

Tracing Combustion Regime Shifts through Char and Soot Black Carbon Records in Beibu Gulf Sediment Cores: Burial Flux Controls and Carbon Storage Assessment

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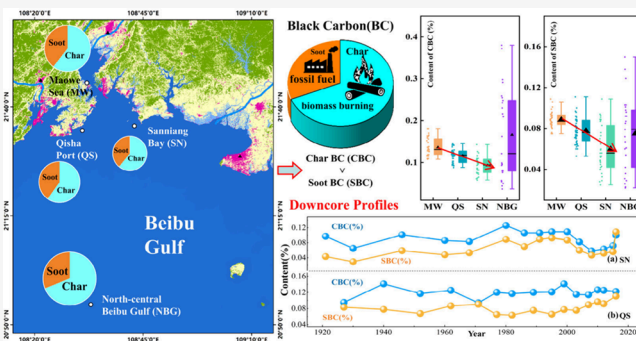
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ABSTRACT: Black carbon (BC) in marine sediments provides a unique archive of combustion history and a reservoir for long-term carbon storage. However, the distinct roles of char BC (CBC) and soot BC (SBC) in combustion-source tracing and carbon-cycle assessment remain poorly resolved in marginal seas. Here, we analyze four sediment cores from the Beibu Gulf, South China Sea, using benzene poly(carboxylic acid) (BPCA) and chemothermal oxidation at 375 °C (CTO-375) methods to resolve subtype-specific BC records. CBC accounted for 52–57% of the estimated total BC burial across all settings, consistent with sustained biomass-burning contributions. SBC exhibited higher spatiotemporal variability and sensitivity to fossil fuel expansion, particularly near industrial zones. Estimated BC burial fluxes varied spatially, largely reflecting differences in representative sedimentation rates rather than BC content. Notably, nearshore sites exhibited higher burial despite lower BC content. Centennial-scale profiles revealed that SBC effectively traced regional transitions from biomass to fossil fuel combustion, while CBC preserved the long-term fire legacy. These findings highlight the complementary roles of CBC and SBC in reconstructing combustion histories and assessing BC burial in marginal seas. Burial of biomass-derived BC can contribute to net atmospheric CO₂ sequestration, whereas fossil-derived BC burial represents the transfer of fossil carbon into long-term sedimentary storage.

KEYWORDS: black carbon, char and soot BC, combustion regime shift, burial flux, carbon storage



1. INTRODUCTION

Black carbon (BC) is a chemically recalcitrant byproduct of incomplete biomass and fossil fuel combustion.^{1–4} Its stability promotes long-term accumulation in marine sediments, reinforcing its role in carbon burial within marginal seas. Marginal seas, especially continental shelf regions, are disproportionately important BC sinks due to high sedimentation rates and substantial terrestrial inputs via atmospheric deposition and fluvial transport.⁵ Although they occupy less than 10% of global ocean area, they sequester more than 90% of sedimentary BC,⁶ underscoring their central role in global BC burial. Here, carbon storage refers to the long-term retention of BC in marine sediments, regardless of source. Burial of biomass-derived BC can contribute to net atmospheric CO₂ sequestration, whereas fossil-derived BC burial represents long-term storage and transfer of fossil carbon.⁴

BC encompasses a continuum of carbonaceous residues formed under varying pyrolytic conditions, with char BC (CBC) and soot BC (SBC) as the dominant subtypes in

marine sediments.^{7,8} CBC is typically associated with lower-temperature biomass burning, whereas SBC is predominantly associated with high-temperature fossil fuel combustion, resulting in distinct physicochemical properties and environmental behaviors. These differences complicate BC quantification when relying on a single analytical method.^{9,10} The benzene poly(carboxylic acid) (BPCA) method targets low-condensation CBC, while chemothermal oxidation at 375 °C (CTO-375) isolates highly condensed SBC, allowing complementary quantification of BC subtypes and their burial behaviors.^{11–15} However, despite their distinct biogeochemical roles, historical records that separately resolve sedimentary CBC and SBC remain exceptionally rare globally,¹⁴ and to our

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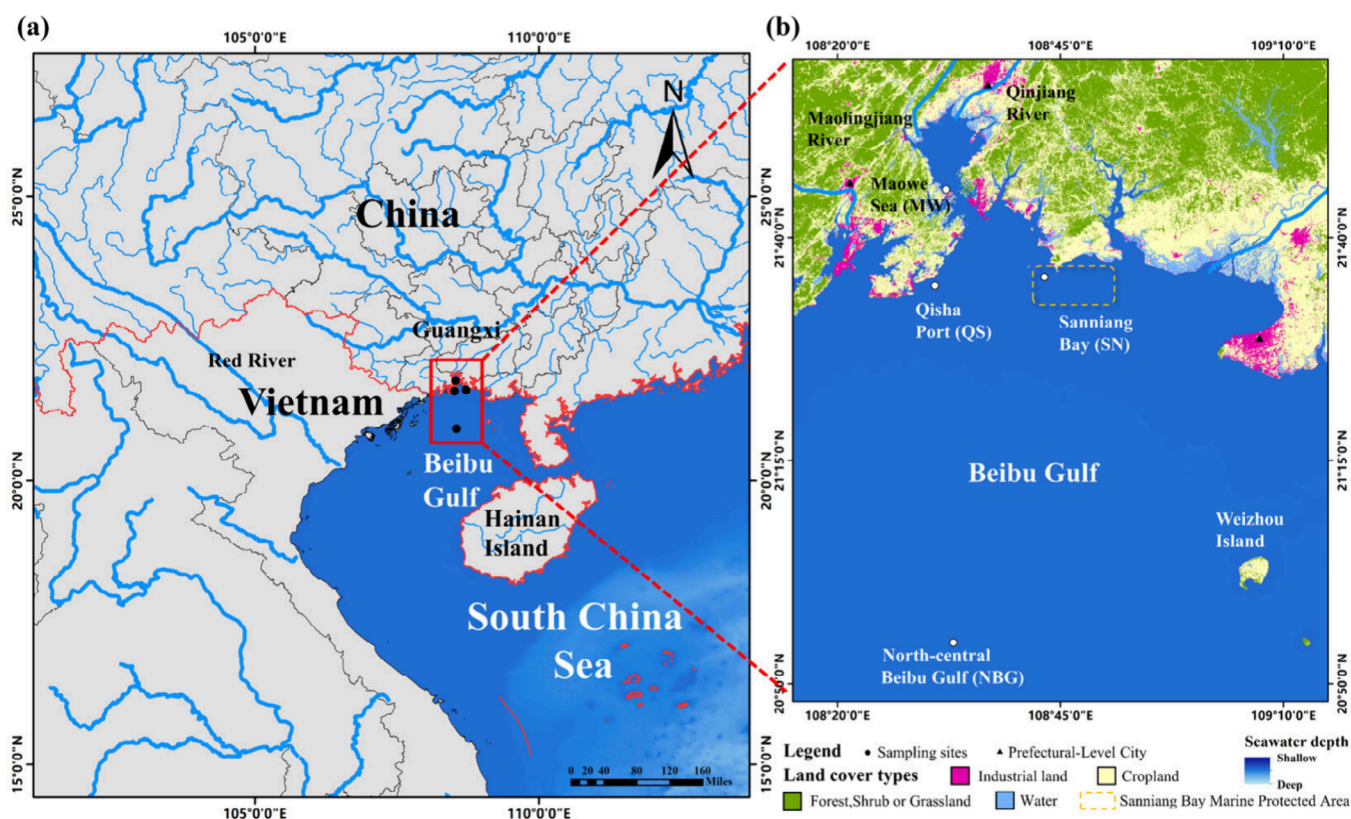


Figure 1. (a) Study area and core locations along a depositional gradient in the Beibu Gulf. (b) Enlarged map showing land cover near the four sites.

knowledge, no such subtype-specific archives have yet been reported for our study region, the Beibu Gulf, South China Sea.

The Beibu Gulf, located on the continental shelf of the South China Sea, is a typical semi-enclosed marginal sea basin, with sedimentary processes shaped by regional circulation patterns.^{16,17} Complex hydrodynamic conditions, combined with inputs from the Red River in Vietnam and local rivers in Guangxi, Hainan, and surrounding regions of China, create pronounced spatial heterogeneity in sedimentary environments.¹⁸ This dual influence makes the Beibu Gulf an effective archive for tracking BC burial and combustion patterns in marginal sea environments.^{15,19,20} Historically, low industrialization but sustained biomass fuel use has preserved pronounced biomass-burning signatures.^{21,22} Ongoing regional infrastructure developments represent potential future drivers of terrestrial inputs and land-sea connectivity. Although macro-engineering projects, such as the Pinglu Canal, are important future variables for the Beibu Gulf's ecological environment, evaluating the immediate impacts of such specific engineering operations is not the objective of this study. Instead, our focus remains entirely on broader marine dynamics and establishing a historical baseline. Future shifts in regional dynamics may alter the relative contributions of riverine CBC and atmospheric SBC; however, any long-term changes in net burial fluxes will be fundamentally governed by broader oceanographic processes controlling sediment accumulation and retention.^{9,15,23} These historical baselines and dynamic mechanisms are critical for carbon-management and climate-mitigation assessments, which must distinguish potential net CO₂ sequestration from fossil-carbon storage under evolving coastal conditions.

Currently, observations in this region are largely restricted to modern snapshots. In surface sediments of the North Beibu Gulf, BPCA-derived sedimentary BC averages $\sim 0.087\%$ and accounts for $\sim 14\%$ of sedimentary organic carbon.¹⁵ However, these surface snapshots reflect only recent deposition, lacking the temporal depth required to track long-term environmental changes. Furthermore, they do not resolve the distinct down-core dynamics of CBC and SBC across contrasting depositional settings. Consequently, centennial-scale BC burial trends and combustion-regime shifts remain poorly constrained, potentially biasing burial-flux assessments. Specifically, estimates based solely on SBC likely underestimate total BC burial by excluding CBC,^{24–26} despite its proven stability and persistence in marine environments.^{14,15,27}

Here, we use the BPCA and CTO-375 methods to quantify CBC and SBC in four sediment cores collected along a depositional gradient in the northern Beibu Gulf, encompassing a semi-enclosed bay, nearshore shelf, and outer-gulf setting. Our objectives are to (1) characterize the spatial distribution and composition of CBC and SBC across depositional settings, (2) evaluate CBC stability via BPCA-derived indicators and its relationship with total organic carbon (TOC), (3) qualitatively assess source contributions and transport implications using the carbon-to-nitrogen ratio (C/N) and BC/TOC as complementary indicators, (4) compare estimated BC burial fluxes to evaluate their spatial variability and potential controls, and (5) reconstruct centennial-scale CBC and SBC changes in two dated nearshore cores to track combustion-regime shifts.

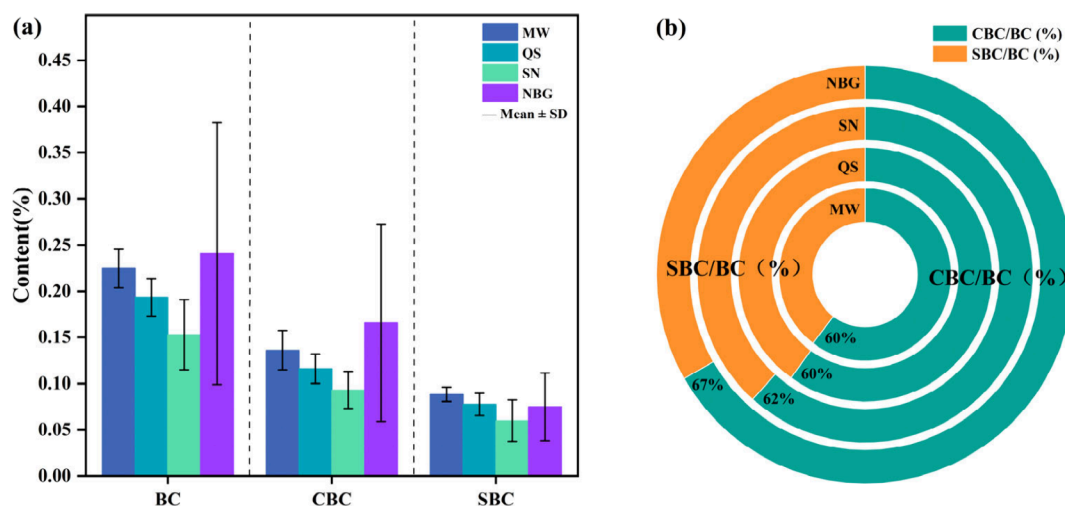


Figure 2. (a) Mean contents ($\pm$ SD) of CBC, SBC, and total BC in sediment cores from four sites along a depositional gradient from the semi-enclosed bay to the outer-gulf site. (b) Percentage contributions of CBC and SBC to the total BC content at each site. Numbers on the rings denote CBC/BC (%) (and SBC/BC = 100 – CBC/BC).

