Non-conservative behaviors of chromophoric dissolved organic matter in a turbid estuary: Roles of multiple biogeochemical processes

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1. Introduction

Dissolved organic matter (DOM) is the largest pool of reduced carbon and plays important roles in many biogeochemical processes in aquatic environments (Benner, 2003; Battin et al., 2008; Jiao et al., 2010). The land–ocean flux of DOM is an important linkage between terrestrial and marine ecosystems. Elements of C, N and P bounded in terrestrial DOM can be released during both photochemical and microbial degradation processes, hence affecting the air-sea CO\textsubscript{2} flux, bioavailable inorganic nutrient levels and aquatic production in coastal oceans (e.g., Moran and Zepp, 1997; White et al., 2010; Bauer and Bianchi, 2011). Fluvial discharge is also a major source of chromophoric DOM (CDOM) in many estuaries and coastal oceans, a fraction of DOM which affects both primary production and the habitat for organisms through absorbing both UV and photosynthetically active radiations (Coble, 2007).

Estuary is a dynamic land–ocean interface with large physical, chemical, and biological gradients (Bauer and Bianchi, 2011). Many biogeochemical processes in the estuary may alter the fluvial DOM (including CDOM) that finally reaches the ocean (e.g., Shank et al., 2010; Fellman et al., 2010; Guo et al., 2011; Osburn et al., 2012; Yang et al., 2013a). Detailed studies on those processes are important for assessing their effects on the concentration, chemical composition, and biogeochemical reactivity of DOM in the estuary and for tracing terrestrial DOM in marine environments. In particular, adsorption-desorption of organic matter between particulate and dissolved phases may play important roles in turbid estuaries (Uher et al., 2001; Shank et al., 2005, 2011; Pisani et al., 2011). However, few studies examine the dissolution of watersoluble chromophoric particulate organic matter (CPOM) throughout an estuary from the freshwater end to the marine end, although such studies would provide significant insights into the factors influencing the level and chemical composition of CPOM and the interaction between CDOM and CPOM (Osburn et al., 2012). The turbidity maximum zone (TMZ) is widely present in global
estuaries and the adsorption-desorption process may be active in TMZ, which is to be studied to better understand the cycling of CDOM and DOM in estuaries (Xie et al., 2012).

The Jiulong Estuary is a shallow subtropical estuary in southeast China, with a TMZ developed in the upper estuary. There are active addition and removal of CDOM in the river-estuary interface (Guo et al., 2007, 2011), but the mechanism has not yet been well studied. This study aimed to: (1) examine dynamics of CPOM in the Jiulong Estuary; (2) compare the concentration and chemical composition of CPOM with those of CDOM and water-soluble chromophoric sediment organic matter (CSOM); and (3) assess the importance of desorption–adsorption in the non-conservative behavior of CDOM in the estuary, in comparison with other biogeochemical processes. These results also have implications for understanding the biogeochemistry of the bulk DOM in estuaries.

2. Materials and methods

2.1. Field sampling and laboratory incubations

Surface water samples were collected from the Jiulong Estuary using Niskin bottles during three cruises in April, August and November 2011 (Fig. 1). Bottom waters were only sampled at few stations in April and August, since the behavior of CDOM in the bottom water was similar to that in the surface water in this shallow estuary (Guo et al., 2011). Samples from stations S1 and S2 were collected in August to examine the inputs from a small stream overflowing through Haicheng Town and the South Jiulong River, respectively (Fig. 1). Salinity was measured using a SeaBird SBE917 Plus self-contained CTD (conductivity–temperature–depth) profiling system (Sea-Bird Electronics Inc., USA). Suspended particulate matter (SPM) was collected on pre-weighted 47-mm-diameter GF/F filter (nominal pore size 0.7 μm) and measured by weighting method in August and November.

For DOC and optical measurements, water samples were filtered through pre-combusted (500 °C for 5 h) GF/F filters. One aliquot of the filtrate was acidified with HCl and stored in a freezer for DOC measurements, while the other was stored in the cold (4 °C) and dark without acidification for CDOM optical measurements. Particles on the GF/F filter were stored in a freezer before the extraction of CPOM in August and November.

