Sources, distributions, and early diagenesis of sedimentary organic matter in the Pearl River region of the South China Sea

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ABSTRACT

Suspended particles from the Pearl River, and surface sediments from the northern South China Sea (NSCS) were analyzed for elemental composition (C, N), stable carbon isotopic composition (δ^{13}C), lignin phenols, and total hydrolyzable amino acids (THAA). Organic matter (OM) in riverine particles was depleted in ^{13}C (avg. −28.3‰) and was derived primarily from plankton and soils, with minor contributions from C3 plant material. The δ^{13}C of sedimentary OM became increasingly enriched in ^{13}C (avg. −21.3‰) from the inner shelf to the slope of the NSCS, and C/N ratios decreased from the inner shelf to the slope, indicating increasing contributions of marine organic carbon (OC). Lignin phenol yields in sedimentary OM decreased from the inner shelf to the slope, indicating declining contributions of terrestrial OC. Lignin phenol compositions in riverine particles and marine sediments reflected a predominately angiosperm source. Degradation indices (DI) of sedimentary amino acids indicated increasing diagenetic alteration of marine OM with water depth and distance offshore. Increasing acid:aldehyde ratios (Ad/Al) in lignin phenols and 3,5-dihydroxybenzoic acid:vanillyl phenols (3,5-BD/V) ratios also indicated a seaward increase in the diagenetic state of terrestrial OM, presumably due to hydrodynamic sorting and biogeochemical processing. A three end-member mixing model based on lignin phenol yields and stable C isotopic compositions was used to distinguish sources of OM. Marine OM accounted for an increasing fraction (62–82%) of sedimentary OC from the inner shelf to the slope, whereas soil-derived OM accounted for a decreasing fraction (39–18%) of sedimentary OC from inner shelf to the slope. The contribution of C3 plant OM was negligible. The significant contributions of terrestrial OM in NSCS sediments are ascribed to the relatively refractory nature of soil OM and the bioavailable nature of marine OM.

1. Introduction

Ocean margins are the repository for ~90% of the organic carbon (OC) buried in marine sediments (Hedges and Keil, 1995). A considerable fraction of this sedimentary OC is derived from the terrestrial environment and is mainly delivered to margins via river runoff (Bianchi et al., 2009; Gordon and Goñi, 2003, 2004; Hedges et al., 1997), coastal erosion (Kuzyk et al., 2008), and aeolian transport (Keil et al., 1998; Sun et al., 1999). These allochthonous sources of organic matter (OM) are widely dispersed and mixed with marine OM (Miltner and Emeis, 2001), resulting in heterogeneous distributions of OM in marine sediments. Primary production in ocean margins provides a much greater source of OM to sediments than riverine transport (Hedges et al., 1997), but marine OM is much more efficiently remineralized than

terrestrial OM. Hence, a significant fraction (~33%) of terrestrial OM discharged from rivers is deposited in marine sediments (Burdige, 2005). Identifying the source and diagenetic history of OM in margin sediments is critical for understanding the roles of ocean margins in the global carbon cycle.

The origins and diagenetic state of OM buried in marine sediments have been investigated using various techniques, including bulk parameters (e.g., C/N ratios and stable carbon isotopic compositions) and organic biomarkers (e.g., lignin phenols and alkanes). Specifically, stable carbon isotopic ratios and C/N ratios are frequently used to distinguish terrestrial and marine sources of sedimentary OM (Bianchi et al., 2002; Gordon and Goñi, 2003; Hu et al., 2006; Yu et al., 2010). Biomarkers derived from terrestrial plants, marine plankton, and bacteria can provide more specific and complementary data for tracing the origins of OM. For example, lignin phenols are very useful tracers of terrestrial OM because they are derived exclusively from vascular plants, and lignin-derived parameters, such as the ratio of syringyl-to-vanillyl phenols (S/V), cinnamyl-to-vanillyl phenols (C/V), and acid to aldehyde (Ad/Al) of vanillyl and syringyl phenols, are indicative of terrestrial plant sources and the extent of diagenetic alterations (e.g., Hedges and

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Mann, 1979; Opsahl and Benner, 1995). Total hydrolyzable amino acid content and composition can also provide insights about OM sources and diagenetic alterations (Cowie et al., 1992; Dauwe and Middelburg, 1998; Kaiser and Benner, 2008; Keil et al., 2000). In addition, some amino acids, such as the D-enantiomers of alanine, glutamic, and aspartic acid, and diaminopimelic acid (DAPA), provide information regarding bacterial sources (Kaiser and Benner, 2008; Lomstein et al., 2009).

The northern South China Sea (NSCS) is characterized by a relatively broad shelf that receives discharge from the Pearl River, the second largest river in China in terms of annual runoff flux (Higginson et al., 2003). Terrestrial OM is a notable component of sedimentary OM in the Pearl River estuary and its western coast (He et al., 2010; Hu et al., 2006; Yang et al., 2011; Yu et al., 2010; Zhang et al., 2009), but concentrations of terrestrial OM decline rapidly across the shelf (Hu et al., 2006). These surveys provide valuable insights about carbon cycling in the Pearl River estuary and adjacent shelf region, but the distributions and fates of terrestrial OM as well as marine OM in the sediments of the NSCS remain poorly characterized. In the present study, we used multiple tracers of terrestrial and marine OM and a three endmember mixing model to further investigate the sources and diagenetic transformations of sedimentary OM in the NSCS.

2. Material and methods

2.1. Study area

The South China Sea is the second largest marginal sea in the world. The deep central basin is bordered by two broad shelves, representing 52% of the SCS area (Higginson et al., 2003). The Pearl River discharges onto the northern shelf of the South China Sea (Hu et al., 2006). This river system is located in a tropical/subtropical region with warm temperatures, high rainfall, and elevated rates of biogeochemical processes (Ni et al., 2008; Ran et al., 2009). Agricultural land (C3 and C4 plants) and conifer-dominated forests (C3 plants) dominate in the lower drainage basin and grasses (mostly C4 plants) dominate the upper drainage basin (Sun et al., 1999). The Pearl River discharges ~80% of its annual water flux (~3.3×10^{11} m^3), and ~94% of its annual suspended sediment flux (~2.5×10^7 t) during flood periods between April and September (Higginson et al., 2003). The flux of particulate OC from the Pearl River is 9.2×10^5 t/year and accounts for ~0.1–0.2% of the total OC exported by the worldwide rivers (Ni et al., 2008). The Pearl River estuary retains ~80% of the river's suspended sediments during the wet season, with the remainder being delivered to the adjacent shelf and slope (Hu et al., 2006 and references therein).

Suspended riverine particulates are dispersed by a complex hydrodynamic system with a seasonally alternating East Asian monsoon as well as deep-water circulation (Fig. 1; e.g., Sun et al., 1999). Surface water circulates cyclonically during the northeast monsoon (from November to March) and anti-cyclonically during the southwest monsoon (from June to September; Zhao et al., 2009). The shelf water in the NSCS exchanges with the East China Sea via a coastal current, and the western Pacific Ocean water enters the South China Sea through the Luzon Strait and flows along the slope (Higginson et al., 2003). The Guangdong Coastal Current flows along the coastal margin to the southwest and results in a cyclonic circulation at Guangzhou Bay (Li et al., 2011). Thus, terrigenous materials exported from the Pearl River could be widely distributed across the shelf, although the dominant transport path is directed to the southwest part of the river estuary (Yu et al., 2010).

