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Research Article

Changes of Parameters Characteristic for Surface Sediments in Oil Spill Sea Area

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Abstract

The explosion induced by Huangwei pipeline leakage on Nov 22, 2013, which provides a better experimental platform for studying the weathering process of oil spill in real marine environment.The study bases on the sediment samples for four times surveys of the southern coastal of Jiaozhou Bay, and by using the technique of Gas Chromatography-Mass Spectrometry (GC-MS), to analyzedistribution characteristics of biomarker of surface sediment in oil spill sea area, the fluctuation pattern of characteristic parameters, and the source of sediment organic matter. Results show: Tricyclicterpane that with different carbon numbers and hopance that with different stereochemistry configuration in terpanes, and cholestane, methylcholestaneand ethylcholestane in steranewere detected in every station. The ratio Ts/Tmwas low, that maybe due to biological degradation; the ratio C31αβ(S/(S+R)) and C29-Steraneααα(S/(S+R))were close to 0.6, it indicated the area was affected by the input of petroleum. The distribution pattern of characteristic parameters of steranes and terpaneswereconsistent in survey stations, indicating that the composition of organic matter in the survey area was consistent. The characteristic parameters of sterane and terpaneswere changing regularly with the change of time, indicating that the surface sediment in oil spill sea area that was contaminated by oil spill is controlled weakly by oil Pollution; it is mainly affected by natural factor such as the input of organic matter. The sterane in survey area is mainly came from mixed organic matter include higher plants, plankton and algae.

Keywords: Characteristic Parameters; Jiaozhou Bay; Oil Fingerprints; Sediments; Sterane; Terpanes

Introduction

The oil spill identification system is constantly improving at present in China. Oil spill identification requires selecting the stable characteristic ratiosthatare affected little by weathering. Sterane and terpanes are important biomarkers in petroleum geochemistry. These substances or their parameters not only characterize the inherent characteristics of oil, but also are affected littlebyweathering degradation in marine environment. Due to the complexity of the geology and conditions of oil generation, each crude oil always displays unique biomarker fingerprints,which play an important role indetermining oil spills, identifying crude oil, investigating hydrocarbon behavior in the environment and monitoring the degradation process and weathering status of crude oil under different environmental conditions [1]. The south bank of Jiao zhou Bay in Qingdao has built the largest deep-water oil terminal and large refinery base in China.

The accident oil pipeline explosionoccurred on November 22, 2013, led about 1 000 m^2 of ground was polluted by crude oil, most of crude oil flowed into Jiaozhou Bay with the municipal drainage culvert, and about 3000 $m^2$of sea covered by oil. It caused serious damagetothe coastal marine environment and marine organism. Yuanyuan Zhang [2] studied the short-term natural weathering characteristics of the oil spillaccident. Xuena Yang [3] and Jianxin Ren [4] have made a preliminary study on the characteristics of organic matter in sediments on tidal flat culture zone and surface sediments near the polluted area, and achieved remarkable results. On the basis of the studies above, my paper bases on the sediment samples of the southern coastal of JiaozhouBay and four times survey datas after 2 years of oil spill,to study environmental evolution process and thefluctuation pattern with time of the identification parameters in oil pollution, and analysis of the types and sources of organic matter. Whichin order to provide a scientific basis for understanding the environmental pollution status of coastal waters affected by oil spill in southern Jiaozhou Bay and the remediation methods of sediment environmental pollution.

Materials and Methods

Sampling

A total of eight sampling sitesin the coastal area of the south bank of Jiaozhou Bayare shown in (Figure 1). Four different cruises wereconducted in November 2015, March 2016, October 2016, March 2017, and respectively.In accordance with the technical requirements of "The specification for marine monitoring" (GB17378-2007), surface sediments samples were collected and stored in a brown glass bottle and returned to the laboratory, and after natural air drying at laboratory temperature to determine.

