Optical approaches to examining the dynamics of dissolved organic carbon in optically complex inland waters

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Abstract
Optical approaches were developed to examine the relationship between the optically active and the optically inactive fractions of dissolved organic carbon in inland waters. A multiple linear regression model was developed on the basis of an extensive dataset from Taihu Lake, and validated employing data from another large shallow eutrophic lake (Chaohu Lake) in southern China. The model was used to estimate the concentration of dissolved organic matter ($n = 191$) using the absorption characteristics of its chromophoric fraction with a high correlation coefficient ($R^2 = 0.62$) and a low root mean squared error (RMSE = 9.67%). This intra-ecosystem validity allows us to improve our understanding of carbon dynamics using optical remote sensing approaches for these optically complex lakes, where multiple sources and sinks of dissolved organic matter were present.

Keywords: CDOM, DOC, lake, optical properties, remote sensing, case 2 waters

1. Introduction

In recent decades, increasing attention has been paid to the dynamics of organic carbon in natural waters. As dissolved organic carbon (DOC) is the largest pool of reduced organic carbon in most aquatic ecosystems (Hedges 2002), an understanding of its spatial and temporal dynamics is fundamental to monitor carbon cycling in marine and lake environments (Chen *et al* 2004). DOC is a major energy source for microbially based aquatic food webs (Deegan and Garritt 1997) and plays an important role in the biogeochemical dynamics and optical conditions of many lakes and rivers. Spectral attenuation by chromophoric dissolved organic matter (CDOM), the colored fraction of DOC, can modify primary productivity as well as reduce UV related stress on aquatic biota (Nieke *et al* 1997).

Identifying a relationship between the chromophoric and non-chromophoric portions of dissolved organic matter allows for the optical analysis of aquatic carbon cycles, particularly important in large lakes and marine environments. This relationship has been investigated in rivers (Del Castillo and Miller 2008), estuarial waters (Spencer *et al* 2009) and coastal systems (Fichot and Benner 2011). Many studies indicate that the spectral absorption characteristics of CDOM ($a_g(\lambda)$) and the concentration of DOC (C_{DOC}) vary independently (Vodacek *et al* 1997, Loiselle *et al* 2009b). However,

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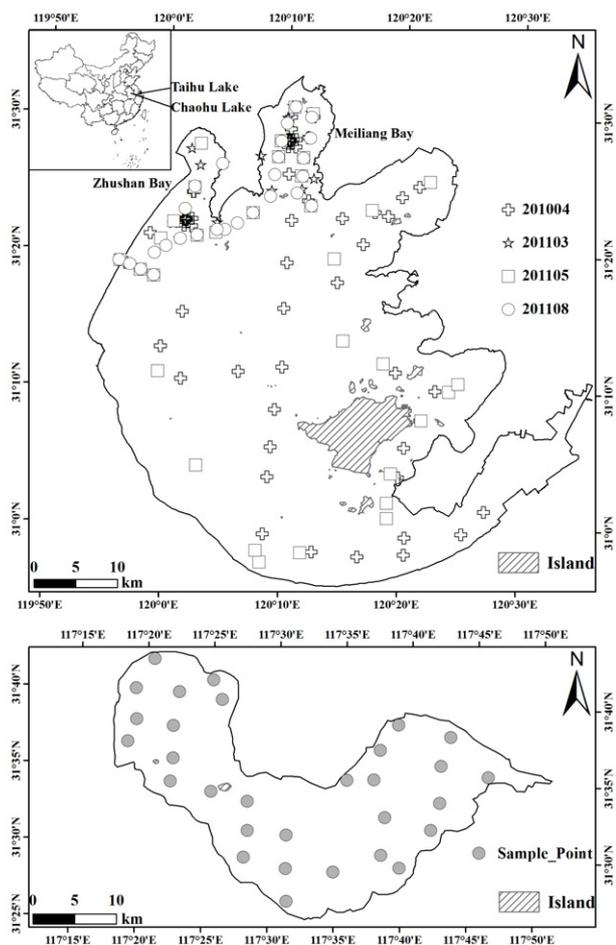
Figure 1. Geographical location of sampling sites in Taihu Lake and Chaohu Lake. For Taihu Lake, overlaid points in Meiliang Bay and Zhushan Bay result from sampling in the same positions in different cruises.

