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PRELIMINARY STUDY ON THE DISSOLVED AND COLLOIDAL ORGANIC CARBON IN THE ZHUJIANG RIVER ESTUARY*

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Abstract This paper reports data on the dissolved and colloidal organic carbon in the Zhujiang (Pearl) River estuary. DOC concentration was 142 to 239 $\mu\text{mol/L}$ in the freshwater taken in March 1997 from the four Zhujiang River tributaries flowing into the Lingdingyang estuary. High concentration was observed in the Humen tributary located near Guangzhou. The rapidly increased DOC concentration at low salinities (~ 5) may be attributed to the exchange between macroparticulate and dissolved organic matter during the early stage of estuarine mixing. DOC concentration overall followed the mixing line until salinity 25, where the Deep Bay is located and where DOC was elevated. This elevated DOC may suggest a local organic matter source from Shenzhen. Using a crossflow ultrafiltration (CFF) system equipped with a Millipore Prep-scale CFF 1 kD regenerated cellulose membrane, we also separated the colloidal organic matter from the truly dissolved fraction (< 1 kD). CFF membranes were carefully evaluated for their applicability (retention characteristics, blank level and mass balance) to separate colloidal organic matter. COC in the study area ranged from 5 to 85 $\mu\text{mol/L}$, representing 3% - 32% of DOC. The highest COC percentage was found at low salinities (< 5) in both winter and summer. Evidence suggests in situ production of colloidal material at this salinity range. Beyond this point, a very modest removal was observable until high salinities. Again, an increase in COC concentration was shown in the samples taken from the Deep Bay.

Key words: dissolved organic carbon, colloidal organic carbon, Zhujiang River estuary

INTRODUCTION

Estuaries comprise a major biogeochemical interface connecting the land and the sea (Mantoura, 1987). The behavior and fate of a particular river-borne substance introduced into an estuary is determined to a large extent by the biogeochemical properties of the substance as well as physical and chemical characteristics of the estuary (Chester, 1990). Knowledge of such behavior is of great importance to our understanding of the marine DOC cycle. The Zhujiang River is one of the largest rivers in China and the most important river flowing into the South China Sea.

Recent studies revealed that a significant fraction of DOC is actually represented by high molecular weight materials that are not truly dissolved but colloidal (1 nm - 1 μm , Vold, R. D. and Vold, M. J., 1983; Carlson et al., 1985; Dai, 1995; Martin et al., 1995; Cauwet and Sidrov, 1996; Dai et al., 2000). Studies on estuarine colloids have also improved our understanding of the processes that influence DOC behavior in estuaries (Dai, 1995 and references therein).

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We report here a preliminary data set on DOC and colloidal organic carbon (COC, defined here as the fraction between 1 kD and 0.4 or 0.7 μm). The main focus of this paper is the behavior of DOC and COC during estuarine mixing. Some essential issues relevant to cross-flow ultrafiltration (CFF) technique that we used for isolating colloidal particles will also be addressed.

METHODS

Study area

The Zhujiang River estuary is a weak-tide estuary with numerous islands. The river mouth has a characteristically strong runoff ($10525 \text{ m}^3/\text{s}$ annually), weak tide energy (mean tide range of 0.86 - 1.6 m), and low silt content ($0.1 - 0.3 \text{ kg}/\text{m}^3$ on average). The mean annual discharge of suspended load was 8745×10^4 tons between 1955 and 1980. The bed load discharge was estimated to be $900 \times 10^4 \text{ t/a}$, more than 90% of which was discharged in the flood period. As a consequence, suspended particle concentration may become a major limiting factor for the primary productivity and the lower primary production is usually observable during the flood season (Huang et al., 1994).

The Zhujiang River has eight mouths (Humen, Jiaomen, Hongqimen, Hengmen, Modaomen, Jitimen, Hutiaomen and Yamen) and empties into the South China Sea through three estuarine areas (Lingdingyang, Modaomen and Huangmaohai). The Lingdingyang estuary chosen as a primary focus for this study is the largest estuary in South China and 70 km long and 4 - 58 km wide. The region has complicated topography with channels, shoals and tidal flats; and has not been fully characterized, but was considered to be a tidally-dominant estuary (Ye and Johnson, 1994). River water discharges from its four tributaries (Humen, Jiaomen, Hongqimen, and Hengmen) average $1740 \times 10^8 \text{ m}^3/\text{a}$. The annual suspended load is 3728×10^4 tons, of which one third comes from the Humen mouth.

