Colored dissolved organic matter in Tampa Bay, Florida

Zhiqiang Chen a,*, Chuanmin Hu a, Robyn N. Conmey a, Frank Muller-Karger a, Peter Swarzenski b

a College of Marine Science, University of South Florida, 140 Seventh Avenue S., St. Petersburg, FL, 33701, USA
b United States Geological Survey, 600 Fourth Street S., St. Petersburg, FL, 33701, USA

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Abstract

Absorption and fluorescence of colored dissolved organic matter (CDOM) and concentrations of dissolved organic carbon (DOC), chlorophyll and total suspended solids in Tampa Bay and its adjacent rivers were examined in June and October of 2004. Except in Old Tampa Bay (OTB), the spatial distribution of CDOM showed a conservative relationship with salinity in June, 2004 (aCDOM(400) = −0.19 × salinity + 6.78, R2 = 0.98, n = 17, salinity range = 1.1–32.5) with little variations in absorption spectral slope and fluorescence efficiency. This indicates that CDOM distribution was dominated by mixing. In October, 2004, CDOM distribution was nonconservative with an average absorption coefficient (aCDOM(400), ∼7.76 m−1) about seven times higher than that in June (∼1.11 m−1). The nonconservative behavior was caused largely by CDOM removal at intermediate salinities (e.g., aCDOM(400) removal >15% at salinity ∼13.0), which likely resulted from photobleaching due to stronger stratification. The spatial and seasonal distributions of CDOM in Tampa Bay showed that the two largest rivers, the Alafia River (AR) and Hillsborough River (HR) were dominant CDOM sources to most of the bay. In OTB, however, CDOM showed distinctive differences: lower absorption coefficient, higher absorption spectral slopes, and lower ratios of CDOM absorption to DOC and higher fluorescence efficiency. These differences may have stemmed from (1) changes in CDOM composition by more intensive photobleaching due to the longer residence time of water mass in OTB; (2) other sources of CDOM than the HR/AR inputs, such as local creeks, streams, groundwater, and/or bottom re-suspension. Average CDOM absorption in Tampa Bay at 443 nm, aCDOM(443), was about five times higher in June and about ten times higher in October than phytoplankton pigment absorption, apha(443), indicating that blue light attenuation in the water column was dominated by CDOM rather than by phytoplankton absorption throughout the year. © 2007 Elsevier B.V. All rights reserved.

Keywords: Colored dissolved organic matter; Dissolved organic carbon; Absorption; Fluorescence; Estuarine-mixing; Tampa Bay

1. Introduction

Tampa Bay is a shallow (average depth of ∼4.0 m), micro-tidal (tidal range ∼1.0 m) estuary located along the west coast of central Florida (Fig. 1). It is the largest estuary in Florida (∼1000 km²) and is one of the 28 estuaries of national significance for the U.S. (Harwell et al., 1995). Significant ecosystem restoration efforts since the mid-1980’s have led to improved water quality and increased expectations that seagrass coverage can again increase (Janicki and Pribble, 2001; Ladika, 2002; Anastasiou et al., 2005). A water quality monitoring program has been established in Tampa Bay since 1974 (Boiler et al., 1991) to track water quality indices such as...
chlorophyll (Chl), nutrient concentrations, water clarity (e.g., Secchi depth and turbidity), and visual conditions (water color in Platinum–Cobalt Units).

Previous studies found some correlation between Chl and light attenuation in Tampa Bay (Janicki and Pribble, 2001). However, Hu et al. (2004) showed that colored dissolved organic matter (CDOM) plays a key role in controlling light attenuation within Tampa Bay. In addition to light attenuation (Clementson et al., 2004), dissolved organic carbon (DOC) affects the transport and bio-availability of trace metals and organic pollutants (Santschi et al., 1997; Guo et al., 2001). Therefore, CDOM and DOC provide means for additional quantitative assessment of ecological conditions in the bay.

Because Tampa Bay is large, it is difficult to monitor water quality parameters synoptically using traditional methods. Remote sensing techniques seem appropriate because they provide synoptic and frequent mapping capabilities. However, the high CDOM concentration makes it difficult to estimate Chl remotely because both CDOM and Chl strongly absorb blue light (e.g., Magnuson et al., 2004). Hence, knowledge of CDOM sources, distribution and its optical properties would enhance our ability to monitor the water quality of Tampa Bay.

Here we discuss absorption and fluorescence of CDOM and the factors that affect these variables in Tampa Bay. We collected observations during two cruise surveys, specifically in June and October, 2004. We examined how CDOM optical properties varied with salinity, Chl, total suspended solids concentration (TSS), and DOC. Our objectives were (1) to characterize the distribution and variability of CDOM in Tampa Bay; and (2) to understand processes that control its origins, dispersal and sinks.

