



Distribution of dissolved organic matter in the Pearl River Estuary, China

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Received 28 January 2003; received in revised form 4 December 2003; accepted 9 February 2004

Available online 2 June 2004

Abstract

Chromophoric dissolved organic matter (CDOM) fluorescence and dissolved organic carbon (DOC) were measured in the Lingdingyang Estuary, a major component of the Pearl River Delta, China, in May 2001 and November 2002. Measurements of CDOM and DOC suggest multiple sources of dissolved organic matter (DOM) in the low-salinity region of the estuary, due to the mixing of four freshwater outlets, Humen, Jiaomen, Honqimen and Hengmen, all with different freshwater endmembers and all flowing into the head of the Lingdingyang. Our 2002 cruise expanded efforts to characterize these four major outlets, allowing for the quantification of CDOM inputs within this complex watershed.

DOC and CDOM appear conservative in mid-salinity (5–20) waters, suggesting that mixing dominates production and removal processes over time scales on the order of 3 days, the residence time of water in this region of the estuary. DOC and fluorescence are linearly correlated in the mid-salinity region of the estuary north of Shenzhen, suggesting that in this region, terrestrial inputs dominate both signals. However, this relationship does not continue out onto the shelf, where water masses of differing optical properties mix. The CDOM/DOC ratio decreases with increasing salinity as would be expected through phototransformation of CDOM into non-fluorescent DOC. Additionally, this ratio at low salinity appears to vary seasonally, with a higher value in Spring (high flow) compared to Fall (low flow).

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Keywords: CDOM; Pearl River Estuary; Fluorescence; Dissolved organic carbon

1. Introduction

Dissolved organic carbon (DOC) is one of the largest pools of reactive carbon in the world's oceans (Hedges et al., 1997). A better understanding of

oceanic DOC dynamics as well as biogeochemical processes within and DOC transport through estuaries and coastal seas is essential to better constrain global carbon models (Bauer and Druffel, 1998; Cauwet et al., 2002). Through high discharge rates and material loading, large rivers and their plumes contribute substantial dissolved and particulate material to continental margins and subsequently to the ocean (Meybeck, 1982; Dagg et al., 2004), the fate of which is not well understood despite the extensive effort being put

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into the field (Sholkovitz, 1978; Mantoura and Woodward, 1983; Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997; Vlahos et al., 2002). For example, with an estimated annual riverine export of 0.25×10^{15} g DOC entering estuaries globally, only a small fraction of oceanic DOC shows a “terrestrial” signature (Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997). Adding more complexity is that recent findings suggest that DOC and particulate organic carbon (POC) being discharged from rivers are generally older, with larger age variability (i.e., across different river systems) than previously believed (Raymond and Bauer, 2001a, and references therein). It is thus clear that more research remains to be carried out in order to understand the fate of this terrestrial organic material (Hedges et al., 1997).

Riverine DOC passes through estuarine systems as it is transported to the ocean. Therefore, estuaries can potentially play a large role in the fate of riverine DOC. Estuaries are unique in that they encompass areas influenced by both terrestrial and marine forces. Conditions are affected not only by seasonal changes and diurnal variability that influence all marine systems, but also by tides, multiple inputs and fluctuating river flows. High nutrient loading from terrestrial sources fuels high in situ DOC production in coastal regions (Kemp et al., 1997). Large riverine and in situ estuarine sources of DOC, in conjunction with adsorption and remineralisation of organic material and complex mixing dynamics within estuaries, result in strong DOC gradients from freshwater sources towards the ocean (Peterson et al., 1994; Alvarez-Salgado and Miller, 1998; Dagg et al., 2004).

Chromophoric dissolved organic matter (CDOM) represents the fraction of the dissolved organic pool which absorbs light in the visible as well as UV-A and UV-B (280–400 nm) ranges. The significance of CDOM to biogeochemical processes has been studied by many researchers with respect to photochemical reactivity (Zafiriou et al., 1984; Moffett and Zika, 1987; Mopper et al., 1991), light attenuation and optical characteristics, which can affect primary production rates (Blough et al., 1993; Nelson et al., 1998; Rochelle-Newall and Fisher, 2002a,b) and the fueling of microbial respiration by photodegraded CDOM (Amon and Benner, 1996; Miller and Moran, 1997; Benner and Biddanda, 1998; Opsahl and Benner, 1998; Reche et al., 1998; Moran et al., 2000). CDOM

has also been used as a tracer of terrestrial sources of DOM to estuarine systems (Zimmerman and Rommets, 1974; Chen and Bada, 1992; De Sousa Sierra et al., 1997; Coble, 1996; Chen, 1999). Because of its photochemical reactivity, much of the CDOM entering estuarine systems is removed, through direct photochemical transformation (bleaching) as well as photodegradation in conjunction with microbial respiration, before it reaches the marine environment (Miller and Moran, 1997; Benner and Biddanda, 1998; Opsahl and Benner, 1998). A recent review of CDOM research (Blough and Del Vecchio, 2002) highlights the need for an increase in CDOM studies conducted in major world rivers, where, because of high discharge rates, terrestrially derived chromophoric material may be transported to marine systems before it is degraded. Biogeochemical as well as photochemical processes in large river systems, with large discharge volumes, cannot be inferred through “scaling up” small-system data, because large buoyant plumes create unique environments for biogeochemical and photochemical activities (Dagg et al., 2004).