CPOM was extracted following a procedure for extracting water-soluble organic compounds from soils and aerosols (Mladenov et al., 2009, 2011). Briefly, particles on the GF/F filter were extracted in dark with 100 mL Milli-Q water (pH = 6.1) at 30 °C for 2 h on a constant temperature shaker. The resultant solution was filtered through GF/F filters and the filtrate was used for measuring water-soluble organic carbon (WSOCp) and optical properties following the procedures for DOC and CDOM optical measurements. The measured WSOCp and absorption coefficient of CPOM were corrected with the volume of water samples filtered in the field for collecting particles. In August, CPOM at stations A3–A8 were measured in triplicate and the mean analytical precisions were 10.4% and 6.5% for WSOCp and absorption coefficient. Most CPOM samples were determined for surface waters and only one was for the bottom water of TMZ in August (station A8).

Surface sediments were grabbed at stations A3–A6 and A8 and stored in a freezer in April. They were freeze-dried and homogenized through gentle grinding for the extraction of CSOM and adsorption experiment following the procedure described by Uhler et al. (2001) and Shank et al. (2005). CSOM from ~50 mg sediments was extracted, filtered and measured with a procedure similar to that for CPOM. To evaluate the adsorption of CDOM to sediments in the turbid upper estuary, ~50 mg of sediments were added into 100 mL filtrates (through GF/F filters) at stations A3–A6 and A8 and shaken in dark at 30 °C for 2 h. The resultant solution was re-filtered for measuring DOC and optical properties after desorption–adsorption. Adsorptions of DOC and CDOM were calculated as the initial contents in the filtrates plus desorption quantities from sediments (as determined in the CSOM extraction experiment) minus the final contents after desorption–adsorption. All the experiments on adsorption for the extractions of CDOM and CSOM and the adsorption were set to 2 h because: (1) the partition of organic matter between solid and liquid phases occurs mainly within 15 min and almost stops after 2 h; and (2) microbial degradation within 2 h can be ignored (Kaiser and Zech, 1998; Zhou and Wong, 2000).

Microbial degradation of CDOM was examined in April following the procedure described by Fellman et al. (2010). Water samples with salinities of 0 and 10 were initially filtered through pre-combusted GF/F filters to remove the majority of microbial biomass. The freshwater filtrate was added with microbial inocula collected at four salinities (0, 10, 22, and 30) with a volume/volume ratio of 9/1. The filtrate with a salinity of 10 was added with the microbial inoculum collected at the same station. At the start of the experiment and after incubations for 7 and 28 days at 25 °C in the dark, the solution was re-filtered for DOC and optical measurements. All incubations were carried out in triplicate and the mean variation coefficients were 6.4%, 1.1%, and 2.7% for DOC, absorption coefficient and fluorescence intensities. Microbial inocula were prepared by filtering whole waters through pre-combusted GF/D filters (nominal pore size 2.7 μm).

2.2. DOC, absorption, and fluorescence measurements

DOC, absorption, and fluorescence were measured using the methods described previously (Yang et al., 2013b). Briefly, the DOC concentration was measured with high temperature catalytic oxidation after removing dissolved inorganic carbon by oxygen purging, using a Multi N/C 3100 TOC-TN analyzer (Analytik Jena, Germany). Each sample was measured in triplicate with an analytical precision of 2%. Solutions of potassium hydrogen phthalate were used as standards and Low Carbon Water and Deep Sea Water (from Dr. D. A. Hansell, University of Miami) were used to verify the accuracy of the measurement.

Absorbance spectra of CDOM were scanned using a Techcomp 2300 UV–Vis spectrometer at wavelengths of 240–800 nm. The absorption coefficient at 280 nm (aCDOM(280)) was used to indicate the abundance of CDOM in this study. The absorption spectral slope of CDOM over 275–295 nm (S275–295) and the slope ratio (Sr: the ratio of the spectral slope over 275–295 nm to that over 350–400 nm) were calculated to trace compositional changes of CDOM (Helms et al., 2008).