2. Methods

Based on different geographic features and salinity regimes, Tampa Bay is conventionally divided into four mainstem segments: Old Tampa Bay (OTB), Hillsborough Bay (HB), Middle Tampa Bay (MTB), and Lower Tampa Bay (LTB) (Lewis and Whitman, 1985) (Fig. 1). Fig. 1 shows sample locations for our surveys on June 1–3 (dry period) and October 12–14 (wet period), 2004. Seventeen stations were collected from three of the four segments. Six samples were collected from the Alafia River (AR) during the dry season in June, 2004. The AR was not sampled in October, 2004, because the river’s effect was readily observable in the bay due to high discharge at that time.

Fresh water inputs of the Alafia and the Hillsborough River, the two largest rivers discharging into Tampa Bay were examined using U.S. Geological Survey National Water Information System (USGS NWIS) data to derive climatological (1973 to 2003) and 2004 daily flow rates (Fig. 2). Fig. 2 clearly shows the general trend of river flow rates (the wet season from June to October and the dry season for the rest of the months of a year) and possible deviation from the typical seasonality for a specific year. From Fig. 2 our sampling dates of June 1–3 and October 12–14, 2004 can be reasonably designated as in the dry and wet seasons, respectively.

2.1. Temperature, salinity, chlorophyll and total suspended solids

Surface water samples for temperature, salinity, chlorophyll, and total suspended solids (TSS) were collected using a bucket from a small boat. Temperature
and salinity were measured immediately using a WTW™ Multi 340i Meter (Aquatic eco-system, FL, USA). Samples were stored in brown plastic bottles in a cooler with ice. They were filtered the same day after returning to the lab through GF/F Whatman filters (pump pressure <120 mm Hg) to determine chlorophyll concentration (Chl) using a Turner-Designs fluorometer (Mueller et al., 2003). Whatman™ Nylon membrane filters (0.2 μm pore size) were used to obtain CDOM filtrates. TSS estimates were based on 500–800 ml water samples filtered through pre-weighed 47 mm Millipore GN filters (0.45 μm pore size). Filters were dried in a desiccator and weighed again. The difference of filter weights between with and without particulates, together with the volume of filtered seawater, was used to calculate TSS (Mueller et al., 2003).

2.2. Dissolved organic carbon

Samples to measure dissolved organic carbon concentration (DOC) were collected directly from surface waters of the bay using 500 ml brown glass bottles previously rinsed three times with Milli-Q water before each sampling. Samples were filtered through pre-combusted (500 °C overnight) 47-mm Whatman® GF/F filters. The initial 250 ml of filtrate was discarded, and 50 ml of subsequent filtrate was preserved in a brown glass bottle poisoned with 30 μl of 1.1 M high purity hydrochloric acid, then stored at −17 °C. A Shimadzu TOC-5000A (using high temperature catalytic oxidation) equipped with the ASI-5000A accessory was used to analyze DOC samples. Milli-Q water was used as an instrument reference blank and to prepare a standard solution of potassium hydrogen phthalate (KHP). The accuracy and precision of the measurements were better than 5%. DOC was not measured during the wet season.

2.3. CDOM absorption coefficient and fluorescence

CDOM abundance was estimated in term of its light absorption and fluorescence properties. A Hitachi U3310 double-beam spectrophotometer (300–850 nm, 2 nm resolution) was used to measure CDOM spectral absorbance \( A(\lambda) \) (dimensionless) in 10 cm quartz cells with Milli-Q water as the blank reference. \( A(\lambda) \) was measured three times and the mean was used to calculate the CDOM absorption coefficient, \( a_{\text{CDOM}}(\lambda) \) (\( \text{m}^{-1} \)) as follows (Hu et al., 2002):

\[
a_{\text{CDOM}}(\lambda) = \ln 10 \times A(\lambda)/L,
\]

where \( L \) is the cuvette pathlength (0.1 m).

A nonlinear least square regression was used to derive spectral slope \( S, \text{nm}^{-1} \) over the wavelength range 350–440 nm:

\[
a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(400) \exp\left[-S(\lambda - 400)\right] + K,
\]

where \( a_{\text{CDOM}}(400) \) is the CDOM absorption coefficient at a reference wavelength of 400 nm, and \( K \) is an offset to account for residual scattering and/or noise.

