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Geochemical Characteristics of Hydrocarbons in Core Sediments From the Southwest Sub-Basin of the South China Sea and Its Implications for the Sedimentary Environment

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Marine sediments are found to record various information for example the evolution of ocean and the exchange of matter and energy between the surrounding continents and oceans. The Southwest Sub-basin is one of the most important tectonic unit in the South China Sea Basin. The geochemical information of the sediments provides potential to understand the sedimentary history of the Southwest Sub-basin of South China Sea. In this paper, the aliphatic hydrocarbon compounds in two core sediments from the Southwest sub-basin were analyzed using lipid biomarker analysis. The average concentration of the total organic carbon (TOC) and the total nitrogen (TN) for both core sediment A and sediment B are similar, falling in the range of 0.64% ± 0.18 and 0.10% ± 0.02%, respectively. The C/N ratios vary from 3.2 to 11.1, reflecting that the organic carbon was a mixture of terrestrial and marine sources with more contributions from marine sources in core sediment B than sediment A. The long-chain *n*-alkanes of both core sediments show an even-odd predominance, reflecting the contributions of terrestrial higher plants and short-chain *n*-alkanes from marine plankton or bacteria. The Pr/Ph of core sediments A and B are 0.3–0.5 and 0.2–0.4, respectively, both of which are far less than 1, indicating that the sedimentary environment was dominated by strong reduction and long-term stability. The odd-even distribution of medium-chain *n*-alkanes (n-C_{14-20}) in the core sediments A and B is due to the reduction of *n*-fatty acids with an odd carbon dominance in a strongly reductive depositional environment.

Keywords: core sediments, organic matter, aliphatic hydrocarbons, Southwest sub-basin of South China Sea, sedimentary environment

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INTRODUCTION

The South China Sea, one of the marginal sea of the Pacific Northwest Sea. According to water depth, topography and geology, and geophysical data, the South China Sea Basin was divided into the Northwest sub-basin, Southwest sub-basin and Eastern sub-basin (Briais et al., 1993; Sun et al., 2009). The Southwest sub-basin is located among the Xisha Islands, Zhongsha Islands and Nansha

Islands. It is a NE-trending triangular basin with a northeast direction of approximately 600 km and a northeast margin of approximately 400 km with a water depth of 3,000–4,000 m (Li, 2011). It is the lowest depression in the South China Sea basin (**Figure 1**). As the interaction zone between the continent and the ocean, the South China Sea's unique geographical location, complex tectonic environment and special ocean currents have formed its complex sedimentary environment, and its sedimentary material sources are various and diverse (Hamilton, 1979; Tapponnier et al., 1982).

Due to bordering on many countries, the Southwest Sub-basin of South China Sea is lack of comprehensive and systematic investigations over decades. Most of the research was concentrated on the northern South China Sea. For the southern South China Sea, organic geochemistry research has also been done (Duan, 2000; Hu et al., 2009; Tahir et al., 2015; Kerimov et al., 2019). However, compared with other sea areas, the geochemical studies in the southern South China Sea also appear to be lagging and weak. There are few reports on the geochemical characteristics, influencing factors and environmental records of hydrocarbon compounds in the core sediments in this area.

Molecular fossils could maintain the carbon skeleton of original biochemical components during the evolution processes of organic matter, recording information about original organisms and thus can be used to reveal information of biological input, sedimentary environment and diagenetic changes (Meyers and Lallier-Vergés, 1999; Meyers, 2003). In this paper, two core sediments collected from the Southwest sub-basin as the research object, analyzed the organic geochemical index of *n*-alkanes and their carbon molecular assemblages, the aim of this study was to trace the source of organic matter and understand the sea-land interaction during modern marine sedimentation in the southwest sub-basin, and to provide a scientific basis for the indication of climate and environment.

SAMPLE AND ANALYSIS METHODS

Sample Collection

The sampling sites were located in the southwest sub-basin of the South China Sea (**Figure 1**). Sediment cores were collected by the "Haiyang 4" ship of the Guangzhou Marine Geological Survey in September 2015, using a large gravity sampler. The sediment cores were collected from water depths of 4,050–4,030 m with their lengths of 4.75 and 5 m, respectively. Man-made damages and obvious biological disturbances were not observed during collection and sampling processes, therefore, the geochemical information can be used as indicators for original sedimentary characteristics. Core sediments were subsampled immediately and stored at −20°C for the further analyses.

Experimental Analysis

Total Organic Carbon (TOC)

Sediments were freeze-dried at −50°C and ground into powder about 200 mesh. Approximately120 mg of powder was put into a crucible, and excess HCl at a concentration of 6 mol/l was added. The samples were laid over night, followed by being heated at 80°C for 2 h to remove the carbonate and rinsed with deionized water until neutral. The cleaned samples were dried at 110°C and measured with LecoC230.

Sample Extraction and Separation of Soluble Organic Matter

The organic matters were extracted by Soxhlet for 72 h with a mixed solvent of dichloromethane/methanol (9:1, volume ratio). Before extraction, the appropriate amount of activated copper sheet was added to the receiving bottle of the extraction liquid to remove the elemental sulfur. The internal standard $C_{20}D_{42}$ was added to the receiving bottle of extraction liquid. After extraction, the extracts were concentrated by rotary evaporation and transferred to a suitable bottle, which was then blown to dryness with nitrogen and get soluble organic matter. The soluble organic matter was saponified with KOH/CH_3OH (1 mol/l) (i.e., 70°C heating reflux 2 h), then neutral components were extracted by adding *n*-hexane. After the organic matter was transferred to a silica gel column, the organic matter was washed with 3 volumes of *n*-hexane to obtain hydrocarbon components.

Gas Chromatography—Mass Spectrometry (GC-MS)

Instrument Model: Thermo Trace GC Ultra-AL/AS3000 GC–MS; ion source for the electron bombardment source (70 eV); ion source temperature: 230°C; inlet temperature: 290°C; number of scans: 0.7911/s; scanning rate: 500 amu/s, 30–750 amu. The carrier gas was high-purity helium.

