

Quantification of Biodegradation: Applied Example on Oil Seeps in Armàncies Fm, Southeastern Pyrenees

Cuantificación de la biodegradación: Aplicación a los indicios de petróleo de la Fm. Armàncies, Pirineo Suroriental

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RESUMEN

La presencia de petróleo expulsado directamente de la roca madre de la Formación Armàncies, constituye un caso único para el estudio de los procesos de biodegradación aeróbica en petróleo. El estado de degradación bacteriana es moderado y está principalmente limitado a la alteración de n-alcános, isoprenoides y algunos aromáticos. La cuantificación ha sido realizada mediante el contenido en sulfuro y con los marcadores moleculares de la fracción aromática. Los resultados obtenidos indican que entre un 50 y un 60% del petróleo se ha consumido debido al proceso de biodegradación.

Key words: biodegradation, oil seeps, quantification, Armàncies Fm

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Introduction

Biodegradation refers to the alteration of hydrocarbons by bacterial action taking place during migration, within the reservoirs, or at the surface in case of oil seepage. For years, these processes have mainly been ascribed to the action of aerobic bacteria (Chosson *et al.*, 1992; Connan, 1984; Connan and Dessort, 1987; Peters and Moldowan, 1993). Recently, Connan *et al.* (1997) have questioned this interpretation, arguing that anaerobic bacteria are of prime importance, particularly in reservoirs in which meteoric recharge appeared unfeasible.

Aerobic and anaerobic microbial degradation causes a preferential loss of chemically simple structured compounds. The loss of light components gives rise to a relative increase of aromatics and polar compounds and consequently to an increase of density.

Water washing may also be responsible for the loss of light components, especially aromatics. Telling the difference between these two alteration phenomena can be difficult in some instances, except when, as a result of biodegradation, a selective loss of isomers of the same compound is observed.

In this study we examine bacterial degradation of several oil samples,

seeping out directly from the source rock (Fig. 1 A and B), in abandoned bitumen mines (Permanyer, 2000). The source rock belongs to the Armàncies Formation of Eocene age (Cuisian) which crops out in the northeastern Pyrenees over a distance of about 100 km. Its thickness is up to 600 m. The formation consists of shales, marls, carbonates and locally sandstones. The sediment facies represents a deep slope depositional system with carbonate slope deposits in an evolving foreland basin. The lower 200 m represent an anoxic event with high organic carbon content (TOC up to 15%). The organic matter is of marine origin with no

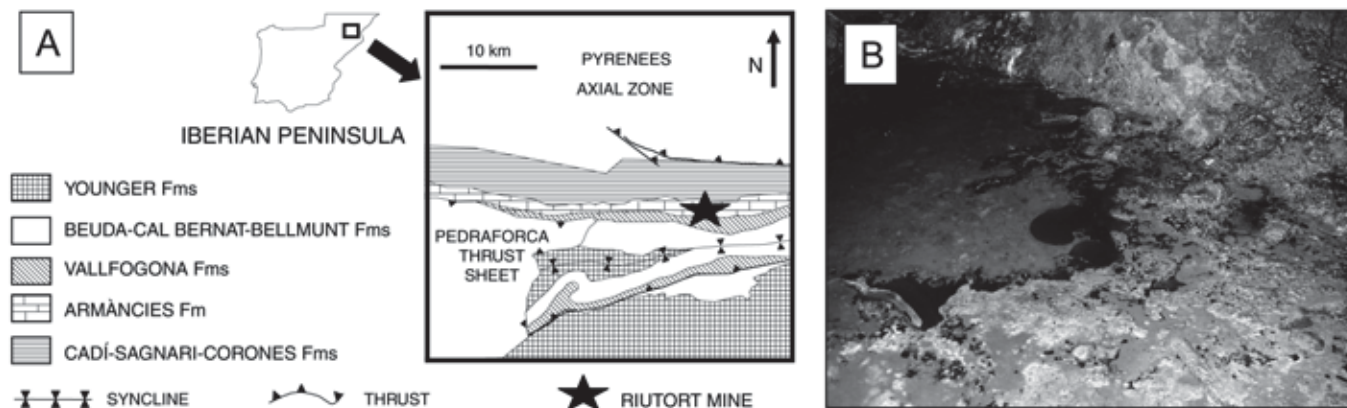


Fig. 1.- A: Location map. B: Oil with bacteria groundmass in flak water from Riutort Mine.

