

MAIN FACTORS CONTROLLING THE COMPOSITIONAL VARIABILITY OF SEEPAGE OILS FROM TRUJILLO STATE, WESTERN VENEZUELA

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The organic geochemistry of eighteen samples of seepage oils from Trujillo State, Western Venezuela, was investigated. These oils are probably derived from the predominantly marine Cretaceous La Luna Formation which is near peak maturity for oil generation. A range of biomarkers (n-alkanes, acyclic isoprenoids, phenanthrene and alkyl-phenanthrenes, as well as dibenzothiophene and alkyl-dibenzothiophenes) were analysed by gas chromatography - mass spectrometry (GC-MS).

The seepage oils have been modified as a result of water washing and biodegradation. A first group of samples were slightly biodegraded with the partial loss of n- and iso-alkanes. Other samples fall into two groups: those that are moderately degraded, with partial depletion of acyclic isoprenoids; and those that are severely altered, as indicated by the partial or total absence of hopanes.

One objective of this work was to evaluate the factors influencing the compositional differences of the three samples sets. In-situ measurements, together with the interpretation of the geochemical data, suggest that diverse factors were responsible for these variations. These included different degrees of alteration due to biodegradation and water washing, as well as differences in flow rate towards the surface.

INTRODUCTION

Seepage oils can be considered in geochemical terms to comprise residual materials derived from mature

crude oils. Seepage oils are characterised by a reduced content of saturated and aromatic hydrocarbons as a result of evaporation, water washing and biodegradation. In general, an oil seep can be considered as part of a migration pathway along which petroleum flows from the source rock to the surface; or as a place where petroleum components escape to the surface through fractures and fissures from a subsurface reservoir or a source rock (Clarke and Cleverly, 1991; Macgregor, 1993). Seepage oils can be used to provide evidence for the presence of an active petroleum system, together with information about the source and maturity of organic matter and the migration route (Rogers *et al.*, 1999; Abrams *et*

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Key words: oil seeps, biodegradation, water washing, hydrocarbon flow rate, Trujillo State, Venezuela.

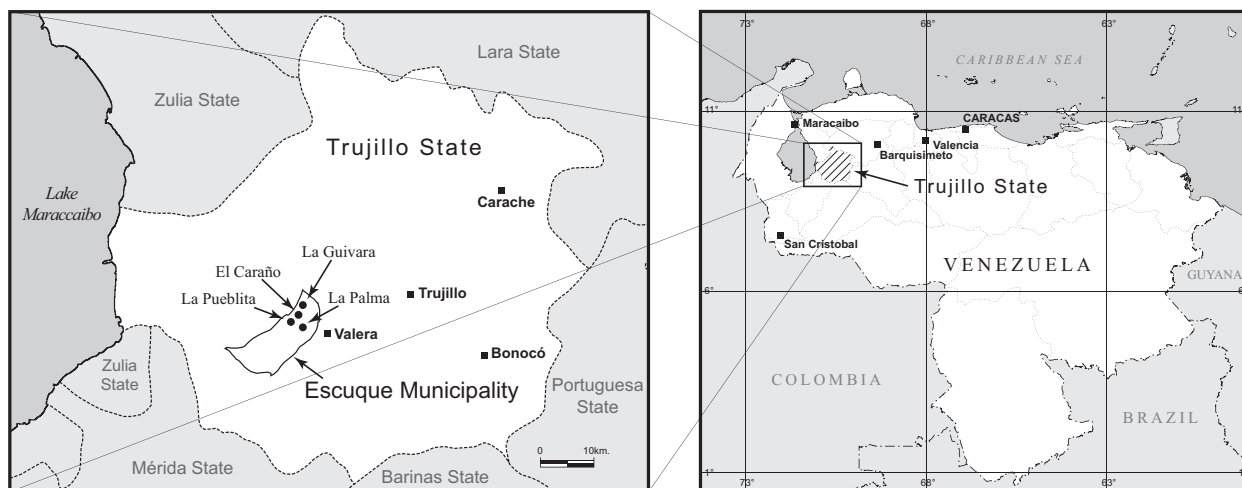


Fig. 1. (a) Location of Trujillo State in NW Venezuela. (b) Location map of the study area. The oil seeps studied in this paper are located in Esecuque Municipality.

al., 2001; Abrams, 2005). Petroleum normally escapes to the surface, together with a variable proportion of natural gases and formation waters, along fractures or faults, generally from pre-existing oil accumulations (Levorsen, 1967).

Seepage oils usually occur as viscous, low-gravity liquids or asphalts due to oxidation and polymerization as a result of atmospheric exposure and bacterial and fungal degradation (Tissot and Welte, 1984; Hunt 1996). Water washing processes may remove the more water-soluble hydrocarbons, leaving behind heavier residual materials (Palmer, 1984; Lafargue and Barker, 1988).

Oil seeps can be classified as active or inactive. At active seeps, the oils are only lightly altered and their composition is similar to that of the precursor petroleum. Active seeps make up approximately 30% of the seeps known worldwide; more than half of these are gas seeps, the remainder comprising light or heavy oils. Active seeps are characterized by a steady or nearly steady flow rate towards the surface (Hobson and Tiratsoo, 1975). By contrast, oils at inactive surface seeps are heavily altered and very viscous. Inactive seeps comprise more than 40% of seeps known worldwide.

Numerous hydrocarbon seeps occur in Venezuela and have been the subject of organic geochemical investigation (Pérez, 1991; Del Olló, 1993; Tocco *et al.*, 1995; Zambrano *et al.*, 2000; Escobar *et al.*, 2007). However, few studies have investigated geochemical characterization of aromatic compounds such as phenanthrene (P), methylphenanthrene (MP), dibenzothiophene (DBT) and their alkyl-substituted homologues (e.g. Olivares, 1998). Even fewer studies have examined the relationship between *in-situ* flow rate and the chemical composition of the seeps.

