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胶州湾表层海水中的正构烷烃及其来源解析

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摘要: 正构烷烃是自然界中普遍存在的有机物质, 其组成和分布与人类活动密切相关, 是表征有机污染物来源的良好标志物。用气相色谱-质谱(gas chromatography-mass spectrometry, GC-MS)对2016年4月胶州湾表层海水中的正构烷烃进行检测, 首次报道了胶州湾表层海水中正构烷烃的分布特征及来源解析。结果表明, 其含量在 $1.756 \sim 39.09 \mu\text{g} \cdot \text{L}^{-1}$ 之间, 主要由连续分布的 $\text{C}_{11} \sim \text{C}_{37}$ 正构烷烃同系物组成, 没有明显的奇偶优势, 但碳数为 $\text{C}_{21} \sim \text{C}_{33}$ 的正构烷烃约占总正构烷烃的95.0%。胶州湾表层海水中正构烷烃的高值区以湾口为主, 在湾内东北部和西部也有出现, 这一分布特征与胶州湾东北部和西部河流带来的工业废水、生活污水和湾口码头附近的船舶航运带来的正构烷烃输入有关。水交换较为充分的湾中部和湾外海域正构烷烃总量在 $1.756 \sim 2.842 \mu\text{g} \cdot \text{L}^{-1}$ 之间, 平均值为 $2.196 \mu\text{g} \cdot \text{L}^{-1}$, 可视为胶州湾正构烷烃的环境背景值。其碳数分布有明显的 C_{24} 主碳峰, 前峰群有微弱的奇碳优势, 后峰群有微弱的偶碳优势, 表明这部分正构烷烃以藻类和海洋细菌等生物自生输入为主。人类活动对胶州湾的影响很大, 输入的正构烷烃主要集中在湾口及湾内近岸海域, 由 $\text{C}_{21} \sim \text{C}_{33}$ 正构烷烃同系物组成, 呈现出有微弱偶碳优势的后峰群单峰形分布特征, 代表高度风化的石油类污染物。其含量在 $9.606 \sim 39.09 \mu\text{g} \cdot \text{L}^{-1}$ 之间, 约占胶州湾总正构烷烃量的83.7%。整体来看, 胶州湾表层海水对正构烷烃的去除机制以蒸发、稀释等物理风化过程为主, 从湾内向湾外风化强度增大。

关键词: 正构烷烃; 来源; 污染评价; 表层海水; 胶州湾

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Distribution and Sources of *n*-alkanes in Surface Seawater of Jiaozhou Bay

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Abstract: Hydrocarbons emitted by human activities probably constitute the largest class of contaminants that are present in coastal areas, because of widespread use of fossil fuels for power generation and logistics, and accidental spillages. The chemical composition of hydrocarbon mixtures found in the marine environment allowed the identification of relative contributions of different natural and anthropogenic sources. Identification of these hydrocarbons, especially *n*-alkanes, could act as tracers for the possible sources. To evaluate *n*-alkanes concentrations with emphasis on source analysis, surface water without visible oil was collected from the cruise in April 2016. Determination and quantification were performed by solvent extraction and gas chromatography-mass spectrometry. Various molecular diagnostic parameters were used to assess the contribution of different sources and origin of *n*-alkanes in surface seawater of Jiaozhou Bay. Concentrations of total dissolved *n*-alkanes ($\text{C}_{11} \sim \text{C}_{37}$) were between $1.756 \sim 39.09 \mu\text{g} \cdot \text{L}^{-1}$ with a high carbon number predominance profile without odd-even carbon number preference. The *n*-alkane concentrations varied spatially depending on the distance away from main input sources and the ability of water exchange. It was at a higher concentration in the northeast and west coastal areas, as well as the mouth of Jiaozhou Bay. And concentrations were relatively lower in the inner area and outside of Jiaozhou Bay. In the sea area with strong water exchange, concentrations of total *n*-alkanes were around $2.196 \mu\text{g} \cdot \text{L}^{-1}$, which could be considered as the environmental background level of *n*-alkanes in Jiaozhou Bay. Those *n*-alkanes were dominated with C_{24} , with a slightly odd carbon number preference in low carbon *n*-alkanes and an even carbon number preference in high carbon *n*-alkanes. The values of CPI for the whole range of *n*-alkanes series, low carbon *n*-alkanes, and high carbon *n*-alkanes were 0.949, 1.026, and 0.980, respectively. Diagnostic indices and curves indicated that the dominant inputs of those *n*-alkanes were from marine biogenic

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input such as algae and marine bacteria. The concentration profiles of *n*-alkanes in other areas were characterized by no odd-even predominance in the range of C_{21} - C_{33} with peaks center at C_{24} which were indicative of anthropic contributions as emission sources. *N*-alkanes dominating with anthropic sources comprised a high proportion (83.7%) of total *n*-alkanes. Activities of harbors and ships were the main contributors of Jiaozhou Bay *n*-alkanes. Physical processes, such as evaporation and dilution, were the principal weathering mechanisms. Because of its sufficient environmental capacity, Jiaozhou Bay was still moderately contaminated with petroleum.

