



Source identification of *n*-alkanes and isoprenoids using diagnostic ratios and carbon isotopic composition on crude oils and surface waters from the Gulf of Mexico

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Abstract Diagnostic ratios and compound-specific isotopic analysis (CSIA) are two tools that can help identify and differentiate the petrogenic and biogenic sources of hydrocarbons found in environmental samples. The present study aims to evaluate the concentration and type of *n*-alkanes and isoprenoids found in the oligotrophic waters of the Gulf of Mexico ($n=14$), and through the typical diagnostic ratios reported for *n*-alkanes and its carbon isotopic composition ($\delta^{13}\text{C}$) to establish and differentiate the possible source of the hydrocarbons. Additionally, crude oil samples ($n=10$) extracted in the Gulf of Mexico were evaluated by CSIA as a possible source of hydrocarbons to the study area. We found that the CSIA of $\delta^{13}\text{C}$ for *n*-alkanes ($n\text{-C}_{11}$ to $n\text{-C}_{30}$) and isoprenoids (pristane and phytane) found in the surface water samples varied from -25.55 to -37.59‰ and from -23.78 to -33.97‰ in the crude oil samples, values which are more related to petrogenic sources. An analysis of the $\delta^{13}\text{C}$ for pristane vs. phytane suggests that only three surface water samples show an origin in common that those observed in

crude oils of the Gulf of Mexico. A low incidence of odd- and even-numbered *n*-alkanes higher than $n\text{-C}_{25}$ in the water samples indicate low to negligible presence of terrigenous sources into the area, which was supported by the carbon isotopic composition of the individual *n*-alkanes.

Keywords *n*-Alkanes · $\delta^{13}\text{C}$ · PAHs · CSIA · Gulf of Mexico

Introduction

In the last decades, compound-specific isotopic analysis (CSIA) has been applied as an additional tool to aid in the identification of the potential sources of individual compounds in environmental samples based on their isotopic composition (Elsner & Imfeld, 2016; Famiyeh et al., 2021; Fiedziukiewicz & Hanley, 2021). In addition, this analysis could provide a useful method to assess the environmental fate of the contaminants such as biodegradation (Alvarez-Zaldívar et al., 2018; Huang et al., 2020). For instance, the determination of the carbon isotopic compositions of individual *n*-alkanes for oil spill identification and its association with possible sources is a common application of CSIA in environmental analysis. Given that the weathering process does not alter the carbon isotopic composition observed for individual *n*-alkanes, this makes the CSIA a powerful tool to be used for the identification

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of hydrocarbon sources (Ankit et al., 2017; Bosch et al., 2015; Wang et al., 2013).

Typically, the sources of *n*-alkanes in the marine environment include anthropogenic and natural inputs, i.e., combustion of fossil fuels and biomass, natural seepages of crude oils, or contributions of *n*-alkanes from terrestrial (C₃, C₄, and CAM photosynthetic pathways) and aquatic plants (Mojiri et al., 2019; Wang et al., 2018). Therefore, characterizing and identifying their potential sources are challenging. Once in the environment, the hydrocarbons can be subjected to a wide variety of weathering processes (chemical, physical, and biological); hence, correlating its fingerprint by applying conventional methods for identifying their origin becomes difficult (Li et al., 2009; Wang et al., 2013).

The Gulf of Mexico is an ocean basin that extends along the northeastern coast of Mexico and is bordered to the north by five states of the USA and to the east by Cuba. It has an area of approximately 1.5 million km², has a maximum depth of approximately 3700 m, and contains one of the largest oil deposits in the world. Because of extensive oil exploitation and transportation carried out in the area, oil spills may occur incidentally, causing damage to marine and terrestrial ecosystems. In addition, the biological productivity in the Gulf of Mexico is strongly affected by the nutrient load from the large freshwater input of the Mississippi River, mainly in the coastal regions near to the northern shelf which exhibits elevated productivity in comparison to offshore oligotrophic regions (Rabalais & Turner, 2019; Tan et al., 2021).

In general, relatively scarce information regarding the isotopic composition of individual *n*-alkanes and isoprenoids is available for the oligotrophic region of the Gulf of Mexico. In contrast, the northern coastline region of the Gulf of Mexico has been studied more intensely, in part due to the high biological productivity in this region, which is frequently associated with the large quantities of nutrients and organic matter discharged from the Mississippi River (Walker et al., 2017).

This study aims to establish a baseline distribution of *n*-alkanes, including the isoprenoids pristane (Pr) and phytane (Ph) in the surface waters of the oligotrophic area of the Gulf of Mexico and to establish and differentiate the possible origins using some typical diagnostic ratios reported for *n*-alkanes and by determining its carbon isotopic composition. Our

hypothesis is that CSIA as a tool can aid in determining and differentiating the sources of hydrocarbons present in this type of marine environment. Additionally, we determined the $\delta^{13}\text{C}$ values for alkanes and isoprenoids in the different crude oils extracted off Mexican coasts because they may represent a possible important source of hydrocarbons towards the Gulf of Mexico.