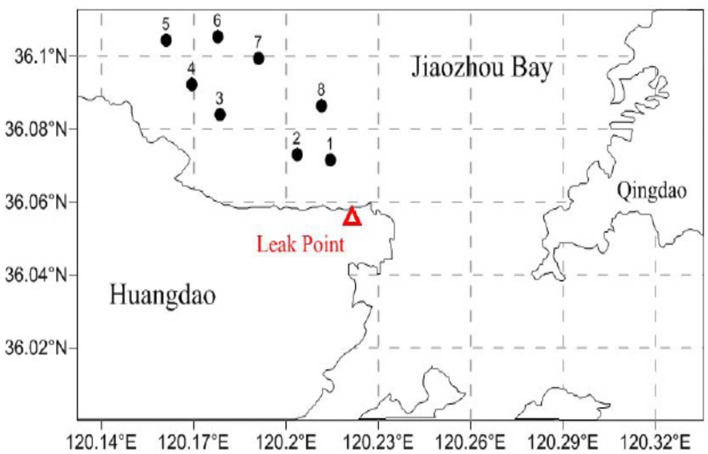


Figure 1: The surface sediment sampling sites.

Instruments and Reagents

Gas Chromatography Mass Spectrometry(GC/MS): GC6890-MS5975, Equipped With Mass Spectrometry Detector(MSD) and HP-5 Capillary Chromatographic Column(Agilent, USA); Rotary Evaporator: BuchiR-3HB, equipped with a diaphragm vacuum pump (Buchi, Germany); Termovap Sample Concentrator: EFCG-11155 (Organization, USA); Ultrasonic Cleaner: KQ5200DE (Kun Shan Ultrasonic Instruments, China); Analytical Balance: KERNABS220-4 (KERN, Germany).n-hexane, GR, ref.110-54-3 (TEDIA,USA); Dichloromethane, GC (TJSHIELD, China); Sodium sulfate anhydrous, GR (Kermel, China); Copper Powder, 99.99% (TJ Hua Zhen, China).

Sample Preparation

Groundthe dried surface sediments samples and pass them through the 100-mesh sieve. Then weigh about 10.0 g of sediment samples and add to 100 μL recovery rate indicator- Phenanthrene (4 mg•L^{-1}) in it. Put the samples in Soxhlet extractor after be wrapped up in worked filter paper. Then add 150 mL of n-hexane-dichloromethane (Volume ratio 1:1) to Soxhlet extractor and extract 24 h (thewater bath temperature is 60 ℃, to ensure that t return 5-6 times per hour). Then add 0.5 g copper powder after extraction to desulfurization. The extract was filtered through anhydrous Na_2SO_4 and concentrated by rotary evaporation to about 2 mL, thentransfer it with n-hexane to l mL nitrogen blowing bottle,transfer it to the gas phase sample bottle after concentration,and finally put it for GC-MS analyses.Blank experiments were performed simultaneously with the sample analyses. The resulting GC-MS spectra showed that the baseline was low and the noise was weak and the target compound was not detected. The sample recovery range is 85.3% -110.2%, up torequirements ofUSA EPA standards (70% -120%).

Sample Analysis

Chromatographic conditions: the initial temperature of 50 ℃for 2 min, then on 6℃•min-1 rose to 300℃, keep 16 min; carrier gas is high purity He, flow rate 1.6 mL • min-1; thecolumn pressure is 94.9 kPa, the inlet temperature is 250˚C, the injection volume is 1 μL, Split less injection, constant current injection mode.

Mass spectrometry conditions: the interface temperature is 250℃,the ion source temperature is 230℃, the quadruple temperature is 150℃, the ionization energy is 70 eV, solvent delay 3 min, the scanning range is 50.00-500.00 amu; SIM way, deuterated (188), Alkane terrene selective ions (191, 217).

Results and Discussion

The Distribution and Characteristic Parameters of Sterane and Terpanes

The Distribution of Steranes and Terpanes

Figure 2 and Figure 3 show the chromatograms of terpanes and steranes in sediment of typical stations. Figure 2 shows that, in the sediments of sea area,tricyclicterpanes that with different carbon numbers and Hopanesthat with different stereochemistry configuration in terpanes, such as Trisnorhopane, moretane and 17α(H),21β(H)-$_{C27, 29, 30, 31}$Hopanes and a small amount of C_{30} rearrangement Hopaneswere detected.