Key words: *n*-alkanes; source; pollution evaluation; surface seawater; Jiaozhou Bay

正构烷烃是一类直链饱和碳氢化合物,在自然界中普遍存在^[1],它们的组成和分布与人类活动密切相关.进入水环境的正构烷烃不但对水生生物有明显的毒害作用,而且会随着地球化学循环过程危及人类健康^[2].自然来源的正构烷烃在水体中浓度很低,通常视为环境背景值^[3].而石油工业、原油运输、港口作业和生活、工业排污等活动都会向环境中引入正构烷烃,使人为输入成为近海水体中正构烷烃的主要来源.不同来源的正构烷烃组成特征各不相同,而且这类化合物结构稳定,是表征有机污染物来源的良好标志物^[4~7].

胶州湾是青岛的母亲湾,其沿岸生物资源丰富,是优良的天然避风港和锚地,也是青岛市经济社会发展的重要条件^[8].随着海运交通和石油储运业的发展,向胶州湾输入的石油类物质来源更趋广泛.黄岛油码头和青岛港是胶州湾正构烷烃的固定输入源,繁忙的船舶活动与航运作业向胶州湾输入大量正构烷烃,此外还有大气沉降、城市排污和无法预估的石油污染事故,种类繁多的输入途径使胶州湾面临石油污染的风险^[9].这些进入胶州湾的石油类污染物给近岸海域的生态环境造成极大威胁,也给栖息于该海区的海洋生物带来很大的压力.

有关胶州湾正构烷烃的研究多集中于沉积物、颗粒物等固相载体,水体中石油烃类多侧重于估算其环境容量^[9~13],至目前针对胶州湾水体中正构烷烃的组成及来源解析研究尚未见到报道,但我国近海其他海域其正构烷烃的研究已有不少报道^[2, 14~18].为研究胶州湾水体中正构烷烃的环境地球化学特征,查明该海域正构烷烃的组成和污染状况,本文报道了2016年4月胶州湾表层海水中正构烷烃的含量、分布与来源,并重点诠释了石油污染对于胶州湾环境的影响,以期为该海区的环境质量评估和环境保护提供科学依据.

1 材料与方法

1.1 样品采集

2016年4月搭载“创新号”科考船对胶州湾进行了调查采样,共设置10个采样站位,如图1所示.

每个站位在考察船上风方向采集0.5~1.0 m水深的表层海水2.5~3.0 L,装入事先灼烧并清洗干净的玻璃瓶中,用磨口玻璃塞旋紧密封,放在阴暗处暂存,并于调查当天15:00之前运回实验室进行下一步处理.

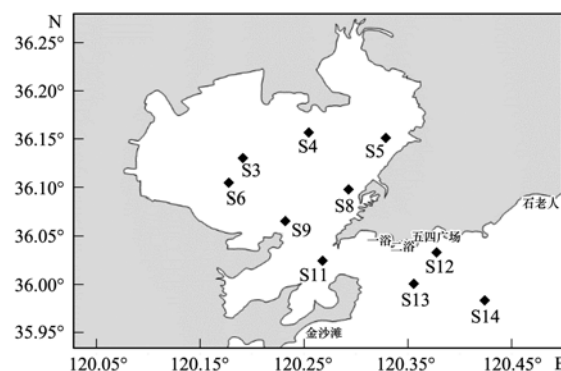


图1 胶州湾2016年4月采样站位示意

Fig. 1 Sampling stations in Jiaozhou Bay during the cruise in April 2016

1.2 仪器与试剂

美国 Agilent 气相色谱-质谱联用仪 7890A/5975C;天津津腾 GM-0.33A 型隔膜真空泵;美国 Thermo Sorvall ST40 ST40R 高性能台式离心机;昆山舒美 KQ-800KDV 台式高功率数控超声波清洗器.

正己烷(德国 Merck 色谱纯);二氯甲烷(德国 Merck 色谱纯);无水 Na_2SO_4 (国药集团化学试剂有限公司,分析纯).

所有玻璃器皿及滤膜均经过马弗炉高温灼烧并用二氯甲烷、正己烷清洗.