CDOM fluorescence spectroscopy was performed according to the method of Coble (1996) using a SPEX Industries Fluoromax-2 spectrofluorometer. Samples with \( A(300) > 0.02 \) were diluted to avoid self-shading (Green, 1992). The fluorescence signal, after corrections for Raman scattering and instrument configuration, was normalized to units of quinine sulfate equivalents (QSE) in ppb using the fluorescence of a diluted series of quinine sulfate dihydrate in 0.05 M sulfuric acid at excitation/emission (Ex/Em) of 350/450 nm. CDOM fluorescence intensity was reported as fluorescence at Ex/Em of 300/420 nm, located in Humic Peak C region (Coble, 1996).
Table 1
Surface salinity, CDOM absorption coefficient at 400 nm ($\alpha_{\text{CDOM}}(400)$, m$^{-1}$) and spectral slope (S, nm$^{-1}$), total suspended solids concentration (TSS, mg/l), chlorophyll concentration (Chl, mg/m$^3$), dissolved organic carbon concentration (DOC, $\mu$M) and normalized CDOM fluorescence (Quinine Sulfate equivalent, QSE) in Tampa Bay and the Alafia River (AR) in the 2004 dry (June, first row per station) and wet (October, second row per station) seasons.

<table>
<thead>
<tr>
<th>Stations</th>
<th>Latitude (°)</th>
<th>Longitude (°)</th>
<th>Salinity</th>
<th>$\alpha_{\text{CDOM}}(400)$ (m$^{-1}$)</th>
<th>Spectral slope ($\times 10^{-3}$, nm$^{-1}$)</th>
<th>TSS (mg/l)</th>
<th>Chl (mg/m$^3$)</th>
<th>DOC ($\mu$M)</th>
<th>Fluorescence (QSE)</th>
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<td>1.41</td>
<td>18</td>
<td>1.8</td>
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<td>13</td>
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<td>82.657° W</td>
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<td>N.D.</td>
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<td>82.599° W</td>
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<td>1.16</td>
<td>18.6</td>
<td>6.6</td>
<td>6.6</td>
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<td>28</td>
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<td>82.598° W</td>
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<td>1.16</td>
<td>18.6</td>
<td>6.6</td>
<td>6.6</td>
<td>374</td>
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<td>27.1</td>
<td>0.92</td>
<td>21.7</td>
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<td>AR 1</td>
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<td>6.96</td>
<td>17</td>
<td>4.4</td>
<td>3.6</td>
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<td>82.320° W</td>
<td>1.7</td>
<td>5.88</td>
<td>16</td>
<td>3.8</td>
<td>5.0</td>
<td>390</td>
<td>83</td>
</tr>
</tbody>
</table>

(continued on next page)
2.4. Phytoplankton pigment absorption coefficient

In the wet season, the spectral absorption coefficient due to particulate matter, \( a_p(\lambda) \), was determined using the quantitative filter technique (Yentsch, 1962). We used a custom-made, 512-channel spectroradiometer (\( \sim 350–850 \) nm) to measure absorption. Pathlength amplification was corrected using the \( \beta \) factor of Carder et al. (1999). Detrital absorption spectra, \( a_d(\lambda) \), were obtained after chemical extraction of phytoplankton pigments from the sample using hot methanol (Kishino et al., 1985). Phytoplankton pigment absorption spectra, \( a_{ph}(\lambda) \), were then calculated by difference:

\[
a_{ph}(\lambda) = a_p(\lambda) - a_d(\lambda).
\]

Because the maximum absorption of phytoplankton occurs near 443 nm, \( a_{ph}(443) \) was chosen to compare with \( a_{CDOM}(443) \). In the dry season when no particulate absorption was measured, \( a_{ph}(443) \) was modeled as (Bricaud et al., 1995; Babin et al., 2003):

\[
a_{ph}(443) = 0.04 \times \text{Chl}^{0.668}.
\]

2.5. Statistical tests

Pearsons’ product moment correlation and linear and nonlinear regression analyses were used to evaluate the statistical relationships between variables. Statistical significance was reported as either not significant (NS) (\( p>0.05 \)), weak (*, \( 0.01<p<0.05 \)), moderate (**, \( p<0.01 \)), and high or strong (***, \( p<0.001 \)).

3. Results

Table 1 lists the results for all stations by segments and seasonal surveys. These results are discussed below.

Table 1 (continued)