Hydrocarbon Detection: The column model was a HP-1 capillary column (60 m *0.32 mm, i.d., *0.25 μm coating). The temperature program was as follows. The initial temperature was 80°C, the temperature was maintained for 3 min, and the temperature was raised to 315°C at 3°C/min for 30 min. Using a splitless injection mode, the carrier gas was high-purity helium with a flow rate of 1.1 ml/min.

RESULTS

The Results of the TOC and Total Nitrogen (TN)

The TOC, total TN and TOC/TN of the two core A and B in the southwest sub-basin are listed in **Table 1**. The mean TOC of core sediment A was 0.64% ± 0.18% (0.29–0.88%). The average concentration of TN was 0.10% ± 0.02% (0.04–0.12%), and the average C/N was 6.91 ± 2.03 (3.22–11.15). The mean TOC of core sediment B was 0.64% ± 0.12% (0.43–0.86%). The average concentration of TN was 0.10% ± 0.01% (0.08–0.11%), and the average C/N was 6.38 ± 1.33 (4.8–9.3). The average TOC of cores A and B were equivalent to 0.7 and 0.53% of the two cores measured by Duan (2000) in the Nansha Sea.

Hydrocarbon Compounds

The hydrocarbons detected in the two cores sediments A and B ranged from C_{14} to C_{33}, mainly including *n*-alkanes and acyclic diolefins (pristane and phytane) (**Table 2**). The concentrations of total *n*-alkanes of core A varied from 716.7 to 2799.8 ng/g (**Table 2**), and the concentration of total *n*-alkanes of core

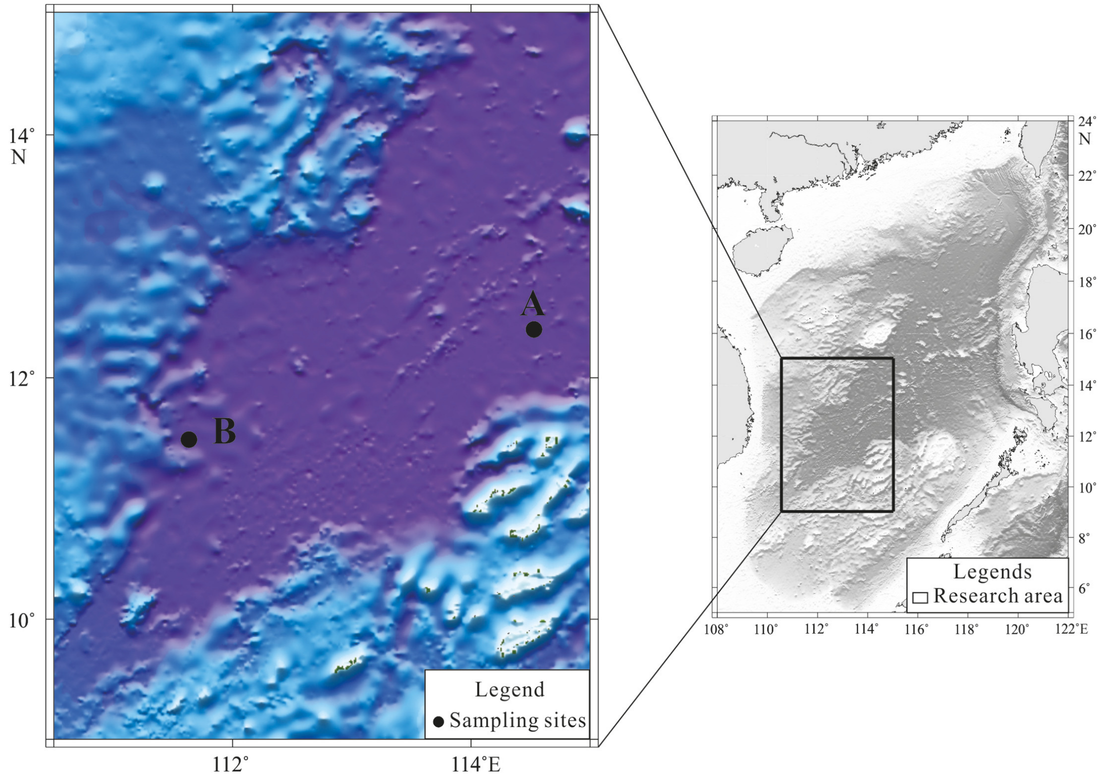

FIGURE 1 | The distribution of sampling sites and the tectonic location of the Southwest Sub-basin.

sediment B were 1008.3–2109.9 ng/g (**Table 3**). In the two core A and B, n-C_{27}, n-C_{29}, and n-C_{31} were the main peak carbons, and the values of CPI_{24-35} of long-chain n-alkanes were 3.6 (2.1–5.0) and 2.9 (1.8–3.6). The sum of the most abundant n-alkanes related to terrestrial origins (n-C_{27}, n-C_{29}, and n-C_{31}) were defined as ΣTer-alkanes, which were 211.4–1004.0 ng/g, accounting for 18.8–48.9% of the total n-alkanes (averaging 31.1%) at station A. The ΣTer-alkanes for B ranged from 224.4 to 670.6 ng/g, representing 14.5–34.0% of the total n-alkanes (averaging 23.4%).

TABLE 1 | The total organic carbon (TOC), total nitrogen (TN), carbon to nitrogen ratio (C/N).

