

Experimental Studies on the Weathering of Chemicals in a Field Trial to Predict their Behaviour in Case of a Spill

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Abstract

World production of vegetable oil increased from 18 million tons annually in 1960 to 84 million tons in 1999. Most of this is transported by sea and, as a result, approximately 850,000 tons of vegetable oil entered and left French harbours in 2001. This trend increases the risk of accidental spills at sea. When spilled at sea, vegetable oil is subject to natural weathering processes that significantly change the oil's physical state and chemical structure. Such modifications often transform non-toxic products into pollutants that can damage the marine ecosystem.

This study was aimed at obtaining experimental data on the behaviour of two vegetable oils (castor oil and soybean oil) and two chemical products (oleic acid and dioctylphthalate) when released at sea, and characterizing the data through sea trial experiments. For this purpose, a sea campaign was organized off Pointe de Penmarc'h, during which 2000 L of each product were released. Two types of measurements were used to monitor the weathering processes that the slicks underwent. First, samples were taken for on-board laboratory analyses and the viscosity, emulsion water content and kinetics, and emulsion stability were studied. Secondly, in-situ analyses were directly performed at a depth of 1 m under each slick to determine product solubility.

Results have shown significant differences between the behaviour of the vegetable oils and the chemical products. In addition, it appeared that the solubility of the vegetable oils was different (castor oil was ten times more soluble than soybean oil). These results underline the importance of field experiments to validate laboratory studies.

1 Introduction

Since 1981, world production of vegetable oil has doubled and in 2001, more than 95 Mt was produced. Soybean oil represents 29% of this total, with 28 Mt produced in 2001. Production of palm oil has quintupled since 1981 and represents 25% of the total production with 24 Mt produced in 2001. Many other vegetable oils are included in this production, including castor oil (0.2 Mt), coconut oil (1.8 Mt), sunflower oil (2.5 Mt), and secondary products such as oleic acid (3 Mt) (Proléa-Documentation, 2003).

Today, vegetable oils are both consumer goods and raw materials used in some industries, primarily the food processing, pharmaceutical and cosmetic industries. Regarded as non-toxic products as consumer goods, vegetable oils may become hazardous to marine life when spilled at sea (Fingas et al., 2001).

The specific gravity of vegetable oils ranges from 0.90 to 0.97 at 20°C (Karleskind, 1992). In this respect, when spilled at sea, such oils will remain on the

surface to spread and form a slick. While their short-term behaviour is similar within the minutes or hours following a spill, their long-term fate depends on several factors, such as the amount spilled, their chemical composition, and the weather conditions at sea, e.g., wind, water temperature, sunshine, and current. Two main weathering processes, emulsification and dispersion, occur under natural conditions and affect all oil spilled at sea. The chemical composition and physical properties of the oil are constantly changing according to its weathering stage. Density increases, part of the oil can disperse naturally in the water column, while the oil remaining on the water surface is emulsified with sea water and oxidized by solar UV. Oil can become increasingly viscous and thus form a new persistent pollutant in the environment.

This study aims at showing how this type of product could react when spilled at sea. The main objective was to obtain experimental data on the behaviour of vegetable oil on the sea's surface and in the water column during a field experiment. For this purpose, castor oil, soybean oil, oleic acid, and dioctylphthalate were released at sea. The dispersion of the oil in the water column was monitored with a fluorimeter (Turner Designs 10AU) and measurements were taken at a depth of 1 m. Several samples of the slick were taken in order to monitor emulsification and viscosity kinetics.

2 Materials and Methods

2.1 Vegetable Oil and Derivative Compounds

Castor oil, soybean oil, oleic acid, and dioctylphthalate were supplied by ACROS Organics, a company of Fisher Scientific International. Their main physico-chemical parameters are listed in Table 1.

