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Sources and accumulation of organic carbon in the Pearl River Estuary surface sediment as indicated by elemental, stable carbon isotopic, and carbohydrate compositions

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Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Organic matter in surface sediments from the upper reach of the Pearl River Estuary and Lingdingyang Bay, as well as the adjacent northern South China Sea shelf was characterized by a variety of techniques, including elemental (C and N), stable carbon isotopic ($\delta^{13}\text{C}$) composition, as well as molecular-level analyses. Total organic carbon (TOC) content was $1.61\pm 1.20\%$ in the upper reach down to $1.00\pm 0.22\%$ in Lingdingyang Bay and to $0.80\pm 0.10\%$ on the inner shelf and $0.58\pm 0.06\%$ on the outer shelf. $\delta^{13}\text{C}$ values ranged from -25.11‰ to -21.28‰ across the studied area, with a trend of enrichment seaward. The spatial trend in C/N ratios mirrored that of $\delta^{13}\text{C}$, with a substantial decrease in C/N ratio from 10.9 ± 1.3 in the Lingdingyang Bay surface sediments to 6.5 ± 0.09 in the outer shelf surface sediments. Total carbohydrate yields ranged from 22.1 to 26.7 mg (100 mg OC) $^{-1}$, and typically followed TOC concentrations in the estuarine and shelf sediments, suggesting that the relative abundance of total carbohydrate was fairly constant in TOC. Total neutral sugars as detected by the nine major monosaccharides (lyxose, rhamnose, ribose, arabinose, fucose, xylose, galactose, mannose, and glucose) yielded between 4.0 and 18.6 mg (100 mg OC) $^{-1}$ in the same sediments, suggesting that a significant amount of carbohydrates were not neutral aldoses. The bulk organic matter properties, isotopic composition and C/N ratios, combined with molecular-level carbohydrate compositions were used to assess the sources and accumulation of terrestrial organic matter in the Pearl River Estuary and the adjacent northern South China Sea shelf. Results showed a mixture of terrestrial riverine organic carbon with in situ phytoplankton organic carbon in the areas studied. Using a two end-member mixing model based on $\delta^{13}\text{C}$ values and C/N ratios, we estimated that the terrestrial organic carbon contribution to the surface sediment TOC was ca. $57\pm 13\%$ for Lingdingyang Bay, $19\pm 2\%$ for the inner shelf, which decreased further to $4.3\pm 0.5\%$ on the outer shelf. The molecular composition of the carbohydrate in surface sediments also suggested that the inner estuary was rich in terrestrial-derived carbohydrates but that the contribution of terrestrial-derived carbohydrates

BGD

7, 2889–2926, 2010

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

decreased offshore. Terrestrial organic carbon accumulation flux was estimated as $1.37 \pm 0.92 \times 10^{11} \text{ g yr}^{-1}$ in Lingdingyang Bay, which accounted for $37 \pm 25\%$ of the terrestrial organic carbon transported to the Bay. The burial efficiency of terrestrial organic matter was markedly lower than that of suspended particulate substance ($\sim 71\%$) suggesting that the riverine POC undergoes significant degradation and replacement during transportation through the estuary.

1 Introduction

The fate of terrestrial organic matter in the ocean is the key to understanding the global carbon cycle (Hedges et al., 1997). It is estimated that rivers transport approximately $1.8 \times 10^{14} \text{ g yr}^{-1}$ terrestrial particulate organic carbon (POC) to the world's oceans (Meybeck, 1982), which is around twice the rate it accumulates in ocean sediment (Keil et al., 1997, and the references therein). Thus, the efficiency of riverine terrestrial particulate organic matter (POM) burial is thought to be quite low. It is reported that $<30\%$ Amazon riverine POM is buried in deltaic sediment (Aller et al., 1996; Keil et al., 1997). This low burial efficiency is enigmatic because most riverine POM is highly degraded soil organic matter (Hedges et al., 1994) and should presumably be recalcitrant to degradation when delivered to the ocean (Hedges and Keil, 1995).

Estuarine and continental shelf sediments have been long recognized as the dominant reservoir for organic carbon burial in the marine environment, and an accurate estimate of the sources of organic carbon in these sediments is essential in order to understand the transformation and the fate of terrestrial organic matter in the ocean. A number of techniques have been applied to trace carbon sources in sediment mixtures. $\delta^{13}\text{C}$ is a common index used to identify the organic sources in sediments and in food webs (Fry and Sherr, 1984; Gearing et al., 1977). However, applications of stable carbon isotopes in internal heterogeneity source identification can lead to confusing results (Hedges et al., 1997). For example, combination of equal parts of C_3 ($\delta^{13}\text{C} = -27\%$) and C_4 ($\delta^{13}\text{C} = -14\%$) plant carbon yields a total organic matter mixture

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

with a $\delta^{13}\text{C}$ (-20.5%), which resembles that of marine plankton. Therefore, combinations of the $\delta^{13}\text{C}$ method with other bulk parameters and/or biomarkers have been used to increase the resolution of the analysis (Andrews et al., 1998; Hedges and Parker, 1976; Peterson et al., 1985).

Carbohydrates occur in polysaccharide forms in which monosaccharide residues are bound to each other via glycosidic bonds. They are ubiquitous in the marine environment with primary importance as both structural and storage compounds of organisms. Together with amino acids, they represent the most abundant constituents of organic matter in marine organisms, suspended and sinking particles, and dissolved organic matter (Cowie and Hedges, 1992a; Hernes et al., 1996). In marine sediments, carbohydrates typically account for 3~10% of sedimentary TOC (Bergamaschi et al., 1999; Burdige et al., 2000; Kerherve et al., 2002; Skoog and Benner, 1997), and are important energy and carbon sources for various heterotrophic organisms in the sediment (Decho, 1990; Tibbles et al., 1994). Recently, it is indicated that carbohydrates preserved in sediments are predominantly structural polysaccharides, the compositions of which are more dependent upon their sources than the particular diagenetic pathway (Hernes et al., 1996). Such a composition at a molecular level is, therefore, potentially powerful in order to distinguish between organic matter with a terrestrial and a marine source (Biersmith and Benner, 1998; Cowie and Hedges, 1984b; da Cunha et al., 2002). Moreover, the molecular composition of carbohydrates may also provide insights of the organic matter biogeochemical cycle (Benner and Opsahl, 2001; Keil et al., 1998).

The Pearl River Estuary is a discharge dominant estuary, which provides $\sim 3.26 \times 10^{11} \text{ m}^3$ of fresh water and $\sim 7 \times 10^7$ tons of sediment annually to the South China Sea (SCS) (Zhao, 1990). Since most of the particles discharged by the Pearl River are deposited in the estuarine and shelf zones, it is thus vital to understand the sources and the transformation undergone in the estuarine systems in order to better examine their input and their response in the shelf system of the SCS. However, the natural cycling and origins of organic carbon within the sediments are still poorly

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



understood in this region. Several studies on the sources of organic matter deposited in the sediments of the Pearl River Estuary and the adjacent SCS by the bulk parameters such as TOC, total nitrogen (TN), and stable isotopic compositions ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) have shown significant spatial variability of the organic carbon deposition due to the complex hydrodynamics and the variable phytoplankton production (Hu et al., 2006a; Jia and Peng, 2003; Zhang et al., 2009). Only a few studies have characterized the origins of organic matter at the molecular level (Hu et al., 2009, 2006b). No studies have thus far been published concerning sediment organic matter with respect to carbohydrates at the molecular level in this highly dynamic estuarine system. In this paper, we present the spatial distribution of elemental (C and N), $\delta^{13}\text{C}$, and carbohydrate composition of the organic matter in surface sediments collected from the upper reach of the Pearl River Estuary, Lingdingyang Bay, and the northern SCS shelf. These bulk organic geochemical parameters in combination with carbohydrate biomarkers are used to further evaluate the sources of the organic matter deposited, and to estimate the accumulation flux of the terrestrial organic matter in the areas studied.

2 Materials and methods

2.1 Site description

The Pearl River consists of three main tributaries – North River (Beijiang), East River (Dongjiang), and West River (Xijiang), which empty into the Pearl River Estuary, and subsequently into the SCS. The Pearl River Estuary consists of three sub-estuaries, namely Modaomen, Yamen and Lingdingyang Bay. This study focuses on the major sub-estuary, Lingdingyang Bay. Lingdingyang Bay consists of four major outlets – Humen, Jiaomen, Hongqimen and Hengmen (Fig. 1). Sedimentation types in the Pearl River Estuary vary, depending upon the hydrodynamics of sedimentation environment. Overall, the western side of the estuary accumulates fine sand due to the dynamic hydrology induced by the water flow from the four outlets while the eastern parts of the

estuary is dominated by silty clays and clay silts (Chen, 1994; Jia and Peng, 2003). Off the Pearl River Estuary and on the SCS shelf, sediments are characterized with clayed silt around Sta. 6A-1 and with a mixture of sand/silt/clay around Sta. 5 (Chen, 1994).