2. MATERIALS AND METHODS

2.1. Study Area and Sediment Cores

During two cruises in 2017 and 2020, four sediment cores were collected from the Beibu Gulf (Figure 1). Sites were selected to represent contrasting nearshore-to-outer-gulf settings and differences in terrestrial input, anthropogenic influence, and depositional conditions. The four sites were (1) the semi-enclosed Maowei Sea (MW, water depth 3.4 m, core length 65 cm), which receives substantial riverine runoff (e.g., Qijiang and Maoling rivers) and associated terrestrial organic matter, (2) the urban–industrial Qisha Port (QS, water depth 6.2 m, core length 76 cm), heavily impacted by localized fossil fuel combustion, maritime shipping, and industrial emissions, (3) Sanniang Bay (SN, water depth 5.6 m, core length 72 cm), a relatively open coastal bay with historically lower anthropogenic intensity, and (4) the outer-gulf site in the north-central Beibu Gulf (NBG, water depth 38.5 m, core length 77 cm), representing a relatively remote, low-energy depositional setting (Figure 1). Collection of the MW, QS, and SN cores was described previously,²⁸ whereas that of the NBG core was reported separately.²⁹ The MW, QS, and SN cores were retrieved using a gravity corer and sectioned into 1 or 2 cm intervals along the core axis. During sectioning, the outer ~1 cm of each segment in contact with the core liner was removed to minimize potential smearing contamination. Each segment was wrapped in aluminum foil and stored continuously at $-20\text{ }^{\circ}\text{C}$ at the School of Marine Sciences, Guangxi University, until analysis. The NBG samples were provided directly by the original sampling team, transported to our laboratory under frozen conditions, and stored at $-20\text{ }^{\circ}\text{C}$ upon receipt. Detailed core metadata are provided in Table S1 of the Supporting Information.

2.2. CBC and SBC Quantification

CBC was quantified using the BPCA method following established protocols.^{14,15,30,31} Detailed procedures are provided in Text S1. Briefly, approximately 100.00 mg of freeze-dried sediment (weighed to ± 0.01 mg precision) was added to a 5 mL polytetrafluoroethylene (PTFE) liner. Then, 2 mL of 65% HNO_3 was added, and the liner was sealed in a stainless-steel autoclave. The autoclave was heated at $180\text{ }^{\circ}\text{C}$ for 8 h. After cooling, the sample was redissolved in 1 mL of Milli-Q water and transferred to a vial for CBC determination.

SBC was determined using the CTO-375 method (Text S2).^{14,15} Briefly, 200.00 mg of freeze-dried sediment (weighed to ± 0.01 mg precision) was evenly distributed in a ceramic crucible and combusted at $375\text{ }^{\circ}\text{C}$ for 24 h in a muffle furnace. The resulting residue was analyzed for SBC content using an elemental analyzer (vario MACRO cube, Elementar, Germany). Method reproducibility and associated

analytical uncertainty are summarized in Texts S1 and S2. Both BPCA-derived CBC and CTO-375-derived SBC are operationally defined, semiquantitative fractions rather than strictly isolated BC types. BPCA-derived CBC may be affected by oxidation efficiency, compound recovery, and the applied conversion factor, whereas CTO-375-derived SBC may be underestimated through oxidative loss or overestimated by charring artifacts.^{14,32} The BPCA method can also detect a fraction of soot-derived BC.^{9,11} Conversely, some highly carbonized wood chars produced at $1000\text{ }^{\circ}\text{C}$ may partially survive CTO-375 treatment and thereby contribute to the operationally defined SBC fraction.³³ Together, these cross-responses indicate that the analytical windows of BPCA and CTO-375 partially overlap across the BC continuum, which may affect the apparent relative contributions of CBC and SBC. Accordingly, comparisons between CBC and SBC should be interpreted as semiquantitative rather than as exact mass proportions.

2.3. TOC and TN Measurements

Approximately 1.00 g (weighed to ± 0.01 g precision) of homogenized sediment was treated with 2 mol/L HCl at room temperature and left to stand for 24 h to remove inorganic carbon. The acid-treated sample was centrifuged and rinsed repeatedly with Milli-Q water until the supernatant reached a neutral pH. After freeze-drying, TOC and total nitrogen (TN) contents were determined using an elemental analyzer (vario MACRO cube, Elementar, Germany). Although commonly used, HCl treatment followed by rinsing may result in the loss of acid-soluble organic carbon during supernatant removal, potentially leading to underestimation of TOC and overestimation of BC/TOC.^{34,35} Because the magnitude of this loss was not quantified in this study, BC/TOC values were interpreted only qualitatively and were not used for quantitative source apportionment.

2.4. Calculation of BC Burial Flux

BC burial flux was calculated using established methods,^{27,36} according to the following formula:

$$F_{\text{burial}} = 10^3 \times C \times \rho \times \omega \times (1 - \phi)$$

where F_{burial} is the burial flux of BC ($\mu\text{g cm}^{-2} \text{ year}^{-1}$), C is the BC concentration at 0–10 cm sediment depth (mg/g), and ρ is the density of dry sediment particles (1.5 g cm^{-3}).^{15,37,38} ω is the sedimentation rate (cm year^{-1} ; Text S3), and ϕ sediment porosity (dimensionless). A representative value of 0.75, corresponding to the midpoint of the commonly reported range of 0.70–0.80 for marine sediment mixed layers, was used to calculate the burial-flux point estimates.^{39–41} Representative sedimentation rates were selected on the basis of published regional values and the depositional setting of