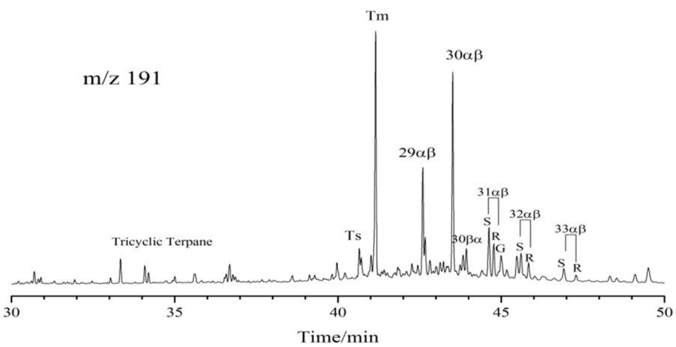


Figure 2: GC-MS Chromatograms of terpanes in sediment from typical sampling station(α, β = 17α (H), 21β (H)-Hopanes; β,α =17β(H), 21α(H)-Hopanes; R and S = C-22 Rand S configuration; G = Gammacerane; Ts = 18α(H)-22,29,30-Trisnorhopane; Tm = 17α(H)-22, 29, 30-Trisnor-hopane)

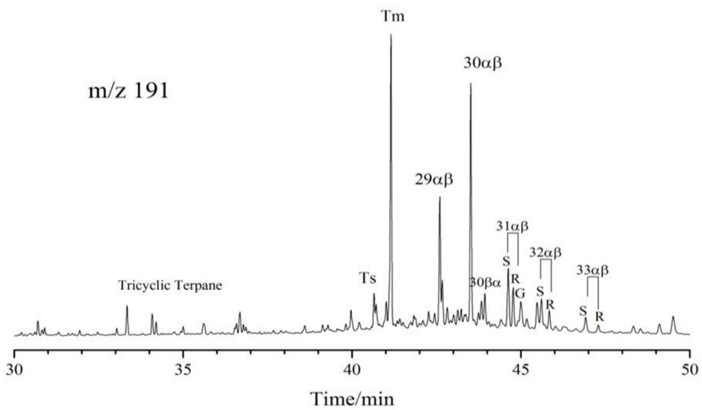


Figure 3: GC-MS Chromatograms of steranes in sediment from typical sampling station(ααα = 5α(H), 14α(H), 17α(H)-steranes; αββ = 5α(H), 14β(H), 17β(H)-steranes. R and S = C-20 R and S configuration).

In the terpanes, the abundance of 17α (H), 21β (H) -22, 29, 30-trisnorhopane (Tm) and 17α (H), 21β (H)-hopance (C30 Hopanes) was the highest. C31, C32 of homo hopance were detected more obviously, and the presence of C31 and C32 homo Hopanes indicated the influence of petroleum input [5]. In addition, all samples were detected gamma cerane, which gammacerane have been found in a lot of crude oiling our country. These indicated that sediments in the survey area may be affected by oil input. (Figure 3) shows that for steranes in the sediments of the investigated sea area, and cholestane, Methyl cholestane and Ethyl cholestane in sterane were detected, in which the geological configuration αββ of Sterane had advantages obviously.

The Characteristic Parameters of Steranes and Terpanes

Table 1.1-1.4 lists diagnostic ratios of steranes and terpanes in sediments of survey sea area for four times samplings. It is observed that the range of Ts/Tm ratio in the four surveys were 0.15-0.25, 0.17-0.31, 0.38-0.62 and 0.43-0.59, and the ratio was lower, and it can be also seen from Figure 2 that Tm abundance was very high, Ts abundance was low.