2.2. Sampling

Suspended particulate matter (SPM) was collected from the mainstream of the Pearl River and the Dongjiang River, a major tributary of the Pearl River, between December 2008 and July 2010 (Table 1). SPM was collected from six sampling sites. Two sites (JK and WLH) were located in reservoirs and the remainder (BL, SW, YZ, LHS) were located in areas with unrestricted river flow. There is a landfill near the JK station, which releases high concentrations OM. Surface water (0.5–1.0 m) was pumped into carboys (HDPE), and SPM was recovered from the water samples using a continuous-flow centrifuge in the laboratory, followed by freeze-drying.

Shelf and slope sediments were collected using a box core during two cruises in August 2008 during the South China Sea Open Cruise (R/V Shiyan 3; South China Sea Institute of Oceanography, Chinese Academy of Sciences) and in April 2010 during the Spring Cruise (National Natural Science Foundation of China). The sampling sites are categorized into three regions: inner shelf, outer shelf, and slope based on water depths of <50 m, 50–300 m, and >300 m, respectively (Fig. 1). Surface sediments (0–5 cm) were collected from the cores. Sediments
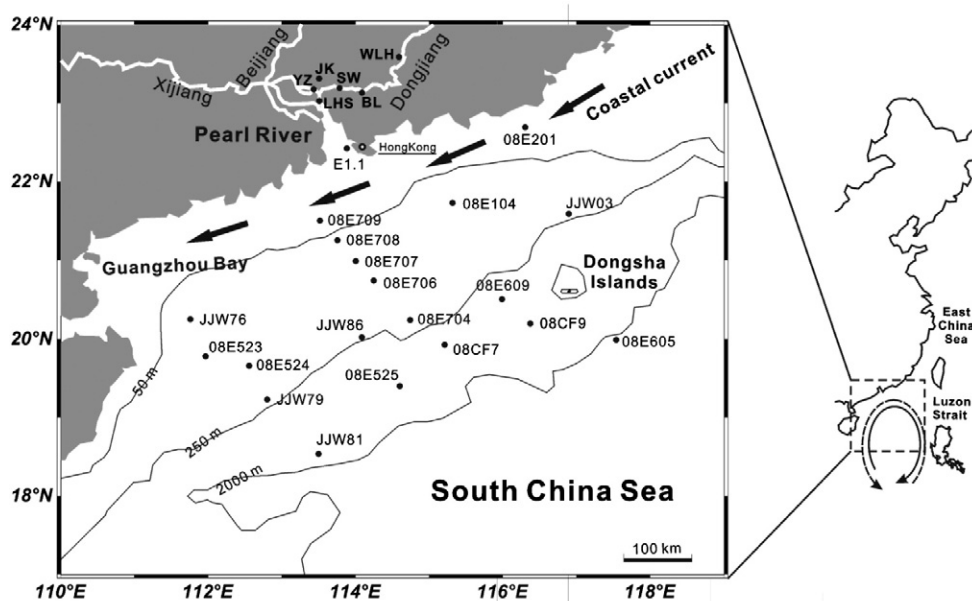

Fig. 1. Sample locations in the Pearl River system and the South China Sea. The solid and the dashed curves with arrows represent the surface circulation in the summer and winter, respectively.

Table 1
Sampling locations and bulk properties of suspended particles from the Pearl River and sedimentary organic matter in the South China Sea. n.a. = not available.

Location	Site	Date	Longitude	Latitude	Depth	SPM	TOC	TN	δ^{13}C	C/N
		(Year/month)	(N)	(E)	(m)	(mg/L)	(%)		(‰)	
Pearl River suspended	*Reservoir*									
particulate matter	WLH	2009/11	114°38′	23°44′	0.5–1	2.12	5.76	0.67	−28.3	10.0
	JK	2010/1	113°30′	23°15′	0.5–1	4.15	19.01	3.82	−36.9	5.8
	River									
	BL	2010/1	114°17′	23°9′	0.5–1	8.21	4.11	0.64	−30.9	7.5
	LHS1	2010/3	113°32′	22°58′	0.5–1	34.4	1.35	0.13	−26.3	12.1
	LHS2	2010/7	113°32′	22°58′	0.5–1	28.6	4.53	0.58	−29.0	9.1
	SW	2010/7	113°51′	23°7′	0.5–1	16.7	3.43	0.50	−28.6	8.0
	YZ1	2008/12	113°25′	23°6′	0.5–1	24.4	6.36	1.05	n.a.	7.1
	YZ2	2009/4	113°25′	23°6′	0.5–1	52.4	4.36	0.43	−26.7	11.8
South China Sea	*Inner shelf*									
sedimentary	E1.1	2010/12	113°45′	22°24′	17		0.90	0.10	n.a.	11.0
organic matter	08E201	2008/8	116°18′	22°41′	30		0.19	0.02	−21.8	10.3
	08E709	2008/8	113°30′	21°30′	43		0.83	0.11	−21.6	8.8
	Outer shelf									
	08E708	2008/8	113°45′	21°15′	63		0.57	0.07	−21.5	9.1
	08E707	2008/8	114°0′	21°0′	80		0.21	0.02	−21.4	10.8
	JJW76	2010/4	111°45′	20°15′	82		0.19	0.03	−21.4	9.0
	08E706	2008/8	114°15′	20°44′	84		0.51	0.07	−21.7	8.4
	08E523	2008/8	111°58′	19°46′	93		n.a.	n.a.	n.a.	n.a.
	08E104	2008/8	115°19′	21°43′	98		0.56	0.07	−21.1	8.8
	08E524	2008/8	112°33′	19°40′	144		0.36	0.05	−21.7	7.9
	08E704	2008/8	114°45′	20°15′	180		0.40	0.05	−21.3	9.1
	JJW86	2010/4	114°5′	20°1′	190		0.25	0.03	−21.3	9.7
	JJW79	2010/4	112°48′	19°14′	247		0.14	0.02	−21.6	10.3
	JJW3	2010/4	116°54′	21°35′	260		0.15	0.02	−21.8	9.0
	Slope									
	08E609	2008/8	115°59′	20°30′	562		0.38	0.05	n.a.	8.6
	08CF9	2008/8	116°23′	20°11′	937		0.55	0.09	−20.5	7.3
	08CF7	2008/8	115°13′	19°55′	1094		0.54	0.07	−20.7	8.7
	08E525	2008/8	114°36′	19°24′	1192		0.75	0.11	−20.9	7.9
	JJW81	2010/4	113°30′	18°32′	1394		0.66	0.10	−20.6	8.1
	08E605	2008/8	117°32′	19°59′	2379		n.a.	n.a.	n.a.	n.a.

were stored in a freezer (−20 °C) until they were freeze-dried in the laboratory. Subsamples of riverine particles and marine sediments were finely ground using mortar and pestle prior to analysis.

