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Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China

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Abstract

The isotopic composition (δ^{13}C and δ^{15}N) and organic carbon (OC) and total nitrogen (TN, organic plus inorganic) content of 37 carbonate-free surficial sediments of the subtropical Pearl River estuary and the adjacent shelf of South China Sea (SCS) was determined. The δ^{13}C values indicate that the sediment organic material is a mixture from two sources, terrestrial and marine. Several of the sediments have extremely low (<4) OC/TN ratios, which could be due to low OC contents and/or to a significant fraction of the TN present as inorganic nitrogen adsorbed on clays. In general, the spatial patterns of OC, TN, δ^{13}C and δ^{15}N are similar. Values are low at the river mouth and on the western coast, suggesting proportionally greater accumulation of terrestrial particulate organic matter relative to marine phytodetritus, which is limited by low productivity in the turbid plume of the Pearl River. Algal-derived organic carbon (al-OC) content is estimated to be low (≤0.06%) at the river mouth and higher (up to 0.57%) on the adjacent inner shelf based on a mixing model of end members.

Keywords: Pearl River estuary; Organic matter; Stable isotopes; South China Sea

1. Introduction

Knowledge of the source(s) of organic matter in estuarine and coastal sediments and factors controlling their distribution are important to the understanding of global biogeochemical cycles. In these transitional systems, primary production generates large amounts of organic matter of which a significant portion sinks through the water column and is ultimately preserved in sediments (Budge and Parrish, 1998). Here we report the organic carbon (OC) and total nitrogen (TN) contents and the isotopic compositions (δ^{13}C and δ^{15}N) of surficial sediments from a subtropical coastal environment, the Pearl River estuary and the adjacent South China Sea.

Due to the complex nature of organic matter in estuarine sediment (Jassby et al., 1993), a variety of parameters (δ^{13}C, δ^{15}N, biomarkers) have been used to determine the sources of organic matter (Sweeney and Kaplan, 1980; Hedges et al., 1988; Schimmelmann and Tegner, 1991; Canuel et al., 1995; Andrews et al., 1998; Naidu et al., 2000; Maksymowska et al., 2000; Zimmerman and Canuel, 2001; Kerhervé et al., 2001, among many others). The usefulness of these parameters lies in the fact that they each exhibit character-

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istic source-specific signatures. For example, the typical $\delta^{13}C$ values of terrestrial C_3 plants range from −26‰ to −28‰ and for marine phytoplankton from −19‰ to −22‰ (Fry and Sherr, 1984; Emerson and Hedges, 1988; Fontugne and Jouanneau, 1987; Boutton, 1991). Likewise, the typical $\delta^{15}N$ values of terrestrial vascular plants range from −5‰ to +18‰ with an average value ~3‰ and marine POC range from 3‰ to 12‰ with a mean value ~6‰ (Wada and Hattori, 1991; Müller and Voss, 1999; Maksymowska et al., 2000). Organic carbon to nitrogen ratios (OC/N) also serve as potentially useful indicators in elucidating the source of sediment organic matter (Andrews et al., 1998; Müller and Voss, 1999; Maksymowska et al., 2000). Generally, marine organic matter and terrestrial organic matter have OC/N of ~5–8 and >15, respectively (Meyers, 1997). However, post-depositional changes in this ratio can occur (Bordovskiy, 1965; Prahl et al., 1980; Roman, 1980), and presence of significant fraction of inorganic nitrogen (adsorbed on clay minerals) can also limit the usefulness of OC/N ratios as source indicators of organic matter in marine sediments.

As for most major estuarine systems world-wide, the Pearl River estuary has been increasingly impacted by anthropogenic activities. In the 1970s large-scale economic reforms were undertaken, and subsequent increases in deforestation and developmental activities resulted in higher sedimentation rates in coastal regions (Owen and Lee, 2004), heavy metal contamination in sediments (Li et al., 2000, 2001), and increased inputs of anthropogenic organic carbon to the estuaries (Li and Lee, 1998). In the last two decades, the Pearl River estuary also received a high flux of anthropogenic nutrients from increased agricultural activities, sewage input and marine fish farming (Huang et al., 2003). As a result of these activities, eutrophication and harmful algal blooms occurred frequently (Yin et al., 2000; Huang et al., 2003). These changes, in turn, have the potential to alter the nature and content of organic matter of marine deposits and their OC/N, $\delta^{13}C$ and $\delta^{15}N$ values (Owen and Lee, 2004).

