

# Composition and Distribution of Aliphatic Hydrocarbon Compounds and Biomarkers in Seafloor Sediments from Offshore of the Leizhou Peninsula (South China)

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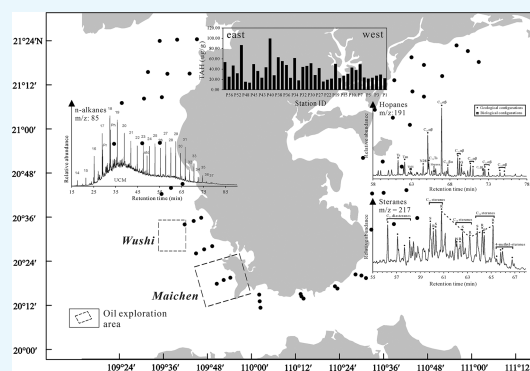
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**ABSTRACT:** The offshore of Leizhou Peninsula (LP, China), which contains unique ecosystems such as mangroves, seagrass beds, and coral reefs, is an environmentally sensitive area. For this reason, the levels of aliphatic hydrocarbon including biomarkers (hopanes, steranes) in the offshore seafloor sediments were analyzed in terms of their composition, distribution, and input sources and aimed to evaluate the extent of possible petroleum hydrocarbon contamination in the sediments of coastal areas. The total aliphatic hydrocarbons (TAH) fraction, the content of total *n*-alkanes ( $nC_{14}$ – $nC_{37}$ ) ( $\sum n$ -alkanes), and content of hopane + sterane are in the range of 13.76–99.53, 1.22–8.33, and 0.02–0.23  $\mu\text{g/g dw}$ , respectively. The presence of unresolved complex mixture (UCM) hydrocarbons hump and petrogenic steranes and hopanes in these seafloor sediments suggest that petrogenic sourced hydrocarbon inputs were present. The stations on the peninsula's southwest side had the lowest values of UCM/resolved aliphatic compounds (UCM/R) and UCM/*n*-alkanes. These findings suggest that seafloor sediments from the southwest offshore of the peninsula were likely contaminated by recently inputted petroleum hydrocarbons. The presence of relatively high  $\sum n$ -alkanes content in seafloor sediments from southwest offshore of the LP, combined with relatively low natural *n*-alkane ratios (NARs), indicates an increased influence of petrogenic hydrocarbons. The elevated levels of recent petrogenic hydrocarbon contamination in the sediments from the LP's southwestern offshore were likely related to petroleum exploitation in the Beibu Gulf's Maichen and Wushi sags.



## 1. INTRODUCTION

Marine sediments are the predominant long-term sink for organic carbon in the biogeochemical reduced carbon cycle as they incorporate organic matter (OM) into the geochemical carbon cycle.<sup>1,2</sup> Despite accounting for only 7.6% of the global ocean, continental shelf sediments receive significant terrestrial and marine organic carbon inputs and account for more than 80% of the organic carbon buried in oceans.<sup>3,4</sup> In recent decades, anthropogenic activities such as industrial discharge, agricultural emission sewage input, marine fish farming, and so on have had extremely significant impacts in the coastal and estuarine regions. It is essential to delineate the origins of OM in seafloor sediments for a quantitative understanding of the global/regional carbon cycle, as well as environmental evaluations and ecosystem preservation.

Hydrocarbons from both natural and anthropogenic sources are ubiquitous in the marine environment. Organic geochemistry played a significant role in the identification and quantification of organic matter sources. Biomarkers, in particular, can provide valuable information on OM origin and transformation processes. The hydrocarbon compounds,

including biomarkers (hopanes and steranes), are widely used in petroleum and environmental geochemical studies.<sup>5–7</sup>