Station	1	2	3	4	5	6	7	8	Mean value
Ts/Tm	0.25	0.19	0.25	0.21	0.15	0.18	0.24	0.22	0.21
$C_{29}\alpha\beta/C_{30}\alpha\beta$	0.69	0.74	0.72	0.75	0.77	0.79	0.78	0.74	0.75
$C_{31}\alpha\beta(S/(S+R))$	0.60	0.60	0.60	0.61	0.61	0.58	0.57	0.61	0.60
$C_{27}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.48	0.48	0.48	0.44	0.44	0.43	0.44	0.44	0.46
$C_{28}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.48	0.45	0.44	0.43	0.50	0.48	0.47	0.49	0.47
$C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.40	0.39	0.39	0.39	0.39	0.39	0.40	0.40	0.39
$C_{27}\alpha\beta\beta/(C_{27}-C_{29})\alpha\beta\beta$	0.28	0.29	0.29	0.29	0.23	0.25	0.26	0.25	0.27
$C_{28}\alpha\beta\beta/(C_{27}-C_{29})\alpha\beta\beta$	0.35	0.31	0.30	0.32	0.38	0.38	0.35	0.37	0.34
$C_{29}\alpha\beta\beta/(C_{27}-C_{29})\alpha\beta\beta$	0.38	0.40	0.40	0.40	0.39	0.37	0.39	0.38	0.39
$C_{29}\alpha\alpha\alpha(S/(S+R))$	0.57	0.56	0.55	0.54	0.55	0.57	0.54	0.55	0.55

Table 1.1: The characteristic parameters of steranes and terpanes in the surface sediments in November 2015.

Station	1	2	3	4	5	6	7	8	Mean value
Ts/Tm	0.17	0.31	0.18	0.31	0.18	0.17	0.25	0.27	0.23
$C_{29}\alpha\beta/C_{30}\alpha\beta$	0.80	0.77	0.92	0.86	0.94	0.88	0.87	0.78	0.85
$C_{31}\alpha\beta(S/(S+R))$	0.50	0.52	0.54	0.51	0.55	0.51	0.51	0.46	0.51
$C_{27}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.39	0.39	0.37	0.37	0.38	0.38	0.37	0.37	0.38
$C_{28}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.70	0.64	0.66	0.72	0.67	0.64	0.63	0.68	0.67
$C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.40	0.40	0.39	0.39	0.38	0.40	0.38	0.41	0.39
$C_{27}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.26	0.30	0.28	0.24	0.30	0.27	0.31	0.27	0.28
$C_{28}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.46	0.40	0.45	0.51	0.44	0.42	0.42	0.45	0.44
$C_{29}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.29	0.31	0.28	0.25	0.26	0.31	0.27	0.28	0.28
$C_{29}\alpha\alpha\alpha(S/(S+R))$	0.51	0.49	0.53	0.54	0.53	0.51	0.51	0.54	0.52

Table 1.2: The characteristic parameters of steranes and terpanes in the surface sediments in March 2016.

Station	1	2	3	4	5	6	7	8	Mean value
Ts/Tm	0.52	0.58	0.53	0.38	0.62	0.52	0.57	0.57	0.54
$C_{29}\alpha\beta/C30\alpha\beta$	0.77	0.84	0.82	0.93	0.84	0.84	0.85	0.85	0.84
$C_{31}\alpha\beta(S/(S+R))$	0.56	0.50	0.52	0.53	0.54	0.53	0.51	0.50	0.52
$C_{27}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.48	0.35	0.37	0.40	0.43	0.47	0.38	0.40	0.41
$C_{28}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.61	0.64	0.59	0.65	0.60	0.59	0.62	0.61	0.62
$C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.38	0.33	0.35	0.36	0.38	0.37	0.37	0.43	0.37
$C_{27}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.35	0.29	0.32	0.31	0.35	0.34	0.31	0.28	0.32
$C_{28}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.40	0.44	0.41	0.41	0.38	0.40	0.43	0.43	0.41
$C_{29}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.25	0.27	0.27	0.28	0.26	0.26	0.26	0.29	0.27
$C_{29}\alpha\alpha\alpha(S/(S+R))$	0.52	0.54	0.54	0.53	0.54	0.52	0.55	0.55	0.54

Table 1.3: The characteristic parameters of steranes and terpanes in the surface sediments in October 2016.