Figure 2. Spectral slopes against wavelength from 250 to 400 nm calculated using non-linear regression at a 20 nm interval in the four cruises in Taihu Lake.

recent studies in coastal waters have shown that where a single DOC source is dominant, DOC concentrations can be estimated using a log-linearized ecosystem specific relationship using two CDOM absorption wavelengths, $a_g(275)$ and $a_g(295)$ (Fichot and Benner 2011). Inland waters, however, usually have multiple processes that modify the relation between the optical and chemical properties of DOC (dilution, photodegradation, flocculation) (Chen *et al* 2004, Loiselle *et al* 2010).

Changes in CDOM absorption characteristics derive directly from solar exposure and indirectly oxidation of the aromatic compounds (Reche *et al* 2000, Loiselle *et al* 2012), which cause losses in humification and aromaticity (Weishaar *et al* 2003). The molecular implications of photobleaching differ depending on the spectral characteristics of the incident solar irradiance. In the ultraviolet B wavelengths (UVB, 280–315 nm), absorption losses of CDOM are related to the degradation of the olefinic components (Loiselle *et al* 2009b). Exposure to UVA (315–400 nm) has been associated to modifications in the CDOM aromatic fraction (Corin *et al* 1996, Ma and Green 2004). Changes in absorption in the visible wavelengths have been associated with a

disruption in the intramolecular charge transfer that is related to the featureless absorption spectrum typical of natural CDOM (Osburn *et al* 2009).

Changes in the optical properties of CDOM can be characterized using individual absorption wavelengths, specific UV absorption $a_g^*(\lambda) = a_g(\lambda)/C_{DOC}$ (Weishaar *et al* 2003), the ratio of absorptions $a_R = a_g(\lambda_1)/a_g(\lambda_2)$ (Helms *et al* 2008) and the absorption spectral slope (S, nm^{-1}): $a_g(\lambda) = a_g(\lambda_0) \exp[S(\lambda_0 - \lambda)]$ where $a_g(\lambda)$ is the CDOM absorption at wavelength λ and $a_g(\lambda_0)$ is the CDOM absorption at a reference wavelength λ_0 (Bricaud *et al* 1981). Changes in S have been shown to reflect changes in the molecular structure and average molecular weight of DOM (Carder *et al* 1989).

Through improving our understanding of the linkages between C_{DOC} and its spectral properties, new insights into organic carbon dynamics can be gained, including the photochemical processes that modify the structure, reactivity and bio-lability of DOC in aquatic ecosystems. In the present study, we explore a modeling approach to estimate DOC from CDOM absorption using an extensive bio-optic dataset. This model is then applied in two shallow inland lakes.

2. Material and methods

Data from two shallow lakes (figure 1) were used in this study. Taihu Lake, the third largest freshwater lake in China with an average depth of 1.9 m, is characterized by severe summertime cyanobacteria blooms (Duan *et al* 2009). Chaohu Lake is another shallow and large hypereutrophic lake in south China, with similar eutrophication problems (Xie *et al* 2005).