Fig. 1. Sampling stations of the Jiulong Estuary in 2011 (NJR: North Jiulong River; WJR: West Jiulong River; SJR: South Jiulong River).
Excitation emission matrix fluorescence spectra (EEMs) were scanned using a Cary Eclipse fluorescence spectrophotometer at excitation and emission wavelengths of 250–450 and 300–600 nm. High absorption samples were diluted to A(350) < 0.02 at 1 cm path length for fluorescence measurements to avoid inner-filter effects (Moran et al., 2000; Kowalczuk et al., 2003). The spectra of each sample were calibrated with the Raman peak of Milli-Q water and subtracted Raman-normalized spectra of Milli-Q water (Stedmon and Markager, 2005). All the EEMs in this study, together with those collected in 2008–2009 in the Jiulong Estuary (Guo et al., 2011), were subject to parallel factor analysis (PARAFAC) (Stedmon and Bro, 2008). Four fluorescence components were identified: humic-like C1 with excitation/emission maxima at ≤250, 325/418 nm and ≥250, 375/458 nm, and protein-like C3 and C4 with excitation/emission maxima at ≥275/348 nm and ≤250, 300/370 nm. These components were similar to those identified in Guo et al. (2011) where only the EEMs collected from the Jiulong Estuary in 2008–2009 were analyzed. Fluorescence intensities of C(1–4) were used to trace changes in their levels while the contribution of protein-like components to the total fluorescence was calculated to examine changes in the chemical composition of fluorescent DOM.

3. Results

3.1. Dynamics of CDOM

The DOC concentration was 0.83–2.67 mg L⁻¹ and correlated negatively with salinity in the Jiulong Estuary (Fig. 2A). The latter indicated that the fluvial discharge was an important source of DOC in the estuary and the estuarine behavior of DOC was dominated by the mixing of freshwater and seawater (Guo et al., 2011). The DOC concentration was elevated at station S1 (3.42 mg L⁻¹) in the small polluted stream that flows through Haicheng Town (Fig. 2), while the DOC concentration at S2 in the South Jiulong River was similar to that at other stations with a similar salinity.

The aCDOM(280) value was 1.78–13.88 m⁻¹ and decreased with increasing salinity, indicating that CDOM was generally conservative in the three cruises of 2011 (Fig. 2B). However, CDOM showed notable non-conservative behaviors in the turbid river-estuary interface (stations A3–A8). In April, a removal of CDOM was evidenced by: (1) aCDOM(280) decreased from 12.8 to 10.2 m⁻¹ while salinity changed little within 0.14–0.16 at stations A3–A5; and (2) the lowered aCDOM(280) from the conservative mixing line in the low-mid salinity (1.5–14.5) zone. In August and November, rapid removal and addition of CDOM were shown by the fluctuated aCDOM(280) values at stations A3–A6. Elevated aCDOM(280) values at stations S1 and S2 suggested that the small stream flowing through Haicheng Town and the South Jiulong River were both additional sources of CDOM for the estuary.

The aCDOM(280) and aCDOM(370) values at stations A3–A9 in August and November were 0.018–0.0218 nm⁻¹ and 0.78–1.54 (Fig. 3), which correlate negatively with the average molecular weight of DOM, both higher in the marine end than in the freshwater end, indicating a lower average molecular weight of marine DOM. Similar to CDOM, the estuarine behaviors of individual fluorescent components were dominated by the mixing between terrestrial and marine DOM, as indicated by negative correlations between fluorescence intensities and salinity (r = −0.63 to −0.95, p < 0.01). The contribution of protein-like components to the total fluorescence increased with increasing salinity, indicating a compositional change of the bulk fluorescent DOM (Fig. 3C). This could be explained by: (1) the mixing of protein-rich marine DOM and humic-rich terrestrial DOM; and (2) the additions of tryptophan-like component from autochthonous production, in particular during the dry season (Guo et al., 2011).

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station A3; except for that, WSOCP was highest at A8–A9 in the TMZ and A5 where elevated turbidity was found. In November, WSOCP was highest at station A6 (the center of TMZ) and was generally higher in the upper than in the lower estuary.

The absorption coefficient of water-soluble CPOM ($a_{\text{CPOM}(280)}$) was $0.11 \pm 4.88 \text{ m}^{-1}$ in the surface water and was as high as $7.94 \text{ m}^{-1}$ in the bottom water at station A8 (Fig. 4C). The $a_{\text{CPOM}(280)}$ was equivalent to 5–46% of $a_{\text{CDOM}(280)}$ in surface waters and 101% of $a_{\text{CDOM}(280)}$ in the bottom water. The spatial distribution of $a_{\text{CPOM}(280)}$ was different from $a_{\text{CDOM}(280)}$ but very similar to SPM (Fig. 4B,C), with maximum values in the TMZ and lower values in the lower estuary. In fact, $a_{\text{CPOM}(280)}$ correlated significantly with SPM in both August and November (Fig. 5). The correlation between $a_{\text{CPOM}(280)}$ and salinity was significant in November but not in August (Fig. 5). Furthermore, regression slopes between $a_{\text{CPOM}(280)}$ and SPM in August and November were similar, which suggested a constant and predictable yield of CPOM desorbed from SPM.