1.3 样品处理

所采水样经灼烧并用有机溶剂清洗过的0.7 μm 玻璃纤维膜过滤,除去颗粒物.取2 L过滤后的表层海水,加入40 mL二氯甲烷,充分振荡萃取20 min后分液.取有机相加入无水 Na_2SO_4 干燥,离心分出上清液,氮吹浓缩至干燥,将溶剂置换成0.2 mL正己烷,转移至气相样品瓶中,待GC-MS检测.

1.4 仪器条件

色谱条件^[19]:HP-5MS 5% Phenyl Methyl Silox (19091S-433)弹性石英毛细管柱(30 m $\times$ 250 μm $\times$ 0.25 μm);柱温:初始温度50℃保持2 min,再以6

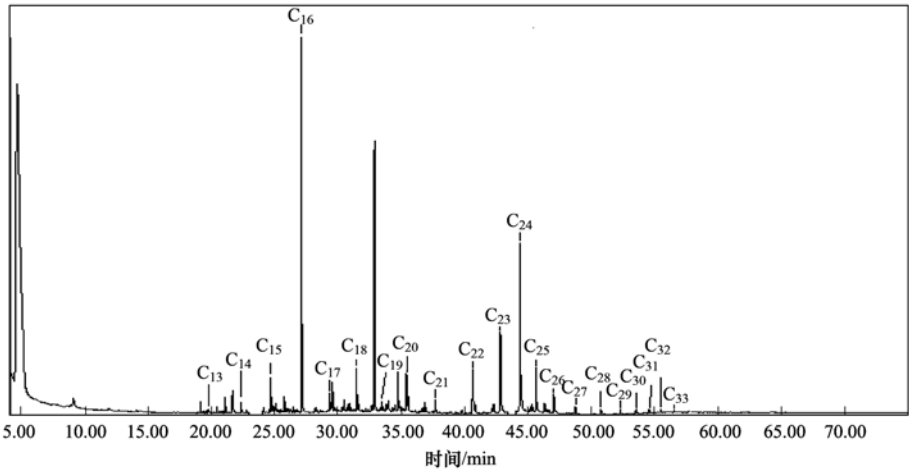


图 2 胶州湾表层海水中的正构烷烃 GC-MS 谱图(以站点 S12 为例)

Fig. 2 GC-MS chromatography of surface seawater extracts in Jiaozhou Bay

从整个胶州湾来看,不同碳数正构烷烃的含量范围如表 2 所示,含量超过总正构烷烃含量 1% 的主要为碳数在 $C_{21} \sim C_{33}$ 之间的正构烷烃,约占全部正构烷烃的 95.0%,其中又以 C_{24} 正构烷烃含量最高,约占正构烷烃总量的 16.3%。胶州湾表层海水

中的正构烷烃由连续分布的 $C_{11} \sim C_{37}$ 同系物组成,从不同碳数正构烷烃的含量看,奇碳数正构烷烃的含量并没有表现出比偶碳数正构烷烃高或低的规律性变化,即胶州湾表层海水中的正构烷烃含量没有明显的奇偶优势(图 4)。

表 2 不同种类正构烷烃的含量及占总正构烷烃含量的比例

Table 2 Concentrations and proportions of different *n*-alkanes

正构烷烃种类	含量范围/ $\mu\text{g}\cdot\text{L}^{-1}$	平均值/ $\mu\text{g}\cdot\text{L}^{-1}$	单种正构烷烃占总正构烷烃的比例/%
C_{11}	N. D. ~0.070	0.070	0.10
C_{12}	N. D. ~0.064	0.064	0.09
C_{13}	0.060 ~0.060	0.060	0.44
C_{14}	0.056 ~0.060	0.058	0.42
C_{15}	0.054 ~0.058	0.056	0.41
C_{16}	0.052 ~0.070	0.060	0.44
C_{17}	0.052 ~0.064	0.055	0.41
C_{18}	0.052 ~0.076	0.061	0.45
C_{19}	0.052 ~0.076	0.058	0.42
C_{20}	0.034 ~0.188	0.075	0.55
C_{21}	0.060 ~0.942	0.280	2.05
C_{22}	0.076 ~2.890	0.843	6.17
C_{23}	0.072 ~5.080	1.626	11.9
C_{24}	0.136 ~6.046	2.232	16.3
C_{25}	0.078 ~5.980	1.978	14.5
C_{26}	0.082 ~5.672	1.728	12.6
C_{27}	0.104 ~4.238	1.224	8.96
C_{28}	0.100 ~3.640	0.977	7.16
C_{29}	0.108 ~2.694	0.745	5.45
C_{30}	0.102 ~2.046	0.574	4.20
C_{31}	0.088 ~0.960	0.363	2.66
C_{32}	0.108 ~0.642	0.254	1.86
C_{33}	0.072 ~0.378	0.157	1.15
C_{34}	N. D. ~0.182	0.118	0.69
C_{35}	N. D. ~0.118	0.086	0.44
C_{36}	N. D. ~0.056	0.056	0.04
C_{37}	N. D. ~0.056	0.056	0.04
胶州湾总正构烷烃含量	1.756 ~39.09	13.66	—