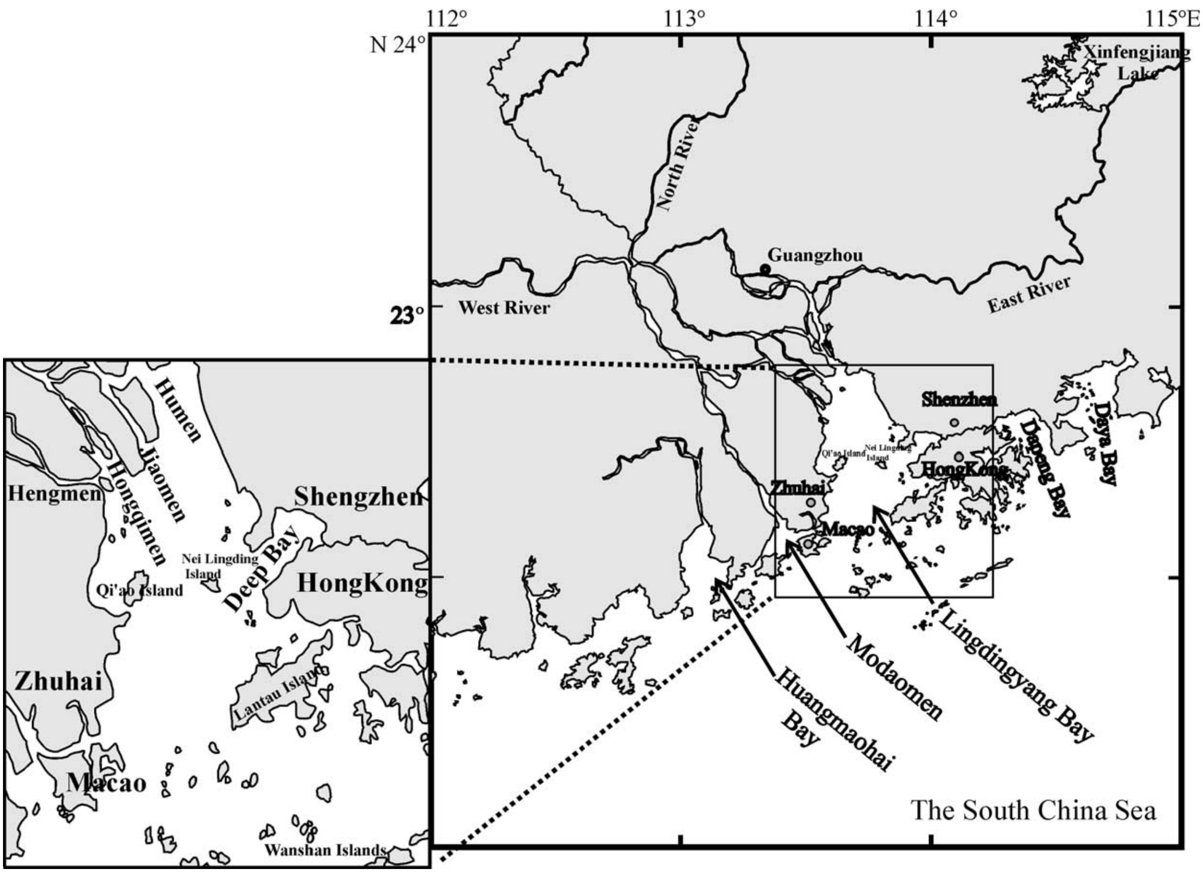

Fig. 1. A map showing the disposition of the Pearl River estuary (Inset of Lingdingyang Estuary shows the location of the main Lingdingyang transect; after Callahan et al. (2004)).

There are many data sets available on nutrients for the Pearl River and estuary (Zhang et al., 1999; Yin et al., 2000, 2001). Additional studies on metal and organic contaminants in sediments in the area have been performed (Li et al., 2000, 2001; Mai et al., 2001; Zheng et al., 2001; Zhang et al., 2002a,b). However, the biogeochemistry of organic matter (carbon) within this estuary remains poorly documented (Dai et al., 2000; Chen et al., 2003, 2004; Jia and Peng, 2003; Callahan et al., 2004). In this study, we report the concentrations of organic carbon (OC) and total nitrogen (TN) and their isotope ratios (δ^{13}C and δ^{15}N) in sediments of the Pearl River estuary and the contiguous shelf of the South China Sea, and elucidate the sources of organic matter deposited in the area.

2. Study area

The study area consists of the Pearl River estuary and the adjacent inner continental margin of northern South China Sea (SCS). Together with the Mekong River, the Pearl River provides the largest inflow of fresh water to the SCS, which is one of the largest marginal seas in the North Pacific. The Pearl River system discharges into the SCS via three subestuaries, Lingdingyang, Modaomen and Huangmaohai estuaries (Fig. 1), and consists of three main tributaries, Beijiang (North River), Dongjiang (East River) and Xijiang (West River). The Xijiang has the greatest freshwater discharge.

The Pearl River is the second largest river in China and the thirteenth largest river in the world in terms of water discharge (~330×10^9 m^3 yr^{-1}) and carries a sediment load of ~80×10^6 t y^{-1} (Tian, 1994; Zhang et al., 1999). It has a catchment area of 45×10^4 km^2 and stretches for 2200 km (Cai et al., 2004). The suspended sediment concentration in the Pearl River is lower compared with other major Chinese rivers, with a mean concentration of about 0.172 kg m^{-3} and an annual flux of ~30.64×10^6 t (Wai et al., 2004). About 94% of the suspended sediment is discharged during the wet season (April to September), ~80% of which is deposited within the Pearl River estuary and the remainder transported to the South