Fig. 1.- A: Mapa de situación. B: Petróleo y bacterias en charcos de agua de la Mina Riutort.

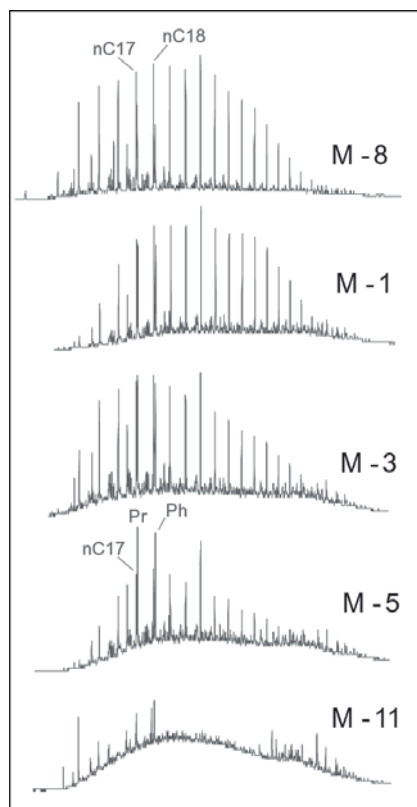


Fig. 2.- Biodegradation pattern on saturate fraction (n-alkanes, iso and cyclic alkanes).

Fig. 2.- Secuencia de biodegradación de la fracción de hidrocarburos saturados (n-alcenos, alcanos ramificados y cicloalcanos).

terrestrial influence, and it is entering the oil window, with R_o around 0.65 % and T_{max} around 440°C (Permanyer *et al.* 1988; Permanyer, 2004).

Methods and samples

Hydrocarbons with various degrees of biodegradation have been sampled at different places in the galleries. They ranged from droplets from the gallery ceilings and walls (samples M 8, M1), to black (M3) and brown (M11) oil floating on water pools and to submerged oil (M5, M4), or oil with bacterial mass (M6, M7). To quantified biodegradation degree hydrocarbons were fractionated into saturated and aromatics. Fractions have been studied by gas chromatography and gas chromatography/mass spectrometry. Likewise, the sulphur content has been determined by elemental analyses.

Results and Discussion

All samples are believed to be affected by biodegradation at varying stages. The M8 sample which showed

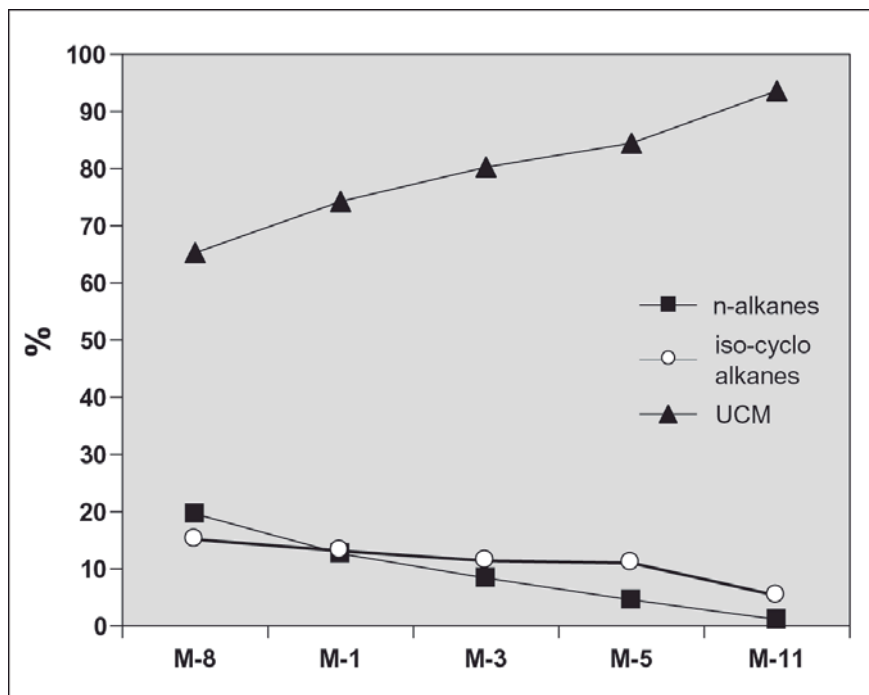


Fig. 3.- Progressive diminution of nalkanes, iso and cyclo alkanes content. The UCM increases with biodegradation.