Sampling

Seawater samples were collected in the Zhujiang River estuary during a cruise in July 1996 and one in March 1997 (Fig. 1). Samples were collected by pumping with a submersible stainless steel pump during the first cruise and an all-Teflon pump during the second cruise via Teflon tubing. Samples were then prefiltered through pre-combusted glass fiber filters (GF/F, 0.7 μm) during the first cruise and through acid-cleaned 0.4 μm polycarbonate Nuclepore filters during the second cruise, and subsequently passed through the CFF system.

CFF processing

Detailed CFF processing procedure was described in Dai et al. (1998). Briefly, our CFF system was composed of a Flojet polypropylene diaphragm pump, plumbing (mostly of teflon) and Millipore Prep/Scale TM-TFF PLAC regenerated cellulose CFF membranes. The prefiltrate mentioned above was continuously passed into a 4-liter fluorinated polyethylene bottle while the CFF was running progressively. During operation the membrane pressure was maintained at 96 - 110 kPa. Subsamples were collected at various times or concentration factors (c_f) from the permeate and retentate lines for OC analysis. CFF was stopped mostly at $c_f = 5 - 8$ while some CFF experiments were processed until $c_f > 10$. The potential impact of different CFF c_f on the calculation of final COC concentration was discussed in Dai et al. (1998).