The aims of this work were to evaluate the type of organic matter and the degree of biodegradation at

three oil seeps in Trujillo State, Western Venezuela (Figs 1, 2), using biomarkers and other geochemical parameters. The seeps were: TR-8, in the El Caraño valley; TR-14, near the La Palma river; and TR-16A, in the La Guivara zone. We also consider previous experimental data (Tocco *et al.*, 1995) on fifteen other nearby oil seeps (Fig. 2). Of these, one is similar to the TR-16A seep, others are similar to TR-14 and the rest to TR-8 oil. The additional seeps are (Fig. 2): TR-1 to TR-4 and TR-16B in the La Guivara zone; TR-5 to TR-7, TR-9 and TR-10 in the El Caraño valley; TR-12A, TR-12B and TR-13 in the La Palma area; and two other seeps, TR-11 and TR-15, located close to La Pueblita de Caus. The marine limestones and calcareous shales of the Cretaceous La Luna Formation are thought to be the principal source rocks for all these oil seeps (Tocco *et al.*, 1995).

GEOLOGICAL SETTING

The study area is located in Esecuque Municipality, Trujillo State, Western Venezuela (Figs 1). The oil seeps studied are in the sandstones of the Eocene Misoa Formation and occur in a zone covering approximately 90 sq. km (Fig. 2).

In terms of regional structure, the study area is located at the margin of the Maracaibo and Trujillo crustal blocks. A complex network of faults is present, the most prominent being the Boconó, Valera, Piñango and Tuñame faults (Audemard *et al.*, 2005) (Fig. 3). The eastern Trujillo block is bounded in the west by the sinistral Main Valera fault and to the south by the right-lateral Boconó fault (Hervouët *et al.*, 2001). The SW-NE trending Main Valera fault system is about 230 km long. To the south of the city of Valera, it splits into two N30°E-trending segments (García and Campos, 1977). To the west is the Maracaibo block whose eastern margin is cut by a series of secondary

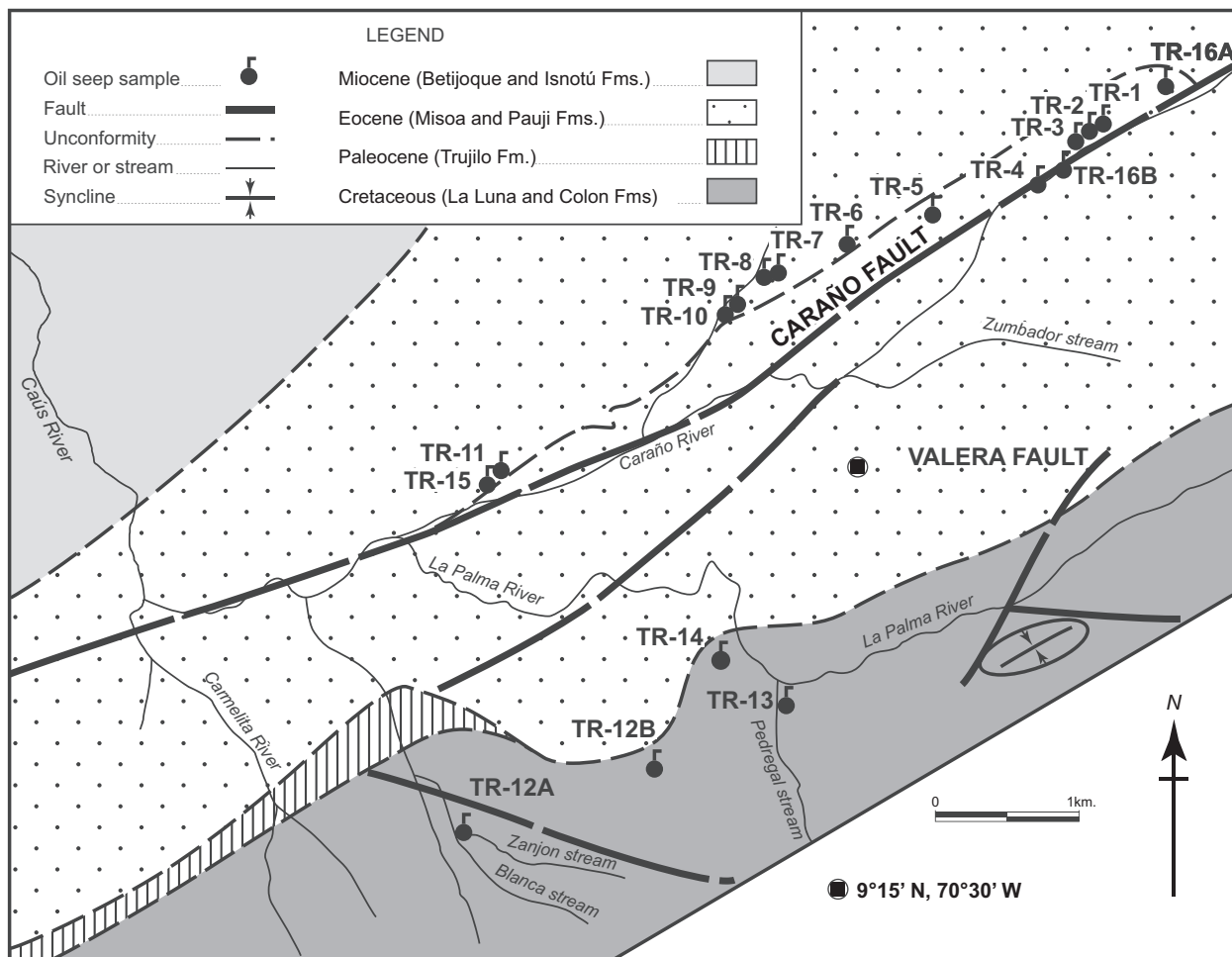


Fig. 2. Location map of the oil seeps in Escuque Municipality, Trujillo State (Western Venezuela), with major structural elements. Seepage oils at locations TR-16A, -14 and 8A were analysed in this study; seepage oils from other locations were analysed by Tocco *et al.*, 1995.

faults paralleling the Main Valera fault and the left-lateral, SW-NE oriented Las Virtudes - Caraña fault (Audemard *et al.*, 2000). The Main Valera and Las Virtudes - Caraña faults are interpreted as listric structures penetrating to mid-crustal depths. These faults, along which the studied oil seeps are located (Fig. 2), formed during different tectonic phases from the Neogene onwards (Backé *et al.*, 2006).