A				B			
Depth	**C (%)**	**N (%)**	**C/N**	**Depth**	**C (%)**	**N (%)**	**C/N**
20 cm	0.76	0.12	6.5	20 cm	0.75	0.11	6.7
60 cm	0.88	0.12	7.3	60 cm	0.65	0.11	5.9
100 cm	0.82	0.12	7.1	100 cm	0.56	0.10	5.7
140 cm	0.55	0.11	5.1	140 cm	0.76	0.09	8.7
180 cm	0.65	0.10	6.3	180 cm	0.43	0.08	5.2
220 cm	0.80	0.10	8.0	220 cm	0.59	0.11	5.4
260 cm	0.37	0.04	9.6	260 cm	0.70	0.10	6.9
300 cm	0.50	0.10	5.1	300 cm	0.86	0.09	9.3
340 cm	0.66	0.10	6.4	340 cm	0.69	0.11	6.2
380 cm	0.60	0.10	6.1	380 cm	0.61	0.11	5.5
420 cm	0.29	0.09	3.2	420 cm	0.69	0.10	6.8
460 cm	0.76	0.09	8.1	460 cm	0.62	0.10	6.0
470 cm	0.67	0.06	11.1	495 cm	0.45	0.09	4.8

Short-chain n-alkanes are attributed to be derived from marine algae and bacteria (Blumer et al., 1971). Low-carbon alkanes show a significant advantage of even carbon number, and the maximum relative abundances are n-C_{16}, n-C_{18}, and n-C_{20}. For core sediment A, the ΣMar-alkanes, defined as the sum of n-C_{15}, n-C_{17}, and n-C_{19}, were 52.2–325.4 ng/g, accounting for 2.7–13.2% (averaging 8.9%) of the total n-alkanes. The ΣMar-alkanes at B were 64.5–266.5 ng/g, accounting for 5.2–12.6% (averaging 8.4%) of the total n-alkanes.

The concentrations of pristane in cores A and B were 10.2–95.9 and 12.3–78.7 ng/g, respectively, and the concentrations of phytane were 32.8–212.5 and 51.9–184.1 ng/g, respectively.

DISCUSSION

Downcore Profiles of TOC and TN in Sediments and Their Source Indication

Carbon and nitrogen form the basis of life and play important roles in many terrestrial and aquatic biogeochemical cycles (Likens et al., 1981). Carbon in marine sediments is an important part of the carbon cycle. Nitrogen is the most basic bioactive element that limits the growth of phytoplankton in the ocean.

TABLE 2 | Concentration (ng/g sed.dry weight) of hydrocarbon in A station of the Southwest Sub-basin.

Depth	20 cm	60 cm	100 cm	140 cm	180 cm	220 cm	260 cm	300 cm	340 cm	380 cm	420 cm	460 cm	470 cm
Compounds													
n-C$_{14}$	36.2	3.1	4.5	3.6	0.6	1.0	0.1	8.3	4.0	2.9	0.7	0.5	3.1
n-C$_{15}$	43.7	9.6	21.5	20.2	6.0	8.3	1.9	14.9	11.9	8.4	5.3	5.1	7.2
n-C$_{16}$	306.4	133.5	157.1	153.8	101.3	115.5	56.1	138.9	120.5	88.5	87.9	59.7	64.8
n-C$_{17}$	187.7	84.6	114.3	110.9	86.4	89.4	59.3	92.0	114.3	34.2	31.0	28.4	25.5
Pr	95.9	40.0	53.4	68.9	45.9	45.6	35.9	47.7	75.3	13.7	11.9	10.7	10.2
n-C$_{18}$	371.1	197.8	203.0	177.4	147.3	156.9	95.3	159.9	180.8	115.1	129.3	100.6	85.9
Phy	212.5	97.3	118.6	140.5	95.4	107.8	69.1	101.4	198.0	44.6	45.2	32.8	32.2
n-C$_{19}$	94.1	40.8	90.7	52.7	37.0	50.5	19.0	36.3	62.0	27.1	25.5	21.9	19.5
n-C$_{20}$	286.1	157.7	153.2	132.2	103.8	113.9	59.3	102.6	100.5	80.2	93.8	74.8	65.3
n-C$_{21}$	97.1	47.6	69.2	54.0	42.3	54.8	21.2	40.6	40.3	33.5	33.8	37.1	32.2
n-C$_{22}$	199.7	99.0	87.0	83.5	67.5	69.5	34.3	62.9	60.1	46.5	61.1	54.5	45.6
n-C$_{23}$	102.7	59.3	56.8	59.4	51.1	58.8	23.4	48.3	45.3	40.3	53.0	74.5	57.5
n-C$_{24}$	132.0	61.4	55.2	59.2	46.7	49.5	21.8	49.1	43.2	35.0	48.0	50.3	41.6
n-C$_{25}$	55.0	69.7	67.1	65.4	61.1	66.7	27.9	55.7	54.0	51.4	69.6	116.5	85.9
n-C$_{26}$	107.5	51.6	77.1	48.5	45.8	48.4	18.5	38.7	38.4	32.4	43.8	51.1	41.7
n-C$_{27}$	91.6	84.6	77.1	81.2	76.7	82.0	37.7	59.3	74.2	75.9	105.6	197.9	157.3
n-C$_{28}$	82.0	55.3	42.6	53.5	43.9	42.8	18.7	33.5	39.8	37.2	44.2	72.5	55.7
n-C$_{29}$	213.1	176.7	147.6	169.7	157.3	157.8	86.1	109.1	150.1	160.8	243.6	382.1	286.1
n-C$_{30}$	53.4	36.8	34.4	39.8	36.2	37.4	13.4	23.0	30.5	28.4	36.5	73.3	58.5
n-C$_{31}$	220.7	193.3	167.4	172.3	172.8	173.4	87.6	119.8	158.8	161.9	244.0	424.0	315.2
n-C$_{32}$	27.5	17.3	18.5	22.2	20.0	20.8	6.5	10.6	14.6	14.3	18.8	41.2	33.0
n-C$_{33}$	92.2	72.1	69.1	79.7	74.5	87.3	28.5	41.5	61.4	59.2	75.9	187.5	133.4
Total *n*-alkanes	2799.8	1651.8	1713.4	1639.1	1378.3	1484.5	716.7	1245.0	1404.7	1133.2	1451.5	2053.5	1615.0
ΣTer-alkanes	525.3	454.6	392.1	423.2	406.7	413.1	211.4	288.2	383.1	398.6	593.1	1004.0	758.6
ΣMar-alkanes	325.4	135.0	226.6	183.7	129.4	148.2	80.3	143.2	188.2	69.6	61.8	55.3	52.2
TAR	1.6	3.4	1.7	2.3	3.1	2.8	2.6	2.0	2.0	5.7	9.6	18.2	14.5
CPI$_{24-33}$	2.1	3.2	2.7	3.0	3.3	3.3	4.0	3.1	3.5	4.0	4.5	5.0	4.7
Pr/Ph	0.5	0.4	0.5	0.5	0.5	0.4	0.5	0.5	0.4	0.3	0.3	0.3	0.3

