Terrestrial Biomolecular Burial Efficiencies on Continental Margins

Pengfei Hou1,2, Meng Yu1,2,3, Meixun Zhao1,3, Daniel B. Montluçon2, Chenglong Su1, and Timothy I. Eglinton2

1Frontiers Science Center for Deep Ocean Multispheres and Earth System, and Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao, China. 2Geological Institute, ETH Zürich, Zürich, Switzerland, 3Laboratory for Marine Ecology and Environmental Science, Qingdao National Laboratory for Marine Science and Technology, Qingdao, China

Abstract The fate of terrestrial organic carbon (OCter) exported from large rivers in marginal seas is an integral component of land-ocean-atmosphere carbon dynamics and influences on atmospheric CO2 concentrations on millennial and longer timescales. In this study, we employ a novel approach to constrain burial efficiencies for source-specific terrestrial biomolecules (long-chain n-alkanes and n-fatty acids) in two river-marginal sea systems. We find for the Pearl River-South China Sea system that 34 ± 19% and 11 ± 4% of n-alkanes and n-fatty acids, respectively, are preserved across the transport pathway from the river mouth to inner shelf. In contrast, terrestrial biomolecular burial efficiencies were markedly higher (64 ± 17% and 84 ± 30% of n-alkanes and n-fatty acids, respectively) in the Yellow River-Bohai Sea/Yellow Sea system. These findings reveal markedly different fates of OCter in these two fluvial-marine systems, as well as sharp contrasts in OCter reactivity within each system.

Plain Language Summary Burial efficiencies of source-specific biomarker compounds in coastal sediments can provide new insights into the fate of terrestrial organic carbon in marine environments. In this study, we determine mineral surface area-normalized loadings of higher plant-derived long-chain n-alkanes and n-fatty acids in two Chinese fluvial/marginal sea systems in order to examine terrestrial organic carbon burial efficiencies. We find marked contrasts in terrestrial organic carbon burial efficiency between both fluvial systems and terrestrial biomolecules. These differences imply sharply contrasting fates of different components of terrestrial organic matter during transport and sedimentation, which in turn shed new light on underlying mechanisms and carry implications for interpretation of past and present-day variations in terrestrial organic carbon sequestered in continental margin sediments.

1. Introduction

Large river-dominated ocean margins are primary interfaces that connect continental and marine carbon reservoirs (Bianchi et al., 2018). On a global basis, it is estimated that approximately 0.20 × 10^15 g year^-1 of particulate organic carbon (POC) and 0.25 × 10^15 g year^-1 of dissolved organic carbon (DOC) is discharged by rivers to the ocean (Galy et al., 2015; Hedges et al., 1997). While most DOC is returned to the atmosphere on relatively short timescales through oxidation, a significant fraction of riverine POC is buried in marine sediments and stored on geologic timescales (Bianchi et al., 2018; Burdige, 2005). In the modern ocean, marginal seas are estimated to account for more than 90% of organic carbon (OC) burial, despite comprising less than 10% of global ocean area (Hedges & Keil, 1995). The majority of this OC accumulates in deltaic and continental shelf sediments, highlighting the importance of coastal zones as loci for sequestration (and remineralization) of terrestrial OC (OCter) (Bianchi et al., 2018).

OCter accumulating in coastal sediments can be separated into two main components: (1) biospheric OC, which includes modern biomass OC from fresh higher plant detritus, aquatic production, and preaged mineral-bound soil OC, and (2) petrogenic OC resulting from erosion of sedimentary rocks or from anthropogenic activities utilizing fossil fuels (Drenzek et al., 2007; Galy et al., 2008; Tao et al., 2016). Biospheric OC comprises the most dynamic component of OCter, with the majority rapidly recycled back to CO2 and returned to the atmospheric reservoir prior to or during transport (Aller & Blair, 2004). Nevertheless, the small proportion that is buried in marine sediments represents an important net carbon sink, with the
balance of sequestration and remineralization of biospheric OC_{terr} modulating the size of the atmospheric C reservoir on millennial and longer timescales (Galy et al., 2015).

Accurate constraints on burial efficiency (BE) are an essential prerequisite for establishing robust carbon budgets, and elucidation of the factors that control OC_{terr} fate in the coastal ocean. It is estimated that on a global basis, approximately one third of fluvially derived OC is preserved in marine sediments (Blair & Aller, 2012), with the rest remineralized primarily during dispersal and deposition over the continental margins. Such estimates are based on the premise that most riverine POC is associated with, and stabilized by, mineral surfaces (Hemingway et al., 2019; Keil & Mayer, 2014; Lutzow et al., 2006), as evidenced by a positive correlation between total organic carbon (TOC) content and mineral-specific surface area (SA) frequently observed in riverine and river-dominated coastal sediments (Bianchi et al., 2018; Blair & Aller, 2012; Goñi et al., 2003; Keil et al., 1997; Mayer, 1994). A method was established to constrain OC_{terr} BEs in marine sediments combining mineral-specific SA-normalized OC contents (OC loadings) with stable carbon isotopic (δ^{13}C) compositions of sediment TOC, the latter being used to apportion terrestrial and marine organic matter (Burdige, 2005; Keil et al., 1997). Resulting estimates of OC_{terr} BE on continental margins range from as low as 21% for the Amazon River delta to as high as ~80% for the Yellow River delta, with a global average of 44 ± 13% (Burdige, 2005; Keil et al., 1997).