Stratigraphic development

The study area is located on the SW margin of the Maracaibo Basin (Martínez, 1976; Gonzalez de Juana *et al.*, 1980), which contains up to 12 km of sediments deposited from the Triassic - Jurassic to the present (White, 1985). In the Caus River area, the following formations are present, from bottom to top: Río Negro, Apón, Aguardiente, Capacho, La Luna, Colón, Mito Juan, Trujillo, Misoa, Pajui, León, El Palmar, Isnotu, and Betijoque (González de Juana *et al.*, 1980). Detailed information on the Cretaceous and Tertiary stratigraphy of the area was provided by Boesi *et al.* (1988).

Parnaud *et al.* (1995) divided the sedimentary column in the eastern part of the Maracaibo Basin into separate tectono-stratigraphic units: a Lower to Upper Cretaceous passive margin succession; a transition to a compressive regime in the Late Cretaceous - Early Paleocene, when the Pacific volcanic arc overrode the South American plate and emplaced the Lara nappes; a Late Paleocene - Middle Eocene foreland basin succession in front of the volcanic arc; and finally a Late Eocene - Pleistocene sequence related to the collision of the Panama arc with the South American plate.

Deposition during the Early Cretaceous occurred during thermal subsidence of the passive margin of South America (De Toni and Kellogs, 1993; Lugo and Mann, 1995). During this phase, coarse fluvial siliciclastics (Río Negro Formation), bioclastic carbonates (Apon Formation) and sandstones (Aguardiente Formation) were deposited. Subsequent deepening resulted in deposition of the open-marine Capacho and La Luna Formations during the Late Cretaceous. These formations are composed of

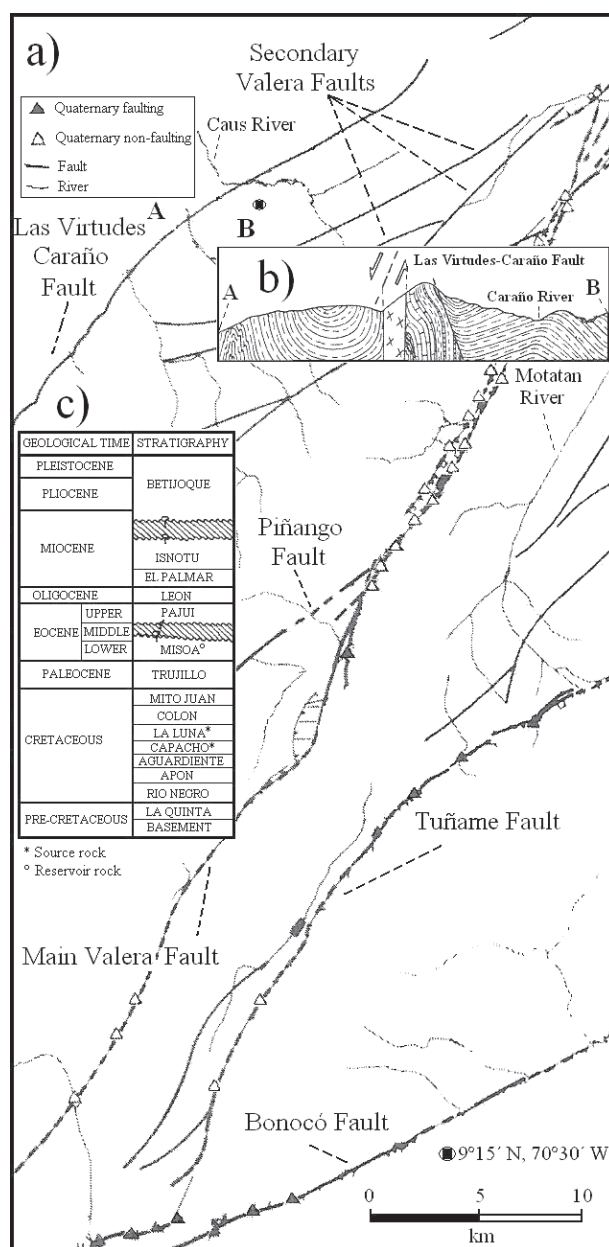


Fig. 3. (a) Regional location map of the northern Maracaibo Basin area showing major fault structures at the margins of the Maracaibo and Trujillo crustal blocks (see text for details). (b) Cross-section A-B; (c) Stratigraphic column for the Caus River area.

anoxic marine limestones, black shales and calcareous shales (Hedberg, 1931), which have exceptional source rock potential, especially in the Maracaibo Basin (Tocco *et al.*, 1995).

A regressive succession, due to oblique collision between the westward-migrating Caribbean island arc and the passive margin of South America (Lugo and Mann, 1995), began in the Maastrichtian with the clay- and shale-rich Colon Formation. The sandstones and shales comprising the Mito Juan Formation also began to be deposited at this time (Zambrano *et al.*, 1971). They are overlain by the paralic-deltaic Trujillo Formation (Paleocene), consisting of sandstones, shales, coals, and siltstones, and the lower Eocene fluvial deposits of the Misoa Formation (Zambrano *et*

al., 1971). Above are paralic to lagoonal facies of the Pajui Formation (upper Eocene) and León Formation (Oligocene) (Notstein *et al.*, 1944). Miocene units include the coastal marine El Palmar Formation and fluvio-deltaic Isnotu Formation. Late Miocene to Recent continental sediments derived from the uplifting Andean orogen form the Betijoque Formation (Sutton, 1946).

Petroleum system

Considering the La Luna source rocks, two phases of generation and expulsion have been recognised in the study area:

(1) Late Eocene – Early Miocene, contemporaneous with the emplacement of the Lara Nappes;

this period was characterized by minor hydrocarbon generation but by significant remigration from pre-existing accumulations, with intense biodegradation (Talukdar and Marcano, 1994).

(2) Early Miocene – Holocene, contemporaneous with Andean uplift and foredeep formation. During this phase, crude oils were generated and expelled from new kitchen areas; condensates and gas were generated in the deepest parts of the basin. These fluids migrated towards the northern flank of the Andes (Tocco *et al.*, 1997).

Hydrocarbons are generated from the La Luna Formation source rocks in active kitchens, and migrate to the surface via along the Valera and Las Virtudes - Caraño faults or other enhanced permeability conduits, resulting in the surface seepages in the study area.