Materials and methods

Sampling collection

In 2015, surface water samples were obtained as part of an oceanographic campaign known as XIXIMI-4, which was part of a larger effort to characterize the central region of the Gulf of Mexico after the Deepwater Horizon oil spill. Samples were collected in an oceanographic campaign conducted from August 25 to September 11, 2015, aboard the ORV Justo Sierra, which is owned by the Universidad Nacional Autónoma de México. The sites where the water samples were collected, which were located within the Exclusive Economic Zone of Mexico, are shown in Fig. 1. For the purpose of sampling, surface water collection was conducted using a 10 L Niskin bottle at nominal depth of 5 m, and a 2 L subsample for *n*-alkane analysis was stored in precleaned amber glass jugs. All samples were preserved with a saturated solution of mercuric chloride and were refrigerated at 4 °C until the analysis. Finally, Petróleos Mexicanos (PEMEX) provided us with 10 samples

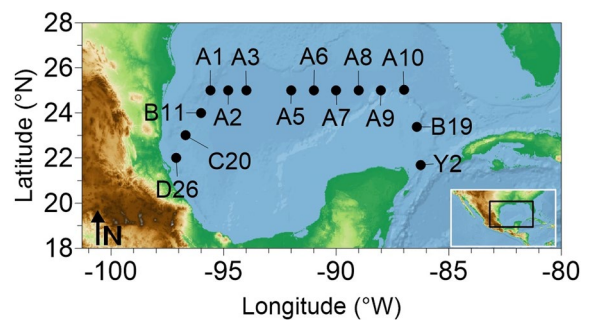


Fig. 1 Sampling locations in the Gulf of Mexico where surface water samples were collected during XIXIMI-IV oceanographic campaign

of crude oils, which are produced from different oil extraction sites or wells in the Gulf of Mexico.

Chemicals and reagents

Silica gel (mesh 70–230; Sigma-Aldrich), alumina (activated, basic, Brockmann I; Sigma-Aldrich), quartz sand (mesh 50–70; Sigma-Aldrich) anhydrous sodium sulfate (ACS grade; VWR Chemicals BDH), and nonvolumetric glassware were baked in a muffle furnace at 400 °C for 4 h as a standard cleaning procedure. Volumetric glassware was cleaned using solvents (MeOH, acetone, and dichloromethane). Finally, all solvents used in the *n*-alkane analysis (MeOH, acetone, dichloromethane, *n*-hexane, iso-octane, water) were of HPLC grade (VWR Chemicals BDH). An analytical standard containing a mixture of *n*-alkanes (*n*-C₈ to *n*-C₄₀, including the isoprenoids Pr and Ph) was purchased from UltraScientific, Inc. (TRPH Standard, Catalog Number SNJ-200-1). The analytical standards 1-chlorooctadecane and 1-docosene were purchased from Dr. Ehrenstorfer (LGC Standards Ltd.), while that secondary isotopic reference *n*-alkane mixture B4 (including *n*-C₁₆ to *n*-C₃₀) was acquired from Indiana University. In addition, the Standard Reference Material (SRM) 2779 containing crude oil from the Gulf of Mexico collected from the Macondo well was purchased from the National Institute of Standards & Technology (NIST).

Extraction and clean-up protocol

To obtain the organic fraction, 1.8 L of the seawater sample was liquid–liquid extracted in a 2 L separatory funnel using dichloromethane (3×60 mL) as the extraction solvent. The samples were placed on a benchtop orbital shaker for 5 min at constant speed. No filtration process was carried out on the samples prior to their analysis. To estimate the recoveries in the samples, 1-docosene was used as a surrogate (Kuppusamy et al., 2020). The obtained extract was further separated in a column chromatography (11×300 mm) packed with 12 cm silica gel and 6 cm basic alumina (both deactivated using 3% HPLC grade water). To recover the *n*-alkanes and the polycyclic aromatic hydrocarbons (PAHs), elution was conducted sequentially with 15 mL hexane (F1) and

40 mL hexane:dichloromethane (70:30 v/v; F2), respectively. Both fractions were concentrated using a Rocket Synergy evaporator and further concentrated with a gentle flow of N₂ gas until a final volume of 0.2 mL was obtained. Finally, 1-chlorooctadecane was used as the internal standard for the quantification of *n*-alkanes (Martinez et al., 2004). Procedural and fortified blanks were included as quality assurance and quality control during the sample analysis process. The mean recovery of spiked surrogate in the samples was 89% ± 24% (± 1 SD).

Quantification and identification of *n*-alkanes and isoprenoids

The concentrations of *n*-alkanes were analyzed using a Hewlett Packard 6890 GC system with a flame ionization detector (GC-FID) operated in splitless mode. A DB-5 column (30 m×320 μm i.d.×0.25 μm film thickness, J&W Scientific) was placed on the GC. Nitrogen grade 5.0 was used as the carrier gas at a constant flow of 1.6 mL/min. The oven temperature was initially held at 70 °C for 3 min. Thereafter, the temperature was ramped up at 7 °C/min to 300 °C and held for 25 min. The injector and detector temperatures were set at 275 °C and 315 °C, respectively.

For calibration purposes, a five-point internal standard calibration curve was prepared using an analytical standard containing a mixture of *n*-alkanes (*n*-C₈ to *n*-C₄₀, including Pr and Ph). 1-chlorooctadecane was used as internal standard for quantification. No detectable concentrations of *n*-alkanes were measured in the procedural blanks. It is important to note that the concentrations reported in this work were not corrected by the percentage recoveries.

δ¹³C analysis for *n*-alkanes and isoprenoids

The CSIA of δ¹³C for *n*-alkanes (*n*-C₁₁ to *n*-C₃₀) and isoprenoids (Pr and Ph) was conducted using continuous-flow isotope ratio mass spectrometry (IRMS). High molecular weight *n*-alkanes (*n*-C₃₁ to *n*-C₄₀) were excluded from the analytical method because their concentrations in the samples were too low for isotopic analysis. A Thermo Scientific Trace 1310 gas chromatograph coupled with an ISQ LT Single Quadrupole MS and a TriPlus RSH autosampler, a GC Isolink II, and a CONFLO IV

interface coupled with a Thermo Scientific Delta V Plus IRMS were used to obtain the $\delta^{13}\text{C}$ values. A Thermo Scientific TG-5MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm film thickness) was used for CSIA, and a splitless injection mode was used. An injection volume of 2 μL was programmed in the analytical method.