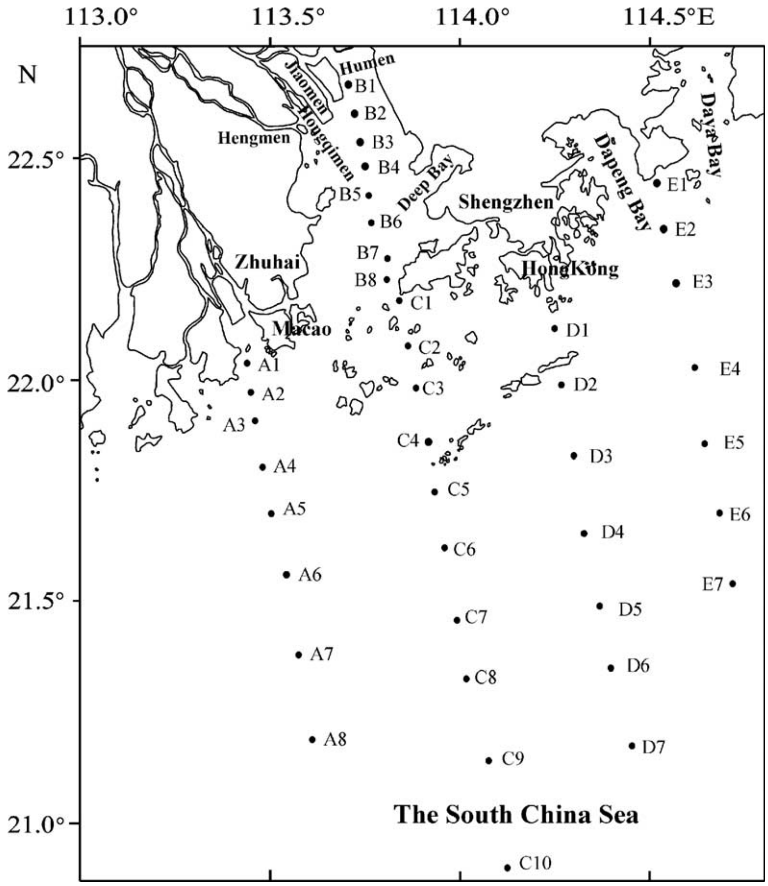

Fig. 2. Locations of sampling sites in the Pearl River estuary and on the adjacent shelf of the northern South China Sea.

China Sea (Wai et al., 2004). However, the sedimentation rates are different in different area in the estuary/shelf system, i.e., they are high in the coast (from 1.13 to 2.34 cm/yr, Jia and Peng, 2003) and low in the shelf (0.2 to 1.0 cm/yr, Owen and Lee, 2004). Generally, the surface samples (10 cm) represent 5 to 10 years. Further description of the environment of the Pearl River Estuary is available in a recent synthesis (*Continental Shelf Research*, *vol.* 24, 2004).

3. Materials and methods

Surface sediment (0–10 cm) samples were collected with a grab sampler in July 2002 at 37 locations in the Pearl River estuary and on the South China Sea shelf (Fig. 2). The samples were stored frozen at −30 °C until analysis. The sediment samples were thawed, dried, homogenized and powdered. Sub-samples for isotope, OC and TN analyses were treated with 4 N HCl to remove carbonate and subsequently rinsed with deionized water to remove salts and dried. The carbonate-free samples were then analyzed for weight percent OC and TN on a Vario EL-III elemental analyzer. Duplicate analyses of every sample were run, and the mean of the two measurements are reported here. Replicate analysis of one sample ($n=5$) gave a 1 σ precision of ±0.02 wt.% C and ±0.003 wt.% TN.

The δ^{13}C and δ^{15}N analyses were on the carbonate-free sediment sample, using a DELTA^{plus} XL mass

Table 1
Study sample and bulk sediment properties

Sample	Latitude (°N)	Longitude (°E)	Water depth (m)	TOC (%)	TN (%)	C/N	$\delta^{13}C_{org}$ (‰)	δ^{15}N (‰)	Fine-grained sediment (%)
A2	21.95	113.45	9	0.89	0.19	5.5 (*9.1*)	−23.5	4.8	99.1
A3	21.88	113.46	19	0.70	0.11	7.4 (*11.6*)	−23.6	4.9	93.0
A4	21.78	113.48	29	0.47	0.11	5.0 (*8.0*)	−22.9	5.1	86.1
A5	21.67	113.50	32	0.29	0.10	3.4 (*5.3*)	−23.3	4.6	70.0
A6	21.52	113.54	37	0.37	0.13	3.3 (*5.4*)	−22.6	4.8	85.3
A7	21.33	113.58	47	0.13	0.03	5.1 (*7.1*)	−22.6	–	14.7
A8	21.13	113.61	–	0.36	0.09	4.7 (*7.4*)	−22.4	4.7	90.1
B2	22.60	113.71	10	0.06	0.04	1.8 (*2.8*)	–	–	0.2
B3	22.54	113.74	9	0.15	0.10	1.8 (*3.0*)	−24.6	3.9	20.0
B4	22.42	113.76	13	0.94	0.12	9.1 (*15.0*)	−24.6	5.8	99.6
B5	22.48	113.75	13	0.79	0.11	8.4 (*14.2*)	−24.6	5.6	94.8
B6	22.35	113.77	8	0.92	0.18	6.0 (*9.9*)	−24.0	5.6	99.4
B8	22.22	113.81	25	0.94	0.13	8.4 (*13.4*)	−23.8	5.0	99.5
C1	22.17	113.84	20	1.02	0.18	6.6 (*10.6*)	−23.4	4.1	99.8
C2	22.06	113.86	16	0.37	0.10	4.3 (*7.0*)	−22.6	4.0	50.7
C3	21.96	113.88	25	0.64	0.15	5.0 (*8.2*)	−22.8	4.4	94.7
C4	21.83	113.92	29	0.58	0.11	6.2 (*9.8*)	−23.4	4.84	93.1
C5	21.72	113.93	39	0.37	0.13	3.3 (*5.3*)	−22.8	4.4	86.6
C6	21.58	113.96	46	0.54	0.14	4.5 (*7.4*)	−23.2	4.6	91.7
C7	21.41	113.99	59	0.54	0.16	3.9 (*6.6*)	−22.6	4.7	91.8
C8	21.28	114.02	69	0.57	0.15	4.4 (*7.1*)	−22.7	4.8	94.2
C9	21.08	114.08	73	0.17	0.08	2.5 (*4.1*)	−23.1	3.9	35.3
C10	20.83	114.13	85	0.33	0.15	2.6 (*4.3*)	−22.2	4.2	77.0
D1	22.01	114.03	–	0.73	0.17	5.0 (*8.2*)	−22.1	5.4	96.8
D2	21.97	114.27	–	0.70	0.17	4.8 (*8.1*)	−22.6	5.5	97.3
D3	21.80	114.30	–	0.58	0.14	4.8 (*7.9*)	−23.3	5.2	89.1
D4	21.62	114.33	–	0.36	0.13	3.2 (*5.5*)	−22.2	5.0	79.9
D5	21.45	114.37	–	0.53	0.12	5.2 (*8.6*)	−22.0	5.1	85.5
D6	21.30	114.40	–	0.44	0.10	5.1 (*8.7*)	−22.8	4.9	88.4
D7	21.12	114.45	–	0.25	0.12	2.4 (*4.1*)	−22.9	4.1	46.6
E1	22.44	114.52	20	0.61	0.11	6.5 (*10.3*)	−22.6	6.4	92.6
E2	22.33	114.54	26	0.56	0.12	5.4 (*8.6*)	−22.9	5.5	88.4
E3	22.21	114.57	33	0.66	0.16	4.8 (*7.8*)	−22.9	5.3	93.4
E4	22.01	114.62	45	0.64	0.18	4.2 (*6.8*)	−22.6	4.8	91.9
E5	21.83	114.64	60	0.63	0.12	6.1 (*10.0*)	−22.1	5.1	91.8
E6	21.67	114.68	70	0.64	0.15	5.0 (*8.1*)	−22.5	4.9	92.0
E7	21.50	114.72	76	0.38	0.10	4.4 (*7.1*)	−22.4	4.5	86.3