<table>
<thead>
<tr>
<th>Stations</th>
<th>Latitude (°)</th>
<th>Longitude (°)</th>
<th>Salinity</th>
<th>( a_{CDOM}(400) ) (m²)</th>
<th>Spectral slope ( \times 10^{-3} ), nm⁻¹</th>
<th>TSS (mg/l)</th>
<th>Chl (mg/m³)</th>
<th>DOC (µM)</th>
<th>Fluorescence (QSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Alafia River</td>
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<tr>
<td>AR 3</td>
<td>27.868° N</td>
<td>82.328°W</td>
<td>4.1</td>
<td>5.74</td>
<td>16</td>
<td>6.0</td>
<td>12.5</td>
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<td>82.348°W</td>
<td>7.4</td>
<td>5.72</td>
<td>14</td>
<td>6.0</td>
<td>16.1</td>
<td>366</td>
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</tr>
<tr>
<td>AR 5</td>
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<td>82.362°W</td>
<td>12.1</td>
<td>4.78</td>
<td>15</td>
<td>5.4</td>
<td>10.4</td>
<td>391</td>
<td>58</td>
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<tr>
<td>AR 6</td>
<td>27.859° N</td>
<td>82.389°W</td>
<td>18.1</td>
<td>3.01</td>
<td>17</td>
<td>18.2</td>
<td>18.3</td>
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<tr>
<td>Dry season average</td>
<td>7.4 (6.6)</td>
<td>5.35 (1.34)</td>
<td>16 (1)</td>
<td>7.3 (5.4)</td>
<td>11.0 (5.9)</td>
<td>414 (56)</td>
<td>70 (17)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:
(1) CDOM absorption spectral slope (\( S \)) was determined over the wavelength range 350–440 nm.
(2) N.D. = “not determined”.
(3) The numbers in parentheses in each average row represent standard deviations.
Station locations can be found in Fig. 1.

3.1. Distributions of TSS and Chl

TSS concentration ranged from 1.6 mg/l in Middle Tampa Bay (MTB) to 18.2 mg/l in the Alafia River (AR). On average, TSS was higher in the wet season than in the dry season, especially in Hillsborough Bay (HB) (Fig. 3A, Table 1), indicative of higher riverine sediment inputs. MTB generally showed the lowest TSS of all bay segments in both seasons. However, looking at individual sampling locations there was no apparent relationship between TSS and salinity (Fig. 3A, Table 2). This suggests that TSS in Tampa Bay was not directly

Fig. 3. Surface salinity versus (A) total suspended solids concentration (TSS) and (B) chlorophyll concentration (Chl). Empty symbols show observations for the dry season, whereas filled symbols for the wet season. These symbols are used in all subsequent figures.
controlled by riverine inputs, but by other processes, such as local bottom resuspension by winds and/or tides, which may play more important roles.

Chlorophyll showed significant seasonal variations. The wet season concentrations exceeded those in the dry season by factors of 2–10 (Table 1). The highest Chl was observed in the wet season in HB (79.0 mg/m³) and MTB (>40.0 mg/m³). In the AR, highest Chl (18.0 mg/m³) was observed in the intermediate salinity range 10.0–20.0, and then Chl decreased with increasing salinity (Fig. 3B, Table 1), consistent with earlier observations (Vargo et al., 1991).

Looking at individual stations, there was a moderate correlation between Chl and salinity in the wet season (Fig. 3B, Table 2). This correlation was attributed to nitrogen supply through rivers in the wet season, as

![Fig. 4. Surface salinity versus $a_{CDOM}(400)$ for Tampa Bay and the AR in the dry and wet seasons (also see Table 3). The dotted line is the conservative mixing line in the dry season in June, 2004, while the dashed dotted line is the hypothesized mixing line for the wet season in October, 2004 ($a_{CDOM}(400) = 16.81 – 1.10 \times (Salinity - 8.8)$).](image)

Table 2
Correlation coefficients ($r$) between surface salinity and TSS and between surface salinity and Chl in Tampa Bay and the AR in the dry and wet seasons

<table>
<thead>
<tr>
<th>Season</th>
<th>Parameter</th>
<th>AR</th>
<th>HB+MTB</th>
<th>HB+MTB+OTB</th>
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</thead>
<tbody>
<tr>
<td>Dry season (June, 2004)</td>
<td>TSS vs salinity</td>
<td>0.58 NS</td>
<td>0.43 NS</td>
<td>0.46 NS</td>
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<tr>
<td></td>
<td>(n=6)</td>
<td>(n=11)</td>
<td>(n=17)</td>
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<tr>
<td></td>
<td>Chl vs salinity</td>
<td>0.77 NS</td>
<td>0.41 NS</td>
<td>0.58*</td>
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<td></td>
<td>(n=6)</td>
<td>(n=11)</td>
<td>(n=17)</td>
<td></td>
</tr>
<tr>
<td>Wet season (October, 2004)</td>
<td>TSS vs salinity</td>
<td>N.D.</td>
<td>0.82 *</td>
<td>0.43 NS</td>
</tr>
<tr>
<td></td>
<td>(n=9)</td>
<td>(n=14)</td>
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<tr>
<td></td>
<td>Chl vs salinity</td>
<td>N.D.</td>
<td>0.79 *</td>
<td>0.73**</td>
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<tr>
<td></td>
<td>(n=9)</td>
<td>(n=14)</td>
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</table>

Note:
1. Statistical significance is reported as either NS ($p > 0.5$), * ($0.01 < p < 0.05$), ** ($p < 0.01$), *** ($p < 0.001$).
2. The numbers in parentheses are numbers of sample used for correlation analysis.
3. N.D. = “not determined”.