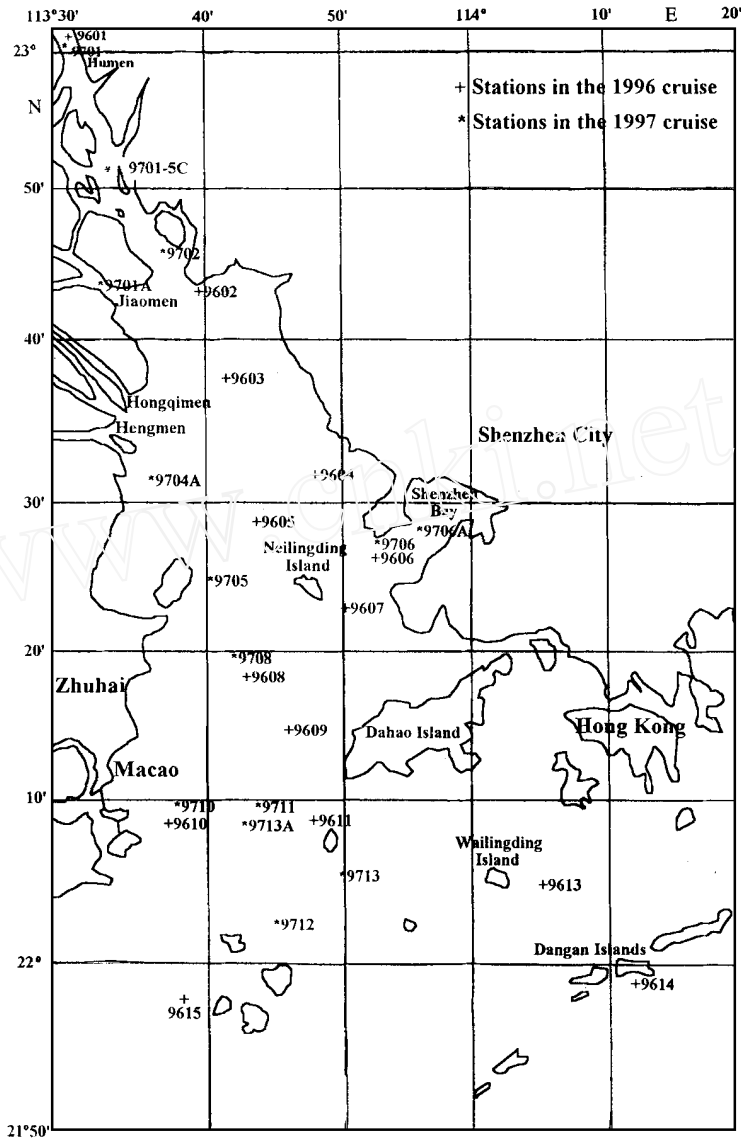


Fig. 1 Map of the Zhujiang River estuary

Before and after a typical sample run, the CFF system was cleaned by flushing with > 20 L nano pure Q-water (Q-water hereafter) followed by 0.01 ml/L NaOH and 0.01 ml/L HCl solutions made from the same Q-water. The base or acid solution was recirculated for at least one hour followed by rinsing with Q-water until pH 7 was reached. Preconditioning with prefiltered seawater (4 - 6 L) followed these cleaning steps. The cleaning was conducted just prior to each sample run.

Colloidal concentration

We define the colloidal fraction as the material that passes through a 0.7 μm or 0.4 μm filter and is retained by a 1 kD CFF membrane (Using standard molecules, 1 kD cutoff is equivalent to a pore size of 1 nm). When analyzing data from the sampling mode, the concentration was calculated at each sampling point when samples were collected. At each sampling point:

$$[\text{colloidal}] = \frac{[\text{retentate}] - [\text{permeate}]}{cf} \quad (1)$$

$$cf = \frac{\text{retentate volume} + \text{permeate volume}}{\text{retentate volume}} \quad (2)$$

and,

$$\text{Sum concentration} = [\text{colloidal}] + [\text{permeate}]$$

The mass balance can then be calculated by comparing the sum with the initial source solution concentration.

Analysis

Subsamples for OC analysis were collected in either 125 ml precombusted glass bottles or 20 ml glass scintillation vials with precleaned Teflon lined caps. Samples were acidified with 50% H_3PO_4 to pH 2 (500 μl for 100 ml sample) immediately upon collection and poisoned with HgCl_2 (at 1 mg/L). OC concentrations in the permeate, retentate or prefiltrate fractions were analyzed, in duplicate, with a high temperature catalytic oxidation (HTCO) analyzer (Peltzer and Brewer, 1993). Instrumental blanks (typically < 10 $\mu\text{mol/L}$) were estimated daily using UV-irradiated Q-water with very close to zero carbon content. Calibration was also run daily using potassium hydrogen phthalate dissolved into aged seawater as standard. The precision of OC measurement was < 2%.

RESULTS AND DISCUSSIONS

Evaluation of CFF performance

1. Blank evaluation

A CFF blank test represents an essential first order check on the performance of the CFF membrane. A low Q-water blank suggests adequate desorption or degradation of the membrane OC foulants and furthermore attests to the lack of carryover of sample solution.

Table 1 shows one example of the evolution of OC concentration during the cleaning and rinsing steps as the CFF system was treated progressively using Q-water, base, and acid solutions after a typical sample run. The source Q-water OC concentration 2 $\mu\text{mol/L}$. Elevated OC concentrations (27.2 $\mu\text{mol/L}$ for the retentate and 7.4 $\mu\text{mol/L}$ for the permeate when $cf = 2$) in the first Q-water rinse (recirculation for 20 - 30 minutes prior to collection) may be related to the release of OC that was retained by the CFF membrane due to sorptive processes, and/or sample solution carryover due to incomplete draining of the system from the proceeding CFF sample. The OC concentration increased in the retentate to 36.6 $\mu\text{mol/L}$ as CFF processing progressed ($cf = 4$), indicating the continued release of OC. A subsequent base rinse appeared efficient at lowering the OC blank of the system (OC = 17.6 $\mu\text{mol/L}$). After the base rinse, the blank of the system was indistinguishable

Table 1 Organic carbon concentrations in Q water and in rinse solutions from the Millipore CFF system

Rinse solution	OC ($\mu\text{mol/L}$)		cf
	Permeate	Retentate	
1st Q-H ₂ O	7.4	27.2	2
	8.3	36.6	4
NaOH ^{a)} (0.01 mol/L)	5.9	N/A ^{b)}	2
	6.4	17.6	4
HCl (0.01 mol/L)	2.3	6.0	2
	1.2	2.0	4
last Q-H ₂ O	1.8	2.0	2
	0.2	0.8	4

cf = concentration factor; a) Rinse the system with Q-H₂O until pH 7 after the base and acid rinses; b) N/A = not available; Source Q-H₂O organic carbon concentration 2 $\mu\text{mol/L}$. The volume of each rinse solution used was 4 liters.

