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Variation of reactivity of particulate and sedimentary organic matter along the Zhujiang River Estuary*

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Abstract —— To investigate organic matter source and reactivity in the Zhujiang River (Pearl River) Estuary and its adjacent areas, particulate organic carbon (POC), particulate hydrolysable amino acids (PHAA), and Chl a during two cruises in July 1999 and July 2000 were measured. The highest POC and PHAA concentration was observed in the waters with maximum Chl a. The spectra distribution, relative content (dry weight in milligram per gram), PHAA-C% POC and other indicators such as the ratios of amino acids vs. amino sugars (AA/AS) and glucosamine vs. galactosamine (Glum/Gal) suggested that particulate amino acids in the water column and sediments in the Zhujiang River Estuary were mainly derived from biogenic processes rather than transported from terrestrial erosion. In inner estuary where high turbidity was often observable, organic matter was mainly contributed by re-suspension of bottom sediments with revealed zooplankton, microbial reworked characteristics, which suggest that these organic matters were relatively "old". In the estuarine brackish region, organic matter in water column is mainly contributed by relatively fresh, easily degradable phytoplankton derived organic matter. During physical - biological processes within the eastuary, organic matter derived from phytoplankton was subjected to alteration by zooplankton grazing and bacterial reworking.

Key words Organic matter, reactivity, amino acids, the Zhujiang River Estuary

INTRODUCTION

Estuarine and continental margin sediments are important depositories of carbon and associated elements because of higher suspended matter inputs of terrestrial sources. On the other hand, enhanced nutrient loading due to urbanization may enhance the primary productivity of coastal waters, thus added marine organic carbon deposits in the sediments. It is estimated that

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about 83% of organic carbon accumulating in modern marine sediments is buried along continental margins, mainly in deltaic and shelf areas (Benner, 1982) . So the coastal seas and continental margins may be a significant sink for anthropogenic CO_2 (Walsh, 1991) . However, estuaries are located in the most complex environments on earth in which freshwater discharge and tidal forcing are changing on time scales of seconds to seasons and turbulent mixing of fresh water and salt water can generate abrupt changes in temperature, salinity, pH and nutrients along the estuary. Up to now, the knowledge of dynamics and fate of terrestrial or marine organic matter in estuaries is still very limited (Hedges *et al*., 1997; Hedges and Keil, 1999) . The formation and degradation of organic matter in an estuary are an integrative process of estuarine ecosystem dynamics. The reactivity of organic matter mainly depends on its sources and in turn it largely determines the possibility and the rate of nutrients regeneration from organic matter (Ittekkot, 1988; Nguyen and Harvey, 1997) . So characterizing reactivity of organic matter from riverside fresh waters to offshore oceanic waters is important for understanding the ecosystem dynamics and sedimentary carbon accumulation in the estuary.

The Zhujiang River is the second largest river in China in terms of water discharge, it enters into the South China Sea through eight distributaries. The discharge in wet season (April to September) accounts for 80% of the total annual discharge. In summer, due to large river runoff, the mean flow pattern inside such an estuary has a strong net seaward surface flow of fresh water and a strong inflow of heavier brackish water at depth, which results in a strong stratification. A number of surveys shows that the nitrate concentration across the estuary is generally high, with a maximum values over 100 μmol/L in surface waters, the ratio of N top is up to 200:1, which is one order higher than the Redfield ratio (Zhang *et al*. , 1999; Yin *et al*., 2000) . Although some marine chemistry studies have been carried out such as nutrients and trace metal distribution (Wang and Peng, 1996; Zhang *et al* ., 1999), carbon budget (Han, 1991), nutrients dynamics and limitation (Yin *et al* ., 2000), only very limited data on spatial distribution and fate of organic carbon have been available in the estuary.

In this paper, we present results from two cruises in July 1999 and July 2000 in the Zhujiang River Estuary. Water, particulate and sediment samples were taken and analyzed for Chl a, POC and particulate hydrolysable amino acid . This paper will focus on organic matter distribution and its reactivity variability in the Zhujiang River Estuary, dynamic of amino acids (AAs) in the estuary will be reported elsewhere.

MATERIALS AND METHODS

Two cruises were conducted on board *Haijian* 74 during July 17 to 28, 1999 and July 22 to 28, 2000 in the Zhujiang River Estuary, sampling was conducted in neap tide periods. The sampling locations were designed to cover the riverine plume, the estuarine plume to the coastal plume and oceanic waters. More details are shown in Fig. 1.