Water samples (192) were collected from Taihu Lake at 5 cm depth in April 2010, March, May and August 2011 (figure 1 and table 1). Discrete samples were immediately filtered through precombusted (6 h at 450 °C) 47 mm Whatman GF/F glass fiber filters (0.70 μm) at a low
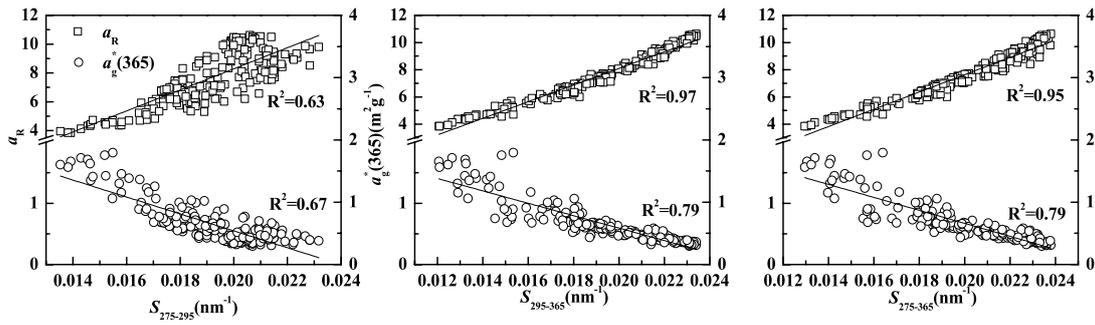
Figure 3. Relationships between slopes (275–295 nm, 295–365 nm, 275–365 nm) and a_R and $a_g^*(365)$.
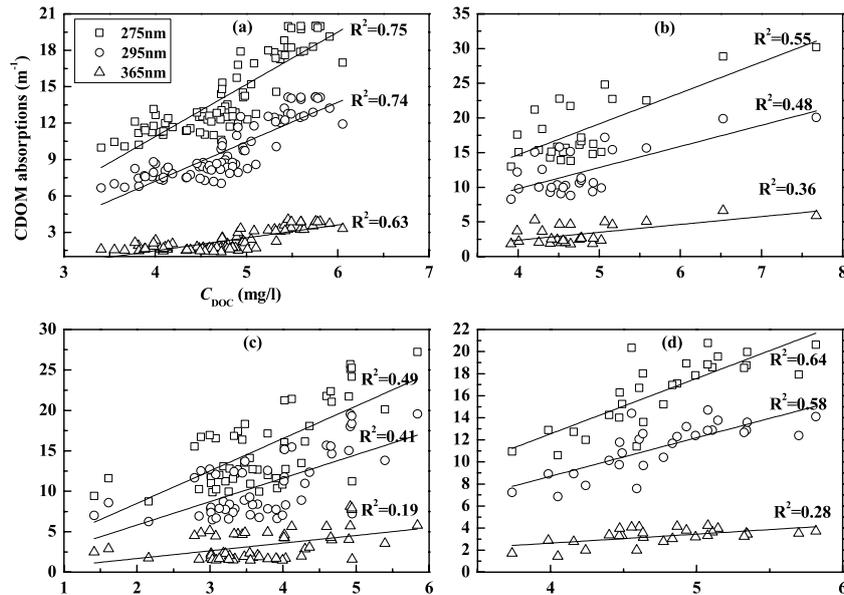
Figure 4. Relationship between CDOM absorptions and DOC concentration in Taihu Lake: (a) 201 004; (b) 201 103; (c) 201 105; (d) 201 108.

Table 1. Descriptive statistics of averages of $a_g(365)$, C_{DOC}, $a_g^*(365)$ and a_R from measurement campaigns in Taihu Lake and Chaohu Lake.

Sampling date	Proxy	Study area	Sampling points	$a_g(365)$ (m^{-1})	C_{DOC} (mg l^{-1})	$a_g^*(365)$ (m^2 g^{-1})	a_R
23 April–2 May 2010	201 004	Taihu Lake	84	2.30 ± 0.83	4.77 ± 0.62	0.47 ± 0.12	8.79 ± 1.34
24–25 March 2011	201 103	Meiliang Bay Zhushan Bay	26	3.27 ± 1.46	4.79 ± 0.80	0.67 ± 0.25	7.99 ± 1.67
1–8 May 2011	201 105	Taihu Lake	54	3.31 ± 1.82	3.70 ± 0.87	0.91 ± 0.45	7.16 ± 2.09
31 August–2 September 2011	201 108	Meiliang Bay Zhushan Bay	27	3.26 ± 0.75	4.75 ± 0.51	0.68 ± 0.14	6.86 ± 0.97
15–16 October 2009	200 910	Chaohu Lake	35	5.92 ± 6.67	9.50 ± 12.88	0.64 ± 0.37	9.46 ± 1.23

vacuum for DOC analysis (C_{DOC}), using a Shimadzu TOC-5000A analyzer following the protocol of Chen *et al* (2004). An aliquot of each sample was filtered through a 0.22 μm Whatman Nuclepore filter pretreated by 10% dilute hydrochloric acid. The filtrate was stored in the dark at a low temperature (4–8 °C) until analysis. The CDOM absorbance spectra were measured on a UV-2401 spectrophotometer with 1 cm quartz cuvettes, after the filtrate reached the room temperature (20 °C). Milli-*Q* water was used as a blank and reference. Absorbance ($A(\lambda)$) from 200 to 800 nm was

determined for each sample and converted to the absorption coefficients as $a_g(\lambda) = 2.303A(\lambda)/l$, where l was the cuvette path length. Baseline correction was performed on the basis of the average absorption coefficients from 700 to 800 nm according to Green and Blough (1994).