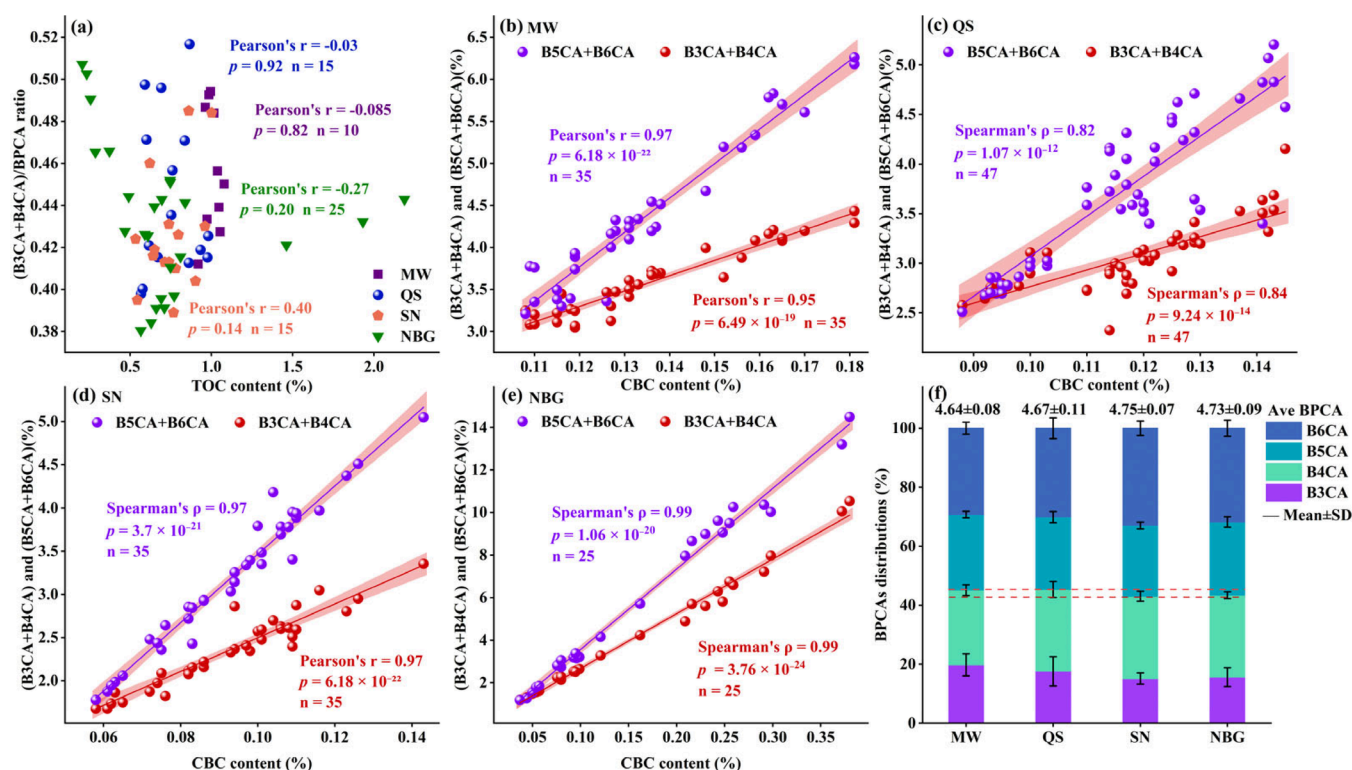


Figure 3. (a) Correlation between TOC content (%) and the (B3CA + B4CA)/BPCA ratio in sediments from four sampling sites. (b–e) Relationships between CBC content (%) and B3CA + B4CA and B5CA + B6CA. (f) Average percentage distributions of B3CA–B6CA and average BPCA numbers.

each site (Text S3): $0.41 \text{ cm year}^{-1}$ for MW, $0.40 \text{ cm year}^{-1}$ for QS, $0.75 \text{ cm year}^{-1}$ for SN, and $0.20 \text{ cm year}^{-1}$ for NBG. These literature-derived rates were treated as fixed representative inputs rather than statistically determined means. Accordingly, the resulting burial fluxes are presented as point estimates conditional on these representative inputs. The propagation of among-sample variability in BC concentrations and the sensitivity of the estimates to the published porosity range are described in Text S4.

2.5. Statistical Analysis

Pearson and Spearman correlation analyses were conducted to evaluate relationships among the measured variables. The choice between Pearson (r) and Spearman (ρ) correlations was based on residual diagnostics from ordinary least squares fits, including tests for normality and homoscedasticity. Spearman correlations were applied when these assumptions were not satisfied. Data visualization was carried out with Origin Pro 2024, and the study area map was generated using ArcGIS 10.4.

3. RESULTS AND DISCUSSION

3.1. Spatial Distribution and Molecular Structure of Sedimentary BC

3.1.1. Spatial Variation and Composition of BC Subtypes. Total BC and its subtypes (char BC and soot BC) exhibited contrasting spatial patterns across the transect (Figure 2). Mean BC contents decreased from the outer-gulf site (NBG; $0.24 \pm 0.14\%$) to Maowei Sea (MW; $0.225 \pm 0.021\%$), Qisha Port (QS; $0.194 \pm 0.020\%$), and Sanniang Bay (SN; $0.153 \pm 0.038\%$). Notably, CBC exhibited a similar pattern, peaking at the outer-gulf site ($0.17 \pm 0.11\%$), followed by the semi-enclosed bays and nearshore sites. In contrast, SBC reached its maximum at MW and decreased progressively at QS, NBG, and SN.

These differences reflect varying depositional environments and levels of anthropogenic disturbance across sites. Maowei Sea receives substantial terrestrial input from the Qinjiang and Maoling rivers, which drain urbanized areas such as Qinzhou City. Along the southern coastline, intensive industrial activity, aquaculture, and land reclamation, together with limited water exchange caused by offshore islands, promote BC accumulation and burial in sediments.^{42,43} Qisha Port has been primarily developed for industrial and urban marine use, is subject to pronounced industrial influence, and also exhibits relatively high BC enrichment. In contrast, Sanniang Bay (Figure 1b), located distant from major industrial hubs in the Beibu Gulf and characterized by historically lower anthropogenic intensity, exhibits relatively low BC enrichment.

Accordingly, contents of BC, CBC, and SBC generally decreased from the semi-enclosed Maowei Sea to the urban–industrial Qisha Port and the Sanniang Bay, consistent with a seaward decline in terrestrial inputs and human activity. This pattern is consistent with previous findings that CBC predominates over SBC in nearshore continental shelf sediments.⁹ However, the outer-gulf site (NBG) displayed the highest BC and CBC contents despite its offshore location, deviating from the expected spatial trend. This deviation likely reflects the combined influence of diverse source inputs and site-specific depositional conditions in marginal seas (Figure 2a).

The NBG core contains silt-rich sediments with particle sizes markedly smaller than those at the other sites.^{28,43,44} Regional cyclonic circulation and tidal forcing promote frequent resuspension and redeposition of fine particles, which enhances the deposition of fine-grained particles in bottom sediments.^{17,43} At the microscale, such particles exhibit