MATERIALS AND METHODS

Three samples (TR-8, TR-14, and TR-16A) were collected from the related surface seeps. The samples were stored in glass jars prior to analysis. The locations of the three oil seeps, and those of another fifteen nearby seeps analysed in a previous study (Tocco *et al.*, 1995), are shown in Fig. 2. Seepage oils were greenish, slightly viscous and smell strongly of kerosene. The TR-16A oil seep occurs in a topographic depression with an oil pond approximately 8 m in diameter and over 1 m deep. The TR-8 and TR-14 seeps are puddles less than 2.5 m in diameter and a few centimetres deep. Flow rate studies at the TR-16A oil seep were performed by oil-capture tent flow measurements (Leifer and Wilson, 2007). An apparatus known as a petrolarium, described by Leifer *et al.* (2007), was used to estimate flow rates at both the TR-8 and TR-14 seep locations.

Approximately 2 g of each sample was separated into constituent fractions (SARA method) using conventional procedures. Asphaltenes were precipitated with *n*-heptane in a 1:40 v/v ratio in accordance with the ASTM D3279 standard method (ASTM, 2005); each sample was passed through a batch-type reactor in constant agitation for 1 hour at 60 °C, followed by a 12-hour rest period (Speight, 1998). Later, malthenes were separated into saturate, aromatic and resin fractions by liquid adsorption chromatography (De la Cruz *et al.*, 1997). Saturates, aromatics and resins were respectively eluted by *n*-hexane, toluene and methanol-trichloromethane (1:1) using a glass column (30 cm in length x 1 cm in internal diameter) filled with activated silica-alumina (50:50).

Alkanes and acyclic isoprenoids were subsequently analysed using gas chromatography combined with a flame ionization detector (FID) at 290 °C. A *Perkin*

Elmer 8500 device and a *DB-5* fused-silica capillary column (30 m x 0.25 mm, film thickness 0.25 µm) were used. The gas chromatograph was also equipped with a splitless injector at 290 °C. Experimental GC conditions were as follows: helium was used as the carrier gas at 25 psi, and the oven was programmed for an initial temperature of 80 °C (hold for 4 min) to 290 °C at 4 °C/min, then to 290 °C for 10 min. Peaks were identified by comparison with data reported in the literature (Galarraga, 1986; Cassani and Eglinton, 1991; Tocco *et al.*, 1995).

The aromatic and saturate fractions were analysed using gas chromatography – mass spectrometry. A *Perkin Elmer Qmass 910* system equipped with a *DB-5* capillary column identical to that described above was used to analyse the aromatics. The saturates were analysed through an *SE-52* capillary column (60 m x 0.25 mm i.d., film thickness 0.25 µm). Helium was used as the carrier gas. The samples were analysed by single-ion monitoring (SIM) mode with a dwell time of 100 ms. The settings for the mass spectrometer which was operated in electron-impact (EI) mode were: interface temperature of 290 °C, 2000 V electron photomultiplier, 220 mA filament current, and 70 eV electron energy. 178, 184, 191, 192, 198, 206, 212, and 218 m/z ions were analysed through mass spectrometry. The aromatic hydrocarbons were identified by comparison with data from the NIST/NBS library and results published in the literature (Mackenzie *et al.*, 1980, 1981, Connan, 1984; Hughes, 1984; Radke *et al.*, 1994).

Sulphur contents were determined (according to the ASTM D-4294/98 method) by means of an energy-dispersive X-ray Panalytical spectrometer (*Axios* model) equipped with a digital signal processor and dual multi-channel analyser. Flame atomic absorption spectrometry allowed the quantitative analyses of vanadium and nickel concentrations (using norm ASTM D-5863/00) through a model *1100B Perkin-Elmer* spectrometer. All the reagents were of analytical grade, and Mill-Q water was used.

RESULTS AND DISCUSSION

Alkanes, isoprenoids and other geochemical characteristics

Geochemical characteristics of the seepage oils are given in Table 1. The TR-15 seepage oil and the La Palma river oils (TR-12A, -12B, -13 and -14) had saturated hydrocarbon concentrations (expressed in weight percent) significantly lower than 70 % (44 and 61-64 %, respectively), whereas the saturated fraction ranged from 70 to 81 % for the other thirteen seepage oils. If the seeps have a common origin (Tocco *et al.*, 1995), the variable saturate fractions may be explained in terms of differences in degree of

Table 1. Geochemical characteristics of the studied oil seeps.

Sample	Area	Saturates	Aromatics	Polars	S	V/Ni	C ₃₀ H/C ₂₉ ST	% 22S	C ₂₇ ST/C ₂₉ ST
TR-1	La Guivara	80	16	4	1.9	4.1	2.7	35.6	1.15
TR-2	La Guivara	70	21	9	1.06	5.2	0.5	41.5	0.82
TR-3	La Guivara	76	21	3	1.1	5	0.8	60.4	1.01
TR-4	La Guivara	74	18	8	1.24	5.4	0.4	<i>n.d.</i>	0.82
TR-5	El Caraño	76	19	5	1.09	5.2	0.5	39.7	0.87
TR-6	El Caraño	75	17	8	1.16	5.7	0.6	37.4	0.84
TR-7	El Caraño	78	18	4	1.2	4.9	0.4	40.2	0.85
TR-8	El Caraño	73	17	8	1.04	5	0.5	42.6	0.9
TR-9	El Caraño	81	15	4	1.12	4.8	0.6	45.1	0.87
TR-10	El Caraño	77	19	4	1.19	5.5	0.7	61.3	1.01
TR-11	La Pueblita	74	17	9	1.21	4.4	0.6	47.9	0.81
TR-12A	La Palma	61	32	7	1.6	5.2	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
TR-12B	La Palma	61	30	9	1.56	5.9	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
TR-13	La Palma	60	28	12	1.52	5	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
TR-14	La Palma	64	19	16	1.45	5.6	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
TR-15	La Pueblita	44	19	37	1.39	6	<i>n.d.</i>	<i>n.d.</i>	1.14
TR-16A	La Guivara	80	15	5	1.99	4.2	0.5	37.9	1.12
TR-16B	La Guivara	77	19	4	1.1	4.5	0.5	44.2	1.07

Notes: % 22S: C₃₁αβ 22S/(22S+22R), 17α,21β(H)-29-homohopane 22S and 22R ratio;

C₃₀H/C₂₉ST: C₃₀-hopane/C₂₉-sterane ratio;

C₂₇ST/C₂₉ST: C₂₇/C₂₉-sterane ratio.