2.3. Elemental composition

Total organic carbon (TOC) and nitrogen (TN) were analyzed with a Vario EL III Elementar analyzer. Prior to analysis, riverine particles (10–20 mg) were treated with HCl vapor to remove carbonates and analyzed in silver boats. Vapor acidification was insufficient to remove carbonates from the sediments collected from the South China Sea (30–50% carbonate). The sediments were directly acidified (4 N HCl) and dried prior to analysis. All samples were analyzed in duplicate. The mean deviations of the duplicate samples for C and N were <0.05%. The relative mean deviations of replicate analyses (n = 4) of one sample for C and N are 0.56% and 0.45%, respectively.

2.4. Stable C isotopic composition

The stable carbon isotopic compositions of carbonate-free particles and sediments were measured using a Finnigan Delta Plus XL. Black carbon (Product ID: GBW04408) was employed as the reference standard and δ^{13}C values (‰) were converted relative to ^{13}C/^{12}C of Peedee belemnite. The precision of δ^{13}C based on replicate analyses was <0.2‰.

2.5. CuO oxidation

Lignin phenols and 3,5-dihydroxybenzoic acid were measured using the alkaline CuO oxidation method (Hedges et al., 1982) as modified by Kaiser and Benner (2012). Freeze-dried sediments were reacted with alkaline CuO under a nitrogen atmosphere in a sealed bomb at 155 °C for 3 h. An internal standard mixture of ethylvanillin and trans-

cinnamic acid was added to the reaction vessel after oxidation. The aqueous hydrolysates were separated from sediments by centrifugation, and the hydrolysates were acidified with sulfuric acid to pH 2 and extracted using solid phase extraction. The lignin oxidation products were eluted with a water/methanol (7/3) mixture followed by 1.5 ml of a dichloromethane/methyl acetate/pyridine (75/20/5) mixture and 1 ml of dry methanol. The combined eluates were dried under a gentle argon gas and dissolved in 500 μL of pyridine. Extracted samples were derivatized with bis(trimethylsilyl) trifluoroacetamide plus 1% trimethylchlorosilane and analyzed by gas chromatography and mass spectrometry using an Agilent 7890 GC and 5975C MS. External calibrations were preformed to quantify the following compounds: vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, *p*-coumaric acid, ferulic acid, *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid, and 3,5-dihydroxybenzoic acid. The precision for individual phenols was <10% for duplicate analyses. The concentrations of individual oxidation products were normalized to the TOC of the samples. The sums of vanillyl phenols (V; vanillin, acetovanillone, and vanillic acid), syringyl phenols (S; syringaldehyde, acetosyringone, and syringic acid), and cinnamyl phenols (C; *p*-coumaric acid and ferulic acid) were calculated.

2.6. Total hydrolyzable amino acids

Total hydrolyzable amino acids (THAA), including two non-protein amino acids and sixteen protein amino acids, were measured using a commercially-available kit (EZ:faast Amino Acid Analysis Kit; Phenomenex) for the purification of acid hydrolyzed samples. Briefly, the hydrolysis of samples was conducted in sealed ampoules with 6 N HCl at 110 °C for 20 h. Aqueous hydrolysates were separated from sediments by centrifugation, and the hydrolyzed amino acids were retained on a solid phase extraction (SPE) column. After rinsing with water,

amino acids were eluted with alkaline n-propanol, derivatized, and analyzed by gas chromatography with flame ionization detection (Agilent 6890). Each amino acid was quantified using an external calibration curve and an internal standard for verification. The precision for the analysis of duplicate samples was <10%.

The concentrations (μmol/g) and carbon-normalized yields (%OC) of THAA were calculated. In addition, we calculated the degradation index (DI) developed by Dauwe and Middelburg (1998) to investigate the dia-genetic alteration of amino acids in the particulate and the sedimentary samples. The DI values were calculated using the following equation:

$$DI = \sum_i \left[\frac{var_i - AVG\ var_i}{STD\ var_i} \right] \cdot fac.coef._i$$

where var is the mole percentage of individual amino acid, and AVG var, STD var and fac. coef. are the mean, the standard deviation and the factor coefficient from Dauwe et al. (1999). Arginine was not determined using the EZ:faast method. Assuming that the mole per-centage of arginine was 6.1% in all the cases to neutralize its effect in the calculations, the compositions of 13 protein amino acids (mol%) were reevaluated and standardized using the equation. A typical range of the mole percentage of arginine in marine sediments is from 3.3% to 5.1% (Dauwe and Middelburg, 1998). However, the item values using 6.1% did not cause significant changes in the DI value.

3. Results and discussion

3.1. Sources and diagenetic state of suspended particulate OM in the Pearl River

The average SPM concentration (21.4 ± 17.1 mg/L) in the Pearl River is significantly lower than in the Yangtze River (68 mg/L; Wu et al., 2007) and Mississippi River (152 mg/L; Kendall et al., 2001), whereas the average TOC concentration (3.7%; Table 1 and Fig. S1) for SPM (except for JK) in the Pearl River is higher than in the Yangtze River (1.1%; Wu et al., 2007) and Mississippi River (1.6%; Bianchi et al., 2007). Soils and plankton can be important sources of SPM in rivers (Hedges et al., 1997), and the TOC concentration in soil is much lower than in plankton (~30%; Cowie and Hedges, 1994). It is noted that the TOC concentration in the SPM of the Pearl River is higher than in the soils (2.1%; Yu et al., 2010) in the Pearl River catchment, probably indicating the occurrence of plankton-derived OM in SPM. Although plant debris with high TOC yields are also potential sources of SPM, this possibility can be ruled out by lignin compositions of SPM in the Pearl River (see the following discussion).

The δ¹³C values of the SPM in the Pearl River ranged from −36.9‰ to −26.3‰, with the lowest value observed in the JK reservoir sample (Table 1). Excluding JK, the average δ¹³C value (−28.3‰) is somewhat depleted in ¹³C compared to several other large rivers, such as Mississippi (−18.5‰ to −26.4‰; Onstad et al., 2000), Columbia (−27.9‰; Kendall et al., 2001), and Yangtze (−24.4‰; Wu et al., 2007). However, these δ¹³C values are comparable to that reported previously for the Pearl River (−28.7‰; Yu et al., 2010). Yu et al. (2010) investigated the stable carbon isotopic compositions of vegetation in the Pearl River catch-ment and reported that C4 plants have enriched δ¹³C (avg. −13.1‰) values compared to C3 plants (avg. −29.0‰) and SPM in the river (Fig. 2). Riverine plankton is also depleted in δ¹³C (avg. −30.0‰; Kendall et al., 2001) and has similar isotopic compositions as C3 vegeta-tion in the Pearl River catchment. Overall, the relatively depleted δ¹³C values of SPM in the Pearl River indicate a minor contribution of C4 plants. However, a relatively enriched δ¹³C of −24.1‰ for the soils indicates that ~30% of soil OC in the Pearl River catchment could be de-rived from C4 plants, which is consistent with the fact that agricultural plants, including sugarcane and corn, are dominant in the downstream catchment (Yu et al., 2010). Furthermore, the C/N ratios (5.8–12.1; Table 1) indicate particulate OM in the Pearl River is largely derived
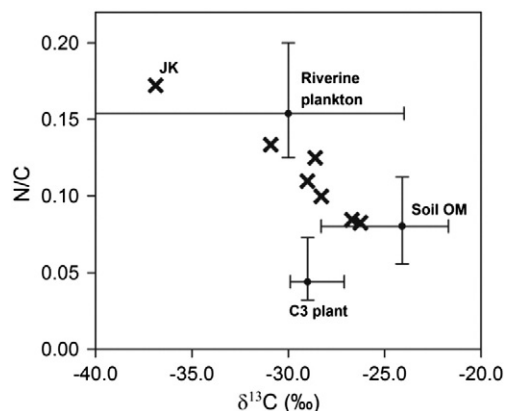

Fig. 2. Stable carbon isotopic compositions (δ¹³C) and elemental ratios (N/C) for suspended particulate matter in the Pearl River. The average compositions and ranges of three organic matter sources are shown: C3 plant material, soil organic matter, and riverine plankton (Kendall et al., 2001; Yu et al., 2010).

from both terrestrial OM (>8.0) and plankton (5.0–8.0). There is a significant correlation between δ¹³C values and N/C ratios ($R^2 = 0.92$) of riverine particles, indicating soil OM and riverine plankton are the major sources of SPM (Fig. 2).