Table 1 Main Physico-chemical Parameters of the Tested Products

Properties	Castor oil	Soybean oil (soya)	Oleic acid (OA)	Dioctylphthalate (DOP)
CAS	8001-79-4	8001-22-7	112-80-1	117-81-7
Melting point, °C	-10	-	13	-50
Boiling point, °C	313	-	286	386.9
Vapour pressure, mm Hg	5	-	0.016 (121°C)	0.07
Vapour density (air=1)	Negligible	-	9.7	-
Density	0.95 g/cm ³	0.92	0.8946	0.98
Solubility in water	Insoluble	Insoluble	Insoluble	0.000034 g/100 mL
Viscosity	-	-	164.20 cp (50°C)	-
Refractive index	1.48 (20°C)	1.47 (25°C)	1.46214 (11.8°C)	1.486 (20°C)

2.2 Experimental Location

The experiment was carried out at the location defined by 47°50'N and 05°10'W, which is 20 miles off the French shoreline in the Iroise sea (Figure 1).

2.3 Operations Schedule

For each product, 2000 L were released at the sea surface by following a line perpendicular to the direction of the main current in order to avoid slick superposition (head to 220, Figure 2). In addition, 200 m between each slick was kept free of oil to

avoid mixing processes (Figure 3). NORDA buoys were used to mark each slick to follow and differentiate them.