A CTD (*Seabird*) and a YSI 6600 (YSI^R, USA) were used to measure *in situ* water depth, salinity, temperature, dissolved oxygen, pH as well as turbidity. Upper (0.5 m below

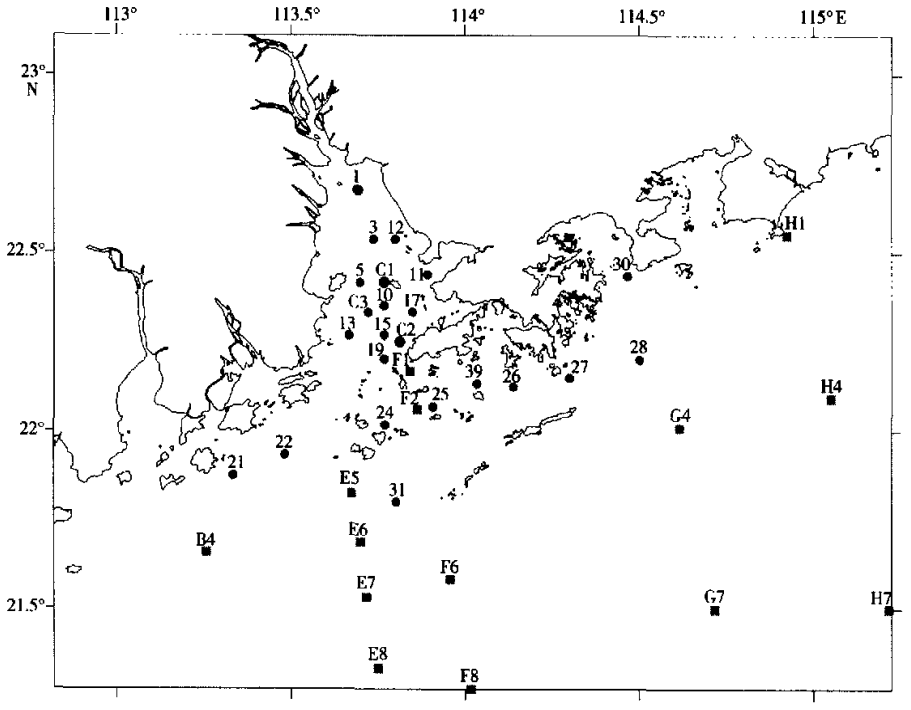

Fig. 1. Sampling stations in the Zhujiang River Estuary. Gray circles stand for stations sampling during July 1999, gray squares mean stations sampling during July 2000, and black circles (1, C1, C2) stand for stations in which samples were taken in both 1999 and 2000.

surface) and lower (1 m above sediments) water samples were taken with a 2.5 L Go-flo sampler. Nutrients and Chl a were analyzed on board according to Chinese National Standard Methods (GB 17378 – 1998). Concentrations of suspended sediment (SS) were weighted after filtered by 0.45 μm cellulose filter.

For POC and PHAA analysis, about 1 000 mL and about 200 mL water samples were filtered by a pre-combusted 47 mm Whatman GF/F filter on a millipore glass filtration set, then the filters were stored in frozen and dark. Sediment samples were taken with a multi-corer. Sub-sampling (in 2 cm slices) was carried out immediately after the multi-corer was brought onto the deck. Then all samples including filters and sediments were freeze-dried in a shore-based laboratory. The dried sediments were homogenously grounded before analysis.

POC and sedimentary organic carbon were determined by Shimadzu TOC 5000A TOC analyzer (using a Solid Sample Module SSM – 5000A) and a Carlo Erba EA1106 CHN analyzer respectively after removing of carbonate on the filters with HCl. The resullt wrer calibrated by acetanilide and organic carbon sediment reference GBW07314, which has been used as national standard.

Amino acids analysis followed a method described previously (Chen *et al.*, 2000).