C/N (italic number) is the C/N values obtained after correcting for inorganic N.

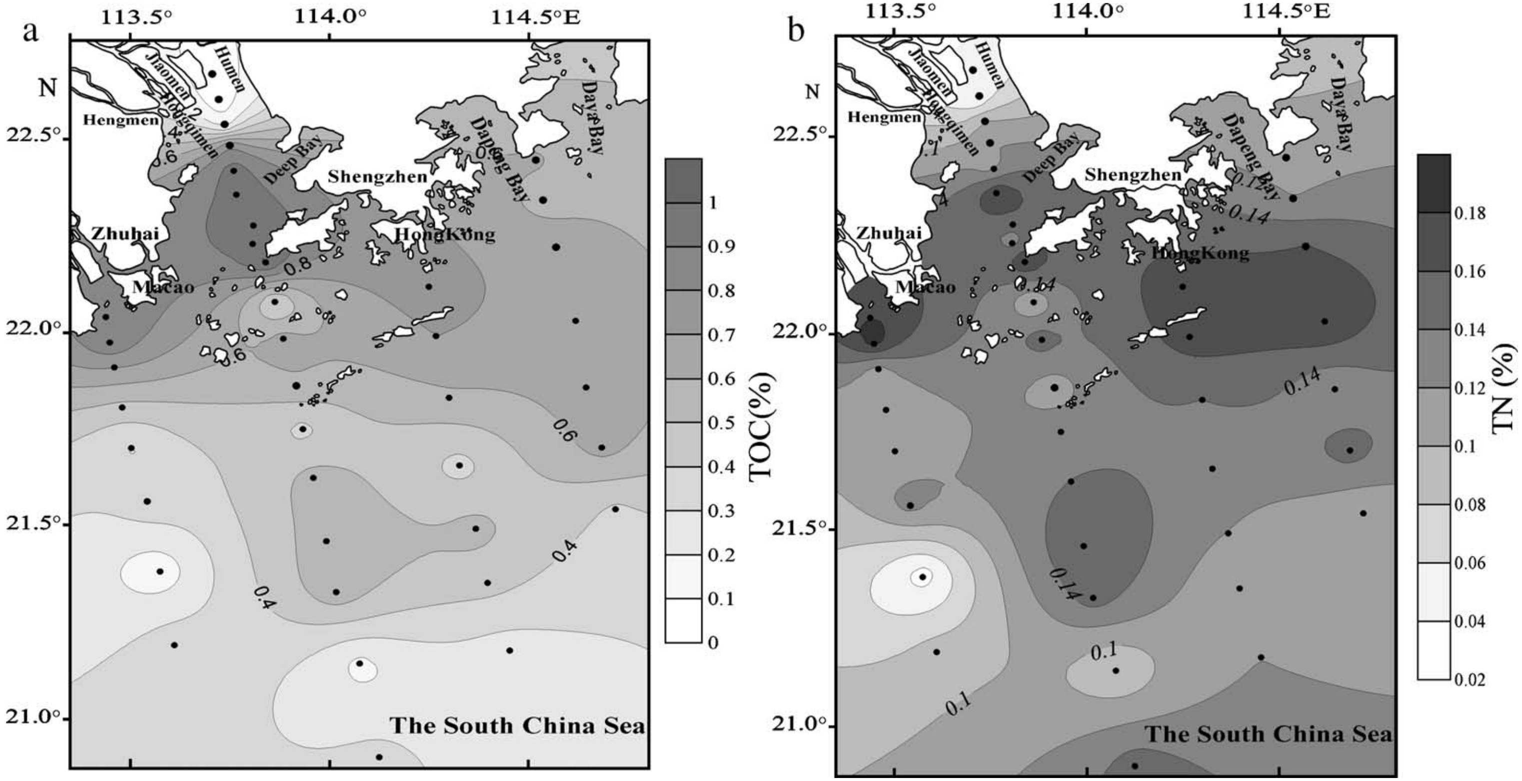

Fig. 3. The distribution of a) TOC (%), and b) TN (%) in surficial sediments from the Pearl River estuary and adjacent shelf, Southern China.

spectrometer. Results are reported in parts per mil (‰) as:

$$\delta(‰) = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}} \times 1000,$$

where δ(‰) stands for δ^{13}C(‰) or δ^{15}N(‰), and R_{sample} and $R_{\text{reference}}$ are the isotopic ratios of the sample and reference, respectively. For carbon the reference is Peedee belemnite (PDB) and for N it is air (δ^{15}N 0‰). Reproducibility based on triplicate analyses of a sample was ±0.2‰ for δ^{13}C and ±0.3‰ for δ^{15}N.