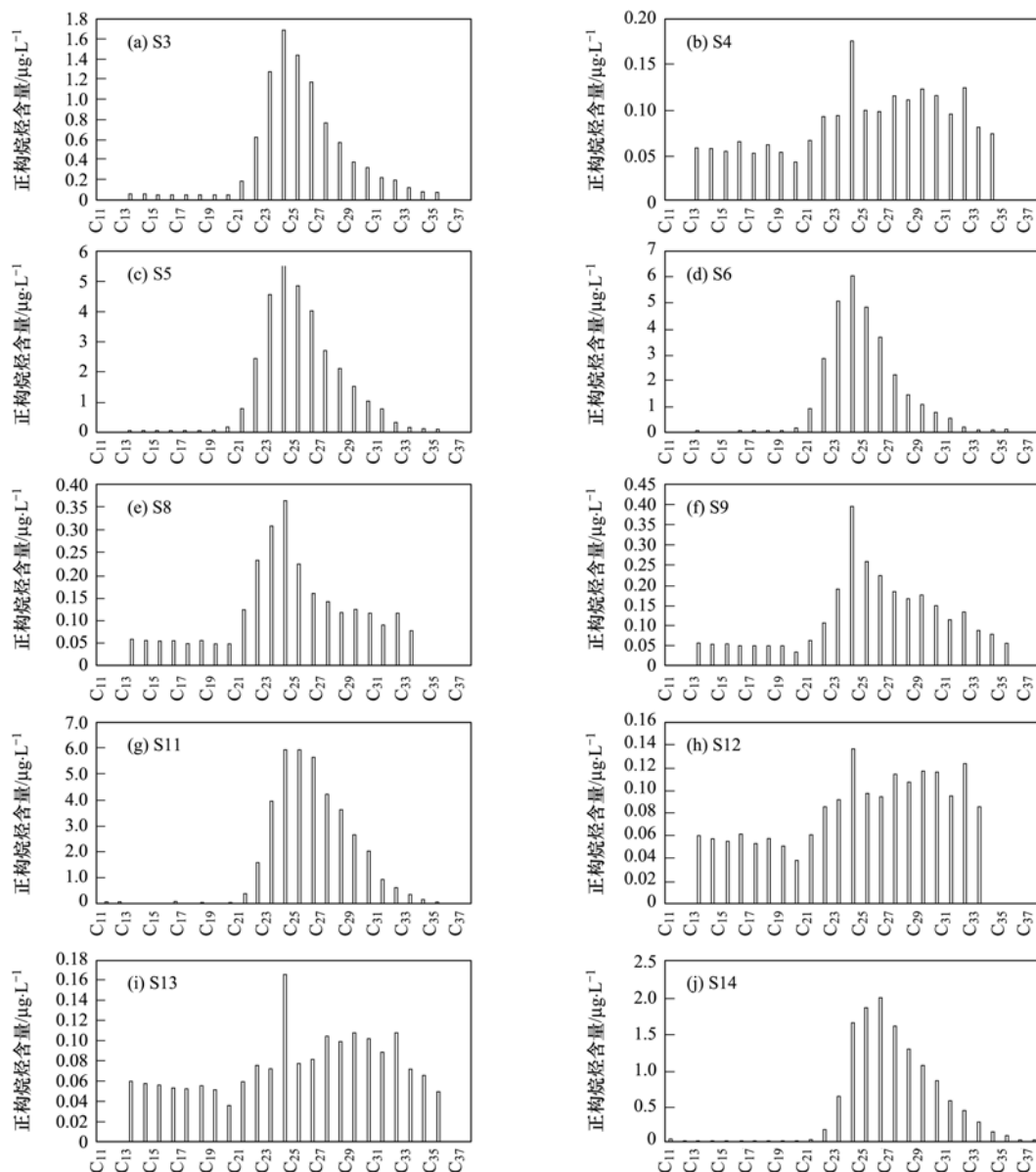


图3 各站位正构烷烃碳数分布

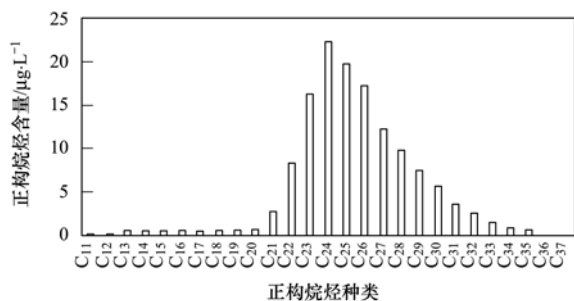
Fig. 3 Distributions of *n*-alkanes in every station