Table 2 Size-fractionated organic carbon concentration in the Zhujiang River estuary and the CFF mass balance

Station	Salinity	cf	DOC ($\mu\text{mol/L}$)	Permeate ($\mu\text{mol/L}$)	Retentate ($\mu\text{mol/L}$)	COC ($\mu\text{mol/L}$)	COC/DOC (%)	R (%)
9601	0.1	29.4	261.5	200.5	517.5	10.81	4.1	80.8
9604	0.5	6.4	240.3	229.1	368.8	21.73	9.0	104.4
9605	1.4	10.5	108.7	90.2	293.0	19.28	17.7	100.7
9606	6.4	5.8	314.5	245.0	307.0	10.64	3.4	81.3
9608	1.2	6.6	162.2	157.2	301.6	22.12	13.6	110.4
9609	9.0	7.5	171.8	165.2	239.1	9.80	5.7	101.9
9610	5.1	5.8	195.5	192.6	259.1	11.44	5.9	104.4
9611	12.9	5.1	189.2	182.2	223.4	8.11	4.3	100.6
9613	15.7	7.2	248.2	226.8	306.5	11.09	4.5	95.8
9614	24.8	13.9	198.7	165.2	344.8	32.10	16.2	89.6
9701A	0.17	8.1	141.7	101.1	442.3	42.2	29.8	101.0
9701	0.28	6.2	238.5	208.9	447.4	38.8	16.3	104.0
9704A	1.3	5.8	150.4	140.9	337.6	33.9	22.5	116.0
9701 - 5C	4.3	6.0	266.0	179.0	N/A	87.0	32.7	N/A
9702	9.9	8.9	191.1	158.5	554.4	44.7	23.4	106.0
9705	15.1	9.1	150.5	131.8	236.0	11.5	7.6	95.0
9710	24.0	3.3	125.9	117.9	159.4	12.6	10.0	104.0
9706	24.0	8.5	193.2	177.6	219.2	4.9	2.5	94.0
9713A	26.1	8.0	169.4	152.4	333.2	22.7	13.4	103.0
9711	29.8	4.8	109.2	102.4	147.3	9.3	8.5	102.0
9713	32.0	8.5	151.8	123.5	338.1	25.3	16.7	98.0

Permeate: < 1kD; Retentate: final concentrated solution from the CFF processing; COC: colloidal organic carbon (1 kD - 0.4 or 0.7 μm); cf: concentration factor; R: Recovery; N/A: not available.

from that of the source Q-water (OC = 2 - 3 $\mu\text{mol/L}$). The last Q-water rinse had an OC concentration equivalent to that of the source Q-water. These results demonstrate that a low bulk OC blank is achievable for the CFF membranes after careful cleaning. Due to differences in our sample media

and Q -water, these OC blanks could not be directly applied as a correction to OC results for seawater processed by CFF, as noted by Buesseler et al. (1996).

2. Retention characterization

The retention coefficient ($RC \% = (1 - [\text{permeate}] / [\text{retentate}]) \times 100$) of a CFF membrane must be known prior to making any determination of sample size distributions based upon CFF data. Moreover, membrane RCs could change with use, and therefore the RC for a CFF membrane must be estimated frequently.

We used prefiltered ($< 0.2 \mu\text{m}$) seawater sample spiked with nmol/L levels of fluorescein tagged dextran (3 kD) standard molecules to estimate RC. Tests were run in recirculation mode, and the RC was calculated using the data when no further losses of standards to the membrane could be observed. Results (Fig. 2) showed that the obtained 93 % retention coefficients for the CFF membrane used in this study accords with the manufacturer's specification.