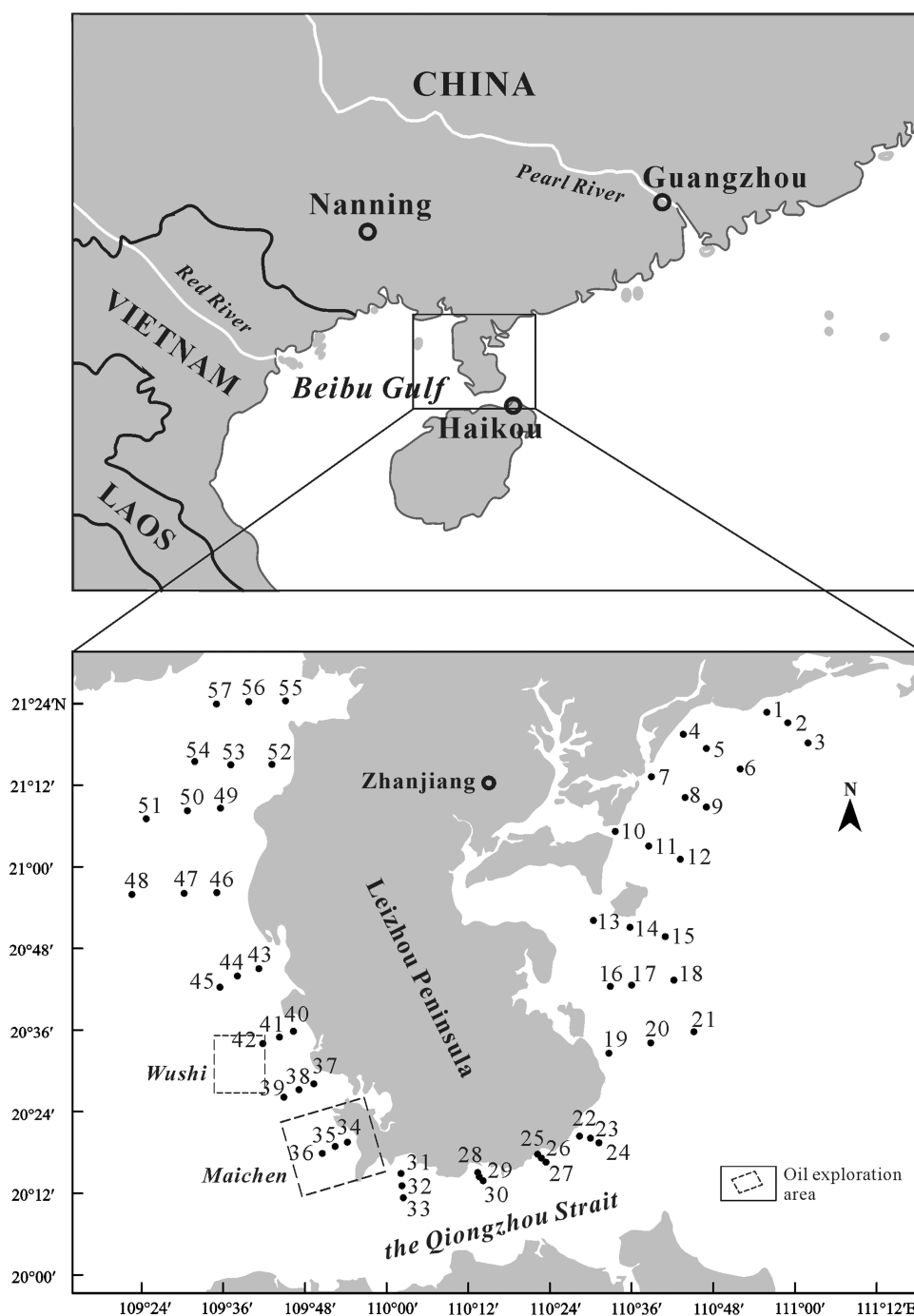
The Leizhou Peninsula (LP) is located on the Chinese mainland's southernmost tip, northwest of the South China Sea. It has a winding coastline with numerous bays and islands, as well as distinctive ecosystems such as mangroves, seagrass beds, and coral reefs. The coastal environment of the LP is complex owing to the influence of the Pearl and Red River plumes, river runoff from the LP and Hainan Island, and saltwater from the South China Sea. Furthermore, the uneven distribution and development of industry and agriculture caused certain disturbances to the surrounding ecosystem. As one of China's most critical subtropical mangrove regions, the LP has significant marginal effects on the carbon pool of offshore marine sediments (Figure 1).<sup>8</sup>

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**Figure 1.** Map of the study area and sampling locations.

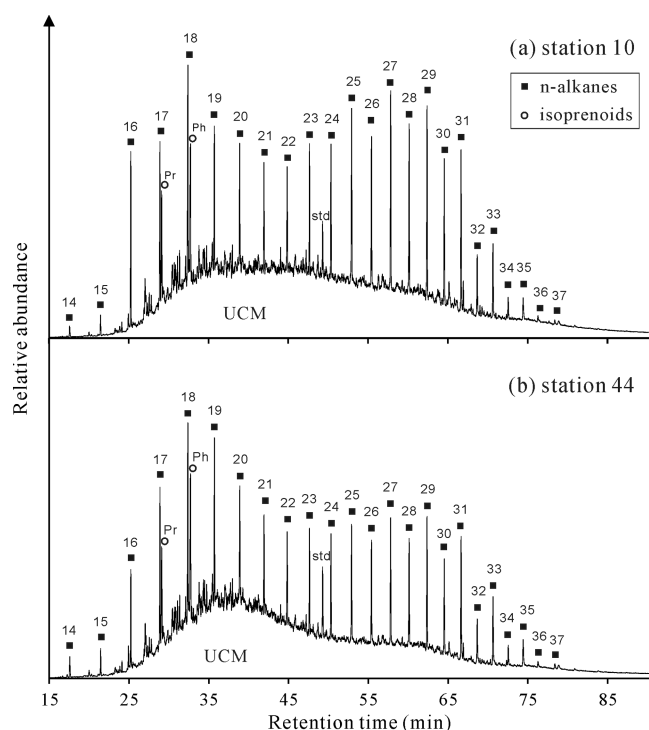
Few studies have been carried out on the organic geochemistry of seafloor sediments in the offshore area of the LP<sup>9–14</sup>. In this study, we report the concentration of *n*-alkanes and biomarker levels in seafloor sediments surrounding the LP and determine their distribution, composition, and sources in this area.

## 2. RESULTS AND DISCUSSION

### 2.1. Content of Total Aliphatic Hydrocarbons (TAHs).

The total aliphatic hydrocarbons (TAHs) in the seafloor sediments from offshore of LP were composed of resolved compounds (e.g., *n*-alkanes and isoprenoids) and unresolved complex mixtures (UCM), as shown in Figure 2. TAH

concentrations ranged from 13.76 to 99.53  $\mu\text{g/g dw}$  (sediment dry weight), all of which were less than 100  $\mu\text{g/g dw}$ , with the highest values recorded at sites P40 and P51 (Table 1). Intertidal and estuarine sediments with TAHs in concentrations lower than 10  $\mu\text{g/g dw}$  are considered unpolluted. Sediments having total aliphatic hydrocarbons contents more than 100  $\mu\text{g/g dw}$ , on the other hand, are associated with petroleum inputs.<sup>15,16</sup> When TAH concentrations are lower than 50  $\mu\text{g/g dw}$ , a more detailed analysis of the hydrocarbon constituents is required to assess the magnitude of contamination.<sup>16</sup> The TAH concentrations in our research were much lower than those reported in severely contaminated areas such as the Xiamen Harbor, China (133–943  $\mu\text{g/g}$



**Figure 2.** Typical gas chromatography–mass spectrometry (GC–MS) chromatograms of *n*-alkanes (squares) and isoprenoids (circles) for seafloor sediments from station 10 (a) and station 44 (b) from the offshore Leizhou Peninsula. Pr for Pristane; Ph for Phytane; UCM for unresolved complex mixtures; std for standard (C24D50).

dw),<sup>17</sup> and New York Bight (500–3000  $\mu\text{g/g}$  dw).<sup>18</sup> In general, seafloor sediment samples in our research contained relatively low levels of TAHs (concentrations < 100  $\mu\text{g/g}$  dw) and are considered slightly polluted.

**2.2. Content and Composition of *n*-Alkanes.** *n*-Alkanes were detected in the range of *n*-C<sub>14</sub>–*n*-C<sub>37</sub>. Except for Site P22, the *n*-alkanes in all samples exhibited bimodal distributions, with *n*-C<sub>17</sub> or *n*-C<sub>18</sub> and *n*-C<sub>27</sub>, *n*-C<sub>29</sub>, or *n*-C<sub>31</sub> as maxima (Figure 2). On a dry weight basis, the total concentrations of *n*-alkanes ( $\sum n$ -alkanes) ranged from 1.22 to 8.33  $\mu\text{g/g}$  dw, with an average value of 4.24  $\mu\text{g/g}$  dw (Table 1). The maximum value was obtained at station P34, while the lowest value was obtained at station P47. The seafloor sediments in our research had higher  $\sum n$ -alkanes values than those from the Pearl River Estuary (0.53–0.87  $\mu\text{g/g}$  dw),<sup>19</sup> Yellow River Estuary (0.356–0.572  $\mu\text{g/g}$  dw),<sup>20</sup> Bohai Sea (0.39–4.4  $\mu\text{g/g}$  dw),<sup>21</sup> Laizhou Bay (0.18–1.42  $\mu\text{g/g}$  dw),<sup>22</sup> and Yangtze River Estuary (0.16–1.88  $\mu\text{g/g}$  dw).<sup>23</sup> The  $\sum n$ -alkanes values of the sediments from two short cores in our study area ranged from 0.37 to 6.03  $\mu\text{g/g}$  dw.<sup>14</sup> The relatively high  $\sum n$ -alkanes concentrations in our study were recorded at stations P31 to P38 located on the southwestern coast of the LP (Figure 1).

There are numerous sources that contribute to the presence of sedimentary *n*-alkanes with varying distribution characteristics. Marine phytoplankton produces mostly short-chain *n*-alkanes, predominantly *n*-C<sub>15</sub>, *n*-C<sub>17</sub>, and *n*-C<sub>19</sub>, and have a strong odd-to-even carbon preference. Both microbial activity and fossil fuel input contribute to the production of short-chain *n*-alkanes, but neither has a strong odd-to-even carbon preference. The Carbon Preference Index (CPI) has been widely used as a source indicator for *n*-alkanes in marine sediments.<sup>24,25</sup> CPI<sub>25–33</sub><sup>26</sup> and CPI<sub>15–19</sub><sup>27</sup> are two parameters

that are frequently used to indicate sources of low-molecular-weight compounds (LMW, *n*-C<sub>14–21</sub>) and high-molecular-weight compounds (HMW, *n*-C<sub>22–34</sub>), respectively. The CPI<sub>15–19</sub> ranged from 0.54 to 1.12 in the sediments collected for this study (Table 1), indicating a weak even-carbon-number predominance. Even-carbon-number preferences in the LMW compounds for marine sediment indicate mainly microbial activity, although petroleum-derived inputs are also possible.<sup>28–30</sup> Terrestrial higher plants produce the long-chain *n*-alkanes *n*-C<sub>25–35</sub> with a strong odd-to-even carbon preference, predominantly *n*-C<sub>27</sub>, *n*-C<sub>29</sub>, and *n*-C<sub>31</sub>. Long-chain *n*-alkanes can also be derived from marine phytoplankton, microorganisms, and oil pollution but with no carbon preference.<sup>15</sup> Furthermore, biological sources of long-chain *n*-alkanes, such as microalgae and cyanobacteria, can also contribute to the abundance of *n*-C<sub>15</sub> and *n*-C<sub>17</sub>. Generally, CPI<sub>25–33</sub> values ranging from 3 to 6 indicate *n*-alkanes derived from terrestrial vascular plants, whereas CPI<sub>25–33</sub> values close to 1 suggest petrogenic hydrocarbon inputs. Furthermore, CPI<sub>25–33</sub> values less than 1 indicate microbial sources of hydrocarbons,<sup>31</sup> while  $1 < \text{CPI}_{25–33} < 3$  are thought to infer oiled sediments.<sup>18</sup> Our sediments had CPI<sub>25–33</sub> values ranging from 1.07 to 1.66 (Table 1). These results indicated that all marine sediments are contaminated with petrogenic hydrocarbons and that a mixture of petrogenic and biogenic hydrocarbons was likely to exist in the sediments.

The natural *n*-alkane ratio (NAR) can be used to distinguish between petrogenic and biogenic sources of *n*-alkanes. A low NAR value (close to 0) may indicate crude oil and petrogenic hydrocarbons. In contrast, a high NAR value (close to 1) usually indicates biogenic inputs. The NAR values obtained from this study's samples ranged from 0.011 to 0.180, with an average of 0.087 (Table 1). The NAR values suggested that the *n*-alkanes in the seafloor sediments predominantly originated from petrogenic hydrocarbon sources. Samples P31–P35, which emerged from the LP's southwestern offshore, had a relatively low NAR (Figure 1).

**2.3. Abundance of Unresolved Complex Mixture.** All samples included UCM containing cycloalkanes, branched alkanes, and other compounds unresolved by the capillary column; which appeared as a “hump” below the resolved compounds.<sup>32</sup> UCM concentrations <10  $\mu\text{g/g}$  dw are common in coastal environments and can be caused by bacterial degradation of OM.<sup>15,33</sup> The presence of UCM and hydrocarbon biomarkers can indicate the input of petrogenic hydrocarbons. In our study, UCM made up the major component of aliphatic hydrocarbons, with concentrations ranging from 10.86 to 81.10  $\mu\text{g/g}$  dw and accounting for 63–84% of the TAH. High concentrations of both TAH and UCM were also found at sites P40 and P51. High UCM concentrations indicate petroleum contamination or a chronically degraded complex hydrocarbon mixture.<sup>23,34</sup> The ratio of UCM to resolved aliphatic compounds (UCM/R) or UCM/ $\sum n$ -alkanes can distinguish contamination from fresh and degraded petroleum.<sup>35–38</sup> Values of UCM/R <4 and UCM/ $\sum n$ -alkanes <10 suggest recent pollution that has been diluted by natural inputs, whereas UCM/R >4 and UCM/ $\sum n$ -alkanes >10 values confirm extensive biodegradation of petroleum-related inputs. Table 1 shows our samples' UCM/R and UCM/*n*-alkanes values, which varied from 1.67 to 5.32 and 1.96 to 20.39, respectively. Almost all of the highest values came from the LP's northwestern coast, indicating a high degree of biodegradation and chronic contamination from

Table 1. Concentrations of TAH,  $\sum n$ -Alkanes, UCM, and Hydrocarbon Geochemical Indexes for Offshore Seafloor Sediments of the Leizhou Peninsula<sup>a,b</sup>