图4 胶州湾表层海水中总正构烷烃的碳数分布

Fig. 4 Distributions of total *n*-alkanes in seawater of Jiaozhou Bay

胶州湾各站位正构烷烃总量在 $1.756 \sim 39.09 \mu\text{g}\cdot\text{L}^{-1}$ 之间, 平均约 $13.66 \mu\text{g}\cdot\text{L}^{-1}$ (表2). 与邻近的青岛市各海水浴场相比, 石老人和金沙滩海水浴

场表层海水中的正构烷烃含量仅略高于胶州湾的最低值, 第一和第二海水浴场的正构烷烃含量高于胶州湾的最低水平, 但仍在平均线以下, 而五四广场附近海域表层海水中的正构烷烃含量则对应胶州湾中的较高水平 (见表3). 这是因为金沙滩和石老人均远离市区, 受人为输入的影响较小, 正构烷烃主要来源于海洋自生^[18]. 此外, 这两个海水浴场均位于开阔海域, 水交换较为充分, 所以有相对较低的含量. 一浴和二浴分别位于汇泉湾和太平湾, 水交换不如金沙滩和石老人充分, 加之与胶州湾相比更靠近市区, 正构烷烃含量稍高. 这两处海域附近均以旅游景区为主, 人类活动对海水正构烷烃水平虽有一定影响, 但幅度不大. 而五四广场近岸海域

所在的浮山湾靠近奥帆码头,受往来船只影响较大,因此有偏高的正构烷烃含量. 结合 2013 年青岛市近岸海域的石油类物质污染情况^[20]分析,即使在正构烷烃含量最高的浮山湾,石油类物质仍在一类海水的水质标准范围内,而本次调查中超过一半站位的正构烷烃含量都低于该处,说明胶州湾石油污染并不严重.

表 3 不同海区正构烷烃的含量比较

Table 3 Comparisons of *n*-alkanes concentrations in surface water from various estuary and coastal regions

地点	正构烷烃含量/ $\mu\text{g}\cdot\text{L}^{-1}$	文献
南极杰拉许湾	0.128~0.241	[21]
墨西哥湾	94~150(2010年) 10.8~34.7(2011年)	[22]
阿根廷拉普拉塔河口	182	[23]
黄河口	0.156~0.400	[16]
长江口	0.19~4.1	[17]
黄东海	0.018~20	[24]
渤海湾	0.811~1.251	[16]
湄洲湾	1.22~1.55	[25]
青岛各海水浴场	1.14(金沙滩) 6.61(一浴) 8.72(二浴) 25.47(五四广场)	[18]
青岛石老人海水浴场	1.21	[26]
胶州湾	1.756~39.09	本研究

相对于长江口、黄河口、渤海湾和湄洲湾等国内其他海域,胶州湾表层海水中的正构烷烃含量明显偏高. 若究其原因,胶州湾表层水体中的正构烷烃主要来自于以石油储运为主的人类活动输入,其浓度必然高于生物自生输入占很大比例的湄洲湾^[25]. 长江口和黄河口的正构烷烃也有石油源输入的特征^[16, 17],其浓度较胶州湾低的原因可能是河口强烈的水动力作用带来较强的稀释作用,同时高颗粒物含量对正构烷烃有显著的吸附作用. 而胶州湾是半封闭海湾,与外海的水交换不充分,加之 4 月降水稀少,又不在休渔期内,航运活动频繁,多因素共同导致本次调查中各站位正构烷烃的含量较高. 渤海湾受石油烃污染也较严重^[16],但其体量远大于胶州湾,对于石油烃污染也有更大的环境容量,这解释了渤海湾表层海水中正构烷烃含量低于胶州湾的问题. 黄东海受多种正构烷烃输入源共同影响,以生物碎屑输入为主,在夏季,浮游生物旺发造成正构烷烃大量进入水体^[24],使其高值接近于本次调查中胶州湾正构烷烃的含量.