2.2 Sampling

5 Surface sediment samples were collected from 16 sites along the Pearl River Estuary and SCS continental shelf during two cruises on board R/V Yanping II in May 2001, and in November 2002, within which three regions have been defined for the purposes of this paper: Lingdingyang Bay, the inner shelf, and the outer shelf (Fig. 1). The biogeochemical characteristics of these samples are shown in Table 1. Eight additional
10 river surface sediments were collected in January 2005 in the fresh water part of the Pearl River Estuary and Dongjiang tributaries (hereafter referred to as the upper reach of the Pearl River Estuary) as the river input end-member (Fig. 1 Table 1). Surface sediments were collected using a sediment grab and/or a box sampler. All samples were kept frozen at -20°C on board upon collection and until subsequent sample
15 processing.

2.3 Elemental and stable carbon isotopic composition ($\delta^{13}\text{C}$) analysis

Sediments were oven-dried at 50°C , ground and homogenized with mortar and pestle, then passed through a mesh sieve (60 mesh). TOC and TN were detected by dry combustion using a Perkin-Elmer 2400 CHNS/O analyzer after removal of inorganic carbon
20 with 1 mol L^{-1} HCl at room temperature for 24 h (Prahl et al., 1994). The precision of the technique is better than 5%.

The stable isotopic composition of the bulk organic matter in sediments was determined using ratio mass spectrometry. Organic carbon was oxidized to CO_2 with high-temperature CuO catalysis after removal of inorganic carbon with 1 mol L^{-1} HCl
25 (Prahl et al., 1994). The CO_2 was purified and the ratio of $^{13}\text{C}/^{12}\text{C}$ was analyzed using MAT252 mass spectrometry (Finnigan MAT, USA). $\delta^{13}\text{C}$ values were expressed in the

BGD

7, 2889–2926, 2010

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

per mil (‰) deviation from the standard Pee Dee Belemnite (PDB). The precision was no more than 0.2‰.

2.4 Carbohydrate analysis

2.4.1 Individual sugar analysis

5 Analysis of carbohydrates is generally initiated with a hydrolysis step that yields a pool of monomers (monosaccharides), which are subsequently detected by either colorimetric or chromatographic methods. Hydrolysis is, therefore, a critical process in the determination of sugar compositions. Various hydrolysis techniques have been employed, depending on the type of sample (Panagiotopoulos and Sempéré, 2005, and
10 the references therein). We chose “mild” hydrolysis, using 4.0 mol L^{-1} trifluoroacetic acid (TFA) to release monosaccharide from marine surface sediments. TFA has been recommended in hydrolyzing dissolved organic matter (Aluwihare et al., 1997) and non-cellulose soil samples (Amelung et al., 1996). Approximately 0.5 g dried sediment was weighed into a precombusted 50 mL glass tube with a Teflon-lined cap. A 4.0 mol L^{-1}
15 TFA solution (5.0 mL) was added to each tube, after which the sample was hydrolyzed at 105°C with magnetic stirring for 4 h. After hydrolysis a certain amount of adonitol (Sigma Co.) was added to the hydrolysate as a gas chromatography (GC) internal standard. The solution was completely homogenized, and then centrifuged for 20 min at 3000 rpm and the supernatant was collected to a 100 mL pear-shaped flask. The so-
20 lution was then rotary evaporated to remove TFA at $\leq 50^\circ\text{C}$. The dried hydrolysate was redissolved in $\sim 2 \text{ mL}$ Milli-Q water, and the solution ($\text{pH}=2\text{--}3$) was then run through a $\sim 25 \text{ mL}$ cation/anion mixed column at a flow rate of $0.8\text{--}1.0 \text{ mL min}^{-1}$ to desalt. The ion exchange column was packed with mixed (1:1 v/v) cation 001 \times 7 (732, Lvyin Co., China) and anion resins 201 \times 7 (717, Lvyin Co., China) and the sugar fraction was
25 eluted with at least three bed volumes of Milli-Q water. The deionized hydrolysate was again rotary evaporated to dryness.

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

We preconditioned the resins as follows: first, the resins were washed thoroughly with Milli-Q water, then soaked in Milli-Q water for 12 h. After the water was removed, the resins were soaked in ethanol for 4 h to remove any alcohol-soluble substance. After the ethanol was washed out, the cationic resins were transformed into hydrogen-type resins by soaking in $\sim 1 \text{ mol L}^{-1}$ HCl solution for 4 h. Finally, the resins were washed with Milli-Q water until $\text{pH}=5\text{--}6$. The anionic resins were soaked in $\sim 1 \text{ mol L}^{-1}$ NaOH solution for 4 h to transform into OH-type resins, followed by Milli-Q water wash until $\text{pH}=7\text{--}8$.

The equilibration and derivatization of sugar were based on the method of Cowie and Hedges (1984b). Briefly, the deionized dried sample was dissolved in double distilled pyridine. An absolute recovery standard (sorbitol) (Sigma Co.) was added to the solution followed by an equal volume of 0.4% (w/v) LiClO_4 in pyridine. The sugar anomers were equilibrated at 60°C for 48 h and derivatized with Regisil reagent (bis(trimethylsilyl) trifluoroacetamide +1% trimethylchlorosilane) for 20 min at 60°C to form trimethylsilyl ether (TMS) derivatives. Analysis of individual sugars was carried out using a Hewlett-Packard (HP) 6890 gas chromatograph equipped with a 30 m by 0.32 mm i.d. fused-silica capillary column (HP-5) with a flame ionization detector (FID). Both the injection port and the FID were maintained at a constant temperature of 300°C . The injection volume was $1 \mu\text{L}$ with a split 5:1. Hydrogen was employed as a carrier gas at $\sim 1.5 \text{ mL min}^{-1}$ in a constant flow mode. Column temperature was programmed from 150°C after an initial delay of 15 min, then increasing at 3°C min^{-1} to 200°C , and after that increasing at $15^\circ\text{C min}^{-1}$ to 280°C and holding for 5 min. Under these conditions the best peak resolution can be obtained, and quantification on the basis of a single clearly resolved peak for each sugar is made possible (Fig. 2). Each monosaccharide was identified using its relative retention time, and quantified by an internal standard. Total neutral sugar (TNS) concentration was calculated as the sum of the individual sugars.

2.4.2 Total carbohydrate

Total carbohydrate (TCHO) concentrations in the sediments were determined using a method modified from the phenol-sulfuric acid (PSA) assay (Miyajima et al., 2001). Briefly, carbohydrates were first hydrolyzed to individual monosaccharides using 4.0 mol L⁻¹ TFA. The hydrolysate was centrifuged and the supernatant was collected and diluted. The dilution was used to analyze TCHO following this PSA procedure. TCHO yields reported here were based on standard curves constructed from glucose standards and presented in units of mg carbohydrate (100 mg OC)⁻¹.

2.5 Quality controls and assessment

In order to control the quality of our elemental and isotope analysis, we chose three sediments from the west Pacific as secondary standards to monitor our analysis process. The carbon isotope composition of these sediments ranged from -20.16 to -20.91‰, which matched well with marine biogenic organic carbon (-20~ -22‰) (O'Leary, 1988). The atomic C/N ratios ranged from 6.4 to 6.6, which were again consistent with the Redfield ratio.

There was a significant positive correlation ($R^2=0.96$; $p < 0.001$) between the TOC and TN in the sediments from the upper reach of the Pearl River Estuary (Fig. 3), indicating the same origin of TOC and TN. The intercept of the regression line was ~0, suggesting that most of the nitrogen measured by our method was related to sedimentary organic carbon and probably in the organic form (Hedges et al., 1986).

A complete description of the QA/QC measures and the results for the measurement of monosaccharide compositions has been published (He et al., 2003). Our method showed a spiked recovery (sample + spike) of 77–115% with a relative standard deviation (RSD) of 1.8–11%, and the detection limits of the TMS-monosaccharide ranged from 0.02–0.06 mg L⁻¹ with a signal to noise ratio of 3. The recovery of the internal standard, adonitol, was 79.8% ($n=6$, RSD=5.2%) throughout the sample processing procedure.