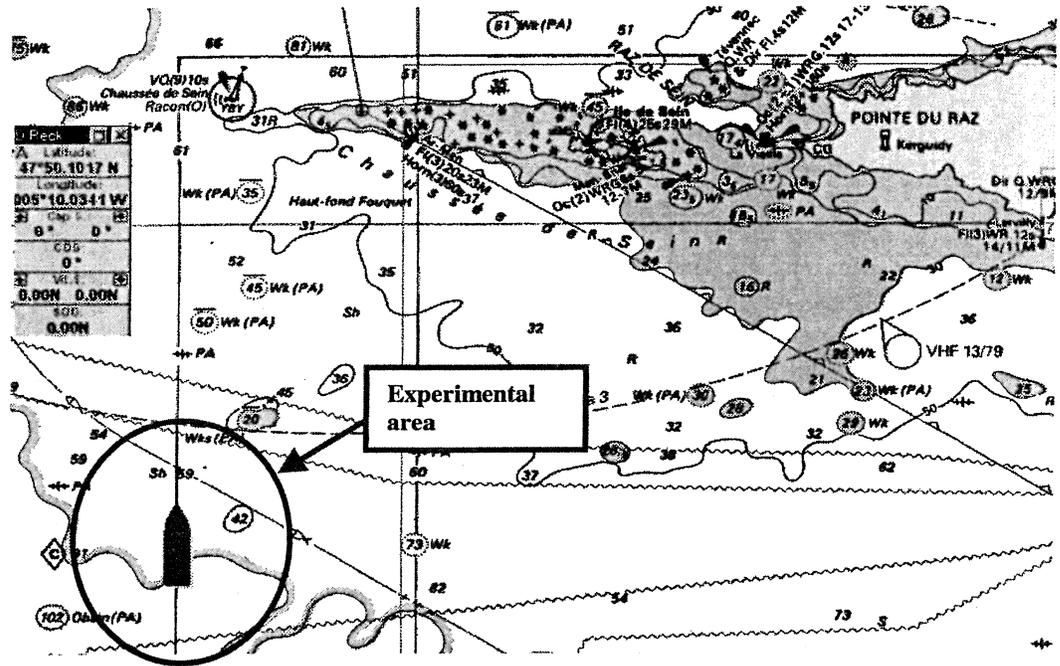


Figure 1 Experimental Area in Iroise Sea

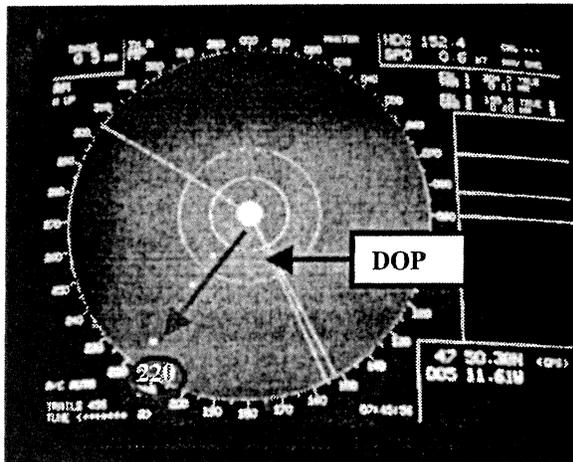


Figure 2 Alignment of Slicks after the Spill

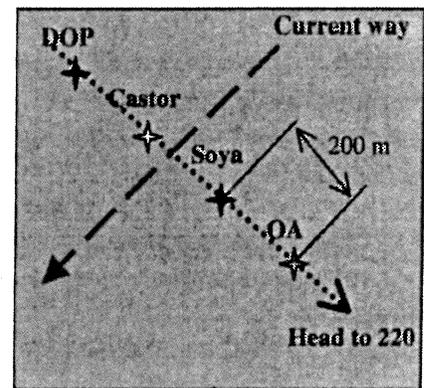


Figure 3 Order of Spill

2.4 Sampling Protocol

Samples of each slick were taken at the sea surface and analyzed in the on-board laboratory for density, viscosity, and water content. The distribution of the dispersed pollutant in the water column was monitored by performing fluorescence measurements at a depth of 1 m with the fluorimeter (SF-UV). The sampling schedule is shown in Table 2.

Table 2 Time Schedule for Operations

	T ₀	T _{+2h}	T _{+8h}	T _{+12h}
Oil released	x			
Slick sampling		x	x	x
Sea water column sampling		x	x	x

2.5 Chemical Analyses

Density - The density of the surface samples was determined according to ASTM method D70-97 (ASTM, 1999a). This measurement gives the real density of the emulsion that would remain on the sea surface.

Emulsification - The emulsification of products was followed up by measuring the evolution of the water content, determined by the Dean & Stark method, ASTM D95-99 (ASTM, 1999b). From these measurements, it was possible to determine the kinetics of emulsification as well as the maximum water uptake.

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

Dispersion - The natural dispersion of products was monitored by means of an UltraViolet Fluorescence instrument (Turner Design UVF fluorimeter, model 10 AU 005). A sea water flow passed continuously through the measuring cell of the fluorimeter which performed a concentration measurement every 3 s. Before the release of the four studied compounds, they were mixed with a dye (red organol, 1 kg per 2000 L) to ensure their detection by fluorescence in the water column.

In addition, 3 samples of sea water were taken at each measuring location (on each slick) and at each sampling time. These were brought back to the laboratory and extracted with dichloromethane and analyzed by gas chromatography coupled to mass spectrometry (GC-MS). Results were used to calibrate the fluorescence response obtained in situ.

2.6 Environmental Monitoring

The main environmental parameters that could influence the product's behaviour are the wind (high wind agitates the sea surface which increases the emulsification process) and the sun (UV rays increase the oil's fluidity).

3 Results and Discussion

3.1 Weather Monitoring and Visual Observations

Early in the morning, the wind was strong enough to induce waves with many whitecaps, corresponding to a 'rough' state on the Douglas scale. In the middle of the day (T +4h), the wind decreased to 5 knots, which corresponds to level 2 on the Beaufort scale ('gentle breeze') with small wavelets. Just after the releases, the sea was agitated enough to influence the behaviour of slicks, particularly the emulsification and dissolution processes. The sea temperature was 12°C and the atmospheric temperature was 15°C.

Visually, it was possible to clearly distinguish between the 4 slicks throughout the experiment (Figure 4) and to observe a particular behaviour for the oleic acid, which can be seen as the more compact slick in Figures 4 and 5.