胶州湾的正构烷烃含量显然与受陆源输入和人类活动影响都很小的南极杰拉许湾^[21]不在同一数

量级. 然而与受石油污染的拉普拉塔河口和墨西哥湾相比,2013 年刚经历过黄潍输油管道泄漏爆炸事故这样大范围溢油事故的胶州湾正构烷烃仍处于较低的水平上,这在反映胶州湾有效的自净能力之余,也从一个侧面表明近年来越加受到重视的污染防控手段有所成效.

胶州湾表层海水中的正构烷烃分布情况如图 5 所示,高值区以湾口为主,在湾内东北部和西部也有出现. 这一分布特征与胶州湾东北部和西部河流带来的工业废水、生活污水和湾口码头附近的船舶航运带来的正构烷烃输入有关. 而湾中部和湾外输入源较少,与外海海水混合充分,正构烷烃浓度相对较低.

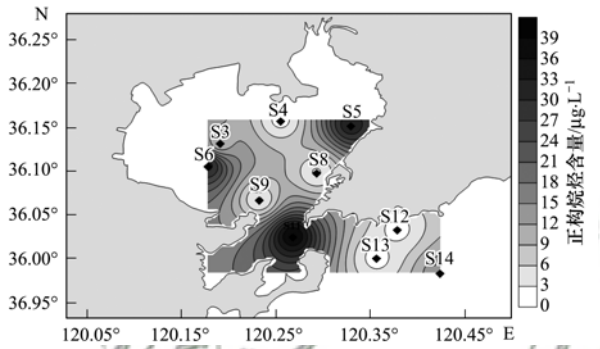


图 5 胶州湾表层海水中的正构烷烃空间分布

Fig. 5 Spatial distributions of *n*-alkanes in surface water of Jiaozhou Bay during the cruise in April 2016

2.2 胶州湾表层海水中正构烷烃的组成特征及来源解析

胶州湾表层海水中的正构烷烃由连续的 $C_{11} \sim C_{37}$ 同系物组成,主要集中在 $C_{21} \sim C_{33}$ 范围内(占正构烷烃总量的 95.7%),没有明显的奇偶优势. 沉积物或颗粒物中通常不会出现这样大范围且明显的中峰群或后峰群优势,这可能是由于表层水除受海洋细菌降解等因素影响以外,还有光降解等降解途径,影响因素更加复杂多样,而低分子量的正构烷烃在生物降解与蒸发因子的共同作用下比高分子量的正构烷烃更容易降解^[27, 28].

如此宽范围且连续的正构烷烃序列通常用以指代石油或化石燃料燃烧等人为源输入,接近于 1 的碳优势指数和奇偶优势指数(表 4)也支持这一假设^[29~31]. 陆源生物贡献的正构烷烃通常具有明显的碳数分布特征,其主要浓度组分集中于 C_{25} 以上的后峰群^[32],具有非常明显的奇碳优势,尤其是碳优势指数这一指标值往往高达 $6 \sim 10$ ^[33, 34]. 即使随时间的推移而风化,表征陆源生物输入的正构烷烃依

然具有较高的碳优势指数和较明显的奇碳优势^[4, 35]。在本次调查中,胶州湾正构烷烃虽然也以后峰群正构烷烃为主要组分,但其碳优势指数近似于1,几乎没有表现出奇碳优势,这排除了陆源生物为主要输入源的可能性。主峰碳也是表征正构烷烃来源的重要参数之一,藻类产生的正构烷烃通常以C₁₅、C₁₇和C₁₉为主峰^[36],高等植物通常是C₂₅、C₂₇、C₂₉和C₃₁占优势^[37, 38]。然而,不同于通常以C₁₆为主要组分这一典型的石油正构烷烃碳数分布特征,胶州湾海水样品的主碳峰分布在C₂₄~C₂₆之间,以C₂₄

为主。对于墨西哥湾“深水地平线”钻井平台溢油的研究^[39]为解释这种现象提供了参考:随着海水中石油的降解程度增大,前峰群优先风化,正构烷烃主碳峰逐渐后移。鉴于风化后的正构烷烃仍然具有连续分布的特征,而且未表现出明显的奇偶优势,推测胶州湾石油烃降解以物理风化过程为主。