sampling site	TOC (% dw)	UCM ( $\mu\text{g/g dw}$ )	R ( $\mu\text{g/g dw}$ )	TAH ( $\mu\text{g/g dw}$ )	$\sum n$ -alkanes ( $\mu\text{g/g dw}$ )	UCM/R	UCM/ $\sum n$ -alkanes	NAR	CPI <sub>15-19</sub>	CPI <sub>25-33</sub>	Pr/Ph	Pr/ <i>n</i> -C <sub>17</sub>	Ph/ <i>n</i> -C <sub>18</sub>
P1	0.28	18.09	4.27	22.36	2.18	4.24	8.30	0.160	0.89	1.61	0.87	0.90	0.94
P2	0.30	23.54	5.97	29.51	3.02	3.94	7.79	0.176	0.91	1.65	0.86	0.90	0.96
P3	0.59	21.27	6.05	27.32	2.95	3.52	7.21	0.168	0.76	1.66	0.78	0.95	0.87
P4	0.35	18.10	5.15	23.26	2.79	3.51	6.49	0.149	0.86	1.57	0.78	0.89	0.89
P5	0.31	16.80	4.74	21.54	2.42	3.54	6.94	0.121	0.79	1.44	0.85	0.91	0.82
P6	0.51	18.63	5.24	23.88	2.94	3.56	6.34	0.169	0.87	1.65	0.96	0.89	0.84
P7	0.55	38.81	10.66	49.47	6.12	3.64	6.34	0.057	0.78	1.17	0.78	0.86	0.84
P9	0.43	29.59	8.71	38.29	5.30	3.40	5.58	0.073	0.78	1.22	0.75	0.87	0.87
P10	0.36	34.54	8.64	43.18	4.05	4.00	8.53	0.134	0.67	1.45	0.78	0.85	0.73
P13	0.19	23.69	6.81	30.51	3.84	3.48	6.17	0.091	0.92	1.27	0.86	1.01	1.04
P15	0.52	20.91	6.46	27.37	4.20	3.24	4.98	0.097	1.08	1.33	0.75	0.58	0.94
P18	0.34	16.29	6.40	22.69	3.97	2.55	4.10	0.056	1.10	1.20	0.82	0.62	0.95
P19	0.34	39.07	11.25	50.32	4.82	3.47	8.11	0.055	0.67	1.17	0.79	0.83	0.70
P21	0.09	16.12	5.60	21.71	2.82	2.88	5.72	0.029	1.06	1.10	0.64	0.39	0.73
P22	0.36	13.90	5.61	19.51	4.12	2.48	3.37	0.050	0.92	1.17	0.26	0.78	0.91
P23	0.33	11.62	4.26	15.87	2.84	2.73	4.09	0.035	0.80	1.13	0.42	0.93	0.86
P27	0.59	31.89	10.24	42.13	5.86	3.11	5.44	0.035	0.64	1.13	0.58	0.89	0.67
P29	0.51	20.82	7.62	28.44	6.05	2.73	3.44	0.042	1.12	1.14	0.64	0.50	0.80
P30	0.29	41.09	10.22	51.31	3.91	4.02	10.51	0.068	0.88	1.14	0.78	0.88	0.90
P31	0.33	33.96	12.34	46.30	8.22	2.75	4.13	0.013	0.79	1.07	0.79	0.82	0.82
P32	0.50	32.25	11.99	44.24	8.19	2.69	3.94	0.024	0.81	1.08	0.74	0.78	0.84
P33	0.34	11.62	6.45	18.07	5.52	1.80	2.11	0.024	1.09	1.11	0.63	0.46	0.76
P34	0.43	47.37	14.09	61.46	8.33	3.36	5.69	0.017	0.54	1.08	0.67	0.80	0.64
P35	0.71	14.43	8.65	23.08	7.38	1.67	1.96	0.011	0.58	1.08	0.51	0.71	0.67
P36	0.52	37.39	10.62	48.01	5.96	3.52	6.27	0.051	0.84	1.15	0.70	0.82	0.90
P37	0.79	43.42	12.20	55.62	6.63	3.56	6.55	0.082	0.93	1.24	0.76	0.91	1.00
P38	0.57	48.99	14.08	63.07	7.21	3.48	6.79	0.051	0.85	1.13	0.73	0.84	0.89
P39	0.70	21.36	6.68	28.04	3.09	3.20	6.91	0.115	0.77	1.40	0.96	0.96	0.87
P40	0.75	81.10	18.43	99.53	6.59	4.40	12.31	0.102	0.87	1.23	0.71	0.88	0.96
P42	0.50	34.99	8.64	43.63	3.41	4.05	10.26	0.131	0.94	1.41	0.83	0.88	0.95
P43	0.23	18.00	5.20	23.20	2.54	3.46	7.09	0.051	0.95	1.12	0.77	0.90	1.02
P44	0.54	29.09	7.37	36.45	3.01	3.95	9.66	0.139	0.95	1.44	0.65	0.80	0.91
P45	0.55	39.59	10.05	49.65	3.87	3.94	10.23	0.120	0.91	1.32	0.70	0.81	0.92
P47	0.20	10.86	2.90	13.76	1.22	3.74	8.90	0.092	0.96	1.26	0.71	0.81	0.90
P48	0.26	12.36	3.13	15.48	1.26	3.95	9.81	0.092	0.95	1.25	0.74	0.86	0.94
P51	0.48	72.98	13.71	86.69	3.58	5.32	20.39	0.142	0.70	1.47	0.82	0.84	0.76
P52	0.23	25.62	6.29	31.91	2.13	4.07	12.03	0.090	0.87	1.24	0.73	0.89	0.95
P54	0.18	38.43	8.49	46.92	2.74	4.53	14.03	0.099	0.75	1.29	0.75	0.81	0.77
P56	0.13	20.56	4.78	25.34	1.68	4.30	12.24	0.093	0.95	1.22	0.67	0.91	1.00
P57	0.53	44.43	9.22	53.64	2.71	4.82	16.39	0.180	0.99	1.57	0.81	0.90	1.00