Specific UV absorption coefficients, $a_g^*(\lambda)$ (m^2 g^{-1}), were calculated by dividing the CDOM absorption at $\lambda = 365$ nm by C_{DOC}. This wavelength was chosen to be consistent with other studies which examine both CDOM absorption and fluorescence (Bari and Farooq 1985). Absorption ratios,

a_R, were determined using CDOM absorptions at 255 and 365 nm: $a_R = a_g(255):a_g(365)$ as given by Helms *et al* (2008).

The distribution of absorption spectral slope was calculated using a non-linear fitting method based on the least squares regression analysis from 250 to 400 nm at a 20 nm wavelength interval following Loiselle *et al* (2009b).

A model validation dataset was constructed using DOC and CDOM measurements on samples obtained in Chaohu Lake (30 stations) in October 2009 (table 1). Sampling and analysis were made following the same methods in both lakes.

3. Results and discussion

3.1. Characteristics of DOC and CDOM in Taihu and Chaohu Lakes

In Taihu Lake, CDOM absorption at 365 nm averaged 2.3 m^{-1} in 2010 and 3.3 m^{-1} in 2011, while DOC concentrations ranged from 3.8 to 4.8 mg l^{-1} (table 1). The two northern bays, Meiling and Zhushan, often linked to algal blooms (Duan *et al* 2009), had similar absorption values to that of whole lake in 2011, but with much higher C_{DOC} values. The Chaohu Lake dataset presented higher $a_g(365)$ and C_{DOC}. The carbon-specific UV absorption, $a_g^*(365)$, was highest in the Taihu Lake May 2011 dataset, averaging almost twice that of the Taihu Lake 2010 dataset obtained in the same period. The two northern bay datasets, obtained in March and September 2011 showed similar values. The average absorption ratio value (a_R) was highest in the Chaohu Lake and 2010 Taihu Lake datasets.

The distribution of the absorption spectral slopes showed the spectral variability of S_λ and significant differences between sampling campaigns (figure 2). A significant and negative relationship was found between the absorption spectral slope ($S_{275-295}$, $S_{295-365}$, $S_{275-365}$) and the carbon-specific UV absorption coefficients, $a_g^*(365)$ (figure 3). As expected, a strong and positive correlation was observed between the absorption spectral slope intervals and a_R. Both terms have been used as indicators of intramolecular structure and weight of DOM (Helms *et al* 2008). Furthermore, the absorption spectral slope is clearly a logarithmic form of the absorption ratio. In the present dataset, these parameters, a_R (or S) and $a_g^*(365)$ were shown to provide comparable information on the CDOM present.

3.2. Estimation of DOC from CDOM

The direct correlation between C_{DOC} and CDOM absorption was spectrally variable and generally poor for most datasets. The highest correlation was found to occur at lower wavelengths (figure 4).

