

Bulk organic $\delta^{13}\text{C}$ and C/N as indicators for sediment sources in the Pearl River delta and estuary, southern China

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ABSTRACT

Preservation of organic matter in estuarine and coastal areas is an important process in the global carbon cycle. This paper presents bulk $\delta^{13}\text{C}$ and C/N of organic matter from source to sink in the Pearl River catchment, delta and estuary, and discusses the applicability of $\delta^{13}\text{C}$ and C/N as indicators for sources of organic matter in deltaic and estuarine sediments. In addition to the 91 surface sediment samples, other materials collected in this study cover the main sources of organic material to estuarine sediment. These are: terrestrial organic matter (TOM), including plants and soil samples from the catchment; estuarine and marine suspended particulate organic carbon (POC) from both summer and winter. Results show that the average $\delta^{13}\text{C}$ of estuarine surface sediment increases from $-25.0 \pm 1.3\text{‰}$ in the freshwater environment to $-21.0 \pm 0.2\text{‰}$ in the marine environment, with C/N decreasing from 15.2 ± 3.3 to 6.8 ± 0.2 . In the source areas, C_3 plants have lower $\delta^{13}\text{C}$ than C_4 plants ($-29.0 \pm 1.8\text{‰}$ and $-13.1 \pm 0.5\text{‰}$ respectively). $\delta^{13}\text{C}$ increases from $-28.3 \pm 0.8\text{‰}$ in the forest soil to around -24.1‰ in both riverbank soil and mangrove soil due to increasing proportion of C_4 grasses. The $\delta^{13}\text{C}_{\text{POC}}$ increases from $-27.6 \pm 0.8\text{‰}$ in the freshwater areas to $-22.4 \pm 0.5\text{‰}$ in the marine-brackish-water areas in winter, and ranges between -24.0‰ in freshwater areas and -25.4‰ in brackish-water areas in summer. Comparison of the $\delta^{13}\text{C}$ and C/N between the sources and sink indicates a weakening TOM and freshwater POC input in the surface sedimentary organic matter seawards, and a strengthening contribution from the marine organic matter. Thus we suggest that bulk organic $\delta^{13}\text{C}$ and C/N analysis can be used to indicate sources of sedimentary organic matter in estuarine environments. Organic carbon in surface sediments derived from anthropogenic sources such as human waste and organic pollutants from industrial and agricultural activities accounts for less than 10% of the total organic carbon (TOC). Although results also indicate elevated $\delta^{13}\text{C}$ of sedimentary organic matter due to some agricultural products such as sugarcane, C_3 plants are still the dominant vegetation type in this area, and the bulk organic $\delta^{13}\text{C}$ and C/N is still an effective indicator for sources of organic matter in estuarine sediments.

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1. Introduction

Preservation of organic matter in estuarine and coastal sediments is an important process in the global carbon cycle as more than 90% of the carbon buried in the oceans is located in continental margin sediments (Emerson and Hedges, 1988; de Haas

et al., 2002). In estuarine areas, organic matter can be supplied both from autochthonous sources (such as plants growing on the sediment surface) and allochthonous sources (organic material transported predominantly by the tide or a river). Better constraints on the sources of organic matter in marine sediments are needed to understand the processes responsible for its preservation (Meyers, 1994). Such understanding will help estimate the possible contribution of different sources of organic matter to the marine organic matter pool, relating to the global cycle of carbon (Schlunz et al., 1999; Gaye et al., 2007).

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Bulk organic $\delta^{13}\text{C}$ and C/N have been widely used to elucidate the source and fate of organic matter in the terrestrial, estuarine and coastal regions (e.g. Hedges and Parker, 1976; Goñi et al., 1997; Chivas et al., 2001; Hu et al., 2006; Kuwae et al., 2007; Harmelin-Vivien et al., 2008; Ramaswamy et al., 2008). Fontugne and Jouanneau (1987) employed carbon isotopes of particulate organic carbon (POC) to examine the distribution of terrigenous sediment within the Gironde estuary, Western Europe, and the terrestrial POC flux into the estuary and the ocean. A good correlation between $\delta^{13}\text{C}_{\text{POC}}$ values and salinity is observed in their study, indicating a general trend of heavier $\delta^{13}\text{C}_{\text{POC}}$ values with increasing salinity seawards. Similar correlations between $\delta^{13}\text{C}_{\text{POC}}$ and water salinity are also suggested in other studies (Middelburg and Nieuwenhuize, 1998; Countway et al., 2007; Middelburg and Herman, 2007; Wu et al., 2007; Zhang et al., 2007). Middelburg and Herman (2007) suggested that the correlation between $\delta^{13}\text{C}_{\text{POC}}$ values and salinity is more significant in river-dominated estuaries, such as the Rhine estuary and the Douro estuary, than in tidal-dominated estuaries such as the Gironde estuary and the Loire estuary. Middelburg and Herman (2007) also pointed out that the range of the $\delta^{13}\text{C}_{\text{POC}}$ values is small in estuaries of high turbidity, between -24‰ and -26‰ (Fontugne and Jouanneau, 1987; Zhang et al., 1997; Tan et al., 2004), which reflects the dominance of terrigenous POC input into the estuary mixed with material from other sources. Bird et al. (2008) estimated the carbon flux from the Ayeyarwady and Thanlwin into the Indian Ocean by examining the $\delta^{13}\text{C}_{\text{POC}}$ of suspended sediments, and suggested that the Ayeyarwady–Thanlwin river system contributes a minimum of 4.6 Mt/yr of POC and an additional 1.1 Mt/yr of dissolved organic carbon (DOC) to the global ocean.

The Southeast Asian area is one of the most densely-populated areas in the world, as well as one of the most industrialized regions. The contribution of organic carbon from land to the ocean via major fluvial systems in this area has not been well estimated. Some studies have been carried out to assess the contribution of terrigenous organic matter to the South China Sea (e.g. Hu et al., 2006), as well as a number of studies investigating the modern-day organic carbon isotopic signature from the Pearl River delta and estuary (Dai et al., 2000; Jia and Peng, 2003; Chen et al., 2003, 2004; Callahan et al., 2004; Zong et al., 2006). However, a detailed understanding of the range of sources of organic matter and their relative contribution to the bulk sediment organic carbon within the estuary is still rather poorly constrained. Detailed investigation of $\delta^{13}\text{C}$ and C/N of the organic matter through the full estuarine complex (from freshwater to marine environments) is one way to address this problem. Here we aim to use this technique to establish the full range of $\delta^{13}\text{C}$ and C/N of the organic matter in the Pearl River estuary from source to sink. We will then assess the suitability of this proxy as an indicator for dominant vegetation type, sediment source and environmental conditions as well as the role of anthropogenic influence on the $\delta^{13}\text{C}$ and C/N in the Pearl River estuary.

2. Materials and methods

2.1. The Pearl River delta and estuary

The Pearl River delta is located at $21^{\circ}20'–23^{\circ}30'N$ and $112^{\circ}40'–114^{\circ}50'E$ (Fig. 1a), and formed during the last 9000 years (Zong et al., 2009). The Pearl River (Zhujiang) is the general name for the three rivers (the East, the North and the West, Fig. 1a) that flow into the Pearl River delta-estuary before entering the South China Sea. It is the second largest river in China in terms of water discharge (about $330 \times 10^9 \text{ m}^3/\text{year}$; Hu et al., 2006). The River is 2214 km in length (the West River), and it drains an area of 425700 km² (Li et al., 1990). The suspended sediment concentration in the Pearl River is

relatively low compared with other major Asian rivers (Zong et al., 2009), with a mean concentration of about 0.172 kg m^{-3} and an annual flux of about $30.64 \times 10^6 \text{ t}$ (Wai et al., 2004). About 92–96% of the suspended sediment is discharged during the wet season (from April to September, monsoon summer), with maximum river discharge occurring in July. The warm/hot wet season is followed by a cool/cold dry season (monsoon winter from October to March). Approximately 80% of sediment influx to the estuary is deposited within the Pearl River estuary, the remainder being transported to the South China Sea (Xu et al., 1985).

The coastal waters in the vicinity of the Pearl River estuary are influenced by three water regimes: Pearl River discharge, oceanic waters from the South China Sea and coastal waters from the South China Coastal Current (Morton and Wu, 1975; Yin et al., 2004). These water regimes are subjected to two seasonal monsoons. In winter, the northeast monsoon prevails, the China Coastal Current dominates the coastal waters of Hong Kong, and freshwater discharge is at its lowest. In summer when the monsoon blows from the southwest direction and the Pearl River discharge reaches the maximum, the interaction of the estuarine plume and oceanic waters from the South China Sea dominate the coastal water regime (Yin et al., 2004).

The Pearl River delta is within the tropical climate zone, with mean annual temperature ranging from 14 to 22 °C across the basin and precipitation ranging from 1200 to 2200 mm year⁻¹ (Zhang et al., 2008). Subtropical and tropical forests are the dominant vegetation type in the Pearl River catchment (Winkler and Wang, 1993). The natural plants in this area are dominantly C₃ plants, mixed with some C₄ grasses, while sugarcane (a C₄ plant) is one of the major agricultural products in the lower deltaic area today.