Fig. 3.- Disminución progresiva del contenido en n-alcenos, iso y cicloalcanos. Los compuestos sin resolver (UCM) aumentan con la biodegradación.

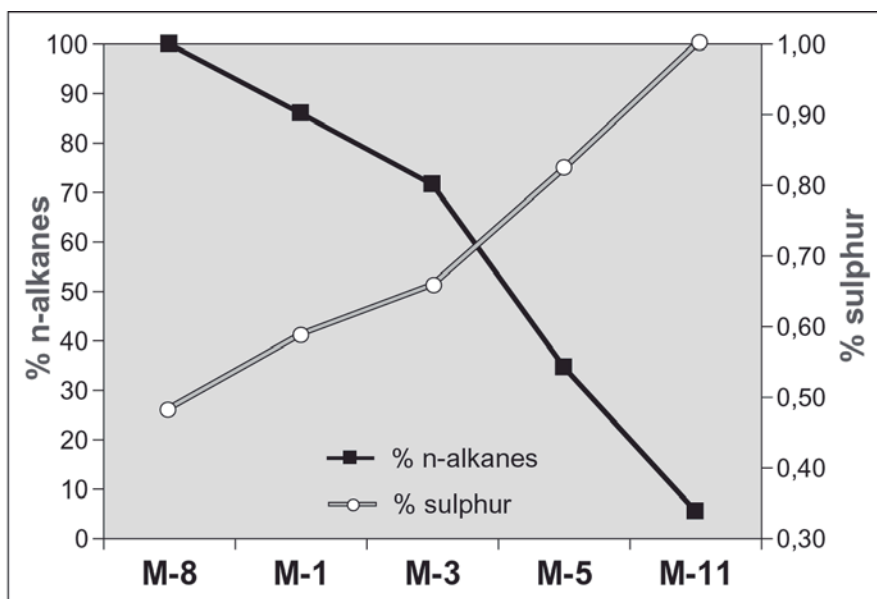


Fig. 4.- Relative sulphur content increases with the biodegradation. Figure shows percent variations of sulphur and n-alkanes according to the biodegradation.

Fig. 4.- El contenido relativo en azufre aumenta con la biodegradación. El la figura se muestra la variación porcentual de azufre y n-alcenos de acuerdo con el grado de biodegradación.

the maximum content of saturated hydrocarbons, especially nalkanes, has been taken as a reference.

Evolution of nalkanes, branched and cyclic alkanes, and UCM (unresolved compounds mixture) of saturated fraction is shown in figure 2 and 3. The degree of alteration observed in the mine

appears in complete agreement with the degree of biodegradation.

The grading degradation of n alkanes is combined with a relative increase in the isoprenoids pristane and phytane up to total degradation (samples M4 and M11). Steranes and hopanes are apparently not altered (Permanyer, 2000). On the basis