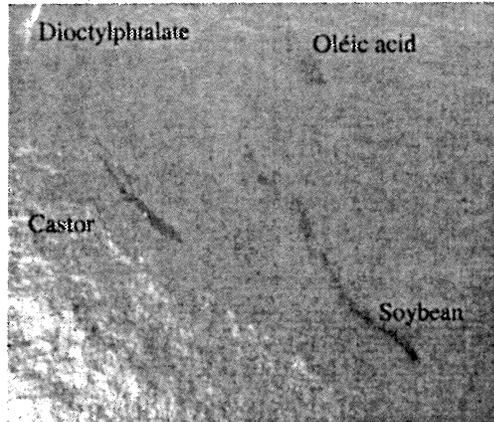


Figure 4 Overall Picture of 4 Slicks at T+8h (Source: French Navy)



Figure 5 Closeup of Oleic Acid Slick at T+8h (Source: French Navy)

3.2 Density

For soybean oil and castor oil, density remained stable throughout the experiment: the density of the weathering product was always very close to that of the original product, with no significant difference observed. The initial density is represented by a dotted line in Figure 6. After 12 hours at sea, the density of the oleic acid was significantly higher than the density of the initial product. The density of dioctylphthalate, however, decreased significantly from 0.98 to 0.81 during the experiment.

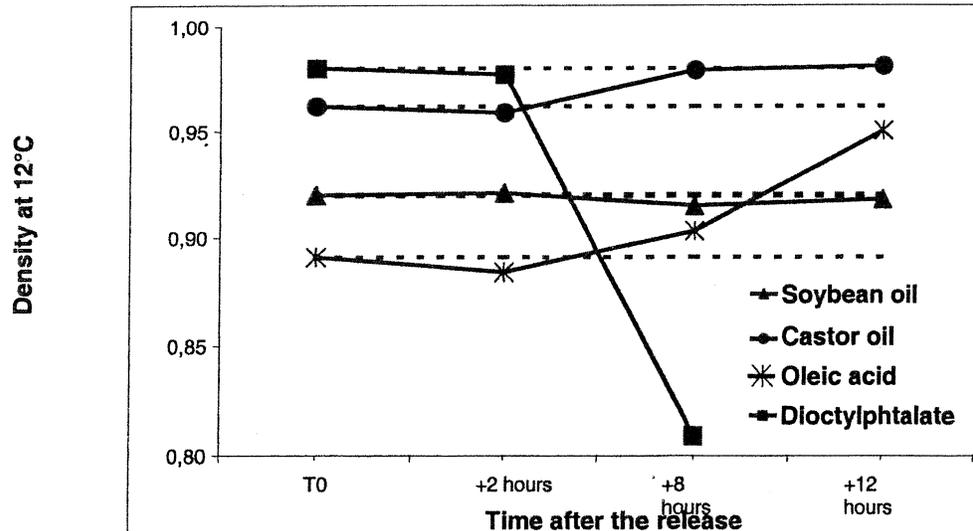


Figure 6 Density Variations of Castor Oil, Soybean Oil, Oleic Acid, and Dioctylphthalate

3.3 Viscosity

The variations in viscosity for the various products are shown in Figure 7. The viscosity of both the soybean oil and the oleic acid was stable throughout the experiment and remained close to the viscosity of the initial product. The viscosity decreased significantly for the castor oil and increased for the dioctylphthalate.