Several limitations are inherent in the above stable carbon isotope-based approach to constrain OC_{terr} fate, with challenges in defining isotopic end-member signatures introducing substantial uncertainty in corresponding budgets. Moreover, bulk OC signatures often lack sufficient diagnostic power for detailed reconstruction of terrestrial paleoenvironments based on fluvially derived sedimentary records. Source-specific biomolecules (biomarkers) can provide direct constraints on the origin of OC accumulating in continental margin sediments and also shed light on depositional histories of OC on continental shelves (Bao et al., 2018; Blair & Aller, 2012; Bröder et al., 2018; Eglinton et al., 1997; Tao et al., 2016). Long-chain n-alkanes and n-fatty acids (n-FAs) are almost exclusively derived from terrestrial higher plant leaf waxes and have been shown to be well preserved in the terrestrial and aquatic environments (Eglinton & Hamilton, 1967; Eglinton & Eglinton, 2008). Consequently, they have been widely used to trace OC_{terr} inputs in rivers and marine sediments (e.g., Bröder et al., 2018; Freymond et al., 2018; Galy & Eglinton, 2011; Tao et al., 2016; Yu, Eglinton, Haghipour, Montluçon, Wacker, Hou, et al., 2019; Yu, Eglinton, Haghipour, Montluçon, Wacker, Wang, et al., 2019). Biomarker concentrations are typically normalized to volume (e.g., ng/L), mass (μg/g dw), or OC content (mg/g OC); however, changes in mineral composition and hydrological sorting in aquatic systems can affect corresponding OC contents when expressed in these units (Blair & Aller, 2012). Normalizing biomarker contents to mineral-specific SA (i.e., “biomolecular loadings”) can account for the effects of changes in mineral compositions and hydrological sorting, offering the potential to further constrain the net loss of OC_{terr} and to distinguish interferences from other carbon pools (e.g., Bröder et al., 2016; Freymond et al., 2018). Biomolecular loadings have previously been determined for river and marine sediments and have revealed significant degradation of OC_{terr} during fluvial and cross-shelf transport (Bröder et al., 2018; Freymond et al., 2018; Tesi et al., 2016). Surprisingly, however, this loadings-based approach has not yet been applied to evaluate BEs of OC_{terr} exported from rivers to the coastal ocean.

Here, we introduce the concept of “biomolecular burial efficiency” (BBE) and apply it in concert with conventional stable carbon isotopic approaches to explore the fate of OC_{terr} in two major river-marginal shelf sea settings that serve as model systems to assess OC_{terr} BEs: the Pearl River-northern South China Sea (PR-SCS) and the Yellow River-Bohai Sea/Yellow Sea (YR-BS/YS) (Figure 1). We determined the δ^{13}C composition of bulk OC and the contents of higher plant-derived biomarker compounds (long-chain n-alkanes and n-FAs) in riverine suspended particulate matter (SPM) and coastal surface sediments of the two systems. Corresponding bulk OC and biomolecular loadings are then used to assess the BEs of fluvially derived terrestrial organic components in adjacent marginal seas.

2. Study Areas
2.1. Pearl River-Northern South China Sea
The PR is the second largest river in China, and the thirteenth largest river globally in terms of both water discharge (~3.5 × 10^{11} m^3 year^{-1}) and suspended sediment flux (~8.5 × 10^7 t year^{-1}) (Zhang et al., 1999), with a POC flux of 5.4 × 10^5 t year^{-1} (Ni et al., 2008).
The PR system discharges into the northern SCS via three subestuaries, the Lingdingyang, Modaomen, and Huangmaohai estuaries (Figure 1b). Sampling sites in this study are located along the Lingdingyang, the largest subestuary that is usually referred to as the PR estuary, and extend from the apex of the estuary (salinity = 0) to the adjacent continental margin (Figure 1b).

The dispersal and spatial distribution of PR-derived sediments in the northern SCS shelf is strongly influenced by the seasonally alternating East Asian monsoon and associated surface circulation patterns. From April to August, the southwesterly summer monsoon winds drive an anticyclonic circulation in the northern SCS, while from November to March the northeasterly winter monsoon winds induce cyclonic circulation (Figure 1b; Chu et al., 1999). Sediment transport in the PR estuary and the adjacent continental margin is modulated by this seasonal oscillation, while the net transport of sediments is toward the southwest along the coast (Liu et al., 2016) (Figure 1b). The sampling locations broadly follow the main sediment transport pathway, spanning a transect that is ~475 km in length (Figure 1b).

### 2.2. Yellow River-Bohai Sea/Yellow Sea

The YR, originating on the Qinghai-Tibet Plateau, flows through the Chinese Loess Plateau in the northwestern China and eastward to the BS, with a total length of 5,464 km. It historically primarily transports $1.1 \times 10^{15}$ g particulate matter, with the suspended sediment load and sedimentary materials discharged to the adjacent BS/YS dominated by inputs of fine-grained materials (<32 μm) and associated POC from highly erodible loess deposits on the Chinese Loess Plateau (Zhang et al., 2013).

The modern YR-derived clayey silt sediment is directly discharged into the western BS with an accumulation rate of 557 Mt/year. A portion of this sediment has escaped from the BS Strait to the YS via the coastal current, building the Shandong subaqueous delta at an accumulation rate averaging ~70 Mt/year (Liu et al., 2004; Yang & Liu, 2007). The study area encompasses the lower reach of YR (Kenli), with sampling locations broadly following the ~620 km-long coastal sediment transport pathway (Figure 1c).
3. Materials and Methods

3.1. Sampling

3.1.1. PR-SCS

Near-surface (upper 0.5 m) SPM samples were collected from the PR at Guangzhou (PR1, salinity = 0), ~3 km upstream of the first PR estuary sediment site (P03, salinity = 0), in April 2017, September 2017, and November 2017. Water depth at PR1 is <4 m and was well mixed vertically during the sampling periods, so SPM samples are considered representative of the overall river suspended sediment load, and the three SPM samples collected over different seasons are taken to reflect the annually integrated OC signal delivered by PR to estuary. In each case, 900–1,600 L of surface water was filtered onto precombusted glass fiber filters (150 mm diameter, 0.7 μm, Whatman), and the filters were freeze-dried upon return to the laboratory. After freeze-drying, particles were then carefully scraped off the filter for subsequent analysis.

Surface sediment (0–2 cm) samples were collected using a box corer from eight sites in the PR estuary during January 2017 (R/V Haishun, Xiamen University) and from four sites on the continental shelf in April 2017 (R/V Haili, Ocean University of China). Sediment samples were stored in a freezer (−20°C) until they were subsequently freeze-dried in the laboratory.