Proteins are more bioreactive than bulk carbon in natural OM, so the fraction of OC as amino acids decreases with increasing decomposition, and THAA yields (%OC) serve as indicators of the diagenetic state of OM (Cowie et al., 1992; Cowie and Hedges, 1994; Davis et al., 2009). The THAA yields (OC%) of riverine SPM ranged from 22.6% to 37.4%

Table 2
Concentrations and carbon-normalized yields of total hydrolyzable amino acids (THAA), degradation indices, and carbon-normalized yields of diaminopimelic acid (DAPA) in suspended particles from the Pearl River and sedimentary organic matter in the South China Sea. n.a. = not available.

Location	Site	THAA		DI	DAPA
		(μmol/g)	(%OC)[a]		(nmol/mg OC)
Pearl River suspended particulate matter	*Reservoir*				
	WLH	256.0	22.6	0.0	4.2
	JK	1321.9	37.4	0.8	5.3
	River				
	BL	285.8	35.6	0.0	4.4
	LHS1	61.6	23.3	0.1	n.a.
	LHS2	247.6	28.2	0.1	4.2
	SW	156.5	22.7	−0.5	6.9
	YZ1	360.0	29.4	0.4	4.4
	YZ2	196.4	23.2	0.2	5.4
South China Sea sedimentary organic matter	*Inner shelf*				
	E1.1	16.4	9.2	−0.3	10.9
	08E201	5.2	13.9	−0.6	n.a.
	08E709	12.9	7.8	−0.2	21.3
	Outer shelf				
	08E708	7.9	7.9	2.0	9.7
	08E707	5.0	12.1	−0.4	13.1
	JJW76	5.6	14.2	−0.7	46.4
	08E706	5.1	4.9	−1.0	n.a.
	08E523	7.5	n.a.	−0.8	n.a.
	08E104	14.1	12.4	−0.8	10.7
	08E524	7.1	9.6	−0.9	19.8
	08E704	5.7	7.1	−0.3	19.9
	JJW86	4.4	8.7	−0.6	29.2
	JJW79	5.7	19.4	−0.2	140.9
	JJW3	3.8	11.8	−1.2	41.1
	Slope				
	08E609	12.8	16.8	−0.7	18.7
	08CF9	8.2	7.4	−1.0	10.8
	08CF7	9.8	8.9	−0.9	13.5
	08E525	13.1	8.3	−1.2	9.4
	JJW81	13.1	9.4	−1.3	14.6
	08E605	13.3	n.a.	−1.8	n.a.

[a] THAA (%OC) is percentage of OC presents as amino acids in sediment TOC.

and were only slightly lower than those (23.8–59.4%; avg. 38.1%) of fresh plankton (Table 2; Cowie et al., 1992; Kaiser and Benner, 2009). The high amino acid yields indicate riverine SPM is relatively fresh and has undergone minimal diagenetic alteration. The yields in higher plant leaves (2.6–2.8%; Jennerjahn and Ittekkot, 1997), soil (3.2%; Wang et al., 1991), and sediment (11.7–16.2%; Chen et al., 2003) in the Pearl River Delta are lower than those observed in SPM. The high THAA (OC%) yields indicate that plankton is an important source of SPM in the lower reach of the Pearl River. In addition, the plankton-derived SPM should be relatively bioavailable. The composition of amino acids also provides insights about the diagenetic state of OM and a degradation index (DI) has been developed for this purpose (Dauwe and Middelburg, 1998). The DI values decrease from positive values (1–1.5) for fresh phytoplankton to negative values (<− 1) for diagenetically-altered OM in deep sea sediments (Dauwe et al., 1999). The amino acid DI values for suspended particles in the Pearl River range from − 0.5 to 0.8 (avg. 0.1) and are generally indicative of minor to moderate alteration.

The carbon-normalized yields of lignin phenols (Λ_8) in riverine suspended particles ranged from 0.06 to 1.12 mg/100 mg OC (Table 3). The reservoir samples (WLH and JK) had low lignin yields, which are consistent with a substantial plankton component in these samples. Overall, the suspended particles in the Pearl River had lower lignin yields than in the Mississippi River (1.40 mg/100 mg OC; Bianchi et al., 2007), the Atchafalaya River (2.82 mg/100 mg OC; Gordon and Goñi, 2003), and several other North American rivers (1.33 mg/100 mg OC; Onstad et al., 2000). Elevated contributions of plankton-derived SPM due to high anthropogenic nutrient input could be responsible for the relatively low

C-normalized yields of lignin in this highly populated and developed region of the Pearl River (Hu and Li, 2009). The ratios of syringyl to vanillyl phenols (S/V) ranged from 0.72 to 1.22, reflecting the predominant contribution of angiosperm vegetation (Table 3; Supplementary data, Fig. S2).

The (Ad/Al)v and (Ad/Al)s ratios in suspended particles ranged from 0.37 to 0.75 and 0.35–0.59, respectively (Table 3). Elevated Ad/Al ratios (>0.4) are indicative of degraded OM material and are commonly observed in soil-derived OM (Gordon and Goñi, 2003). Based on Ad/Al ratios, it appears soil OM was present in SPM from the Pearl River. In addition, the CuO oxidation product, 3,5-dihydroxybenzoic acid (3,5-BD), accumulates in soils relative to vanillyl phenols, and elevated ratios of 3,5-BD/V (>0.1) provide additional evidence of soil-derived OM (Gordon and Goñi, 2003; Houel et al., 2006; Kuzyk et al., 2008; Louchouarn et al., 1997). The 3,5-BD/V ratios ranged from 0.06 to 1.12 in this investigation (Table 3), further indicating that soils were an important source of terrigenous OM in suspended particles.

Seasonal variability in the composition of particulate OM from the Pearl River could influence OM distributions and cycling in NSCS. However, sediment accumulation rates are 1.65 cm/year in the Pearl River estuary (Ye et al., 2012), and 0.29, 0.062, and 0.011 cm/year in the NSCS inner shelf, outer shelf, and slope (Zhao et al., 2009). This indicates that the buried OM in the 0 to 5 cm depth interval represents years to centuries of sediment accumulation, during which time physical processes and bioturbation will thoroughly mix the upper layers of the sediments. The C/N and lignin signatures are quite similar in the surface sediments from NSCS between the two cruises (Table S1), indicating seasonality in the Pearl River SPM composition does not appear to have a large influence on surface sediments from the NSCS.