Table 3
Results of regression analyses between $a_{CDOM}(400)$ and surface salinity in Tampa Bay and the AR in the dry and wet seasons

<table>
<thead>
<tr>
<th>Region</th>
<th>Regression equation ($R^2$)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry season (June, 2004)</td>
<td>$a_{CDOM}(400) = -0.19 \times \text{salinity} + 6.77$</td>
<td>0.90**</td>
</tr>
<tr>
<td></td>
<td>$a_{CDOM}(400) = -0.19 \times \text{salinity} + 6.72$</td>
<td>0.90**</td>
</tr>
<tr>
<td>AR, HB+MTB</td>
<td>$a_{CDOM}(400) = -0.19 \times \text{salinity} + 6.78$</td>
<td>0.98***</td>
</tr>
<tr>
<td>HB+MTB+OTB</td>
<td>$a_{CDOM}(400) = -0.077 \times \text{salinity} + 3.27$</td>
<td>0.29 NS</td>
</tr>
<tr>
<td>Wet season (October, 2004)</td>
<td>$a_{CDOM}(400) = 43.70 \times \exp (-0.11 \times \text{Salinity})$</td>
<td>0.98***</td>
</tr>
</tbody>
</table>

Note:
1. Statistical significance is reported as either NS ($p > 0.5$), * ($0.01 < p < 0.05$), ** ($p < 0.01$), *** ($p < 0.001$).

Tampa Bay phytoplankton are generally nitrogen limited (Vargo et al., 1991).

3.2. Light absorption by CDOM

The CDOM absorption coefficient generally decreased with increasing salinity. The lowest CDOM absorption values occurred in MTB in the dry season (Fig. 4, Table 1). The relationships between $a_{CDOM}(400)$ and salinity, however, varied with bay segments and seasons.

In the dry season, except in Old Tampa Bay (OTB), $a_{CDOM}(400)$ was highly correlated with salinity,

Table 4
Correlation coefficients ($r$) between $a_{CDOM}(400)$ and TSS and between $a_{CDOM}(400)$ and Chl in Tampa Bay and the AR in the dry and wet seasons

<table>
<thead>
<tr>
<th>Season</th>
<th>Parameter</th>
<th>AR</th>
<th>HB+MTB</th>
<th>HB+MTB+OTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry season (June, 2004)</td>
<td>TSS vs $a_{CDOM}(400)$</td>
<td>0.43 NS</td>
<td>0.60 NS</td>
<td>0.36 NS</td>
</tr>
<tr>
<td></td>
<td>Chl vs $a_{CDOM}(400)$</td>
<td>0.74 NS</td>
<td>0.55 NS</td>
<td>0.24 NS</td>
</tr>
<tr>
<td>Wet season (October, 2004)</td>
<td>TSS vs $a_{CDOM}(400)$</td>
<td>N.D.</td>
<td>0.79 *</td>
<td>0.73**</td>
</tr>
<tr>
<td></td>
<td>Chl vs $a_{CDOM}(400)$</td>
<td>N.D.</td>
<td>0.77 *</td>
<td>0.73**</td>
</tr>
</tbody>
</table>

Note:
1. Statistical significance is reported as either NS ($p > 0.5$), * ($0.01 < p < 0.05$), ** ($p < 0.01$), *** ($p < 0.001$).
2. The numbers in parentheses are numbers of sample used for correlation analysis.
3. N.D. = “not determined”.

indicating that riverine CDOM was dominant. CDOM from the AR was conservatively mixed into the MTB. In the wet season, however, a CDOM(400) in HB and MTB showed an exponential decrease with increasing salinity (Fig. 4, Table 3), showing that CDOM was not conservatively mixed. We estimate that N15% of a CDOM(400) had been removed at the salinity of about 13.0 (the median salinity in October, 2004) when compared with the hypothesized conservative mixing line. In both seasons, CDOM absorption in OTB was significantly lower than those in HB and MTB, indicative of possible differences in CDOM sources in OTB (Fig. 4).

CDOM absorption exhibited significant seasonal variations. Average a CDOM(400) in the wet season was about four, seven and ten times higher than in the dry season for OTB, MTB and HB, respectively (Table 1).