Station	1	2	3	4	5	6	7	8	Mean value
Ts/Tm	0.56	0.55	0.50	0.53	0.59	0.43	0.53	0.51	0.53
$C_{29}\alpha\beta/C30\alpha\beta$	0.81	0.76	0.80	0.81	0.84	0.80	0.78	0.81	0.80
$C_{31}\alpha\beta(S/(S+R))$	0.63	0.64	0.63	0.64	0.62	0.64	0.64	0.60	0.63
$C_{27}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.43	0.42	0.43	0.46	0.44	0.48	0.42	0.47	0.44
$C_{28}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.50	0.48	0.48	0.52	0.51	0.55	0.50	0.51	0.50
$C_{29}\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$	0.43	0.41	0.42	0.41	0.43	0.38	0.40	0.43	0.41
$C_{27}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.30	0.30	0.31	0.31	0.31	0.32	0.31	0.32	0.31
$C_{28}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.32	0.32	0.31	0.33	0.33	0.36	0.33	0.32	0.33
$C_{29}\alpha\beta\beta/(C_{27}\text{-}C_{29})\alpha\beta\beta$	0.37	0.38	0.38	0.36	0.36	0.32	0.36	0.36	0.36
$C_{29}\alpha\alpha\alpha(S/(S+R))$	0.62	0.59	0.60	0.60	0.60	0.57	0.61	0.59	0.60

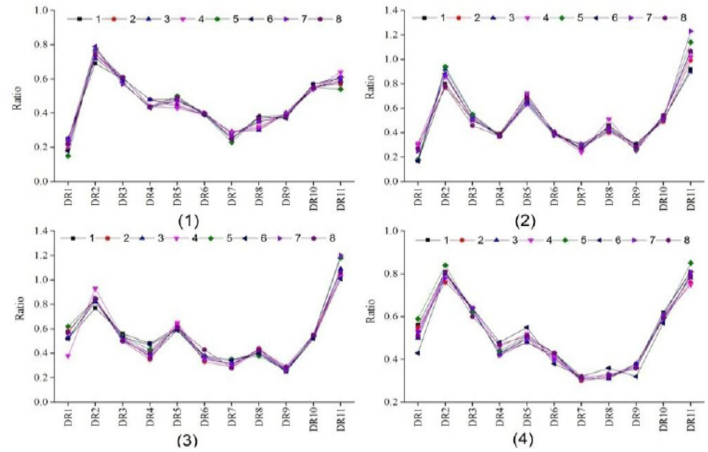
Table 1.4: The characteristic parameters of steranes and terpanes in the surface sediments in March 2017.

According to the study of J P, Bao [6], it is found that the ratio of Ts/Tm decreases with the increase of biodegradation intensity. Therefore, it was inferred that the lower Ts/Tm ratio may be related to biodegradation in four surveys.The component percentage ofR and S configuration in steranes and terpanes is the important indicatorinassessment of thermal maturity of organic matter, such as C_{31}~$_{35}$αβ(S/(S+R)) and C_{29}ααα(S/(S+R)), etc. They generally show different ranges with different maturity: low maturity organic matter show between 0.52-0.55, fully mature equilibrium value show of 0.6 or so[7,8]. Therefore, these parameters are often used to distinguish between oil and non-oil inputs. The ranges of C_{31}αβ (S/(S+R)) ratio in the four surveys were 0.57-0.61, 0.46-0.55, 0.50-0.56 and 0.60-0.64, which all around 0.6; the ranges of C_{29}ααα (S/(S+R)) ratio were0.54-0.57, 0.49-0.54, 0.52-0.55and 0.57-0.62. All of aboveindicated that the survey area had been affected by oil input.

The regular C_{27}-C_{28}-C_{29}sterane series (Cholestane, Ergostane, and Stigmastane) is most common in oils, and because of its high oil source characteristics, the correlation ratios of it are commonly used in chemical fingerprint studies.Steranes include both biological configuration (5α14α17α) and geologic configuration (5α14β17β), and the biological configuration isomers are gradually transformed into geologic configuration isomers with the degree of thermal evolution increased, so we usually use αββ/ (αββ+ααα) to indicatethe maturity of crude oil.In the four surveys, the mean value of C_{27}αββ/(αββ+ααα) were 0.46,0.38,0.41 and 0.44 respectively; the mean value of C_{28}αββ/(αββ+ααα) were 0.47,0.67,0.62 and 0.50 respectively; the mean value of C_{29}αββ/(αββ+ααα)were 0.39,0.28,0.37 and 0.41 respectively. All of aboveindicated that the survey area had been affected by oil input.