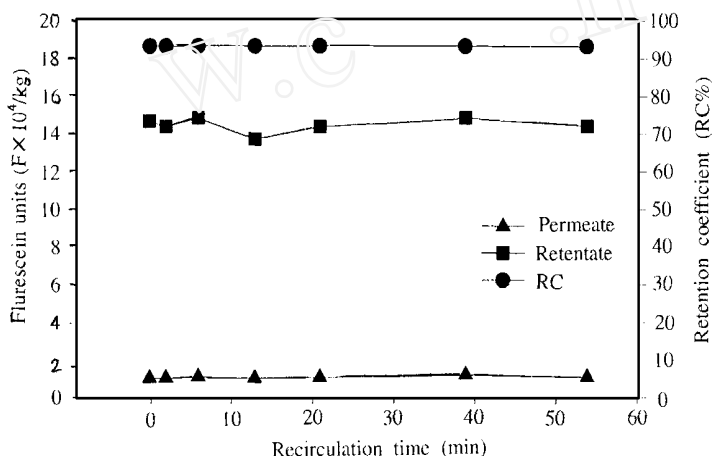


Fig. 2 Recirculation mode test using a 3 kD fluorescein tagged dextran standard.

This figure shows the variation of the fluorescein both in the permeate and the retentate fractions.

Retention coefficient of the CFF membrane for the dextran standard can be then calculated:

$RC = \text{retention coefficient}$ ($RC \% = (1 - [\text{permeate}] / [\text{retentate}])$), the average RC from this experiment is 93 %

3. Bulk organic carbon mass balance

A showing of proper mass balance represents an essential first order check of the performance of any CFF experiment. Table 2 shows the mass balance of organic carbon from the CFF processing. For most samples processed, we obtained quite acceptable recoveries (90 % - 110 %) as far as the CFF system was preconditioned. The low recovery for the sample 9601 was probably due to losses of OC onto the membrane at the high concentration factor. Using a permeation model, Dai et al. (1998) noticed high molecular weight breakthrough at high concentration factors. The low recovery for sample 9606 was odd, something we cannot fully explain.

DOC and COC concentrations

DOC concentration observed in this study was significantly lower than that obtained by Cai and Han (1990). In this study, DOC concentration ranged from 142 $\mu\text{mol/L}$ to 239 $\mu\text{mol/L}$ (March, 1997) in the freshwater taken from four tributaries of the Zhujiang River flowing into the Lingdingyang estuary. Elevated concentration was found at Humen located near Guangzhou. DOC concentration at Humen was the highest among the four tributaries. This elevated concentration might suggest some extent of anthropogenic input at this region. Trace metal concentration was also highest at Humen (Trincherini, personal communication). For example, total dissolved Pb and Cd in the Humen tributary were consistently higher (by a factor of 2) than those in the other three tributaries. A very striking feature at Humen was the very low pH (6.96 at the surface and 7.05 at the bottom) observed during the March, 1997 cruise. In the other three tributaries, pH ranged from 7.86 - 8.03. This dramatic pH drop was due probably to some point sources of acidic waste discharges that could increase the concentrations of metals and likely of organic matter. It is also noteworthy that the nitrate concentration (dissolved oxygen concentration) at Humen was nearly 10 (half) that at the other three tributaries. The low dissolved oxygen content is not surprising given the higher DOM concentration at Humen.

During the July 1996 cruise, we took only one freshwater sample from Humen, and so were not able to make any comparison with the other three tributaries. However, DOC at this region (Station 9601 in Table 2) was 261 $\mu\text{mol/L}$, close to the concentration observed in March 1997 (239 $\mu\text{mol/L}$, Station 9701).

Elevated DOC concentration was also observed in the Deep Bay (9606 and 9706, Table 2). Due to the difference in seawater intrusion, DOC varied from 314.5 $\mu\text{mol/L}$ in July (salinity 6) to 193 $\mu\text{mol/L}$ in March (salinity 24). Overall though, the elevated DOC concentration at this station was evident: for example, in March 1997, DOC concentration at Station 9710 with salinity similar to that at Station 9706 was 70 $\mu\text{mol/L}$ lower than that at Station 9706, which would suggest there existed some local contamination sources. According to Qi and Zhang (1995), there was a significant amount of agricultural waste containing mainly organic manure and pesticides, discharged into the Deep Bay. Consistently, the highest DDTs concentration was found in the sediments of the Deep Bay's inlet (Hong, 1998).

COC in the study area ranged from 8 - 22 $\mu\text{mol/L}$ in July to 5 - 85 $\mu\text{mol/L}$ in March 1997, representing about 3% - 32% of DOC. The overall COC percentage was consistent with the results of previous studies in various estuarine regions (Dai, 1995), suggesting that the majority of DOC occurs as low molecular weight organic matter. Overall, COC in March was higher than that in July. Since the dominant components of the suspended loads in the Zhujiang River are minerals, river borne colloids could not be a dominant source for the COC in the estuary. Hence, in-situ production by precipitation of truly dissolved organic carbon and/or by biological activity is the most likely source for COC. In this regard, primary productivity in winter was overall higher than that in the flood period due to the limitation by turbidity. The primary production in March, 1997 was 6 times that in July 1996 (Hong, 1998).

Behavior of DOC and COC during estuarine mixing

In light of the complexity of the estuary input sources, high-resolution samples are obviously needed to fully understand the biogeochemical processes that determine the organic carbon behavior during estuarine mixing. Here we take the second cruise data as an example to briefly discuss the mixing processes of organic carbon.

Besides the above mentioned two "hot" spots at Humen and in the Deep Bay where additional input other than mixing occurred, DOC concentration increased rapidly at low salinities (~ 5) (Fig. 3). This is consistent with the highest COC concentrations at this salinity, which may be attributed to the exchange between macroparticulate and dissolved organic matter during the early stage of estuarine mixing or the in-situ formation of colloidal material caused by coagulation of the dissolved organic carbon. Indeed, the truly dissolved organic carbon (< 1 kD) is relatively low in terms of its percentage in DOC at this salinity. Beyond this point, DOC concentration overall follows the theoretical dilution line. For COC, a very modest removal was observable until higher salinities. But this minor removal did not seem to affect the bulk DOC distribution though the removal might have significant impact on particle-reactive elements. Truly dissolved organic carbon has an overall trend similar to that of DOC at the salinity range of 5 - 25. A modest elevated concentration for all the three organic carbon fractions was again observed at salinity 25 in the Deep Bay, which might represent a local organic matter source from Shenzhen as mentioned earlier.

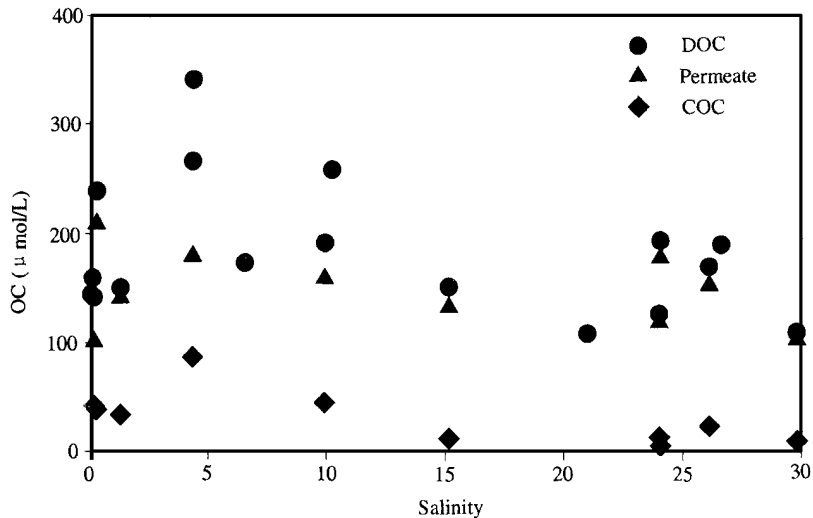


Fig. 3 Distribution of organic carbon fractions as a function of salinity (March, 1997)

SUMMARY

This study yielded some preliminary results on the size fractionated organic carbon in the Lingdingyang estuary. DOC distributed non-linearly along the salinity gradient, indicating the existence of other sources of organic matter in the estuary. Due to the complexity of the estuary system, high-resolution samples will have to be taken in order to better define the river-end member concen-

trations and to more comprehensively describe the behavior of organic carbon in the estuary. On the other hand, the impact of human activity induced by the economic boom in the region during the last 15 years has been emerging. This is particularly obvious at Humen and in the Deep Bay. In this context, the localized pollutant discharge should also be better identified so as to distinguish the processes at the natural level and the impact by the economic development in the region.

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