Most world estuarine systems are also experiencing increasing pressure from anthropogenic forcing. This is particularly true in the Pear River (Zhujiang) estuary. The cities and towns surrounding the Pearl River Estuary have undergone rapid changes following China’s economic reforms of 1978. Containing two cities (Zhuhai and Shenzhen) designated Special Economic Zones in 1978, as well as the delta region as a whole having been declared an Open Economic Region in 1985, the area currently encompasses one of the fastest growing regions in China (Lin, 2001). This urbanization, industrialization and economic growth have resulted in increased sediment loading of Pb, Cu and Zn over the past 20 years (Li et al., 2000, 2001). Metal contaminants are transported to the estuary via the main river channels as well as through aeolian deposition, a primary source pathway for Pb to the system (Li et al., 2001).

In addition to increased levels of metal contamination since the mid-1980s, increased inputs of anthropogenic organic carbon to the system have led to the current situation, where anthropogenic carbon is now reported to make up 50% of the carbon pool in the eastern Deep Bay area, adjacent to the Pearl River Estuary (Li and Lee, 1998). Further studies have

included measurements of PCBs and other industrial organic contaminants, abundant in sediments in the area, which have increased during the same time period (Mai et al., 2001; Zheng et al., 2001; Zhang et al., 2002a,b). To date, very limited work has been conducted to determine the size fractionation and cycling of organic carbon within the estuary (Dai et al., 2000), yet no studies have been published concerning CDOM distribution within this, one of the most complex estuarine systems in the world.

This study aims to investigate the distribution of DOC and CDOM in the Pearl River Estuary, as well as the identification of major sources of these organic materials to the complex estuarine system. Conclusions are based upon data collected during two cruises, using both real-time underway analysis for CDOM as well as discrete sampling techniques for DOC and CDOM. As the Pearl River is the thirteenth largest river in the world in terms of dis-

charge, research of this nature is essential for further study of carbon exchange dynamics between the Pearl River and the South China Sea. This will in turn add to our understanding of carbon exchange between marine and terrestrial systems as well as the effect of estuarine processes on coastal ocean carbon cycling.

2. Study area

Along with the Mekong River, the Pearl River provides the largest inflow of fresh water to the South China Sea, the largest marginal sea in the North Pacific, delivering 350 km^3 of fresh water ($11,100 \text{ m}^3/\text{s}$) and 85×10^6 tons of sediment annually to the South China Sea (Zhang et al., 1999). It is China's second largest River in terms of water discharge, with a length of 2214 km and a watershed of $230,000 \text{ km}^2$.

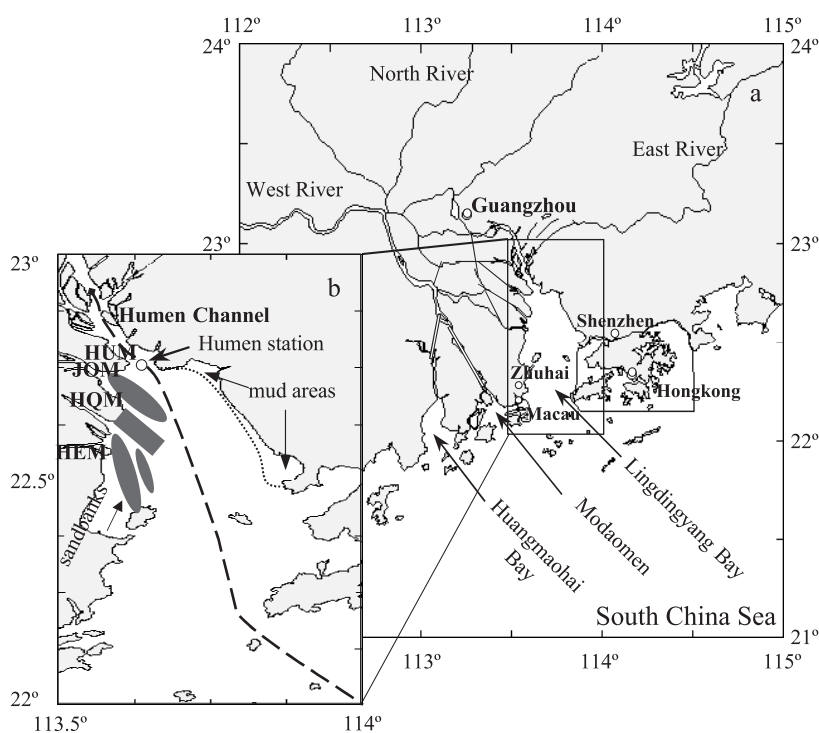


Fig. 1. Lingdingyang Estuary and Pearl River Delta. Inset of the Lingdingyang Estuary shows the main Lingdingyang transect (dashed line bisecting the estuary) as well as the cross-shelf transect (dashed line from NW to SE). Discrete samples, as well as in situ measurements, were taken along these main transects. The 2002 sampling track follows that of the May 2001 cruise, with the addition of discrete sample collections at major outlets: Humen, Hongqimen, Hengmen and Jiaomen. JOM—Jiaomen Outlet; HQM—Hongqimen Outlet; HEM—Hengmen Outlet.

The Pearl River consists of three main tributaries—Beijiang (North River), Dongjiang (East River) and Xijiang (West River), which empty into the Pearl River estuary forming the Pearl River Delta region (Fig. 1).

Roughly 70–80% of the fresh water delivered by the Pearl River to the South China Sea occurs during the wet season (April–September), with the remaining entering between October and March. Levels of riverine dissolved and particulate organic carbon transported to the estuary through the main tributaries are highest during high flow periods (Gao, 2000; Gao et al., 2002). This seasonality of flow regimes will presumably affect biogeochemical cycling within the estuary over time scales of months.