Pr, pristane; Phy, phytane; CPI, carbon preference index; ΣTer-alkanes, $\Sigma C_{27+29+31}$; ΣMar-alkanes, $\Sigma C_{15+17+19}$; TAR, ΣTer-alkanes/ΣMar-alkanes; N.D., not detected.

Therefore, it is very important to study the distribution of carbon and nitrogen in core sediments.

The downcore profiles of TOC, TN and TOC/TN with depth of core sediment A are shown in **Figure 2**. From bottom to top, according to the vertical concentration changes of TOC and TN, 4 stages were identified: (1) Under the layer below a depth of 380 cm, the concentration of TOC was low and varied significantly. The concentration first increased from the bottom, dropped to the lowest value (0.29%) at 420 cm, and then increased again. The concentration of TN had a similar trend but did not change as strong as TOC; (2) At depths between 380cm and 340 cm, the concentration of TOC was low and consistent; the concentration of TN was also relatively uniform; (3) The concentration of TOC varied greatly at depths between 340m and 220 cm, and the lowest TN value were found at a depth of 260 cm (0.04%); (4) Above the depth of 220 cm, the concentration of TOC showed a high, rising, but fluctuating trend; however, the change was small; the concentration of TN generally rose, with the highest value (0.04%) appearing at the depth of 60 cm. Overall, the vertical concentration variation trends of TOC and TN in core sediment A was generally the same, with differences in individual locations.

The curves of TOC, TN and TOC/TN with depth for core sediment B are shown in **Figure 3**. From bottom to top, 3 stages were identified. (1) In the layer below 300 cm, the TOC of core sediment B changed slightly, showing an upward trend overall, with a high value (0.86%) at a depth of 300 cm and a low value of TN (0.09%). (2) At a depth of 300–180 cm, the concentration of TOC showed a downward trend, and the concentration of TN fluctuated greatly. (3) At a depth above 180 cm, the TOC showed an upward trend but fluctuated while the concentration of TN increased gently. According to the change of TOC, we can find that the trend of TOC and TN are the same at a depth of 340 cm and below, while TOC and TN have an opposite trend at a depth of 340 cm and above.

The C/N of organic matter in marine sediments can be used to determine the source of organic matter. Organic matter is usually thought to originate from marine organisms at a C/N of 5-7 (Redfield et al., 1963), while the C/N of organic matter in higher plants from terrestrial sources is generally greater than 15 (Meyers, 1997). As seen from **Figures 2**, **3**, the C/N of the core A and B vary greatly with depth, and the average C/N of core sediment A is 6.91 ± 2.03, ranging from 3.22 to 11.15 and indicating that organic carbon in sediments is a mixed source

TABLE 3 | Concentration (ng/g sed.dry weight) of hydrocarbon in B station of the Southwest Sub-basin.

Depth	20 cm	60 cm	100 cm	140 cm	180 cm	220 cm	260 cm	300 cm	340 cm	380 cm	420 cm	460 cm	495 cm
Compounds													
n-C_{14}	18.6	8.7	42.2	0.9	4.7	1.9	0.4	0.3	0.7	19.6	24.4	6.9	30.7
n-C_{15}	26.5	25.8	31.1	11.2	15.2	11.2	5.0	4.1	8.5	22.5	31.2	26.9	66.9
n-C_{16}	235.9	166.8	204.3	104.8	181.4	148.1	98.9	86.5	142.0	175.2	183.2	226.8	296.7
n-C_{17}	78.4	70.1	80.1	54.2	58.2	52.8	41.0	32.0	61.6	55.6	56.1	88.2	124.4
Pr	32.1	26.2	24.1	26.9	21.6	20.9	18.9	12.3	26.7	22.4	22.4	39.4	78.7
n-C_{18}	245.4	206.4	228.5	143.6	218.6	195.9	199.1	135.0	224.4	190.5	176.1	227.1	282.4
Phy	113.8	101.9	98.5	78.4	90.2	80.7	75.1	51.9	92.0	77.7	80.8	124.1	184.1
n-C_{19}	60.4	44.5	60.1	36.9	55.8	41.1	38.9	28.5	50.1	43.8	41.4	62.1	75.3
n-C_{20}	165.4	109.2	164.3	75.7	163.3	139.1	133.5	98.6	171.0	129.7	118.8	155.9	185.3
n-C_{21}	71.8	47.1	68.1	40.4	63.6	50.1	38.8	36.5	65.8	55.1	52.3	68.9	88.0
n-C_{22}	88.5	91.9	94.9	58.2	93.1	74.4	65.5	60.8	102.5	76.4	69.8	87.7	109.8
n-C_{23}	71.6	85.7	71.3	81.4	71.1	59.4	55.5	42.8	77.3	65.3	55.8	71.8	92.5
n-C_{24}	59.8	86.4	60.2	70.0	56.8	46.8	42.2	38.0	78.6	58.5	52.2	60.2	69.0
n-C_{25}	62.0	96.8	70.9	114.4	76.3	65.2	54.7	47.4	72.7	67.1	61.8	67.4	63.1
n-C_{26}	43.4	91.8	51.6	78.7	53.6	41.4	40.4	35.9	64.4	48.3	41.1	46.6	59.3
n-C_{27}	40.5	80.8	52.7	153.0	75.4	71.5	62.7	50.7	69.1	70.1	63.7	56.4	68.9
n-C_{28}	28.7	64.4	38.0	89.2	52.6	41.1	30.8	28.1	51.2	38.5	42.2	45.3	51.0
n-C_{29}	94.1	164.2	113.1	265.0	184.3	166.4	127.7	101.8	149.1	151.7	136.5	136.9	169.0
n-C_{30}	20.8	47.8	25.2	85.7	33.3	26.0	23.6	21.3	33.0	29.3	30.1	24.1	32.0
n-C_{31}	89.7	196.0	115.5	252.6	174.4	147.6	129.7	108.9	151.3	157.8	146.3	136.2	170.6
n-C_{32}	10.8	36.0	12.7	64.5	15.4	11.3	10.6	10.5	14.1	12.8	14.1	12.4	14.5
n-C_{33}	30.7	98.5	42.9	190.8	69.2	52.2	39.8	40.6	54.6	54.5	54.3	48.8	60.5
Total *n*-alkanes	1542.7	1818.9	1627.6	1971.3	1716.4	1443.5	1238.8	1008.3	1642.0	1522.2	1451.4	1656.7	2109.9
ΣTer-alkanes	224.4	441.0	281.3	670.6	434.2	385.5	320.2	261.4	369.5	379.6	346.5	329.4	408.5
ΣMar-alkanes	165.2	140.4	171.4	102.3	129.2	105.1	84.8	64.5	120.2	121.9	128.7	177.2	266.5
TAR	1.4	3.1	1.6	6.6	3.4	3.7	3.8	4.1	3.1	3.1	2.7	1.9	1.5
CPI_{24-33}	2.5	2.3	2.6	2.8	3.2	3.6	3.4	3.1	2.6	3.3	3.1	1.8	2.9
Pr/Ph	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.4

Pr, pristane; Phy, phytane; CPI, carbon preference index; ΣTer-alkanes, $\Sigma C_{27+29+31}$; ΣMar-alkanes, $\Sigma C_{15+17+19}$; TAR, ΣTer-alkanes/ΣMar-alkanes; N.D., not detected.

of terrigenous and marine. Meanwhile, the average C/N of core sediment B is 6.38 ± 1.33 (4.79–9.34), which also reflects the input of both terrigenous and marine organic matter. The C/N of A and B are both lower, indicating that the organic carbon is mainly from a marine source, while the lower C/N value of B indicates that the contribution of marine sources to organic carbon in core sediment B are larger than that of A.

In the two cores, the TOC and TN have a positive correlation (**Figure 4**), the positive relationship of TOC and TN suggests that TN measured in the sediments mostly exists in the form of organic nitrogen (Goñi et al., 1998). In addition, Qian et al. (1997) also proposed a method to quantitatively estimate the concentration of aquatic organic carbon (Ca), terrestrial organic carbon (Ct), aquatic nitrogen (Na) and terrestrial nitrogen (Nt). According to this method, assuming that the TOC/TN ratios of aquatic and terrestrial organic matter are 5 and 20, respectively (as a zero-order approximation) (Jia et al., 2002), the above parameters have the following relationship:

$$TOC = Ca + Ct$$

$$TN = Na + Nt$$

$$Ca/Na = 5$$

$$Ct/Nt = 20$$

Among them, TOC and TN represent the measured values. The solution of this equation formed by the above relationship calculates the available aquatic organic carbon and terrestrial organic carbon as follows:

$$Ca = (20TN - TOC)/3$$

$$Ct = 4(TOC - 5TN)/3$$

The concentrations of aquatic organic carbon (Ca) and terrestrial organic carbon (Ct) in the core sediment A are 72.2 and 27.8% of the TOC, as calculated by the above formula; aquatic nitrogen (Na) and terrigenous nitrogen (Nt) account for 87.2 and 22.8% of the TN, respectively. Therefore, TOC and TN in the core sediment A are mainly marine sources. The concentration of aquatic organic carbon (Ca) and terrestrial organic carbon (Ct) in core sediment B account for 74.9 and 25.1% of the total organic carbon, and aquatic N and Nt account for 90.8 and 9.2% of the total nitrogen, respectively. Therefore, organic carbon and

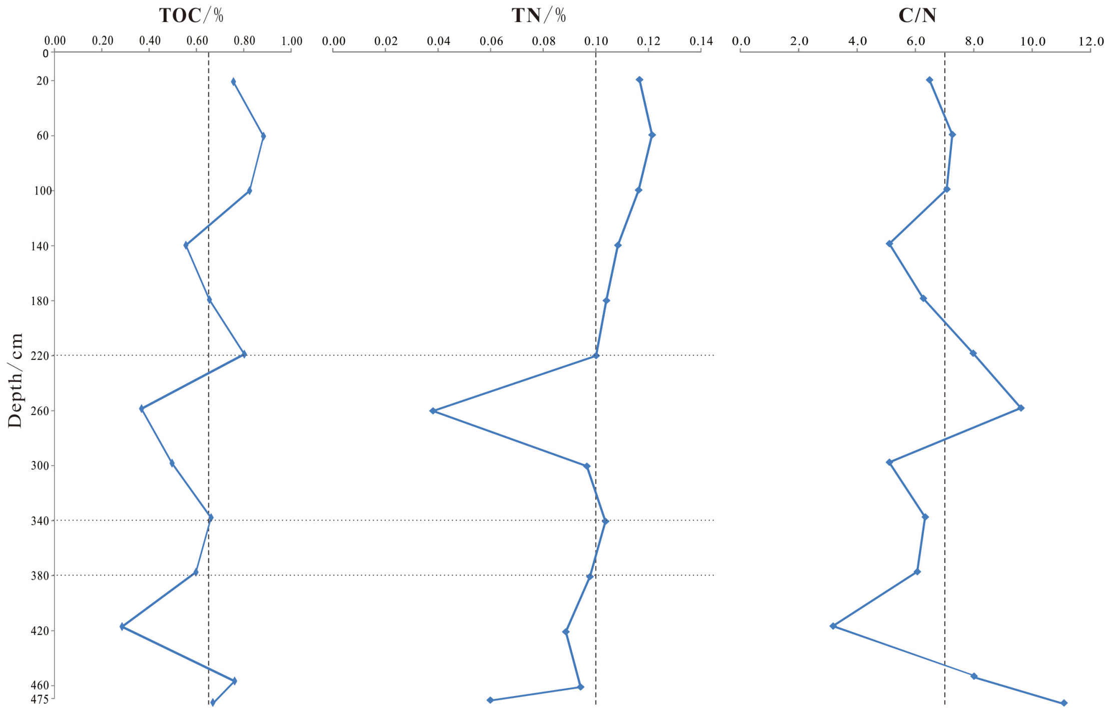

FIGURE 2 | Vertical profiles of TOC, TN, and CN in core sediment A.

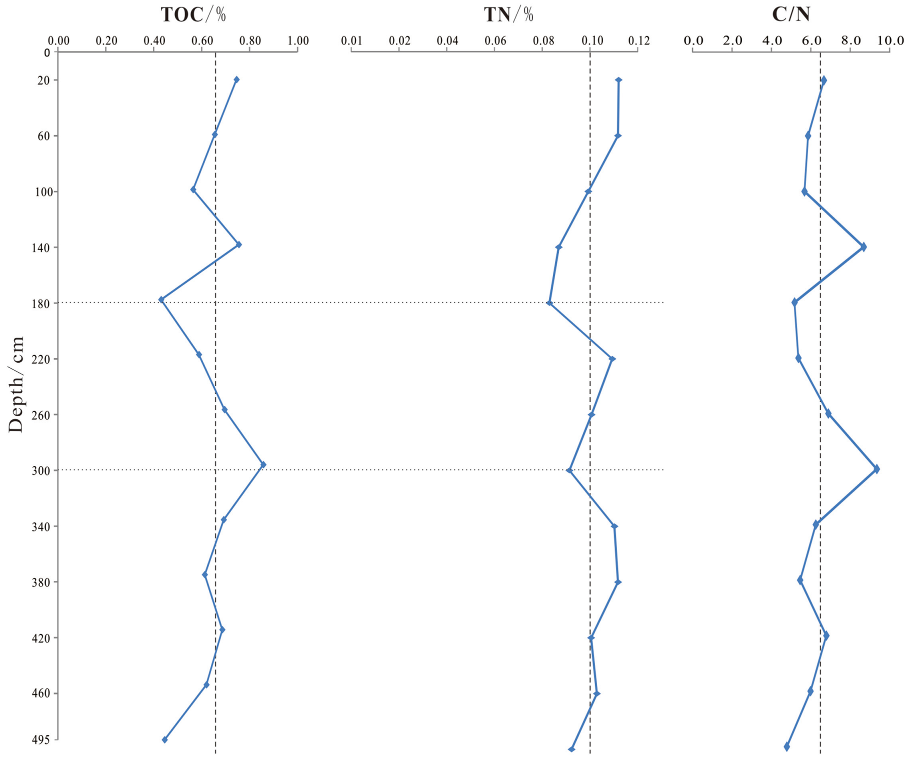

FIGURE 3 | Vertical profiles of TOC, TN, and C/N in core sediment B.

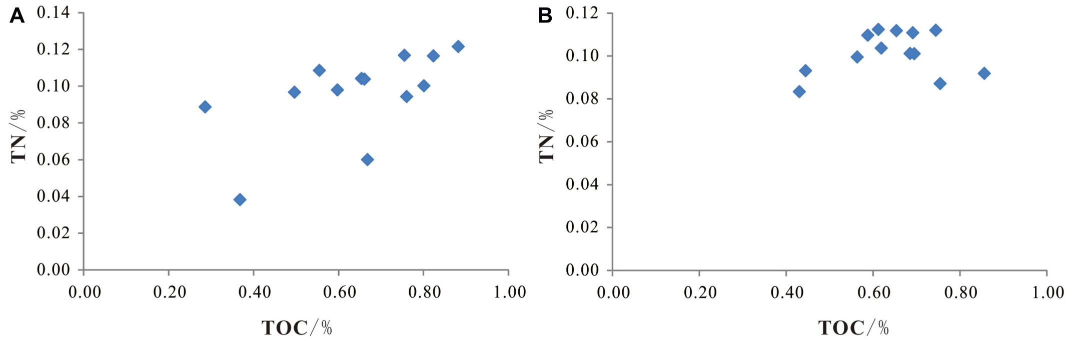

FIGURE 4 | The correlation of TOC and TN in core sediments **(A,B)**.

