified with the Low Carbon Water (LCW) and Deep Sea Water (DSW) from University of Miami.

Results and discussion

Absorption characteristics of CDOM in Yundang Lagoon CDOM absorption coefficient in Yundang Lagoon typically decreased with increasing wavelength in the UV and visible regimes. The variation trend was roughly exponential (Fig. 2), indicating that optical properties of CDOM derived from sewage discharge was similar to CDOM samples from various natural environments [5-7]. However, shoulders were conspicuous over 255-280 nm for many samples. Such phenomenon has also been reported in Taihu Lake and coastal environments [15, 16].

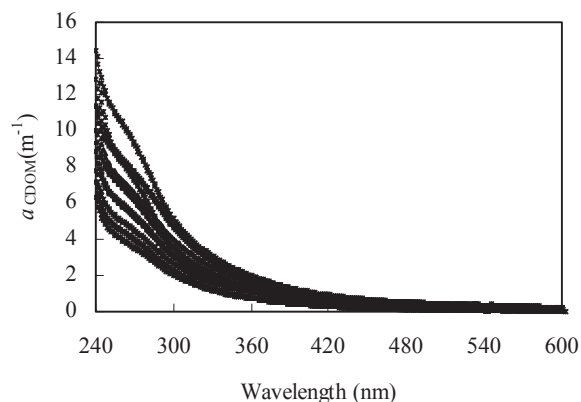


Fig. 2 Absorption spectra of CDOM for all samples collected in 9 April, 2008

Spatial and temporal variation of a_{280} and S_R

Fig. 3 shows the monthly variation of absorption coefficient a_{280} in six typical stations in the lagoon. It is clear that a_{280} showed similar temporal variation at all stations except St.1, which is located at the inlet of outer seawater into the lagoon. The highest a_{280} were observed at St.8 and St.3. St.8 was located at the main canal, where a great amount of domestic sewage directly discharged into the lagoon from upstream Songbai Lake. St.3 was located at the outlet of a sewage treatment plant in Xiamen. Although the municipal wastewater has been treated by this plant, the organic matter concentration in the treated wastewater is still high [12]. These results demonstrated that sewage discharge was still the main sources of CDOM in this lagoon. Such input resulted in the high CDOM abundance in both inner and outer lagoon. This was showed

by the similar variation trend of a_{280} at St.5 and St.4 to these two stations. Low a_{280} at St. 1 and relatively high a_{280} confirmed that the engineering measures to introduce seawater from Xiamen Bay into the lagoon at high tide period and to flow out the lagoon water at low tide period can actually be effective in diluting the organic pollution.

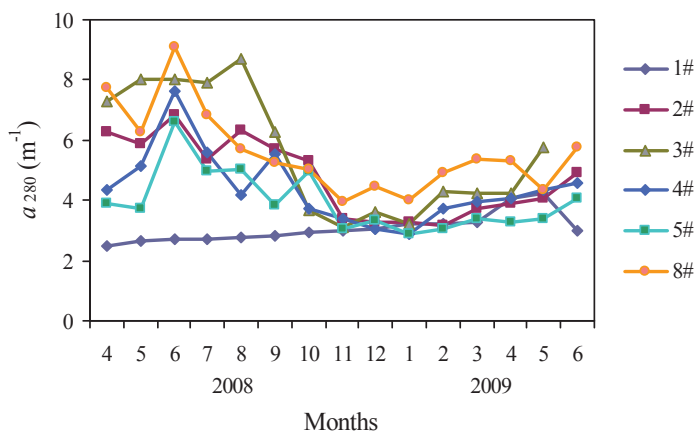


Fig. 3 Temporal variation of a_{280} in Yundang Lagoon

During the winter of 2008 and spring of 2009, a_{280} at most stations showed a significant decrease. The nutrient (i.e. ammonium, nitrate, nitrite, phosphate) concentrations also demonstrated the similar decrease tendency. This may be due to several reasons. The secondary sewage treatment plant near St.3 was closed in the middle of 2008. In addition, the municipal works constructed in the upstream of the lagoon also reduce the amount of sewage discharged into the lagoon. Furthermore, the production of sewage is notably lower in winter than in summer due to the less consumption of domestic water by citizens during cold weather period.

The spectral slope ratio (SR) has been proposed to be inversely related to the DOM molecular weight [14]. The weight-average molecular weight (Mw) decreased with the increase of SR. Generally, terrestrial DOM is characterized by relatively low SR while marine DOM has higher SR values. It is noteworthy that most SR values were >1 (Fig. 4), especially for samples collected at St.8 and St.5. These results implied that the molecular weight of DOM in Yundang Lagoon was relatively small compared with the normal terrestrial DOM. This is consistent with the strong biological reactivity of sewage DOM. One exception was the lowest values of SR (<1) for St. 3 samples during the spring of 2008. DOM in St.3 during this period was derived mainly from the secondary sewage plant. Large amounts of DOM with a low molecular weight in the sewage had been degraded significantly, resulting in the discharge of DOM with a higher molecular weight into the lagoon.

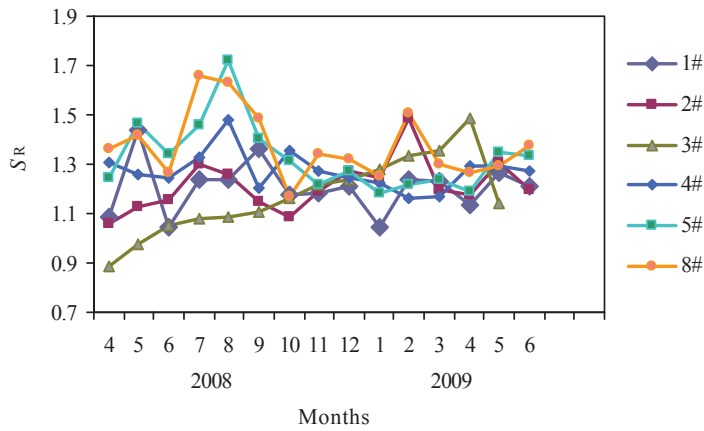


Fig. 4 Temporal variation of SR in Yundang Lagoon

Relationship between a_{280} and the DOC concentration

CDOM represents the fraction of total DOM pool absorbing ultraviolet-visible (UV-Vis) light, while DOC indicates the total carbon contents of DOM. As the measurement of DOC is more difficult and time-consuming, an alternative spectroscopic proxy for DOC quantification is preferable. The linear relationship analysis indicated a positive correlation between a_{280} and the DOC concentration (Fig. 5) for all samples. This suggested that CDOM optical properties can be used as an indicator to trace the DOC concentration and the degree of organic pollution in highly-polluted environments.

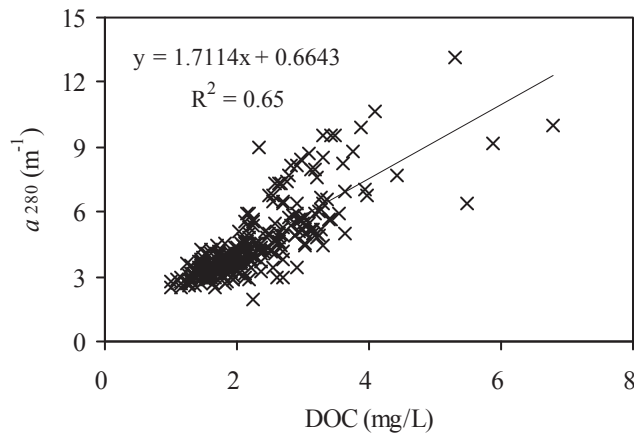


Fig. 5 Relationships between a_{280} and DOC concentrations

Summary

A monthly consecutive sampling has been carried out in Yundang Lagoon, China from April 2008 to June 2009 in order to study the optical properties of chromophoric dissolved organic matter (CDOM) in the

highly polluted aquatic environment. The absorption spectra of DOM from this polluted saline lake resembled that of DOM from other natural environments. The spatial distribution of absorption coefficients at 280 nm (a_{280}) indicated that sewage discharge was the main source of CDOM in this lagoon. A notable decrease of a_{280} from spring to winter of 2008 indicated that the CDOM abundance was sensitive to the variation of sewage discharge from anthropogenic activities. Most values of the spectral slope ratio (S_R) of CDOM absorption were >1 , implying that the sewage-derived DOM has a low molecular weight. A close correlation between a_{280} and DOC concentrations illustrated the feasibility of DOM optical properties as an indicator of the degree of organic pollution in highly-polluted aquatic environments.

Acknowledgements

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