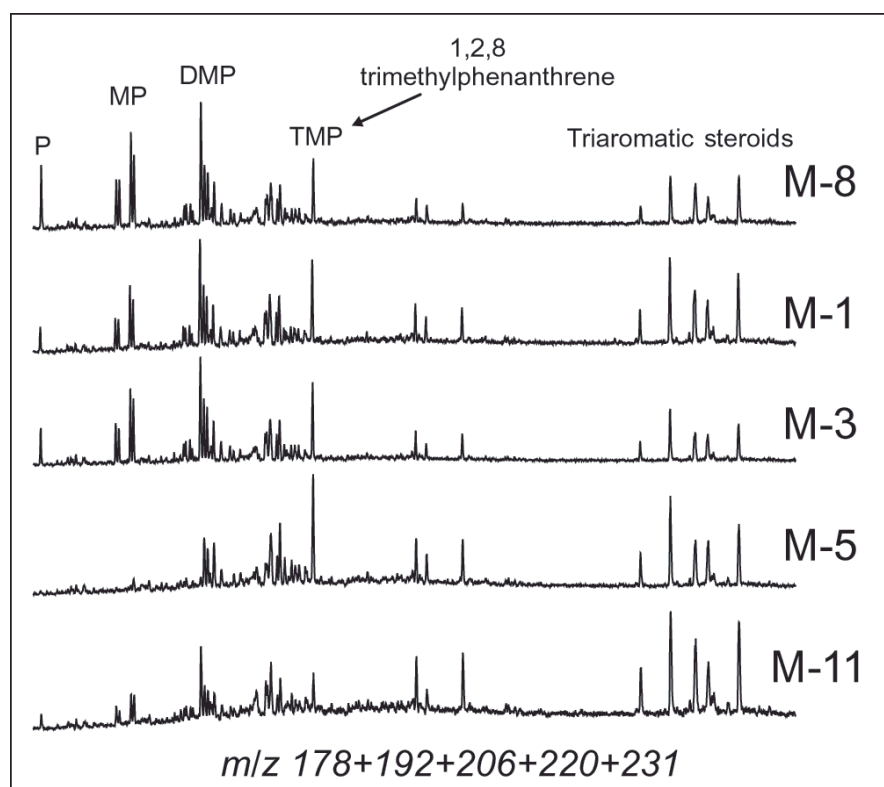


Fig. 5.- Aromatic hydrocarbons: reconstructed chromatograms using selected mass fragmentograms. P: phenanthrene; MP: methylphenanthrene; DMP: dimethylphenanthrene.

Fig. 5.- Hidrocarburos aromáticos: cromatogramas reconstruidos a partir de fragmentogramas de masa. P: fenantreno; MP: metilfenantreno; DMP: dimetilfenantreno.

of these data, biodegradation reached the level 34 according to Peters and Moldowan (1993) scale. However, as a relative increase in tricyclic terpanes between C19 and C26 has been observed, it is not excluded that the hopane series could be also slightly affected.

The sulphur content increases with biodegradation, from 0.39% to 1% (Fig. 4). Assuming that a negligible quantity of organic sulphur is incorporated to the oil during the biodegradation process and that the sulphur-bearing compounds are refractory to biodegradation at these stages, a maximum of 65% biodegradation can be estimated using the sulphur content.

Analyses of aromatic fraction (Fig. 5) shows that the alteration of aromatics is globally consistent with biodegradation of saturates except for the long chain nalkylbenzene series, which completely disappeared in all the samples. Some molecular series disappeared (phenanthrene series) or are temporary concentrated (triaromatic steroids, 1,2,8 trimethylphenanthrene) according to the progression of biodegradation. In sample M11 (the most biodegraded) the 1,2,8 TMP, being

less refractory than the triaromatic steroids, is consumed.

Quantitative analyses appear to be more adequate than molecular ratios to describe evolution of the biodegradation, particularly because the various molecular series are biodegraded according to different rates (Fig. 6A and 6B).

Relative quantity of aromatic molecular markers (Fig. 6A) shows:

- the obvious dilution of the biodegraded oil by an input of non biodegraded oil (M-3 and M-11),
- the relative stability of the concentration of triaromatic steroids, showing their effective biodegradation,
- the relative decrease of the phenanthrene series showing that these compounds are biodegraded early in aerobic conditions, and
- the increase, then the decrease of the concentration of 1,2,8 TMP reflecting its medium sensitivity to the biodegradation

In M-5 sample concentration of 1,2,8 TMP increases up to 150% respect to the less biodegraded M-8 sample. That may indicate that the C15⁺ aromatic fraction has lost at least 1/3 of its mass at this

stage of biodegradation. The behaviour of this compound is typical of products moderately refractory to biodegradation, same as hopanes for instance. Concentration of such products reaches a maximum before their own biodegradation begins.

Occurrence of heavy refractory compounds (e.g. organosulphur compounds) allows quantifying biodegradation which can reach about 60%.