For example, at TB17, a CDOM(400) in the dry season was 1.50 m \(^{-1}\) (salinity=27.3), but increased to 16.80 m \(^{-1}\) in the wet season (salinity=8.8). The average a CDOM(400) over the entire bay increased about seven fold from \(\sim 1.11 \text{ m}^{-1}\) in the dry season (salinity=27.9) to \(\sim 7.76 \text{ m}^{-1}\) in the wet season (salinity=14.3). Furthermore, extrapolations from regression analysis between a CDOM(400) and surface salinity in the dry season and from the hypothesized conservative mixing line in the wet season indicate that a CDOM(400) of the river end member in the wet season (N26.5 m \(^{-1}\) at salinity =0.0) was significantly higher than that in the dry season (about 6.78 m \(^{-1}\)). The difference suggests a seasonal difference in land-based CDOM sources.

CDOM absorption showed no significant correlation (\(p>0.05\)) with TSS or Chl in the dry season (Fig. 5A and B, Table 4). In the wet season, however, CDOM was

![Fig. 5. a CDOM(400) versus (A) TSS and (B) Chl and (C) a CDOM(443) versus a ph(443) for Tampa Bay and the AR in the dry and wet seasons (also see Table 4).](image)

![Fig. 6. CDOM absorption spectral slope (S) versus surface salinity for Tampa Bay and the AR in the dry and wet seasons. The dashed and solid lines represent the average spectral slope without OTB samples in the dry and wet seasons, respectively. Student's t-test showed that these average values were significantly smaller than those from OTB in both seasons (\(p<0.01\)).](image)
moderately correlated with Chl over most of Tampa Bay (Fig. 5B, Table 4), likely as a result of the coincidence that both high loads of nutrients and CDOM were delivered into the bay in the wet season.

As a result of the high concentrations of CDOM, CDOM absorption of blue light was significantly higher than that due to phytoplankton pigment absorption, consistent with the results of Hu et al. (2004). Average $a_{CDOM}(443)$ was about five and ten times higher than $a_{ph}(443)$ in the dry and wet seasons, respectively (Fig. 5C). The ratios of $a_{CDOM}(443)$ and $a_{ph}(443)$ ranged from three to eleven for the different bay segments and seasons with maximum in HB in the dry season and MTB in the wet season. The minima were observed in OTB in both seasons (Table 5).

CDOM absorption spectral slope ($S$) within the AR, HB, and MTB stations were similar in both seasons ($p < 0.05$). Higher spectral slopes were, however, found in OTB in both seasons, especially in the dry season (Fig. 6). This implies that CDOM chemical composition might be different in OTB, possibly due to photo-bleaching or due to different CDOM sources in OTB as discussed below.

### 3.3. DOC

During the dry season, DOC varied from 200 to 500 μM with higher concentration in the AR and OTB and lower in the HB and MTB. Unlike CDOM, however, DOC in the AR did not decrease with increasing salinity but remained almost constant along the AR salinity gradient (Fig. 7). When comparing CDOM absorption with DOC, OTB showed consistently lower ratios of CDOM absorption to DOC (Fig. 8), suggesting that DOC in OTB may have originated from different sources.

### 3.4. CDOM fluorescence efficiency

The ratio of fluorescence to absorption, or “equivalent fluorescence efficiency”, was relatively constant throughout the bay and the AR during the dry season (Fig. 9), consistent with the observations that most CDOM was
derived from river inputs, and that CDOM was conservatively mixed in most of Tampa Bay. In contrast, the OTB CDOM showed slightly higher fluorescence efficiency than those in other areas (Fig. 9, Table 6). This coincided with differences in other optical properties: lower CDOM absorption, higher spectral slopes, and lower ratios of CDOM absorption to DOC.

4. Discussion

4.1. CDOM sources and sinks

Previous studies have shown that CDOM in estuarine and coastal waters is mainly of terrestrial origin (Blough and Del Vecchio, 2002; and references therein). In Tampa Bay, we found a high correlation between CDOM and salinity along a salinity gradient from the Alafia River (AR) to Middle Tampa Bay (MTB) in both seasons (June and October 2004, respectively), showing that riverine inputs were the dominant CDOM sources. Based on river flow rates, there are four “major rivers” discharging into Tampa Bay (Fig. 1) with the largest being the Hillsborough River (HR) and Alafia River (AR) (Robinson, 2004). Statistically similar slopes and intercepts from the AR, HB and MTB (Fig.4) indicate that CDOM properties from the HR and AR might be optically similar. A single conservative mixing behavior (or effectively the same riverine end-member) was observed. Indeed, Hastings et al. (2004) suggested that CDOM from the HR and AR was optically not distinct. This optical similarity of CDOM may be related to their similar watersheds because watersheds seem to play important roles in determining CDOM quantity and quality (Chen et al., 2004). For example, although the Atchafalaya and Mississippi River systems share almost identical fresh water sources, the Atchafalaya has higher CDOM loads than the Mississippi, which was attributed to the remarkable differences in downstream watersheds between these two river systems (Chen and Gardner, 2004). Similarly, in Tampa Bay, CDOM from the Little Manatee River (LMR) and Manatee River (MR) showed higher CDOM fluorescence/absorption ratios than those from the HR and AR. The AR and HR are associated with similar urban watersheds (Estevez et al., 1991), but the LMR and MR are related to more rural, agriculture-intensive watersheds (Hastings et al., 2004).