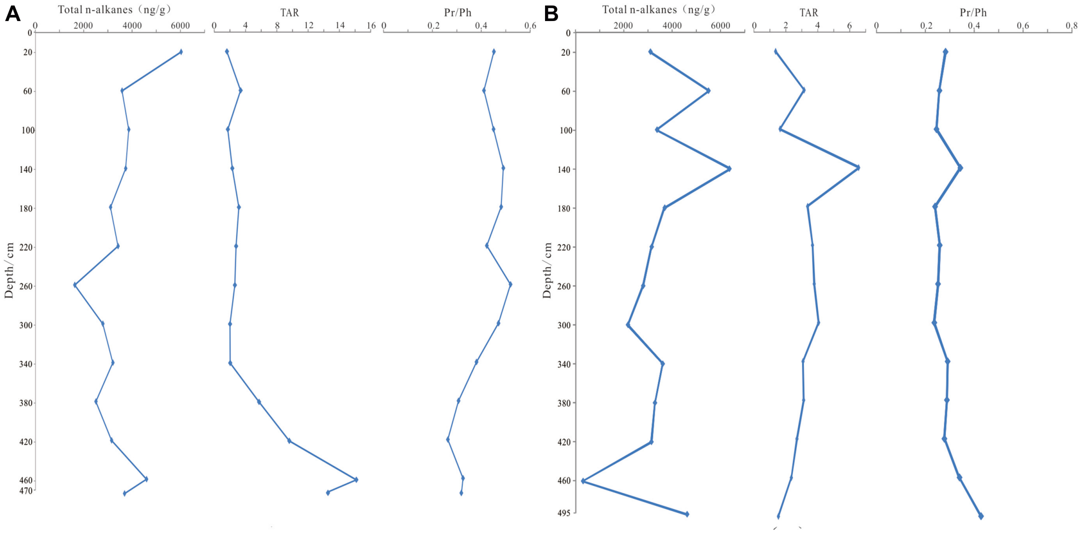

FIGURE 5 | Vertical profiles of the typical molecular compositional patterns of core **(A,B)**.

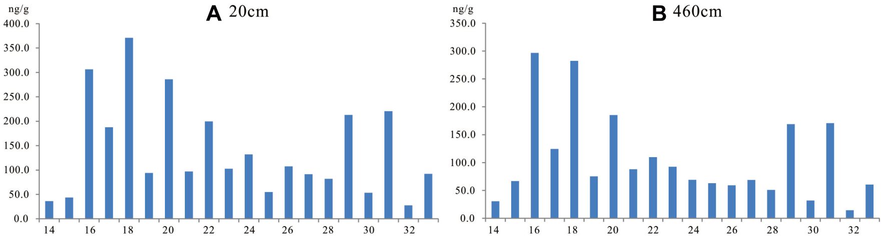

FIGURE 6 | Distribution of *n*-alkanes in the representative horizon in the core sediments **(A,B)**.

nitrogen in the core sediment B are also mostly marine sources, which is consistent with the result of the C/N.

Molecular Composition of Hydrocarbons and Indication Sedimentary Environment

n-alkanes are widely distributed in organisms such as bacteria, algae and higher plants. The *n*-alkanes derived from specific organisms usually with distinct distribution patterns and compositions (Parker et al., 1967; Han and Calvin, 1969; Winters et al., 1969). The distribution of *n*-alkanes detected in sediment samples was $C_{14} - C_{33}$, with an average CPI_{24-33} of long-chain *n*-alkanes for A and B stations being 3.6 and 2.9, respectively, while the CPI was 2–10, which is a hallmark of terrestrial organic matter inputs in typical marine sediment (Clark and Blumer, 1967). Short-chain *n*-alkanes are derived from marine plankton or bacteria (Blumer et al., 1971). In addition, *n*-C_{29}, *n*-C_{31} and *n*-C_{33} are the main peak carbons of long-chain *n*-alkanes

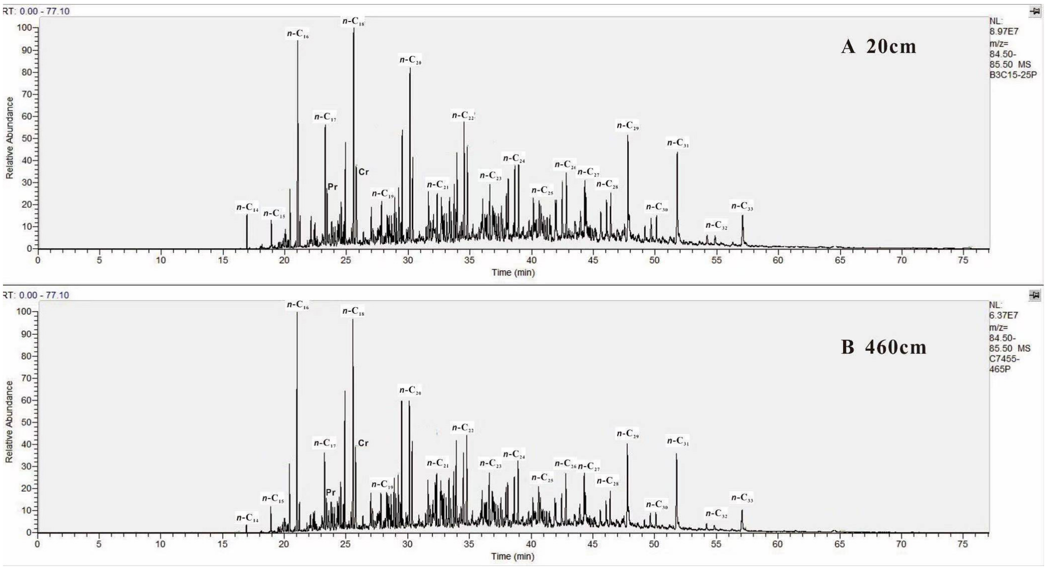

FIGURE 7 | The chromatogram of the typical samples in core sediments **(A,B)**.

in all layers of sediments, reflecting the organic characteristics of typical modern sediments (Bray and Evans, 1961; Eglinton et al., 1962; Eglinton and Hamilton, 1963; Clark and Blumer, 1967; Cranwell, 1973; Weete, 1976; Meyers, 2003), in which the n-C_{27} and n-C_{29} represent the input of woody plants and n-C_{31} and n-C_{33} represent the inputs of herbs (Meyers, 2003; Cranwell, 2010); pristane and phytane are mainly produced from degradation products of chlorophyllophyton-based side chains from photosynthetic plants (Powell and McKirdy, 1973). There are isotope data on the surface sediments of the Southwest Sub-basin. Most of the hydrocarbons cannot be detected due to their low concentration. The carbon isotope composition detected is between $-25.41 \sim -32.41‰$ (Wan et al., 2019).