Table 3
Carbon-normalized yields of lignin phenols and ratios of C/V, S/V, (Ad/Al)v, (Ad/Al)s and 3,5-BD/V in suspended particles from the Pearl River and sedimentary organic matter in the South China Sea. n.a. = not available.

Location	Site	V	S	C	Λ_8[a]	C/V	S/V	(Ad/Al)v[b]	(Ad/Al)s[b]	3,5-BD/V
		(mg/100 mg OC)								
Pearl River suspended particulate matter	*Reservoir*									
	WLH	0.02	0.02	0.03	0.06	1.43	0.93	0.61	0.35	0.42
	JK	0.02	0.03	0.03	0.07	1.12	1.19	0.75	0.57	1.12
	River									
	BL	0.12	0.15	0.10	0.38	0.84	1.22	0.74	0.59	0.19
	LHS1	0.48	0.48	0.16	1.12	0.33	1.00	0.50	0.46	0.11
	LHS2	0.40	0.32	0.11	0.84	0.27	0.80	0.42	0.40	0.06
	SW	0.20	0.23	0.11	0.54	0.55	1.13	0.66	0.54	0.17
	YZ1	0.39	0.28	0.10	0.77	0.25	0.72	0.48	0.47	0.11
	YZ2	0.38	0.31	0.13	0.83	0.35	0.81	0.37	0.37	0.06
South China Sea sedimentary organic matter	*Inner shelf*									
	E1.1	0.52	0.47	0.14	1.12	0.27	0.90	0.44	0.39	0.08
	08E201	0.17	0.12	0.03	0.32	0.17	0.69	0.44	0.38	0.13
	08E709	0.09	0.07	0.03	0.19	0.37	0.79	0.45	0.41	0.12
	Outer shelf									
	08E708	0.09	0.06	0.04	0.19	0.40	0.70	0.59	0.53	0.14
	08E707	0.03	0.02	0.02	0.07	0.52	0.55	0.61	0.45	0.58
	JJW76	0.07	0.04	0.02	0.13	0.36	0.63	0.59	0.50	0.35
	08E706	0.02	0.01	0.01	0.03	0.33	0.73	0.81	0.60	0.68
	08E523	n.a.	n.a.	n.a.	n.a.	0.37	0.63	0.77	0.49	1.10
	08E104	0.09	0.05	0.03	0.16	0.31	0.58	0.58	0.51	0.23
	08E524	0.13	0.08	0.02	0.23	0.13	0.66	0.58	0.51	0.28
	08E704	0.07	0.05	0.02	0.13	0.24	0.81	0.73	0.60	0.36
	JJW86	0.02	0.02	0.01	0.04	0.36	0.73	1.04	0.54	1.38
	JJW79	0.07	0.05	0.02	0.14	0.34	0.69	0.69	0.49	0.58
	JJW3	0.08	0.05	0.01	0.14	0.14	0.70	0.49	0.41	0.28
	Slope									
	08E609	0.18	0.12	0.03	0.33	0.16	0.64	0.68	0.59	0.37
	08CF9	0.04	0.03	0.01	0.08	0.38	0.90	0.76	0.54	0.65
	08CF7	0.03	0.02	0.01	0.07	0.49	0.78	0.93	0.65	0.68
	08E525	0.02	0.02	0.02	0.06	1.01	0.87	0.96	0.71	0.99
	JJW81	0.02	0.02	0.02	0.05	0.96	0.86	1.17	0.61	1.23
	08E605	n.a.	n.a.	n.a.	n.a.	0.58	0.94	1.01	0.66	0.70

[a] V, S, and C are yields of total vanillyl, total syringyl, and total cinnamyl phenols, respectively.

[b] Λ_8 = V + S + C; (Ad/Al)v and (Ad/Al)s are the ratios of acid to aldehyde of vanillic and syringic phenols, respectively.

3.2. Sources of sedimentary OM in the NSCS

Total organic carbon (TOC) concentrations were <1.0% in sediments throughout the NSCS, with relatively elevated values occurring on the inner shelf and slope (Table 1). A linear regression of TN versus TOC in sediments had an intercept of zero, indicating sedimentary nitrogen is predominantly of organic origin (Supplementary data, Fig. S1). The C/N ratio in sedimentary OM ranged from 7.3 to 11.0, which is within the range of values in SPM from the Pearl River (Table 1). The C/N ratios decreased with increasing water depth, suggesting an increasing contribution of marine OM in outer shelf and slope sediments (Fig. 3A).