The GC oven conditions were programmed as follows: 50 $^{\circ}\text{C}$ for 1 min, 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$ for 30 min, and 30 $^{\circ}\text{C}/\text{min}$ to 320 $^{\circ}\text{C}$ for 3.5 min. Helium was used as the carrier gas at a constant flow of 1.4 mL/min. The injection inlet and MS transfer line were set at 250 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. Furthermore, the ion source and quadrupole temperatures were set at 230 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$, respectively. Data acquisition were conducted by electron impact ionization in the full scan mode (50–650 amu). The combustion reactor on the GC Isolink II was operated at 940 $^{\circ}\text{C}$.

The secondary isotopic reference *n*-alkane mixture B4 acquired from Indiana University was used daily to evaluate the accuracy and precision of the instrument. Two-point linear normalization for the measured $\delta^{13}\text{C}$ values of the samples was done using a commercially available secondary reference material for *n*-alkanes (GC-IRMS Alkane Standard *n*-C₁₁, *n*-C₁₅, *n*-C₂₀; CHIRON AS, Catalog Number 0451.3–150-CY) traceable to the international standard Vienna Pee Dee Belemnite (VPDB), which was analyzed daily by triplicate. The standard deviation of the secondary isotopic reference for each *n*-alkane was lower than 0.4‰ for $\delta^{13}\text{C}$ ($n=24$). All samples were analyzed by triplicate. A series of pulses of CO₂ as the reference gas was included at the beginning and end of each analysis, and the $\delta^{13}\text{C}$ data for individual *n*-alkanes were reported in standard δ per mil notation (‰) relative to the CO₂ reference gas calibrated to the VPDB scale:

$$\delta^{13}\text{C} = \left[\frac{\delta^{13}\text{C}_{\text{sample}} - \delta^{13}\text{C}_{\text{std}}}{\delta^{13}\text{C}_{\text{std}}} \right] \times 1000. \quad (1)$$

Diagnostic ratios for *n*-alkanes and isoprenoids

To identify the possible sources of hydrocarbons found in water samples collected from the Gulf

of Mexico, diagnostic ratios such as carbon preference index (CPI), Pr/Ph, Pr/*n*-heptadecane (Pr/C₁₇), Ph/*n*-octadecane (Ph/C₁₈), lower-molecular weight (sum of *n*-alkanes from *n*-C₉ to *n*-C₂₃) *n*-alkanes over high-molecular weight (sum of *n*-alkanes from *n*-C₂₄ to *n*-C₃₆) *n*-alkanes (LMW/HMW), and natural *n*-alkane ratio (NAR) were calculated.

The CPI ratio indicates the possible predominance of odd *n*-alkanes or even *n*-alkanes or the absence of predominance. A CPI value near one suggests that there is no preference between odd and even *n*-alkanes, which is commonly associated with petrogenic inputs and other anthropogenic sources. By contrast, CPI values largely different from 1 indicate a biological origin. For example, higher CPI values (>3) indicate a contribution of *n*-alkanes from terrigenous sources (El Nemr et al., 2016; Leider et al., 2013). The CPI ratios were calculated as follows:

$$\text{CPI} = \frac{\sum(C_{23} - C_{21})_{\text{odd } n\text{-alkanes}} + \sum(C_{25} - C_{33})_{\text{odd } n\text{-alkanes}}}{2 \sum(C_{24} - C_{32})_{\text{even } n\text{-alkanes}}}. \quad (2)$$

The terrigenous/aquatic ratio (TAR) is commonly used to differentiate the terrestrial contribution from aquatic sources of *n*-alkanes using long- and short-chain odd *n*-alkanes (Bourbonniere & Meyers, 1996). The TARs were calculated using the following formula:

$$\text{TAR} = \frac{C_{27} + C_{29} + C_{31}}{C_{15} + C_{17} + C_{19}}. \quad (3)$$

NAR is the proposed ratio for estimating the proportions of natural and petroleum *n*-alkanes. Petrogenic inputs have ratios close to 0, whereas biogenic inputs such as terrestrial or marine plants have ratios close to 1 (Mille et al., 2007). The NARs were calculated using the following formula:

$$\text{NAR} = \frac{n\text{-alkanes } \sum(C_{19} - C_{32}) - 2 \sum \text{even } n\text{-alkanes } (C_{20} - C_{32})}{\sum n\text{-alkanes } (C_{19} - C_{32})}. \quad (4)$$

Furthermore, the isoprenoids to *n*-alkane ratios (Ph/C₁₈ vs. Pr/C₁₇) was used to evaluate the thermal maturity of the crude oils (Abogllila et al., 2010; Shanmugam, 1985).

Results and discussion

Total *n*-alkanes in surface water

The concentrations of total *n*-alkanes (*n*-C₉ to *n*-C₄₀) in surface water ranged from 382 to 3100 ng/L, with a mean value of 1037 ± 811 ng/L (± 1 SD). The samples collected in sites A5, A9, and B11 showed the highest concentrations of *n*-alkanes in the study area, while the minimum concentrations of total *n*-alkanes were found at stations A10 and C20 (Fig. 2). In general, it was observed that most of the sites had concentrations of total *n*-alkanes close to 1 µg/L, which were 3 to 10 times lower than those reported in surface waters of Louisiana continental shelf in northern Gulf of Mexico after Deepwater Horizon oil spill (2.8 to 10.6 µg/L for dissolved *n*-alkanes) and around 10 to 30 times less (10.8 to 34.7 µg/L for dissolved *n*-alkanes) than those reported one year later (Liu et al., 2016). For surface seawater in the northeastern South China Sea, Gong et al. (2020) found concentrations of total *n*-alkanes ranging from 11.2 to 287.9 µg/L (mean: 89.3 ± 9.1 µg/g), with the higher values located around the shore. Moreover, in less disturbed marine environments such as the Antarctic Ocean, lower values of total concentration of *n*-alkanes have been reported for subsurface water samples (depth < 0.5 m), which varied from 272 to 553 ng/L (Stortini et al., 2009), and were within the ranges observed in the sites A2, A7, A10, and C20 (382 to 452 ng/L) which could suggest low anthropogenic impact in these areas. In contrast, the sites A5 and A9 which were located at the longitude -88°W and -93°W had the highest total concentrations of