4. Results

The OC (%), TN (%), δ^{13}C and δ^{15}N values of sediments are shown in Table 1. There is a wide spatial variation in OC contents (0.06% and 1.02%; mean 0.54%). The distribution of OC from the Pearl River mouth to the shelf of the South China Sea displays some notable trends (Fig. 3a). The lowest OC content occurs at the Humen River mouth. In the inner shelf, OC contents progressively increase seaward, leading to the highest values (>0.9%) south of Neilingding Island. Beyond the inner shelf, the OC concentrations generally decrease seaward. An exception is the slightly higher (>0.5%) OC contents at sites C_6, C_7, C_8 and D_5, where higher proportions of fine-grained sediment, predominantly composed of silts and clays (<63 μm), are encountered (Table 1).

Generally, the distribution of TN% in the sediments is similar to OC%, showing a progressive increase in the values seaward from the Humen River mouth to the outer shelf (Fig. 3b). There is also a general gradient showing a decrease in OC/TN ratios from the river mouth to the shelf (Fig. 4). A significant correlation (R^2=0.71) exists between OC% and TN% (Fig. 5a).

The $\delta^{13}C_{org}$ values vary between −24.6‰ and −22.0‰ (Figs. 5b,c and 6). The most depleted values (<−23.6‰) generally occur at, or close to the river mouth, as well as along west part of the coast (Fig. 6). Southward to the South China Sea, the $\delta^{13}C_{org}$ values generally increase. The δ^{15}N values of sediments range from 3.9‰ to 6.4‰ (Figs. 5c and 7), with the most depleted δ^{15}N value occurring at and close to the river mouth (Fig. 7).

5. Discussion

As described above, there is a general seaward increase in both OC% and TN% from the estuary to the shelf (Fig.

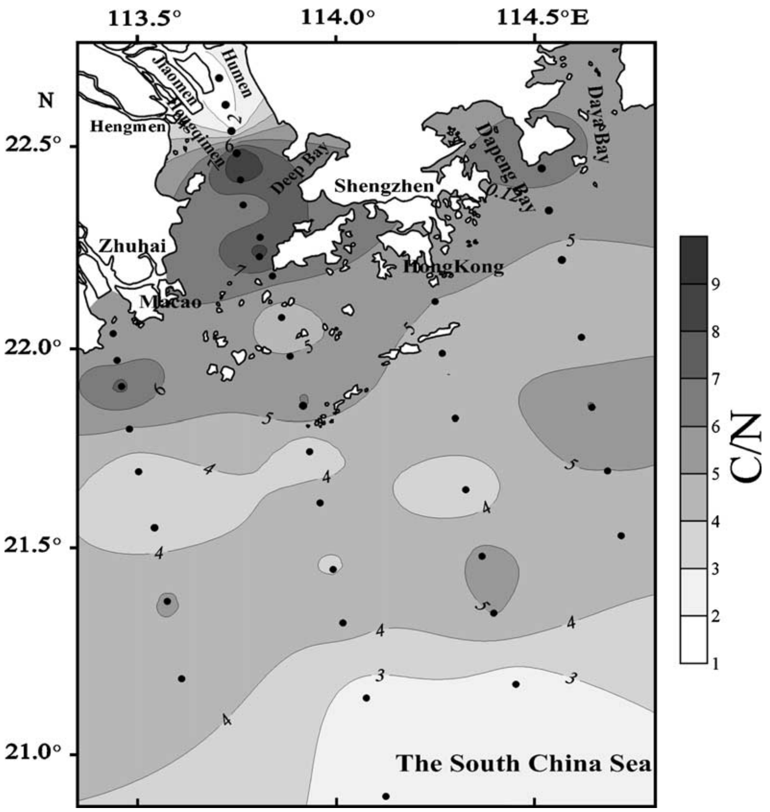

Fig. 4. Contour plot showing the spatial variation in C/N ratios in surficial sediments in the Pearl River estuary and adjacent shelf, Southern China.

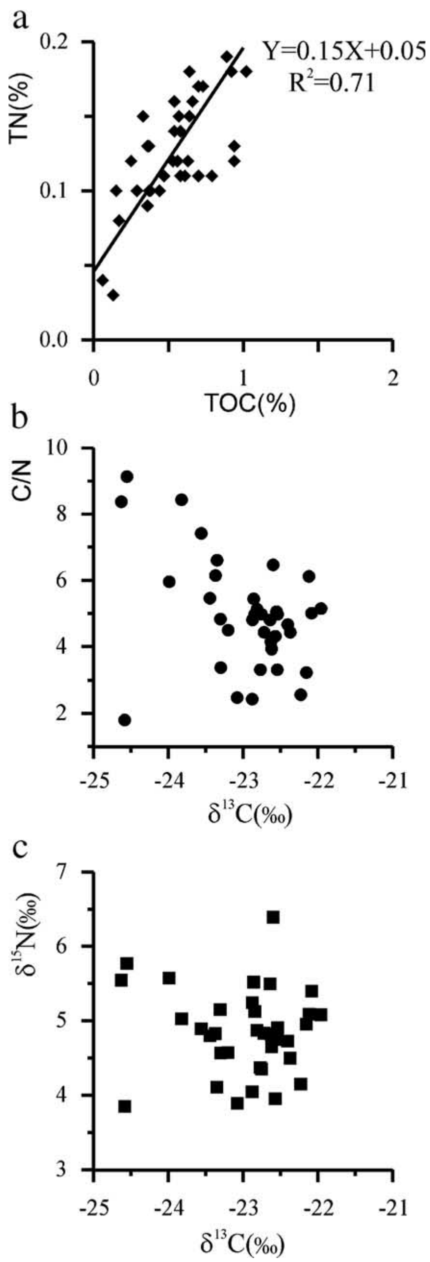

Fig. 5. Correlations between a) TOC and TN, b) $\delta^{13}C_{org}$ and C/N, and c) $\delta^{13}C_{org}$ and $\delta^{15}N$.

3a and b), with relatively low values at the river mouth. A simple explanation for this distributional pattern is given in context of a progressive decrease seaward in the current-wave-tidal energy. With the decrease seaward in the hydraulic transport competency, it is to be expected that progressively more of the fine-grained sediment and lighter organic matter will be deposited seaward of the river mouth. It is, therefore, not surprising that OC and TN (both of which are tied with organic matter) and fine-grained sediment contents have similar distributional pattern in the study area (Figs. 3 and 8a) and that a strong covariance exists between fine-grained sediment% and OC% (Fig. 8b). Further, given the presence of high current/wave energy and turbidity at the river mouth and nearshore it is to be expected that there will be a greater deposition there of coarse inorganic particles and limited primary production (Zhang et al., 1999). The water column chl *a* concentration also showed the status of the primary production. Chl *a* was <16.0 mg m^{-2} in and along the estuary, increased to 20–30 mg m^{-2} beyond the estuary, and reached the maximum at the edge of the estuarine coastal plume south of Hong Kong (Yin et al., 2004). Furthermore, the water column chl *a* fraction >5 μm made up more than 80% of total chl *a* at the river mouth and decreased downstream (Yin et al., 2004). Consequently, at the mouth and nearshore the overall depositional flux of OC and TN from phytodetritus will be less, and organic matter will be diluted by inorganic particles.

OC/TN ratios, and $\delta^{13}C$ and $\delta^{15}N$ values have been widely used as effective markers to estimate the relative proportions of terrigenous and marine organic matter in coastal and marginal sediments (Fry and Sherr, 1984; Meyers, 1997; Naidu et al., 2000; Stein and Macdonald, 2004 and references therein). In our study, we have interpreted the spatial variations in sediment OC/TN, $\delta^{13}C$ and $\delta^{15}N$ in this context. It is generally assumed that land plants and marine algae have different OC/N ratios (N taken as organic nitrogen): cellulose- and lignin-rich vascular land plants have higher OC/N ratios (>15), whereas marine protein-rich algae have lower OC/N ratios (<6). Therefore, the strong river mouth-estuary to shelf decreasing trend in OC/TN (Fig. 4) is attributed to a progressive decrease seaward in the deposition of terrigenous organic matter and increase in marine organic matter inputs.

An important assumption in the above approach is that all of the sedimentary TN exclusively reflects N bound to organic matter. Accordingly, a close covariance between OC and TN of sediments is expected and regression of these two variables must result in a line that intersects at zero values of OC and N. In contrast, Fig. 5a suggests that a significant fraction (39%) of the TN in these sediments is inorganic (presumably as NH_4^+ adsorbed on clays, Müller, 1977; Meyers, 1997). If this amount of N is subtracted from each sample, the C/N ratios would range from 2.8 to 15.0 (Table 1), which are similar to those reported by Owen and Lee (2004). Alternatively, the procedure of rinsing of samples after acidification prior to element analyses might also influence the C/N ratios. Taking into account potential causes of the low

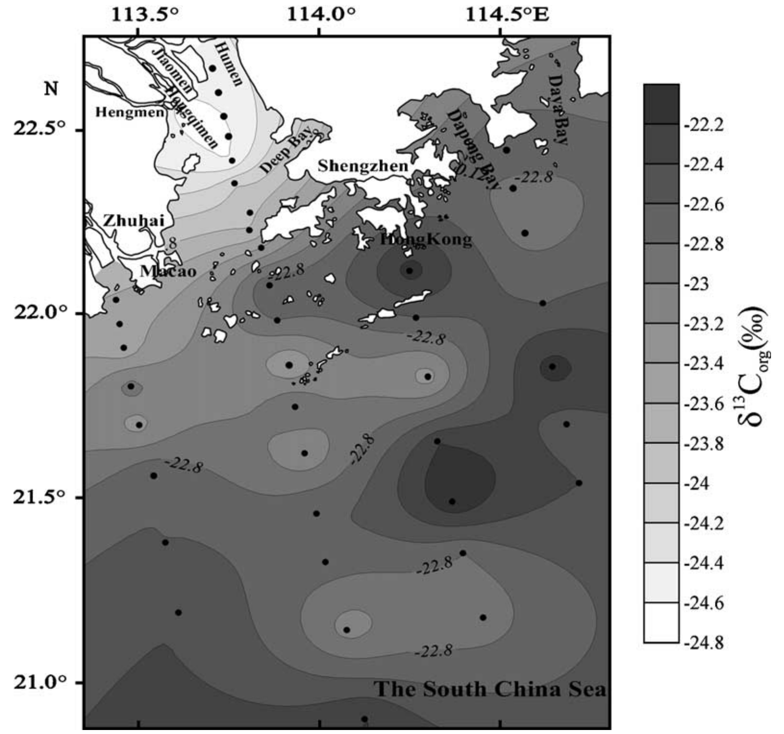

Fig. 6. Spatial variation in $\delta^{13}C_{org}$ in surficial sediments in the Pearl River estuary and adjacent shelf, Southern China.