The other data are expressed in weight percentages, except V/Ni ratio; *n.d.*, not determined.

Results previously obtained (Tocco *et al.*, 1995) are in italics.

biodegradation (Connan, 1984).

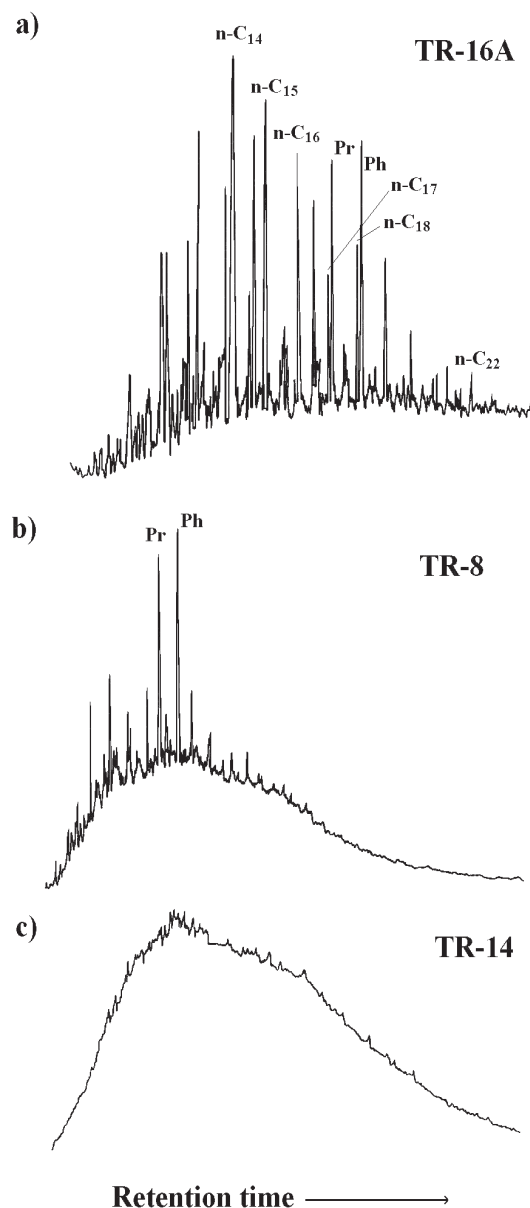
Gas chromatograms of the saturate fractions of the TR-16A and -1 oil seeps are closely similar. The chromatograms show characteristic peaks of the C₁₂-C₂₁ alkanes with a maximum at C₁₄, and acyclic isoprenoids (Fig. 4a). The partial absence of *n*-alkanes in both hydrocarbon seeps indicates "level 2" biodegradation according to the "PM" side proposed by Peters and Moldowan (Peters *et al.*, 2005). C₁₅₊ compounds in both oils show no dominance of odd over even *n*-alkanes. The carbon preference index (CPI) for these samples (approximately one) is consistent with source rocks which are in the oil window (Marteau *et al.*, 2002). However, *n*-alkanes are the first compounds to be removed during biodegradation (Wenger *et al.*, 2002), and CPI values could consequently be due to alteration as opposed to the maturity of the source rocks.

V/Ni ratios (~4), API gravities (~25°), and the similar sulphur contents (ca. 2 %; see Table 1) of the TR-16A and TR-1 oils may corroborate a marine origin for the precursor organic matter of these oil seeps from the shaly limestones of the La Luna Formation which were deposited under anoxic conditions

(Talukdar *et al.*, 1985). Despite the fact that the concentrations of both V and Ni can be influenced by biodegradation and water washing or during migration, the V/Ni ratio tends to be stable due to the structural similarities of the organometal compounds which contain vanadium and nickel (Lewan and Maynard, 1982; Lewan, 1984). In addition, the low C₁₅₊ alkane contents may also be explained if the two oils were mature light oils generated from marine source rocks (Tocco *et al.*, 1995). Low organic sulphur contents in the oils can be indicative of water washing (Lafargue and Barker, 1988).

By contrast, the TR-8 oil (Fig. 4b) shows a GC with an unresolved hump due to the presence of naphthene components, as well as the complete absence of alkanes and the partial depletion of acyclic isoprenoids. No significant variations in gas chromatograms of the saturate fractions were observed in the seepage oils from the La Guivara area (excluding TR-1 and TR-16A), TR-11 and the remaining oil seeps in the El Caraño valley. These natural seepage oils could be ranked on the PM scale at "level 4" which corresponds to moderate biodegradation.

Fig. 4a, b and c. Gas chromatograms of the TR-16A, TR-8 and TR-14 seepage oils. Seep locations are in Fig. 2. The oils are biodegraded to different degrees (see text for details), as indicated by the marked variations in *n*-alkane contents (data in Table 1).



A representative GC for the TR-15, TR-14 and the other La Palma seepage oils is shown in Fig. 4c. These seeps have the lowest saturated hydrocarbon contents (Table 1) and are biodegraded beyond PM “level 5”, which means they are so severely altered that alkanes and acyclic isoprenoids are absent (Peters *et al.*, 2005).

Most of the seepage oils have Pr/Ph ratios of approximately 0.8 and unimodal distributions of *n*-alkanes, consistent with generation from organic matter deposited in a marine environment under reducing conditions (Tissot and Welte, 1984). However, the relative proportions of pristane and phytane are governed by complex processes (e.g. Dzou *et al.*, 1995), and Pr/Ph ratios are known to be affected by maturation (Koopmans *et al.*, 1999) and biodegradation (Peters *et al.*, 2005). Pr/Ph ratios should therefore be interpreted with caution.