The stable carbon isotopic composition of sedimentary OM ranged from −21.8‰ to −20.5‰ (avg. −21.3‰) and indicated a predominantly marine origin (Fig. 3B; Tesi et al., 2007). The $\delta^{13}C$ values gradually became more enriched in ^{13}C from the inner shelf (−21.7‰) to the outer shelf (−21.5‰) and slope (−20.7‰). This pattern was consistent with declining C/N ratios along this gradient, further supporting the increasing contributions of marine OM offshore. Goñi et al. (1998) and Gordon and Goñi (2003) observed a similar enrichment of $\delta^{13}C$ values in northern Gulf of Mexico sediments. They attributed this trend, in part, to an increasing contribution of C4 grass-derived soil OM from the Mississippi River drainage basin. Soils in the Pearl River drainage basin have an average $\delta^{13}C$ composition of −24.1‰ (Yu et al., 2010), indicating a potential contribution of C4-derived OM to sediments in the NSCS margin.
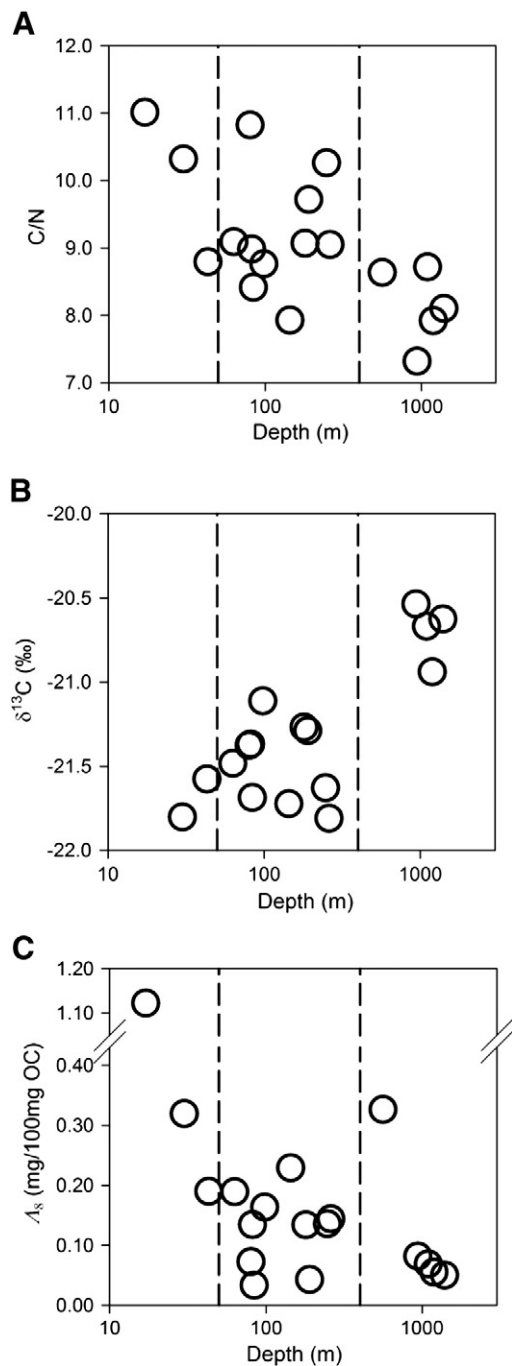
Lignin yields ranged from 0.03 to 1.12 mg/100 mg OC and generally decreased from the inner shelf to the slope (Fig. 3C). Yields in NSCS sediments were generally lower than those in other marginal sediments (e.g., Prahl et al., 1994; Requejo et al., 1991; Sánchez-García et al., 2009). The NSCS shelf is relatively broad (250 km), resulting in extensive remobilization and decomposition before burial (Blair and Aller, 2012; Burdige, 2005). The highest lignin yield (1.12 mg/100 mg OC) was found in the Pearl River estuary. Declining lignin yields across the shelf most likely result from biodegradation and hydrodynamic sorting. The latter process can lead to the retention of coarse plant debris in the delta and estuary, and the preferential delivery of fine soil OM to offshore sediments (Keil et al., 1998). An apparent exception to this trend is observed at slope station 08E609, which had an elevated lignin yield (0.33 mg/100 mg OC). Terrigenous input from the nearby Dongsha Islands could be responsible for the elevated lignin yield at station 08E609. As with SPM samples from the Pearl River, the S/V ratios (0.55–0.94) indicate a predominant angiosperm source of lignin in NSCS sediments (Supplementary data, Fig. S2).
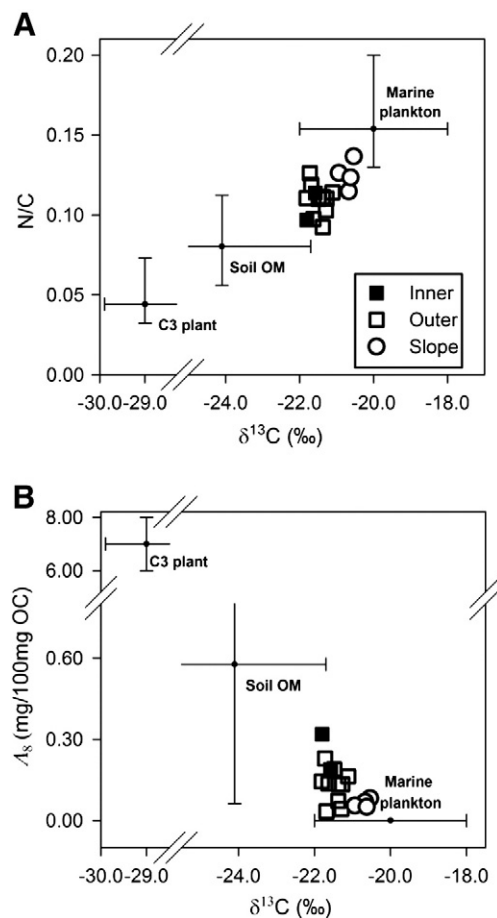

Fig. 3. Depth distributions of C/N ratios, stable carbon isotopic compositions, and carbon-normalized lignin concentrations (Λ_8) in marine sediments. The inner shelf, outer shelf, and slope sediments are separated by two dashed lines.

Fig. 4. Atomic N/C ratios (A) and carbon-normalized lignin yields (Λ_8) (B) vs. stable carbon isotope compositions ($\delta^{13}C$) for marine sediments and sources. The average compositions and ranges of the sources are based on Yu et al., 2010; Tesi et al., 2007; and this study.

No consistent pattern in C/V ratios occurred from the shelf to the slope (Supplementary data, Fig. S2), which is similar to patterns observed in sediments of the Washington margin (Hedges and Mann, 1979) and the Gulf of Mexico (Gordon and Goñi, 2004). The occurrence of C phenols is indicative of the contribution of herbaceous plant material (Hedges and Mann, 1979). The most likely explanation for the variable pattern of C/V ratios in NSCS sediments is that OM source, hydrodynamic sorting and biodegradation all play a role in shaping the observed distributions.

DAPA is a unique amino acid that is found in the cell wall polymer, peptidoglycan, of Gram negative bacteria (Jørgensen et al., 2003). The occurrence of DAPA in marine sediments is indicative of both living bacteria and remnants of bacterial cells (Lomstein et al., 2009). The DAPA yields in the majority of NSCS sediments (Table 2) are similar to those found in marine bacteria (Supplemental data Table S2), indicating bacteria are an important source of amino acids in these sediments.

A qualitative evaluation of the sources of sedimentary OM based on N/C ratios and δ^{13}C compositions is presented in Fig. 4A. In general, sedimentary OM appears to be a mixture of marine plankton and soil-derived OM. A similar evaluation based on lignin yields and δ^{13}C compositions leads to the same general conclusion (Fig. 4B) (See the Section 3.4).

3.3. Diagenesis of sedimentary OM in NSCS

The amino acid DI values in NSCS sediments ranged from −1.8 to −0.2, with the exception of 08E708 (Table 2). The DI values decrease from the inner shelf to the slope, indicating an increasing degree of diagenetic alteration with water depth (Fig. 5A). Amino acids comprised a major fraction of SPM in the Pearl River, but it is unlikely they survive transport from the river to marine sediments due to their high reactivity (Chen et al., 2004). In addition, marine OM appears to be the dominant source of amino acids in these NSCS sediments. Previous studies in the South China Sea reported primary production was

406 mg C m^{-2} d^{-1} (Liu et al., 2007), and it appears >99% of the carbon is degraded/remineralized before burial in sediments (Zhao et al., 2009).

The THAA (%OC) values ranged from 4.9 to 19.4% in NSCS sediments and were in the range (12 ± 10%) reported for ocean margin sediments (Keil et al., 2000), with the highest value obtained at JJW79 (19.4%). The highest concentration (140.9 nmol/mg OC) of DAPA was also obtained in JJW79, indicating that bacteria were a particularly important source of sedimentary amino acids at this site. No consistent pattern of THAA (%OC) was observed from inner shelf to slope sediments (Fig. 5B). No significant correlation was observed between THAA (%OC) and the DI. It appears the different sources of amino acids in sedimentary OM have variable THAA (%OC) yields and amino acid composition leading to varying patterns in the yields and compositions of amino acids in NSCS sediments.