<sup>a</sup>CPI<sub>15-19</sub> =  $(1/2)[(nC_{15} + nC_{17} + nC_{19}) / (nC_{14} + nC_{16} + nC_{18}) + (nC_{15} + nC_{17} + nC_{19}) / (nC_{16} + nC_{18} + nC_{20})]$ ; <sup>b</sup>CPI<sub>25-33</sub> =  $(1/2)[(nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}) / (nC_{24} + nC_{26} + nC_{28} + nC_{30}) + (nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33}) / (nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})]$ .



degraded petroleum. Lower UCM/R and UCM/ $\sum n$ -alkanes ratios at stations P31 to P35, on the other hand, indicated a recent input of fresh oil. Meanwhile, concentrations of  $\sum n$ -alkanes were higher at those stations. Stations P31–P35 are near the oil exploration regions of Wushi and Maichen (Figure 1).<sup>39</sup> Oil spills and leaks may have occurred recently during oil exploration and transportation processes, resulting in the input of petroleum-related hydrocarbons.<sup>40</sup>

**2.4. Content of Isoprenoid Hydrocarbons.** Pristane (Pr) and phytane (Ph) are common components in petroleum; high Pr and Ph concentrations, associated with low Pr/Ph ratios (<1), can indicate that these components originated from fossil hydrocarbons.<sup>41</sup> All sediment samples contained Pr and Ph, with concentrations ranging from 0.01 to 0.37  $\mu\text{g/g dw}$  and 0.05 to 0.52  $\mu\text{g/g dw}$ , respectively. The Pr/Ph value was within 0.26 to 0.96, suggesting petrogenic rather than biogenic sources. The Pr/ $n$ -C<sub>17</sub> and Ph/ $n$ -C<sub>18</sub> ratios ranged from 0.39 to 1.01 and from 0.64 to 1.04, respectively, and averaged 0.82 and 0.87. The Ph/ $n$ -C<sub>18</sub> and Pr/ $n$ -C<sub>17</sub> ratios were less than 1, indicating a recent oil input, which was consistent with the scenario suggested by the UCM/R and UCM/ $\sum n$ -alkane values.<sup>36,42</sup>

**2.5. Content of Hopanes and Steranes.** Petroleum biomarkers such as hopanes and steranes are common constituents of crude oils and petrogenic hydrocarbons. The presence of these molecular fossils in the marine environment suggests inputs from petrogenic hydrocarbons.<sup>27,35</sup> The typical mass chromatograms of hopanes ( $m/z$  191) and steranes ( $m/z$  217) of our sample determined by GC–MS are shown in Figure 3. All samples contained a series of hopanes (C<sub>27</sub> to C<sub>34</sub>, excluding C<sub>28</sub>); C<sub>30</sub> hopane was the dominant homologue. The

distribution of homohopanes showed a decreasing pattern, from C<sub>31</sub> to C<sub>34</sub>. Gammacerane was also present. These biomarkers were detected in our seafloor sediments at concentrations ranging from 0.02 to 0.23  $\mu\text{g/g dw}$  (Table 2). These values were lower than those found in sediment cores from a tropical Brazilian estuarine system (0.15–1.63  $\mu\text{g/g dw}$ )<sup>37</sup> and those recorded in core sediments from coral Islands in the Persian Gulf, Iran (0.59–7.58  $\mu\text{g/g dw}$ ).<sup>7</sup> The similarly low values of Hop/ $\sum n$ -alkanes (Table 2) also suggested that the biomarker inputs were probably diluted by natural inputs.

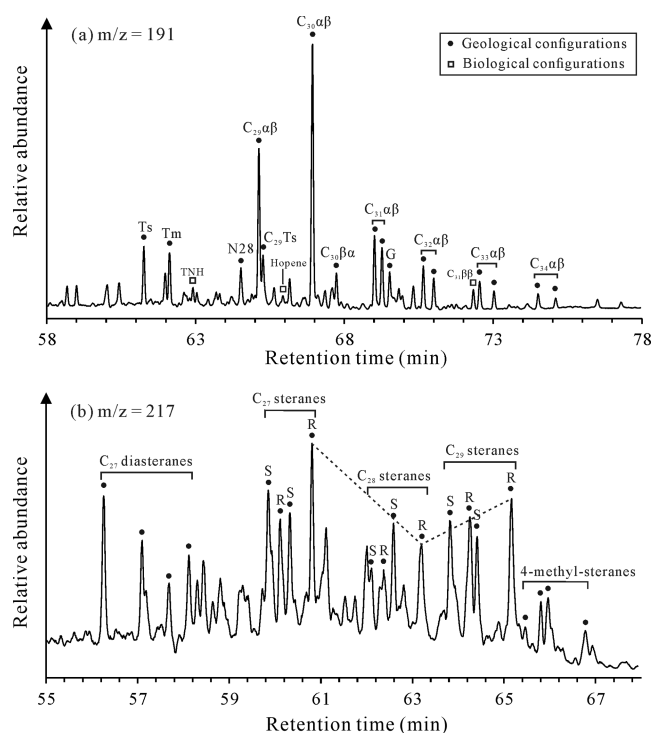
**2.6. Possible Source Inputs of Aliphatic Hydrocarbons in Seafloor Sediments.** There are a variety of hydrocarbon sources that could have contributed to the petrogenic hydrocarbon background in marine sediments, both naturally and anthropogenically. Natural oil seeps or erosion of carbon-rich formations are natural sources of petrogenic hydrocarbons. Anthropogenic petrogenic hydrocarbons can enter marine systems through petroleum extraction, crude oil transportation, sewage discharge, and roadside runoff.

Residual oil stains, asphaltic sandstones, and organic-rich mudstones have been found in exposures in Hanoi and Dong Ho, Vietnam,<sup>43</sup> as well as on islands in the Beibu Gulf.<sup>44</sup> Oil seeps occur on and off the shore of Vietnam, as well as off the southwestern coast of Hainan Island.<sup>45</sup> The Beibuwan Basin, a Cenozoic sedimentary basin covered by the Beibu Gulf and the LP, is rich in oil and gas reservoirs.<sup>46</sup> According to our previous research,<sup>14</sup> natural petroleum sources contributed to the petrogenic hydrocarbon background in the southern and southwestern offshore areas of Leizhou Peninsula, although the exact sources are uncertain. Natural petroleum sources could potentially contribute to petrogenic hydrocarbons in seafloor sediment from offshore of the LP.

Several cities along or near the coast of the LP are home to oil refineries. The Qiongzhou Strait is an important traffic channel. The ports of Zhanjiang and Maoming are vital traffic hubs and maritime terminals. Zhanjiang, a city located on the LP, discharges a large quantity of industrial and domestic sewage into its coastal waters every year. Marine transportation, offshore drilling in the Beibu Gulf, nearshore refining, roadside runoff, and sewage discharge may all contribute petrogenic hydrocarbons to the sea around the coast of the LP.

### 3. CONCLUSIONS

Seafloor sediments collected from offshore areas of the Leizhou Peninsula had relatively low concentrations of TAHs compared to those reported for highly contaminated areas, but higher than those from pristine environments. The coexistence of UCM, high Pr and Ph concentrations, low Pr/Ph ratios, and sterane and hopane biomarkers suggested that petrogenic hydrocarbons contaminated the sediments collected for our study. The UCM/R and UCM/ $\sum n$ -alkanes values higher than 4 and 10, respectively, were recorded in northwestern coast sites, indicating contamination by degraded/weathered petroleum in those areas. The southwestern coast had the lowest UCM/R and UCM/ $\sum n$ -alkanes values, which coupled with the higher  $\sum n$ -alkanes concentrations, indicating fresh oil inputs. The highest concentration of  $\sum n$ -alkanes came from the Wushi and Maichen oil exploration area in the Beibu Gulf. Further research is needed to determine the specific origins of the petrogenic hydrocarbons found off the coast of the Leizhou Peninsula.



**Figure 3.** Mass chromatograms of  $m/z = 191$  and  $m/z = 217$  for hopanes (a) and steranes (b) in the seafloor sediments from site 10. Note: Ts for 22,29,30-trisnorhopane; Tm for 22,29,30-trisnorhopane; TNH for 25,28,30-trisnorhopane; N28 for 28-norhopane; C<sub>29</sub>Ts for 30-norhopane; and G for gammacerane.

Table 2. Content of Hopanes and Steranes in Offshore Seafloor Sediments of the Leizhou Peninsula<sup>a,b</sup>

sampling site	Hop ( $\mu\text{g/g dw}$ )	Ster ( $\mu\text{g/g dw}$ )	Hop + Ster ( $\mu\text{g/g dw}$ )	Hop/ <i>n</i> -alkane
P1	0.08	0.02	0.10	0.04
P2	0.12	0.03	0.15	0.04
P3	0.08	0.02	0.10	0.03
P4	0.14	0.03	0.16	0.05
P5	0.07	0.02	0.09	0.03
P6	0.10	0.03	0.13	0.03
P7	0.12	0.03	0.15	0.02
P9	0.09	0.03	0.12	0.02
P10	0.09	0.03	0.12	0.02
P13	0.06	0.02	0.08	0.02
P15	0.12	0.03	0.15	0.03
P18	0.07	0.02	0.08	0.02
P19	0.06	0.02	0.08	0.01
P21	0.05	0.01	0.07	0.02
P22	0.03	0.01	0.04	0.01
P23	0.04	0.01	0.05	0.01
P27	0.07	0.02	0.09	0.01
P29	0.05	0.02	0.07	0.01
P30	0.05	0.02	0.07	0.01
P31	0.07	0.02	0.09	0.01
P32	0.04	0.02	0.06	0.00
P33	0.03	0.01	0.04	0.00
P34	0.09	0.03	0.12	0.01
P35	0.05	0.02	0.07	0.01
P36	0.10	0.03	0.13	0.02
P37	0.09	0.03	0.12	0.01
P38	0.07	0.03	0.09	0.01
P39	0.06	0.02	0.07	0.02
P40	0.10	0.04	0.14	0.02
P42	0.07	0.02	0.10	0.02
P43	0.03	0.01	0.04	0.01
P44	0.04	0.02	0.06	0.01
P45	0.05	0.02	0.07	0.01
P47	0.01	0.01	0.02	0.01
P48	0.02	0.01	0.03	0.01
P51	0.18	0.05	0.23	0.05
P52	0.04	0.02	0.06	0.02
P54	0.07	0.02	0.09	0.02
P56	0.02	0.01	0.03	0.01
P57	0.06	0.02	0.08	0.02