The concentration of total n-alkanes in core A was ranging from 716.7 to 2799.8 ng/g (**Table 2**), with the lowest content was found in the middle layer and higher contents were observed in the top and bottom layers. The concentration of total n-alkanes in core B was varying from 1008.3 to 2109.9 ng/g (**Table 3**), and the vertical variation was quite fluctuant. TAR($\mathrm{TAR} = \Sigma C_{27} + C_{29} + C_{31}/\Sigma C_{15} + C_{17} + C_{19}$) was used to evaluate the relative contributions of ternary alkanes from terrestrial and marine sources (Meyers, 1997). The TAR in the core sediment A range from 1.6 to 18.2 with an average of 5.4 (**Table 2**). The TAR ranged from 1.4 to 6.6 in the core sediment B with an average of 3.1 (**Table 3**), it shows that the contribution of terrestrial organic matter to n-alkanes is dominant in the two core sediments. The vertical features of TAR in the core sediment A can be divided into two sections: TAR values were bigger below the depth of 340 cm in the core sediment A, while those above the depth of 340 cm remained stable, indicating that the terrigenous organic matter had a greater contribution to n-alkanes at the bottom of the core sediment A.

Pr/Ph is usually used as a parameter for the degree of oxidation-reduction of sedimentary environments and reconstruction of paleoenvironment (Powell and McKirdy, 1973; Didyk et al., 1978). Both pristane and phytane are derived from phytol, which is favorable for the formation of Pr under oxidative conditions during the evolution process, whereas production of Ph is favored in reducing conditions (Didyk et al., 1978). Therefore, it is generally believed that $\mathrm{Pr/Ph} < 1.0$ indicates a depositional environment of anoxia reduction, whereas $\mathrm{Pr/Ph} > 1.0$ reveals an oxidized depositional environment (Peters and Moldowan, 1993). The Pr/Ph value of core sediment A was 0.3–0.5, with an average of 0.4, and was slightly increased downward the vertical direction. The Pr/Ph value of the core sediment B was 0.2–0.4 with an average of 0.3, and it vertically decreased. The Pr/Ph values of the both cores are far less than 1, similar to the Pr/Ph values of 0.44–0.73 in the four samples measured by Duan et al. (1996) in the Nansha Sea area. The Pr/Ph values of the core sediments remain the same with depth (**Figure 5**), which shows that the depositional environment was strongly reduced and stable over long term, which is beneficial for the preservation of marine organic matter. These conclusions thus highlight the contribution of marine organic matter (Meyers, 1997; Hu et al., 2013) and are consistent with the conclusion of the C/N ratio of both core sediments.

Indication of Medium-Chain *n*-Alkanes Distribution

The even/odd predominance patterns in the n-alkane (n-C_{14-20}) of core A and B (**Figures 6**, **7**) show an anomalous sedimentary environment (Kuhn et al., 2010). It is generally believed that this phenomenon may be caused by (1) high-salt carbonate environments (Dembicki et al., 1976; Guoying et al., 1980; Ten Haven et al., 1985); (2) anthropogenic fossil fuel contamination or hydrocarbon leaks in the underlying high-maturity formations (Lichtfouse et al., 1997); (3) the strong reduction of the environment and the reduction in the *n*-fatty acids with an odd carbon dominance (Welte and Ebhardt, 1968; Welte and Waples, 1973).

Both cores were predominantly comprised of medium-fine sand and clay silt, suggesting that the presence of high-salt carbonate environments is impossible. The distribution of *n*-alkanes (CPI = 1.8–5.0) of both cores shows the characteristics of modern sedimentation. Therefore, it is also impossible for the even/odd predominance patterns in the medium-chain *n*-alkane in sediments to be dominated by the fossilization of modern fossil fuels or the leakage of hydrocarbons from deeper strata to lower strata (CPI $\approx$ 1) (Nishimura and Baker, 1986; Freeman and Colarusso, 2001). The ratio of Pr/Ph in the sediment ranged from 0.2 to 0.5, indicating a strong reduction depositional environment, and strong reduction makes the odd-carbon *n*-fatty acids reduce to even-carbon *n*-alkanes. Therefore, we speculate that the even/odd predominance patterns in the *n*-alkane (*n*-C_{14-20}) of core A and B are results from the intense reduction environment during deposition.

CONCLUSION

(1) The mean TOC of core sediment A is 0.64% ± 0.18%, and the average concentration of TN is 0.10% ± 0.02% (0.04–0.12%). The average concentration of TOC of core sediment B is 0.64% ± 0.12%, and the average concentration of TN is 0.10% ± 0.01%. The C/N ratio reflects that the organic carbon in the sediments is a mixture of terrestrial and marine sources, the contribution of marine sources to organic carbon in core sediment B is bigger than that of A.

(2) The long-chain *n*-alkanes in all layers of the both core sediments show an odd-even predominance, with *n*-C_{29}, *n*-C_{31} and *n*-C_{33} being the main carbons, which reflect the contribution of terrigenous higher plants and short-chain *n*-alkanes from marine plankton or bacteria. The Pr/Ph of core A and B were 0.3–0.5 and 0.2–0.4, respectively, which are both far less than 1, and the Pr/Ph values remained the same with depth changes, indicating that the sedimentary environment was dominated by strong reduction and long-term stability.

(3) The even-odd distribution patterns of medium-chain *n*-alkanes (*n*-C_{14-20}) in the core A and B possibly caused by the strong reductive depositional environment. The strong reduction allowed the conversion of odd-carbon *n*-fatty acids to even-carbon *n*-alkanes.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author/s.

AUTHOR CONTRIBUTIONS

XW: writing-original draft, experimental analysis, and data analysis. ZW: main idea, methodology, writing—review and editing, project administration, and funding acquisition. CC: data analysis and writing—review and editing. SC: experimental analysis. All authors contributed to the article and approved the submitted version.

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