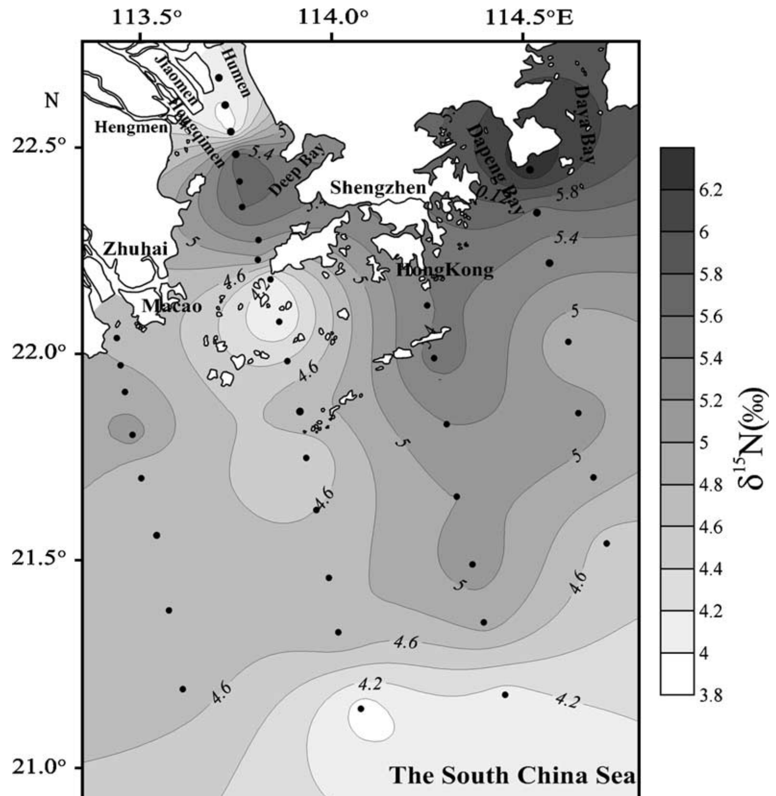

Fig. 7. Spatial variation in $\delta^{15}N$ in surficial sediments in the Pearl River estuary and adjacent shelf, Southern China.

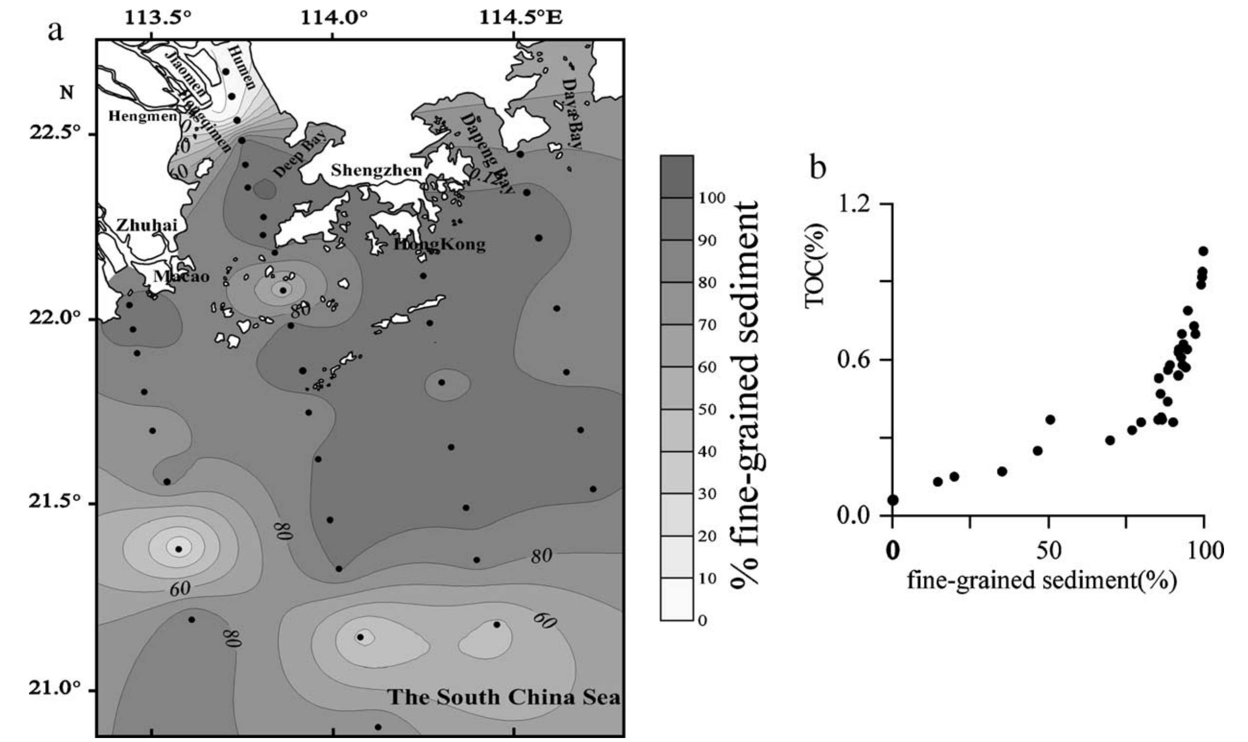

Fig. 8. a) Contour plot showing the distribution of fine-grained sediment (<63 μm) in the Pearl River estuary and adjacent shelf, Southern China, and b) relationship between TOC (%) and fine-grained sediment (<63 μm, %) content.

values, these C/N ratios indicate the deposition of terrigenous and marine organic matter in the studied area.

As shown in Figs. 6 and 7, there is a net increase seaward in δ^{13}C and δ^{15}N in sediments from the Pearl River through the estuary and open shelf in the study area. A straightforward explanation for this trend is a progressive seaward decrease in the proportions of terrigenous organic matter relative to marine organic matter. This explanation is also consistent with the seaward decrease in OC/TN. However, while the spatial distributions of each parameter share similarities (Figs. 4, 6 and 7) they are only correlated weakly (Fig. 5b and 5c). The lack of stronger correlations is likely due to the influence of inorganic N on OC/TN and δ^{15}N values. Clearly therefore, limitations exist for the application of the above parameters for inference of sources of sedimentary organic matter. A comprehensive investigation on the partitioning of nitrogen, defining proportions of organic and inorganic N (Schubert and Calvert, 2001), will help to refine our interpretations.