Briefly, sediment samples, filters or filtered waters were hydrolyzed with 5 mL 6 mol/L HCl for 22 h under argon. An aliquot of hydrolysate was dried at 40℃ under argon in order to remove remaining HCl. The residue was dissolved with 10 μl 0.1 mol/L HCl, derived with fluorescence reagent (AQC, Waters^{R}) and then analyzed on Waters 600E HPLC system according to the procedures developed by Cohen and Dennis (1993). The system included the Waters 600E solvent delivery unit, ACCQ－TAG column for amino acids separation, 474 fluorescence detector, 717 auto-sampler and Millennium 32 chromatography workstation. Two additional secondary amino acids (β-alanine, γ-aminobutyric acid, sigma) and two amino sugars (glucosamine, galactosamine, sigma) were added into a mixture amino acid standard sample (Pierce, USA) which contained 17 individual primary amino acids and ammonium, thus the new amino acid standard mixture has contained 19 amino acids and 2 amino sugars. The internal standard of α-aminobutyric acid was added during treating and analyzing the standard and samples. Amino acids and amino sugars were identified from retention time and their amount were calculated by comparing standard peaks and samples peaks, which were corrected with an internal standard. Relative error in duplicate analysis is less than 5% for total amino acids, less than 10% for total amino sugars, and less than 10% for individual amino acids and amino sugars.

RESULTS AND DISCUSSION

Spatial distribution and sources of POC from fresh waters to oceanic waters

Figure 2 shows mixing diagrams of POC, PHAA and Chl a vs. salinity and graphs of organic matter vs. Chl a. At the freshwater end-members, concentrations of POC and PHAA in surface layer vary from 0.32 to 1.15 mg/L and 0.23 to 0.95 mg/L respectively. Higher values occur in mid-salinity waters (Fig. 2a). POC and PHAA concentrations are generally lower in bottom layer than those in surface layer in waters of low to mediate salinity, while POC and PHAA are higher in oceanic bottom waters, which indicates that those higher concentration organic matter in mid-salinity waters will settle when surface waters move seaward. The diluted curves of POC and PHAA against salinity are rather complicated, showing that physical mixing is not a dominant factor controlling POC and amino acids contents in the estuary. POC and PHAA distribution are quite similar to that of Chl a, the regressions of POC vs. Chl a and PHAA vs. Chl a are all significant (Fig. 2e), indicating that most of the particulate organic matter of the Zhujiang River Estuary is derived from plankton. Generally, the distribution patterns of PHAA relative content (dry wt in milli grarn per grorm) against salinity and Chl a are significantly linear in surface waters, suggesting that PHAA relative content in bulk particulate matter increases from fresh waters to oceanic waters. The higher Chl a concentration is in the waters, the higher relative PHAA content in the bulk particulate matters (Fig.2d). Much lower PHAA relative content in bottom water (Fig. 2f) suggests decomposition of organic matter during settling or resuspension of sediments with lower PHAA relative content.