BGD

7, 2889–2926, 2010

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Sources and
accumulation of
organic carbon in the
Pearl River Estuary**

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Given the primary importance of hydrolysis in the determination of individual sugars, we compared the 4.0 mol L^{-1} TFA hydrolysis method with the strong sulfuric acid method (Cowie and Hedges, 1984b). The latter was recommended for terrestrial samples rich in α -cellulose. Strong hydrolysis may also be used for marine samples containing “refractory” structural polysaccharides (Kerherve et al., 2002; Pakulski and Benner, 1992). Strong hydrolysis is usually performed in two steps. Samples were treated with 12 mol L^{-1} sulfuric acid at room temperature, after which the acid was diluted to 1.2 mol L^{-1} and heated in a boiling water bath with stirring. The individual neutral monosaccharide yields of the same sediment samples using these two hydrolysis methods are presented in Table 2. The results showed that the TFA hydrolysis method gave comparable yields of lyxose (LYX), arabinose (ARA), fucose (FUC), rhamnose (RHA), galactose (GAL) and glucose (GLU), but significantly higher yields of xylose (XYL) and ribose (RIB), than those of the strong H_2SO_4 hydrolysis method. Previous studies also find that hydrolysis with 2 mol L^{-1} TFA for spruce holocellulose and with 4 mol L^{-1} TFA for soil samples give higher yields of all monosaccharides (except glucose) than 12 mol L^{-1} H_2SO_4 (Amelung et al., 1996; Fengel and Wegener, 1979). Pentoses are reported to be more fragile than hexoses and are partially destroyed after strong hydrolysis, especially for the RIB (Mopper, 1977; Panagiotopoulos and Sempéré, 2005). The higher yields of XYL and RIB are likely to be due to less destruction of these monosaccharides during mild hydrolysis.

Strong hydrolysis generally gave a higher yield of glucose due to the more efficient cleavage of α -cellulose. However, for our sediment samples, strong hydrolysis did not give a higher yield of glucose. This result was probably due to the fact that our sediment samples for the comparison experiments contained a low content of α -cellulose because the sediment samples were collected from the inner shelf (Sta. 7-1), which contained less than 20% terrestrial organic matter (see discussion below).

3 Results

3.1 Bulk characteristics of the river sediments

TOC and TN content of the eight riverine sediments analyzed in this study spanned a range from 0.60 to 4.41% and 0.06 to 0.23% by weight, reflecting the wide variety of sedimentary environments and sediment textures. Atomic C/N ratios ranged from 11.7 to 22.4. The highest C/N ratio along with the highest content of TOC and TN was observed at station R01 near Guangzhou where wastewater discharge containing large amounts of organic matter and ammonia occurred. The concentrations of TOC and TN were highly correlated with those in the sediments collected from the upper reach of the estuary except for the highly polluted station R01 (Fig. 3). The linear regression equation was as follows:

$$\text{TN}\% = 0.092\text{TOC}\% - 0.004, \quad R^2 = 0.96 \quad (1)$$

The slope of the regression line indicated a best-fit atomic C/N ratio of 12.7, suggesting that most of the TOC in the upper reach of the Pearl River Estuary was attributable to soil derived organic matter. Soil organic matter tends to have a lower C/N ratio (8–14) than plant organic matter (>20) due to the retention of nitrogen by microbes during organic matter demineralization in soils (Hedges and Oades, 1997). The $\delta^{13}\text{C}$ values of $-23.05 \sim -26.05\%$ with an average of $-24.91 \pm 0.94\%$ also closely matched soil attributes (Prahl et al., 1994), implying that the bulk organic carbon in the river sediments was ultimately derived from land plants and would have undergone extensive biotransformation and/or biodegradation before deposition. This conclusion seemed surprising since there were other potentially significant sources of organic carbon for these sediments, including phytoplankton production and the sewage input in the upper reach of the estuary. We attributed this to selected degradation of autochthonous and sewage-derived POM resulting in the stable terrestrial organic carbon (TrOC) being dominantly preserved in the sediments. The high Chl-*a* concentration coupled with permanent oxygen depletion in this study area may lend additional evidence for the

BGD

7, 2889–2926, 2010

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



selected removal of labile POM in the water column or sediment water interface. As compared to the $\delta^{13}\text{C}$ and C/N ratio of the in situ phytoplankton ($\delta^{13}\text{C}$: -31.23% to -25.83% , C/N ratio: 6.5 to 8.4, our unpublished data), sediment TOC had significantly heavier $\delta^{13}\text{C}$ and higher C/N ratios ($\delta^{13}\text{C}$: -26.05 to -23.05% , C/N: 11.7–22.4). Such enrichment in $\delta^{13}\text{C}$ and elevation in the C/N ratio of sediments suggested again the preferential removal of light phytoplankton carbon during degradation of POM.

3.2 Carbohydrate composition of the river sediments

Samples from the upper reach of the estuary were also analyzed for TCHO and individual neutral carbohydrate. TNS yields, estimated as the sum of neutral monosaccharides analyzed using GC-FID and normalized to TOC (in units of mg carbohydrate $(100\text{ mg OC})^{-1}$), and individual neutral carbohydrate composition (wt% of individual aldose relative to the total aldoses) are reported in Table 3. Nine major neutral sugars in the sediment samples were identified and quantified (Fig. 2a, b).

TNS yields of the sediments in the upper reach of the Pearl River Estuary ranged from 4.3 to 10.8 mg $(100\text{ mg OC})^{-1}$ with a mean of 7.9 ± 2.4 mg $(100\text{ mg OC})^{-1}$, which were much lower than the TCHO yields analyzed using the PSA method for the same sediment samples (10.3–26.5 mg $(100\text{ mg OC})^{-1}$, Table 3). The TNS yields observed here were consistent with the values reported in other riverine sediments (Jennerjahn and Ittekkot, 1999). The most abundant neutral sugars were GLU ($29.2\pm 5.7\%$) followed by RHA ($17.5\pm 7.8\%$), GAL ($14.6\pm 3.3\%$) mannose (MAN, $12.4\pm 3.3\%$), XYL ($8.3\pm 3.4\%$), FUC ($7.9\pm 1.2\%$) and ARA ($7.7\pm 2.8\%$). RIB and LYX were minor components and present only in small amounts, $2.0\pm 0.8\%$ and $0.8\pm 0.1\%$, respectively. As compared to plant tissues (Cowie and Hedges, 1984b) and phytoplankton (Hernes et al., 1996), the Pearl River sediments had a significantly higher percentage of RHA and FUC. Although FUC is the monomer of a storage polysaccharide in phytoplankton (Cowie and Hedges, 1984b), the association of FUC with RHA strongly suggest a bacterial origin for both these deoxyhexoses (Bhosle et al., 1992; Ogier et al., 2001). This high abundance of deoxysugars further confirmed that the organic matter in this

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

area has undergone extensive biodegradation or biotransformation. This suggestion was also supported by the relatively high ratios of (FUC+RHA)/(ARA+XYL) (Table 3). Guggenberger et al. (1994) state that (FUC+RHA)/(ARA+XYL) ratios exceeding 0.5 correspond to microbially-altered organic matter.

3.3 Bulk characteristics of estuarine and shelf sediments

There was a general decreasing trend in TOC offshore, with a mean value of $1.00 \pm 0.22\%$ in Lingdingyang Bay decreasing to $0.58 \pm 0.06\%$ on the outer shelf. A similar trend was observable for the atomic C/N ratio, which ranged from 8.4–13.0 in Lingdingyang Bay to 6.9–8.4 on the inner shelf, and to 6.5–6.6 on the outer shelf, showing the relative enrichment of nitrogen seaward. Meanwhile, $\delta^{13}\text{C}$ became progressively heavier from the estuary ($-23.86 \pm 0.96\text{‰}$) to the inner shelf ($-21.48 \pm 0.04\text{‰}$) and to the outer shelf ($-21.36 \pm 0.11\text{‰}$) sediments, indicating the different contribution of terrestrial materials to the sediment TOC in different zones.

3.4 Carbohydrate composition of the estuarine and shelf sediments

Surface sediments of seven stations along the salinity gradient from the Pearl River Estuary to the SCS shelf were chosen to analyze TCHO and individual neutral sugars. At these selected stations TCHO yields typically followed TOC concentrations and ranged from 22.1 to 26.7 mg (100 mg OC)⁻¹ (Table 3) suggesting that TCHO were a constant fraction of TOC. TNS yields ranged from 4.0 to 18.6 mg (100 mg OC)⁻¹, which were similar to typical values reported for coastal surface sediments (5–20 mg (100 mg OC)⁻¹) (Bergamaschi et al., 1997; Burdige et al., 2000; Cowie and Hedges, 1984a; Kerherve et al., 2002). The contribution of TNS to TCHO varied typically from 18 to 51%, which was consistent with the value (18–47%) reported for the Mandovi Estuary sediment (Khodse et al., 2008), indicating that more than half of the bulk carbohydrates were not neutral aldoses. A probable reason which may explain this difference between the chromatographic and spectrophotometric methods is that carbohydrates

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

determined by the PSA method include neutral monosaccharides and their methyl derivatives including uronic acids (Dubois et al., 1956). Moreover, the differences may also be due to structural changes of individual aldoses incorporated into refractory DOC molecules that can still be characterized by the PAS method but not by the GC method (Khodse et al., 2008).