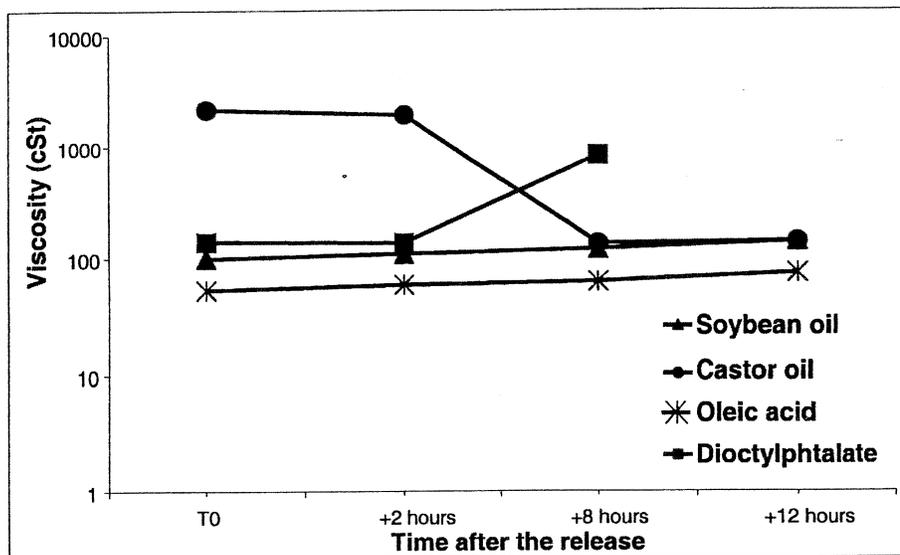


Figure 7 Viscosity Variations of Castor Oil, Soybean Oil, Oleic Acid, and Dioctylphthalate

3.4 Emulsification

The castor oil did not emulsify during this experiment; the water content was always lower than 5% as shown in Figure 8. Emulsification kinetics were different for each of the other three products. For oleic acid and dioctylphthalate, emulsification started 8 hours after the release. Soybean oil was emulsified immediately: at T+2 hours, the water content reached 20%. Nevertheless, this water percentage was not stable over time: 7% at T+8 hours and 20% at T+12 hours. These results describe a mesostable emulsion for the soybean oil which was encouraged by the weather conditions at sea.

3.5 Natural Dispersion

The concentrations of sea water in the vegetable oils during the field trial are shown in Figure 9. Immediately after the release (T+2 hours), it was possible to detect oil at a 1-m depth: oil was widely dispersed in the water column. Castor oil reached a concentration of 49 g/L after 8 hours of weathering. Soybean oil was less dispersed and reached only a concentration of 3 g/L, approximately 16 times lower than castor oil. Nevertheless, for both oils, sea water concentrations were essentially due to direct emulsification processes (droplets of oil under the sea surface). Concerning the transfer of an oil from the surface to the water column, it seems that two vegetable oils can have significantly different behaviours.

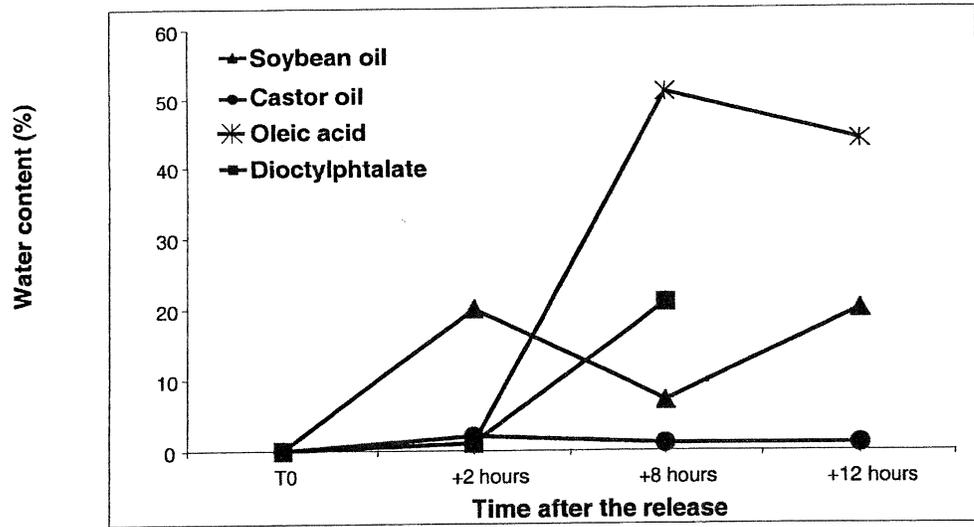


Figure 8 Water Content Variations of Castor Oil, Soybean Oil, Oleic Acid, and Dioctylphtalate