n-alkanes (2539 and 3100 ng/L, respectively), area that is commonly influenced by Loop Current and associated Eddies. It has been reported that through the Yucatan current, the water masses from the Caribbean Sea enter the Yucatan Channel towards the Gulf of Mexico favoring the formation of the Loop Current which later leaves the Gulf through the Straits of Florida (Portela et al., 2018). The Loop Current Eddies (with diameters between 200 and 400 km) can eventually detach from the Loop Current moving westward of the Gulf of Mexico commonly over the latitudes 24°N and 26°N (Hamilton et al., 2019; Portela et al., 2018; Weisberg & Liu, 2017). In addition to this, the main water masses in the Gulf of Mexico present from surface to 3000 m include the Caribbean Surface Water remnant (CSWr), the Gulf Common Water (GCW), the Tropical Atlantic Central Water (TACW), the Antarctic Intermediate Water (AAIW), the North Atlantic Subtropical Underwater (NASUW) and the North Atlantic Deep Water (NADW). Only CSWr and GCW have been reported at depths between 50 and 150 m (Portela et al., 2018). Our results suggest that the distribution of *n*-alkanes in surface waters in the deep zone of the Gulf of Mexico could be associated with the accumulation centers of the water masses, particularly to the Loop Current Eddies commonly found in this area.

In our study, sea surface temperatures ranged from 29.4 to 30.6 °C (30.2 °C ± 0.3 °C; mean ± 1 SD) while surface water salinities ranged from 33.2 to 36.6 (36.1 ± 0.9; mean ± 1 SD), which may indicate a strong presence of water masses from the GCW in the study area (Online Resource 1, Table S1). Seasonally, the presence of mixed-layer fresh water from the Mississippi River can decrease the observed values of salinity from surface to 50 m depth (Portela et al., 2018), which maybe the case observed in the slight decrease in salinity observed at sites A6, A7, A8, and A9. The warmer sea surface temperatures we observed at all sites (around 30 °C), were within the expected range of sea surface temperatures (29 °C to 30 °C) commonly measured during the summer for the Gulf of Mexico (Allard et al., 2016), which is 1 °C lower than those previously reported for the coastal area in the northern Gulf of Mexico during sampling carried out in August 2010 (Liu et al., 2016).

Generally, the composition of *n*-alkanes in the samples can provide information about their source and diagenesis. Diagnostic ratios were calculated to

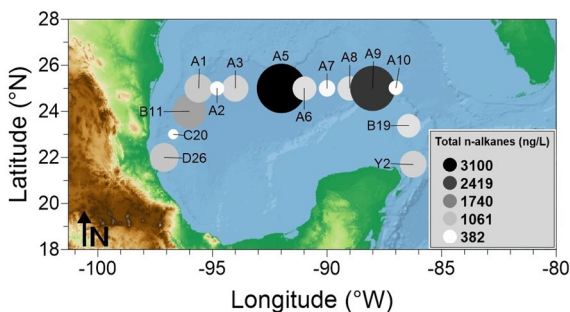


Fig. 2 Spatial distribution of the total concentrations of *n*-alkanes (*n*-C₉ to *n*-C₄₀) in surface water samples of the Gulf of Mexico

identify the origin of the *n*-alkanes found in the surface water samples (marine/terrestrial, petrogenic/biogenic) In our work, the samples collected showed an absence of high-molecular weight *n*-alkanes (greater than *n*-C₃₄), and a dominance of light *n*-alkanes (lower than *n*-C₂₂) was observed. Based on the abundance of *n*-alkanes, a slight to moderate even-numbered *n*-alkane preference was found in the samples, except at station D26, where a slight odd-numbered *n*-alkane preference was observed. This result further suggests that a terrestrial organic matter contribution in the site seems unlikely because the samples did not show a predominance of odd-numbered *n*-alkanes higher than *n*-C₂₃ (mainly C₂₇, C₂₉, C₃₃, and C₃₅) that are typical of these sources (Liu et al., 2016; Sainakum et al., 2021).

In our work, the CPI values ranged from 0.22 to 2.06, with a predominance of petrogenic contributions or a mixture of sources over terrigenous contributions. Sites A2, A6, A10, and B11 showed CPI values around 1, which is typical of petroleum hydrocarbons (Mille et al., 2007; Sainakum et al., 2021; Vaezzadeh et al., 2015). However, stations A1, A3, A5, and C20 showed CPI values near 2 with a predominance of lower odd-numbered *n*-alkanes especially *n*-C₁₇; this is commonly related to a biogenic origin such as phytoplankton (El Nemr et al., 2016; Sainakum et al., 2021; Wang et al., 2009). It should be noted that most of the sites with a biogenic component had total concentrations of *n*-alkanes above 1 µg/L including the site A5 site which had the highest concentrations of total *n*-alkanes found in this work (3160 ng/L). The CPI values of stations B19, D26, and Y2 could not be estimated because of the absence of even *n*-alkanes from *n*-C₂₀ to *n*-C₃₂. In contrast, the lower values of CPI (around 0.5) found in the sites A2, A7, A8, and A9 usually is associated to *n*-alkanes derived from mixed-origin (Elfadly et al., 2017).