2.2. Field data collection

2.2.1. Terrestrial organic matter

TOM includes land plants and soil organic matter (SOM) (Fig. 1b; Table 1). A range of C₃ and C₄ plants were sampled. C₄ plants include general C₄ grasses, such as *Panicum maximum* Jacq. and sugarcane (*Saccharum officinarum*). As this study also examines $\delta^{13}\text{C}$ and C/N of agricultural plants, it is necessary to separate sugarcane from other non-agricultural grasses. The 'general C₄ grasses' are the non-agricultural, naturally-growing C₄ grasses in this area. C₃ plants sampled include: general C₃ plants (e.g. *Pteris semipinnata*, *Pinus* sp.), mangrove (*Avicennia*, *Kandelia obovata*, *Bruguiera gymnorhiza*, *Acanthus ilicifolius*, *Aegiceras corniculatum*, *Avicennia marina*, *Ficus microcarpa*) and agricultural plants e.g. banana (*Musa acuminata*), lotus (*Nelumbo nucifera*), reed (*Phragmites australis*) and rice (*Oryza sativa*). Here, the 'general C₃ plants' are the non-agricultural, naturally-grown C₃ plants in this area. Representative plant organs, e.g. leaves and roots, were collected and stored in paper bags then dried at 50 °C overnight in an oven. Soil samples were collected from c. 3 cm depth (to avoid fresh plant roots and disturbed soil, Liu et al., 2003), and stored in polyethylene tubes in a refrigerator before sample preparation and analysis. As both C₃ and C₄ plants grow in the terrestrial area, organic matter in terrestrial soil samples is a mixture of both kinds of plants. Soil samples are placed into the following groups: forest soil, mangrove soil, riverbank soil and agricultural soil, depending on sample location as well as the dominant vegetation type. Plants and soil samples were collected in June 2006, except for agricultural plants (banana, lotus, reed, rice and sugarcane) and agricultural soil samples which were collected in August 2007.

2.2.2. Estuarine organic matter

Samples of estuarine organic matter include seasonally collected particulate organic carbon (POC) and estuarine surface sediments (Figs. 1b and 2; Tables 2 and 3). A total of 49 POC samples (PE41–92 except PE76 and 77) were collected in winter (December

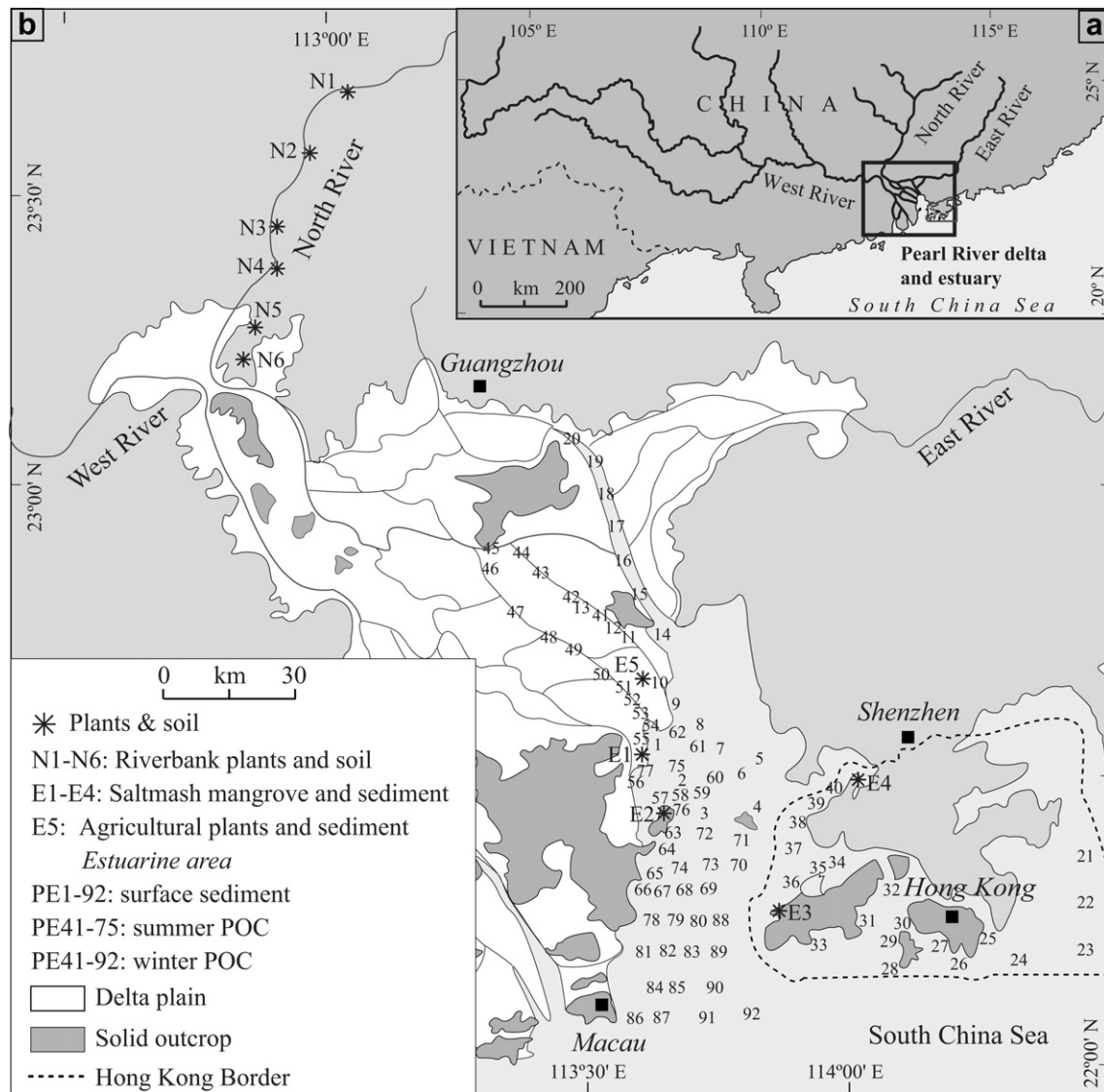


Fig. 1. Location of study area, Pearl River delta and estuary, in East Asia (a) and sample sites (b) within the estuary. Surface sediment and winter/summer POC are from the same sample sites. There is no surface sediment from site PE43, no winter/summer POC from site PE1-40, and no winter POC from site PE76 and 77.

2006), and 45 POC samples (PE41-75) in summer (June 2006). Most of the POC samples were collected by filtering water samples using a fibreglass filter paper (Fisher Brand MF200) in the laboratory, the exception being 10 samples from June 2006 collected using a 70 μm net (the net was not used in winter due to small size of the boat). Samples were then washed from the net into a sampling tube, and refrigerated prior to analysis. POC samples were only collected from the western estuary where suspended sediment concentration was

high enough to allow measurements to be made. A total of 91 surface sediment samples (PE1–PE92, except PE43; Fig. 1b) were obtained using a grab sampler from a boat. The top 10 cm sediment was collected, which potentially represents sediment deposited during the past 6–10 years, according to the sedimentation rate of around 0.8 cm/year on shoals within the estuary (Li et al., 1990). Samples were sealed in polyethylene tubes and stored in a refrigerator at 2–3 °C before analysis.

Table 1
Results of the plants samples and their sampling sites.

| | | $\delta^{13}\text{C}$ | %C | %N | C/N |
|----------------------------|------------------------------------------------|-----------------------|------------|-----------|-------------|
| C ₃ plants (52) | General terrestrial C ₃ plants (33) | -29.9 ± 1.3 | 42.3 ± 3.5 | 2.4 ± 1.1 | 21.7 ± 10.7 |
| | Agricultural C ₃ plants (7) | -28.2 ± 1.4 | 40.3 ± 3.0 | 3.0 ± 0.5 | 13.7 ± 2.7 |
| | Mangroves (12) | -27.1 ± 1.7 | 44.6 ± 2.4 | 1.7 ± 0.6 | 31.0 ± 12.5 |
| | Ave. | -29.0 ± 1.8 | 42.6 ± 3.4 | 2.3 ± 1.0 | 22.7 ± 11.6 |
| C ₄ plants (9) | Ave. | -13.1 ± 0.5 | 40 ± 2.0 | 1.9 ± 1.0 | 24.6 ± 9.4 |
| Soil samples | Forest soil (2) | -28.3 ± 0.8 | 3.3 ± 0.9 | 0.2 ± 0.0 | 17.9 ± 3.6 |
| | Riverbank soil (8) | -24.1 ± 1.0 | 2.1 ± 1.0 | 0.2 ± 0.1 | 12.5 ± 2.3 |
| | Mangrove soil (12) | -24 ± 1.9 | 1.9 ± 1.0 | 0.2 ± 0.1 | 12.4 ± 3.6 |
| | Agricultural soil (3) | -21.7 ± 0.7 | 1.9 ± 0.4 | 0.2 ± 0.1 | 8.9 ± 1.1 |

'(n)' shows the number of samples; Values are presented in the format of 'average value ± standard deviation (SD)'.