Conservative mixing of CDOM is common in estuarine systems because high CDOM concentration tends to mask small variations caused by other processes, such as photochemical and biological processes (Nieke et al., 1997; Blough and Del Vecchio, 2002; Rochelle-Newall and Fish, 2002; Kowalczyk et al., 2003; Chen et al., 2004). CDOM absorption in Tampa Bay is indeed relatively higher compared to those reported for other estuaries. For instance, at salinity of 25.0, $a_{\text{CDOM}}$ (400) in Tampa Bay in the dry season was about 1.50 m$^{-1}$, while it was about 0.50 m$^{-1}$ in the Chesapeake Bay (Rochelle-Newall and Fish, 2002) and about 0.70 m$^{-1}$ in the Mississippi River plume (Hu et al., 2003). Thus CDOM distribution in Tampa Bay is primarily determined by the processes controlling its high concentration such as the river inputs and subsequent mixing between river and oceanic waters.

The poor correlation between $a_{\text{CDOM}}$ (400) and Chl in the dry season, and particularly the lack of corresponding CDOM increase in Chl peaks in the AR further indicate that phytoplankton played minor role in regulating CDOM abundance in the dry season in Tampa Bay. While $a_{\text{CDOM}}$ (400) showed a moderate correlation with Chl in the wet season, this correlation likely resulted from a coincidence between high concentrations of nutrients (therefore Chl) and CDOM, rather than indicating an inherent cause-and-effect relationship between Chl and CDOM. Little contribution of CDOM from phytoplankton in estuaries was also observed in other estuaries, such as in the Chesapeake Bay (Rochelle-Newall et al., 1999; Rochelle-Newall and Fish, 2002). Similarly, the poor correlation between $a_{\text{CDOM}}$ (400) and TSS suggests that CDOM contribution from sediment resuspension was also negligible. However, further study is required to provide more direct evidence for the relationship between CDOM variation and sediment resuspension events in Tampa Bay, since previous studies in other coastal and estuarine waters have suggested that CDOM could be derived from bottom sediments (e.g., Boss et al., 2001; Burdige et al., 2004).

Several processes have been reported to be responsible for CDOM removal, such as flocculation and precipitation of sediments in estuaries (Uher et al., 2001), microbial transformation and photobleaching (Blough and Del Vecchio, 2002; and references therein). Our observations of no significant correlation between CDOM and TSS in either season suggest that TSS in Tampa Bay (1.6–18.2 mg/l) may be lower than that required for a substantial CDOM removal by sediment adsorption (Uher et al., 2001).

CDOM removal by photobleaching might also be negligible in the dry season. Previous studies have found that photobleaching usually takes weeks to months to effect a noticeable removal of CDOM, depending on solar illumination and water column stability (e.g., Vodacek et al., 1997). Numerical modeling of Tampa Bay, however, suggested that the...
e-folding time (the time required for the number of particles in a grid cell to decrease by 65%) in Lower Tampa Bay (LTB) and in the adjacent deep channel was about 10 days or less (Burwell et al., 2000). Furthermore, the water column was generally well mixed in the dry season, which would further limit photobleaching. This hypothesis is consistent with the little variation in the spectral slope (Fig. 6) and fluorescence efficiency (Fig. 9) along the salinity gradient from the AR to MTB.

In the wet season, at least 15% of $a_{\text{CDOM}}(400)$ might have been removed at salinity $\sim 13.0$, assuming no CDOM was added from other processes (Fig. 4). Indeed, if we hypothesize that conservative mixing yields $a_{\text{CDOM}}(400) = 0.00 \text{ m}^{-1}$ at salinity $= 36.0$ from the riverine $a_{\text{CDOM}}(400) = 43.0 \text{ m}^{-1}$ at salinity $= 0.00$ (Fig. 4), then CDOM removal at salinity $\sim 13.0$ would be $> 50\%$ (observed $\sim 10.0$ as opposed to hypothetical $\sim 27.0 \text{ m}^{-1}$). This substantial CDOM removal in the wet season was likely due to photobleaching, because (1) in the wet season Tampa Bay becomes more stratified due to buoyancy input from freshwater and heat (Burwell et al., 2000); (2) CDOM delivered via rivers in the wet season may be younger and therefore susceptible to degradation (Zanardi-Lamardo et al., 2004).