由于前峰群的缺失,总正构烷烃/C₁₆比值和短链/长链正构烷烃比值这两个参数远远偏离正常值范畴,不具有协助指示胶州湾海水中正构烷烃来源的作用。

表 4 正构烷烃来源表征参数						
Table 4 Characteristic parameters of <i>n</i> -alkanes						
站位	正构烷烃总量 / $\mu\text{g}\cdot\text{L}^{-1}$	主峰碳 C _{max}	碳优势指数 CPI	奇偶优势指数 OEP	陆源/水源正构 烷烃比 TAR	总植物蜡碳数 /%
S3	9.606	C ₂₄	0.963	0.919	8.709	0.76
S4	1.930	C ₂₄	0.881	1.095	2.049	0.79
S5	32.19	C ₂₄	0.971	0.915	25.57	1.00
S6	30.89	C ₂₄	0.970	0.929	20.08	1.24
S8	2.682	C ₂₄	0.984	1.072	2.220	1.62
S9	2.842	C ₂₄	0.928	0.987	3.000	0.65
S11	39.09	C ₂₄ , C ₂₅	0.943	0.916	44.84	0.41
S12	1.768	C ₂₄	1.009	1.114	2.025	0.88
S13	1.756	C ₂₄	0.942	1.113	1.875	0.88
S14	13.81	C ₂₆	0.952	0.959	20.30	0.14
平均值	13.66	—	0.954	1.002	13.07	0.82

对胶州湾表层海水中的正构烷烃数据做主成分分析(如图6),发现主成分1解释了95%的差异,主成分2仅解释了4.9%的差异。在主成分分析中,S4、S8、S9、S12和S13可归为一类,结合这些站位的位置发现,它们均位于水交换相对充分的湾外或湾中部海域,具有相似的碳数分布特征和较低的正构烷烃含量,可以视为胶州湾正构烷烃的环境背景值。而S5和S6也具有相似的碳数分布特征,结合其位置发现这两个站位都在胶州湾近岸海域,而且都在河口附近,可能代表径流输入的正构烷烃特征。

胶州湾正构烷烃的环境背景由C₁₃~C₃₅组成,正构烷烃总量介于1.756~2.842 $\mu\text{g}\cdot\text{L}^{-1}$ 之间,平均值为2.196 $\mu\text{g}\cdot\text{L}^{-1}$ 。各站位均以C₂₄为主峰碳(表5),其含量在总正构烷烃环境背景值中所占的比例介于7.69%~13.9%之间,远远高于其他种类的正构烷烃。这种具有C₂₄显著高值的分布模式在南极罗斯海和圣路易斯石灰岩样品中也有报道^[21, 40],通常用以表征海洋细菌或硅藻等微生物的输入。以C₂₄为界,分前后两段计算碳优势指数,发现两个计算值均近似于1,但前峰群有微弱的奇碳优势,类似于藻类输入的正构烷烃特征,后峰群有微弱的偶碳

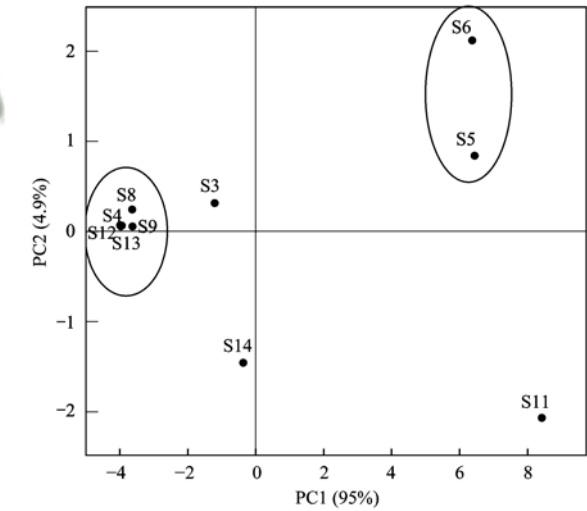


图 6 胶州湾表层海水中的正构烷烃主成分分析

Fig. 6 Principal component analysis on *n*-alkanes from surface seawater of Jiaozhou Bay

优势,类似于海洋细菌合成或分解产生的正构烷烃特征,这表明胶州湾正构烷烃的环境背景以藻类和海洋细菌等生物自生输入为主。

减去环境背景值后,剩余的正构烷烃可以视为全部来自人类活动输入。这一部分正构烷烃占胶州湾正构烷烃总量的83.7%,主要由C₂₁~C₃₃正构烷

烃同系物组成,呈现出有微弱偶碳优势的后峰群单峰形分布特征(表6),与渤海湾受石油输入影响较大海域的正构烷烃碳数分布特征相似^[16],可能是石油的风化产物. S5和S6这两个站位水样中的正构烷烃具有非常相似的总含量和碳数分布特征,可能因为它们都位于河口近岸海域,接受径流排污的程度和水交换带来的风化程度相似.