$S_{275-295}$ and $S_R$ of CPOM ($S_{275-295(\text{CPOM})}$ and $S_R(\text{CPOM})$) were $0.0115–0.0133 \text{ nm}^{-1}$ and $1.20–1.38$ in August and $0.0106–0.0159 \text{ nm}^{-1}$ and $1.17–2.83$ in November (Fig. 6). Both of $S_{275-295(\text{CPOM})}$ and $S_R(\text{CPOM})$ correlated positively with salinity in November ($r = 0.81$, $p < 0.01$ and $r = 0.65$, $p < 0.05$, respectively), suggesting that the average molecular weight of water-soluble POM probably decreased with increasing salinity. This was likely due to the estuarine mixing of more humified (with larger molecular weight) terrestrial POM and fresher marine POM.
The concentration of water-soluble organic carbon desorbed from sediments (WSOC) was 0.28–0.49 mg L$^{-1}$ at a re-suspended sediment concentration of 500 mg L$^{-1}$ (Table 1). Correspondingly, absorption coefficient of CSOM ($a_{CSOM}(280)$) ranged from 0.42 to 4.08 m$^{-1}$. Both WSOCS and $a_{CSOM}(280)$ were highest for clayey sediments from stations A4 and A5 while lowest for sandy sediment from A8, suggesting that the content of water-soluble organic matter in the sediment was probably associated with the sediment properties. Generally, the bulk organic carbon content of sediment is dependent on its grain size (Keil et al., 1997). In addition, $S_{275-295(CSOM)}$ varied within 0.0090–0.0113 nm$^{-1}$, while $S_{R(CSOM)}$ was 1.08–1.46 at stations A3–A7 and 2.13 at A8. Generally, both $S_{275-295(CSOM)}$ and $S_{R(CSOM)}$ increased from A(3–4) to A(5–6) and to A8, likely suggesting a downstream decrease in the average molecular weight of water-soluble sediment organic matter.

### 3.3. Adsorption of CDOM to re-suspended sediments

When sediments were added to estuarine waters, there was active partition of organic matter between the solid and liquid phases. At a re-suspended sediment concentration of 500 mg L$^{-1}$, the adsorption quantities of DOC and $a_{CDOM}(280)$ within 2 h were 0.57–0.78 mg L$^{-1}$ and 0.34–3.04 m$^{-1}$ (Table 2). They were equal up to 32% of the initial DOC and 4–26% of the initial $a_{CDOM}(280)$. Nevertheless, the two proxies for the chemical composition of DOM ($S_{275-295(CDOM)}$ and $S_{R(CDOM)}$) changed little (<5%) in the adsorption experiment (data not shown), suggesting that the removal of DOM by adsorption to particles was probably not selective for different molecular-weight DOM components.

### 3.4. Microbial degradation of CDOM at the river-estuary interface

When the freshwater DOM sample was added with microbial inocula with salinities of 0–30, DOC and $a_{CDOM}(280)$ decreased by 11–25% and 23–38% after 28-day incubation (Table 3). DOC and $a_{CDOM}(280)$ in the estuarine sample (salinity: 10) decreased by 7% and 22%, respectively after 28-day incubation with local bacteria. $S_{275-295(CDOM)}$ and $S_{R(CDOM)}$ generally decreased during the incubation, suggesting an increase in the average molecular weight of DOM (preferential loss of low molecular weight components and/or production of high molecular weight components).

![Fig. 5](image_url)

Fig. 5. Relationships between the absorption coefficient of CPOM ($a_{CPOM}(280)$) and (A) the concentration of suspended particulate matter (SPM) and (B) salinity in the Jilulong Estuary in 2011.

![Fig. 6](image_url)

Fig. 6. Spatial variations of $S_{275-295}$ and $S_{R}$ of CPOM in the Jilulong Estuary in 2011, compared with those of CDOM.

### Table 1

<table>
<thead>
<tr>
<th>Station</th>
<th>Sediment type</th>
<th>WSOCS (mg L$^{-1}$)</th>
<th>$a_{CSOM}(280)$ (m$^{-1}$)</th>
<th>$S_{275-295(CSOM)}$ (*10$^{-2}$ nm$^{-1}$)</th>
<th>$S_{R(CSOM)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>Silt</td>
<td>0.39</td>
<td>0.98</td>
<td>0.96</td>
<td>1.15</td>
</tr>
<tr>
<td>A4</td>
<td>Clay</td>
<td>0.49</td>
<td>4.08</td>
<td>0.90</td>
<td>1.08</td>
</tr>
<tr>
<td>A5</td>
<td>Clay</td>
<td>0.49</td>
<td>3.49</td>
<td>1.07</td>
<td>1.20</td>
</tr>
<tr>
<td>A6</td>
<td>Sand-clay</td>
<td>0.34</td>
<td>1.12</td>
<td>1.07</td>
<td>1.46</td>
</tr>
<tr>
<td>A8</td>
<td>Sand</td>
<td>0.28</td>
<td>0.42</td>
<td>1.13</td>
<td>2.13</td>
</tr>
</tbody>
</table>

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The protein-like C3 and C4 were removed while the humic-like C1 and C2 were produced in most groups. The tryptophan-like C3 was highly susceptible to the microbial degradation. C4 was removed by the bottom water of TMZ in August (337 mg L\(^{-1}\)) and after they were deposited as sediments.

Table 2 Adsorption quantities and their percentages in the initial contents of DOC and CDOM.

<table>
<thead>
<tr>
<th>Station</th>
<th>DOC (mg L(^{-1}))</th>
<th>DOC (%)</th>
<th>(\Delta_{CDOM}(280)) (m(^{-1}))</th>
<th>(\Delta_{CDOM}(280)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>0.57</td>
<td>25</td>
<td>2.16</td>
<td>18</td>
</tr>
<tr>
<td>A4</td>
<td>(A_4)</td>
<td>(A_4)</td>
<td>3.04</td>
<td>26</td>
</tr>
<tr>
<td>A5</td>
<td>0.71</td>
<td>30</td>
<td>1.69</td>
<td>15</td>
</tr>
<tr>
<td>A6</td>
<td>0.78</td>
<td>32</td>
<td>1.32</td>
<td>13</td>
</tr>
<tr>
<td>A8</td>
<td>(A_8)</td>
<td>(A_8)</td>
<td>0.34</td>
<td>4</td>
</tr>
</tbody>
</table>

* The calculation of adsorption quantity might show large uncertainties when the adsorption was much smaller than the initial or final content. These data were excluded because they showed large variation coefficients of triplicate analysis (Relative standard deviation (RSD) > 20%).

4. Discussion

4.1. Dynamics of CPOM in the estuary

Dissolution of CPOM was observed in the Jiulong Estuary, similar to some recent studies (Shank et al., 2011; Pisani et al., 2011; Osburn et al., 2012). In particular, based on the correlation between \(\Delta_{CPOM}(280)\) and SPM in both August and November (Fig. 5), our results demonstrated that the amount of desorbed CPOM was largely dependent on the concentration of SPM. This also suggested a relatively constant yield of CPOM desorbed from SPM in the estuary, although the desorption of CPOM might be affected to some extent by the particle properties. In addition, the desorption of CPOM in the field may be also affected by environmental conditions such as temperature, pH and salinity, which should be examined in the future. However, the advantage of extracting all samples using the similar water media in our and other studies (e.g., Mladenov et al., 2009, 2011; Osburn et al., 2012) is that such a method makes the extracted CPOM from a series of samples comparable. Although fluorescence measurements are affected by pH, the effect is probably limited in most natural waters that normally have pH between 5 and 9 (Hudson et al., 2007). The desorption of CPOM was in particular important in TMZ, where the highest \(\Delta_{CPOM}(280)\) was observed (Fig. 4C). At a high concentration of SPM such as that in the bottom water of TMZ in August (337 mg L\(^{-1}\)), \(\Delta_{CPOM}(280)\) could be as high as that of \(\Delta_{CDOM}(280)\). Desorption of CPOM could provide an important additional source for CDOM in the TMZ, which might explain in part the non-conservative behavior of CDOM in this area (e.g., Xie et al., 2012).

Similar to CDOM, CPOM showed notable changes in the chemical composition in the estuary. Both of \(S_{275–295}(CPOM)\) and \(SR_{CPOM}\) correlated positively with salinity in November in the Jiulong Estuary. Similarly, \(SR_{CPOM}\) correlated positively with salinity in the Neuse River Estuary (Osburn et al., 2012). This result suggested that the average molecular weight of watersoluble POM probably decreased with increasing salinity, likely due to the estuarine mixing of more humified (with larger molecular weight) terrestrial POM and fresher marine POM. The spectral compositional proxies (such as \(S_{275–295}(CPOM)\) and \(SR_{CPOM}\) in this study) may be useful tools for tracing changes in the source of POM in estuaries.

4.2. Comparison of CPOM with CSOM and CDOM

Similar to suspended particles, sediments from the Jiulong Estuary also contained water-soluble chromophoric organic matter (Table 1). Both \(S_{275–295}\) and \(SR\) of CSOM were close to those of CPOM at stations A3–A8, suggesting that CSOM and CPOM probably had some similarities in chemical composition. However, the \(\Delta_{CSOM(280)}\) ranged from 0.42 to 4.08 m\(^{-1}\) at a re-suspended sediment concentration of 500 mg L\(^{-1}\), while \(\Delta_{CPOM(280)}\) was up to 7.94 m\(^{-1}\) at a SPM concentration of 337 mg L\(^{-1}\). The \(\Delta_{CPOM(280)}\) would be \(> 10\) m\(^{-1}\) if the linear regression between \(\Delta_{CPOM(280)}\) and SPM was extrapolated to a particle concentration of 500 mg L\(^{-1}\). Therefore, the content of CSOM was lower than that of CPOM at a similar particle concentration, which was probably due to the removal of CPOM both when they settled down through the water column and after they were deposited as sediments.

The \(\Delta_{CPOM(280)}\) was 5–46% (average: 22% \(\pm\) 13%) of \(\Delta_{CDOM(280)}\) in surface waters and 101% of \(\Delta_{CDOM(280)}\) in the bottom water of station A8. This suggested that the level of water-soluble CPOM was generally lower than that of CDOM in the Jiulong Estuary. In addition, while \(\Delta_{CDOM(280)}\) generally decreased with increasing salinity, \(\Delta_{CPOM(280)}\) showed maximum values in TMZ at salinity 5.6–10.6 in August and at salinity 0.3–3.1 in November. Correlation analysis showed that the CPOM level was affected more by the SPM concentration while the CDOM level was dependent mainly on salinity. Therefore, CPOM and CDOM had de-coupled spatial variations and their relative importance in the total light-absorption might vary in estuaries.

Fluorescence intensities of CPOM were very low, suggesting a low fluorescence quantum yield (the fluorescence to absorption ratio) of CPOM in the Jiulong Estuary. Similarly, fluorescence intensities of based-extracted POM were much lower than those of CDOM in the Neuse River Estuary (Osburn et al., 2012). The lower fluorescence quantum yield of CPOM suggested that CPOM and CDOM probably had different chemical compositions that might be associated with different sources and biogeochemical transformation histories. For example, POM generally has undergone less microbial reworking than DOM in estuaries (e.g., Loh et al., 2006) and the fluorescence quantum yield would be increased by microbial degradation (Romera-Castillo et al., 2011). CPOM and CDOM had different \(S_{275–295}\) and \(SR\) values in the Jiulong Estuary, which also indicated differences in their chemical composition. The extracted POM also had much higher \(SR\) values than CDOM in the Neuse River Estuary (Osburn et al., 2012). However, when compared with proxies for CDOM, the lower \(S_{275–295}(CPOM)\) suggested a higher average molecular weight while the higher \(SR_{CPOM}\) suggested a lower average molecular weight of CPOM in the Jiulong Estuary. This is probably because that CPOM and CDOM had different relationships between \(S_{275–295}\) and/or \(SR\) and average molecular weight.

4.3. The importance of desorption–adsorption in the non-conservative behavior of CDOM in the estuary and comparison with other biogeochemical processes

The importance of land–ocean transfer of organic matter in the global carbon cycle has been recognized for a long time. Accumulating evidences show that the river-estuary system is an area where active biogeochemical processing of organic matter occurs (e.g., Battin et al., 2008; Bauer and Bianchi, 2011; Dai et al., 2012; Yang et al., 2013a). In the Jiulong Estuary, the non-conservative behavior of CDOM was most notable in the turbid river-estuary
interface, with significant additions and/or removals from station A3 to A8 (Guo et al., 2011). Since the water residence time was short for the Jiulong Estuary (~2 days, Hong and Cao, 2000), the dominant processes for the non-conservative behavior of CDOM must occur rapidly. On one hand, both suspended particles and sediments contained water-soluble organic matter that could rapidly desorb into the water; in addition to other additional sources for CDOM in the estuary. Water-soluble CPOM was distributed throughout the whole estuary both vertically and horizontally, but was most abundant in the turbid river-estuary interface. On the other hand, CDOM could be removed rapidly by being adsorbed to particles. The adsorption experiments showed significant reductions of CDOM within 2 h (e.g., 4–26% (average 15%) of the initial \(a_{\text{CDOM}}(280)\)). Similarly, 9–39% (average 21%) of riverine CDOM can be removed through adsorption to particles in the Tye Estuary (Uher et al., 2001). Previous studies on soils and wastes also show that the partition of organic matter between solid and liquid phases occurs rapidly (Kaiser and Zech, 1998; Zhou and Wong, 2000). Thus, the partition between CPOM and CDOM represented a rapid process that could change the level of CDOM in the Jiulong Estuary and likely other turbid estuaries. The solid–liquid partition of organic matter might be most significant in the river-estuary interface (including the TMZ) due to its highest turbidity, thus this zone might play an important role in the land–ocean flux of DOM.

In addition to the water-soluble CPOM, there are other additional sources of CDOM in the complex estuarine environment such as the Jiulong river-estuary interface (e.g., the inflow of small tributaries, vertical diffusion of CDOM from sediment pore water and inputs from surrounding mangrove ecosystems, Guo et al., 2011). For example, the South Jiulong River and the small stream flowing through Haicheng Town both had higher \(a_{\text{CDOM}}(280)\) (at stations S2 and S1, respectively) than the surrounding estuarine stations, suggesting that they may bring additional CDOM to the estuary. However, the role of these small tributaries may be limited by their water discharges, since the stream flowing through Haicheng Town is very small and the drainage area of South Jiulong River is only 4.5% of the whole Jiulong River. The limited influence of South Jiulong River was indicated by the fact that \(a_{\text{CDOM}}(280)\) at the adjacent stations A7 and A8 fell on the conservative mixing line during the three cruises, even though two cruises were conducted in the wet season.

In addition to adsorption to particles, microbial and photochemical degradations are another two important processes that would lead to non-conservative behaviors of CDOM in estuaries.

The \(a_{\text{CDOM}}(280)\) in the freshwater and estuarine water decreased by 22–38% after 28 days in the microbial incubation experiment of this study. While being limited in the turbid river-estuary interface of Jiulong Estuary, the photo-degradation of CDOM may become important in the lower estuary and adjacent coastal ocean. Although multiple biogeochemical processes probably all occur in the estuarine environments, they appear to have different effects on the chemical composition of CDOM. Water-soluble CPOM had different \(S_{295}^{+} - 295\) and \(S_{6}^{+} \) values from CDOM. \(S_{295}^{+} - 295\) and \(S_{6}^{+}\) changed little in the adsorption experiment but was decreased by microbial degradation. The protein-like components were preferentially removed in the microbial degradation experiment. There is significant increase in absorption spectral slope and preferential loss of humic-like components in photo-degradation experiments (e.g., Guo et al., 2012). Therefore, adsorption to particles appeared to be less selective for various DOM constituents than microbial and photochemical degradations.

### 5. Conclusions

Both suspended particles and sediments contained water-soluble chromophoric organic matter and had similar chemical compositions, although the content of CPOM was higher. Desorption of CPOM and CSOM would provide additional sources for CDOM in the estuary, in particular in the turbid estuaries and the turbidity maximum zone. The level of CPOM correlated significantly with the concentration of suspended particulate matter while the chemical composition of CPOM was affected by the mixing of terrestrial and marine organic matter. Significant amounts of CDOM could be adsorbed rapidly to re-suspended sediments, but the process had little effects on \(S_{275}^{+} - 295\) and \(S_{6}^{+}\) of CDOM. \(S_{275}^{+} - 295\) and \(S_{6}^{+}\) of CDOM decreased and only the protein-like but not the humic-like components were removed by microbial degradation. In conclusion, desorption—adsorption of chromophoric organic matter between particulate and dissolved phases was a rapid process for the non-conservative behavior of CDOM in the estuary (especially in the turbidity maximum zone) and may play important roles in turbid estuaries.

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