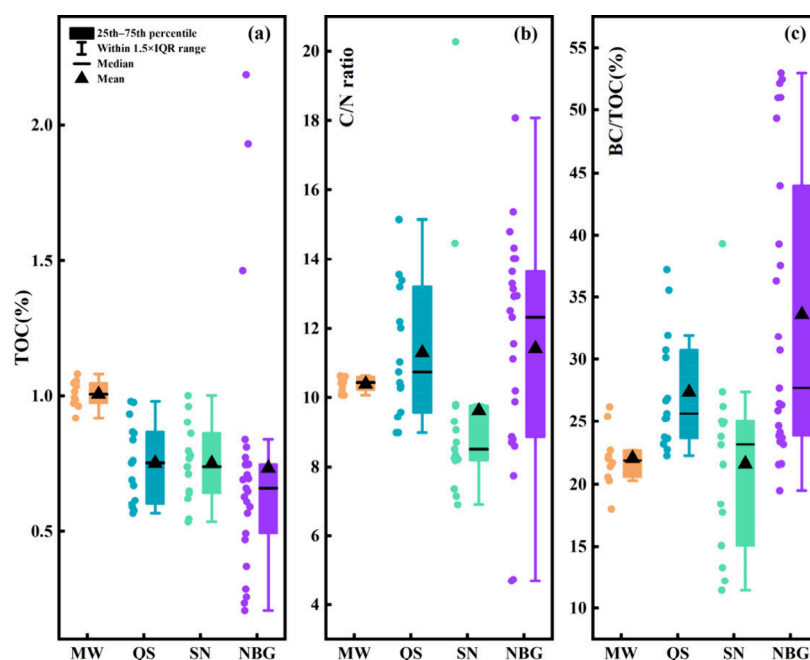


Figure 4. Ranges of TOC, C/N ratio, and BC/TOC in four sediment cores along a gradient from the semi-enclosed bay to the outer-gulf site.

high specific surface areas and abundant sorption sites, serving as efficient carriers of organic matter (OM). These physicochemical attributes enhance BC retention and burial in fine-grained sediments.^{26,36,43,45–47}

Additionally, BC accumulation at the NBG site is influenced by inputs from Weizhou Island, rivers along the Guangxi coast, and material transported northward from northwestern Hainan Island via Beibu Gulf circulation.²⁰ Before the 2000s, both islands relied mainly on agriculture and small-scale fisheries, with limited industrialization and low fossil fuel use. Since then, rapid tourism and shipping development has intensified island-based emissions,^{48,49} notably polycyclic aromatic hydrocarbons (PAHs, SBC precursors) from maritime traffic around Weizhou,^{50–52} while biomass burning remains the dominant BC source in southwestern Hainan.⁵³ The NBG site may also receive long-range CBC from frequent biomass burning in Vietnam and other tropical Southeast Asian countries, delivered via the Red River and other fluvial systems under Beibu Gulf circulation.^{16,19,54–56}

CBC and SBC originate from distinct sources and follow different transport pathways. CBC, generated by low-temperature biomass combustion, is typically delivered via surface runoff and riverine flow, whereas SBC, formed during high-temperature fossil fuel combustion, is mainly transported through long-range atmospheric pathways.^{8,57} At the outer-gulf site (NBG), CBC accounted for approximately 67% of total BC, the highest among all sites, while SBC content was lower than at Maowei Sea (MW) and Qisha Port (QS) and only slightly higher than at Sanniang Bay (SN) (Figure 2a and b). This pattern is consistent with the preferential accumulation of CBC in fine-grained sediments at NBG, whereas limited fossil fuel inputs may constrain SBC levels. Overall, biomass burning likely contributed substantially to CBC enrichment at NBG.

3.1.2. Reliability and Structural Indicators of BPCA-Derived CBC. B3CA and B4CA detected via the BPCA method may partially derive from non-BC organic matter, especially at higher TOC levels, which can affect BC quantification.⁵⁸ However, other studies have shown that

B3CA and B4CA mainly derive from BC during oxidation, suggesting that TOC has limited influence and supporting the specificity of these markers.⁵⁹ In this study, despite the highest TOC in MW and the lowest in NBG, their (B3CA + B4CA)/BPCA ratios were similar, 0.45 ± 0.03 and 0.43 ± 0.03 , respectively (Tables S4 and S5 and Figure 4a). No significant correlation was observed between the (B3CA + B4CA)/BPCA ratio and TOC in any core. In contrast, both (B3CA + B4CA) and (B5CA + B6CA) showed strong correlations with CBC across all sites (Figure 3a–e). Moreover, under our analytical conditions, the OC load during BPCA oxidation remained below the recommended 5 mg OC threshold for reducing artificial BPCA formation from non-pyrogenic organic matter.⁵⁸ These results suggest that interference from non-BC organic matter was likely limited in this study.

The average percentage distribution of BPCAs across sediment cores from different depositional settings was highly consistent (Figure 3f), supporting the exceptional molecular stability of BC. Furthermore, the distribution of BPCAs can help trace combustion sources.⁶⁰ A higher proportion of B5CA and B6CA indicates more condensed BC structures typically formed under high-temperature combustion, mainly as soot and char.^{33,61} In this study, average BPCA values ranged from 4.5 to 4.9 (Tables S2–S5), at the lower end of reported values (4.5–5.5) and below typical SBC signatures,⁶¹ consistent with CBC identification using the BPCA method.

In this study, the (B5CA + B6CA)/BPCA ratio and average BPCA values were slightly higher in the SN and NBG cores than in Maowei Sea (MW) and Qisha Port (QS) (Figure 3f). Significant positive correlations between CBC and SBC were observed in Sanniang Bay (SN; $n = 35$, $r = 0.59$, $p < 0.01$) and the outer-gulf site (NBG; $n = 25$, $r = 0.97$, $p < 0.01$), whereas no such relationship occurred in MW ($n = 35$, $r = -0.23$, $p > 0.05$) or QS ($n = 47$, $r = 0.03$, $p > 0.05$) (Figure S1). This pattern suggests that high-temperature biomass combustion in SN and NBG, under limited industrial influence, produced more condensed CBC. Given the continuous nature of the BC

spectrum, a fraction of less-condensed SBC may also originate from biomass combustion.⁸

3.2. Interactions between Sedimentary Organic Matter and BC

3.2.1. TOC and C/N Ratios as Proxies for Organic Matter Sources. TOC contents generally declined with increasing distance from shore. The highest mean TOC was observed in Maowei Sea (MW; $1.01 \pm 0.05\%$), followed by Qisha Port (QS; $0.75 \pm 0.15\%$) and Sanniang Bay (SN; $0.75 \pm 0.14\%$), while the outer-gulf site (NBG) showed the lowest TOC ($0.74 \pm 0.47\%$) with high variability (Figure 4a). This spatial pattern is consistent with previous findings that terrestrial organic matter preferentially accumulates in nearshore areas of the Beibu Gulf.^{19,43} Alongshore, TOC and BC both declined from MW to QS and SN, suggesting strong terrestrial influence along the nearshore gradient. At NBG, TOC was the lowest among all sites, consistent with the general offshore-decreasing trend, whereas BC and CBC contents were the highest. This TOC–BC decoupling is consistent with early diagenetic organic matter degradation concepts, in which bulk TOC comprises organic components with contrasting reactivity. Preferential remineralization of labile organic matter during early diagenesis can reduce bulk TOC while refractory BC persists, thereby contributing to elevated BC/TOC ratios.⁶² As a refractory component, BC is more resistant to degradation and preferentially retained during burial, while labile organic matter is more susceptible to early diagenetic degradation and microbial remineralization.⁶³ In addition, the weak hydrodynamics, fine-grained texture, and high specific surface area at NBG promote the selective retention of BC.^{64,14} The relatively low TOC at NBG may therefore reflect preferential remineralization of labile organic matter and heterogeneity in organic matter composition.

The C/N ratio is a widely used indicator for distinguishing marine and terrestrial organic matter sources. Marine organic matter typically shows low C/N values, with phytoplankton averaging ~ 7 and algal inputs ranging from 4 to 10. In contrast, terrestrial sources exhibit higher values: >15 for land-derived material, 5–15 for soil microbial inputs, ≥ 20 for vascular plants, and >30 for C_4 plants.^{64–67} These thresholds are widely applied to distinguish source contributions in marine sediments.

In this study, mean C/N values were 11.4 ± 3.3 at the outer-gulf site (NBG), 11.3 ± 1.9 at Qisha Port (QS), 10.4 ± 0.2 at Maowei Sea (MW), and 9.6 ± 3.4 at Sanniang Bay (SN) (Figure 4b). Most values clustered around 9–12, indicating mixed contributions from marine phytoplankton, soil-derived material, and terrestrial vegetation.²⁰ This contrast aligns with earlier findings that C/N values in the Maowei Sea (7–12) exceed those in Sanniang Bay, reinforcing the C/N ratio as a source indicator across sedimentary gradients in the Beibu Gulf.⁴³

Notably, elevated C/N values were observed at 44–50 cm in NBG (14.8–18.1) and at 30 cm in SN (20.3) (Tables S2 and S5), approaching or exceeding the vascular plant threshold (>15). These excursions likely reflect episodic delivery of vascular plant material, especially at NBG, where biomass-burning signals and multiple terrestrial inputs are evident. Using the local sedimentation rate ($0.20 \text{ cm year}^{-1}$; Text S3), the corresponding layers are estimated to date to the late 18th to early 19th century, a period of frequent regional conflicts,

intensified land-use change in southern China, and flood disasters. These disturbances likely increased terrestrial runoff and biomass burning, contributing to a disproportionate increase in CBC relative to SBC during this interval. Further dating is required to confirm this interpretation. A volcanic source is unlikely, as eruptions on Weizhou Island ceased $>10\,000$ years ago.⁶⁸

At SN, a similar C/N excursion occurred at 30 cm and co-occurred with a sharp decline in TN, a moderate decrease in TOC, and minor increases in CBC and SBC, indicating combined effects of diagenetic alteration and terrestrial input. The paired increases in CBC and SBC suggest a modest rise in combustion-derived material; however, the magnitude of the C/N excursion is more plausibly driven by preferential remineralization of labile, nitrogen-rich organic matter (algal and microbial), leading to substantial N loss and elevated C/N despite minor changes in TOC.⁶⁹ This demonstrates that the C/N ratio responds to both source variations and early diagenetic processes in coastal settings.

3.2.2. Relationships between BC and TOC and Their Source Implications. BC–TOC coupling differed by site (Figure S2a–d). BC and TOC were positively correlated at Qisha Port (QS; $n = 15$, $r = 0.62$, $p < 0.05$) and the outer-gulf site (NBG; $n = 25$, $\rho = 0.78$, $p < 0.01$), but not at Maowei Sea (MW; $n = 10$, $r = -0.36$, $p > 0.05$) or Sanniang Bay (SN; $n = 15$, $r = -0.16$, $p > 0.05$). This pattern likely results from variable terrestrial and marine inputs contributing to TOC composition.⁷⁰ At QS, nearshore runoff, and at NBG, combined riverine and atmospheric sources, enhanced terrestrial input and coaccumulation of BC with TOC. In MW, terrestrial input is substantial. However, high primary productivity contributes labile marine organic matter, which dilutes the BC–TOC association.^{36,46} SN shows a similar pattern, with the lowest average C/N ratio indicating dominance of autochthonous marine organic matter (Figure 4b). These results indicate that BC–TOC correlations provide complementary qualitative evidence for source differences across the depositional gradient.⁶⁴

Mean BC/TOC (%) decreased from NBG ($34 \pm 12\%$) to QS ($27.4 \pm 4.7\%$), MW ($22.1 \pm 2.4\%$), and SN ($21.6 \pm 7.3\%$) (Figure 4c). These values are consistent with reported ranges in marginal seas and continental shelves, such as the Mediterranean (5–38%), Swedish shelf (2–47%), Taiwanese coastal waters (12–40%) and the East China Sea (14.1–47.1%).^{12,25,71,72} In the Bohai and Yellow Seas, reported ranges were 0.8–34.2 and 4.3–45.2%, respectively.⁴¹ Full site-specific BC/TOC ranges are listed in Tables S2–S5. The relatively high measured BC/TOC at NBG, although potentially affected by TOC loss during pretreatment, is consistent with refractory-carbon enrichment. This pattern may reflect preferential degradation of labile organic matter (OM) under prolonged oxygen exposure at low sedimentation rates, together with selective BC retention by fine-grained, high-surface-area particles. Given the unquantified uncertainty associated with TOC pretreatment, BC/TOC (%) is interpreted only as qualitative supporting evidence for differences in BC input and preservation across nearshore and shelf environments.

BC serves as an indicator of both terrestrial input and anthropogenic activity.^{12,23} BC/TOC (%) tends to be lower in rural areas than in urban centers, due to spatial differences in combustion intensity and organic matter composition.⁷³ A BC/TOC ratio above 50% is generally used to indicate dominance of fossil-fuel-derived BC.^{74,75} In this study, most