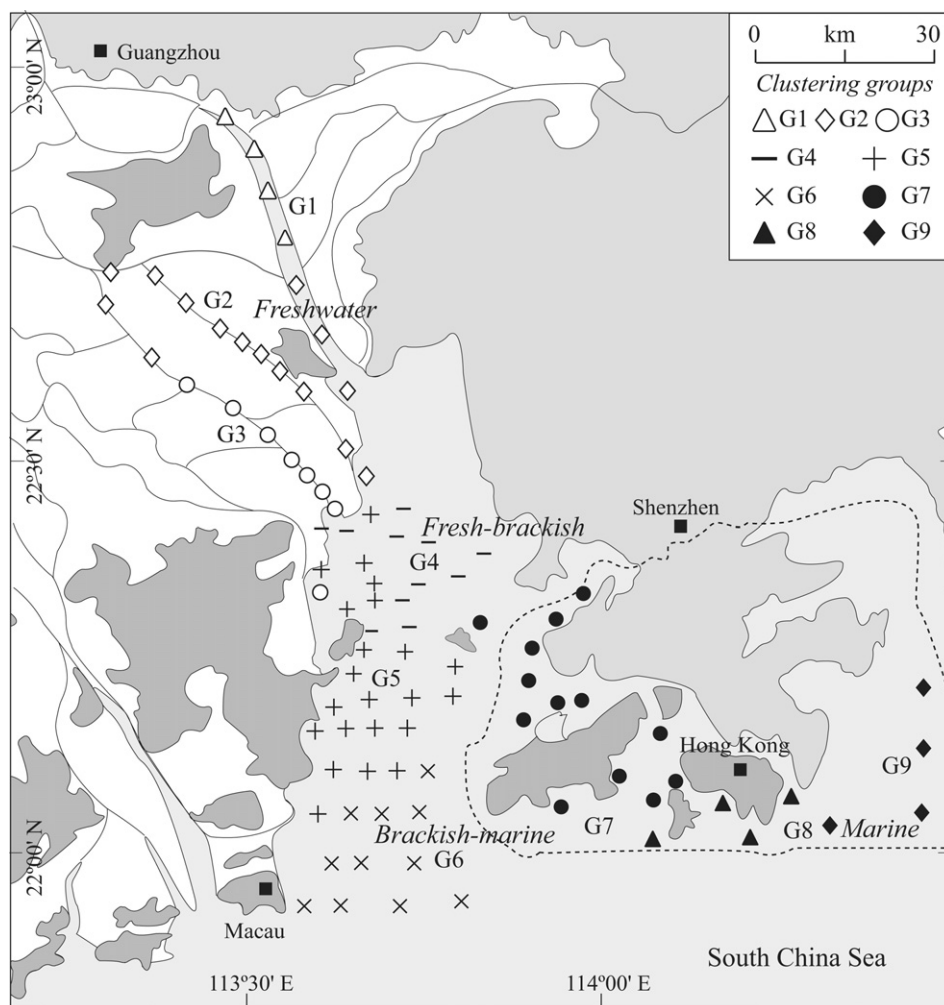


Fig. 2. Map of the Pearl River estuary showing location of cluster groups for the estuarine surface sediment samples and POC samples identified by winter salinity and sand concentration. Groups G1–G3 are from freshwater areas; groups G4–G7 are from brackish areas and G8–G9 are from marine areas.

Samples were collected during three field campaigns. Surface sediment samples PE01–40 were collected in June 2005, samples PE41–77 were collected in June 2006 and samples PE78–92 were collected in December 2006. Summer POC samples PE41–75 were collected in June 2006 and winter POC samples PE78–92 were collected in December 2006.

2.2.3. Estuarine environmental variables

Environmental variables including water salinity, water depth, pH, total dissolved solid and water temperature, were measured from the same sampling sites as the POC samples (Fig. 1b). Summer water salinity and mean water depth of sites PE78–PE92 along with mean water salinity and mean water depth from PE1–PE40, PE76 and PE77 were interpolated based on maps of the area. Mean water salinity for sites PE41–PE92 is the mean value of seasonal values measured. Water salinity was measured using the Practical Salinity Scale at a depth of 50 cm below the water surface using a YSI meter.

2.3. Laboratory methods

2.3.1. Sample preparation

Soil and sediment samples were prepared using 100 mL of 5% HCl to remove carbonates. They were then washed 3 times with deionised water through fibreglass filter paper, before being dried

at 50 °C overnight, homogenised in a pestle and mortar, and weighed (25–50 mg) for $\delta^{13}\text{C}$ and C/N analysis.

Plant samples were placed in a freezer overnight at -80 °C then freeze dried for 24 h. These samples were then crushed and homogenised in a ball mill and then weighed (1–2 mg) for $\delta^{13}\text{C}$ and C/N.

POC samples on the filter paper were dried in the field. Possible samples were gently removed from the filter paper, however some samples could not be removed and were analysed still attached to the filter paper. The POC samples still attached to the filters had insufficient material to allow absolute measurement of TOC and TN. However C/N ratios could still be calculated. To test whether there is contamination of the filter paper on $\delta^{13}\text{C}$ or C/N measurements, a blank filter paper was run and there was no signal detected that was distinguishable from baseline conditions within the mass spectrometer.

2.3.2. Sample analysis

Carbon isotopes and C/N analyses were performed by combustion in a Carlo Erba NA1500 (Series 1) on-line to a VG Triple Trap and Optima dual-inlet mass spectrometer, with $\delta^{13}\text{C}$ calculated to the VPDB scale using a within-run laboratory standards (BROC) calibrated against NBS-19 and NBS-22. Replicate analysis of well-mixed samples indicated a precision of $\pm <0.1\%$ (1SD). C/N was determined by reference to an Acetanilide standard. Replicate

Table 2
Mean values of the POC samples and water conditions of the clustering groups.

| Gr.(n) | Winter season | | | | | | Summer season | | | | | | | |
|--------|---------------------------|-----------|-------------|-----------|------------|-------------|---------------|---------------------------|-----------|------------|-----------|-----------|------------|------------|
| | $\delta^{13}\text{C}$ (‰) | C/N | Sal | pH | TDS (g/L) | DO (%) | Temp (°C) | $\delta^{13}\text{C}$ (‰) | C/N | Sal | pH | TDS (g/L) | DO (%) | Temp (°C) |
| G2(7) | -27.6 ± 0.8 | 6.8 ± 0.6 | 0.2 ± 0.3 | 7.5 ± 0.1 | 0.3 ± 0.4 | 93.5 ± 4.1 | 17.1 ± 0.4 | -24.9 ± 0.7 | 8.7 ± 0.5 | 0.1 ± 0.0 | 7.4 ± 0.0 | 0.1 ± 0.0 | 85.6 ± 5.6 | 28.7 ± 0.4 |
| G3(5) | -24.5 ± 1.3 | 7.2 ± 0.6 | 16.6 ± 10.3 | 7.9 ± 0.1 | 20.2 ± 8.9 | 109.3 ± 2.3 | 18.1 ± 0.7 | -25.4 ± 0.7 | 8.9 ± 0.7 | 2.6 ± 2.5 | 7.7 ± 0.1 | 3.9 ± 2.8 | 82.0 ± 4.3 | 28.2 ± 0.4 |
| G4(8) | -25.8 ± 1.0 | 7.3 ± 0.4 | 3.1 ± 4.0 | 7.7 ± 0.1 | 4.0 ± 4.4 | 95.7 ± 9.9 | 17.4 ± 0.4 | -24.0 ± 0.9 | 9.4 ± 1.5 | 0.1 ± 0.0 | 7.6 ± 0.1 | 0.2 ± 0.0 | 79.3 ± 6.8 | 27.8 ± 0.1 |
| G5(21) | -23.6 ± 1.2 | 7.6 ± 1.0 | 22.2 ± 7.6 | 8.0 ± 0.1 | 24.0 ± 7.2 | 109.8 ± 8.6 | 17.6 ± 0.6 | -24.3 ± 1.1 | 9.5 ± 1.2 | 5.4 ± 5.7 | 8.1 ± 0.1 | 3.3 ± 2.9 | 89.6 ± 6.7 | 28.4 ± 0.5 |
| G6(11) | -22.4 ± 0.5 | 6.3 ± 0.5 | 33.1 ± 1.7 | 8.1 ± 0.1 | 32.7 ± 1.6 | 96.7 ± 2.2 | 19.2 ± 0.3 | | | 24.1 ± 3.5 | | | | |

'Gr.(n)' shows the number (n) of samples in each clustering groups (Gr.); Sal = Salinity; TDS = total dissolved solid; DO = dissolved oxygen; Temp = temperature; Values are presented in the format of 'average value ± SD'; Water salinity was measured using the Practical Salinity Scale.

analysis of well-mixed samples indicated a precision of $\pm <0.1\%$. The isotopic ratios are expressed as $\delta^{13}\text{C}$, in units of per mille (‰).

Organic matter is depleted in ^{13}C relative to VPDB, so $\delta^{13}\text{C}$ of organic material is negative. The weight ratio of total organic carbon (%TOC) to total nitrogen (%TN), giving C/N, is usually measured alongside $\delta^{13}\text{C}$ and helps to distinguish carbon sources.

Particle size analysis was carried out using a laser granular meter (Coulter LS 13200). Values of the $\delta^{13}\text{C}$, C/N, particle size and environmental parameters in this paper are presented in the format of 'average value ± standard deviation (SD)'. Values of $\delta^{13}\text{C}$ or C/N of some samples are not available due to low content of organic matter in those samples.

3. Results

3.1. Hierarchical cluster analysis

All 92 samples were subjected to Hierarchical Cluster Analysis (using SPSS for Windows 15.0) based on winter salinity and sand concentration. The cluster analysis defined 9 groups (G1–G9) with a clear geographical control (illustrated in Fig. 2; Table 3). All surface sediment samples had sufficient material for analysis except sample PE43.

The 9 groups defined by selected environment variables clearly highlight a trend from the fully-freshwater environment (G1–G3) to the fully-marine environment (G8–G9), via brackish areas (G4–G7) (Fig. 2; Table 3). The freshwater groups have low annual average water salinity of 3.4 ± 3.6 , which increases to between 15.8 ± 5.3 and 28.4 ± 3.1 in the brackish-water areas and reaches 32.9 ± 0.8 in the fully marine environment (Table 3). Mean water depth is lower than 5 m in the freshwater area, getting deeper seawards (>20 m in the fully marine area). Meanwhile, average particle size gets finer offshore with a reduction in sand component. All environmental parameters tend to be less variable in the marine area than in the freshwater area (Table 3).

In addition to the spatial diversity of the environmental conditions, seasonal variability in salinity and sediment concentration is also observed. Winter and summer measurements taken from sites in groups G2–G5 show significantly higher salinity and sediment concentration (total dissolved solids) during winter (see Table 2).

3.2. Terrestrial organic matter

3.2.1. Plants

Plant samples collected in this study are composed of two main groups: C₃ plants (dominant vegetation in the Pearl River delta), and C₄ plants. Taken as an overall average C₃ plants have lower $\delta^{13}\text{C}$ (average of $-29.0 \pm 1.8\%$) compared to C₄ plants (average of $-13.1 \pm 0.5\%$, Fig. 3a). The general C₃ plants have the lowest $\delta^{13}\text{C}$ of $-29.9 \pm 1.3\%$, followed by the agricultural C₃ plants (e.g. rice, lotus and banana) then mangroves, with $\delta^{13}\text{C}$ values of $-28.2 \pm 1.4\%$ and $-27.1 \pm 1.7\%$ respectively (Fig. 3b). C₄ plants (mostly grasses) have $\delta^{13}\text{C}$ of $-13.2 \pm 0.5\%$, slightly lower than sugarcane which has $\delta^{13}\text{C}$ of $-12.7 \pm 0.2\%$ (Fig. 3b).

C/N of C₃ and C₄ plants are widely variable (7.4–61.8 for C₃ plants and 8.2–40.3 for C₄ plants) and overlap significantly, with the average value of 22.7 ± 11.6 , and 24.6 ± 9.4 respectively (Fig. 3a). It is impossible to distinguish between the two plant types based on C/N alone. Within the C₃ plants, agricultural plants have lower C/N (13.7 ± 2.7) than general C₃ plants (21.7 ± 10.7) and mangroves (31.0 ± 12.5) (Fig. 3b).

3.2.2. Terrestrial soil

The $\delta^{13}\text{C}$ of terrestrial soil samples ranges between -28.9% and -19.3% , and C/N between 7.7 and 20.4 (Fig. 4a). As expected soil

Table 3
Mean values of the surface sediment and environmental variables of the clustering groups.

| | Gr.(n) | $\delta^{13}\text{C}$ (‰) | C/N | TOC (%) | TN (%) | Mean Sal. | Sand (%) | Clay (%) | Silt (%) | WD (m) |
|----------------|--------|---------------------------|----------------|---------------|---------------|----------------|-----------------|----------------|-----------------|-----------------|
| Freshwater | G1(4) | -25.0 ± 1.3 | 15.2 ± 3.3 | 2.2 ± 1.2 | 0.1 ± 0.0 | 3.1 ± 1.6 | 32.7 ± 8.2 | 20.6 ± 4.0 | 46.7 ± 4.4 | 2.2 ± 0.1 |
| | G2(14) | -23.9 ± 1.2 | 13.0 ± 1.8 | 1.0 ± 0.4 | 0.1 ± 0.0 | 4.1 ± 4.6 | 33.6 ± 20.0 | 17.8 ± 8.1 | 48.6 ± 13.8 | 3.7 ± 2.2 |
| | G3(8) | -23.0 ± 1.6 | 11.1 ± 1.3 | 1.0 ± 0.3 | 0.1 ± 0.0 | 2.3 ± 2.1 | 15.2 ± 9.3 | 22.8 ± 5.4 | 62.0 ± 8.0 | 4.3 ± 1.7 |
| | Ave. | -23.8 ± 1.5 | 12.7 ± 2.3 | 1.2 ± 0.7 | 0.1 ± 0.0 | 3.4 ± 3.6 | 27.8 ± 17.7 | 19.8 ± 7.0 | 52.4 ± 12.7 | 3.7 ± 2.0 |
| Fresh-brackish | G4(11) | -24.0 ± 1.1 | 14.1 ± 2.7 | 1.2 ± 0.4 | 0.1 ± 0.0 | 14.5 ± 6.7 | 30.1 ± 17.1 | 20.1 ± 7.7 | 49.8 ± 10.7 | 8.3 ± 5.4 |
| | G5(22) | -23.1 ± 0.4 | 10.4 ± 1.3 | 1.1 ± 0.3 | 0.1 ± 0.0 | 16.4 ± 4.4 | 18.2 ± 7.9 | 28.0 ± 7.4 | 53.8 ± 4.5 | $9.0 \pm 0.4.3$ |
| | Ave. | -23.4 ± 0.8 | 11.6 ± 2.5 | 1.1 ± 0.3 | 0.1 ± 0.0 | 15.8 ± 5.3 | 22.1 ± 12.8 | 25.3 ± 8.3 | 52.5 ± 7.2 | 8.8 ± 4.6 |
| Mainr-brackish | G6(11) | -23.1 ± 0.2 | 9.7 ± 0.5 | 1.1 ± 0.2 | 0.1 ± 0.0 | 27.7 ± 2.7 | 17.0 ± 2.0 | 25.7 ± 3.9 | 57.3 ± 3.3 | 8.3 ± 2.5 |
| | G7(13) | -23.1 ± 0.9 | 10.4 ± 3.0 | 0.9 ± 0.3 | 0.1 ± 0.0 | 29.1 ± 3.4 | 18.0 ± 13.2 | 24.9 ± 5.7 | 57.2 ± 10.1 | 11.3 ± 9.1 |
| | Ave. | -23.1 ± 0.6 | 9.7 ± 1.0 | 1.0 ± 0.3 | 0.1 ± 0.0 | 28.4 ± 3.1 | 17.5 ± 9.7 | 25.3 ± 4.9 | 57.2 ± 7.7 | 9.9 ± 6.9 |
| Marine | G8(4) | -21.7 ± 0.6 | 8.2 ± 1.2 | 0.9 ± 0.5 | 0.1 ± 0.0 | 32.4 ± 1.0 | 17.8 ± 6.0 | 19.8 ± 4.1 | 62.4 ± 3.4 | 15.8 ± 3.5 |
| | G9(4) | -21.0 ± 0.2 | 6.8 ± 0.2 | 0.7 ± 0.1 | 0.1 ± 0.0 | 33.4 ± 0.1 | 13.7 ± 7.2 | 23.2 ± 3.9 | 63.0 ± 5.5 | 27.0 ± 3.2 |
| | Ave. | -21.4 ± 0.5 | 7.5 ± 1.1 | 0.8 ± 0.3 | 0.1 ± 0.0 | 32.9 ± 0.8 | 15.8 ± 6.5 | 21.5 ± 4.2 | 62.7 ± 4.2 | 21.4 ± 6.8 |

'Gr.(n)' shows the number (n) of samples in each clustering groups (Gr.); Values are presented in the format of 'average value \pm SD'; Annual mean water salinity was measured using the Practical Salinity Scale.

samples from different areas of vegetation cover have different $\delta^{13}\text{C}$ and C/N values. Soil samples from pine forest have the lowest $\delta^{13}\text{C}$ of $-28.3 \pm 0.8\text{‰}$, but the highest C/N of 17.9 ± 3.6 . Soil samples from riverbanks and mangrove areas have similar $\delta^{13}\text{C}$ and C/N, around -24.1‰ and 12.5 respectively, though more variable in the mangrove soil (Fig. 4b). Soil samples from farmlands have the highest $\delta^{13}\text{C}$ of $-21.7 \pm 0.7\text{‰}$ and the lowest C/N of 8.9 ± 1.1 (Fig. 4b).

3.3. Estuarine particulate organic carbon

Viewed overall the $\delta^{13}\text{C}$ of POC shows very little if any seasonal variation (Fig. 5a), the average $\delta^{13}\text{C}$ of POC in summer (-24.5‰) is within error of winter values (-24.2‰) (there is slightly more variation in winter (SD = 1.9) than in summer (SD = 1.0)). C/N of the

winter POC ranges between 6.0 and 9.0 (mean value of 7.1 ± 0.9) and is slightly lower than the summer POC, ranging between 8.0 and 10.2 (averaging 9.2 ± 1.1) (Fig. 5a).

Estuarine POC is composed of organic carbon from fine-size plankton and relatively coarse TOM. POC was also collected by a 70 μm net to compare the relative contribution of these two sources of organic matter. As the size of plankton (e.g. diatoms) is usually smaller than 80 μm , organic matter collected on the filter paper has a higher proportion of plankton/algae, while material collected in a 70 μm net has a higher proportion of TOM. Results show that the POC samples from the 70 μm net have a lower average $\delta^{13}\text{C}$ of $-25.6 \pm 1.0\text{‰}$, compared to the filter paper samples from the same location ($-24.3 \pm 1.0\text{‰}$, Fig. 5b). The average C/N of the POC from the net samples is 10.7 ± 4.5 , which is higher and more variable than that of the POC collected on filter paper of 9.4 ± 1.1 (Fig. 5b). POC values from the samples collected using the

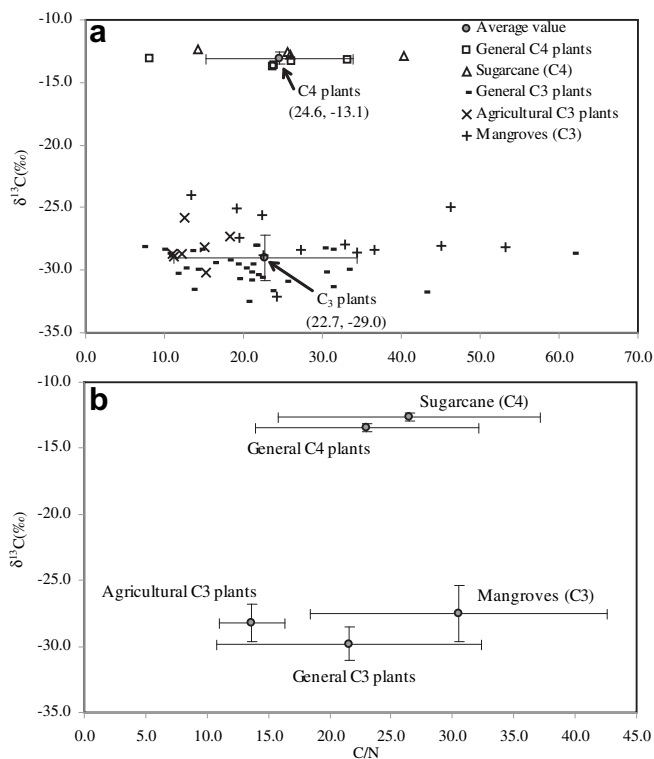


Fig. 3. $\delta^{13}\text{C}$ and C/N bi-plot of C₃ and C₄ plants. a: individual values for each plant with the average value of C₃ and C₄ plants; b: average values of different types of plants within the C₃ and C₄ groups (error bars are the standard deviation).

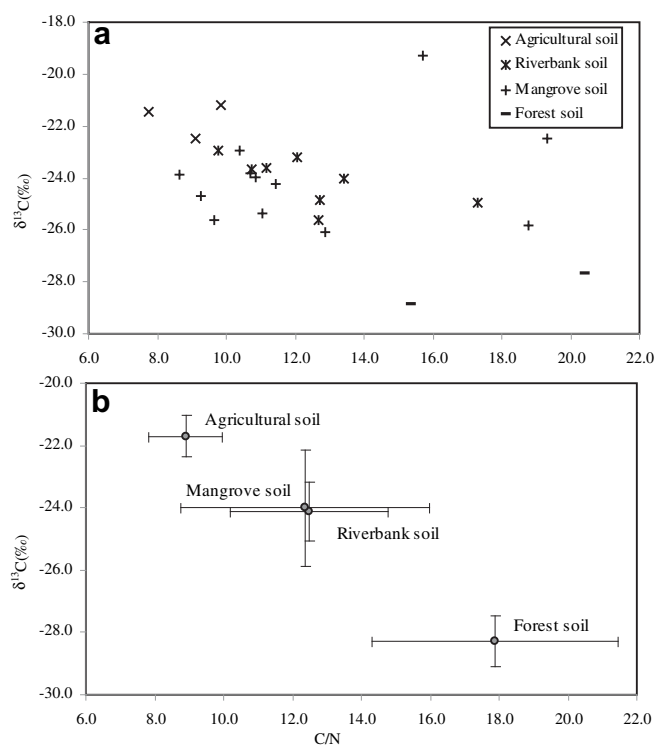


Fig. 4. $\delta^{13}\text{C}$ and C/N bi-plot of terrestrial soil samples. a: individual values for each soil sample; b: average values of different types of soil with stand deviation.

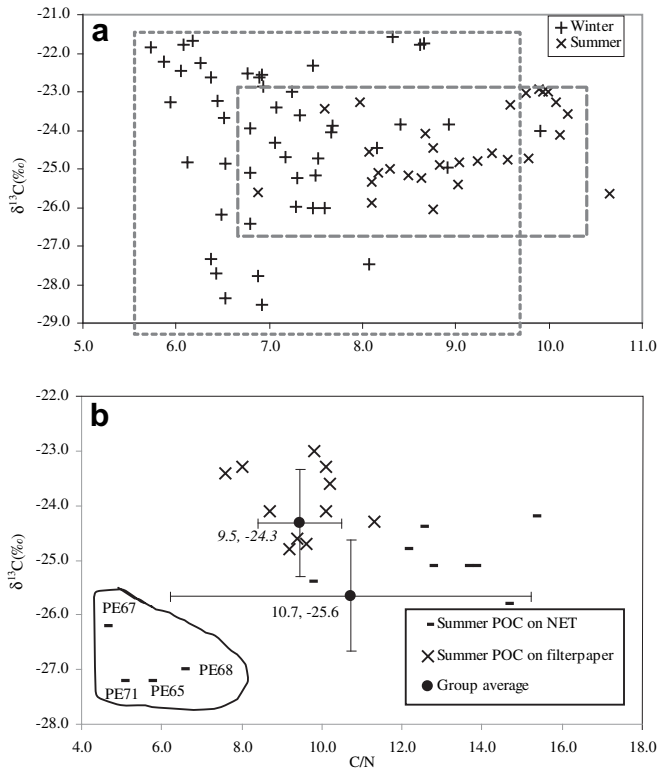


Fig. 5. a: $\delta^{13}\text{C}$ and C/N bi-plot of seasonal POC samples; b: Comparison $\delta^{13}\text{C}$ and C/N values between the POC on 70 μm net and summer POC on filter paper.

net fall into two groups. POC from locations further seaward, such as PE65, PE67, PE68, and PE71 (Fig. 1b), tend to have lower $\delta^{13}\text{C}$ and C/N than those from the inner estuarine area (Fig. 5b).

When the POC data are plotted by cluster group average (groups G2 – G6) spatial and seasonal variability becomes clearer (Fig. 6). In winter, there is a clear gradient of increasing $\delta^{13}\text{C}$ from freshwater through to marine-brackish water ($-27.6 \pm 0.8\text{‰}$ for G2 increasing

to $-22.4 \pm 0.5\text{‰}$ for G6, Fig. 6a). This is particularly clear when $\delta^{13}\text{C}$ is plotted against salinity (Fig. 6c). Variation in C/N of winter POC between groups is not as significant (Fig. 6a). In summer, the $\delta^{13}\text{C}_{\text{POC}}$ and C/N data from individual groups show no clear trends with generally overlapping values (Fig. 6b and d).

3.4. Estuarine surface sediment

The estuarine surface sediment samples have $\delta^{13}\text{C}$ ranging from -27.0‰ to -20.8‰ and C/N ranging between 20.1 and 6.5, with $\delta^{13}\text{C}$ and C/N negatively correlated (Fig. 7a). A clear trend is observed in both $\delta^{13}\text{C}$ and C/N values across the environmental gradient from the fully freshwater to fully marine conditions. $\delta^{13}\text{C}$ becomes progressively higher from G1 to G9, increasing from $-25.0 \pm 1.3\text{‰}$ in G1 to $-21.0 \pm 0.2\text{‰}$ in G9 (Fig. 7b), with increasing water salinity (Table 3). Meanwhile, C/N also shows a clear trend decreasing from 15.2 ± 3.3 in G1 to 6.8 ± 0.2 in G9. The exception to this trend is samples from G3 which have higher $\delta^{13}\text{C}$ and lower C/N values than expected (ie. the group average sits out of sequence in Fig. 7b). Also the variability in both $\delta^{13}\text{C}$ and C/N is significantly decreased in the marine compared to the freshwater environment (Fig. 7b and Table 3).

4. Discussion

4.1. Terrestrial organic matter and its sources

Plants from the study area can be placed in two main groups, C₃ and C₄ plants, based on the way they fix carbon from atmospheric CO₂ during the photosynthetic process. This process produces significant difference in the $\delta^{13}\text{C}$ signature of the organic carbon from these two groups of plants. C₃ plants use the Calvin–Benson cycle (C₃ pathway) (Craig, 1953; Park and Epstein, 1960), through which they absorb and conserve ¹²C from atmospheric CO₂ more effectively compared to the Hatch–Slack pathway used by C₄ plants (Hatch and Slack, 1970). This results in greater discrimination against ¹³C in C₃ plants than C₄ plants, with C₃ plants producing lower $\delta^{13}\text{C}$ around -28.1‰ (Craig, 1953; Deines, 1980; Fry and Sherr, 1984; O’Leary, 1985) than C₄ plants with values around

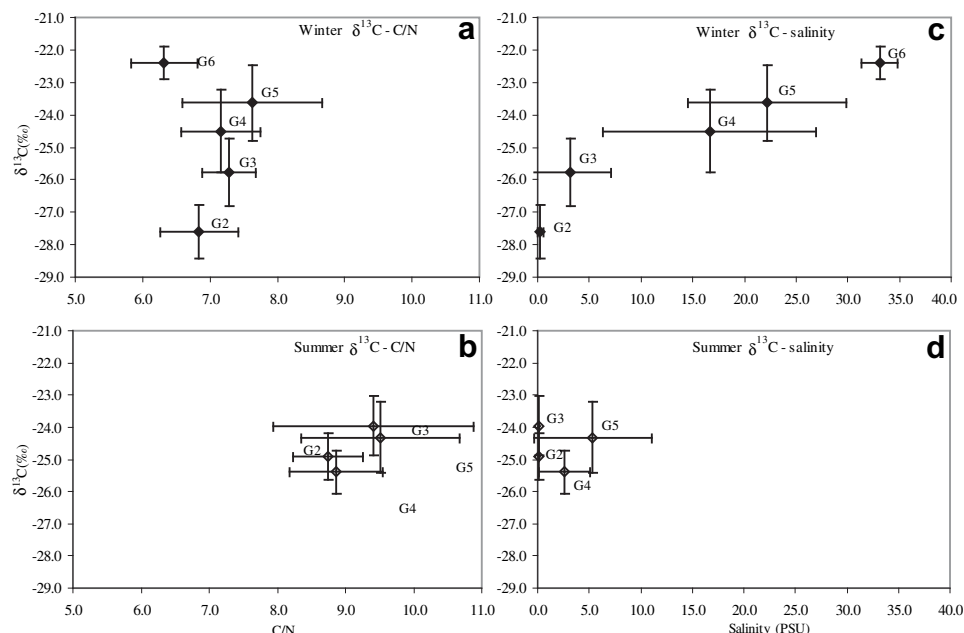


Fig. 6. $\delta^{13}\text{C}$ and C/N bi-plot of seasonal POC samples summarized into cluster groups (a: winter and b: summer) and $\delta^{13}\text{C}$ plotted against water salinity (c: winter and d: summer).

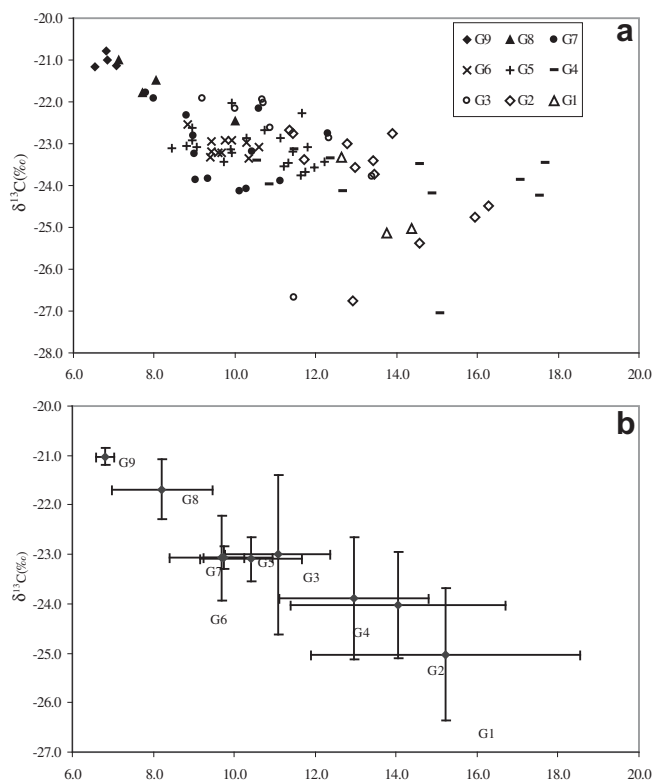


Fig. 7. $\delta^{13}\text{C}$ and C/N bi-plot of surface sediment samples plotted as (a) individual samples; and (b) average $\delta^{13}\text{C}$ and C/N values of the seven groups with standard deviation shown.

–13.0‰ (Bender, 1971; Fry and Sherr, 1984; Emerson and Hedges, 1988). The C_3 plants analysed in this study have an average $\delta^{13}\text{C}$ of –29.9‰ (Fig. 3), about 1.8‰ lower than values reported by other studies. This might be due to the high precipitation in the Pearl River delta area, with precipitation over 1500 mm/yr (Li et al., 1990). A similar case has been reported by Austin and Vitousek (1998) where $\delta^{13}\text{C}$ of C_3 plants shifts from –29.9‰ to –25.6‰, when the sampling site changed from an area of 5000 mm/yr precipitation to an area of only 500 mm/yr. The average $\delta^{13}\text{C}$ of C_4 plants from this study is –13.1‰ (Fig. 3), similar to other studies (e.g. Bender, 1971; Fry and Sherr, 1984; Emerson and Hedges, 1988).

Terrestrial soil is one of the direct sinks of the organic carbon from the surface vegetation and its organic carbon signature depends greatly on the dominant vegetation type. This explains the variation in organic carbon $\delta^{13}\text{C}$ found in soil samples from different areas of the Pearl River delta, e.g. forest, riverbank and tidal flats (Fig. 4). Soils from the forest mainly receive organic carbon from C_3 plants (e.g. trees), and tend to have low $\delta^{13}\text{C}$ of $-28.3 \pm 0.8\text{‰}$, but high C/N of 17.9 ± 3.6 (Fig. 4b). Riverbank soil samples are from the flood plain along the North River, dominated by shrubs and grass. The increasing proportion of C_4 grass on the flood plain produces relatively higher $\delta^{13}\text{C}$ in the riverbank soil ($-24.1 \pm 1.0\text{‰}$) compared to the forest soil (Fig. 4b). Similar $\delta^{13}\text{C}$ and C/N values are found in the riverbank and mangrove soil ($-24.0 \pm 1.9\text{‰}$) and are due to the similar proportion of C_4 plants growing on the flood plain and the tidal flat. Other studies also report the $\delta^{13}\text{C}$ of soils from C_4 -dominated areas as being around –21.0‰, reducing to around –24.0‰ from areas with a mixture of C_3 and C_4 plants (Driese et al., 2005; Saia et al., 2008). Many studies have used $\delta^{13}\text{C}$ of terrestrial soil to reflect different vegetation types (Mackie et al., 2005; Fan et al., 2007; Cao et al., 2008; Driese et al., 2008; Saia et al., 2008). C/N ratios are lower in the soil samples from

this study compared to either C_3 or C_4 plants, agreeing with previous studies showing soil C/N below 20. Although there is a trend in the C/N ratio from the soils samples presented here (forest soils being higher than the other samples, Fig. 4b) there is considerable overlap, hence C/N alone cannot distinguish different sources of the TOM.

4.2. Estuarine particulate organic carbon and its sources

In the Pearl River delta, TOM enters the river system in the form of plant fragments and SOM, and mixes with *in situ* (freshwater, brackish-water and marine) plankton and algae within the estuary. Accordingly, within the estuarine area, the POC is derived from the TOM and *in situ* aquatic organisms. The terrigenous freshwater POC, having $\delta^{13}\text{C}$ around –28.7‰ (Figs. 5a and 6), is delivered into the estuarine system by the river runoff. It dilutes the signal produced by the brackish-water and marine POC which usually has $\delta^{13}\text{C}$ around –21.2‰ and C/N ≤ 11.0 (Figs. 5a and 6). Higher $\delta^{13}\text{C}$ in marine POC compared with riverine POC has also been reported from other coastal areas (Middelburg and Nieuwenhuize, 1998; Countway et al., 2007; Bianchi et al., 2007; Middelburg and Herman, 2007; Zhang et al., 2007; Bird et al., 2008). Wu et al. (2007) report $\delta^{13}\text{C}$ of the POC varying from –24.4‰ in the Yangtze River to –21.0‰ on the East China Sea Shelf.

In the Pearl River estuary, the balance between TOM and *in situ* plankton in the estuarine POC is strongly influenced by the strength of the freshwater runoff. It is, therefore, the strength of runoff that controls the spatial and temporal variation of the $\delta^{13}\text{C}$ signature of the estuarine POC. In winter, significant reduction in monsoonal precipitation results in a remarkable reduction in the TOM input into the estuary, and therefore the POC within the estuary is dominated by *in situ* phytoplankton (e.g. diatoms, dinoflagellates, green algae, euglenoides). $\delta^{13}\text{C}$ of the winter POC shows a clear trend from freshwater areas (around –28.0‰) to the marine-brackish areas (around –22.0‰), reflecting the variation in $\delta^{13}\text{C}$ and C/N of plankton under different environments (Fig. 6a). In the Pearl River estuary, $\delta^{13}\text{C}$ of the freshwater POC typically ranges from –30‰ to –25‰, and the brackish POC typically ranges from –26‰ to –22‰ (Fig. 6 c and d), similar to values reported from other estuaries (Lamb et al., 2006; Middelburg and Herman, 2007; Tesi et al., 2007). The low C/N (7.1 ± 0.9) of winter POC supports the assumption that winter POC is dominated by plankton, as the phytoplankton tends to have low C/N of 5–7 (Lamb et al., 2006). In summer the high freshwater flux brings larger amounts of TOM into the estuary (clearly seen in the amount of sediment collected by the filter in the summer compared to the winter in this study) resulting in a higher proportion of TOM in summer POC, suggested by the relatively higher C/N. At the same time the influence of the strong freshwater flux extends further seawards through the estuary, and produces a relatively uniform mix of POC within the estuary. This mixing and homogenisation of the POC throughout the estuary reduces the spatial variability in $\delta^{13}\text{C}$ of the summer POC. This is indicated by the considerable overlap in $\delta^{13}\text{C}$ and C/N of the summer POC from groups G2 to G5 across the estuary (Fig. 6b).

The POC collected with the 70 μm net is assumed to have a higher proportion of plant fragments than the POC collected on the filter paper as a higher proportion of the relatively smaller phytoplankton can pass through the net, but are trapped on the filter. The POC from the net would, therefore, be expected to record (on average) lower $\delta^{13}\text{C}$ and have higher C/N than the POC from the filter paper. This is indeed the case (Fig. 5b) with POC samples from the net having an average $\delta^{13}\text{C}$ of –25.6‰, and C/N of 10.7 compared to values of –24.3‰ and 9.5 for samples from the filter paper. Previous studies suggest that the range of $\delta^{13}\text{C}_{\text{POC}}$ is small in estuaries of high turbidity, between –26‰ and –24‰ (Fontugne

and Jouanneau, 1987; Tan et al., 2004), which reflects the dominance of terrigenous POC input into the estuary over other sources. This further supports the suggestion that in this and other river-dominated systems, the proportion of TOM in the POC is one of the main factors influencing $\delta^{13}\text{C}$ and C/N of POC, while the strength of the freshwater flux controls seasonal and spatial distribution of the TOM in the POC. However, during periods of reduced freshwater flux (during winter in the Pearl River estuary area for example) *in situ* productivity will tend to be the dominant source of POC and, hence, be the important control on spatial variability of $\delta^{13}\text{C}$ of POC (illustrated by winter distribution of $\delta^{13}\text{C}$, Fig. 6a).

4.3. Estuarine surface sediment and its sources

Comparison of $\delta^{13}\text{C}$ and C/N from a wide range of potential sources of sediment to the Pearl River estuary with measurements of bulk sediment samples from the estuary makes it possible to identify the dominant sources of organic material to the estuary floor. Organic matter within the surface sediment is mainly composed of the POC, especially the marine surface sediment (Liu et al., 2007), while the organic matter of the surface sediments from freshwater environments is a combination of freshwater *in situ* plankton and TOM. Spatially, $\delta^{13}\text{C}$ increases from -25.0‰ to -21.0‰ from river tributaries to marine areas with C/N decreasing from 15.2 to 6.8. This trend indicates a decreasing TOM contribution into the surface sediment organic matter, with increasing POC contribution seawards. Inner estuarine areas near the river mouth predominantly receive TOM delivered by the freshwater runoff. The proportion of TOM in the surface sediment organic matter decreases seawards as the influence of the freshwater runoff becomes weaker. In the marine area, surface sedimentary organic matter is dominated by the POC as TOM flux is weakened by tidal influence.

Applicability of $\delta^{13}\text{C}$ and C/N of the surface sediment for indicating sources of the sediment has been explored in previous studies in the estuarine and continental areas (Hedges and Parker, 1976; Goñi et al., 1997; Hu et al., 2006; Ramaswamy et al., 2008). Hu et al. (2006) examined organic carbon, total nitrogen, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of surface sediments from the Pearl River estuary and adjacent shelf, suggesting proportionally higher terrestrial-derived organic carbon at the river mouth and the western coast compared to marine-origin organic carbon. Using a mixing model (Schultz and Calder, 1976), Hu et al. (2006) further suggest the algal-derived organic carbon content is estimated to below ($\leq 0.06\%$) at the river mouth and higher (up to 0.57%) on the adjacent inner shelf. A decreasing contribution of TOM in the surface sediment organic matter seawards is also suggested by Zong et al. (2006) by examining the bulk organic $\delta^{13}\text{C}$ and C/N of the surface sediment, as well as diatom records.

Detailed bulk organic $\delta^{13}\text{C}$ and C/N of the organic matter from potential source areas of the surface sediment in the Pearl River estuary investigated in this study support the spatial distribution of the TOM and POC in the estuarine area. Different dominant organic matter sources between the freshwater and marine environments generate the lower $\delta^{13}\text{C}$ but higher C/N in the freshwater sediment compared to the marine sediment (Fig. 7b). Surface sediments from the freshwater area of this study have low $\delta^{13}\text{C}$ (e.g. -23.9‰ for surface sediment and -26.3‰ for the POC on average in G2). Surface sediments from the brackish/marine environment, with little freshwater influence, have high $\delta^{13}\text{C}$ (e.g. -21.0‰ in G9, Fig. 7b) due in part to higher $\delta^{13}\text{C}$ of the marine POC (-24.0‰ on average in G5 and -22.4‰ for G6, Fig. 6). C/N is useful for separating algae and TOM, with algae having C/N between 5 and 8, while TOM has C/N typically higher than 15 (Meyers, 1994). Low C/N of the surface sediments at the marine end (e.g. 6.9 for G9, Fig. 7b)

suggests higher organic matter contribution from marine algae (Hu et al., 2006; Wu et al., 2007).

To access relative proportions of TOM present in estuarine surface sediments, a simple $\delta^{13}\text{C}$ -based two end-member mixing model based on the model derived by Calder and Parker (1968) and Schultz and Calder (1976) has been applied to this area. The equation used is as follows.

$$\% \text{ TOM} = \left(\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{Org}} \right) / \left(\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{terrestrial}} \right) \times 100\%$$

Where $\delta^{13}\text{C}_{\text{marine}}$ is the measured $\delta^{13}\text{C}$ of the marine end member = -21.0‰ ; $\delta^{13}\text{C}_{\text{terrestrial}}$ is the measured $\delta^{13}\text{C}$ of the terrestrial end member = -25.0‰ ; and $\delta^{13}\text{C}_{\text{Org}}$ is the measured $\delta^{13}\text{C}$ of a given sample. C/N values are not considered in the estimation of the terrigenous contribution to TOM because they are nearly linearly correlated to $\delta^{13}\text{C}$ (Fig. 7). The marine end member is taken as -21.0‰ (average value of G9). This value is similar to other studies, e.g. -20.5‰ from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea (Ramaswamy et al., 2008). The terrestrial end member is taken as -25.0‰ (average value of G1), similar to the average of the $\delta^{13}\text{C}$ values of POC of Ayeyarwady and Salween Rivers (Bird et al., 2008). Using this equation a contour map of the proportion of TOM in the surface sediment has been generated showing generally more than 50% TOM contribution to the sedimentary organic matter (Fig. 8). This map shows a higher proportion of TOM contribution to the sediment in the inner estuary compared to the outer estuary due to the higher freshwater influence (fluvially delivered TOM) in this area. There is also an east–west gradient (higher proportion of TOM in the west) due to the increased freshwater influence on the western side of the estuary due to general estuarine circulation.

Factors that influence the organic $\delta^{13}\text{C}$ signature of POC, therefore, also become significant for the signature of the surface sediment, i.e. stronger freshwater flux. Sediments near the river mouth are suggested to have higher TOM contribution than some fluvial surface sediment (Fig. 8). This might be due to higher agricultural influence on fluvial surface sediment. For example, the fertilization has resulted in elevated $\delta^{13}\text{C}$ in samples derived from farming fields (O'Leary, 1985). Thus higher $\delta^{13}\text{C}$ values from these fluvial samples should indicate higher agricultural influences due to its location, which is close to farming fields, rather than higher marine influences. The contribution of marine algae to the sedimentary organic carbon pool is limited by the turbidity and nutrient content of the water column (Huang et al., 2003, 2004; Yin et al., 2004). Turbidity is higher at the river mouth (nearer the source of sediment flux), hence the contribution of *in situ* phytoplankton productivity to the sediment signal is less here than further down the estuary towards the inner-shelf area. A similar phenomenon has been reported from other estuaries, e.g. the Gironde estuary, western Europe (Fontugne and Jouanneau, 1987) and the Yangtze River estuary, China (Wu et al., 2007).

4.4. Influences on the bulk organic $\delta^{13}\text{C}$ and C/N

4.4.1. Anthropogenic influences

It has been suggested that anthropogenic influence from the Pearl River delta, such as agricultural products, human waste and industrial inputs, has become an important factor influencing the organic $\delta^{13}\text{C}$ signature of the surface sediments in the estuary (Jia and Peng, 2003; Owen and Lee, 2004). Our results show that agricultural C_3 plants have marginally higher $\delta^{13}\text{C}$ ($-28.2 \pm 1.4\text{‰}$) than general C_3 plants ($-29.9 \pm 1.3\text{‰}$), as well as the agricultural C_4 plants and general C_4 grass (Fig. 3). Correspondingly, $\delta^{13}\text{C}$ decreases from

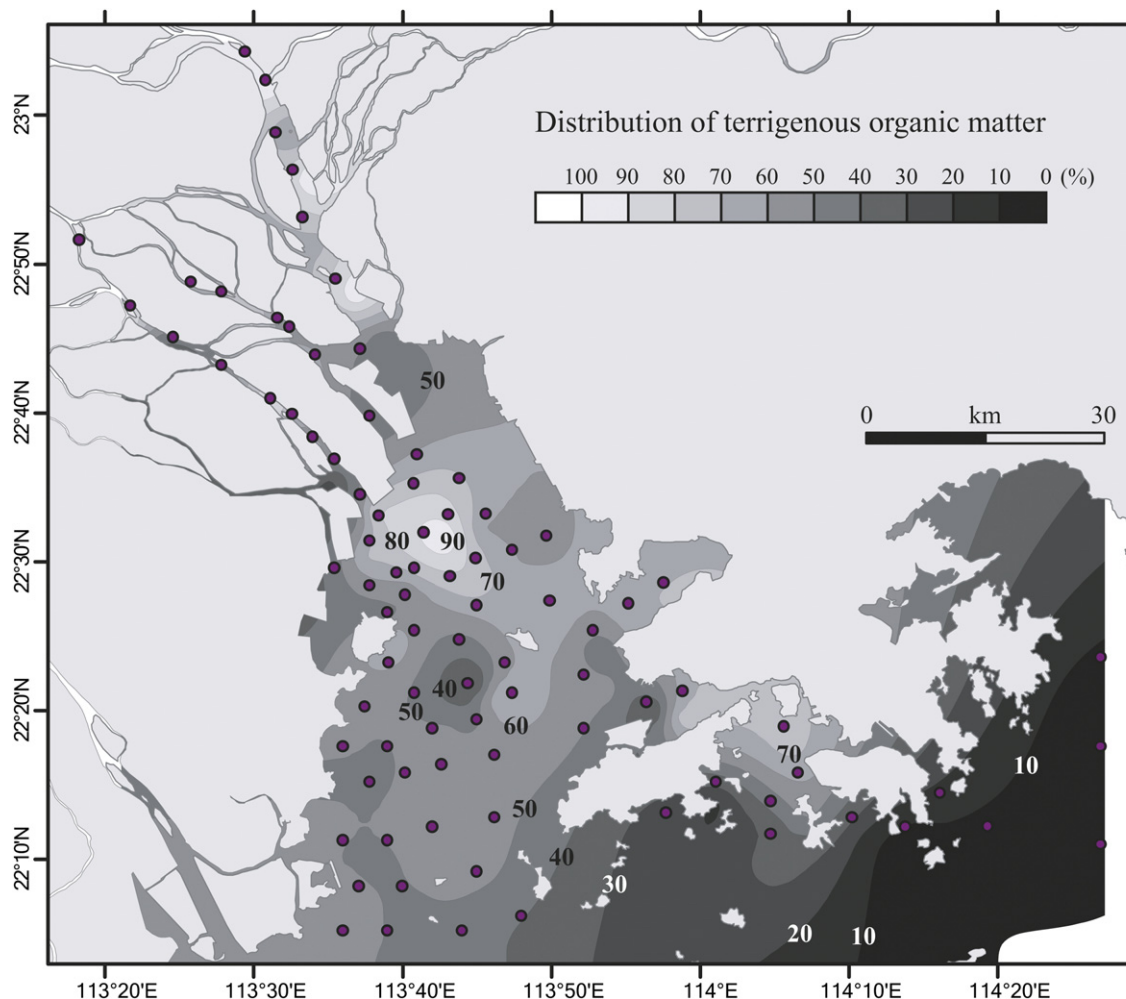


Fig. 8. Contour map of contribution of TOM to the surface sediment samples.

agricultural soil samples to riverbank and mangrove soil, with the forest soil having the lowest $\delta^{13}\text{C}$ (Fig. 4). C/N increases through these soil types, with the forest soil having the highest C/N. This increase in $\delta^{13}\text{C}$ and decrease in C/N found in agricultural soil might be due to the fertilization process (O'Leary, 1985). Sediments deposited during recent decades tend to have elevated $\delta^{13}\text{C}$, which appear to coincide with rapid urbanisation, industrialisation and reclamation in this area (Owen and Lee, 2004; Hu et al., 2008). For example, well-nourished plants show higher $\delta^{13}\text{C}$ than plants deficient in nitrogen and/or potassium (less fertilized) (O'Leary, 1985).

As a relatively densely populated area, sewage could be a potentially important contributor to the sediment organic matter in the Pearl River estuary. Sediments from Victoria Bay, Hong Kong, were significantly contaminated by sewage (Hsieh, 2006). The $\delta^{13}\text{C}$ of these sediments varies from -28.59 to -22.60‰ , and C/N from 10.71 to 14.73 (Hsieh, 2006), which must include the influence of sewage. Initial biomarker analysis of the Pearl River surface samples (David Strong, pers. comm.) show they lack coprostanol and other 5- β stanols indicating that sewage is an insignificant contributor to the organic carbon in these sediments. The main organic pollutants found in the estuarine area are the polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) and organochlorinate pesticides (Kang et al., 2000). Concentrations of the total PAHs, PCBs and organochlorinate pesticides in surface sediments from the river to the estuarine area are $1167\text{--}21329 \mu\text{g g}^{-1}$, $10.2\text{--}485.5 \mu\text{g g}^{-1}$ and $5.8\text{--}1658 \mu\text{g g}^{-1}$

respectively (Kang et al., 2000). When compared to the TOC values from surface samples analysed here of 0.5–2% TOC (i.e. $5000\text{--}20\,000 \mu\text{g g}^{-1}$) the concentration of these pollutants is actually very low. Sediments with the highest concentration of these organic pollutants are from areas near Guangzhou and Maucou according to Kang et al. (2000). For example, concentration of organochlorinate pesticides in sediments from areas investigated by this study is usually between 5 and $70 \mu\text{g g}^{-1}$ (Kang et al., 2000). Overall we consider that the contribution of organic carbon from these pollutants is insignificant.

A possibly more important contributor that might influence $\delta^{13}\text{C}$ value of the sediment is crude oil. The light oil from the Pearl River estuary is characterized by low density (less than 0.83g cm^{-3}), high contents of saturated hydrocarbons (71%–93%) and no asphaltenes (Guo and He, 2006). $\delta^{13}\text{C}$ of the crude oil from Pearl River estuary is between -27.09‰ and -26.48‰ (Guo and He, 2006), slightly heavier than that of C_3 plants. However, according to biomarker results (David Strong, pers. comm.), the total amount of lipids from crude oil in samples from this study ranges from 100 to $500 \mu\text{g/g}$, which compared to the average TOC values of 0.5–2% (i.e. 5–20 mg/g, Table 3), indicates a maximum concentration of 10% (0.5%–10%). Furthermore, biomarker results also suggest that the apolar fractions found in the crude oil would most likely already include the PCBs.

These data indicate that sedimentary organic carbon contributors other than plants, planktons and algae, such as human waste, organic pollutants and crude oil, are less important. The maximum

concentration of organic carbon from these anthropogenic sources is less than 10%. Thus, in spite of the influences of organic carbon from other sources, bulk organic $\delta^{13}\text{C}$ and C/N is still a good indicator for the source of estuarine sediment at the broadest scale from terrestrial, estuarine or marine areas.

4.4.2. Degradation

Change in bulk sediment organic $\delta^{13}\text{C}$ and C/N over time due to decomposition is an important consideration in coastal palaeoenvironmental research (e.g. Wilson et al., 2005; Lamb et al., 2006). For example, in the coastal wetlands of Louisiana, USA, differences in $\delta^{13}\text{C}$ between sediment and the surface vegetation are between -0.5‰ and -3.3‰ (Chmura et al., 1987). Changes in C/N can also occur during decomposition, particularly in the early stages (Valiela et al., 1985). Lamb et al. (2006) reviewed different studies and concluded that in inter-tidal and supra-tidal sediments, this may result in much lower surface sediment C/N compared with the overlying vegetation, whereas in sub-tidal sediments, C/N is commonly slightly higher than in the suspended sediment phase.

The influence of degradation varies across the Pearl River delta area and estuary. In the Pearl River delta, results show that SOM generally has higher average $\delta^{13}\text{C}$ but lower C/N than that of overlying vegetation (Table 1). For example, average $\delta^{13}\text{C}$ of mangrove soil is 3.1‰ higher than that of overlying mangrove plants, and average C/N of mangrove soil is 12.4 compared to 31.0 for that of mangrove plants. Degradation is likely to play a key role in producing these offsets.

In the Pearl River estuary, sedimentary organic matter is mainly derived from fluvial and marine sources (Zong et al., 2006). Much of the terrigenous component of fluvial organic matter may have already been extensively degraded on land or further upstream and should be relatively resistant to further degradation (Hedges and Keil, 1995). Degradation of *in situ* POC might, however, be significant for surface sediment $\delta^{13}\text{C}$. Cifuentes (1991) reported differences in $\delta^{13}\text{C}$ values between the two phases from the Delaware Estuary, southeast USA. In the upper estuary, $\delta^{13}\text{C}$ of POC (-28.9‰) was lower than that of surface sediment (-26.3‰), whilst in the lower estuary, suspended sediment $\delta^{13}\text{C}$ (-20.1‰) was higher than surface sediment $\delta^{13}\text{C}$ (-23.5‰). However, changes in $\delta^{13}\text{C}$ between POC and surface sediment in the Pearl River estuary are not significant when POC from both summer and winter are taken into consideration. For example, in G2, average $\delta^{13}\text{C}$ values are -23.9‰ for surface sediment and -26.3‰ for POC, which is about -2.4‰ lighter in POC. Similar results are found in freshwater group, G3. Differences in $\delta^{13}\text{C}$ between surface sediment and POC become less significant for brackish-water groups. For example, in G5, $\delta^{13}\text{C}$ of POC is only about 0.8‰ lighter than that of surface sediments. These results indicate a similar trend in differences between POC and surface sediment observed by Cifuentes (1991).

Results show that POC from both seasons exhibit much lower C/N ratios than surface sediments (Tables 2 and 3). The contrast is particularly clear in freshwater areas (e.g. G2, G4), and becomes more clear in marine area (e.g. G6). A similar phenomenon in C/N ratio has been reported by Cifuentes (1991) from the Delaware Estuary, southeast USA. Our results suggest that differential decomposition of organic detritus may partially explain differences between POC and surface sediment values (particularly C/N values), but seasonality may also be important in the Pearl River estuary.

Degradation can have a potentially significant influence on both sediment $\delta^{13}\text{C}$ and C/N. Early loss of labile material in vascular vegetation can lead to significant shifts in soil $\delta^{13}\text{C}$ and C/N but is insufficient to prevent the distinction between sediments from C₃ and C₄ vegetated soil. The degradation of POC in estuarine areas suggests that using either proxy in isolation might produce misleading results. It is important to combine $\delta^{13}\text{C}$ and C/N when

indicating sediment sources and environmental changes from coastal areas (Wilson et al., 2005; Zong et al., 2006).

5. Conclusions

1. In the Pearl River delta, C₃ plants have lower $\delta^{13}\text{C}$ than C₄ plants, $-29.0 \pm 1.8\text{‰}$ and $-13.1 \pm 0.5\text{‰}$, respectively, while C/N of both C₃ and C₄ plants are vary widely with considerable overlap.
2. $\delta^{13}\text{C}$ and C/N of SOM are highly related to the source of organic matter. Soil samples from C₃-plant-dominant areas (e.g. forest) tend to have lower $\delta^{13}\text{C}$ than those from C₄-grass-dominant areas (e.g. riverside areas). Their C/N, however, are widely variable and significantly overlap. Thus, while the $\delta^{13}\text{C}$ of soil can be used to indicate the predominant vegetation type, C/N cannot.
3. $\delta^{13}\text{C}$ and C/N of POC show significant variability due to seasonal variation of freshwater flux resulting in changes in the balance between the TOM and *in situ* phytoplankton in the POC.
4. $\delta^{13}\text{C}$ of surface sediment in the estuary increases from -25.0‰ at the freshwater end to -21.0‰ at the marine end, with C/N decreasing from 15.2 to 6.8, suggesting a weakening terrestrial/freshwater input and a strengthening marine contribution seaward.
5. Organic carbon from other sources might influence $\delta^{13}\text{C}$ of surface sediments. Agricultural input might elevate $\delta^{13}\text{C}$ of sedimentary organic matter due to the enhanced fertilization process and, more significantly, by an increase in the proportion of C₄ plants such as sugarcane grown in the catchment area. Organic carbon contributed from crude oil and other anthropogenic inputs such as PAHs, PCBs and organochlorinate pesticides, accounts for less than 10% of the TOC in the sediment according to biomarker results. This material might elevate the organic $\delta^{13}\text{C}$ of the sediment.
6. Degradation accounts for some of the shift in $\delta^{13}\text{C}$ and C/N between soil samples and overlying vegetation, as well as between surface sediments and POC. However, the change is not significant enough to prevent the application of $\delta^{13}\text{C}$ and C/N analysis as indicators for dominant overlying vegetation type and sediment source.
7. A contour map of the contribution of TOM to the estuarine surface sediments shows a greater contribution in the inner estuary (>50%) decreasing seawards to less than 10% in the outer-most samples. The volume of freshwater flux is one of the main factors controlling this distribution pattern.
8. Based on the analysis of modern samples of organic matter from source to sink in the Pearl River catchment, delta and estuary, we conclude that it is possible to use $\delta^{13}\text{C}$ and C/N of bulk organic matter to indicate the source of the organic matter and vegetation type in the source area. It is possible to distinguish at a broad scale between terrestrial, estuarine and marine sources of organic material and, hence, make an assessment of the nature of the sedimentary environment for a sample analysed.

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