Accepting those uncertainties, we have made attempts to assess the relative proportions of terrestrial and marine organic matter present in sediments of the study area. The approach is based on the mixing model of Schultz and Calder (1976), which assumes δ^{13}C values of various terrestrial and marine end-members. For the study area we have taken −27‰ as the δ^{13}C value of the terrestrial end-member based on the δ^{13}C value of sediments at the mouth of the Pearl River and its tributaries (Table 1). This value is close to that of C_3 plants, which is consistent with the paucity of C_4 plants in the drainage basin. Likewise, we have assumed a value of δ^{13}C of −20.5‰ for the marine end-member (Jia and Peng, 2003) for these calculations.

Adopting the above end-ember values, the relative percent of land-derived organic matter (f %) in individual sediment of the study area was estimated based on the following equation (Schultz and Calder, 1976; Minoura et al., 1997):

$$f\% = \frac{\delta^{13}C_{marine} - \delta^{13}C_{org}}{\delta^{13}C_{marine} - \delta^{13}C_{terrestrial}} \times 100 \quad (1)$$

the contribution of marine algae (f') to the TOC could be estimated by the following expression:

$$f' = 1 - f \quad (2)$$

The content of algal-derived organic carbon (al-OC) is obtained from the following equation:

$$\text{al-OC} = \text{TOC} \cdot f' \quad (3)$$

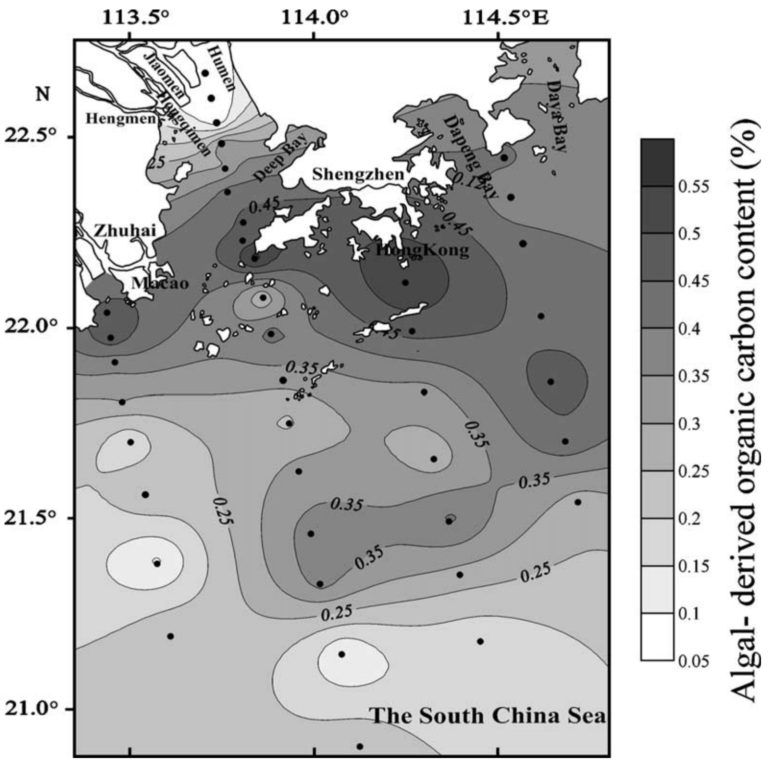

Fig. 9. Spatial variation in algal derived organic carbon content (al-OC %) in surficial sediments in the Pearl River estuary and adjacent shelf, Southern China.

The resulting estimates for the distribution of the algal-derived organic carbon contents in sediments are summarized in Fig. 9. As is to be expected the al-OC concentrations are low at the river mouth and high in the nearshore, presumably reflecting spatial variations in marine primary production over the study area. This is consistent with the earlier suggestion of limited production at the river mouth constrained by high turbidity there (Zhang et al., 1999) and the water column chl *a* concentrations during summer (Yin et al., 2004). On the inner shelf, the al-OC contents are relatively high, likely as a result of increased eutrophication and enhanced production in the vicinity of enhanced of nutrients from anthropogenic sources in the Pearl River Delta. Further offshore, the al-OC contents progressively decrease, presumably due to a reduction in marine production.

6. Conclusions

The spatial distributions of TOC, TN, $\delta^{13}C_{org}$ and $\delta^{15}N$ in surficial sediments from the Pearl River estuary and the adjacent South China Sea shelf are broadly similar. The low TOC contents and depleted $\delta^{13}C_{org}$ values at the river mouth and along the western coast indicate higher terrestrial particulate organic matter deposition there and lower primary production due to enhanced turbidity within the Pearl River plume.

The $\delta^{13}C_{org}$ values of surficial sediments (−24.8‰ to −22.0‰) indicate that the sedimentary organic matter is derived from both marine algae and terrestrial plants. C/N ratios are depressed due to contributions from inorganic nitrogen and low TOC concentrations. C/N ratios are especially low at the Humen River mouth. Estimates of algal-derived organic carbon (al-OC) based on a two-end member mixing model show that organic matter inputs from marine algae are low (≤0.06%) at the river mouth. On the inner shelf, al-OC contents are relatively high (max. = 0.57%), which may reflect increased eutrophication and enhanced production in the region resulting from influx of nutrients from anthropogenic sources in the Pearl River Delta. Farther offshore in the outer South China Sea, the al-OC contents progressively decrease, presumably due to a reduction in marine primary production.

The $\delta^{15}N$ compositions fall in the range of 3.9‰ to 6.4‰. The low $\delta^{15}N$ values at the river mouth and the western coast may reflect preferential deposition of terrestrial particulate organic matter relative to marine phytodetritus constrained by low productivity in the turbid plume of the Pearl River.

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