Overall, the neutral sugar composition of the Pearl River Estuary and SCS shelf showed a high spatial variability (Table 3). There is a general consensus that large variability may exist in neutral sugar composition in the world's riverine sediments due to differences in the local biota (animal and vegetal) and their selective consumption of the carbohydrate fraction of the organic matter (Artemyev, 1996). On average, GLU was also the major monosaccharide ($26.0 \pm 6.4\%$), followed by GAL ($18.0 \pm 5.8\%$), RHA ($15.0 \pm 5.4\%$), MAN ($11.1 \pm 3.1\%$), XYL ($10.6 \pm 2.4\%$), ARA ($9.4 \pm 4.3\%$), FUC ($5.8 \pm 1.5\%$), RIB ($3.3 \pm 1.2\%$) and LYX ($0.8 \pm 0.1\%$).

4 Discussion

4.1 Terrestrial organic carbon contribution to sediments from the Pearl River Estuary and SCS shelf

The sources of sediment organic matter can be indicated by the C/N ratio and the carbon isotopic composition (Hayes, 1993; Middelburg and Nieuwenhuize, 1998). In order to determine the potential sources for the sedimentary organic matter, a simple mixing model based on C/N ratio and $\delta^{13}\text{C}$ of the sediment was used to estimate the contribution of terrigenous organic matter to the sediment samples from the Pearl River Estuary and SCS shelf (Liu et al., 2007). It was assumed that our sedimentary system receives terrigenous organic matter input from a single riverine source, and mixing with marine organic matter. The postulate is probably reasonable in this discharge dominant estuary. Then both the C/N ratio (R) and the $\delta^{13}\text{C}$ value (δ) of the mixture may be expressed as a function of the fraction of terrigenous organic matter (f_t) as

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

follows:

$$R = R_t f_t + (1 - f_t) R_m \quad (2)$$

$$\delta = (f_t R_t \delta_t + (1 - f_t) R_m \delta_m) / R \quad (3)$$

where R_m and R_t represent the marine and terrestrial C/N ratios; and δ_m and δ_t represent the marine and terrestrial $\delta^{13}\text{C}$ values.

The mixing curves are shown in Fig. 4. For the model calculation, surface sediments collected from the upper reach (fresh water part) of the Pearl River Estuary were chosen as the riverine end-member and represented the relatively long term compositional average of the potential riverine input (TrOC) to the ocean, similar to the method described by Prahl et al. (1994). This end-member may provide a better representation of the bulk property of riverine input to the ocean than the universal vascular plant debris end-member, because the recent investigations have shown that terrigenous organic matter is heterogeneous in composition, including at least soils and plant debris sources (Gordon and Goni, 2004, and the references therein). Meanwhile, sediments collected from the west Pacific were chosen as the marine end-member.

The carbon isotope composition and C/N ratio plot (Fig. 4) showed that the mixing of the riverine end-member with the marine end-member can well explain the carbon isotope composition and C/N ratio variations of the sediments along the estuary and continental shelf. The gradual decrease of C/N ratios, consistent with progressive enrichment in $\delta^{13}\text{C}$ from the estuary to the inner shelf and to the outer shelf sediments, suggests a higher fraction of marine organic matter offshore. Based on the two end-member mixing model, Eqs. (2) and (3), we can estimate the fraction of terrigenous organic matter (f_t) contributed to the sediments from the Pearl River Estuary and the SCS shelf, as summarized in Table 1. The contribution of terrigenous organic carbon to sediment TOC accounted for, on average, $57 \pm 13\%$ in Lingdingyang Bay, $19 \pm 2\%$ in the outer estuary, and $4.3 \pm 0.5\%$ on the SCS shelf. Our data concerning TrOC contribution to the sediment TOC were relatively high but comparable to the results reported by Zhang et al. (2009). The contribution of terrigenous organic carbon to the sediment

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



TOC in Lingdingyang Bay was also consistent with the value (63–70%) observed in the Amazon delta (Keil et al., 1997). Our results supported the view that terrestrial organic matter is deposited primarily in the estuaries and inner continental shelves and that little is exported to the outer shelves (Gearing et al., 1977; Hedges and Parker, 1976).

4.2 Source characterization of carbohydrates in the Pearl River Estuary and on the SCS shelf

Carbohydrates are classified as storage and structural polymers. Storage carbohydrates are labile and are rapidly utilized by the in situ heterotrophic organisms. This results in the accumulation of relatively inert structural carbohydrates in marine sediments (Burdige et al., 2000; Hernes et al., 1996; Jensen et al., 2005). So carbohydrate compositions in the sediment are likely to be more dependent upon their source than on diagenetic status. The monosaccharide composition of carbohydrates in sediment is a useful tool for identifying the sources of carbohydrates (Campiano and Romano, 1998; Cowie and Hedges, 1984a; Ittekkot et al., 1984; Kerherve et al., 2002; Khodse et al., 2008).

Based on the $\delta^{13}\text{C}$ and C/N ratio, we estimated the contribution of terrigenous organic matter to sediment TOC in the Pearl River Estuary and SCS shelf as summarized in Table 1. We separated sediment samples into groups with high ($\geq 50\%$) and low ($\leq 25\%$) contributions of terrigenous organic carbon. The average neutral sugar compositions of sediment samples rich in TrOC were compared to those poor in TrOC (Fig. 5). Statistical comparisons (t-test) of the means showed that TrOC-rich sediment was enriched in % ARA ($p < 0.1$, not statistically significant) and % GLU ($p \leq 0.05$, significant); and depleted in % RIB ($p \leq 0.05$, significant) and % GAL ($p \leq 0.01$, very significant) relative to TrOC poor sediment. This comparison clearly shows the differences in neutral sugar composition between sediments from different sources (terrestrial versus marine). Our results supported the view that neutral sugar composition combined with their ratios is useful for distinguishing terrestrial and marine sources in sediment (Cowie and Hedges, 1984a).

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Sources and
accumulation of
organic carbon in the
Pearl River Estuary**

B. He et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

GAL is the second most abundant monosaccharide in surface sediments from the estuary and the shelf, and is enriched seaward. GAL is abundant in terrestrial non-woody plant tissues (Cowie and Hedges, 1984a), and is one of the major constituents of some phytoplankton cell walls and also bacteria (Cowie and Hedges, 1984a; Hecky et al., 1973). Moreover, the relative abundance of GAL increases during a phytoplankton bloom (Ittekkot et al., 1982). Therefore, this monosaccharide may be derived from the mixture of phytoplankton, bacteria and/or terrestrial plant sources. The mixed sources of organic matter in the sediments are also characterized by fatty acids (Hu et al., 2006b) and by lipids (Hu et al., 2009).

ARA and XYL together accounted for 14.5–32.9% of the TNS in the estuarine and the shelf sediments. Such high abundance of these sugars is not observed in the organic matter derived from phytoplankton because neither of these sugars contributes much to the whole cell or cell wall material of diatoms (Biersmith and Benner, 1998) as well as net plankton (Hernes et al., 1996). However, both are abundant in terrestrial plants as constituents of arabinoxylan and arabino-glucuronoxylan (Cowie and Hedges, 1984a; Guggenberger et al., 1994; Ogier et al., 2001). A relatively high % ARA was observed in the estuarine sediments as compared to the inner shelf and outer shelf sediments. Moreover, a positive correlation between the % (XYL + ARA) and the ratio of GLU/RIB was found in the estuarine and SCS shelf sediments (Fig. 6). Previous studies suggest that terrestrial carbohydrates have a higher GLU/RIB ratio than marine carbohydrates (Cowie and Hedges, 1984a). A high GLU/RIB ratio coupled with a high % (XYL + ARA) was observed in Lingdingyang Bay (Sta. 15, 30 and 8-1), whereas a low GLU/RIB ratio along with a low % (XYL + ARA) was observed on the SCS shelf (Sta. 7-1, 6A-1 and 5), indicating that terrestrially derived carbohydrate contributed a higher portion to the estuarine sediment and decreased seaward. This notion was further supported by the enrichment of $\delta^{13}\text{C}$ and decrease of the C/N ratio offshore.

Relatively high RHA (10.3–24.0%) was observed in Pearl River Estuary and SCS shelf sediments as compared to other estuarine and coastal sediments (Hamilton and Hedges, 1988; Hedges et al., 1994). RHA is abundant in bacteria, fungi and

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



phytoplankton (Cowie and Hedges, 1984a; D'Souza et al., 2005; Hicks et al., 1994). An unusually high value of RHA was found at Sta. 8-1 (20.9%) and at Sta. 5 (24.0%). According to Hicks et al. (1994), who analyzed the carbohydrate compositions of different organic materials (vascular plants, zooplankton, phytoplankton and bacteria), only bacteria contain such a high proportion of RHA. This high proportion of RHA strongly suggests a bacterial origin, which is also supported by the high percentage of bacterial fatty acids of the sediments in the Pearl River Estuary and SCS shelf (Hu et al., 2006b).