Ratios of (Ad/Al)v and 3,5-BD/V can be used to indicate the extent of diagenetic alterations and sources of terrestrial OM (Gordon and Goñi, 2003; Houel et al., 2006; Kuzyk et al., 2008). Ratios of (Ad/Al)v and 3,5-BD/V ranged from 0.44 to 1.17 and 0.08 to 1.38, respectively, in the NSCS sediments (Table 3). Most of the sediments had high ratios of Ad/Al (>0.40) and 3,5-BD/V (>0.10), and are consistent with a soil OM source (Kuzyk et al., 2008). Furthermore, the slope sediments exhibited 3,5-BD/V and (Ad/Al)v ratios which are similar to those of mineral-bound soil OM, whereas the inner shelf sediments have ratios indicating contributions from the surface litter layer of soils (Fig. 6). Increasing ratios of (Ad/Al)v and 3,5-BD/V were observed from shelf to slope sediments, indicating increasing diagenetic states of terrestrial OM with water depth (Fig. 5C and D). Given that most (Ad/Al)v and 3,5-BD/V ratios of the NSCS sediments fall in the ranges of those of the Pearl River SPM, hydrodynamic sorting appears to be responsible for the trends. Hydrodynamic sorting, which leads to the preferential delivery of soil OM to offshore sediments (Keil et al., 1998), could lead to increasing (Ad/Al)v and 3,5-BD/V with water depth. Several high (Ad/Al)v ratios in the outer shelf sediments indicated diagenetically-altered OM,
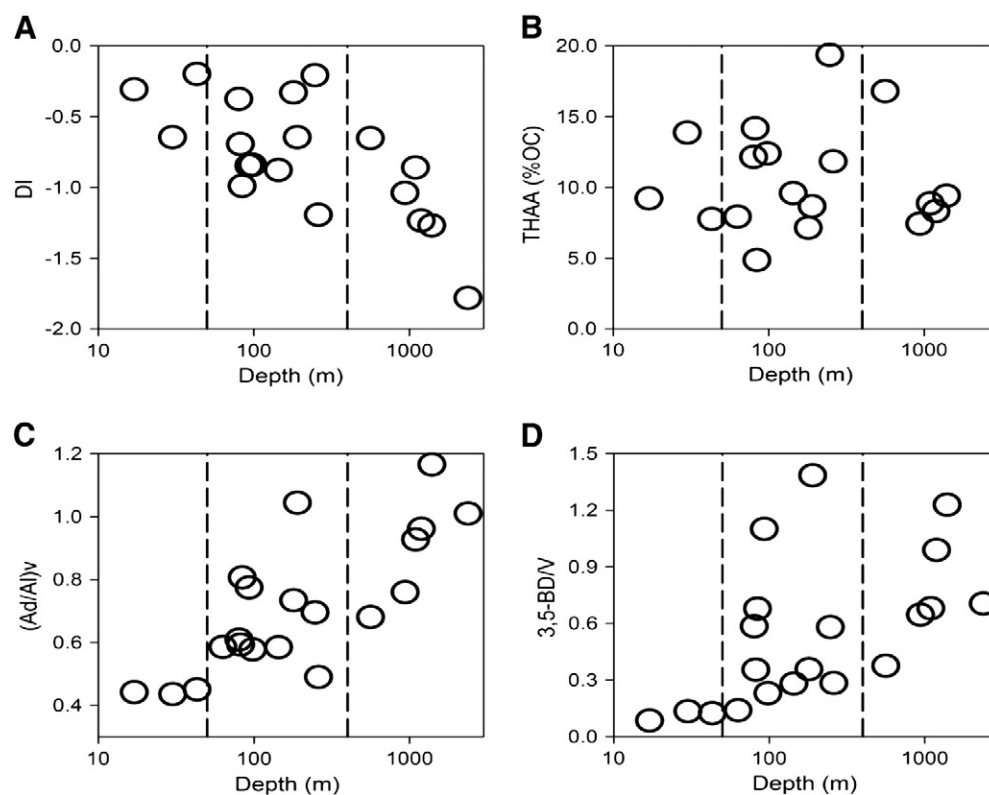

Fig. 5. Depth trends of diagenetic indicators: amino acid degradation index (DI) (A), carbon-normalized THAA yields (%OC) (B), ratios of vanillic acid to vanillin ((Ad/Al)v) (C), and ratios of 3,5-dihydroxybenzoic acid to vanillyl phenols (3,5-BD/V) (D). The inner shelf, outer shelf, and slope sediments are separated by two dashed lines.
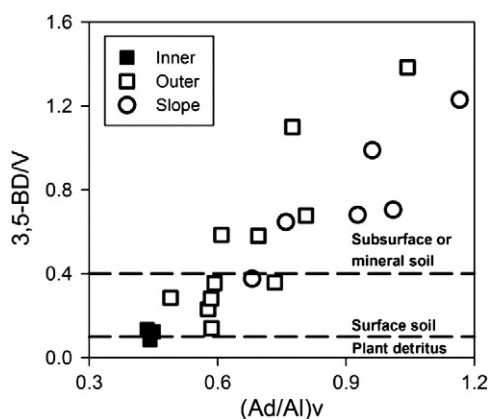
Fig. 6. Ratios of 3,5-dihydroxybenozic acid to vanillyl phenols (3,5-BD/V) and vanillic acid to vanillin ((Ad/Al)v) in sediments. The approximate ranges of 3,5-BD/V for plant debris, surface soils, and subsurface soils are also shown (Kuzyk et al., 2008).

which was consistent with the 3,5-BD/V diagenetic indicator. It is worth noting that some (Ad/Al)v and 3,5-BD/V ratios are significantly higher than the maximum of those Pearl River SPM. This could suggest a degradation of terrestrial OM during delivery to the NSCS. Macroalgae, such as kelp, are a possible source of 3,5-BD (Goñi et al., 2000), but the strong correlation between 3,5-BD/V and (Ad/Al)v ratios indicated most of the 3,5-BD was derived from land. The 08E609 and 08CF9 samples generally exhibited lower ratios than other slope samples did, but their ratios were comparable with those in outer shelf sediments. This observation is consistent with terrestrial inputs from the Dongsha Islands, as indicated by the elevated lignin concentrations and C/N ratios.

3.4. Quantitative assessment of terrigenous and marine OM in NSCS sediments

Two end-member mixing models using a single tracer have been widely used to provide quantitative estimates of the contributions of terrigenous and marine OM to marine sediments (e.g., Hedges and Mann, 1979; Hu et al., 2006). These models have been very useful, but they do not consider the possibility of more than a single source of terrestrial OM. We chose to use a three end-member mixing model with two tracers to distinguish three potential sources of OM in NSCS sediments: C3 plant material, soil OM, and marine plankton (Gordon and Goñi, 2003). The equations in the three end-member mixing model are based on stable carbon isotopic compositions and lignin yields:

$$f_{plant} \times \delta^{13}C_{plant} + f_{soil} \times \delta^{13}C_{soil} + f_{marine}\delta^{13}C_{marine} = \delta^{13}C_{sample}$$
$$f_{plant} \times \Lambda_{8,plant} + f_{soil} \times \Lambda_{8,soil} + f_{marine} \times \Lambda_{8,marine} = \Lambda_{8,sample}$$
$$f_{plant} + f_{soil} + f_{marine} = 1$$