For *n*-alkanes, a NAR close to 0 indicates a petrogenic origin, whereas a NAR value of 1 can suggest the biogenic contribution of marine or higher terrestrial plants (El Nemr et al., 2016). The NAR for the water samples ranged from 0.01 to 0.44 (mean=0.23), thus indicating that a moderate to strong petrogenic component exists in the samples, particularly in the sites A5, A10, C20 and Y2, in which the presence of an unresolved complex mixture (UCM) is also observed. NAR values that are

typically a related to a mixture of hydrocarbons from petroleum and high vascular plant sources (terrestrial or marine origin) were mainly found at sites A7, A8, A9, and D26. In general, the presence of mid-chain *n*-alkanes (*n*-C₂₃ and *n*-C₂₅) in the water samples can indicate the contribution of *n*-alkanes from submerged plants, i.e., aquatic macrophytes (Liu et al., 2015); otherwise, the low incidence of long-chain *n*-alkane homologs (mainly *n*-C₂₉, *n*-C₃₁, and *n*-C₃₃) suggests the limited contribution of *n*-alkanes from terrestrial and emergent plants, a trend that was observed in stations A1, A3, and A5 (Babcock-Adams et al., 2017; Chikaraishi & Naraoka, 2003). Furthermore, the TAR for all samples was lower than 1 (ranging from 0.13 to 0.64), thus suggesting the predominance of *n*-alkanes from aquatic sources (Bourbonniere & Meyers, 1996; Keshavarzifard et al., 2020). Typically, TAR values greater than 1 suggest a higher contribution of terrestrial higher plants (Gong et al., 2020) The LHW/HMW ratios showed values ranging from 2.9 to 25, which is commonly associated with fresh oil inputs of petrogenic sources (Vaezzadeh et al., 2015).

Isoprenoids in surface water

The biomarkers Pr and Ph are used as a proxy of the level of maturity and depositional environmental of alkanes and are frequently associated with the degradation of the chlorophyll phytyl side chain under oxidative and reductive pathways or are produced by bacteriochlorophylls (Gong et al., 2020; Luo et al., 2018; Rontani & Bonin, 2011). Furthermore, these biomarkers are infrequently found as dominant constituents in the terrestrial biota (Babcock-Adams et al., 2017). In this study, the concentrations of isoprenoids in the surface water samples (Online Resource 1, Table S2) ranged from 32.0 ng/L to 128.7 ng/L (mean value of 50.9 ng/L ± 34.0; ± 1 SD) for Pr, and from 27.8 to 140.1 ng/L for Ph (mean value of 60.6 ng/L ± 32.4 ng/L; ± 1 SD). Diagnostic ratios such as Pr/C₁₇, Ph/C₁₈, and Pr/Ph have been widely used as indicators of biodegradation for oil spills. The isoprenoids ratios in the samples ranged from 0.44 to 2.25 for Pr/C₁₇, 0.39 to 0.74 for Ph/C₁₈, and 0.58 to 2.14 for Pr/Ph (Table 1). In this work, the samples showed a Pr/Ph ratio of approximately 1; this suggests a petrogenic source because Ph is a component that is commonly found in crude oil and is rarely produced by

Table 1 Concentrations of *n*-alkanes (sum of *n*-C₁₀ to *n*-C₄₀) and the calculated diagnostic ratios for surface water samples collected from the Gulf of Mexico

Station	Total <i>n</i> -alkanes (ng/L)	Diagnostic ratios						
		CPI	Pr/Ph	Pr/C ₁₇	Ph/C ₁₈	TAR	LMW/HMW	NAR
A1	966	2.01	0.63	0.67	0.56	0.61	4.06	0.23
A2	409	0.53	0.82	0.70	0.46		12.99	0.29
A3	856	1.74		0.59		0.53	2.88	0.12
A5	3100	1.98	0.83	0.74	0.40	0.64	4.21	0.01
A6	718	0.89	0.91	0.63	0.46	0.22	4.23	0.26
A7	452	0.22	0.59	0.44	0.57		8.20	0.44
A8	733	0.36	0.85	0.60	0.58		3.36	0.33
A9	2539	0.48	0.72	0.58	0.39	0.20	3.51	0.33
A10	412	0.78	0.58	0.48	0.63	0.29	4.79	0.20
B11	1376	1.21	0.72	0.50	0.47		6.32	0.14
B19	699		0.71	0.54	0.51			0.17
C20	382	2.06	0.59	0.55	0.67	0.38	6.74	0.11
D26	1001		2.14	2.25	0.74	0.13	25.01	0.41
Y2	868		0.63	0.53	0.54	0.18	21.40	0.14