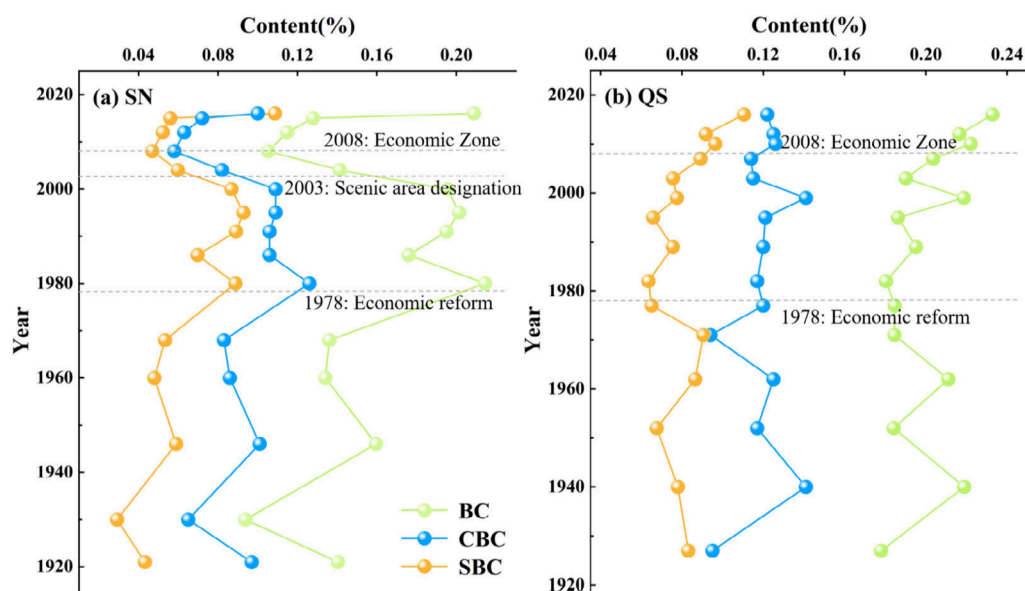


Figure 5. Historical variations of BC, CBC, and SBC in sediment cores from SN and QS, with selected socio-economic milestones indicated by horizontal dashed lines.

measured BC/TOC ratios fell below this threshold, suggesting a substantial biomass-burning contribution. Occasional values exceeding the threshold may reflect localized fossil fuel inputs, although potential TOC loss during pretreatment may also elevate BC/TOC. Spatial patterns of BC/TOC (%) were broadly consistent with C/N ratios, suggesting joint influences of source and depositional processes. The combined use of BC/TOC and C/N provides complementary qualitative evidence for interpreting source differences and early diagenetic effects in marginal sea sediments.⁹

Source attribution remains uncertain because CBC and SBC are not uniquely associated with biomass and fossil fuel combustion, respectively.^{8,9} The proxies used here may also be influenced by transport and environmental processing.^{15,25} Accordingly, our source interpretations are qualitative and based on multiple complementary indicators rather than quantitative source apportionment.

3.3. Spatial Patterns and Controls of BC Burial

BC burial flux reflects the net accumulation of refractory organic carbon, often of terrestrial origin. It serves as an indicator of land–ocean carbon transfer in marginal seas.²⁷ Under the representative parameter set used here, the estimated total BC burial flux was highest at Sanniang Bay (SN; $420 \mu\text{g cm}^{-2} \text{ year}^{-1}$) and lowest at the outer-gulf site (NBG; $140 \mu\text{g cm}^{-2} \text{ year}^{-1}$), whereas Qisha Port (QS) and Maowei Sea (MW) yielded similar intermediate point estimates of 340 and $320 \mu\text{g cm}^{-2} \text{ year}^{-1}$, respectively (Figure S3). The higher estimate at SN primarily reflected the higher representative sedimentation rate for this site ($0.75 \text{ cm year}^{-1}$; Text S3). Sediment texture may also influence organic carbon retention at SN.²⁸ In contrast, although NBG had the highest BC content, it had the lowest estimated burial flux because of the lower representative sedimentation rate for this site (Text S3). Even with very fine particles ($\sim 7 \mu\text{m}$) which may promote BC retention,^{18,21,76} the lower sedimentation-rate input resulted in a lower burial flux. The contrast between SN and NBG illustrates that high BC content does not necessarily translate into high estimated burial flux and highlights

sedimentation rate as an important control on burial-flux estimates.

CBC and SBC burial fluxes show consistent subtype contrasts across the transect, with CBC exceeding SBC at all sites. The estimated CBC burial fluxes at SN, QS, MW, and NBG were 220 , 190 , 170 , and $73 \mu\text{g cm}^{-2} \text{ year}^{-1}$, respectively; the corresponding SBC fluxes were 200 , 150 , 150 , and $61 \mu\text{g cm}^{-2} \text{ year}^{-1}$. At all sites, CBC accounted for approximately 52–57% of the estimated total BC burial flux, compared with 43–48% for SBC. This pattern was observed across contrasting depositional settings, including industrially influenced QS and the semi-enclosed, terrestrially influenced MW. This pattern indicates sustained biomass-derived inputs as a major contributor to BC burial in the Beibu Gulf. Considering SBC alone would underestimate total BC burial flux by more than half.

To place the range of estimated total BC burial fluxes among individual samples (130 – $590 \mu\text{g cm}^{-2} \text{ year}^{-1}$) in a broader marginal sea context, we compiled published fluxes from representative systems (Table S6). These fluxes fall within the ranges reported for other marginal seas, including Qinzhou Bay (58 – $1848 \mu\text{g cm}^{-2} \text{ year}^{-1}$, BPCA method), the Bohai and Yellow Seas [4 – $1100 \mu\text{g cm}^{-2} \text{ year}^{-1}$, thermal/optical reflectance (TOR) method], and the East China Sea (10 – $3360 \mu\text{g cm}^{-2} \text{ year}^{-1}$, CTO-375 method).^{15,41,77} Compared with the Gulf of Thailand ($212 \pm 228 \mu\text{g cm}^{-2} \text{ year}^{-1}$, TOR method),⁷⁸ burial fluxes in the Beibu Gulf are generally higher, likely due to stronger terrestrial input and faster sedimentation. In contrast, burial fluxes in the Beibu Gulf are orders of magnitude higher than those in the open ocean, such as the South Atlantic (0.5 – $7.8 \mu\text{g cm}^{-2} \text{ year}^{-1}$, CTO-375 method).²⁴ However, they remain substantially lower than values reported for the Pearl River Estuary (197 – $6480 \mu\text{g cm}^{-2} \text{ year}^{-1}$, TOR method),²⁷ a region with intense anthropogenic influence. These comparisons highlight the Beibu Gulf's capacity for long-term sedimentary BC storage along continental margins.

3.4. Temporal Shifts in BC Subtypes and Combustion Source Changes

This section analyzes two dated sediment cores (Sanniang Bay and Qisha Port) from the Beibu Gulf shelf to trace centennial-scale changes in BC deposition associated with anthropogenic activity and energy transitions. The precise chronological frameworks of the SN and QS cores were established using ^{210}Pb and ^{137}Cs dating methods and published in a previous study.²⁸ Both the MW and NGB cores were excluded due to the absence of reliable $^{210}\text{Pb}/^{137}\text{Cs}$ chronologies.