3.1.2. YR-BS/YS

Near-surface (upper 0.5 m) SPM samples were collected from the YR at Kenli (37.61°N, 118.54°E, ~50 km upstream of the river mouth) on various occasions between June 2011 to July 2013 and between June 2015 to May 2016. This sampling encompasses different seasons and includes both natural and human-dominated flood events. Given the shallow water depth during most months (ave., 1.5 m), the SPM samples are considered representative of the overall river suspended sediment load (Tao et al., 2018; Wang et al., 2012; Yu, Eglinton, Haghipour, Montluçon, Hou, et al., 2019; Yu, Eglinton, Haghipour, Montluçon, Wang, et al., 2019). About 100 to 150 L of surface water were filtered through precombusted and preweighed glass fiber filters (150 mm diameter, 0.7 μm, Whatman) and then freeze-dried prior to further laboratory analysis.

Seven surface sediments (0–5 cm) in the BS/YS region were collected by using a box sampler during the open cruise of National Natural Science Foundation of China (R/V DongfanghongII, Ocean University of China) in August 2015. All samples were stored at −20°C and subsequently freeze-dried prior to laboratory analyses.

3.2. SA and Mean Grain Size

Freeze-dried samples of ~1.0 g were heated at 350°C for 12 hr (Mayer, 1994) and gently cooled to room temperature to remove organic matter. Mineral-specific SA was measured by a 5-point BET method using NOVA 4000 SA analyzer (Quantachrome Instrument). Mean grain size was measured using a Malvern laser diffraction grain sizer.

3.3. Bulk Analyses

For YR-BS/YS samples, methods for TOC% and TOC-δ¹³C analyses have been described in Tao et al. (2015) and Yu, Eglinton, Haghipour, Montluçon, Hou, et al. (2019). To remove the inorganic carbon, samples were pretreated with 12 N HCl fumigation (60°C, 72 hr) and NaOH neutralization (60°C, 72 hr). TOC% and TOC-δ¹³C values of YR SPM samples collected during 2011–2013 were measured at the Stable Isotope Facility within the Climate Geology group at ETH (Tao et al., 2015). For YR SPM samples collected during 2015–2016, as well as the surface sediment samples in this study, TOC% and TOC-δ¹³C values were determined by the coupled EA-IRMS-AMS online system at the Laboratory for Ion Beam Physics, ETH Zürich (McIntyre et al., 2017).

For PR-SCS samples, they were rinsed with 6 M HCl (12 hr/room temperature). After repeated rinsing (five times) with deionized water and drying in an oven at 55°C, the carbonate-free samples were measured for TOC using a Thermo Flash 2000 Elemental Analyzer. TOC-δ¹³C values were determined using a Thermo Delta V mass spectrometer (continuous-flow mode).

3.4. Extraction, Purification, and Quantification Methods of Lipid Biomarkers

Methods for the extraction of lipid biomarkers in YR-SPM samples (sampled during 2015–2016) have been described in Yu, Eglinton, Haghipour, Montluçon, Hou, et al. (2019). Briefly, about 5 g of freeze-dried and homogenized suspended sediment was microwave-extracted with dichloromethane/methanol (DCM/
MeOH 9:1, 25 min at 100°C). After saponification with KOH in MeOH (0.5 M, 2 hr at 70°C), the neutral fraction and acid fraction (after acidification to pH = 2) were obtained by solvent extraction. n-alkanes were further isolated from the neutral fraction by eluting through SiO2 column with hexane. Fatty acids in the acid fraction were derivatized to corresponding fatty acid methyl esters (FAMEs) with MeOH:HCl (95:5, 12 hr at 70°C). Saturated FAMEs were further purified by eluting through SiO2 column with DCM/hexane (2:1) and AgNO3-SiO2 column with DCM. n-Alkanes, and FAMEs were quantified against external standards on a gas chromatograph with flame ionization detection (GC-FID; Agilent Technologies 7890A) equipped with an Agilent VF-1 column (30 m × 250 μm i.d., 0.25 μm film thickness). The temperature program for n-alkanes started with a 1 min hold time at 80°C, followed by (1) a 20°C/min ramp to 200°C; (2) a 4°C/min ramp to 250°C; 3) a 1.7°C/min ramp to 300°C with a 6 min hold time; (3) a 5°C/min ramp to 310°C with a 5 min hold time at 320°C.

Methods for the extraction of lipid biomarkers in sediment samples and PR-SPM samples are modified from Xing et al. (2011). Freeze-dried samples were extracted (four times) with dichloromethane (DCM)/MeOH (3:1, v/v) by sonication, after addition of C19 n-alkanoic acid (n-FA) and n-C24D50 alkane as internal standards. Each total lipid extract was saponified in KOH/MeOH (6%, sonication/2 hr) and separated into neutral and acidic lipids via liquid-liquid extraction. A nonpolar fraction (containing n-alkanes) was eluted from the neutral lipid fraction by silica gel chromatography using hexane and was dried under a N2 stream prior to analysis. Acidic lipids (containing fatty acids, FAs) were recovered following addition of 6 M HCl (until pH = 2) and liquid-liquid extraction (four times) with 10 ml Hexane: DCM (4:1). This fraction was subsequently transesterified (10 ml [v/v = 5:95] HCl:MeOH; 70°C, 12 hr), and resulting methylated FAs were extracted by hexane (four times) before instrumental analysis. n-alkanes and FAs were quantified on a gas chromatograph with flame ionization detection (GC-FID; Agilent Technologies 6890N) equipped with an Agilent HP-1 column (50 m × 320 μm i.d., 0.17 μm film thickness). The temperature program for n-alkanes started with a 1 min hold time at 80°C, followed by (1) a 25°C/min ramp to 200°C; (2) a 4°C/min ramp to 250°C; 3) a 1.7°C/min ramp to 300°C with a 6 min hold time; (3) a 5°C/min ramp to 310°C with a 5 min hold time. The temperature program for n-FA started with a 1 min hold time at 80°C, followed by (1) a 20°C/min ramp to 140°C; (2) a 4°C/min ramp to 300°C with a 7 min hold time; and (3) a 5°C/min ramp to 315°C with a 4 min hold time.

4. Results

4.1. Mineralogical Characteristics

Mineral-specific SA and mean grain size of the PR-SPM collected over three different months ranged from 26.2 to 34.1 m²/g and from 9.6 to 28.7 μm (sediment flux-weighed ave., 30.6 ± 2.4 m²/g and 17.5 ± 6.7 μm), while SA and mean grain size of the 12 PR-SCS surface sediment samples ranged from 12.0 to 24.8 m²/g and from 12.9 to 53.9 μm, respectively (Table 1).

The SA of YR-SPM sampled across 18 different months ranged from 11.0 to 30.1 m²/g (sediment flux-weighed ave., 20.8 ± 4.4 m²/g) and mean grain size ranged from 13.3 to 39.6 μm (flux-weighed ave., 20.5 ± 5.3 μm). The SA and mean grain size of the 7 BS/YS surface sediment samples ranged from 10.2 to 17.0 m²/g and from 17.9 to 31.1 μm, respectively (Table 2).

4.2. TOC-Based Properties

TOC contents of PR-SPM samples varied between 2.38% to 4.91% (sediment flux-weighed ave., 2.89 ± 1.17%; Table 1). PR-SPM from different months exhibited relatively constant TOC-δ¹³C values ranging from −27.3‰ to −28.5‰ (OC flux-weighed ave., −27.7 ± 0.4‰, Table 1). For the YR-SPM samples, the TOC contents were much lower (0.12 to 0.75%, sediment flux-weighed ave., 0.31 ± 0.04%; Table 2), and the TOC-δ¹³C values were higher (−23.3‰ to −24.9‰, OC flux-weighed ave., −23.7 ± 0.3‰; Table 2) than PR-SPM.

TOC contents of PR-SCS surface sediments ranged from 0.54% to 1.69% (Table 1). The TOC-δ¹³C values of PR-SCS sediments exhibited marked variability from −22.7‰ to −26.6‰ (Table 1). Lower values observed in the upper PR estuary rapidly increase along the estuary and then stabilize on the shelf (Table 1). TOC contents of BS/YS surface sediments ranged from 0.26% to 0.41%, and BS/YS sediments exhibited a narrower range of TOC-δ¹³C values, varying from −21.6‰ to −22.4‰ (Table 2).
The average values of SPM samples were calculated as the sediment flux average values (except for the OC-δ^{13}C, which was calculated as the OC flux average value).

### 4.3. Biomolecular Loadings

Loadings of long-chain \( (n-C_{27} - C_{31}) \) \( n \)-alkanes in PR-SPM varied from 109 to 264 ng m\(^{-2} \) over the three different months (sediment flux weighted ave., \( 141 \pm 48 \text{ ng m}^{-2} \); Table 1), while corresponding loadings for long-chain \( (n-C_{26} - C_{30}) \) \( n \)-FAs ranged from 269 to 1,064 ng m\(^{-2} \) (sediment flux weighted ave., \( 861 \pm 407 \text{ ng m}^{-2} \); Table 1).

The \( n \)-alkane loadings on PR-SCS surface sediments varied from 15 to 109 ng m\(^{-2} \) (Table 1) and displayed a decreasing trend along the transport pathway (Figure 2c). Long-chain \( n \)-FA loadings of PR-SCS surface sediments varied from 49 to 141 ng m\(^{-2} \) (Table 1) and also revealed a general decreasing trend particularly in the upper part of the PR estuary (Figure 2c).

Long-chain \( n \)-alkanes loadings of YR-SPM ranged from 31 to 118 ng m\(^{-2} \) (sediment flux-weighted ave., \( 43 \pm 12 \text{ ng m}^{-2} \); Table 2) and long-chain \( n \)-FAs loadings of YR-SPM ranged from 34 to 114 ng m\(^{-2} \) (sediment flux-weighted ave., \( 60 \pm 22 \text{ ng m}^{-2} \); Table 2). Corresponding \( n \)-alkane loadings of BS/YS surface sediments varied from 22 to 40 ng m\(^{-2} \) (Table 2) and showed a slight decreasing trend along the transport pathway (Figure 2d). The \( n \)-FAs loadings varied from 32 to 77 ng m\(^{-2} \) (Table 2) and also slightly decreased along the transport pathway (Figure 2f).

### 5. Discussion

#### 5.1. Evolution of OC\(_{terr}\) and Biomolecular Loadings Along Sediment Transport Pathways

The concept of SA-normalized OC loadings of continental margin sediments was developed by Keil et al. (1994) and Mayer (1994) and subsequently applied in conjunction with stable carbon isotopic information by Burdige (2005) and Keil et al. (1997) in order to assess OC\(_{terr}\) loadings and corresponding BEs in marine sediments. The latter approach has proven to be a powerful tool for examining carbon exchange and transport between land-ocean reservoirs (Burdige, 2005). Here, we adopt this approach to assess the fate of OC\(_{terr}\) in PR-SCS and YR-BS/YS surface sediments. In parallel, we examine changes in biomolecular loadings of two groups of terrestrial vascular plant-derived biomarker compounds—long-chain \( n \)-alkanes and \( n \)-
FAs—in order to derive independent constraints on OCterr BEs along the fluvial sediment export-transport pathway.

The conventional approach to quantify the fractional contribution of OCterr (OCterr%) in sedimentary organic matter involves the use of a binary mixing model that assumes δ13C values of terrestrial and marine end-members (Burdige, 2005). In this study, values of −20.5‰ and −20‰ were chosen for the marine end-members in PR-SCS and YR-BS/YS, respectively (Hu et al., 2006; Jia & Peng, 2003; Xing et al., 2014). The corresponding terrestrial end-members are based on the OC flux weighted average TOC-δ13C value of PR and YR SPM, that is, −27.7‰ and −23.7‰, respectively (Tables 1 and 2). OCterr% was then estimated based on the following equation (Burdige, 2005; Minoura et al., 1997; Shultz & Calder, 1976):

$$\text{OCterr} = \frac{\delta^{13}C_{\text{marine}} - \delta^{13}C_{\text{sample}}}{\delta^{13}C_{\text{marine}} - \delta^{13}C_{\text{terr}}} \times 100\%.$$  (5.1)

The resulting OCterr% in PR-SCS surface sediments ranged from 31% to 85%, and corresponding OCterr loadings ranged from 0.12 to 0.58 mg m−2 (Figure 2a). BS/YS surface sediments exhibit a narrower range of OCterr% values (43% to 65%), as well as systematically lower OCterr loadings (0.09 to 0.16 mg m−2; Figure 2b) than surface sediments from the PR-SCS. We attribute the difference between two systems to the dominance of loess-derived material as a component of SPM transported by the YR and exported to the adjacent to BS/YS. Differences in clay mineral composition between the YR and PR may also influence OC protection (Liu et al., 2016; Yang et al., 2003), but as we did not carry out clay mineralogy analysis, we
are unable to evaluate this alternative mechanism. The YR exhibits low OC\textsubscript{terr} loadings (0.16 mg m\textsuperscript{-2}; Table 2) in contrast to OC\textsubscript{terr} discharged from the PR, which is primarily derived from fresher soil OC characterized by higher OC\textsubscript{terr} loadings (0.94 mg m\textsuperscript{-2}; Table 2) (Tao et al., 2015; Zhang et al., 2014). This discrepancy in OC\textsubscript{terr} loading on SPM from the two rivers is larger than that exists between sediments from the two adjacent coastal settings.

Marginal sea sediments from both systems exhibit a trend of decreasing OC\textsubscript{terr} loadings along the sediment transport pathway (Figures 2a and 2b). This decrease could reflect several factors including hydrodynamic sorting, production of new SA via authigenic clay mineral formation (Michalopoulos & Aller, 2004), and OC\textsubscript{terr} degradation. Mean mineral grain size does not vary systematically along the PR-SCS transport pathway (Figure S1a), while mean grain size slightly increases along the YR-BS/YS transport pathway (Figure S1b). Hydrodynamic sorting processes therefore are unlikely to influence OC\textsubscript{terr} loadings. Furthermore, hydrodynamic particle sorting processes are unlikely to be a primary factor given normalization of concentrations to SA (Bao et al., 2019; Freymond et al., 2018). We therefore interpret the decrease in OC\textsubscript{terr} loadings as a consequence of OC\textsubscript{terr} degradation during lateral transport. Entrainment of fine-grained sediments in repeated deposition-resuspension loops associated with sediment translocation has been argued as a mechanism for removal of organic matter (Bao et al., 2018; Blair & Aller, 2012).

Although the conventional stable isotope-based approach provides important constraints on OC\textsubscript{terr} fate, it carries limitations that may hinder development of accurate budgets and obscure underlying processes (Bianchi et al., 2002; Burdige, 2005). OC\textsubscript{terr} derived from C\textsubscript{3} vegetation is generally more depleted in \textsuperscript{13}C (i.e., exhibits

---

**Figure 2.** Variations in bulk and biomolecular OC\textsubscript{terr} loadings in SPM (solid color symbols) and surface sediments (lighter shaded symbols) along sediment transport pathways. Upper panels: OC\textsubscript{terr} (a) PR-SCS; (b) YR-BS/YS; middle panels: \textit{n}-alkanes (c) PR-SCS; (d) YR-BS/YS; bottom panels: \textit{n}-FAs (e) PR-SCS; (f) YR-BS/YS.  

10.1029/2019JG005520
lower \(\delta^{13}C\) values) than marine organic matter (Fry & Sherr, 1989). The drainage basins of both fluvial systems are considered to be dominated by C3 plants (Guo et al., 2006; Lin et al., 2019; Liu et al., 2003; Wei et al., 2010); however, only TOC-\(\delta^{13}C\) values for Pearl River SPM (ave. = 27.7‰) are consistent with the typical \(\delta^{13}C\) range for C3 plant OC (−25‰ to −28‰) (Hedges et al., 1997). In contrast, the narrower range and higher \(\delta^{13}C\) values of sediment OC in the YR-BS/YS fall between typical end-member values for C3 plant OC and marine OC. This likely reflects the dominance of aged and degraded terrestrial OC characterized by higher \(\delta^{13}C\) values (−21.4‰ to −24.8‰) (Liu et al., 2003; Tao et al., 2015) contributing to YR SPM, leading to correspondingly higher OC-\(\delta^{13}C\) values (−23.7‰). Thus, if we use a typical C3 plant \(\delta^{13}C\) value (approximately −27‰) as the end-member, not considering such contributions, we would underestimate the OC\(_{terr}\)% (and BE) in the BS/YS sediments based on stable carbon isotope signatures. The reduced isotopic contrast between terrestrial and marine end-members also introduces greater uncertainty with respect to source attribution based on \(\delta^{13}C\) values.

Complications in source apportionment may also arise from OC contributions to riverine SPM from petrogenic inputs and from aquatic productivity, both of which may have variable and poorly constrained stable carbon isotopic compositions (Masiello & Druffel, 2001). Furthermore, hydrodynamically induced differential sorting of terrestrial OC (Goñi et al., 1997) may further confound end-member isotopic assignments.

Given the heterogeneity and associated ranges in chemical composition, reactivity, and degrees of particle association of riverine OM, complementary approaches to constrain OC\(_{terr}\) fate are warranted. In order to obviate the above complications, here we extend this approach to two groups of biomarkers unequivocally derived from terrestrial plants. Two groups of higher plant-derived leaf wax lipids—long-chain n-alkanes (here, we focus on \(nC_{27} + C_{29} + C_{31}\)) and n-FAs (\(nC_{26} + C_{28} + C_{30}\))—are among the most extensively used biomarkers to trace OC\(_{terr}\) input in aquatic sediments (Bröder et al., 2018; Eglinton & Hamilton, 1967; Freymond et al., 2018; Galy & Eglinton, 2011; Tao et al., 2016; Yu, Eglinton, Haghipour, Montluçon, Hou, et al., 2019; Yu, Eglinton, Haghipour, Montluçon, Wang, et al., 2019) and to develop paleo-records of terrestrial ecosystems and climate from continental margin sedimentary sequences (e.g., Jaeschke et al., 2018; Schefuß et al., 2003; Weijers et al., 2009). Their abundances and distributions have previously been examined in the PR estuary and adjacent marginal sea (Hu et al., 2009) as well as the YR-BS/YS (Tao et al., 2015, 2016; Yu, Eglinton, Haghipour, Montluçon, Hou, et al., 2019). Although these biomarkers generally comprise only a minor portion of bulk OC in these and other sediments, they retain key information relating to the terrestrial precursor vegetation when deposited in the marine system and are, except under particular circumstances (Gong & Hollander, 1997), immune to interferences from other carbon pools (Blair & Aller, 2012; Eglinton et al., 1997).

By examining the changes between SA-normalized concentrations of terrestrial OC at bulk and the biomolecular level in riverine SPM and in fluvially influenced marine sediments, we further explore variations in BEs along dispersal transects and assess OC\(_{terr}\) degradation subsequent to discharge from the river. Similar to bulk OC\(_{terr}\) loadings, terrestrial biomarker loadings decrease for both systems along the transport pathway, reflecting degradation during dispersal and sedimentation (Figures 2c-2f). Moreover, as for bulk OC\(_{terr}\), the gradient of decreasing loadings with increasing transit distance is shallower in the YR-BS/YS than the PR-SCS system. This contrasting behavior is especially notable for the n-FA loadings. The latter for PR-SPM (861 ng m\(^{-2}\); Table 1; close to n-FA loadings of Danube sediments in previous study: 0.4–1.5 \(\mu g\) m\(^{-2}\;\); Freymond et al., 2018) are ~14 times higher than those of YR-SPM (60 ng mg\(^{-2}\); Figures 2e and 2f), while corresponding loadings in PR-SCS sediments are only approximately two times higher than those of BS/YS sediments. We attribute this sharp contrast to the highly degraded and preaged nature of OC\(_{terr}\) transported by the YR prior to its delivery to the adjacent marginal seas (Tao et al., 2018; Yu, Eglinton, Haghipour, Montluçon, Hou, et al., 2019), as well as a closer association with its mineral host. Together, these characteristics hinder further decomposition in the marine environment. Terrestrial biomarker loadings of SCs sediments were only slightly higher than those of BS/YS sediments despite supply of SPM replete in long-chain n-FAs from the PR. This implies extensive degradation of long-chain n-FAs between discharge in the PR suspended load and its accumulation in estuarine sediment, with further, slower, reduction of terrestrial biomolecular loadings during subsequent along-shelf transport, resulting in only a small fraction that is ultimately buried. Traversing the ~150 km-long PR estuary (between Stations P03 and F401), long-chain n-alkane and n-FA loadings decreased by 4.2%/10 km and 3.8%/10 km, respectively, while beyond the estuary (from Stations E1 to G2) corresponding biomolecular loadings decreased by a further 0.4%/10 km and 1.0%/10 km. Because most of the relatively labile OC\(_{terr}\) degraded
quickly in the estuarine area, likely as a consequence of strong hydrodynamic forcing that results in protracted exposure to oxygen (Aller, 1998), degradation of the residual, more recalcitrant OC slowed down on the shelf. In contrast, terrestrial biomarkers in the first BS/YS sediment station did not exhibit substantial degradation compared with YR SPM, but long-chain n-alkane and n-FA loadings decreased by 0.7%/10 km and 1.1%/10 km, respectively, along the ~550 km-long BS/YS system transport pathway (between Stations B67 to H02). Very different degradation patterns for the two systems are evident if the degradation gradients are simply evaluated by comparing transport distance-normalized loadings between the first sediment station and the last station. However, the two systems exhibited low and comparable degradation gradients along their respective shelf regions.

The two groups of biomarker compounds examined in this study derive from the same nominal source (i.e., cuticular leaf waxes of higher plants), while there are substantial differences in their relative losses upon delivery to the marine environment. From PR to the estuary, the long-chain n-FA loadings decreased more dramatically than those of corresponding long-chain n-alkanes. Similar decreases of plant wax biomarker loadings were observed with increasing transport distance over the Laptev Sea continental shelf, while a larger decrease was observed for two other groups of higher plank biomarkers—lignin phenols or cutin acids (Bröder et al., 2016). These varying degrees of loss for different biomolecules are attributed to preferential degradation of more labile terrestrial components.

5.2. Contrasting Burial Efficiencies in the Two Systems

The above discussion reveals changes in loadings of OC$_{terr}$ at both the bulk and molecular level upon fluvial discharge to the sea and during subsequent transport over continental shelves. To quantify the changes, we adopt the concept of BE, which is usually calculated with respect to riverine input of OC$_{terr}$ to the oceans utilizing measurements of OC content, bulk stable carbon isotopic composition, and mineral-specific SA (Burdige, 2005; Keil et al., 1997):

$$\text{OC}_{terr} \ BE = \frac{\text{OC}_{terr} \ loading \ sediment}{\text{OC}_{terr} \ loading \ riverine \ SPM} \times 100\%.$$  (5.2)

The BE of OC$_{terr}$ in PR-SCS sediments sharply decreases from 62% to 16% along the axis of the estuary and becomes relatively constant on the shelf (ave., 16% ± 2%), implying extensive degradation of labile OC along the transport pathway and especially in the estuarine area. Corresponding OC$_{terr}$ BEs in the YR-BS/YS system (56% to 100%) are much higher than that in PR-SCS system, with a higher the BE of OC$_{terr}$ near the YR delta (B67 site; 100%) than previously estimated (~80%; Keil et al., 1997). Nevertheless, both values indicate high BE for OC$_{terr}$ transported by YR. Previous studies have shown that relatively refractory and aged OC emanating from erosion of loess deposits is delivered by YR, leading to its efficient burial in BS/YS sediments (Tao et al., 2016). In contrast, a portion of the “aged” OC$_{terr}$ in the PR stems from the coupled action of carbonate weathering (“hard water” effect; Rea & Colman, 1995) and uptake of this carbon into biomass from aquatic photosynthesis (Lin et al., 2019; Liu et al., 2017). This carbon is highly labile and subject to extensive degradation before it may be buried in PR estuary and SCS sediments.

OC$_{terr}$ BEs vary significantly among continental margins (Blair & Aller, 2012), with passive margins (such as Amazon subaqueous delta) generally characterized by efficient remineralization (i.e., low BE), relative to small mountainous river systems developed in active margin settings with narrow continental shelves (Aller & Blair, 2006; Blair & Aller, 2012; Galy et al., 2007; Kao et al., 2006; Keil et al., 1997). Comparing with published data, the calculated OC$_{terr}$ BE in SCS shelf area (ave. 16% ± 2%) is lower than the global average for river-dominated margins (22 ± 5%; Burdige, 2005), including the East China Sea inner shelf (24.7 ± 4.5%; Wu et al., 2013). This implies enhanced OC$_{terr}$ remineralization processes in PR-SCS system, with the majority of OC decomposition taking place within the estuary. In contrast, OC$_{terr}$ BE in the BS/YS shelf is much higher (71% ± 16%) than either the SCS shelf area or the global average, but comparable with previously reported value for this system (Keil et al., 1997). These contrasting results suggest that the nature of exported OC, in addition to the geomorphic setting, exerts a strong influence on its subsequent fate.

Loadings of different terrestrial biomarkers provide an alternative perspective that may shed further light on processes affecting the fate of OC$_{terr}$, thereby placing further constraints of BEs. The potential of this approach has been previously shown for assessment of OC$_{terr}$ during riverine and across shelf transport.
but it has not previously been used to constrain OC<sub>terr</sub> exported from rivers to the coastal ocean or to determine BBEs. Here, we compare loadings of terrestrial biomarkers from the same nominal sources (leaf waxes of vascular plants), but different stabilities, in marine sediments with those in riverine SPM. For long-chain n-alkanes,  

$$BBE_{n-alkanes} = \frac{n \text{-alkane loading sediment}}{n \text{-alkane loading riverine SPM}} \times 100\%.$$  

Similarly, the same approach can be applied to long-chain n-FAs:  

$$BBE_{n-FAs} = \frac{n \text{-FA loading sediment}}{n \text{-FA loading riverine SPM}} \times 100\%.$$  

BBE<sub>n-alkanes</sub> gradually decreased from 77% in the upper reach of PR estuary to 11% in SCS shelf sediments (Figure 3a), with average value for the estuary of 44 ± 15% and 15 ± 3% for the SCS shelf. In contrast, BBE<sub>n-FAs</sub> were low and comparatively stable throughout the PR-SCS sediment transport pathway, varying from 6% to 16% (estuarine ave., 12 ± 4%; shelf ave., 9 ± 3%; Figure 3a). This implies that more than ~85% of long-chain n-FAs are degraded prior to sedimentary burial. These low BBEs may reflect extensive degradation as a consequence of sediment reworking due to current-driven sediment resuspension processes within the estuary (tidal pumping) and over the continental shelf that promote organic matter exposure to oxygenated bottom waters and enhance the decomposition of OC (Aller, 1998, 2004).

In the YR-BS/YS system, BBE<sub>n-alkanes</sub> and BBE<sub>n-FAs</sub> decreased from 92% to 51% (ave., 64 ± 17%; Figure 3b) and from 128% to 53% (ave., 84 ± 30%; Figure 3b), respectively, indicating less extensive loss of terrestrial OC along the riverine sediment transport pathway. The >100% BE at some sites may reflect additional biomarker inputs in the estuary or from coastal regions. Nevertheless, while n-FA loadings from stations B67 and B71 are slightly higher than the average value of YR SPM (Figure 2f), leading to the BBE<sub>n-FAs</sub> values >100%, they fall within the range of those from YR SPM. Seasonal variations in the composition of YR SPM may introduce uncertainties in estimation of absolute BE values and therefore focus primarily on the overall trend along the transport pathway in comparison with YR system. This overall pattern of BBEs contrasts sharply with that in PR-SCS, which exhibited a sharp decrease within the estuary and relatively stable but low BBEs on the shelf. We attribute this difference to the predominance of preaged, mineral-associated plant biomarkers in the YR (Tao et al., 2015; Yu, Eglinton, Haghipour, Montluçon, Wang, et al., 2019) that have resided in intermediate reservoirs (loess and mineral soils) before fluvial export and are thus less prone to subsequent degradation (Bao et al., 2018). In contrast, the higher initial plant biomarker loadings (implying less mineral protection and greater lability) of the Pearl River results in more extensive loss, and hence markedly lower BBEs in the adjacent SCS.

Despite higher BBE<sub>n-alkanes</sub> and BBE<sub>n-FAs</sub> in the YR-BS/YS system, PR estuary/SCS sediments have similar or slightly higher bulk and biomolecular OC<sub>terr</sub> loadings compared with those in the BS/YS sediments.
Differing loci of labile OC removal in these two systems (i.e., within the watershed versus within the estuary) influence OC*terr* BE in corresponding marginal sea sediments. BBEs in the two systems showed clear positive relationships with corresponding OC*terr* BE (Figure 3a, n-alkane: $R^2 = 0.85, p < 0.001$; n-FAs: $R^2 = 0.28, p < 0.05$; Figure 3b, n-alkane: $R^2 = 0.83, p < 0.005$; n-FAs: $R^2 = 0.49, p < 0.05$), indicating their potential to yield an independent assessment of the fate of OC*terr*. In the PR-SCS system, BBE*subscript-n-alkanes* is slightly higher than OC*terr* BE, while both are much higher than corresponding BBE*subscript-n-FAs* (Figures 3a and 4a). This is likely reflecting selective degradation of different OC*terr* components wherein the PR delivers relatively fresher OC*terr* (most strongly reflected by n-FAs) mixing with degraded OC*terr* (manifested more strongly in n-alkanes). In contrast, n-alkanes, n-FAs, and bulk OC*terr* exhibit uniformly high BBES in the YR-BS/YS system, varying in the order n-FAs > OC*terr* > n-alkanes (Figures 3b and 4b). Differences in BE among components may be induced by the highly degraded and pre-aged nature of mineral-associated OC*terr* transported by the YR. Furthermore, mineralogical contrasts between YR and PR suspended sediments, such as the abundance of different clay minerals (e.g., PR consists mainly of kaolinite [46%] and illite [35%], with scarce amount of smectite [1%]; YR consists dominantly of illite [62%], with 12% of smectite and 10% of kaolinite; Yang et al., 2003; Liu et al., 2016) may influence the balance between loss and burial of OC*terr* (Blattmann et al., 2019; Hemingway et al., 2019; Kennedy et al., 2002). The reasons for these differences in BBES between biomarkers and between river-ocean systems remain unresolved at present but must carry further biogeochemical information, such as the provenance and mode of particle association of specific OC*terr* constituents. Further studies, such as those involving bulk and molecular-level 14C analysis, may provide further insights into underlying causes.

In addition to the relevance of BBES for understanding the fate of OC*terr* in the ocean, this information may also have implications for the interpretation of proxy signals carried by these same biomarkers (Eglinton & Eglinton, 2008). In particular, it sheds light on potential biases that may be introduced by variable degrees of preservation of primary signals. Further investigations, such as those involving bulk and molecular-level 14C analysis, would shed light on mechanisms controlling the BE of OC*terr* in the river-dominated margins.

**Figure 4.** BBES of different terrestrial organic components along the sediment transport pathway of (a) PR-SCS and (b) YR-BS/YS.
6. Conclusions

Loadings and BEs of OC\textsubscript{terr} at both the bulk and molecular level were determined for two major river-marginal shelf sea settings. Decreased terrestrial organic component loadings with increasing distance along the PR-SCS and YR-BS/YS sediment dispersal pathways indicate transport-induced loss of OC\textsubscript{terr}, following fluvial export. OC\textsubscript{terr} losses are most extensive in PR-SCS system and occur primarily within the estuary. In contrast, the YR-BS/YS system is characterized by a lesser and more gradual decrease in loadings. These differences are attributed to the contrasting degrees of OC\textsubscript{terr} oxidation and aging, and to the extent of mineral association, prior to fluvial export.

The BEs of terrestrial organic components calculated based on bulk and biomolecular loadings reveal marked contrasts between both fluvial systems as well as between different terrestrial biomolecules. In the PR-SCS system, around 28 ± 14% of bulk OC\textsubscript{terr} is preserved across the 475 km transport pathway, while corresponding values for higher plant-derived n-alkanes and n-FAs are 34 ± 19% and 11 ± 4%, respectively. BEs of terrestrial organic components in the YR-BS/YS system were markedly higher than in PR-SCS, with 71% ± 16% of bulk OC\textsubscript{terr} and 64 ± 17% and 84 ± 30% of n-alkanes and n-FAs, respectively, preserved across the 620 km transport pathway.

Further assessments of BEEs encompassing different river-marginal settings and different terrestrial components are warranted to shed light on underlying processes, to improve carbon budgets, and to refine interpretation of sedimentary records.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All the data supporting this study are available online (at https://doi.org/10.1594/PANGAEA.906750).

References

Aller, R. C. (1998). Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. Marine Chemistry, 61(3-4), 143–155. https://doi.org/10.1016/s0304-4203(98)00024-3
Aller, Robert C. (2004). Conceptual models of early diagenetic processes: The muddy seafloor as an unsteady, batch reactor. Journal of Marine Research, 62(6), 815–835. https://doi.org/10.1137/00224402880837
Aller, R. C., & Blair, N. E. (2006). Carbon remineralization of organic carbon in the Gulf of Papua deltaic complex (Papua New Guinea): Net loss of terrestrial C and diagenetic fractionation of C isotopes. Geochimica et Cosmochimica Acta, 68(8), 1815–1825. https://doi.org/10.1016/j.gca.2003.10.028
Aller, R. C., & Blair, N. E. (2006). Carbon remineralization in the Amazon-Guianas tropical mobile mudbelt: A sedimentary incinerator. Continental Shelf Research, 26(17–18), 2241–2259. https://doi.org/10.1016/j.csr.2006.07.016
Bao, R., Blattmann, T. M., McIntyre, C., Zhao, M., & Eglinton, T. I. (2019). Relationships between grain size and organic carbon $^{14}$C heterogeneity in continental margin sediments. Earth and Planetary Science Letters, 505, 76–85. https://doi.org/10.1016/j.epsl.2018.10.013
Bao, R., Uchida, M., Zhao, M., Haghjoupoor, N., Montluçon, D., McNichol, A., et al. (2018). Organic carbon aging during across-shelf transport. Geophysical Research Letters, 45, 8425–8434. https://doi.org/10.1029/2018gl078904
Bianchi, T. S., Cui, X., Blair, N. E., Burdige, D. J., Eglinton, T. I., & Galy, V. (2018). Centers of organic carbon burial and oxidation at the land-ocean interface. Organic Geochemistry, 115, 138–155. https://doi.org/10.1016/j.orggeochem.2017.09.008
Bianchi, T. S., Mitra, S., & McKee, B. (2002). Sources of terrestrially-derived organic matter in the ocean. Annual Review of Marine Science, 4(1), 401–423. https://doi.org/10.1146/annurev-marine-120709-142717
Blattmann, T., Liu, Z., Zhang, Y., Zhao, Y., Haghjoupoor, N., Montluçon, D., et al. (2019). Mineralogical control on the fate of continental derived organic matter in the ocean. Science, 366(6466), 742–745. https://doi.org/10.1126/science.aax5345
Bröder, L., Tesi, T., Andersson, A., Semiletov, I., & Gustafsson, O. (2018). Bounding cross-shelf transport time and degradation in Siberian-Arctic land-ocean carbon transfer. Nature Communications, 9(1), 806. https://doi.org/10.1038/s41467-018-03192-1
Bröder, L., Tesi, T., Salvadó, J. A., Semiletov, I. P., Dudarev, O. V., & Gustafsson, Ö. (2016). Fate of terrigenous organic matter across the Laptev Sea from the mouth of the Lena River to the deep sea of the Arctic interior. Biogeosciences, 13(17), 5003–5019. https://doi.org/10.5194/bg-13-5003-2016
Burdige, D. J. (2005). Burial of terrestrial organic matter in marine sediments: A re-assessment. Global Biogeochemical Cycles, 19, GB4011. https://doi.org/10.1029/2004gb002368
Chu, P. C., Edmons, N. L., & Fan, C. (1999). Dynamical mechanisms for the South China Sea seasonal circulation and thermohaline variabilities. Journal of Physical Oceanography, 29(11), 2971–2989. https://doi.org/10.1175/1520-0485(1999)029<2971:DMFTSC>2.0.CO;2