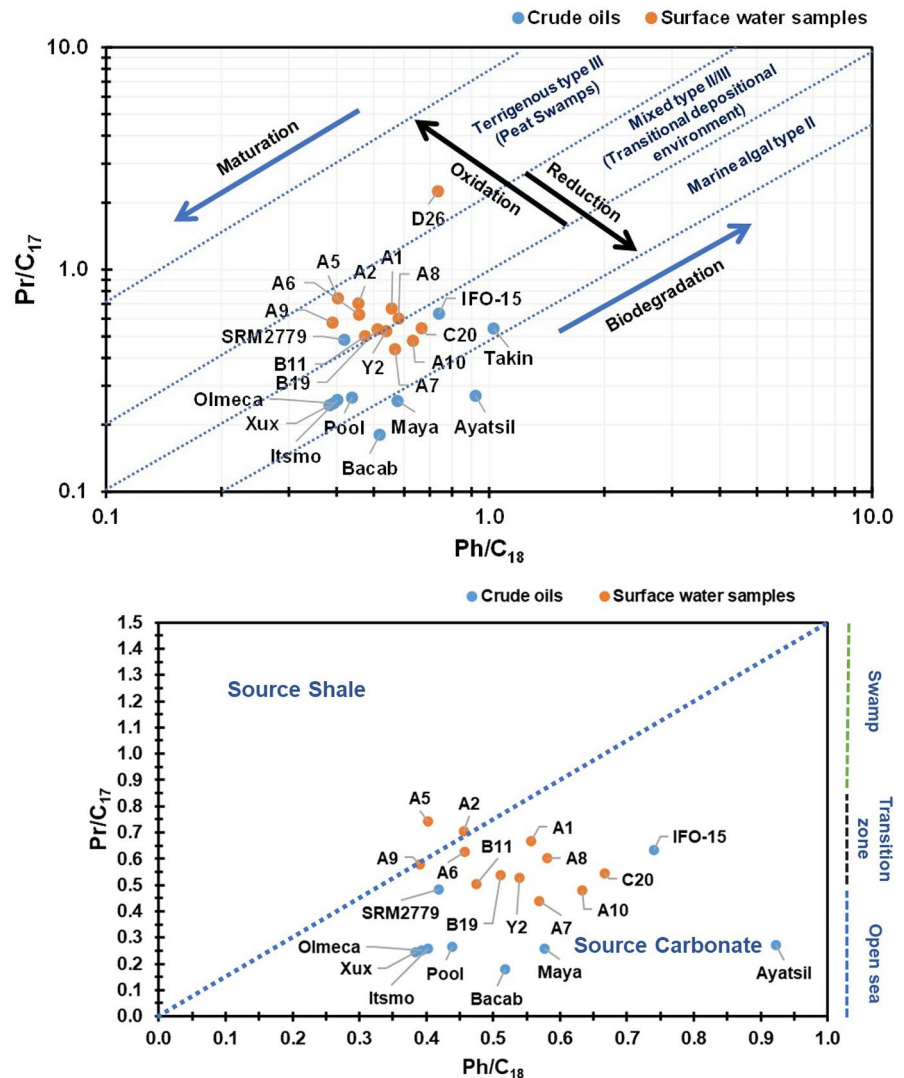
biogenic sources (Babcock-Adams et al., 2017; Caro Gonzalez et al., 2020). A high value of Pr over Ph usually suggests a biological marine source (Zrafi-Nouira et al., 2009), which was observed only at station D26. Often, Pr/Ph values lower than 1 are related to aquatic depositional environments under reducing conditions (Gong et al., 2020; Onojake et al., 2015).

It has been reported that biodegradation indicators such as Pr/C₁₇ and Ph/C₁₈ remain unaltered in lightly weathered oils, even if a significant degradation or evaporation of low-molecular weight *n*-alkanes occurs (Wang & Fingas, 1997). Typically, high ratios of Pr/C₁₇ and Ph/C₁₈ suggest that there was a biodegradation effect over the *n*-alkanes, and this is mainly associated with bacteria or planktonic algae (Babcock-Adams et al., 2017; Gong et al., 2020). In this work, we found that Pr/C₁₇ and Ph/C₁₈ showed values of approximately 0.5 in all samples, except in site D26, which has a Pr/C₁₇ value of 2.25 which could indicate that planktonic algae played an important role in the biodegradation of the *n*-alkanes found in this site (Gong et al., 2020). Ph/C₁₈ values lower than 1 suggests a low effect by biodegradation of the hydrocarbons over the samples. Ratio values ranging from 0.44 to 1.35 for Pr/C₁₇ and from 0.16 to 0.65 for Ph/C₁₈, and a relatively high Pr/Ph ratio (ranging from 1.88 to 4.05), were reported for highly matured crude oils from Nigeria (Onojake et al., 2015). Furthermore, CPI values around 1, with mean values of

0.28 for Pr/C₁₇ and 0.15 for Ph/C₁₈, were found on crude oils from Egypt (El Nady et al., 2016).

To estimate the thermal maturity and the degree of weathering in surface water *n*-alkanes and crude oils, the isoprenoids to *n*-alkane ratios (Ph/C₁₈ vs. Pr/C₁₇; Fig. 3) were evaluated using the criteria suggested by Shanmugam (1985). This figure indicates that the origin and type of organic matter found in the crude oils extracted in Mexico are derived from kerogen type II materials, predominantly from marine algal sources preserved under strongly reducing conditions (Shanmugam, 1985; Zeinalzadeh et al., 2018). Additionally, the data suggest that the SRM 2779 crude oil obtained from the Macondo well (related to the Deepwater Horizon oil spill) in the Gulf of Mexico originated in a transitional depositional environment with mixed-type II/III kerogen (marine/terrigenous organic matter), which differs from the crude oils extracted in Mexico. Furthermore, the Ph/C₁₇ vs. Pr/C₁₈ diagram (Fig. 3) suggests that all crude oils samples were associated with carbonate source rocks reservoirs in marine to transition environments (Mathur et al., 1988; Zeinalzadeh et al., 2018). Additionally, most of the *n*-alkanes found in the surface water samples were originated from transitional depositional or marine algal type II environments, except for site D26, which was one of the closest sites to the coastal zone and was mainly associated with terrigenous type II environments.

Fig. 3 Ph/C₁₈ versus Pr/C₁₇ ratios diagram showing the thermal maturity (up) and depositional environment (down) for the surface water and crude oil samples. The diagrams are based on the proposed by Shanmugam (1985) and Mathur et al. (1988), respectively



Additional data are given in the Online Resource 1, which includes examples of typical chromatograms observed for the crude oils and surface water samples (Fig. S1 to S3). Physical and chemical parameters at sampling stations during the XIXIMI-4 campaign, including the concentration values of individual *n*-alkanes and isoprenoids in the surface water samples were summarized in the Online Resource 1, Tables S1 to S3.