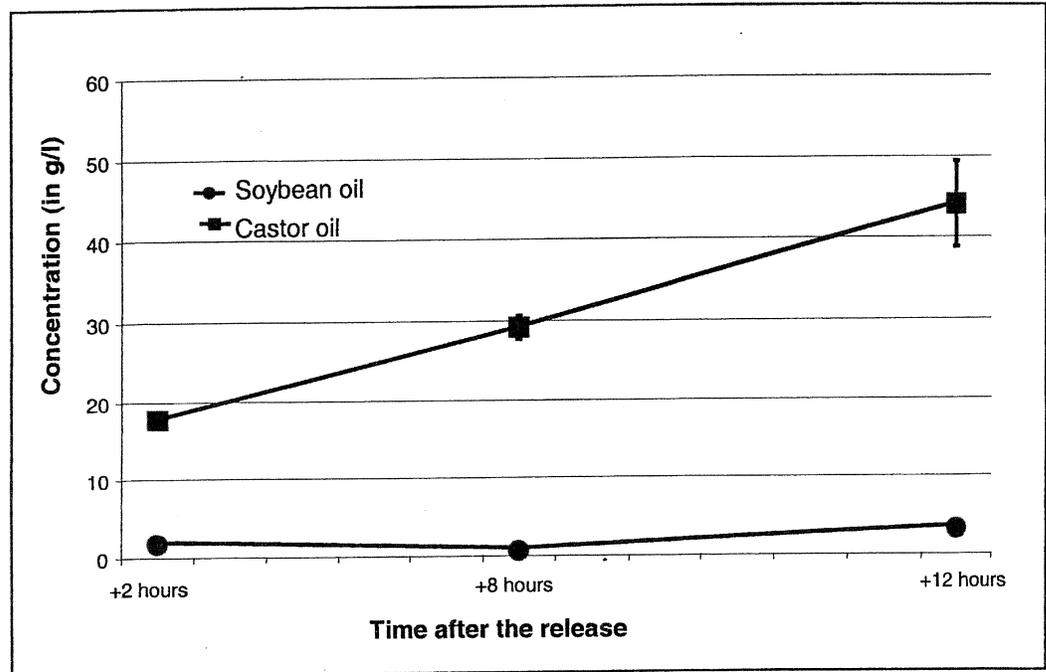


Figure 9 Sea Water Concentrations of Castor Oil and Soybean Oil at 1 m Depth

Concentrations of oleic acid and dioctylphtalate were always lower than 1 g/L but they were detectable 2 hours after their release at a 1-m depth (Figure 10). Even if the concentrations were weak, dioctylphtalate reached a concentration of $26 \cdot 10^{-3}$ g/L after 12 hours and oleic acid a concentration of $2,9 \cdot 10^{-3}$ g/L.

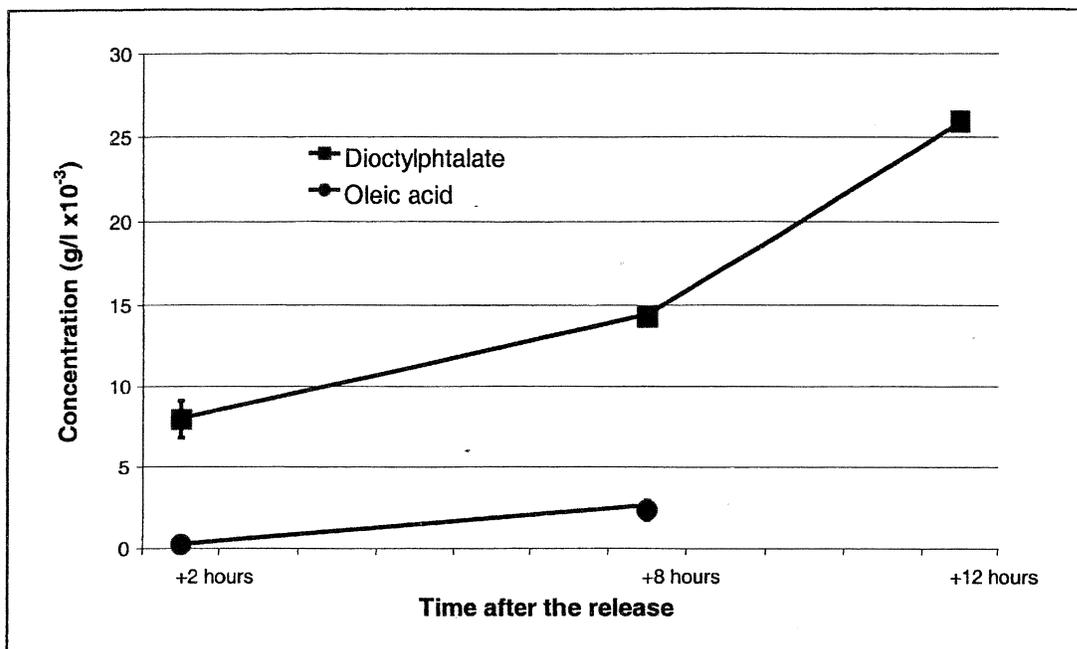


Figure 10 Sea Water Concentration of Oleic Acid and Diethylphthalate at 1 m Depth

4 Conclusion

The objective of this field experiment was to characterize the behaviour of two vegetable oils (castor oil and soybean oil), a derived product of vegetable oil (oleic acid), and diethylphthalate after their release at sea.

This study confirms that the behaviour of these 4 products is largely dependent on the nature of the product and the weather conditions (wind and sea surface state). For the soybean oil, the main weathering process was emulsification, which could reach 20% after 2 hours. For the castor oil, the main weathering process was dispersion. It is clear that the Standardised European Behaviour Classification (SEBC) code, which lists these oils as persistent floaters (Fp), should take other parameters than the physico-chemical parameters into account (Bonn Agreement, 1994). Other parameters to be included should include the emulsification capacity of the product. In addition, from an operational point of view, after an accidental spill of a large amount of castor oil, dispersant should be considered for treating this type of slick as the density did not change significantly during the experiment and natural dispersion could be high.

The floater characteristic of the oleic acid was maintained throughout the experiment, significant emulsification was observed, and only a small amount of dispersed oleic acid was detected in the water column. These results are in accordance with the SEBC code which lists oleic acid as a persistent floater (Fp). In case of an accidental spill at sea, emergency responders should first consider pumping and then the use of dispersants.

The behaviour of the diethylphthalate was particularly interesting: its viscosity, water content, and dispersibility in the water column increased during the first 8 hours of the experiment, while its density decreased. In addition, after 8 hours,

it was not possible to sample the slick due to solidification processes even if small quantities were detected in the water column (Figure 11). In this case, emergency responders should focus on adapted techniques such as trawling.

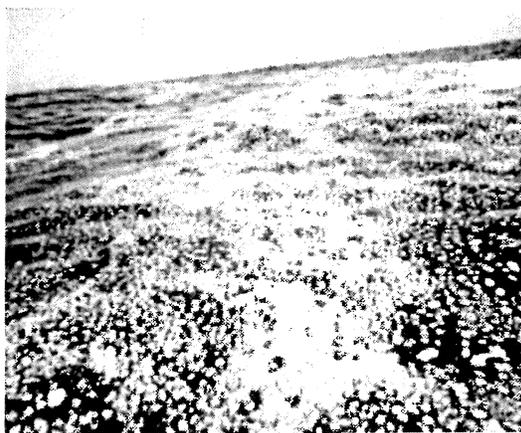


Figure 11 Diocetylphthalate Slick at T +12 Hours

5 References

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