It is interesting to note that the highest percentage abundance of ARA and XYL along with the lowest percentage of RIB, MAN, FUC and GAL among the estuarine and shelf sediment samples was found at Sta. 8-1 in Lingdingyang Bay, indicating the dominant contribution of terrestrial carbohydrate. This conclusion deduced from carbohydrate composition fits well with the organic source estimated from the bulk property $\delta^{13}\text{C}$ and C/N ratio at this station.

4.3 Carbohydrate remineralization and diagenesis

Given their abundance in living organisms, their diversity and their biodegradation, carbohydrates have potential as tracers of source and of alteration processes in natural waters. Prior research shows that the distribution and molecular composition of hydrolysable neutral sugars may be reflective of the preferential utilization of monosaccharides by microorganisms (Biersmith and Benner, 1998; Kerherve et al., 2002; Skoog and Benner, 1997). In addition, neutral sugars are proposed as indicators of the bioactivity and diagenetic status of natural samples (Amon and Benner, 2003; Skoog and Benner, 1997). For example, GLU and GAL are abundant as cellular storage products (β -glucan and galactan polymers) in vascular plants and phytoplankton (Kerherve et al., 2002, and the references therein), which are easily degraded by heterotrophic organisms (Cowie and Hedges, 1992b; Hama and Yanagi, 2001; Hernes et al., 1996). Another hexose, MAN, is rich in the extracellular, high molecular weight, dissolved organic matter of the marine diatom *Thalassiosira weissflogii* and is preferentially removed during heterotrophic decomposition (Aluwihare et al., 1997). Therefore, a high

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

abundance of hexoses may suggest a more “fresh” organic matter. In contrast, fucoidan is resistant to hydrolysis in bottom water as well as in the surface sediment (Arnosti, 2000), and the deoxysugars FUC and RHA have been suggested as good indicators of degraded organic matter (da Cunha et al., 2002; Hedges et al., 1994).

5 Therefore, the ratio of $(\text{GAL}+\text{MAN})/(\text{RHA}+\text{FUC})$ may be used as an indicator to discriminate fresh and refractory organic matter. We excluded the GLU in which concentration varies sharply with source, environmental conditions and diagenetic status.

The ratios of $(\text{GAL}+\text{MAN})/(\text{RHA}+\text{FUC})$ in the Pearl River Estuary were low when compared to those of marine net phytoplankton (2.0–4.0, Pacific) (Hernes et al., 1996) or terrestrial plant tissue (Cowie and Hedges, 1984a). The lowest value of $(\text{GAL}+\text{MAN})/(\text{RHA}+\text{FUC})$ was found at Sta. 8-1 followed by Sta. 7A. The low level of GAL and MAN at these two stations (Table 3) might be associated with the selective degradation of these two monosaccharides. Selective degradation of hexoses was also observed for POM in a Mediterranean river (da Cunha et al., 2002) and for macromolecules in marine diatom culture (Aluwihare et al., 1997). It has also been demonstrated that structural features can significantly affect the degradation rates of carbohydrates (Arnosti, 2000; Arnosti and Repeta, 1994). In addition, Sta. 8-1 and 7A had the lowest neutral sugar yields $(4.0 \text{ mg } (100 \text{ mg OC})^{-1})$, indicating that the organic matter was highly degraded in these areas. The lowest TNS to TCHO proportion further confirmed that these carbohydrates have undergone intensive bio-alteration or biodegradation at these two stations. The sources of this highly degraded organic matter were unclear but might be associated with the erosion of the bed-rock sediment of Dayushan Island due to the heavy development of this area, such as building Hongkong International Airport and Hongkong Disneyland.

25 4.4 Accumulation of terrestrial organic carbon in the Pearl River Estuary and SCS shelf

Lingdingyang Bay is a large sub-estuary of the Pearl River Estuary. The four outlets are located close together in the north or west of the bay. Influenced by Coriolis deflection,

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

waters into the bay flow along the west part of the bay, leading to the coarse suspended accumulation of matter at the bottom along the flow path. In contrast, waters in the east part of the bay are relatively still, due to the absence of a river outlet, and fine silt is deposited gradually at the bottom (Chen, 1994; Liu et al., 1998). The sedimentation rates reported for the estuary and the SCS shelf are summarized in Fig. 7. Sedimentation rates differ strongly throughout the estuary. In the west part of the bay, the sedimentation rates are 1.48–3.85 cm yr⁻¹ (Lin et al., 1998), while in the east part, the sedimentation rates are 0.37–0.50 cm yr⁻¹ (Liu et al., 1998) and data in this paper). Between the west and east part there is a the mid-rate sedimentary area with a sedimentation rate of 1.5–2.5 cm yr⁻¹ (Chen, 1992). In the north of the bay the sedimentation rate was 0.85 cm yr⁻¹ (data in this paper). The sedimentation rates decrease to 0.29–0.88 cm yr⁻¹ on the inner shelf (Zhang et al., 2009; Zhang et al., 1998) and to 0.21 cm yr⁻¹ on the outer shelf.

An approximation of the sediment deposition flux can be estimated using Eq. (4):

$$F_S = R_S \times d_S \tag{4}$$

The organic carbon accumulation flux can be estimated using Eq. (5):

$$F_{org} = C_{org} \times R_S \times d_S \tag{5}$$

where F_S and F_{org} represent the sediment and organic carbon burial flux; C_{org} is organic carbon concentration in the sediment; R_S is the sediment accumulation rate; and d_S is sediment dry density. The deviation of F_{org} was calculated with Eq. (6):

$$\sigma_{F_{org}} = \left(\left(\frac{\partial F_{org}}{\partial C_{org}} \right)^2 \sigma_{C_{org}}^2 + \left(\frac{\partial F_{org}}{\partial R_S} \right)^2 \sigma_{R_S}^2 + \left(\frac{\partial F_{org}}{\partial d_S} \right)^2 \sigma_{d_S}^2 \right)^{\frac{1}{2}}$$

$$\sigma_{F_{org}} = F_{org} \left(\frac{\sigma_{C_{org}}^2}{C_{org}^2} + \frac{\sigma_{R_S}^2}{R_S^2} + \frac{\sigma_{d_S}^2}{d_S^2} \right)^{\frac{1}{2}} \tag{6}$$

**Sources and
accumulation of
organic carbon in the
Pearl River Estuary**

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Based on the average sedimentation rate of $1.90 \pm 1.16 \text{ cm yr}^{-1}$ (Fig. 7) and the average sediment dry density of $0.79 \pm 0.13 \text{ g cm}^{-3}$ from the literature (Lin et al., 1998), we can estimate the sediment deposition flux as $1.51 \pm 0.95 \text{ g cm}^{-2} \text{ yr}^{-1}$. The average organic concentration of the Lindingyang Bay was $1.00 \pm 0.22\%$. The organic matter sedimentary flux in the bay was calculated as $15.1 \pm 9.4 \text{ mg C cm}^{-2} \text{ yr}^{-1}$. The surface area of Lindingyang Bay is $\sim 1600 \text{ km}^2$ (digitization from the navigation map, 2005 version), and thus the sediment accumulation in this area was estimated as $2.41 \pm 1.51 \times 10^{13} \text{ g yr}^{-1}$, while the organic matter accumulation was estimated as $2.41 \pm 1.51 \times 10^{11} \text{ g yr}^{-1}$. TrOC accounted for $57 \pm 13\%$ of the TOC in this area, thus the TrOC accumulation in Lindingyang Bay should be $1.37 \pm 0.92 \times 10^{11} \text{ g yr}^{-1}$.

Long term average river transport of suspended substances to Lindingyang Bay is estimated as $3.39 \times 10^{13} \text{ g yr}^{-1}$, most of which occurs during the flood season (Zhao, 1990). The particle organic content of the lower Pearl River is $1.09 \pm 0.29\%$ ($n=5$) during the flood season, which is similar to that of Amazon River suspended particulate substances (1.01 for the coarse particle, and 1.19 for the fine particle) (Hedges et al., 1986). As a result, the terrestrial POC transported to Lindingyang Bay was $\sim 3.70 \times 10^{11} \text{ g yr}^{-1}$. So the accumulation of TrOC in the bay only accounted for $37 \pm 25\%$ of the total POC loads, whereas sediment deposition accounted for $\sim 71\%$ of the suspended substances transported to the bay. The accumulation efficiency of TrOC was around half of the sediment burial efficiency in the bay. A low burial efficiency of riverine POC is also found in the Amazon Delta ($\sim 25\%$), Columbia and Fly ($< 50\%$) deltaic systems (Keil et al., 1997). Moreover Keil et al. (1997) find that the loss of TrOC occurs in all size fractions, indicating that physical sorting of organic-rich fine particles to distal sites would not be a reasonable explanation for the carbon deficit. In our study, this low accumulation efficiency of TrOC along with the absolute TOC content of sediment declined seaward and the portion of TrOC decreased offshore indicating that riverine POC is likely to have undergone a significant degradation and replacement during transportation throughout the Pearl River Estuary. This high degradation of TrOC was also reflected in the molecular-level identification of the carbohydrate composition of

the same sediments.