The $\delta^{13}\text{C}$ of *n*-alkanes and isoprenoids in surface water samples and crude oils

The $\delta^{13}\text{C}$ of individual *n*-alkanes (*n*-C₁₁ to *n*-C₃₀) found in the samples varied from -25.6 to -37.6‰ ,

whereas that in crude oils varied from -23.8 to -34‰ (Fig. 4; Online Resource 1, Tables S4 and S5, Fig. S4). Average $\delta^{13}\text{C}$ values in the surface water samples and crude oils were $-29.11\text{‰} \pm 0.97\text{‰}$ (± 1 SD) and $-29.73\text{‰} \pm 0.77\text{‰}$ (± 1 SD), respectively. The $\delta^{13}\text{C}$ for both, surface water samples and crude oils were more consistent with the values reported for petrogenic than biogenic sources such as marine primary production ($-21.2\text{‰} \pm 1.5\text{‰}$) and riverine-terrestrial inputs ($-24.6\text{‰} \pm 1.3$), which are more enriched in ^{13}C (Chanton et al., 2018). In the Gulf of Mexico, values of $\delta^{13}\text{C}$ from -26.6 to -33‰ were previously reported for different reservoirs of crude oils (Babcock-Adams et al., 2017; Natter et al., 2012), which is similar to the values that were found

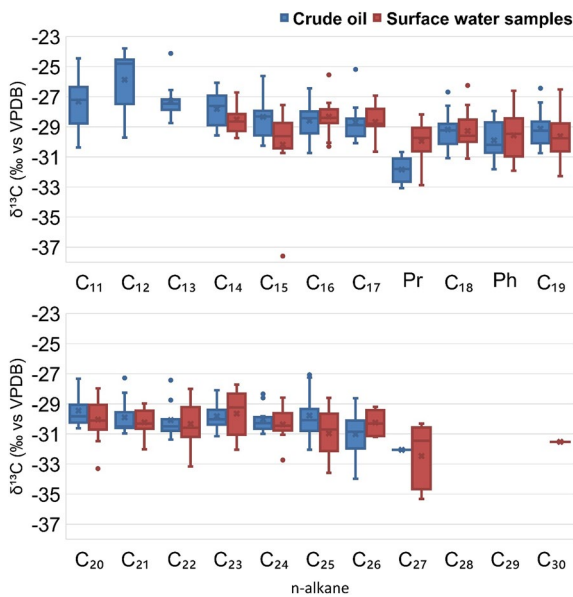


Fig. 4 Comparison of the isotopic composition of individual *n*-alkanes ($\delta^{13}\text{C}$) found in the crude oils and the surface water samples obtained from the Gulf of Mexico

in our study. The carbon isotopic composition of the crude oil released from the Deepwater Horizon oil spill in 2010 had average values around -27.0‰ (Carmichael et al., 2012; Graham et al., 2010; Natter et al., 2012). In addition to this, Reddy et al. (2012) reported that the saturated hydrocarbon fraction of the oil released by the Deepwater Horizon oil spill event was more ^{13}C depleted (-27.9‰) than that those observed in the aromatic hydrocarbon fraction (-26.5‰).

In vascular plants, the reported values of $\delta^{13}\text{C}$ can vary according to the photosynthetic pathway used for carbon fixation. In the shelf and open Gulf of Mexico, it has been reported that samples from rivers, influenced by organic matter, show more positive $\delta^{13}\text{C}$ values than the organic matter produced by marine sources. (Rosenheim et al., 2016). Rosenheim et al. (2016) reports that the Gulf of Mexico sedimentary organic material had mean $\delta^{13}\text{C}$ values of $-21.4\text{‰} \pm 1.9\text{‰}$, with more enriched values in sites with an admixture of C_4 vegetation (-18‰ to -12‰) than those with C_3 vegetation (-23‰ to -22‰). O’Malley et al. (1997) reported that combustion-derived *n*-alkanes/*n*-alkenes from C_4 plants had $\delta^{13}\text{C}$ values in the range of -25.3‰ to -20.6‰ , whereas combustion-derived

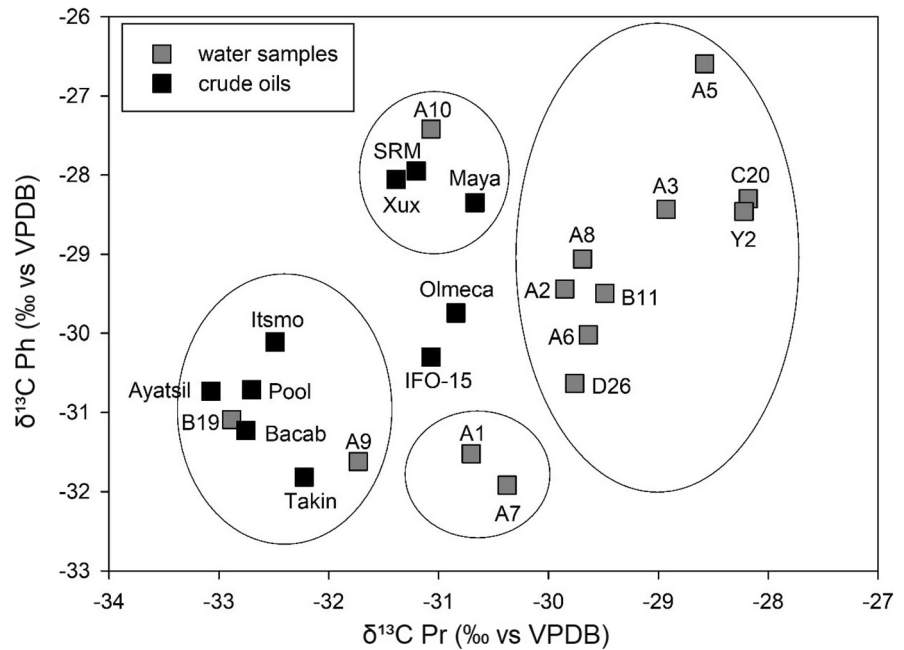
n-alkanes/*n*-alkenes from C_3 plants ranged from -32.9 to -29.2‰ ; in which both categories were dominated by odd-numbered alkanes from *n*- C_{21} to *n*- C_{33} . After the 2010 oil spill event, Natter et al. (2012) found that $\delta^{13}\text{C}$ values for oiled sediments dominated by C_4 plants in the coastal salt-marsh in Louisiana were $-20.8\text{‰} \pm 2.0\text{‰}$, which was isotopically lighter than the marsh plants ($-14.8\text{‰} \pm 0.6\text{‰}$). Similarly, Chanton et al. (2018) reported that plankton collected in the Gulf of Mexico during the years 2010 to 2014 had values of $\delta^{13}\text{C}$ of $-21.2\text{‰} \pm 1.5\text{‰}$. In general, we found that the $\delta^{13}\text{C}$ values for the surface water *n*-alkanes were not within the range reported for biogenic sources such as phytoplankton blooms or from terrigenous inputs, which are relatively more enriched in $\delta^{13}\text{C}$ than those observed in our samples and are more related to the carbon isotopic signature observed in fossil fuels.