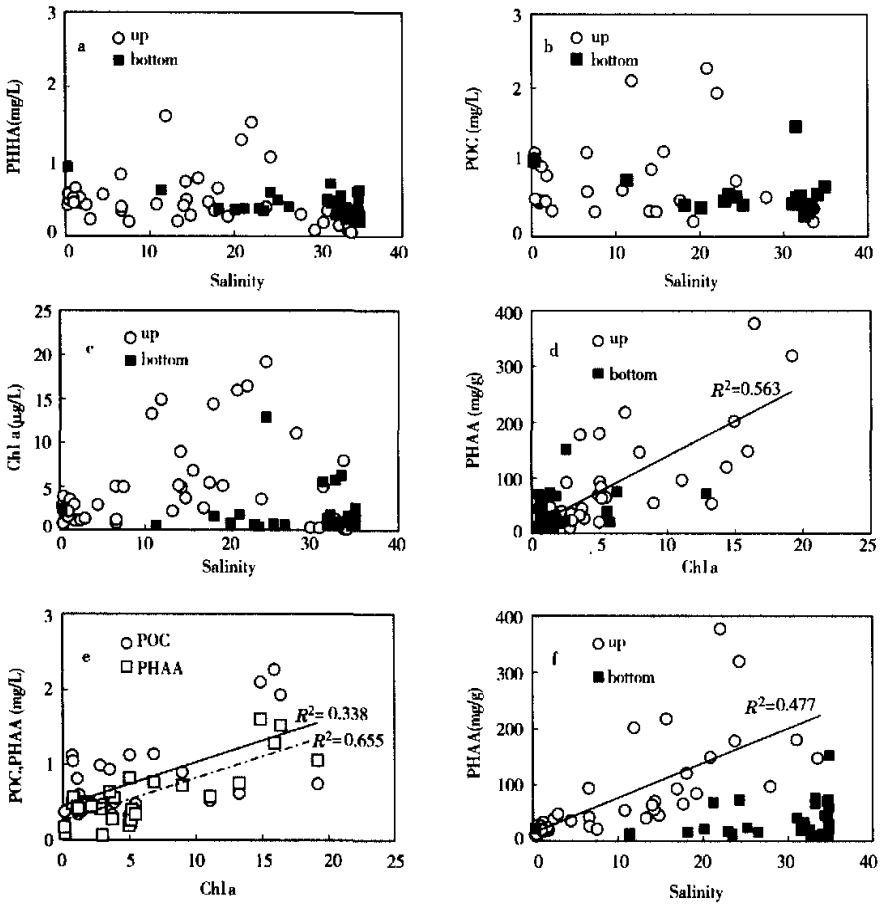

Fig. 2. The mixing digrams of POC, PHAA and Chl a vs. salinity (a-c) and graphs of organic matter vs. Chl a (d-f) based on all data set of cruises 1999 and 2000. Regression is significant when $R^2>0.122$, $n=32$, $\alpha=0.05$

Reactivity of particulate organic matter in the the Zhujiang River Estuary

The Zhujiang River discharges an average amount of 85 M/a of sediment (Zhang *et al.*, 1999). How much organic matter in the the Zhujiang is derived from these suspended matter? Table 1 shows the relative content of amino acids in dry weight in milligram per gram in different sample sets. As easily degradable organic matter, more AAs in bulk material means more fresh organic matter in bulk particulate matter. The amino acid content of Chinese loess is very low, usually less than 0.15 mg/g (Liu, 1985). Low amino acid content (0.80 mg/g, see PRD-soil in Table 1) is also measured in soils from the suburb of Guangzhou in the Zhujiang River Delta area (Wang *et al.*, 1991). In the Zhujiang River Estuary, amino acid relative content in particulate matter is usually one to two orders of magnitude higher than that in soils

from the Zhujiang River Delta, even in the waters with maximum turbidity. This suggests that soil is not likely a major source of amino acids in the estuary. However, it should be noted that upstream of the river can produce amino acid via plankton growth which may discharge into the estuary afterwards. Zhang *et al*. (1992) found that when the turbidity of the Huanghe River was much higher and nearly no fresh plankton in wet seasons, PHAA relative content varied from 1.2 to 1.5 mg/g (dry weight) and was quite similar to that in the soil. But the value increased up to 6.9 to 44.4 mg/g (dry weight) in dry season when higher Chl a was measured. This supports our previous suggestion that riverine or estuarine biological production accounts for most of the PHAA in water column in the estuary. Amino acid relative content in sediments of the Pearl River Estuary ranges from 0.9 to 2.9 mg/g. It only represents 1% of that in biogenic particulate matter and less than 10% of that in the turbidity maximum particulate matter. This dramatic decrease in the amino acid relative content in the estuary indicates that most of the PHAA have been lost before it is ultimately preserved in the sediments.

Orgonic matter is easily degraded into amino acids when it is freshly produced. The percentage of amino acids in bulk fresh organic material is higher than that in old organic matter (Cowie and Hedges, 1994; Chen *et al*., 1999). Thus, the percentage of organic carbon presented in amino acids (here combined as PHAA-COC) could be a significant indicator for organic matter reactivity. Table 2 shows PHAA-COC variations in samples from the Zhujiang River Estuary and in the material from different sources. PHAA-COC in turbid or biogenic particulate matter of our sample set can be comparable with that in previous reports about other large rivers (Ittekkot, 1988) or plankton (Cowie and Hedges, 1992). PHAA-COC in terrestrial materia-

Table 1. Amino acid relative contents (dry weight) in particulate matter, sediments from Zhujiang River Estuary and a comparison of its contents with different sources

	Chines loess	Pacific sediments	PRD soil	Zhujiang River Estuary			
				Bio.PM-up	Turb.PM-up	PM-bottom	sediments
Average (mg/g)	0.08	0.5	0.8	88.0	27.8	29.9	1.5
Maximum (mg/g)	0.15	0.7	2.8	138.0	48.8	74.9	2.9
Minimum (mg/g)	0.04	0.4	0.4	62.0	9.8	17.9	0.9

Notes: Bio.PM means biogenic particulate matter with Chl a > 5 μg/L and SS < 10 mg/L, Turb.PM means turbidity particulate matter with SS > 20 mg/L. Up and bottom means sampling at 0.5 m below the surface and 1 m above the bottom. Data of Chinese loess (Liu *et al*., 1985), soil from the Zhujiang River Delta (PRD) in Guangdong province (Wang *et al*., 1991) and sediments from deep central Pacific Ocean (Chen, unpublished data).

Table 2. Comparison of amino acids derived particulate organic carbon (PHAA－CPOC) between Zhujiang River Estuary particulate matter and potential amino acids source materials

	Higher plants	PRD soil	YR PM (wet season)	YR PM (dry season)	Plankton	Zhujiang River Estuary	
						Turb.PM	Bio.PM
Average	3.6	3.4	8.5	25.0	42.0	22.3	40.0
Maximum	6.8	7.4	12.5	33.0	58.0	36.3	52.0
Minimum	2.6	1.4	6.5	18.0	33.0	14.3	25.0

Notes: Higher plants data from Jennerjahn and Ittekkot (1997). Data of the Zhujiang River Delta soil (PRD soil) from Wang *et al*. (1991), data of the Huanghe River particulate matter (YR PM) in wet and dry season from Zhang *et al*. (1992), plankton data from Cowie and Hedges (1992), Turb.PM and Bio.PM mean turbidity particulate matter and biogenic particulate matter respectively, see Table 1.

ls, such as higher plants (Jennerjahn and Ittekkot, 1997) and soil (Wang *et al.*, 1991), is very low. PHAA-COC in riverine suspended matter from the Huanghe River in wet season is much lower than that in the dry season (Zhang *et al.*, 1992). Based on the comparisons above, it can be further deduced that PHAA in the Zhujiang River Estuary is derived from riverine or estuarine biological production processes, thus, it is quite reactive and easily degradable.

Amino acids spectra and compositional modification in the Zhujiang River Estuary

The spectra of PHAA are shown in Fig. 3. The dominant AAs are, in a descending order, glycine, glutamic acid, proline, aspartic acids, alanine, serine, leucine, isoleucine, lysine and phenylalanine. The mole percentages of these amino acids are all greater than 5%. The AAs spectra of PHAA in the Zhujiang River Estuary are quite similar to those on plankton sample, sediment trap materials and the previous reports on plankton (Cowie and Hedges, 1992; Jennerjahn and Ittekkot, 1997), but different from that in soil (Wang *et al.*, 1991), which indicates that plankton is the dominant source of organic matter. However, there are still significant differences among the average spectra of biogenic particles, turbidity particles and benthic sediments (Table 3). The most pronounced feature is that there are higher glutamic acid (Glu) and proline (Pro) in biogenic particles than those in turbid particles and benthic sediments, while non-protein amino acids, such as β-alanine (b-Ala) and γ-aminobutyric acid (g-Aba), are higher in benthic sediments than those in other two sources. Non-protein amino acids such as β-alanine is absent in living organisms, therefore, higher β-alanine indicates active modification of the released AAs from phytoplankton.

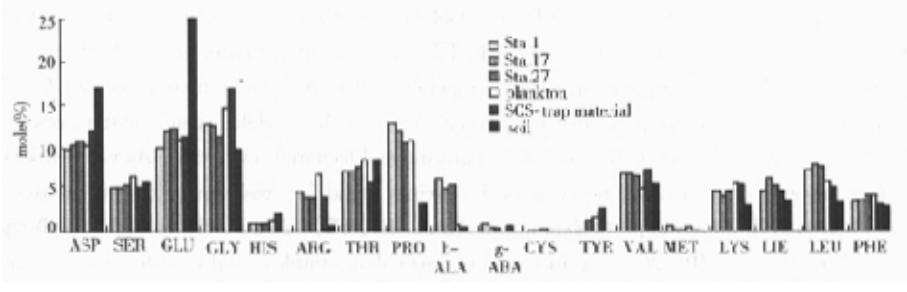

Fig. 3. Amino acids spectra of particulate matter in the Zhujiang River Estuary and a comparison with those in plankton, settling particulate matter and soil. Plankton represents *in situ* culture bloom sample in the Zhujiang River Estuary in July 1999, SCS trap material represents sediment trapmaterial in the South China Sea (Chen *et al.*, 1999) and soil represents surface soil from the Zhujiang River Delta (Wang *et al.*, 1991).

The ratio of amino acids to amino sugars (AA to AS) is a useful proxy for differentiating organic matter derived from phytoplankton and zooplankton (Degens and Mopper, 1976; Ittekkot *et al.*, 1984). Amino sugars are mainly derived from cutin material which is a major component of zooplankton with high depeletion in phytoplankton. If organic matter is dominat-

ed by phytoplankton-derived material, the ratio of AA to AS will be high. With an increasing input of zooplankton-derived organic matter, the ratio decreases. The ratio of glucosamine to galactoamine (Glum to Gal) is helpful in differentiating bacterial biomass from organic matter (Ittekkot, 1984; Haake *et al*., 1993). Table 4 shows a comparison of Glum/Gal of different materials. Bacterial cell walls have nearly equal amounts of the two amino sugars, hence, the ratio is usually no more than 1~3 in bacteria (Kandler, 1979). In the subarctic ocean where bacterial activity was much less than tropical oceans, the ratio is up to 20 in sediment trap material (Haake *et al*., 1993). In contrast, glucosamine is far more abundant than galactoamine in zooplankton (Müller *et al*., 1986). The ratio of (Asp + Glu) to (b-Ala + g-Aba) (combined as AA − p/AA − np) could be used as an indicator of degradation stages of organic matter (Ittekkot *et al*., 1984, Cowie and Hedges, 1994). Non-protein amino acids, such as β-alanine and γ-aminobutyric acid, are absent in living cells as they are decomposition products of aspartic acid and glutamic acid. Thus, the ratio of parent to daughter could be a good indicator of organic matter reactivity.

Table 3. Average amino acids spectra (mole percnetages) in biogenic particles, turbid particles and sediments in the Zhujiang River Estuary and adjacent areas

	ASP	SER	GLU	GLY	HIS	ARG	THR	ALA	PRO	b-ALA	g-ABA	CYS	TYR	VAL	MET	LYS	LIE	LEU	PHE
Biogenic particles	10.2	5.9	13.2	12.4	1.0	4.6	7.0	0.3	11.2	3.8	0.2	0.1	0.3	6.9	0.2	4.8	5.1	7.6	3.9
Turbid particles	9.7	5.4	8.9	11.1	0.5	3.4	6.3	0.0	9.4	4.4	0.8	0.0	0.0	6.4	0.1	3.8	4.5	6.2	3.5
Sediments	10.6	6.3	9.4	16.0	0.8	4.8	7.1	0.9	0.9	7.1	2.0	0.3	1.8	6.4	0.2	3.9	3.6	5.7	3.2

Notes: Biogenic particles repesent samples of Chl a>5 μg/L and SS<10 mg/L, and turbid particles repesent samples of SS>20 mg/L

Figure 4 shows that AA/AS and Glum/Gal increase along the estuary. Decreasing trend was observed from biogenic matter (Stas F1, F2, 31), turbidity matter (Stas. 1, 3) to sediments (Stas. 1 − C3), suggesting that phytoplankton-derived organic matter account for the most part of particulate biogenic matter in oceanic end-member, while organic matter preserved in sediments is that modified by zooplankton grazing and bacterial reworking. As we mentioned before, relative content of amino acids in dry weight stand for freshness of organic matter in bulk material. In biogenic particulate matter (Stas. F1, F2), AAs reachs as high as 200 mg/g, it drops down to 10~20 mg/g in turbidity particulate samples, and in sediments it is only less than 2 mg/g. So organic matter preserved in sediments is relative "old".

Table 4. Ratio of Glum/Gal in different materials

	Bacteria	Soil	YR PM	SCS-trap material	Stn.p trap material	Foraminifera
Glum/Gal	1.3	1.5	1.6	3.3	10.5	6.8
Reference	1	2	3	4	5	6

YR PM represents River particulate matter, SCS-trap material represents sediment trap material from the South China Sea, and Stn.P trap material represents sediment trap material from Sta. P in subarctic Pacific Ocean. 1 indicates Kandler (1979), 2 indicates Degens *et al*. (1976), 3 indicates Zhang *et al*. (1992), 4 indicates Chen *et al*. (1999), 5 indicates Haake *et al*. (1993) and 6 indicates Chen *et al*. (2000).

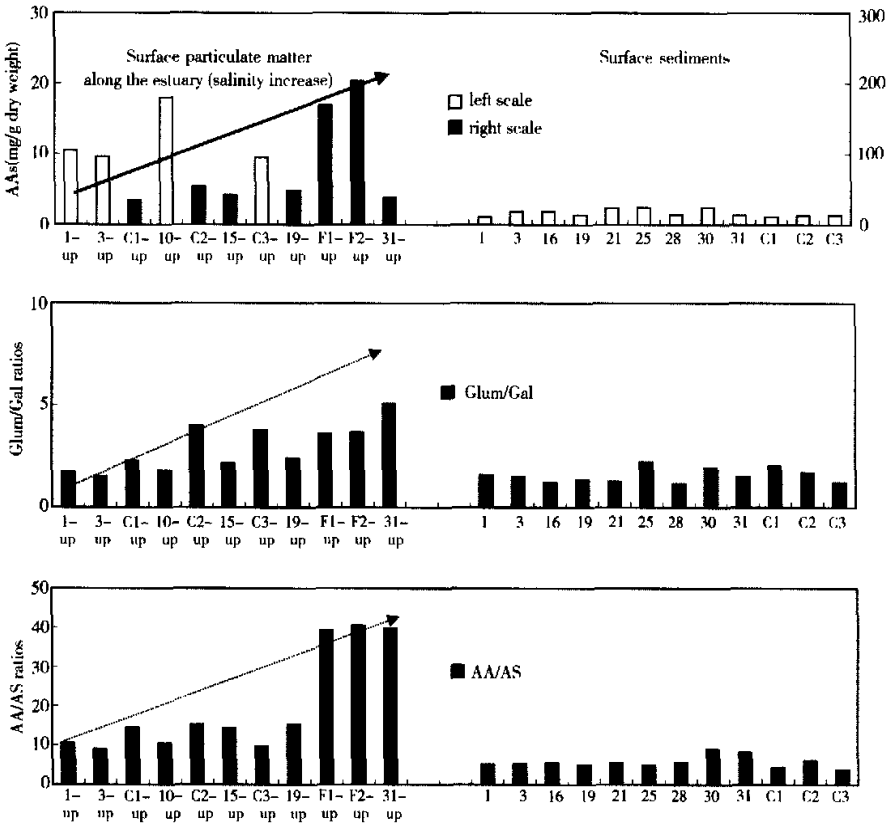

Fig.4. Particulate amino acids relative contents (AAs) and ratios of Glum/Gal, AA/AS along the estuary and a comparison with those in the Zhujiang River Estuary

(1 - up means particulate matter at 0.5 m water depth, the others are the same mean; surface sediments: 0~2 cm)

The top two graphs of Fig.5 show the salinity distribution in surface and bottom layers in the Zhujiang River Estuary during sampling period. According to the salinity gradient, the estuary could be divided into two parts: western waters and eastern waters. Western waters are more fresher waters and turbider than eastern one, due to three tributaries pouring into western part while there is no bigger river discharging into east part. Other 6 graphs of Fig. 5 show the distributing differences of AA/AS, AA - p/AA - np and Glum/Gal between the surface and the bottom layer of the Zhujiang River Estuary. There are significant differences between west and east, surface and bottom, inner and outer of the estuary. In general, ratios of AA to AS, Glum to Gal and AA - p to AA - np increase with the salinity gradient increasing which indicate that the freshness of particulate organic matter increases as one moves downstream into the coastal plume. In the bottom waters, phytoplankton produced amino acids beyond the estuarine plume might sink and could be transported back with the salt wedge, being modified by zoopl-

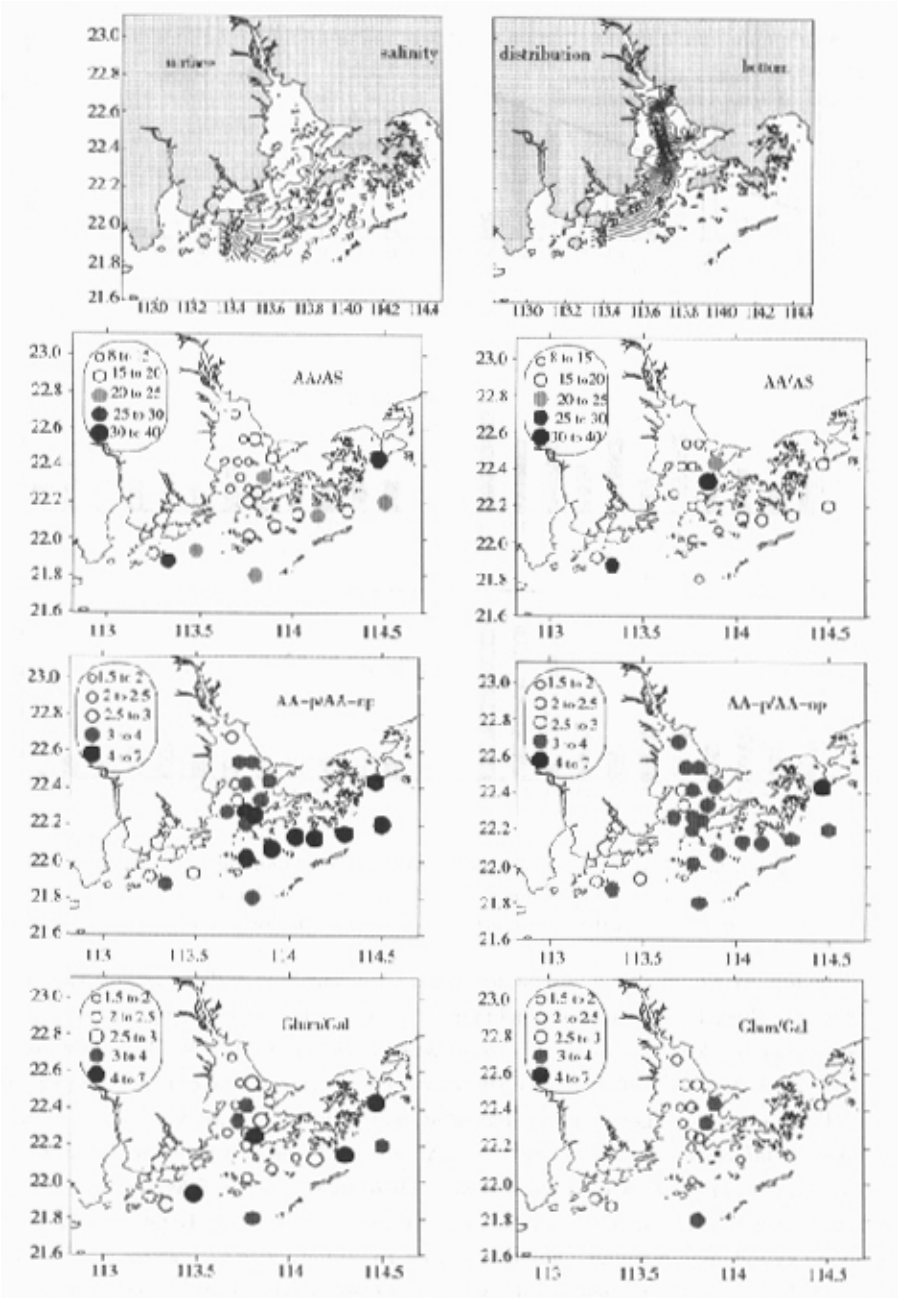

Fig. 5. Amino acids related ratios and organic matrix spatial variation along the PRE.
Left represens surface layer and right represents bottom layer.

ankton grazing and bacteria reworking. Re-suspension of sediments might have contributed to bulk amino acids in waters with higher turbidity.

CONCLUSIONS

Biological processes coupled with the physical processes such as water masses circulation control the production, degradation and transformation of particulate organic matter of the Zhujiang River Estuary. When fresh water flows into the estuary, suspended solids gradully decrease along the estuarine－coastal plume, which improves light penetration correspondingly and benefits for phytoplankton blooms. However the low nutrients of oceanic watecs limit phytoplankton blooms. As a result, the region of Chl a maximum occurs at an intermediate salinity waters of the coastal plume. Biological processes starting from phytoplanton growth dominate production of particulate organic matter in the estuary. On the other hand, higher PHAA concentration near the fresh water is largely attributed to higher SS of turbidity waters, whose relative content is quite low. In estuarine physical-biological processes, organic matter derived from phytoplankton is subject to modification of zooplankton grazing and bacterial reworking as shown by the ratios of AA to AS, AA－p to AA－np and Glum to Gal. Most of organic matter is degraded and transformed within the estuary and only a minor part, mainly modified by zooplankton grazing and bacterial reworking, would ultimately be preserved in sediments.

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