CDOM in OTB showed distinctive properties relative to other bay segments, including lower $a_{\text{CDOM}}(400)$, higher spectral slopes ($S$), lower ratios of CDOM absorption to DOC and higher fluorescence efficiency. These differences suggest that CDOM in OTB may have different chemical composition. The higher spectral slopes might be an indicator of photobleaching due to loss of the CDOM fraction with higher molecular weight (Twardowski and Donaghay, 2002), in agreement with the longer water residence time in OTB ($> 140$ days) (Burwell et al., 2000) allowing for sufficient photobleaching (Vodacek et al., 1997). The longer water residence time also implies that the CDOM exchange through water circulation is weaker in OTB compared with in the HB and MTB, making local processes (phytoplankton production/degradation, CDOM released by sediment resuspension, photobleaching) more effective in determining its optical properties. The differences in CDOM properties in OTB may directly arise from different sources of CDOM, including local creeks, streams, rivers, and/or groundwater. This hypothesis is consistent with distinctive location and bathymetric features in OTB (e.g., the lack of a deep channel).

4.2 Seasonal variation in CDOM absorption

Average Tampa Bay $a_{\text{CDOM}}(400)$ in the wet season was $\sim 7.76 \text{ m}^{-1}$, about 7-fold higher than in the dry season ($\sim 1.11 \text{ m}^{-1}$). These values are near the upper limit of published ranges of CDOM absorption coefficients in coastal and estuarine waters (Kowalczyk et al., 2003). Indeed, extrapolated $a_{\text{CDOM}}(400)$ of riverine end member (salinity $= 0.0$) are about 7.00 $\text{ m}^{-1}$ and 26.50 $\text{ m}^{-1}$ in the dry and wet seasons, respectively, indicating that about 4-fold higher CDOM was present in rivers in the wet season than in the dry season. This seasonality is clearly linked to the variation in river flow rates (Fig. 2), suggesting that CDOM in Tampa Bay was primarily derived from river inputs. Events such as hurricanes or tropical storms in the wet season may transport extra CDOM from watersheds into local rivers and then into estuaries (e.g., Avery et al., 2004). In 2004, four major hurricanes (Category three or greater) affected Tampa Bay, likely resulting in even more CDOM delivered into the bay. The variations in freshwater inputs may also alter CDOM composition, as observed in other southern Florida estuarine and coastal waters (e.g., Zanardi-Lamardo et al., 2004).

4.3 Implications for water clarity monitoring and remote sensing

The absorption of blue light was dominated by CDOM rather than by phytoplankton pigments (Fig. 5C). Our results show that CDOM and phytoplankton pigments covary in the wet season, which is likely the primary reason that earlier studies concluded that chlorophyll could account for the variation in light attenuation (e.g., Janicki and Pribble, 2001). However, this correlation is seasonal, and not common in the dry season. A better index of water clarity is CDOM absorption or fluorescence, since this serves as a proxy for CDOM concentration and light absorption. This is a simple measurement that will benefit a water quality monitoring program.

The high ratio of CDOM to pigment absorption in Tampa Bay makes it difficult to reliably estimate Chl using the sea spectral reflectance band-ratio algorithms that are applied in Case I waters (O’Reilly et al., 2000). In complex CDOM-rich coastal environments, chlorophyll fluorescence line height (FLH) observations help assess synoptic patterns of Chl distribution (Hu et al., 2005). Both MODIS (Moderate Resolution Imaging Spectroradiometer Sensor) and MERIS (Medium Resolution Imaging Spectrometer); full resolution at 300-m per pixel) fluorescence data over Tampa Bay should be evaluated for application in Tampa Bay.

5. Summary and conclusions

Two surveys, in June and October of 2004, were conducted in Tampa Bay to study the applicability of
optical observations to assess water quality indices. The results show that colored dissolved organic matter (CDOM) dominates the absorption of blue light relative to phytoplankton pigments. Average $a_{\text{CDOM}}(443)$ was five and ten times higher than phytoplankton pigment absorption, $a_{\text{ph}}(443)$, in the dry and wet seasons, respectively. The Alafia River and the Hillsborough River were the main CDOM sources to Tampa Bay. These rivers showed $a_{\text{CDOM}}(400)$ of about 7.00 m$^{-1}$ and 26.50 m$^{-1}$ at zero salinity in the dry and wet seasons, respectively.

CDOM absorption coefficient within Tampa Bay showed significant seasonal variations with average $a_{\text{CDOM}}(400)$ of 1.11 m$^{-1}$ and 7.76 m$^{-1}$ in the dry and wet seasons, respectively. In the dry season, except for Old Tampa Bay, CDOM distribution was primarily controlled by conservative mixing between the riverine inputs from the Alafia and Hillsborough Rivers, and coastal waters near the mouth of Tampa Bay. For a better understanding of the interactions between CDOM and rivers, sediment and phytoplankton, more intensive sampling is required.

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