In this work, we found that *n*-alkanes with higher molecular weights (*n*- C_{20} to *n*- C_{30}) in the samples and crude oils were slightly more ^{13}C depleted than the shorter carbon ranges (Fig. 4). Furthermore, *n*-alkanes that are typically observed in land plants as *n*- C_{27} and *n*- C_{29} were not frequently found in the samples; thus, their $\delta^{13}\text{C}$ values could not be determined. O’Malley et al. (1997) and Seki et al. (2006) observed a similar trend in low molecular weight *n*-alkanes (*n*- C_{11} to *n*- C_{19}), which were generally more enriched in ^{13}C compared to the high molecular weight *n*-alkanes (*n*- C_{20} to *n*- C_{30}).

We found that in the surface water samples, $\delta^{13}\text{C}$ for isoprenoids Pr and Ph varied from -28.2 to -32.9‰ ($-29.9\text{‰} \pm 1.3\text{‰}$; mean ± 1 SD) and -26.6 to -31.9‰ ($-29.6\text{‰} \pm 1.6\text{‰}$; mean ± 1 SD), respectively. Additionally, we found that $\delta^{13}\text{C}$ values of crude oils varied from -30.7 to -33.1‰ ($-31.9\text{‰} \pm 0.9\text{‰}$; mean ± 1 SD) for Pr, whereas ranged from -28 to -31.9‰ ($-29.9\text{‰} \pm 1.4\text{‰}$; mean ± 1 SD) for Ph. Average values of -29.8‰ for Pr and -31‰ for Ph were reported in diesel fuels (Lichtfouse et al., 1997), which fall in the range of $\delta^{13}\text{C}$ values observed in the surface water samples. In contrast, the $\delta^{13}\text{C}$ values for Pr observed in the sites A3, A5, C20, and Y2 (from -29‰ to -28‰), suggest that *n*-alkanes originated from microalgae or zooplankton material (Seki et al., 2006).

To evaluate the origin of the *n*-alkanes in the water samples, the $\delta^{13}\text{C}$ values for the isoprenoids

Fig. 5 Scatter plot of $\delta^{13}\text{C}$ for isoprenoids pristane (Pr) versus $\delta^{13}\text{C}$ phytane (Ph) for crude oils and surface water samples analyzed from the Gulf of Mexico



Pr and Ph were plotted together with the crude oils using scatter plots (Fig. 5). Pr and Ph were selected because these compounds have shown resistance to weathering processes. In addition, we found that the $\delta^{13}\text{C}$ values of Pr observed in the crude oils were more depleted in ^{13}C than those found in the surface water samples. Based on the results, there were at least five different sources of *n*-alkanes in the study area. Three stations (A9, A10, and B19) were associated with petrogenic sources because they showed similar carbon isotopic compositions to those found for crude oils that were analyzed from the Gulf of Mexico, while most samples can be related to a mixture of sources (petrogenic and marine). These sites are located at the northern region of the Gulf of Mexico, an area where mesoscale eddies and the Loop Current are involved as the dominant features that regulate the surface currents (Beyer et al., 2016). Otherwise, the mesoscale eddies in this region typically have a wide extension covering 200–300 km in diameter and lifetimes of up to 1 year (Oey et al., 2005); therefore, these mesoscale eddies could contribute to the transport and distribution of *n*-alkanes with a common source in the area. The carbon isotopic pattern observed among the surface water samples suggests at least two other different sources of hydrocarbons that are

generally more ^{13}C -enriched than those found for the crude analyzed in the present study.

Conclusions

The *n*-alkane distribution, combined with some diagnostic ratios and carbon isotopic composition, indicated a predominance of the petrogenic contribution of the hydrocarbons in the area. We found that the values of $\delta^{13}\text{C}$ for Pr in the crude oils were more depleted in ^{13}C than that found in the surface water samples. When we analyzed the carbon isotopic composition of *n*-alkanes ($\delta^{13}\text{C Pr}$ vs. $\delta^{13}\text{C Ph}$) of the surface water samples, only three sites showed similarities with the local crude oil samples from PEMEX; meanwhile, the majority of the sites could be related to mixtures of petrogenic and marine sources. No evidence of terrigenous inputs of *n*-alkanes were found in the water samples, and this is supported by the low incidence of odd- and even-numbered *n*-alkanes, particularly in the range of *n*-C₂₇ to *n*-C₃₁, which are the predominant *n*-alkanes found in vascular plants.

We found that the isotopic composition of crude oil samples from the Gulf of Mexico indicates few differences in their $\delta^{13}\text{C}$ values, thus suggesting a possible common origin or formation, which was

mostly derived from marine algal sources (kerogen type II) preserved under strongly reducing conditions. Additionally, for potential identification purposes, Pr may be the most significant isoprenoid with a distinctive $\delta^{13}\text{C}$ value for all crude oils measured. As expected in the surface water samples, these showed a faster degradation of the alkanes $n\text{-C}_{17}$ and $n\text{-C}_{18}$ than their corresponding isoprenoids. Finally, the low concentrations of n -alkanes found in oligotrophic waters of the Gulf of Mexico make it a challenge to assess the possible sources of hydrocarbons using CSIA.

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Data availability Data available within the article or its supplementary materials.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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