The Distribution Pattern of Characteristic Parameters of Steranes and Terpanes

(Figure 4) Show that the comparison of eleven oil fingerprint parameters of steranes and terpanesin sediments at eight stationsamong the four times surveys. It can be seen from the figure that there wereslightly difference of the distribution pattern of characteristic parameters of steranes and terpanes in different surveys. However, in the single survey, the ratio values of steranes and terpaneswere no significant difference in different stations, and the distribution pattern of characteristic ratioswere consistent, which indicated that the characteristic parameters of steranes and terpanes of sediments at different stations in the survey area was consistent.



Note: DR1: Ts/Tm DR2: C_{29}αβ/C_{30}αβ DR3: C_{31}αβ(S/(S+R)) DR4: C_{27}αββ/(αββ+ααα) DR5: C_{28}αββ/(αββ+ααα)DR6: C_{29}αββ/(αββ+ααα) DR7: C_{27}αββ/(C_{27}-C_{29})αββ DR8: C_{28}αββ/(C_{27}-C_{29})αββ DR9: C_{29}αββ/(C_{27}-C_{29})αββ DR10: C_{29}ααα(S/(S+R))DR11: C_{27}/C_{29}sterane

Figure 4: The distribution diagram of characteristic parameters of steranes and terpanes in four samplings

Time Variation of the Characteristic Parameters of Steranes and Terpanes

The steranes and terpanes in the marine environment are highly stable and are less susceptible to weathering. HengzhenXu[9] found that the characteristic parameters of terpanes and steranes in the oil change less than 10% after weathering 1 year (or indoor natural place 4 years). ZhendiWang[10] had used steranes and terpanes to identify oil spill that weathering 22 years in the environment. G. Mille[11] found that the biomarkers are very stable in the salt marsh environment and remain unaltered even after a 13-year period.

As shown in (Figure 5), in the four surveys, each ratio parameters showed a certain regular fluctuation over time, and its variation pattern is roughly divided into two categories: the ratios C_{29} αβ /C_{30} αβ, C_{28} αββ /(αββ+ααα), C_{28}αββ/ (C_{27}-C_{29})αββ,C_{27}/C_{29}changedin shape “Ù”. And the ratios C_{31} αβ (S/(S+R)), C_{27} αββ / (αββ+ααα), C_{29} αββ/(αββ+ααα), C_{29}αββ/(C_{27}-C_{29})αββ,

C_{29} ααα(S/(S+R)).Changed in shape "Ú" The ratio Ts/Tmincreased 1-2 times in the previous two surveys, and the difference between the maximum and the minimum values of C_{27}/C_{29} steranes was about 1 times and the fluctuation was significant. The characteristic parameters of steranes and terpanes varied regularly with the change of time indicated that the organic matter in the sediments of the survey area may no longer be controlled by the oil input of the oil spill, but be influenced by the natural factors such as the input of organic matter in the marine environment.

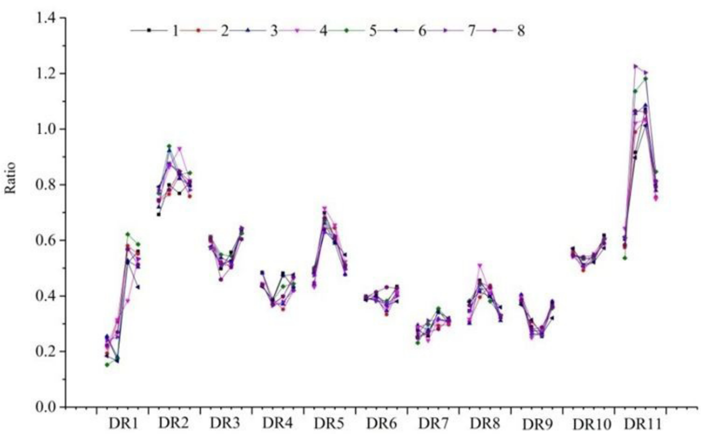


Figure 5: Time variation of the characteristic parameters of steranes and terpanes.

Analysis of Source of Sediment Organic Matter

Steranes are widely found in petroleum and its products, and they have strong resistance to environmental degradation. It can be a good indication of oil sources [12]. The triangular diagram of C_{27}-C_{28}-C_{29}ααα steranes distribution can determine the source of sediment organic matter. C_{27}steranes are mainly marine sources, derived from lower aquatic organisms and algae organic inputs; C_{29}steranesare mainly higher plant sources; C_{28}steranes play a less prominent role in the sources because important terrigenous as well as marine sources may existfor the sterols[13].Figure 6 shows the triangular diagram of C_{27}-C_{28}-C_{29}ααα steranes distribution at each site in four times survey. It can be seen that all the stations in the four surveys fell in the mixed source region, indicated that the steranes in the sediments of the sea area were mainly derived from the mixed organic matter input from higher plants, plankton and algae. The relative distribution of C_{27}, C_{28}, C_{29}αααsteranes had a V-type distribution, which may be due to the organic matter in the study area was affected by the mixed input of petroleum products and their derivatives and higher plants.

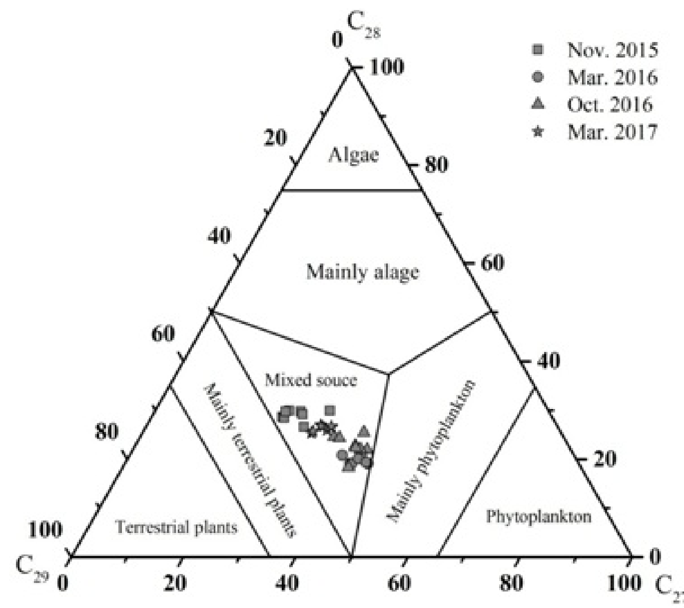


Figure 6: The triangular diagram of C_{27}-C_{28}-C_{29}αααsteranes distribution in four times survey.

Conclusion

In the surface sediment of the southern coastal of Jiaozhou Bay, tricyclic terpanes that with different carbon numbers, Hopanes, C_{30}rearranged Hopanes, cholestane, methylcholestane and ethylcholestanewere detected in every station. The distribution range of characteristics parameters Ts/Tm of the survey area was wider, was 0.15-0.62, with a mean of 0.38, and the ratio was low, which may be related to biodegradation. The distribution range of characteristics parameters C_{31}αβ(S/(S+R)) and C_{29}-sterane ααα(S/(S+R)) were narrow, were 0.46-0.64 and 0.49-0.62respectively, they were all close to 0.6. The distribution range of characteristics parametersC_{29}αββ/(αββ+ααα) was 0.33-0.43, the mean value was 0.39, the component percentage of geological configuration was high.All of above indicated the area was affected by the input of petroleum.

The distribution pattern of characteristic parameters of steranes and terpanes were consistent in survey stations, indicating that the composition of organic matter in the survey area was consistent. The characteristic parameters of sterane and terpanes were changing regularly with the change of time, indicating that the surface sediment in oil spill sea area that was contaminated by oil spill is controlledweakly by oil pollution; it is mainly affected by natural factor such as the input of organic matter.The sterane in survey area is mainly came from mixed organic matter include higher plants, plankton and algae.The relative distribution of C_{27}, C_{28}, C_{29}αααsteranes had a V-type distribution, which may be due to the organic matter in the study area was affected by the mixed input of petroleum products and their derivatives and higher plants.

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