The SN core (Figure 5a) showed synchronous fluctuations in BC, CBC, and SBC concentrations during the 1930s–1950s. All three fractions decreased from the 1920s to the early 1930s, likely reflecting reduced energy use during domestic turmoil (e.g., the First Revolutionary Civil War, 1924–1927). They then increased from the 1930s–1940s, possibly reflecting intensified combustion during the Second Sino-Japanese War (1937–1945).⁷⁹ CBC concentrations consistently exceeded SBC, indicating biomass burning as the dominant BC source in the SN core. After the war ended in the late 1950s, combustion activity weakened, and BC levels declined accordingly.

BC, CBC, and SBC concentrations increased markedly during the 1960s–1980s, consistent with industrial recovery and growing energy demand under China's planned economy. Quadratic fits (Figure S8a) showed that CBC peaked at 0.15% in 1967 ($R^2 = 0.33$), while SBC reached a maximum of 0.089% in 1978 ($R^2 = 0.45$). The earlier and higher CBC peak corresponds to widespread biomass use during the early phase of China's Third Front construction (1964–1970), while the later SBC maximum reflects the onset of economic reform (initiated in 1978) and increased fossil fuel consumption.

BC emissions declined steadily from the 1990s to 2010s, driven by market-oriented reforms and strengthened environmental regulations.^{80,81} The most pronounced reductions occurred in the 2000s, reflecting energy restructuring and stricter policy enforcement. The designation of Sanniang Bay as a tourism scenic area in 2003 promoted ecological conservation, restricted industrial expansion, and reduced combustion-related inputs to local sediments. The launch of the Guangxi Beibu Gulf Economic Zone in 2008 triggered intensified industrialization and fossil fuel consumption, which led to a moderate increase in BC, CBC, and SBC concentrations (Figures S4 and S5). CBC remained dominant, suggesting sustained biomass contributions despite rising fossil fuel use. The 2016 surface sample exhibited anomalously high BC without corresponding increases in regional energy use. It was excluded from regression analysis to avoid skewing long-term trends.

Under minimal industrial influence, the SN record was consistently dominated by biomass burning,⁵⁷ with CBC concentrations exceeding SBC throughout the profile. Fossil fuel signals were also evident, as SBC regression exhibited a slightly higher R^2 than CBC, indicating its greater sensitivity to combustion source variability. The SN core thus represents a stable sedimentary archive of long-term biomass-burning trends and background conditions in marginal seas.

In the QS core (Figure 5b), BC and CBC rose sharply in the 1930s, likely due to increased biomass combustion during the Second Sino-Japanese War (1937–1945).⁷⁹ Both declined sharply by the 1950s, coinciding with the cessation of wartime activities. In contrast, SBC declined gradually, likely reflecting wartime disruption of energy infrastructure. Between the 1950s

and 1960s, BC, CBC, and SBC increased markedly, reflecting renewed industrial activity in Qisha Port during the early planned-economy period. The rise in SBC, in particular, suggests greater fossil fuel combustion, primarily diesel, occurring alongside continued biomass burning.⁸¹

During the 1960s to 1980s, BC, CBC, and SBC displayed divergent trajectories. BC declined steadily, indicating reduced overall energy demand. CBC initially decreased, likely due to curtailed biomass burning during the Cultural Revolution, and later rebounded as rural biomass use intensified. SBC continued to rise into the early 1980s, driven by increased fossil fuel combustion, primarily coal, associated with the Third Front construction, and then declined sharply during the late Cultural Revolution amid widespread industrial disruption. The relative resilience of CBC throughout this period highlights the persistent contribution of biomass-derived inputs (Figures S4 and S6).

From the 1990s to 2020s, BC and SBC increased steadily under ongoing economic reforms (initiated in 1978) and industrialization, while CBC remained relatively stable. Although CBC was still the most abundant fraction, SBC became the primary driver of BC variability, reflecting the expanding influence of fossil fuel combustion.^{8,82} Elevated PAH concentrations in multiple Beibu Gulf cores corroborate this trend, since PAHs are molecular precursors of SBC.^{50,83–85} Regional fossil fuel consumption, mainly coal and petroleum, increased continuously from 1981 to 2018, further confirming the growing fossil fuel contribution to BC (Figure S7).

Quadratic fits for the QS core highlight this contrast (Figure S8b). The CBC curve is nearly flat with low variability ($R^2 = 0.07$). In contrast, the SBC curve shows a pronounced concave shape and a substantially higher R^2 value (0.42), indicating stronger responsiveness to socio-political disruptions and energy transitions. These patterns demonstrate that SBC responds dynamically to combustion shifts, whereas CBC remains the dominant fraction, providing a stable signal of long-term biomass combustion. Accordingly, although CBC remained abundant, control over BC variability in the QS record gradually shifted to SBC, reflecting energy restructuring under regional socio-economic transformation. These results underscore the value of the QS core as a high-resolution archive for reconstructing combustion-source evolution and assessing long-term anthropogenic impacts in marginal seas.

These contrasting subtype dynamics reflect marked spatial heterogeneity in combustion patterns and regulatory influences. SN represents a stable regime dominated by biomass combustion, whereas QS shows greater sensitivity to increasing fossil fuel inputs. This comparison shows that combustion histories are preserved differently across sites, yet a persistent biomass-burning signal remains due to CBC dominance. Collectively, these findings shed light on the mechanisms linking anthropogenic activity to long-term carbon cycling in shelf sediments.

To the best of our knowledge, this study provides one of the first systematic comparisons of sedimentary BC subtypes (CBC and SBC) across diverse depositional settings in the Beibu Gulf, revealing pronounced spatial heterogeneity in sedimentary BC distribution. Our results are based on a nearshore–outer-gulf transect and reflect BC preservation and burial under coastal depositional conditions. SBC is highly sensitive to fossil fuel combustion in nearshore industrial zones, whereas CBC dominates across the study sites, reflecting a long-term legacy of biomass burning. Enhanced

anthropogenic activity has reshaped BC composition and promoted the accumulation and burial of SBC in coastal areas. In the outer-gulf setting, lower sedimentation rates and association with fine particles favor the selective preservation of CBC. Structural characteristics further support the highly condensed nature of CBC and its potential for long-term preservation in sediments. These findings underscore that marginal sea sediments can both record combustion history and provide long-term sedimentary BC storage, with net atmospheric CO₂ sequestration attributable primarily to biomass-derived CBC. Separating CBC and SBC is therefore crucial for evaluating BC burial in marginal seas under increasing anthropogenic pressure.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.6c06586>.

Detailed procedures for CBC and SBC quantification, site-specific sedimentation rates, geochemical and stratigraphic data from four sediment cores, vertical profiles and statistical correlations of TOC, BC subtypes, and BPCA markers, energy consumption records in Guangxi, and regression analysis of combustion-source transitions (PDF)

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■ NOTES

The authors declare no competing financial interest.

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