Saturate and aromatic biomarkers

The mass fragmentograms of terpanes (m/z 191) and regular steranes (m/z 218) of the TR-16A (Fig. 5) and TR-8 samples are very similar to those of the majority of seepage oils. Exceptions are the TR-15 and La Palma oils which completely or partially lack regular steranes and terpanes. Most of these oils have nearly identical sterane and hopane distributions to those of extracts of the La Luna Formation (Tocco *et al.*, 1995). The seepage oils are characterized by high concentrations of tricyclic terpanes and a dominance of the C_{23-3} homologue (Fig. 5b) with respect to the other tricyclic terpanes, together with C_{29} sterane : C_{30} $\alpha\beta$ hopane ratios > 0.33 , and approximately equal proportions of C_{27} 20R 5 α (H)-sterane compared to C_{29} 20R 5 α (H)-sterane (Waples and Machihara, 1991; Peters *et al.*, 2005), as well as an absence of 18 α (H)-oleanane (Moldowan *et*

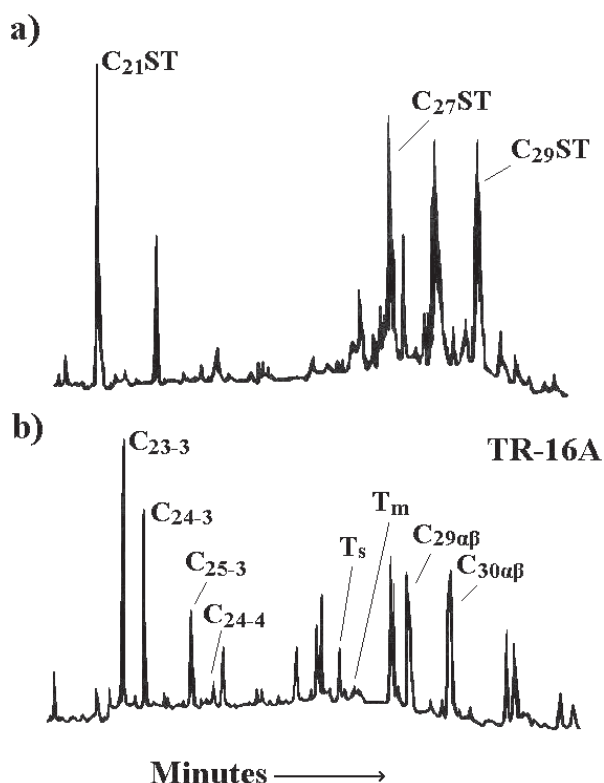


Fig. 5 (a) and (b). m/z 218 and m/z 191 fragmentograms for the TR-16A seepage oil. T_m = 17α (H) 22, 29, 30-trisnorhopane; T_s = 18α (H) 22, 29, 30-trisnorneohopane.

al., 1994). The relatively low content of large hopanes and the quasi-absence of moretanes may indicate that the oils are thermally mature (Seifert and Moldowan, 1978).

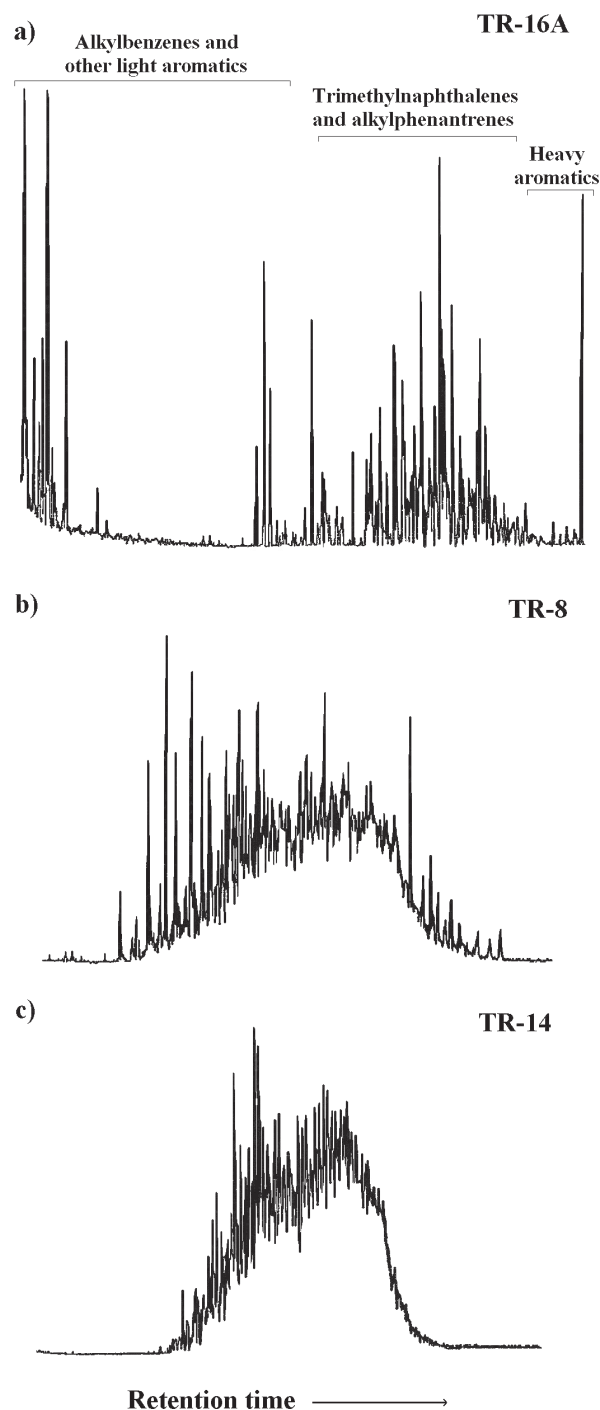
The results of GC-MS analyses of the aromatic fractions in all these samples, except the TR-16A (Fig. 6a) and TR-1 seepage oils, indicate that some low molecular-weight monoaromatic hydrocarbons and alkyl-homologues, dibenzothiophene and alkylated dibenzothiophenes, as well as light and heavy polycyclic aromatic hydrocarbons, among others, are nearly or totally depleted (Figs. 6b and 6c). A similar observation has previously been reported (e.g. Radke *et al.*, 1994; Hunt, 1996; Fisher *et al.*, 1998; Barman Skaare *et al.*, 2007), and may be due to the influence of biodegradation and/or water washing on the concentrations of aromatic compounds present in crude and seepage oils.