where f_{plant}, f_{soil}, and f_{marine} are the fractions of C3 plant material, soil OM, and marine plankton in sedimentary OC, and $\delta^{13}C$ and Λ_8 are stable carbon isotopic compositions and the lignin yields, respectively. The C3 plant end-member value for $\delta^{13}C$ was −29.0‰ (Yu et al., 2010) and was 7.00 mg/100 mg OC for Λ_8 (Tesi et al., 2007). The soil end-member value was −24.1‰ for $\delta^{13}C$, which represents an average $\delta^{13}C$ value of soils in the Pearl River (Yu et al., 2010; Zhang et al., 2012). The marine endmember values for $\delta^{13}C$ and Λ_8 were −20.0‰ and 0 mg/100 mg OC, respectively (Fig. 4B; Tesi et al., 2007). A lignin yield for the soil end-member was chosen based on an approach used by Gordon and Goñi (2003). In this study, an average Λ_8 of 0.58 mg/100 mg OC for SPM in the Pearl River and its reservoirs was chosen for a soil end-member. It is possible this Λ_8 value underestimates the lignin content of soil based on the observed contributions of plankton to the Pearl River SPM. Therefore, the sensitivity of the model to varying Λ_8 values for

the soil endmember was tested (Table S3). No significant change in source apportionment is observed by using 0.58 and 0.75 mg/100 mg OC as a soil endmember. The use of 1.39 mg/100 mg OC cited from Gordon and Goñi (2003) in our model would increase the contribution of soil OC by 8–18% and decrease that of marine OC by 4–10% relative to the chosen value 0.58 mg/100 mg OC. However, the plant contribution in the mixing model decreases and becomes more negative as the soil endmember value increases, which indicates the value from Gordon and Goñi (2003) is too high for the Pearl River system.

Model results show that unmodified C3 plant OM is, at most, a minor component of NSCS sedimentary OM (Fig. 7). In contrast, marine-derived OM comprised most of the sedimentary OM. The contributions of marine OC increase from 62 ± 6% in the outer shelf to 82 ± 5% in the slope, whereas the contributions of soil-derived OC decrease from 39 ± 7% to 18 ± 5%. Although soil contributions to sediment OC are less important than marine contributions, the soil contribution to sedimentary OC is significant.

Hu et al. (2006) and Yu et al. (2010) used two end-member mixing models for the Pearl River estuary and observed a major marine source (70–90%) to sediments, which is larger than estimated (59%) for the corresponding area in the present study. Hu et al. (2006) used a $\delta^{13}C$ of −27‰ for the terrestrial endmember, which is closer to C3 plant material than soil, and Yu et al. (2010) used a $\delta^{13}C$ (−25‰) for riverine sediments to calculate the terrestrial contribution. The contributions of soil OC were hardly considered in previous evaluations of terrestrial OC in the NSCS, which appears to have resulted in an overestimation of marine OC. Based on the present study, terrestrial OM buried in NSCS sediments is predominantly soil-derived. We also tested a two endmember mixing model with $\delta^{13}C$ values for soil and marine plankton OM and observed an insignificant difference (<5%) in results between the two and three endmember mixing models.

The proportion (39 ± 7%) of terrestrial OM in NSCS sediments is significantly higher than that (16 ± 4%) estimated in non-deltaic margins (Burdige, 2005). This phenomenon can be explained by the observation that the remineralization of terrestrial OM in the oceans is much less efficient than that of marine OM (Burdige, 2005). Terrestrial OM in SPM from the Pearl River is primarily derived from soil OM, which is resistant to biodegradation and is transported to shelf and slope sediments. The amino acid components in NSCS sediments are extensively degraded as indicated by the low DI values, suggesting marine OM is remineralized before burial. The occurrence of high dissolved oxygen concentrations in deep water of the SCS also enhances remineralization rate of sinking marine particles (Zhao et al., 2009). As a result, marine OM buried in the SCS sediments presumably accounts for only 0.1–0.2% of primary production (Zhao et al., 2009), which is lower than the estimate (<1.3%) for global continental margins by Burdige (2005). In addition, the SCS has relatively low primary production (406 mg C m⁻² d⁻¹; Liu et al., 2007), implying a high remineralization rate of marine OM
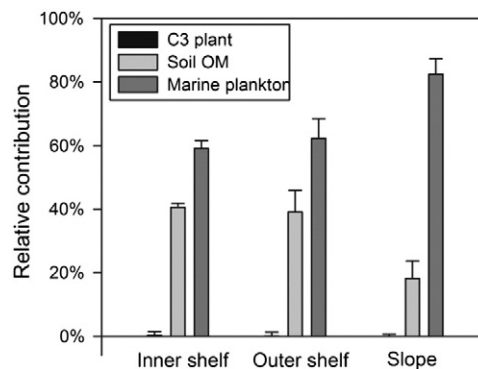

Fig. 7. Relative contributions of C3 plant, soil OM, and marine plankton to sedimentary organic carbon from the inner shelf to outer shelf and slope. The mean values for the three regions are presented and the corresponding error bars represent one standard deviation.

before burial. All these factors lead to an apparently low burial efficiency of marine OM in the NSCS sediments.

The contribution of terrestrial OM is more important to sedimentary OC in the Washington margin and the northern Gulf of Mexico than in the NSCS (Prahl et al., 1994). Terrestrial OM accounted for 60% and 30% of TOC in sediments of Washington shelf and slope, respectively, which is considerably greater relative to shelf and slope sediments in the NSCS. This difference can be ascribed to differences in the depositional environment on these margin systems. Terrestrial OM is more effectively buried in active margins, such as the Washington margin, rather than in passive margins, such as the northern NSCS (Blair and Aller, 2012). It is found that lignin yields (avg. 2.75 mg/100 mg OC) and (Ad/Al)v ratios (0.35) in the Washington margin (Prahl et al., 1994) are significantly higher than those in the NSCS. In addition, sediment accumulation rates on the Washington margin (67–102 mg cm^{-2} year^{-1}; Hartnett et al., 1998) are significantly higher than those in the NSCS (~14 mg cm^{-2} year^{-1}; Huang and Wang, 1998). However, sediment accumulation rates are not the only factor controlling the OM burial. For example, the Mississippi River-dominated northern Gulf of Mexico also has a relatively-high sediment accumulation rate (120–450 mg cm^{-2} year^{-1}; Gordon and Goñi, 2004) and a low dissolved oxygen content (Turner et al., 2008). A significant fraction (~70%) of buried OM in its inner shelf is land-derived (Gordon and Goñi, 2003). The lignin yields (avg. 1.42 mg/100 mg OC) in the shelf of northern Gulf of Mexico are significantly higher than those in the NSCS.

4. Conclusion

Suspended particles in the Pearl River are primarily derived from riverine plankton and soil material, with minor contributions from plant detritus. Hydrodynamic sorting appears to be important in the distribution of sedimentary material in the NSCS, resulting in plant debris being retained in estuarine sediments and refractory soil OM being widely dispersed in NSCS sediments. The application of a three end-member mixing model revealed soil OM accounts for 18–39% of sedimentary OC with decreasing contributions from shelf to the slope sediments. The fraction of terrestrially-derived OC in NSCS sediments is significantly higher than previously considered. Marine OM accounts for 62–82% of sedimentary OC and increases from shelf to slope sediments. Marine OM is rich in amino acids, and the marine OM in NSCS is highly diagenetically-altered based on its amino acid composition. This observation is consistent with a previous study indicating a small fraction of plankton production in surface waters is preserved in NSCS sediments. The low efficiency of marine OM preservation in NSCS sediments can be attributed to high dissolved oxygen concentrations in the water column and low sediment accumulation rates.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.marchem.2013.11.003.

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