5 Conclusions

The combination of elemental and isotope composition analysis showed that the terrigenous organic carbon fraction contributed $57\pm 13\%$ of the TOC accumulation in Lingdingyang Bay. The portion decreased gradually to $19\pm 2\%$ on the inner shelf and to $4.3\pm 0.5\%$ on the outer shelf.

Monosaccharide composition and ratios indicated that the organic matter in the sediments from the Pearl River Estuary and SCS shelf was derived from bacteria, phytoplankton and terrestrial material. The impact of terrestrial material, however, was more evident for the estuarine sediments than for the shelf sediments. The TNS yields along with the relative abundance of neutral monosaccharides suggested that these compounds undergo intensive degradation before settling.

A preliminary sediment budget based on calculated regional accumulation rates showed that only $37\pm 25\%$ of terrestrial POC was accumulated in Lingdingyang Bay. In contrast to the $\sim 71\%$ sediment burial efficiency, this markedly lower accumulation efficiency of terrestrial organic matter suggested again that the terrestrial POC undergoes a significant degradation and replacement during transportation throughout the Pearl River Estuary.

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BGD

7, 2889–2926, 2010

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

References

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BGD

7, 2889–2926, 2010

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Sources and
accumulation of
organic carbon in the
Pearl River Estuary**

B. He et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Hedges, J. I. and Oades, J. M.: Comparative organic geochemistries of soils and marine sediments, *Organic Geochemistry*, 27, 319–361, 1997.
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**Sources and
accumulation of
organic carbon in the
Pearl River Estuary**

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Sources and
accumulation of
organic carbon in the
Pearl River Estuary**

B. He et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Sources and accumulation of organic carbon in the Pearl River EstuaryB. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Organic geochemical data for surface sediments in the upper reach of the Pearl River Estuary, Lingdingyang Bay and the SCS shelf.

Stations	Sampling date	Location		TOC (%)	TN (%)	Atomic C/N	$\delta^{13}\text{C}$ (‰)	f_t (%)
		Latitude	Longitude					
Upper Reach								
R01	Jan 2005	23.115	113.219	4.41	0.23	22.4	−24.89	
R02	Jan 2005	23.086	113.434	0.95	0.08	13.9	−26.05	
R03	Jan 2005	23.058	113.492	1.97	0.18	12.9	−25.54	
R04	Jan 2005	23.042	113.514	0.95	0.07	15.8	−24.33	
R05	Jan 2005	23.050	113.525	0.60	0.06	11.7	−23.05	
R06	Nov 2008	22.905	113.558	1.34	0.13	11.8	−25.49	
R07	Jan 2005	22.943	113.614	1.52	0.13	13.6	−25.39	
R08	Jan 2005	22.891	113.573	1.14	0.10	13.3	−24.56	
Mean±sd				1.61±1.20	0.12±0.06	14.4±3.5	−24.91±0.94	
Outer Shelf								
Sta. 5	Nov 2002	21.002	114.990	0.54	0.1	6.6	−21.28	4.6
Sta. 5A	Nov 2002	21.258	114.747	0.62	0.11	6.5	−21.44	3.9
mean±sd				0.58±0.06	0.10±0.01	6.5±0.09	−21.36±0.11	4.3±0.5
Inner Shelf								
Sta. 6A-1	May 2001	21.798	114.205	0.66	0.11	8.4	−21.52	22
Sta. 6A-2	Nov 2002	21.801	114.208	0.91	0.13	8.1	−21.44	19
Sta. 7-1	May 2001	22.000	113.996	0.79	0.13	6.9	n.a.	n.d
Sta. 7-2	Nov 2002	22.001	113.995	0.84	0.12	7.9	−21.49	17
mean±sd				0.80±0.10	0.12±0.01	7.8±0.6	−21.48±0.04	19±2
Lingdingyang Bay								
Sta. 7A	May 2001	22.170	113.852	0.67	0.07	10.8	−22.26	50
Sta. 8-1	May 2001	22.228	113.797	0.67	0.06	13.0	−23.56	77
Sta. 8-2	Nov 2002	22.264	113.785	0.84	0.08	11.9	−23.09	63
Sta. 12	May 2001	22.423	113.876	0.86	0.12	8.4	−24.91	35
Sta. 14	Nov 2002	22.365	113.637	1.32	0.15	10.5	−23.48	51
Sta. 18	Nov 2002	22.432	113.674	1.11	0.13	9.7	−25.11	50
Sta. 15	May 2001	22.555	113.721	1.24	0.12	12.3	−24.99	78
Sta. 21	Nov 2002	22.510	113.737	0.93	0.10	10.7	−23.27	52
Sta. 30	Nov 2002	22.572	113.699	1.12	0.12	11.4	−23.41	60
Sta. 29	Nov 2002	22.752	113.639	1.26	0.14	10.4	−24.47	55
mean±sd				1.00±0.22	0.11± 0.03	10.9±1.3	−23.86±0.96	57±13

f_t = the fraction of terrigenous organic matter; n.a.= no analysis

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Table 2. Monosaccharide yields from surface sediment using different hydrolytic procedures.

Methods	Monosaccharide yields (mg g ⁻¹ dsw ^a)								
	LYX	ARA	RIB	FUC	RHA	XYL	MAN	GAL	GLU
H ₂ SO ₄ method ^b	3.5±0.7	39.6±6.5	7.8±0.7	66.7±4.4	75.1±4.1	39.5±0.5	58.7±0.8	128.1±12.0	117.1±10.2
TFA method ^c	4.5±0.4	47.0±4.0	22.5±3.1	61.2±0.02	72.2±0.6	62.8±3.8	75.8±7.3	145.6±4.8	139.1±4.0

^a dsw = dry sediment weight

^b H₂SO₄ method: samples are treated with 12 mol L⁻¹ sulfuric acid in room temperature for 3 h, after which the acid is diluted to 1.2 mol L⁻¹ and heated in a boiling water bath with stirring (Cowie and Hedges, 1984b).

^c TFA method: samples are treated with 4 mol L⁻¹ TFA and heated in a 105 °C oil bath with stirring. Surface sediments from Sta. 7-1 are used for the method testing, and the results are expressed as the mean±sd (n=5).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

Table 3. TCHO and TNS yields, neutral sugar compositions and relative abundances in the selected riverine, estuarine and SCS shelf sediments.

Site	Monosaccharide composition (wt %)								TCHO	TNS	TNS/TCHO	Relative abundance				
	LYX	ARA	RIB	FUC	RHA	XYL	MAN	GAL	GLU	mg (100 mg OC) ⁻¹	(%)	GAL+MAN/FUC+RHA	FUC+RHA/XYL+ARA	GLU/RIB		
Upper Reach	R01	0.81	9.6	2.0	7.6	15.3	11.0	10.6	15.9	27.2	10.3	4.8	46.6	1.2	1.1	13.7
	R02	0.68	2.6	n.d.	9.6	33.7	1.7	6.0	9.4	36.3	23.3	4.3	18.6	0.4	10.0	
	R03	0.82	8.4	1.4	7.3	13.7	11.6	16.0	16.2	24.8	19.2	9.2	48.1	1.5	1.1	18.1
	R04	0.65	10.1	3.1	9.0	9.93	7.9	12.0	17.9	29.4	21.4	10.8	50.7	1.6	1.1	9.4
	R05	0.90	5.5	1.1	5.9	14.3	8.1	14.7	11.7	37.8	26.5	8.2	30.8	1.3	1.5	35.0
	R06	0.91	7.7	2.7	8.2	20.7	6.7	13.8	12.9	26.5	23.3	8.1	34.9	0.9	2.0	9.9
	R07	0.71	10.1	1.5	7.6	14.6	10.9	13.7	18.1	22.7	20.1	9.7	48.2	1.4	1.1	15.7
Outer Shelf	Sta.5	0.71	4.8	4.8	3.9	24	9.7	12.3	21.4	18.5	24.3	8.9	36.6	1.2	1.9	3.9
Inner Shelf	Sta.6A-1	0.65	8.4	3.7	7.7	10.3	10.9	12.4	24.4	21.7	26.2	13.5	51.4	2.0	0.9	5.8
	Sta. 7-1	0.87	5.9	4.3	7.8	11.8	10.3	12.0	24.5	22.6	26.7	8.4	31.3	1.9	1.2	5.2
Lingdingyang Bay	Sta. 7A	0.70	7.6	3.3	5.8	14.8	7.2	10.0	12.8	37.8	22.4	4.0	18.0	1.1	1.4	11.5
	Sta. 8-1	1.03	17.7	1.2	5.9	20.9	15.2	4.6	9.3	24.3	22.1	4.0	18.2	0.5	0.8	20.9
	Sta. 15	0.71	10.0	3.3	4.3	11.8	9.8	13.1	17.4	29.7	25.2	7.9	31.4	1.9	0.8	9.0
	Sta. 30	0.77	11.6	2.9	5.2	11.2	11	13.3	16.4	27.6	23.2	18.6	80.0	1.8	0.7	9.7

n.d.= non detectable

LYX = lyxose; ARA = arabinose; RIB = ribose; FUC = fucose; RHA = rhamnose; XYL = xylose; MAN = mannose; GAL = galactose; GLU = glucose.