<sup>a</sup>Hop: Hopanes. <sup>b</sup>Ster: Steranes.

#### 4. MATERIALS AND METHODS

**4.1. Sampling.** Seafloor sediments were collected using a gravity box sampler deployed from the R/V Hai Long of the Guangdong Ocean University (GDOU) in autumn 2017 (September 29 to October 7). A total of 41 seafloor sediment samples (0–5 cm) were collected from 57 predetermined sampling sites (Figure 1). All surface samples were placed in sample bags and stored at  $-20\text{ }^{\circ}\text{C}$  for subsequent processing.

**4.2. Analysis of Aliphatic Hydrocarbons.** The aliphatic hydrocarbon analysis was carried out in accordance with the method described by Li<sup>47</sup> and Jia.<sup>48</sup> Sediment samples were freeze-dried using a vacuum freeze dryer (cold trap at  $-50\text{ }^{\circ}\text{C}$ ), ground in an agate mortar, and sieved to obtain  $<150\text{ }\mu\text{m}$  fine particles. Approximately 50 g of the sediments were Soxhlet extracted continuously for 72 h with dichloromethane (DCM)/methanol solution (93:7, v/v). Activated copper was added to the solvent to remove elemental sulfur from the samples. After extraction, the solvent was concentrated by

rotary evaporation, and the extract was weighed. Asphalt fractions were collected through precipitation separation using *n*-hexane. The saturates, aromatics, and resins fractions were separated and eluted using silica gel column chromatography, with *n*-hexane, *n*-hexane/dichloromethane (3:2, v/v), and methanol, respectively. The saturated fractions were concentrated to 1 mL using a rotary evaporator. Per-deuterated *n*-tetracosane-*d*<sub>50</sub> ( $\text{C}_{24}\text{D}_{50}$ ) was added to the extract as an internal standard for the instrumental analysis. A gas chromatograph-mass spectrometer (GC–MS) analysis of the aliphatic hydrocarbons was performed using an ISQ 7000 (Thermo Scientific) system interfaced with a TRACE 1300 gas chromatograph. Chromatographic separation was achieved by a 30m DB-5 capillary column (diameter = 0.25 mm, film thickness = 0.25  $\mu\text{m}$ ; J&W Scientific). The samples were injected in splitless mode at an injector temperature of  $280\text{ }^{\circ}\text{C}$ . For the GC analysis, the oven was programmed to increase from  $80\text{ }^{\circ}\text{C}$  (3 min) to  $300\text{ }^{\circ}\text{C}$  (15 min) at  $3\text{ }^{\circ}\text{C}/\text{min}$ , with the

total duration time of the GC run 91.3 min. The mass spectrometer was operated in the electron ionization mode (70 eV). Mass scanning combined selective ion monitoring with full-scan detection between  $m/z$  50 and 650 amu, with the ion source temperature of 300 °C. The flow rate of the carrier gas, helium, was constant at 1 mL/min. Concentrations of *n*-alkanes were determined based on their peak areas compared to the internal standard. The UCM fraction was calculated by subtracting the peaks of identifiable alkane from the total aliphatic fraction. The total aliphatic hydrocarbons (TAHs) and the unresolved complex mixture (UCM) were quantified by assuming a response factor of 1.0 based on *n*-alkanes. The total area of resolved peaks and the total area obtained previously from a stored column compensation (blank) run are subtracted from the total detector response. The remaining area is assigned to UCM.<sup>5</sup> The steranes and hopanes in the saturated fraction of the samples were quantified against the per-deuterated *n*-tetracosane-*d*<sub>50</sub> ( $m/z$  66; relative concentration values), and their identification was validated by GC–MS based on their mass spectral features, peak sequence, and previous research.

The quantification of hydrocarbons was performed using the internal calibration method. Method blanks were also used to check for contamination. The solvents used throughout (DCM, hexane, and methanol) were chromatographic grade. Silica used for chromatography was solvent extracted, and glassware was cleaned and heated at 450 °C for 4 h. Analysis of the blanks confirmed no noticeable introduced contamination or other interference over the whole experiment.

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## Notes

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