Conclusions

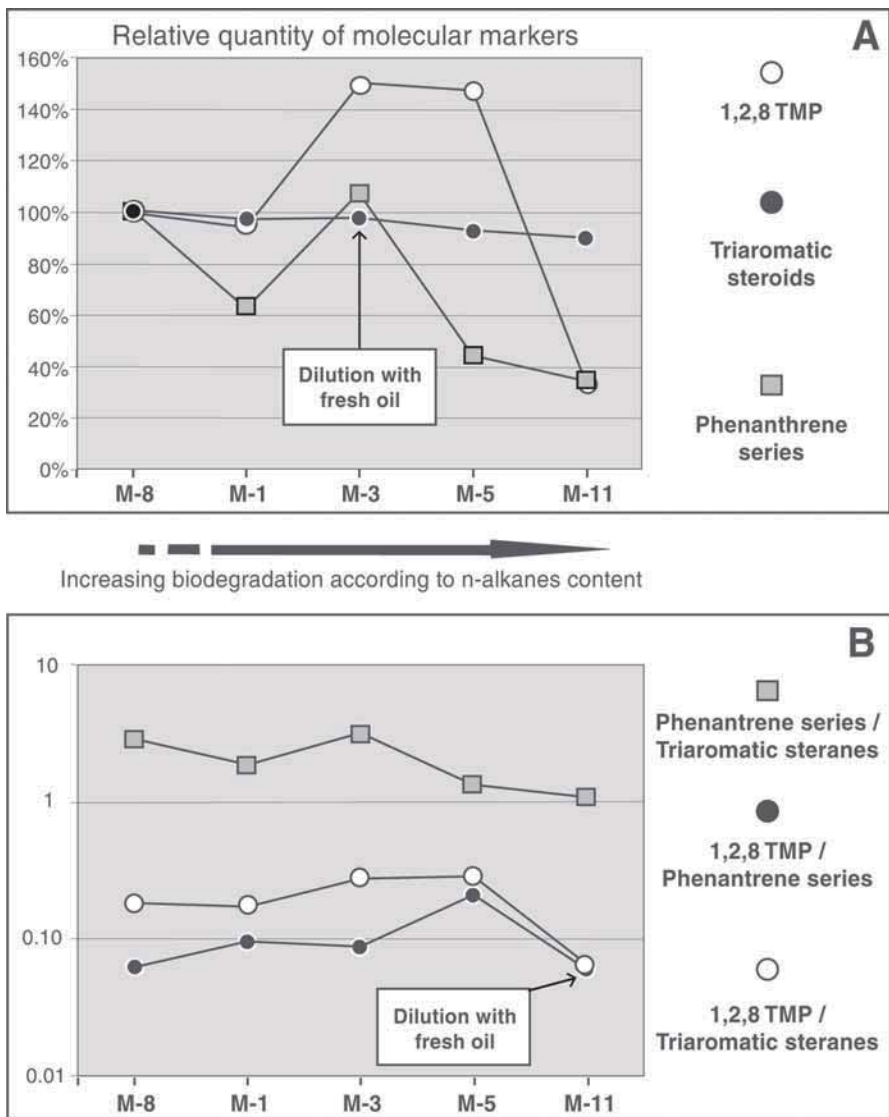
The biodegradation observed in oil samples from Riutort Mine is apparently comparable to biodegradation affecting generally oil seeps at surface, out abiotic oxidation. Biodegradation occurs in the presence of oxygen and water, at quasi constant temperature (15°C), from aerobic bacterial action.

The data obtained indicate that biodegradation does not surpass stage 3-5 for saturates in the Peters and Moldowan (1993) scale. This should be interpreted as an indication of a re-alimentation of the pools by fresh oil expelled from the source rock. In these circumstances, bacterial degradation remains rather moderate and is primarily limited to alteration of n-alkanes, isoprenoids and some aromatics (such as naphthalene, phenanthrene and alkybenzene series).

At this stage of biodegradation, quantification can be assessed by the sulphur content, as well as by quantitative analyses of molecular markers in aromatic fraction. Results indicate that between 50 to 60% of oil has been lost due to biodegradation process.

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Fig. 6.- Aromatic hydrocarbons. A: relative quantity of molecular markers, and B: selected molecular ratios.

Fig. 6.- Hidrocarburos aromáticos. A: cantidad relativa de marcadores moleculares, y B: variación de relaciones moleculares seleccionadas.