Contents of total neutral sugar (TNS) are calculated by summing all neutral monosaccharide contents and normalized to organic carbon. Values of individual neutral monosaccharides are expressed as weight percentage related to the TNS. Total carbohydrate (TCHO) yields reported here are determined by phenol-sulfuric acid and quantified based on standard curves constructed from glucose standards and presented in units of mg carbohydrate (100 mg OC)⁻¹.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

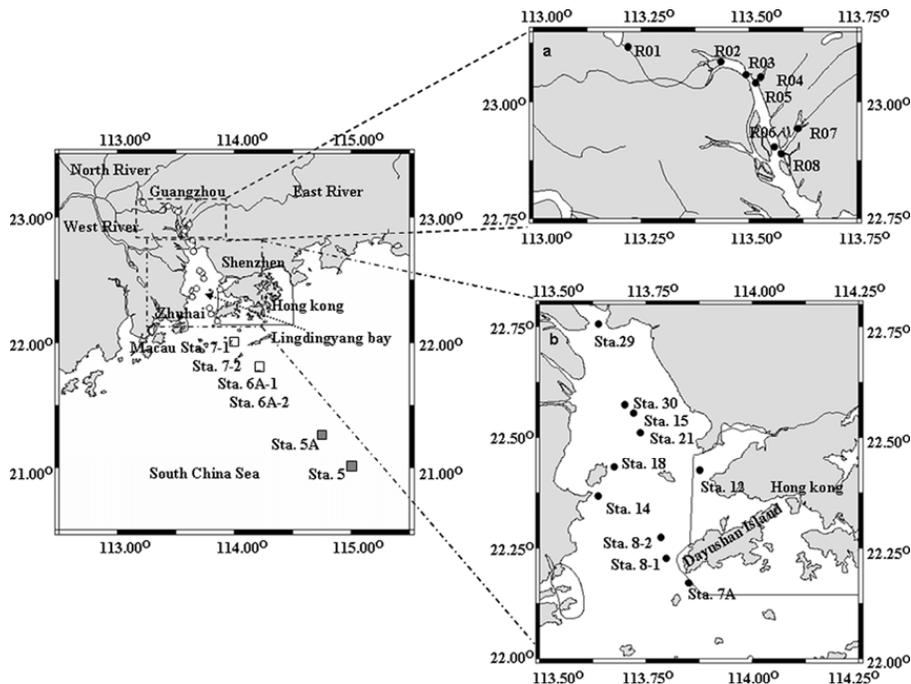


Fig. 1. Map of the Pearl River Estuary and South China Sea (SCS) shelf showing sampling stations: **(a)** in the upper reach (freshwater part) of the Pearl River Estuary; **(b)** in Lingdingyang Bay. The SCS shelf is defined as inner shelf (open squares) and outer shelf (closed squares) for convenient discussion in this study.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

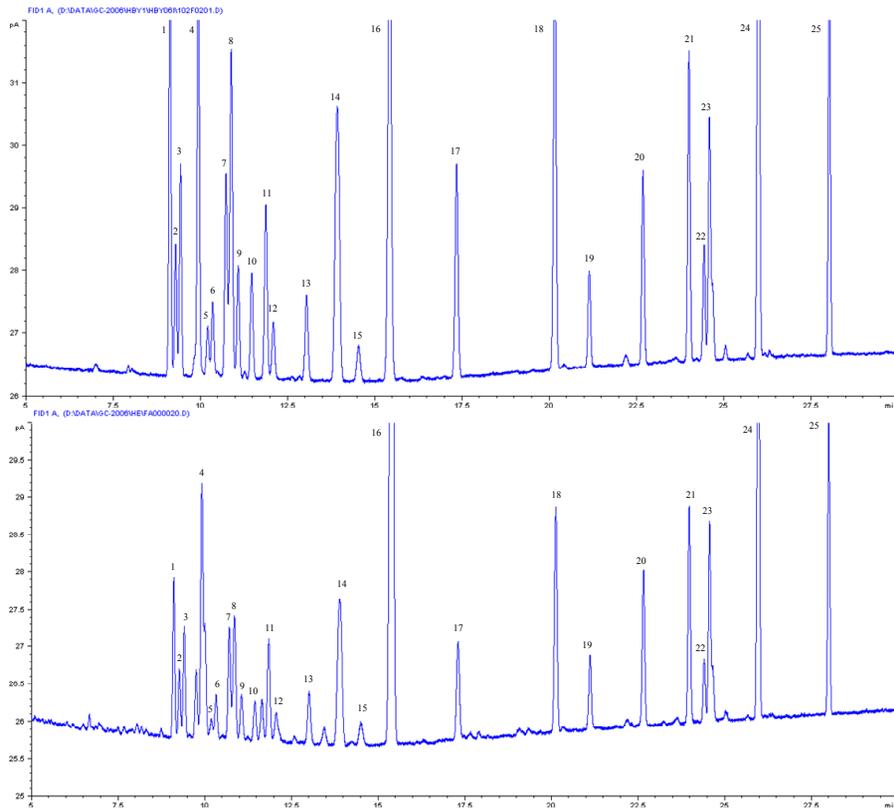


Fig. 2. Gas chromatograms of TMS derivatives of monosaccharides. **(a)** a standard mixture; **(b)** a hydrolysate from the Pearl River Estuary sediment. Twenty five peaks are identified, and the peaks with “*” are isomers used for quantification: 1. LYX1*; 2. ARA1; 3. ARA2*; 4. LYX2, RHA1, XYL1; 5. RIB1; 6. FUC1; 7. ARA3; 8. RIB2, LYX3; 9. LYX4; 10. RIB3*; 11. FUC2*; 12. ARA4; 13. RHA2*; 14. XYL2, FUC3; 15. FUC4; 16. Adonitol; 17. XYL3*; 18. MAN1*; 19. GAL1; 20. GAL2*; 21. GLU1; 22. MAN2; 23. GAL3; 24. Sorbitol; 25. GLU2*.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

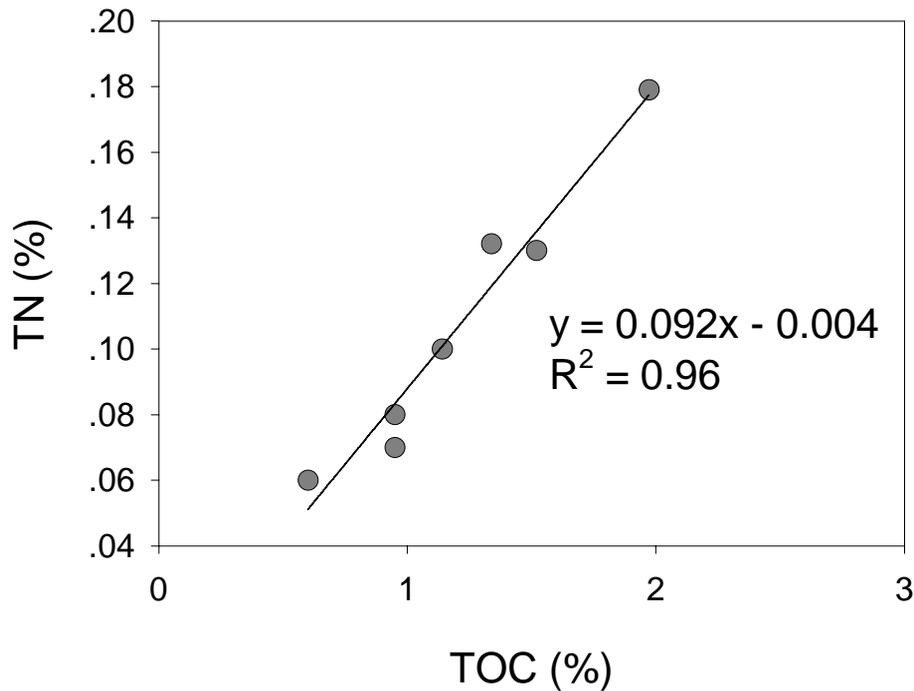


Fig. 3. The scatter plot of total organic carbon and nitrogen content in sediments from the upper reach (freshwater part) of the Pearl River Estuary. The line represents the regression function.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