The relationship between multiple wavelengths was explored using a multiple regression approach. In the recent work by Fichot and Benner (2011), a multiple regression analysis of the logarithm of CDOM absorption at 275 and 295 nm was used to estimate DOC concentrations in a coastal waters ecosystem. A similar approach, using the extensive
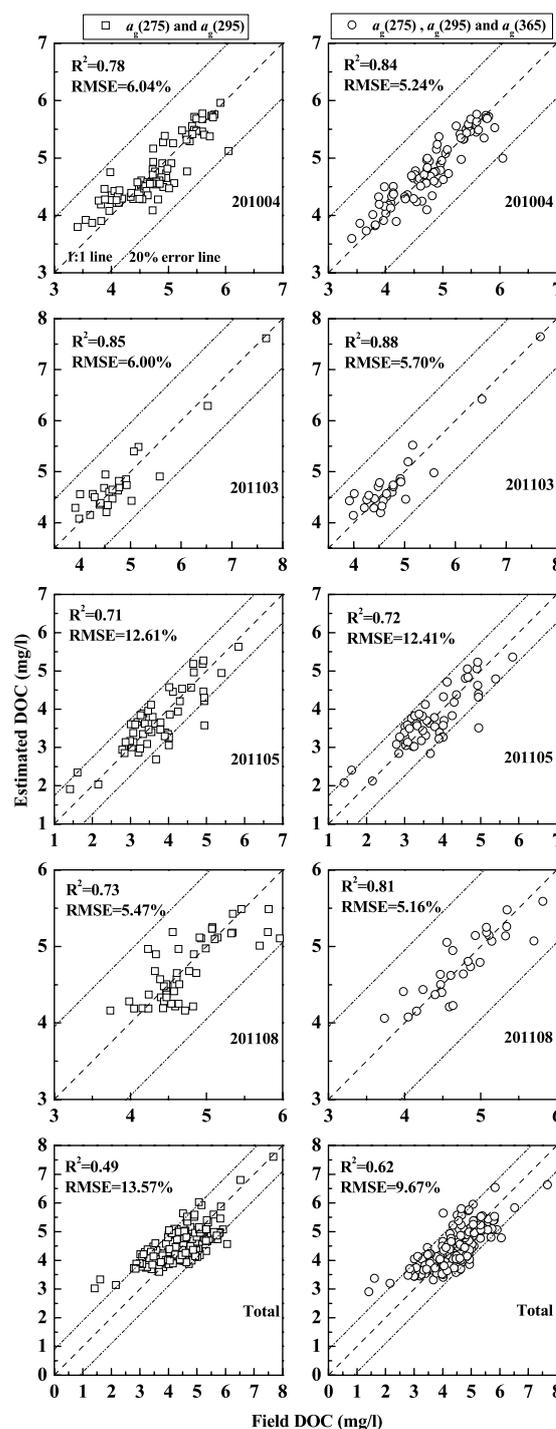
Figure 5. Determination of DOC concentrations from CDOM absorptions using multiple linear regressions of DOC concentrations against two and three CDOM absorptions.

datasets from Taihu Lake was used to determine dataset specific and lake specific algorithms following: $C_{DOC} = \alpha + \beta a_g(275) + \gamma a_g(295)$, where α, β and γ are regression coefficients. The resulting algorithms (figure 5) provided good results for each dataset ($0.71 < R^2 < 0.85$), but did not present a strong correlation when the Taihu datasets were combined ($R^2 = 0.49$, RMSE = 13.57%).
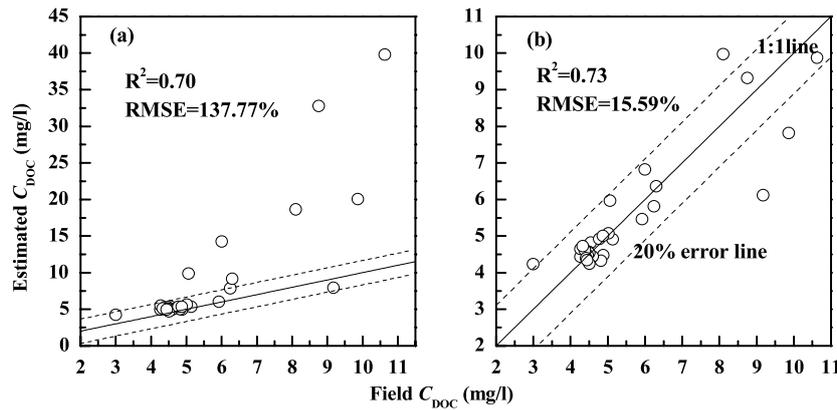
Figure 6. Validation of the Taihu Lake two wavelength model (a) and three wavelength model (b) to estimate DOC concentrations in Chaohu Lake.

We then examined a three wavelengths regression using CDOM absorption at 275, 295 and 365 nm:

$$C_{\text{DOC}} = \delta + \varepsilon a_{\text{g}}(275) + \zeta a_{\text{g}}(295) + \eta a_{\text{g}}(365) \qquad (1)$$

where δ, ε, ζ and η are regression coefficients. Longer UV wavelengths were chosen to provide information related to changes in structure and sources of organic matter. The selection of these wavelengths was also related to absorption wavelengths used in other studies. The three wavelength algorithms provided significantly higher correlations between the estimated and measured DOC for all but one measurement campaign (201 105) (figure 5). Using the complete Taihu Lake dataset, the resulting three wavelength algorithm showed a significantly higher correlation with DOC ($R^2 = 0.62$, RMSE = 9.67%).

$$C_{\text{DOC}} = 1.81 + 0.72 a_{\text{g}}(275) - 0.79 a_{\text{g}}(295) \qquad (2)$$
$$C_{\text{DOC}} = 1.48 - 0.03 a_{\text{g}}(275)$$
$$\qquad\quad + 0.60 a_{\text{g}}(295) - 0.99 a_{\text{g}}(365). \qquad (3)$$

To examine the specificity of these algorithms developed for Taihu Lake, we tested the two regressions employing the Chaohu Lake dataset. The two wavelength model failed to show a significant estimation of C_{DOC} in Chaohu Lake. However, the three waveband model, optimized for Lake Taihu, provided a good estimate of Chaohu Lake C_{DOC} (figure 6). The RMS error was 15.59% and the errors were uniformly distributed around the 1:1 line. It should be noted that many samples are clustered around 4.5 mg l^{-1}, but the relationship remains robust when part of these values are removed.

A separate three band model was developed using the dataset in Chaohu Lake, yielding the regression coefficients $\delta = 2.02$, $\varepsilon = -0.07$, $\zeta = 0.49$ and $\eta = -0.49$, which were very similar to those of the Taihu Lake dataset ($R^2 = 0.75$, RMSE = 15.05%) (figure 7).

4. Conclusion

The possibility of a direct relationship between DOC concentration and CDOM absorption is limited to ecosystems
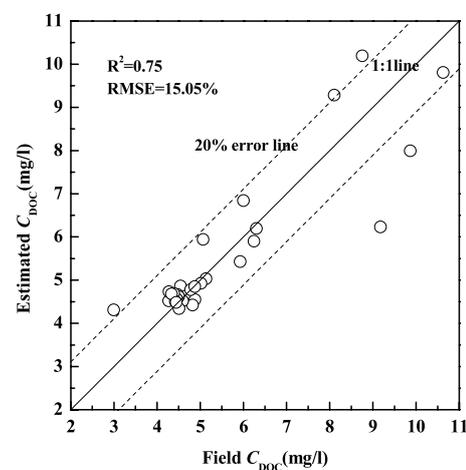
Figure 7. DOC concentration estimated using the three wavelength model based on Chaohu Lake data.

where a single DOC source undergoes dilution or conservative mixing (Del Vecchio and Blough 2004). The lack of such a correlation indicates that multiple sources and sinks are present. Lake Taihu, similar to most inland water bodies, presents a combination of DOC sources and sinks, which vary spatially as well as temporally. In most productive inland ecosystems, both terrestrial and algal-derived DOC sources are present. In shallow unstratified lakes, upwelling and resuspension also bring DOC into the surface waters. Bacterial activity and photodegradation will usually dominate loss processes in large lake ecosystems. Both mechanisms have spatial and temporal variability in Taihu Lake, which has been confirmed in the spatial and temporal variability in the S_λ (Loiselle *et al* 2009a) and $a_{\text{g}}^*(365)$.

Based on the temporally and spatially distinct datasets from Taihu Lake, a multiple linear regression approach using three absorption wavelengths provided a viable estimation approach to estimate DOC concentrations, in particular when a heterogeneous dataset was considered. Furthermore, the same model was found to provide a good estimate of DOC concentrations in a different shallow lake ecosystem. The results show a high determination coefficient $R^2 = 0.73$ and

a low RMS error 15.59%, indicating that the model was significantly robust for exploring DOC dynamics in this second lake.

Although the methodology may be applied to other aquatic ecosystems, re-parameterization of the model may be required where differences in geochemical and biological processes influence the optical properties of DOM. The links between the optical and chemical properties of DOM improve our understanding of the temporal and spatial variability of its molecular characteristics. Furthermore, such information makes it possible to examine relationships between optically active and optically inactive components of the DOM and to determine spectrally distinct degradation rates in relation to exposure to solar radiation (photodegradation), a major transformation process of dissolved organic carbon.

Acknowledgments

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