The GC-MS analyses show the characteristic signals of phenanthrene (m/z 178), methylphenanthrenes (m/z 192), dimethyl phenanthrenes (m/z 206), dibenzothiophene (m/z 184), methyl dibenzothiophenes (m/z 198) and dimethyl dibenzothiophenes (m/z 212) in sample TR-16A (Figs. 7a-7c and 8a-8c, respectively). By contrast, the La Palma samples, for example TR-14, lack phenanthrene (Fig. 7g), dibenzothiophene (Fig. 8g), 1- and 2-methylphenanthrenes (Fig. 7h), and methyl dibenzothiophene (MDBT) homologues (Fig. 8h), whereas dimethyldibenzothiophenes (Fig. 8i) and 3- and 9-isomers of methylphenanthrene (Fig. 7h) were

not completely removed. GC signals for samples TR-1 and TR-15 are very similar to those of TR-16A and TR-8, respectively. The same mass fragmentograms of the aromatics from TR-8 and the rest of the samples show a complete absence of dibenzothiophene (Fig. 8d) and the 1-isomer of methyl dibenzothiophene (Fig. 8e), as well as the partial depletion of phenanthrene (Fig. 7d), methyl-substituted phenanthrenes (Fig. 7e), dimethyl dibenzothiophene (DMDBT) isomers (Fig. 8f), and methylated dibenzothiophenes (Fig. 8e), with the sole exception of the 1-methyl dibenzothiophene. Finally, the dimethylphenanthrene (DMP) homologues are intact or only very slightly depleted in all the oil seeps (Fig. 7c, 7f and 7i).

The relationship between sulphur contents and the DBT/P ratio in the TR-16A sample (both exceeding unity) may be another indication that the oil seeps were generated from organic matter deposited in a carbonate-dominated marine environment (Hughes *et al.*, 1995). However, the relative abundance of the methyl dibenzothiophenes from the TR-16A oil seep varies in the order: $4 > 2+3 > 1$. Therefore, neither oil shows the distribution pattern for the methyl dibenzothiophene homologues corresponding to carbonate lithologies (Hughes, 1984). This may be explained by the substantial amount of shale in some parts of the La Luna Formation, which may be due to the lack of preservation of limestone below an oxygen minimum zone or to a local input of clay-rich turbidites (Erlich *et al.*, 1999).

Fig. 6 (a), (b) and (c). Chromatograms of the aromatics fractions from the TR-16A, TR-8 and TR-14 seepage oils. Seep locations are in Fig. 2.



Coniacian – Santonian palaeogeographic maps of NW Venezuela show an outer shelf-slope region dominated by shaly-carbonate rocks of the La Luna Formation in Trujillo State (Erlich *et al.*, 1999). These are probable source rocks for the seepage oils under study. But it is not possible to preclude that the Escuque oil seeps were generated from other La Luna source facies in nearby areas (e.g. the central part of the Maracaibo Basin) which have shale contents of 50% or more (Erlich *et al.*, 1999).

Thermal maturity determination of the organic matter which generated the Escuque seepage oils is problematic, since *n*-alkanes, isoprenoids, steranes,

phenanthrenes and dibenzothiophenes, among other biomarkers, can be affected by biodegradation (Seifert and Moldowan 1979; Williams *et al.*, 1986) or water washing (Palmer, 1984). Indeed, according to Tocco *et al.* (1995), several samples display anomalous values of parameters such as the 20S/(20S+20R) ratio. In addition, methylphenanthrene to phenanthrene ratios (Radke, 1987) and methyl dibenzothiophene indices (Schou and Myhr, 1987; Wang and Fungas, 1995) for these seepage oils are not conclusive. Furthermore, values of the hopane isomerization ratio (% 22S, Table 1) should be considered with care both because of the biodegradation of these biomarkers

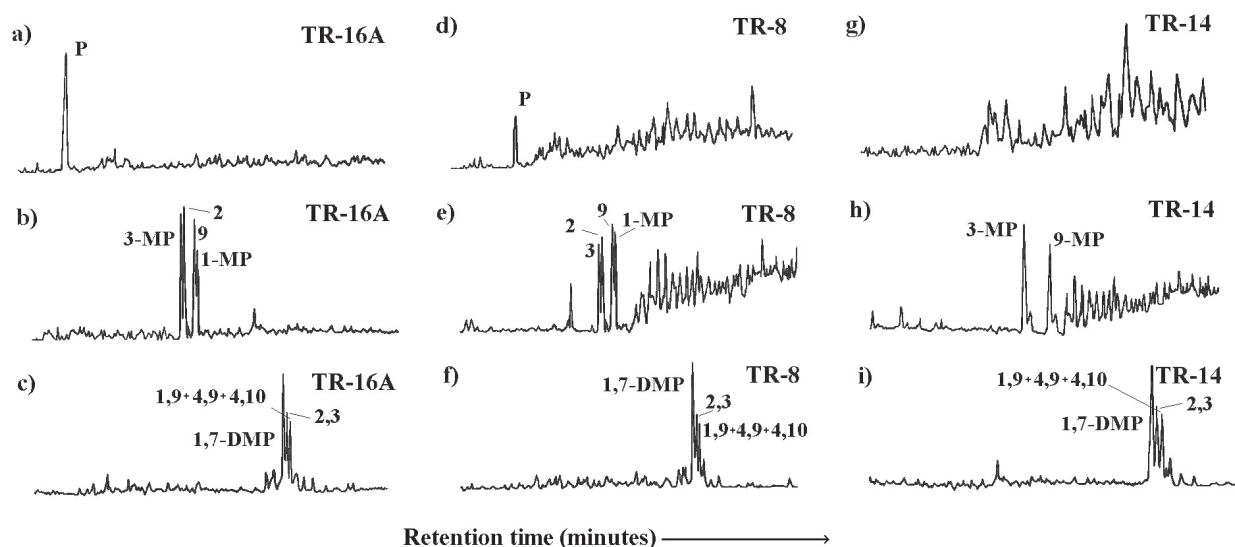


Fig. 7. m/z 178, m/z 192 and m/z 206 mass fragmentograms for the TR-16A seepage oil (a, b, and c, respectively); the TR-8 seepage oil (d, e, and f); and the TR-14 seepage oil (g, h, and i).

Key: P: phenanthrene; MP: methylphenanthrene; DMP: dimethyl phenanthrene.