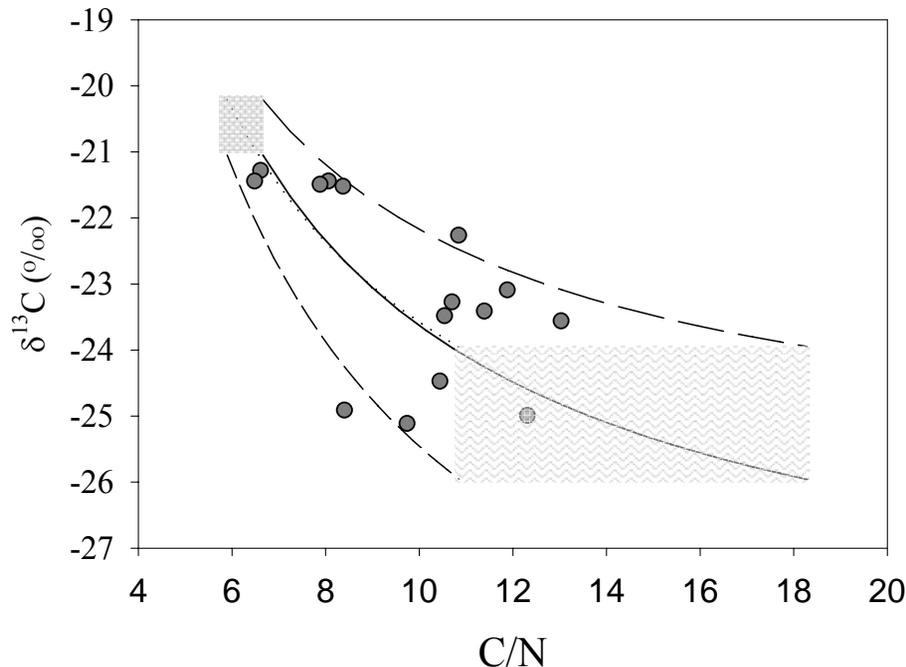


Fig. 4. Scatter plot of the $\delta^{13}\text{C}$ value of organic carbon in the Pearl River Estuary and SCS shelf versus C/N ratio. The curves represent mixing between a terrigenous end-member ($\delta^{13}\text{C} = -24.91 \pm 0.94\text{‰}$, $\text{C/N} = 14.4 \pm 3.5$, down-right shadow) and marine end-members ($\delta^{13}\text{C} = -20.64 \pm 0.42\text{‰}$, $\text{C/N} = 6.5 \pm 0.1$, up-left shadow). Sediments from the upper reach (freshwater part) of the estuary served as the terrigenous end-member, while sediments from the west Pacific served as the marine end-member (see text). Organic carbon isotope compositions ($\delta^{13}\text{C}$), elemental compositions, and C/N ratios of both end-members are listed in Table 1.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

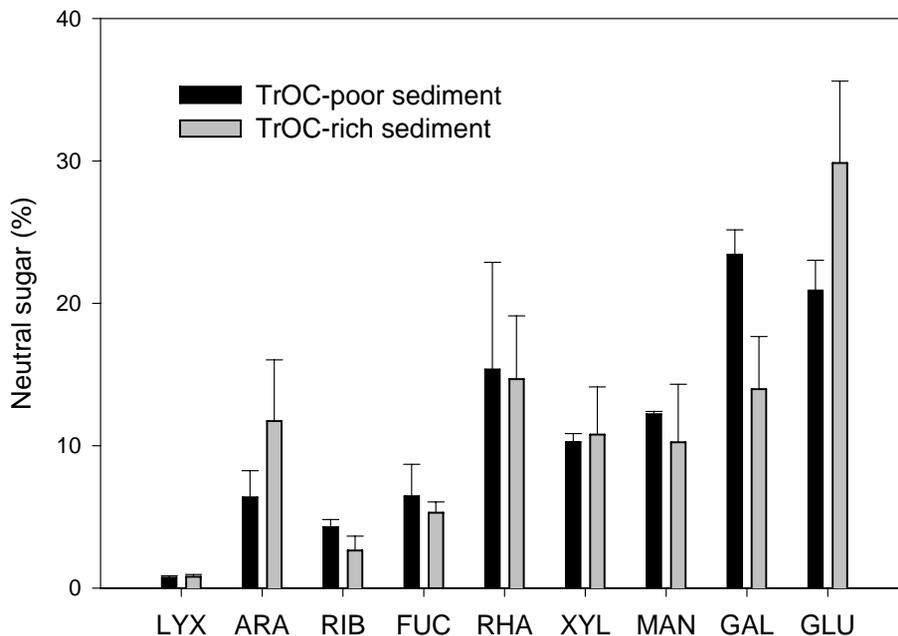


Fig. 5. Average neutral sugar composition (wt %) of surface sediments from Lingdingyang Bay rich in terrestrial organic carbon ($\geq 50\%$) and from SCS shelf poor in terrestrial organic carbon ($\leq 25\%$). The distinction between TrOC-rich and TrOC-poor is explained in the text. Error bars represent the standard deviation.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

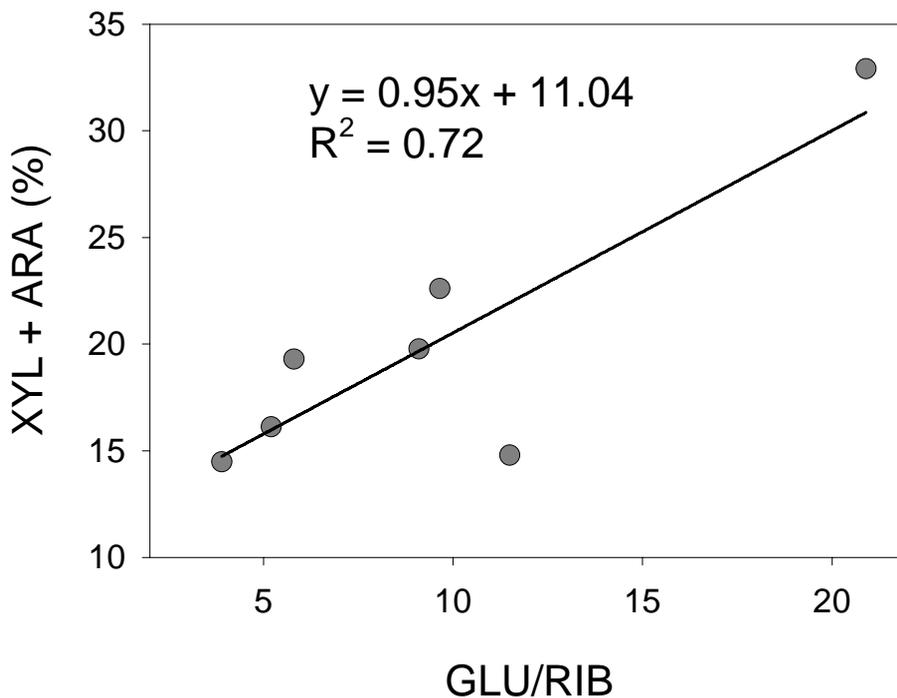


Fig. 6. wt % (xylose + arabinose) versus glucose/ribose ratio in the surface sediments from Lingdingyang Bay and the SCS shelf. The line represents the regression function.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Sources and accumulation of organic carbon in the Pearl River Estuary

B. He et al.

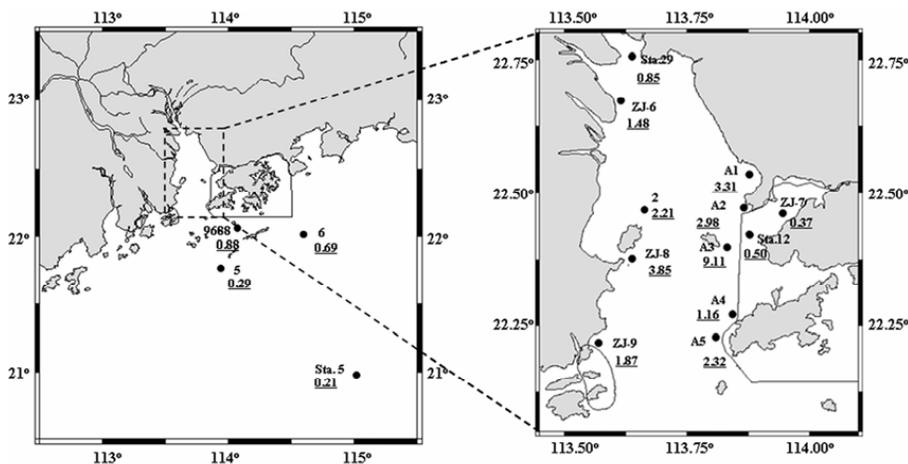


Fig. 7. The spatial distribution of ^{210}Pb sedimentary rates (the underlined data, in the unit cm yr^{-1}) in Lingdingyang Bay and the SCS shelf. ZJ-6, ZJ-7, ZJ-8, and ZJ-9 are after Lin et al. (1998); A1, A2, A3, A4, A5 are after Chen (1992); 2, 5 and 6 are after Zhang et al., (2009); 9688 is after Zhang et al. (1998); and data of Sta. 29, Sta. 12 and Sta. 5 are from this study.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion