

**FATE AND BEHAVIOR OF DIESELS (B0, B10, B30) AND BIODIESELS (FAME, HVO)
IN CASE OF AN ACCIDENTAL SPILL**

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ABSTRACT

Following an accidental spill of biodiesel in inland waters (France, 2016), Cedre with the support of TotalEnergies decided to initiate a project to better understand the behavior fate of diesels and biodiesels in case of accidental spill in fresh or marine waters. Three diesels (B0, B10 and B30) and two biodiesels (FAME – Fatty Acid Methyl Ester - and HVO – Hydrogenated Vegetable Oil) were studied during a 4-years project. The influence of natural weathering processes were assessed at laboratory and pilot scale in Cedre’s flume tank. The different parameters measured were density, viscosity, emulsification, oil adhesion to oleophilic material, natural dispersion and biodegradability. An efficiency test of a drum skimmer on diesel B10 (fresh and weathered) was also integrated in the study.

After one day of weathering, both diesels and biodiesels tended to mix with water and form a sort of “emulsion”. However, this mixture did not appear stable if the agitation was stopped. After one week of weathering, the total dispersion of B0, B10 and B30 was measured in the water column (formation of a white cloud of droplets). This result highlights that in turbulent condition (i) diesels and biodiesels disperse naturally after a few days of weathering, (ii) mechanical recovery will be effective only during the first 2 to 3 days after the spill occurs. If the agitation was stopped, oil droplets recoalesced to form a slick of weathered diesel. Additionally

to this re-coalescence, a foam-like substance was also observed at the water surface. The formation of this very sticky “foam” (not soluble in solvents such as methylene chloride, hexane, pentane, acetone) was also observed in the field and caused a lot of problems during mechanical recovery. As regard to the weathering processes, the evaporation / biodegradation rate reach a maximum of 62% for B0, 69% for B10 and 72% for B30.

Regarding the biodiesels FAME and HVO, as observed for the diesels, during the first day, they tended to emulsify and then, after few days of weathering, they tended to dispersed naturally for an agitated environment. As regard to the weathering processes, no dissolution or evaporation were measured. Biodegradation of the two products reached 99% in lab conditions.

All the results of and feedback from real spill involving diesels or biodiesels have been summarized and are available as a chemical response guide.

INTRODUCTION

In France, in 2015, the Energy Transition for Green Growth Act clearly laid out the intent to establish a solid, sustainable energy model on a national and international scale. Faced with depleting fossil fuel reserves, environmental protection requirements and economic challenges, biofuels, manufactured from renewable materials, represent the primary alternative in the transport sector (Ballerini, 2011).

The refinery's conversion is generating substantial traffic in new feedstocks (animal fat, used cooking oil, vegetable oils) and outgoing products, notably B7, B10, B30, HVO, FAME, aviation fuels (Biojet and Avgas[®]) and Adblue[®], a reducing agent used in a technology to reduce NOx emissions from heavy machinery (trucks, buses, construction equipment, etc.). Given the

increase in pollution risks associated with the growth in transport volumes, the adaptation of local emergency plans is becoming essential.

The production of new fuels inevitably requires an adaptation of the refineries normally used to process crude oil. Concerning the FAME production, after a refining stage to remove the free fatty acids and traces of water present in used fats and oils, conversion to biodiesel is achieved by a transesterification reaction.

Depending on the raw materials used to produce them, FAMES are considered:

- 1st generation when derived from vegetable oils;
- 2nd generation when they are derived from animal fats or used vegetable oils.

All of these products must technically meet the AFNOR NF-EN 14214 standard in order to be placed on the European market. FAME can then be used directly as biodiesel (B100) or blended with "conventional" diesel (B0) to form B5, B7, B10 diesels (the number designating the maximum percentage of FAME used).

Regarding the HVO (hydrogenated vegetable oil), this product is another way of converting fatty acids of plant or animal origin into biodiesel. Compared with FAMES, this product offers advantages in terms of NO_x emission limitation during combustion, storage stability and cold flow properties (European Alternative Fuels Observatory, 2021). HVO can be produced from fatty acids, or even directly from triglycerides. In the case of triglycerides, triple hydrogenation leads to the formation of saturated triglycerides, fatty acid, then propane, water and finally linear alkanes. It is these latter that, after a final treatment to ensure their resistance to cold, are used in a mixture with B0 to produce B30 (30% HVO) or "pure" as a biodiesel (B100) (Cedre, 2023).

As for crude oil, the weathering of diesels and biodiesels released in environment is complex as different natural degradation processes (evaporation, dispersion, emulsification, photo-oxidation,

etc.) occur simultaneously. Numerous studies have explored the fate of a spill of such products (Hollebone and Yang, 2009; Hollebone et al., 2008). In order to improve our knowledge of the weathering and fate of diesels and biodiesels, Cedre launched an experimental study in 2017.

MATERIAL AND METHODS

All of the materials and protocols described hereafter are detailed in Guyomarch et al. (2012).

FLUME TEST PRESENTATION

Tests at pilot scale were conducted in Cedre's flume tank: the Polludrome (Figure 1). The hydraulic canal, set in an air-conditioned room (0°C to 30°C), consists of a loop through which water can be circulated. The tank is equipped with a wave generator with an adjustable period, a current generator and UV lights. With this equipment, it is possible to weather dedicated oil in similar climatic conditions to those encountered in the oil field from which it is extracted or in the area of shipment. This equipment is used to study the behavior and weathering of chemicals and oils, in particular in the framework of the response to real accidents. Details of the Polludrome are given in Table 1.



Figure 1. Polludrome®

Table 1. Cedre flume tank details

Flume (circulation) length - inner wall	16.4 m
Flume (circulation) length - outer wall	20.2 m
Flume height	1.4 m
Flume width	0.6 m
Wind speed	1.2 m/s
Seawater depth	0.90 m
Surface area	8 m ²
Water volume	7.2 m ³
Temperature	20°C
Oil volume	20 L
Wave height	25 cm
Wave frequency	6 s
Current speed	20 cm/s
Wind speed	3 m/s

The effect of solar rays was simulated by two UV units (Hönle UV technology lamps, 2000 W each). The weathering trials were conducted for a minimum duration of one week and oil samples were regularly taken at the water surface (Table 1). This operation was implemented using a large funnel fitted with a tap to separate the free water from the oil which was then transferred into a separatory funnel. To facilitate sampling, the slick was temporarily concentrated into a thick layer by a boom installed across the width of the tank.

Table 1. Sampling times.

Sample reference	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Time (h)	1	2	4	6	8	14	24	26	30	48	53	72	77	144	149	168

MEASUREMENT METHODS

Flash Point

The flash point was measured according to the NF EN ISO 13736 standard (AFNOR, 2008) by using Anton Paar ABA 4 Flash Point Tester. This parameter was assessed until it

reached 100°C, considering this value as a reasonable limit in terms of the risk of ignition of an oil slick.

Density

The density of the samples of surface oil was determined according to the ASTM method ASTM D5002: 2013 (ASTM, 2013) by using an Anton Paar D4500 density meter. This measurement gave the real density of the emulsion that would remain on the sea surface.

Viscosity

The viscosity of the oil samples was measured by establishing the rheological curve using a Haake VT 550 viscosimeter at test temperature, to determine the evolution of the viscosity at dedicated shear rates (e.g. 1, 10, 100 s⁻¹).

Oil Adhesion

The evolution of oil adhesion was measured by weighing the amount of oil that sticks to a given oleophilic plate. This test provides information on the possibility of using oleophilic skimmers.

Emulsification

Emulsification was assessed by measuring the water content in the oil samples in three different ways:

- the water which separated naturally from the oil.
- the water which settled after addition of 0.1% demulsifier (*Demulsip*),

- the water that was distilled using the ISO Dean & Stark method, equivalent to the ASTM D95-05 (2010) Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation.

From these measurements, it was possible to determine the kinetics of emulsification as well as the maximum water uptake. The assessment of the stability of the emulsion resulted from the comparison of these data.

Evaporation and Chemical Composition

The saturate and aromatic fractions were analyzed using gas chromatography. Chromatograms of these compounds at different weathering times show the evolution of their distributions. To assess the evaporation rate of the whole oil, a calibration curve was established from samples of the initial oil evaporated in the laboratory by distillation at various temperatures (typically topped at 150, 200 and 250°C).

Oil Biodegradation

A protocol adapted from De Mello et al. (2007) was used to simulate the biodegradation process. Around 10 mg of product, dissolved in 50 μ L of acetone, was biodegraded at the laboratory scale, in a 125 mL glass bottle containing 100 mL of seawater. Nutrients were added to the water, in accordance with the French standard NFT 90-347 (AFNOR, 1990). This method is applied within the French dispersant approval procedure, and aims at assessing the biodegradation of dispersed oil. The hydrocarbon-degrading microorganisms came from a chronically contaminated site. The bottles were loosely plugged with autoclaved cotton wool, placed onto a shaker table, in the dark and agitated for 28 days. The residual oil was extracted and purified prior to analysis by GC-FID (Gas Chromatography coupled to a Flame Ionization

Detector). The GC was an HP 7890N (Hewlett-Packard, Palo Alto, CA, USA equipped with a split/splitless injector (Splitless time: 1 min, flow 50 mL/min). The injector temperature was maintained at 300°C. The GC-FID temperature gradient was from 50°C (1 min) to 300°C (20 min) at 5°C/min. The carrier gas was Hydrogen at a constant flow of 1 ml/min. The capillary column used was an HP-5 MS: 30 m×0.25 mm ID×0.25 µm film thickness.

RESULTS

Physico-Chemical Properties of the Oils

B0 (diesel), HVO and FAME (Table 2) were provided by TotalEnergies refineries of Donges (France) for B0 and La Mede (France) for HVO and FAME. B10 and B30 were prepared by mixing at ambient temperature these two products at a ratio of 90 / 10 (B0 / FAME) for B10 and 70/30 (B0/HVO) for B30.

Table 2. Physico-chemical properties of B0, B10 and FAME.

Product name	Density	Viscosity (mPa.s@20°C / 10 s ⁻¹)	Flash point (°C)
B0	0.838	4	51.0
B10	0.842	3	62.5
B30	0.851	5	67
FAME	0.880	5	>100
HVO	0.779	3	>100

Visual Comparison of Oil Behaviors

All the pictures taken the weathering tests are presented in Figure 2.

After the spill, a translucent slick form on the surface. No visual changes were observed during an initial phase lasting from 8h (HVO) to ~ 24h (FAME, B0, B10 and B30). Diesel and biodiesels then tend to form unstable emulsions (in the form of whitish-yellowish foams) under

agitated conditions. After a few days of weathering (ranging from 3 days for B30 to 6 days for FAME, B0 and B10), a natural dispersion of the products is observed. The products then appear either in the form of a plume of droplets uniformly distributed in the water column, or as a haze in the water column. As soon as the agitation is stopped, the surface slick forms again after a few minutes. A phase shift can be observed after settling (B0 and B10), characterised by an upper phase composed of aged hydrocarbons and a lower phase in the form of white agglomerates.

The table below summarizes the different weathering stage for these products.

Table 3. Different stages of weathering for B0, B10, B30, FAME and HVO.

	B0	B10	B30	FAME	HVO
Stage 1 : formation of a slick at the surface	0 - 1 day			0 - 1 day	0 - 8 hours
Stage 2 : formation of a foam on the surface (unstable emulsion if not agitated)	1 – 3 days			1 – 6 days	8 hours – 3 days
Stage 3 : - with agitation: natural dispersion - without agitation: oil slick at the surface	after 3 days		after 6 days	after 6 days	after 3 days

	T0 (oil release)	T~24h	T3d-6d	
B0	 Yellow liquid	 Formation of an unstable yellowish emulsion	 For agitated conditions, oil dispersion is observed	 Slick samples after settling
B10	 Yellow liquid	 Formation of an unstable yellowish emulsion	 Without agitation, oil droplets resurface to form an oil slick	 Slick samples after settling
B30	 Yellow liquid	 Formation of an unstable yellowish emulsion	 For agitated conditions, oil dispersion is observed	
FAME	 Yellow liquid	 Formation of an unstable whitish emulsion	 Without agitation, oil droplets resurface to form an oil slick	 For agitated conditions, oil dispersion is observed
HVO	 Incolor liquid	 Formation of an unstable whitish emulsion	 For agitated conditions, oil dispersion is observed	

Figure 2. Appearance of products after spillage and after a few days' weathering in the Polludrome®.

Evolution of Viscosity

Figure 3 presents the measures of viscosity for the 5 products studied. For B0 and B10, an increase of viscosity can be seen. Regarding B0, the viscosity after one week of weathering reach 200 mPa.s due to the variability in results, this evolution in viscosity could not be modelled. Nevertheless, the values obtained tended to remain below 100 mPa.s.

The FAME did not show such a strong increase in viscosity and it remained below 100 mPa.s. It is worth noting that this evolution follows a sigmoidal pattern, with a sudden increase in viscosity observed between 30 and 48 hours.

Concerning the HVO and B30, there are no evolution of viscosities measures for the first one and very slight increase for the B30.

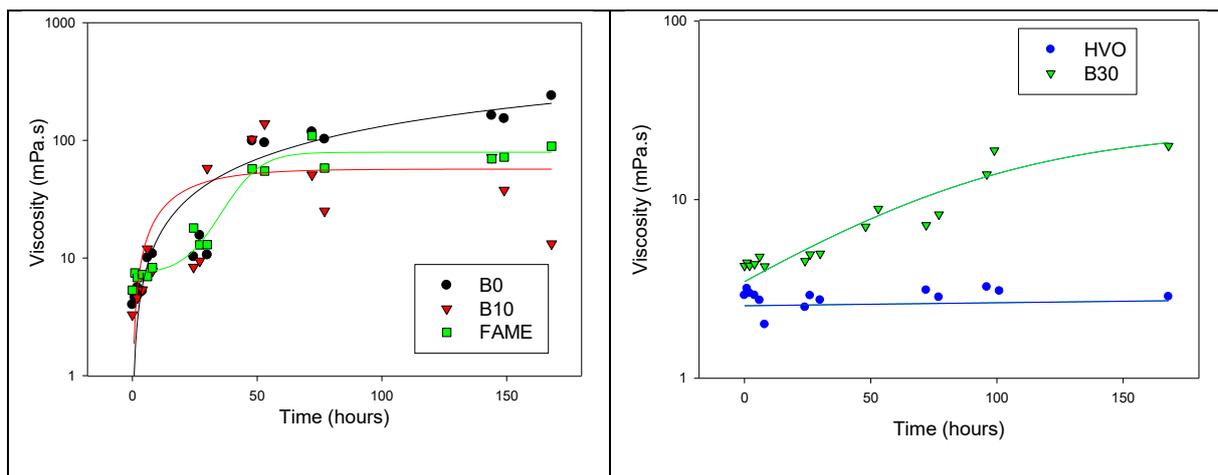


Figure 3. Evolution of viscosity (mPa.s) of B0, B10 and FAME (left) and HVO, B30 (right) as a function of weathering time (hours).

Evolution of Evaporation

Due to their chemical composition, FAME and HVO are not affected by the evaporation process.

As for the biodiesels, the evaporation rate was calculated from the changes in the linear alkane distributions. Even if there is a difference in evaporation rates measured after 7 days of

weathering (32% and 40% for B0 and B10 respectively), the evaporation kinetics of these two products are very similar.

B30 evaporation (data not presented) reached a maximum of 26% after one week of weathering.

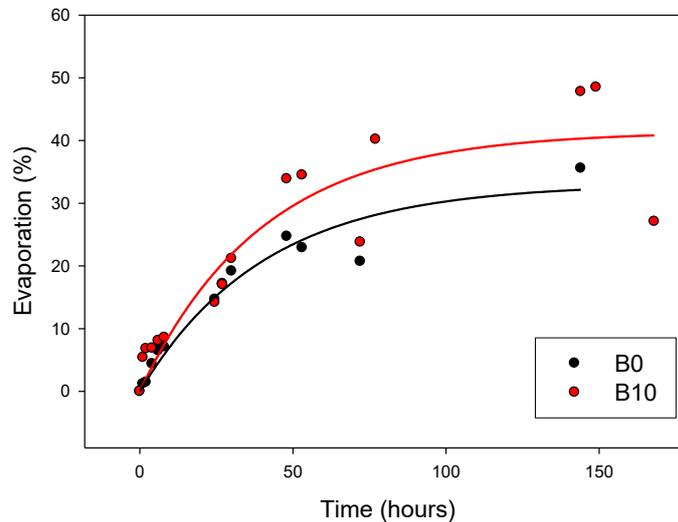


Figure 4. Evolution of evaporation (%) in B0 and B10 as a function of weathering time (hours).

Evolution of Water Content

Figure 5 presents the evolution of water content for the different products immediately after sampling. As reported for viscosity measurements, the evolution of water content values could only be modelled for B0 and B30, which plateaued at a water content of approximately 25% for B0 and 20% for B30. The variability of measures highlights the instability of the emulsion especially for B0 for the latest samples.

As regard to the FAME, water was incorporated progressively over the first 3 days of weathering, after which the maximum of 50% was reached. Concerning the HVO, no emulsification was measured in the samples collected during the weathering experiment.

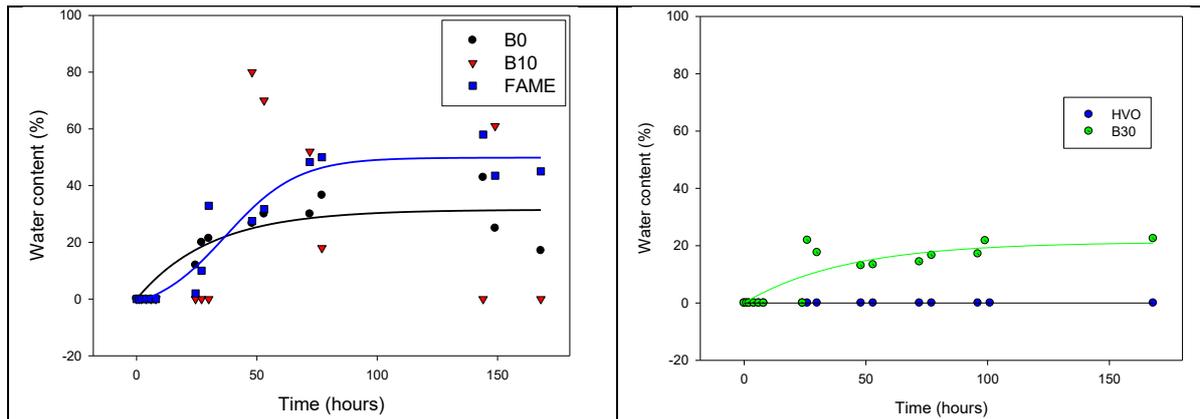


Figure 5. Evolution of water content (%) of B0, B10 and FAME (left) and HVO, B30 (right) as a function of weathering time (hours).

Evolution of Density

For the diesels (B0, B10 and B30), the increasing density (Figure 6) of the water-in-oil emulsions can be related to the evaporation of the lightest compounds together with the incorporation of water. For B0, surprisingly, this increase appeared to be almost linear. However, these results should be interpreted with caution due to the difficulty in obtaining homogeneous oil samples. For B10 and B30, the density values had increased respectively by 3% (0.842 to 0.865) and 5% (0.851 to 0.893) after one week of weathering. For these products, the density values remained below freshwater densities. Consequently, unless matter in suspension (organic or mineral matter) in the water column is incorporated, no immersion of slick will occurred.

For the FAME, the evolution in density follows a sigmoidal pattern in the same way as that of the viscosity values. After 3 days of weathering, the density stabilized at 0.950. Unless matter in suspension is incorporated, this oil is not liable to sink in inland waters. However, FAME can submerge for agitated conditions.

Regarding the HVO, as noticed for viscosity and density measurements, there was no evolution of density during one week of weathering.

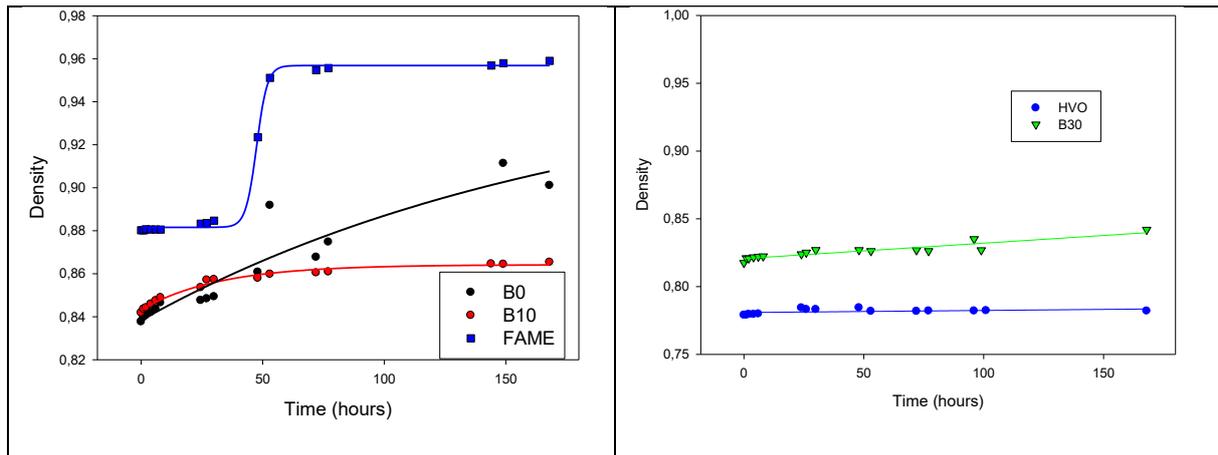


Figure 6. Evolution of density of B0, B10 and FAME (left) and HVO, B30 (right) as a function of weathering time (hours).

Biodegradability

The fresh oils and their corresponding biodegraded samples were analyzed by GC-FID. This method provides a general view of the oil, from the light compounds (around 10 carbons) to the heaviest (around 30 carbons). In order to establish a reliable mass balance, in addition to the two samples mentioned previously, the residues collected after distillation at 250°C were analyzed. The chromatograms obtained for fresh, evaporated and biodegraded samples of B10, B30, HVO and FAME are presented in **Error! Reference source not found.**

All the chromatograms were processed in the same way: assuming that the C26 – C30 fraction of the chromatogram remains stable (no biodegradation, evaporation or dissolution), quantities of oil remaining after degradation or evaporation were expressed relatively to this fraction, which allowed the comparison of the different analyses even if injected amounts of oils were different.

The biodegradation rates were calculated assuming that the evaporation process would be completed, and were therefore calculated relatively to the 250°C+ residues. After 28 days of experimentation, biodegradation of FAME and HVO appeared almost completed. As regard to B0 (chromatograms not presented), B10 and B30, biodegradation + evaporation rates reach 62%, 69% and 72% respectively.

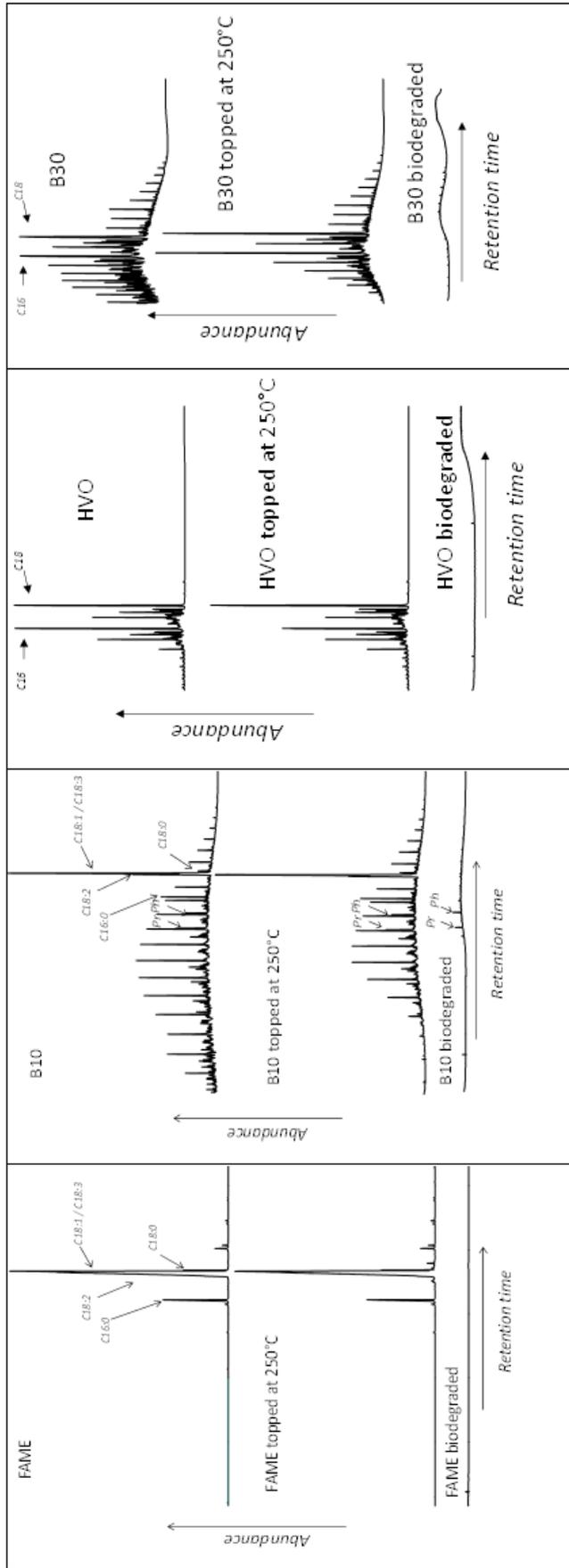


Figure 7. Chromatograms of fresh, evaporated and biodegraded samples of FAME, B10, HVO and B30.

CONCLUSION

In order to better understand the behavior of diesels and biodiesels in the event of accidental pollution, weathering studies were carried out at the Cedre Polludrome[®] on 3 diesels (B0, B10 and B30) and 2 biodiesels (FAME and HVO). A number of information have been concluded from these trials:

- Persistence in the environment: biodegradation process will contribute to the natural cleaning of biodiesels (FAME and HVO) contaminated sites. In the same way, for diesels (B0, B10 and B30), their degradation rates (biodegradation and evaporation process) will reach 62%, 69% and 72% respectively;
- Density: for the 5 products tested, the density values remained below the densities of freshwater and seawater. Consequently, unless matter in suspension (organic or mineral matter) in the water column is incorporated, oil slicks would not be expected to sink;
- Viscosity: the maximum viscosity value measured is 200 mPa.s for the B0. Considering the values as well as adherence measurements (not presented in this paper), weir skimmers or oleophilic skimmers can be used to recover even very weathered slicks;
- Mixture of oil and water: all the products tend to incorporate water droplets quickly. However, this mixture remains very unstable and a settling period of a one hour is sufficient to separate the aqueous and organic phases. This settling period is recommended in order to significantly decrease the volumes of waste to be treated.
- Natural dispersion: this phenomenon was observed systematically for both diesels and biodiesels.

All the results and information gathered during this study have been included in an operational guide available on Cedre's website (<https://wwz.cedre.fr/en>).

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