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 described to aerobic bacteria. Recently, some authors 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 and hydrogen-rich compounds. The loss of light components gives rise to a relative increase of heavy aromatics and polar compounds and consequently to an increase of density.

In this study we examine bacterial degradation of several samples of oil, seeping out directly from the source rock, in ancient bitumen mines. 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 in the order of 600 m. The lower 200 m represent an anoxic facies with elevated organic carbon content (TOC 15%). The organic matter is of marine origin with weak terrestrial influence, and its maturation is relatively low ± 0.65 % PRV and Tmax = 435°C.

Methods

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-2, M-8, M-1), to black (M-3) and brown (M-5, M-11) oil floating on water pools, to submerged oil (M-4), or oil with bacterial mass (M-6, M-7). Samples have been studied using gas chromatography and mass spectrometry. The sulphur content has also been measured.

Results and Discussion

All samples are believed to be affected by biodegradation at varying stages. The sample, which showed the maximum content of saturated hydrocarbons, especially n-alkanes, has been taken as a reference sample (M-2).

As a first result, the degree of biodegradation observed from the chromatograms of saturated and aromatic hydrocarbons is in complete agreement with the alteration visually observed.

The evolution of n-alkanes, branched and cyclic alkanes and UCM (unresolved compounds) is shown in Fig.1. On the other hand, sulphur contents increase with biodegradation, from 0.51% to 1%.

The grading biodegradation of n-alkanes is combined with a relative increase of isoprenoids pristane and phytane and by its final degradation (samples M-4 and M-11). Steranes and hopanes are apparently not selectively affected by biodegradation. On the basis of these data, biodegradation reached the level 3-4 according to the Peters & Moddovan's scale. However, as the relative increase of tricyclic terpanes between C19 and C26 has been observed, it is not excluded than the hopane series has been biodegraded.

The alteration of aromatics is generally consistent with the biodegradation of saturates except for the long chain n-alkylbenzene series which completely disappeared in all samples. The relative decrease of the abundance of the phenanthrene series (fig.1) shows that these compounds are biodegraded early in aerobic conditions, except for 1,2,8 trimethylphenanthrene, more resistant to the biodegradation.
The occurrence of heavy refractory compounds (i.e., aromatic steroids) allows to quantify the biodegradation which can reach about 50% compared to the reference sample.

**Conclusions**

The biodegradation observed in oil samples from Riutort Mine is apparently comparable to biodegradation affecting generally oil seeps at surface, out abiotic oxidation. In the present case, however, hydrocarbons did not migrate, except for primary migration and expulsion, because the gallery shaft is considered as the porous medium adjacent to the source rock. Biodegradation occurs in the presence of oxygen and water, at quasi constant temperature (15°C), from aerobic bacterial action.

The data obtained so far indicate, that biodegradation does not surpass stage 3-4 for saturates in the Peters & Moldowan's 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 and isoprenoids and some aromatics (such as naphthalene, phenanthrene and alkylbenzene series).

![Figure 1](image_url)

**Figure 1.** -- TIC (left) and m/z 178+192+206+220+231 mass chromatograms