表5 胶州湾环境背景值特征参数
Table 5 Characteristic parameters of background *n*-alkanes in Jiaozhou Bay

站位	主峰碳	C _{max} 占该站位总正构烷烃的比例/%	CPI (>C ₂₅)	CPI (<C ₂₃)
S4	C ₂₄	9.12	0.890	0.954
S8	C ₂₄	13.6	1.059	1.028
S9	C ₂₄	13.9	0.951	1.135
S12	C ₂₄	7.69	1.048	0.993
S13	C ₂₄	9.45	0.952	1.021
平均值	—	10.8	0.980	1.026

表6 人为输入的正构烷烃特征参数
Table 6 Characteristic parameters of anthropic *n*-alkanes

站位	主峰碳	低分子量/高分子量正构烷烃比值(LMW/HMW)	CPI	OEP
S5	C ₂₄	0.007	0.972	0.909
S6	C ₂₄	0.007	0.971	0.923
S3	C ₂₄	0	0.963	0.894
S11	C ₂₅	0.006	0.943	0.911
S14	C ₂₆	0.012	0.952	0.950
平均值	—	0.006	0.960	0.917

根据现有报道,陆源生物产生的有机质是近海水体和沉积物有机质含量的主要贡献者^[4, 25, 41~43],而在本次调查中,胶州湾表层海水中的正构烷烃却没有表现出陆源生物输入为主的特征.其原因可能是陆源生物有机质主要以生物遗骸或花粉、落叶等形式进入近海环境,这些有机质更倾向于以颗粒态的形式存在,并逐渐沉降于沉积物中积累、留存,因此,在近海沉积物中,陆源生物输入的有机质通常占据总有机质含量的主体部分.表层海水中有有机质的含量与分布特征对于输入与风化过程的响应更加迅速,与沉积物相比,能更加准确地反映出相对即时的信息.结合物候规律分析,采样所在的4月上旬,青岛市仍处于气象学冬季,大部分植物尚未进入繁盛期,陆源输入量少,在仍然较低的水温下,正构烷烃的溶出量更少.因此,相较于船舶和码头作业输入的正构烷烃量,陆源生物输入不是胶州湾表层海水中正构烷烃的主要输入源.

生物对石油的利用通常表现出碳数选择性,其降解产物有明显的奇偶优势^[44].而本次调查中胶

州湾正构烷烃的碳数分布连续,前峰群明显缺失,CPI和OEP平均值分别为0.960和0.917,仅有微弱的偶碳优势,这些现象都表明正构烷烃的风化以物理过程为主,可能伴有一定程度的微生物作用.随着采样站位离岸距离的增加,正构烷烃的主碳峰后移,根据对墨西哥湾溢油风化产物的研究^[45],这种现象表示样品的风化程度增大.这表明,胶州湾从湾内向湾外,随着水交换强度的逐渐增加,环境对正构烷烃污染物的风化强度也相应加剧.

3 结论

(1) 2016年4月胶州湾表层海水中的正构烷烃由连续分布的C₁₁~C₃₇正构烷烃同系物组成,主要集中在C₂₁~C₃₃范围内,没有明显的奇偶优势,但碳数为C₂₁~C₃₃的正构烷烃约占总正构烷烃的95.0%.各站位正构烷烃总量为1.756~39.09 μg·L⁻¹,平均值为13.66 μg·L⁻¹.

(2) 胶州湾表层海水中正构烷烃的高值区以湾口为主,在湾内东北部和西部也有出现,这一分布特征与胶州湾东北部和西部河流带来的工业废水、生活污水和湾口码头附近的船舶航运带来的正构烷烃输入有关.

(3) 在水交换比较充分的湾中部和湾外海域,正构烷烃总量介于1.756~2.842 μg·L⁻¹之间,平均值为2.196 μg·L⁻¹,可视胶州湾正构烷烃的环境背景值.其碳数分布有明显的C₂₄为主碳峰,前峰群有微弱的奇碳优势,后峰群有微弱的偶碳优势,表明这部分正构烷烃以藻类和海洋细菌等生物自生输入为主.

(4) 人类活动对胶州湾影响很大,输入的正构烷烃主要集中在湾内近岸及湾口海域,主要由C₂₁~C₃₃正构烷烃同系物组成,呈现出有微弱偶碳优势的后峰群单峰形分布特征,代表高度风化的石油类污染物.其含量介于9.606~39.09 μg·L⁻¹之间,约占胶州湾总正构烷烃量的83.7%.

(5) 风化后的正构烷烃呈现连续分布的后峰群单峰形碳数分布特征,且从湾内向湾外主碳峰位置后移,表明胶州湾表层海水对正构烷烃的去除机制以蒸发、稀释等物理风化过程为主,从湾内向湾外对正构烷烃的风化强度增大.

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