(Peters *et al.*, 2005), and also because of possible differences in the chemical composition of the Type II kerogen in the La Luna Formation as a result of variations in the input of organic matter (Erlich *et al.*, 1999; Rey *et al.*, 2004).

Classification of the seepage oils

The seepage oils can be classified into three groups on the basis of the samples' saturate and aromatic biomarker distributions and their SARA data. The marine carbonate-sourced oils reached the surface after passing through the Misoa Formation sandstones under uniform conditions of pH and temperature. The TR-1 and TR-16A oil seeps are characterised by high fluxes (~20 litres per day) compared to the other sixteen oil seeps (only a few tens of millilitres per day). The differences in flow rate, together with differences in surface conditions, biodegradation and water washing, may influence compositional variations in the seepage oils, and explain the presence of a range of biodegradation levels from minor to severe.

The biomarker signatures of the saturate hydrocarbons (*n*- and *iso*-alkanes, phytane, and pristane) and aromatics (phenanthrene, dibenzothiophene and their alkyl derivatives) in the TR-16A and TR-1 seepage oils show that they were slightly altered as a result of biodegradation or water washing. This indicates that migration rate to the surface has controlled the composition of these two active seeps. The measured hydrocarbon flux from the subsurface was significantly higher than the rate of seepage oil biodegradation in both cases. These results are not consistent with observations by Wenger and Isasken (2002). These authors found that hydrocarbons in "macro seeps" (high oil-seep

concentration and/or flux of migrated oil) are more heavily biodegraded than those in "micro seeps" with fluxes of only a few millilitres per day. Wenger and Isasken (2002) proposed that low concentrations of oil could be sequestered on clay and mineral surfaces, and were not therefore available to biological activity.

As regards the other sixteen seepage oils, compositional differences can be explained in terms of the effects of biodegradation processes and not to differences in flow rates from the subsurface. The absence of biomarkers such as *n*- and *iso*-alkanes, acyclic isoprenoids, phenanthrene, 1- and 2-isomers of methylphenanthrene, and of the four isomers of methyl dibenzothiophene in samples TR-12A, TR-12B, -13, -14 and -15 is consistent with severe biodegradation and, to a lesser extent, water washing (e.g. Connan, 1984; Palmer, 1984; Volkman *et al.*, 1984; Watson *et al.*, 2007; Elias *et al.*, 2007; Permanyer *et al.*, 2010; Ross *et al.*, 2010). According to criteria previously established in the literature (Palmer, 1984; Peters *et al.*, 2005), the rest of the oil seeps appear to be moderately biodegraded and water-washed, considering the significant depletion in acyclic isoprenoids, phenanthrene, 1- and 2-isomers of methylphenanthrene, as well as 2-, 3-, and 4-methyl dibenzothiophenes.

CONCLUSIONS

The principal conclusion of this study is that biodegradation, water washing and flow rate have controlled the compositional variability of eighteen seepage oils collected from four locations in Trujillo State (Western Venezuela). Field observations, *in-situ* measurements of flow rate, and organic geochemical

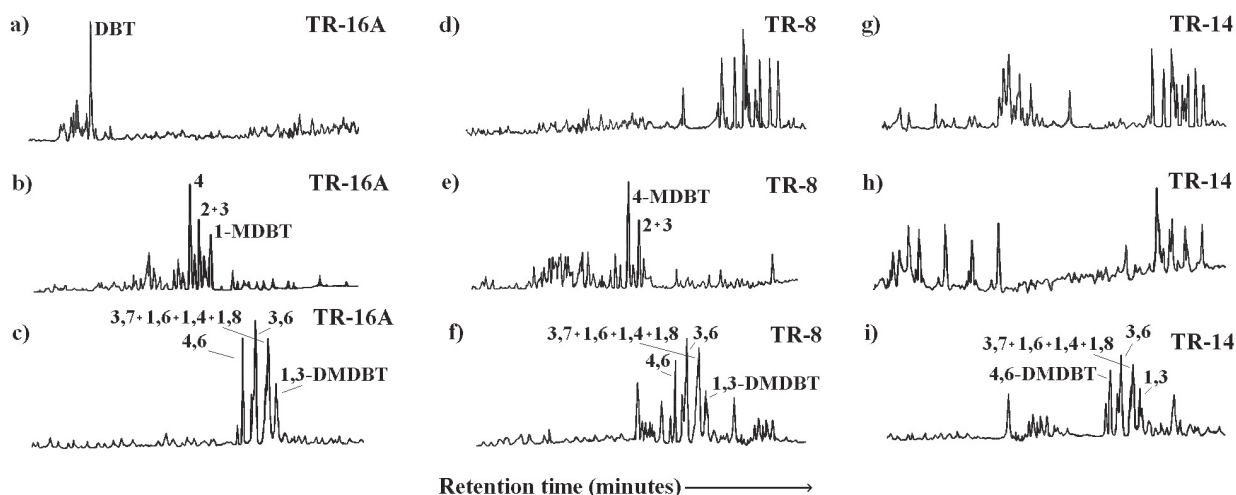


Fig. 8. m/z 184, m/z 198 and m/z 212 mass fragmentograms for the TR-16A seepage oil (a, b, and c, respectively); the TR-8 seepage oil (d, e, and f); and the TR-14 seepage oil (g, h, and i).

Key: DBT: dibenzothiophene; MDBT: methyl dibenzothiophene; DMDBT: dimethyl dibenzothiophene.

results point to the conclusion that these eighteen oils can be divided into three groups. Thus, oil samples from the TR-16A and TR-1 active seeps have undergone slight processes of biodegradation and water washing, indicating that flow rate is the main factor controlling the composition of the seepage oils. By contrast, the compositional characteristics of the other sixteen oil seeps are principally controlled by bacterial and fungal biodegradation. The TR-12A, -12B, -13, -14 and -15 seepage oils are strongly affected by biodegradation and less severely altered by water washing; the other eleven oils show moderate biodegradation and significant alteration due to water washing.

The analytical results (excluding the methyl dibenzothiophene distributions) confirm that the seepage oils are residual hydrocarbons derived from mature high-gravity crude oils generated by marine carbonate source rocks in the La Luna Formation.

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