The Pearl River Estuary consists of three sub-estuaries, namely Maodaomen, Yamen and Lingdingyang estuaries (Fig. 1). This study focuses on the major sub-estuary, the Lingdingyang Estuary, which is commonly referred to as the Pearl River Estuary. The Lingdingyang Estuary consists of four major outlets—Humén, Jiaomen, Hongqimen and Hengmen. In terms of yearly averages, these outlets contribute 35%, 33%, 12% and 20% of the total discharge to the Lingdingyang, respectively. These percentages vary slightly during wet and dry seasons (Kot and Hu, 1995).

The Lingdingyang Estuary is a typical salt-wedge system, with salt water entering the estuary at depth and freshwater discharge flowing toward the sea at the surface (Yin et al., 2001). The average residence time of the constrained estuary is on the order of 3 days (Yin et al., 2000), and the extent of the fresh water-influenced plume varies seasonally in accordance with river discharge. During periods of high flow (Spring and Summer), the Pearl River plume extends to the South China Sea shelf and has been measured extending northeast to 300 km offshore (Cai et al., 2004).

3. Methods

Samples were collected during two cruises onboard the R/V Yanping II in May of 2001 and November of 2002. It was expected that DOM dynamics would differ between May, the wet season and November, the dry season.

3.1. Underway fluorescence measurements

Underway measurements were carried out to examine complex mixing and multiple inputs, and discrete samples were taken for ground-truthing underway measurements as well as providing information which could not be measured underway. While performing cross-salinity transects between the estuary and shelf waters, CDOM fluorescence was measured using a SeaTech flash lamp fluorometer ($\lambda_{\text{ex}} = 330$ nm, $\lambda_{\text{em}} = 450$ nm). Surface water was continuously pumped through the shipboard pumping system from a side intake at a depth of ~ 2 m. Temperature and conductivity were measured continuously (recorded every 10 s) using a SEACAT thermosalinograph system (CTD, SBE21, Sea-Bird). This underway CTD system was calibrated at Sea-Bird in 2000. Sample flow for CDOM fluorescence was split between the underway CTD system mounted on deck and a custom-made polycarbonate flow-through vessel, in which the fluorometer was mounted. This allowed for real-time data collection and concomitant monitoring of salinity, temperature and CDOM fluorescence.

3.2. Discrete sample collection for DOC and fluorescence

During the same cross-salinity transects, replicate discrete samples were collected and filtered through pre-combusted Whatman GF/F filters (0.7 μm) for DOC and fluorescence analysis. Samples were collected in precombusted (500 °C for 6 h) 40-ml glass vials (clear for DOC and amber for fluorescence). DOC samples were acidified with H_3PO_4 to pH=2, and all samples were frozen for storage and transport.

In addition to underway discrete samples, Go-Flo bottle samples were taken at fixed stations throughout the estuary and shelf region over a 30-day period. Station sampling consisted of hydrocasts conducted with a rosette fitted with twelve 2.5-l Go-Flo bottles. Protocols for the collection and storage of station samples were identical to those of underway samples.

3.3. Sample analysis

For samples collected during the 2001 cruise, measurements of both DOC and fluorescence were conducted in Xiamen University's Environmental Sci-

ence Research Center. Using a Shimadzu TOC5000A with a high-sensitivity platinum catalyst, acidified samples were run in triplicate for DOC and calibrated using a five-point calibration curve using the standard DOC calibration compound, potassium hydrogen phthalate (KHP). Standards were run and slopes calculated every 8 h during sample analysis. Values were checked by running reference Low Carbon Water (LCW) and Milli-Q water for system blank subtraction and reference Deep Seawater (DSWR) to ground-truth concentrations (Miller et al., 1993; Sharp et al., 1988; Peltzer and Hayward, 1996; Peltzer et al., 1996; Sharp, 1997). LCW and DSWR were provided by D. Hansell's lab at the University of Miami.

Analyses of 2001 fluorescence samples were performed using a Hitachi F4500 fluorometer. Samples were run using an excitation wavelength of 340 nm, the predetermined “natural humic” peak, and emission spectra were collected from 350 to 650 nm. Integrated spectra were subsequently converted to quinine sulfate units (QSU) as per Chen et al. (2002).

Samples collected during the 2002 cruise were shipped frozen to UMass Boston for analysis. DOC analysis of acidified samples was conducted using a Pelzer-style high temperature combustion apparatus (Peltzer and Hayward, 1996; Vlahos et al., 2002). KHP calibration curves were determined at the beginning and end of each 8-h analysis. System blanks were quantified using LCW and Milli-Q water every hour, and DSWR was used to ground-truth concentrations.

Using a Photon Technologies International QM-1 spectrofluorometer, 2002 fluorescence samples were

analyzed. All slit widths were set to 4 nm. Spectra were blank subtracted (to remove water Raman scattering peak) and converted to QSU using a 4–5-point calibration curve of quinine sulfate (pH = 2) standards, run at the start and end of each day that samples were analyzed. CDOM fluorescence is expressed as QSU, where 1 QSU is equivalent to the fluorescence emission of 1 $\mu\text{g/l}$ quinine sulfate solution integrated from 350 to 600 with an excitation wavelength of 337 nm (Chen et al., 2002).

4. Results

4.1. Estuarine DOC and CDOM distribution

In situ CDOM fluorescence measurements taken throughout the Lingdingyang transect began upstream of the mouth of Humen, the zero-salinity endmember station located at the main channel feeding into the Pearl River Estuary, and extended offshore to salinity (S) = 33.5 (Fig. 2). Complex mixing dynamics within the riverine region of the transect result in zero salinity waters with high spatial variability.

Variability in the low-salinity region may reflect a loss of DOC through adsorption or flocculation at $S = 1–2$ as well as the incomplete mixing of different zero salinity sources of DOC to the estuary. The observed decrease in DOC in mid-salinity waters ($S = 2–12$) outside of the river mouth is expected, as high-DOC riverine source waters mix with relatively low-DOC marine water. At higher salinity ($S \sim 25$),

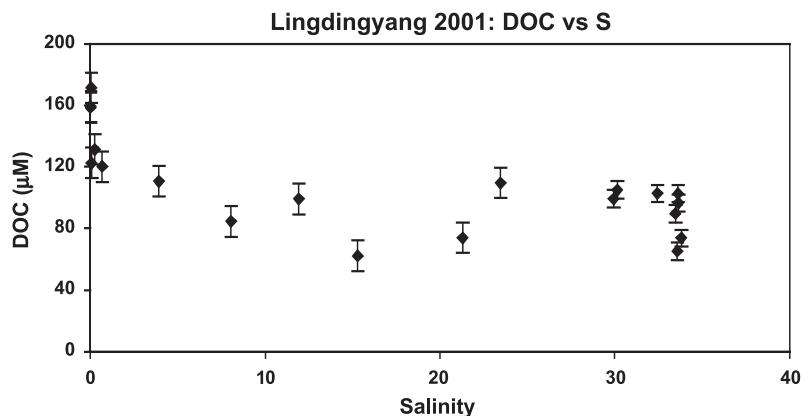


Fig. 2. DOC measurements of underway, discrete samples collected on the Lingdingyang transect.

however, the DOC concentration increases, suggesting a local organic carbon source in the region. This DOC distribution pattern has been seen in this region of the estuary in previous cruises, conducted in 1996 and 1997 (Dai et al., 2000). The region of elevated DOC, located in Deep Bay, south of the highly industrialized city of Shenzhen, is suggestive of a local organic matter source, possibly from Shenzhen (labeled in Fig. 1).

The in situ fluorescence versus salinity plot from the Lingdingyang transect follows the same pattern as DOC in the zero-salinity region, with a sharp drop in CDOM fluorescence between zero and 2 (Fig. 3). The curvature of this plot within mid-salinity waters ($S \sim 5$) may reveal a small mid-estuarine production of fluorescent material, although a temporal variation in river discharge cannot be ruled out as the source of the curvature in the graph, as observed in other estuaries (Morris et al., 1978; Loder and Reichard, 1981; Cifuentes et al., 1990). Fluorescence appears conservative in the $S=5-20$ range due to rapid mixing, while at high salinity ($S>23$), the mixing of several mid- to high-salinity water masses may be responsible for the observed variability in fluorescence values.

A second high-salinity transect covering the salinity range from 22.5 to 33.5 was conducted to further explore variation in CDOM fluorescence in this re-

gion. The mixing of water masses on the shelf, as evidenced in the temperature versus salinity plot (Fig. 4a) yield fluorescence measurements (Fig. 4b), which cannot be described by a simple two-endmember mixing model. While there is clearly an inverse relationship between fluorescence and salinity in this region, the fluorescence versus salinity relationship is not linear. The temperature–salinity diagram associated with this transect displays complex mixing dynamics in the $S=24-29$ and $S=32-33.5$ regions, which may be responsible for the non-conservative behavior of CDOM in the same regions.

Discrete DOC and fluorescence samples collected over a 30-day period at stations within the Lingdingyang Estuary and shelf region are consistent with single-day-transect samples. Results of these analyses are plotted versus salinity in Fig. 5a and b. Reflective of the transect data discussed above, there exists an overall inverse relationship between DOC and salinity and fluorescence and salinity, but, again, two-endmember mixing cannot fully describe the data. The variability in CDOM and DOC at zero salinity and at high salinity is most likely reflective of the mixing of water masses with different CDOM/DOC concentrations and composition, as discussed previously. Mid-salinity variability could likewise be the result of incomplete mixing, with the hypothesis of an influx of high-DOC waters from Deep Bay, off the coast of Shenzhen ($S=22-25$), supported by this station data as well.

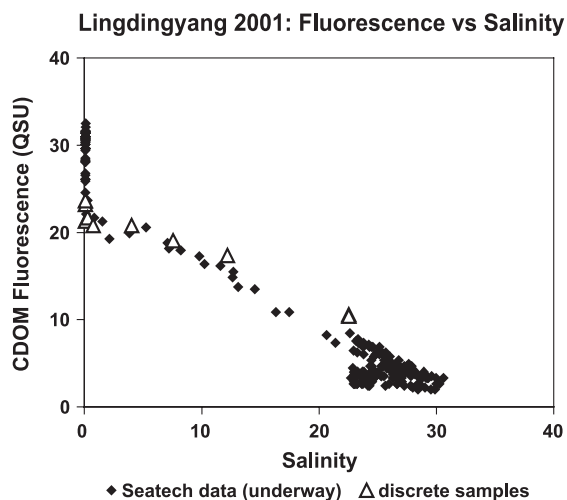


Fig. 3. Fluorescence versus salinity for underway, in situ measurements, as well as discrete samples, taken along the Lingdingyang transect.

4.2. Normalized fluorescence intensity distribution

In addition to CDOM fluorescence and DOC concentrations, the ratio of fluorescence intensity to DOC concentration varies with salinity in the Lingdingyang Estuary (Fig. 6). In low-salinity regions, there is a relatively high proportion of fluorophores within the DOC pool. At higher salinities, CDOM fluorescence as a proportion of total carbon decreases considerably, presumably as a result of photo-transformation of CDOM into non-fluorescent material, as surface waters are transported to sea.

As mentioned previously, the Lingdingyang Estuary is a salt–wedge system, with high-salinity seawater intruding at depth and fresh water discharged at the surface. This type of estuary enables high levels of photodegradation, or bleaching, of fluorescent material as these compounds, highest in river discharge,

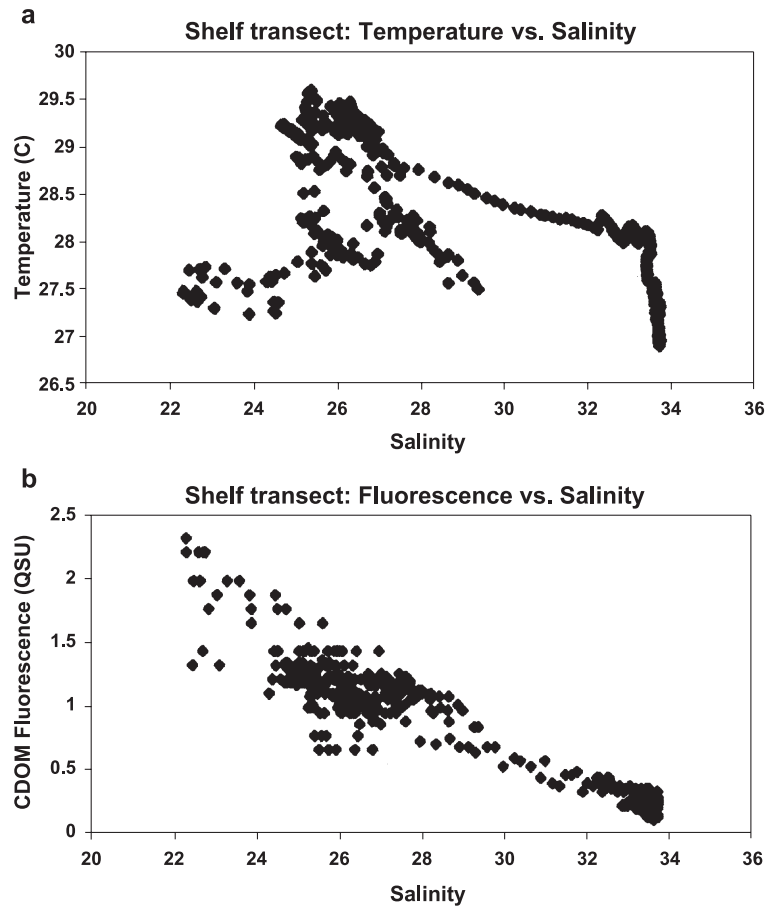


Fig. 4. SCS shelf transect: (a) temperature versus salinity; (b) fluorescence versus salinity.

are kept at the surface where solar irradiance is highest (Del Vecchio and Blough, 2002).

High-salinity data from both 2001 and 2002 samples show a relatively low level of fluorescence per unit carbon (Fig. 6). Values of fluorescence/DOC at salinities above 20 are consistent between years, with variation between years at most ± 0.02 QSU/ μM carbon. On-deck photodegradation experiments conducted during the 2001 cruise showed that most photodegradation of riverine CDOM takes place during the first 48 h of bleaching in natural sunlight (Fig. 7). Surface CDOM in the Lingdingyang Estuary, which has a residence time of 3 days, could therefore be degraded considerably before reaching the shelf.

The consistency of CDOM/DOC values at high salinity (Fig. 6) in conjunction with evidence from incubation experiments showing fluorescence deple-

tion within 48 h, further support the hypothesis that terrestrial fluorophores are transformed to non-fluorescent compounds through photobleaching as they are transported to sea.

Low-salinity data from the two cruises, unlike high salinity values, differ in fluorescence intensity per micromole carbon. May, 2001 cruise samples were between 0.06 and 0.11 QSU higher in fluorescence per unit carbon than those collected in November of 2002. Cruise samples were handled differently after the two cruises, with 2002 samples transported to Boston for analysis, while 2001 samples were analyzed in China. Because the high-salinity samples ($S > 20$) of the two cruises are in agreement, however, there is little evidence for sample deterioration.

Further seasonal studies must be conducted to determine whether there is a consistent pattern of

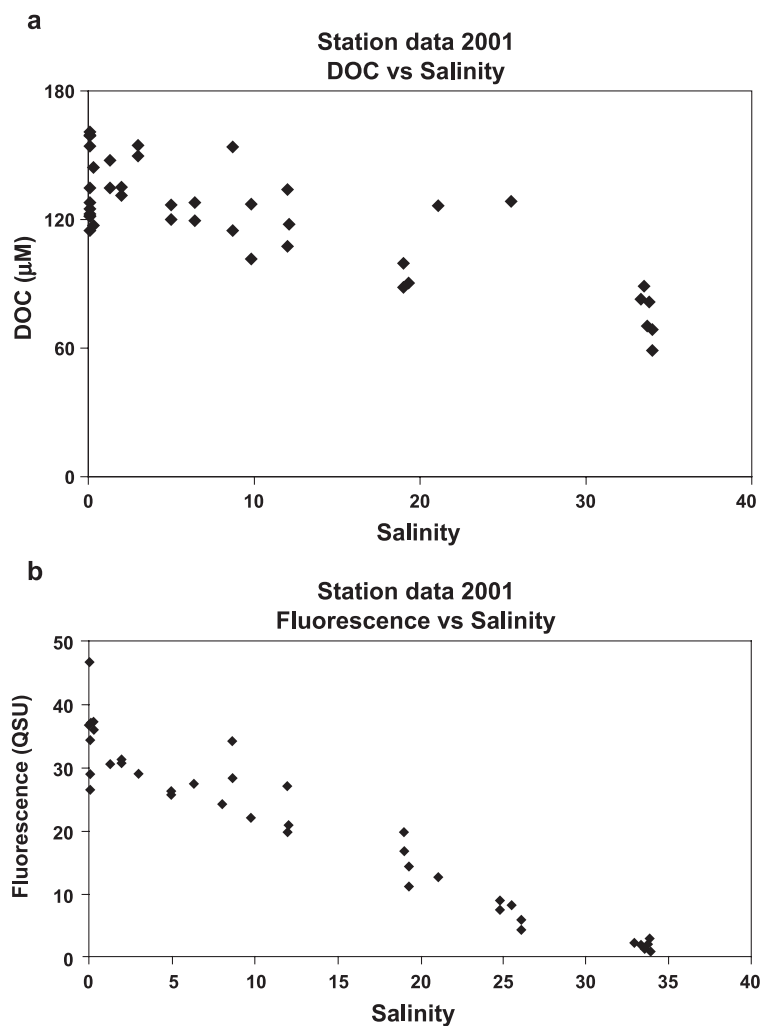


Fig. 5. Discrete station samples collected for DOC and CDOM analysis during the May 2001 cruise reflect the same trends as underway discrete and in situ samples.

higher CDOM fluorescence per unit carbon in this system in the Spring (high flow) than in the Fall (low flow).

4.3. Low-salinity endmembers—2002 cruise

The cruise track for the 2002 Lingdingyang transect is the same as that followed during the May, 2001 cruise (Fig. 1). In addition to transect sample collection, however, the four main outlets emptying into the Lingdingyang, Humen, Jiaomen, Hongqimen and Hengmen, were sampled from a small fishing vessel

in order to characterize these important fresh water endmembers. DOC and CDOM data are plotted versus salinity, and CDOM is plotted versus DOC for transect and outlet samples in Fig. 8a,b,c. Of the outlets under study, Humen is highest in both fluorescence and DOC levels (25 QSU and 187 µM, respectively). This result, in terms of DOC, is consistent with high DOC measured previously in the region (Dai et al., 2000). The plot of CDOM Fluorescence versus DOC (Fig. 8c) shows Humen samples to have a relatively lower fluorescence value as compared with underway samples of similar DOC, observable

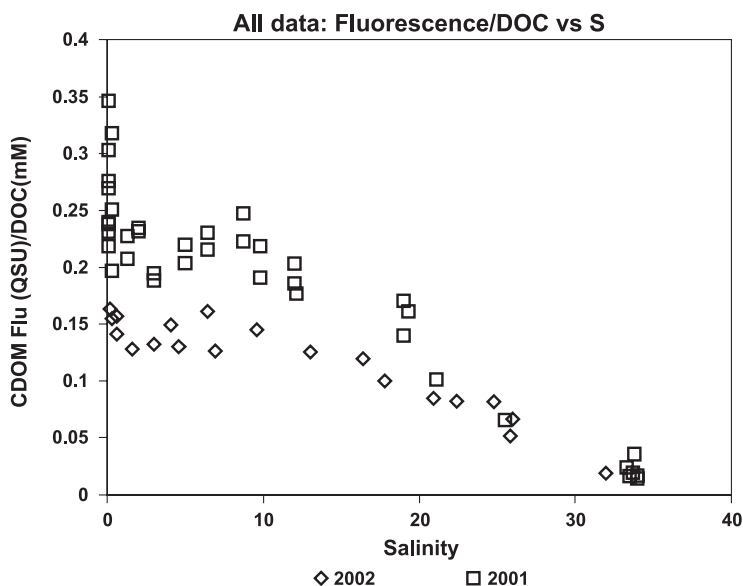


Fig. 6. Fluorescence per unit carbon (QSU/ μ M) versus salinity.

when plotted together on the same graph. This may indicate a significant non-chromophoric fraction of DOC entering the estuary through the Humen source. Humen, as seen on the estuary map (Fig. 1), is the location where the main tributary channel of the Pearl

River empties into the Lingdingyang Estuary. This outlet carries sewage discharge from Guangzhou, one of the largest cities of southern China.

Samples collected at Jiaomen are considerably lower in both DOC concentration and fluorescence intensity than Humen samples. The watershed surrounding the Jiaomen outflow differs greatly from that of Humen, in that land within the Jiaomen system is comprised of small, unindustrialized towns while the Humen system is heavily polluted with industrial waste and sewage. As might be predicted from watershed conditions, water from the Jiaomen outlet has relatively high dissolved oxygen and low temperature as compared with the high temperature and very low dissolved oxygen levels measured at Humen during this cruise (Zhai et al., 2003).

Riverine samples collected upstream of the mouth of the Hengmen outlet contain the same concentration of DOC and $\sim 5\%$ lower fluorescence than that of Jiaomen, a minor difference in fluorescence intensity. Water at the Hengmen sampling site is shallow (< 5 m), while Jiaomen has a higher discharge and has been channeled to create a deeper outlet. Thus photobleaching at the Hengmen site may play a role in the depletion of fluorescence in this sample. The Jiaomen and Hengmen outlets, which essentially fall together on each of the three graphs in Fig. 8, can be seen as collectively

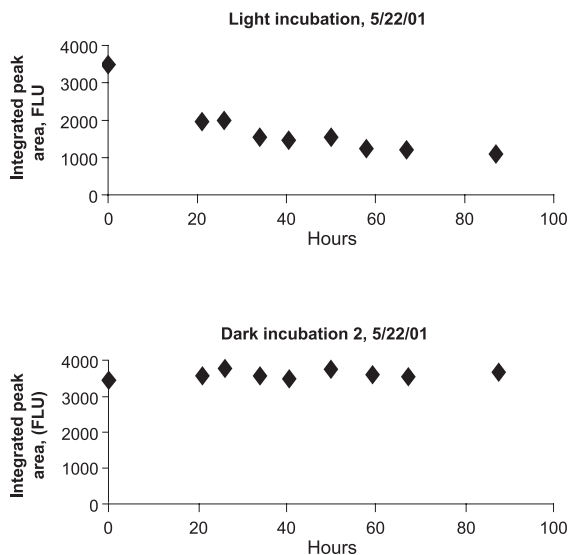


Fig. 7. Results of on-deck incubation experiments—fluorescence intensity versus time. Fluorescence is given in fluorescence units, to be used as a comparison of treatments in this experiment only.

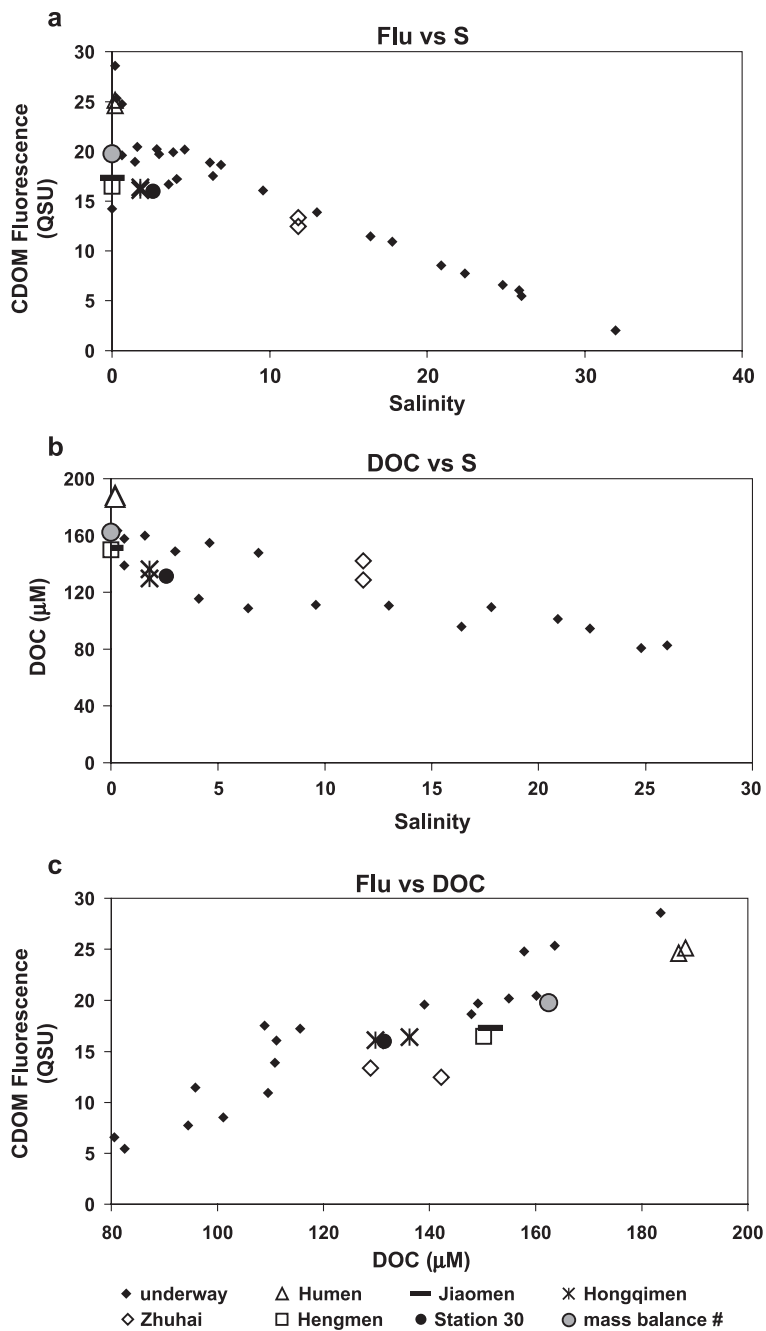


Fig. 8. November 2002 cruise data: DOC (a) and fluorescence (b) versus salinity, and fluorescence versus DOC (c). Major tributaries are labeled. Station 30 is located downstream of the Humen outlet. The calculated “endmember” is also plotted with a large circle, indicated as “mass balance #”.

contributing a relatively low fluorescence, low DOC signature, in comparison to the Humen input.

The Hongqimen outlet lies within the estuary between Hengmen and Jiaomen, and has the same fluorescence intensity as Hengmen. DOC concentration from Hongqimen, however, is 10% lower than Jiaomen, indicating a higher percentage of CDOM within its DOC complement.

Another nearshore sample was collected off the coast of Zhuhai, the location of which is presented in Fig. 1. Fluorescence values of Zhuhai samples fall well below underway sampling points of the same salinity, as displayed in Fig. 8a, indicating that this region is depleted in CDOM relative to other outlets as well as the estuary as a whole. Despite the low fluorescence signature, the Zhuhai samples contain relatively high concentrations of DOC. The depleted fluorescence signature of these samples is responsible for its relatively low fluorescence/DOC ratio. The low-CDOM, high-DOC signature could be reflective of a large anthropogenic plume from Zhuhai, similar to that seen off the coast of Shenzhen, as described earlier.

4.4. Fluorescence mass balance

In order to investigate the relative contribution of each outlet to total CDOM within the Lingdingyang Estuary, we used published discharge data for each outlet. During the dry season, Humen contributes 37.5% of the yearly flow, Jiaomen contributes

32.5%, Hongqimen contributes 9.4% and Hengmen contributes 20.4% (Kot and Hu, 1995). Using these data, we calculated the relative fluorescence (at excitation $\lambda=337$ nm) input from each outlet, then summed them together. Likewise, we calculated the relative DOC contribution of each outlet and summed. Results are presented in Table 1. The resultant fluorescence and DOC “endmember” values are plotted as “mass balance no.” in Fig. 8.

Because the DOC mass balance point plots within the measured DOC values of underway samples, there is little reason to believe that there is a major unaccounted terrestrial DOC source in the low-salinity region. CDOM fluorescence intensity of the calculated endmember likewise plots within measured transect values.

5. Discussion

Microbial respiration has been shown to play a significant role in estuarine DOC transformation, depleting estuarine waters of up to 10% of their riverine DOC input (Raymond and Bauer, 2001b). Microbial transformation of DOM is particularly significant in systems containing high levels of anthropogenic DOC, such as the Scheldt Estuary in the Netherlands (Abril et al., 2001). Microbial communities may be responsible for the transformation of non-chromophoric compounds to fluorescent material, as suggested by Nelson et al. (1998) in the Sargasso Sea and Rochelle-Newall and Fisher (2002a,b), in culture experiments. It is possible that in the highly eutrophic Lingdingyang system, microbial transformation of non-fluorescent DOM into fluorescent products may produce part of the high-fluorescence signature at low salinity ($S=1-5$). The depletion of dissolved oxygen ($DO < 1$ mg/l) in surface water at the Humen river mouth as well as high pCO_2 (>4800 μ atm) measured in the area (Zhai et al., 2004) may be indicative of such processes. The low DO appears to be persistent in this particular region based upon recent observations (Zhai et al., 2004). Furthermore, an on-deck incubation experiment from a parallel study during our May 2001 cruise revealed a very high pelagic respiration rate of 48.7 $mmol$ O_2 m^{-3} day^{-1} (Zhai et al., 2004) and hence a dynamic organic matter transformation, including microbial transformation.

Table 1
Fluorescence and DOC “mass balance” calculation for the Lingdingyang

	Fraction of flow (ff)	FLU	ff \times FLU
Humen	0.355	25.1	8.911
Jiaomen	0.327	17.3	5.657
Hongqimen	0.116	16.2	1.879
Hengmen	0.202	16.5	3.333
		sum =	19.78
	Fraction of flow (ff)	DOC	ff \times DOC
Humen	0.355	188.3	66.84
Jiaomen	0.327	151.5	49.53
Hongqimen	0.116	136.2	15.80
Hengmen	0.202	150.2	30.34
		sum =	162.4

Values used for flow fractions of each outlet are from Kot and Hu (1995).

In addition to microbial production of CDOM, marsh areas and wetlands within estuarine systems can also be important regions of production of fluorescent material. For instance, the Atchafalaya freshwater endmember in the Mississippi Delta system has a 34–48% (varying seasonally) higher fluorescence signal than the main Mississippi River endmember. This increased fluorescence is most likely due to CDOM production in the highly productive wetland basin through which Atchafalaya waters flow before being discharged to Atchafalaya Bay (Chen and Gardner, 2004). Lingdingyang Bay is similar to the main Mississippi River in that it is a highly engineered system with little direct exchange with vegetation and wetlands. Since the 1970s, extensive land reclamation and silting projects have been conducted in the area, destroying most of the natural wetlands in the region. For this reason, CDOM production from wetlands is assumed to be negligible.

DOC and CDOM follow an inverse relationship with respect to salinity in the Pearl River Estuary. This relationship is nonlinear in several locations within the estuary. First, at the mouth of the Pearl River at Humen, DOC and CDOM drop off dramatically, possibly as a result of flocculation of terrestrial material due to salinity effects. Additionally, because of the complex system of minor tributaries emptying into the Lingdingyang Estuary, CDOM and DOC signatures vary greatly in low-salinity samples. For this reason, there is no linear relationship between fluorescence and S , DOC and S or DOC and fluorescence at $S < 5$. Second, at salinity ~ 25 , in Deep Bay, anthropogenic effects play a major role in carbon trends. A large input of material from the city of Shenzhen appears to affect the DOC signature in this region. Finally, in high-salinity shelf waters, the mixing of water masses of differing chemical and optical properties results in apparently non-linear DOC and CDOM versus salinity profiles.

As DOC and CDOM decrease with increasing salinity, so does the ratio of CDOM to DOC. While low-salinity samples from the two cruises differed in their intensity of fluorescence per unit carbon, data from each of the years shows a decrease in CDOM/DOC as salinity increases, and high-salinity samples from the two cruises were consistent. This phenomenon is most likely due to the transformation of fluorescent compounds to non-fluorescent material

through photobleaching as it is transported from upstream within the estuary to the shelf.

These seasonal studies of CDOM and DOC in one of the major estuaries of the world demonstrate the complexity of studying carbon cycling in coastal areas. Seasonal variability, multiple freshwater sources, mixing of multiple water masses on the shelf, anthropogenic influences both in source of organic matter and the removal of natural wetlands, and in situ production and removal processes such as photodegradation and microbial production all influence DOC and CDOM distributions and the proportion of DOC that is optically active. However, with high-resolution spatial and temporal measurements such as those used in this paper, many of these complex variables can be differentiated.

Acknowledgements

This work was funded by a US NSF Dissertation Enhancement Grant, China NSF grants 499825162 and 49976021 and the Office of Naval Research Award N00014-00-1-0325. We thank Zhaozhang Chen, Ganning Zeng and Weidong Zhai for assistance with CTD data collection and processing and graphic preparation. Wuqi Ruan and Fan Zhang along with the crew of Yanping II provided much help during the sampling cruises. This manuscript was greatly improved by the constructive comments of Dr. Chuanmin Hu and another anonymous reviewer.

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