

EXPERIMENTAL STUDIES ON THE WEATHERING OF VEGETABLE OILS IN OPEN POOLS TO PREDICT THEIR BEHAVIOUR IN CASE OF A CASUAL SPILLAGE

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ABSTRACT

Vegetable oil world production raised from 18 millions tons yearly in 1960 to 84 millions in 1999. Most of it is transported by sea and, as a result, approximately 850,000 tons of vegetable oils entered and left French harbours in 2001. This trend induces an increasing risk of accidental release in the marine environment. When spilled at sea, vegetable oil is subject to weathering processes under natural conditions, which induce important changes in the oil physical state and chemical structure. Such modifications often transform non-toxic product into a pollutant that can damage the marine ecosystem. This study aimed at getting experimental data on the behaviour of vegetable oil when released at sea and at characterizing it through *in situ* experiments. For this purpose, experimental open pools were built and settled in the Bay of Brest, each of them made of a 9-square-metre surface surrounded with a 2-metre-high nylon skirt set on a metallic structure. As pool walls are flexible, the contained water was submitted to the swell and waves influences. As they are uncovered, sea surface was submitted to atmospheric influences (wind, sunshine and rain). After oil release at the water surface, weathering processes were studied by measuring the viscosity, the emulsion water content and the corresponding kinetics, the emulsion stability and solubility in the water column. These experiments were carried out in two stages: *in situ* analyses to characterize solubility in the water column and then sampling for laboratory analyses to measure viscosity and emulsification rates. Two vegetable oils were tested, twice each, and the results demonstrated significant difference in the way they behaved at sea.

INTRODUCTION

Since 1981, the world production of vegetable oil has doubled, and in 2001, this production exceeded 95 Mt. Soybean oil holds the first place of vegetable oil product in the world with 28 Mt in 2001 and it represented 29 % of the production of the whole vegetable oil in the world. Since 1981, the world production of palm oil has quintupled, and held in 2001 the second place after soybean oil with 24 Mt, that is to say 25 % of the whole vegetable oil production in the world. In this production many various types of vegetable oils are included, such as castor oil (0,2 Mt), coconut oil (1,8 Mt), sunflower oil (2,5 Mt)... and secondary products as oleic acid (3 Mt; Proléa-Documentation, 2003). Nowadays, vegetable oils are both consumer goods and raw materials in some industries. It is mainly used by food processing, pharmaceutical and cosmetic industries. Regarded as non-toxic products as they are consumable goods, vegetable oils may however 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, such oils will remain at sea surface to spread and form a slick. However, if 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 (wind, temperature of the sea, sunshine, current,...). Two main weathering processes, emulsification and dispersion, occur under natural conditions and affect the whole of the 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 oxidised by solar UV. Oil can get increasingly viscous and become a new persistent pollutant in the environment.

This study aimed at showing how this type of product could react when spilled at sea. The main objective was to get experimental data on the behaviour of vegetable oil at the sea surface and in the water column during an *in situ* experiment. For this purpose, castor oil and oleic acid were released in open mesocosms based at sea and a fluorimeter (Turner Designs 10AU) was used to monitor the oil dispersion process in the water column (measurements were performed at three depths). Samples of the slick were daily collected during one week in order to monitor emulsification and viscosity kinetics.

MATERIALS AND METHODS

Vegetable oil

Castor oil and oleic acid were supplied by ACROS Organics, subsidiary of the Fisher Scientific International company. The main physico-chemical parameters are listed (Table 1).

Experimental design: equipment, sampling procedure and schedule

These tests were carried out in six floating mesocosms, each consisting of an area of 9 m² contained within a flexible boom fixed on a metallic structure, set in a sheltered harbour (Picture 1). The walls of the booms (2 metres high) were flexible and the surface of the water was subjected to wind and agitation due to waves created by passing ships. The volume of sea water contained in each mesocosm was 18 m³.

For each test, 50 litres were poured onto the water surface of a mesocosm (2 x 50 litres of castor oil and 2 x 50 litres of oleic acid). Samples were collected daily and brought back to the laboratory for viscosity and water content determinations (Table 2). In addition, the distribution of the dispersed pollutant in the water column was monitored by performing fluorescence measurements at 4 positions (A, B, C and D) in each mesocosm and at 3 different depths (25, 50 and 100 cm for the fourth positions). This procedure allows to get data at 12 locations in the water column (Figure 1).

This procedure allows to study oil behavioural processes in a systematic and reproducible way over a period of up to 5 days. As these processes are linked to weather conditions, prevailing sunshine, wind speed and temperatures (air and sea) were recorded.

Analyses

Density. The density of the samples of surface oil was determined according to the ASTM method D70-97 Standard Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials (Pycnometer Method) (ASTM, 1999). This measurement gives the real density of the emulsion that would remain on the sea surface.

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

Viscosity. The viscosity of the oil samples was measured by establishing the rheological curve using a Haake VT 550 viscosimeter to get 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 Ultra Violet Fluorescence instrument (Turner Designe 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.

In addition, at each measuring location (point and depth) and at each sampling time, a sea water sample was taken, brought back to the laboratory, extracted with dichloromethane and analysed by gas chromatography coupled to mass spectrometry (GC-MS). Results were used to calibrate the fluorescence response obtained *in situ*.

RESULTS AND DISCUSSION

Environmental monitoring

The main environmental parameters which could have an influence on the oil behaviour are the wind (high wind results in sea surface agitation which increases emulsification process) and the sun (UV increase the oil fluidity). At the beginning, the weather was strong enough to induce moderate waves, many white horses (Beaufort Force scale between 5 and 6), but after the first day (T_{+48h}), it became gentle (Beaufort Force scale between 0 and 3; Table 3).

The sea surface agitation was strong enough only during the first 24 hours to have an influence on the behaviour of the slick, particularly on the emulsification and dissolution processes.

Density

For oleic acid (mesocosms 1 and 4), the density evolutions were not significant: densities of the weathered product were always very close to the density of the pure product (initial density of oleic acid is represented by dotted line; Figure 2).

As regard castor oil, it is possible to observe two different behaviours: during the first 72 hours, the oil density in the mesocosm 5 is always lower than the density of the initial product. For the oil in the mesocosm 2, it is the contrary (Figure 2). This result could be explained by differences of exposure to weather conditions between mesocosms 5 and 2: mesocosm 2 is more exposed to the roughness of wind and sea, and mechanical energy accelerates significantly the emulsification kinetics.

The variation of the density strictly depends on the emulsification process. These two products show a different behaviour during this five-day experiment.

Emulsification

Oleic acid was not able to produce emulsion during this experiment: the water content was always lower than 5% (Figure 3). Concerning castor oil, the emulsification kinetics were different between mesocosms 2 and 5: after 48 hours, in mesocosm 2, the water content reached 42% whereas it was only 11% in mesocosm 5. This result is in accordance with those obtained for the density: the oil density in mesocosm 5 increased due to the higher level of emulsification process. In addition, the castor oil emulsion seems to be unstable: beyond T+48h when the weather became more gentle, the water contents decreased in both mesocosms.

Viscosity

In both case (oleic acid and castor oil), viscosity remained stable during all experiments.

Natural dispersion

Figures 4a and 4b represent the concentration (g/l) of castor oil in mesocosms 5 and 2 (Figure 4). Immediately after the release (T+3h), it is possible to detect oil at the three depths: oil was widely dispersed in the sea water column (1 to 4 g/l). Nevertheless, results in mesocosm 5 were lower and more homogeneous than in mesocosm 2: oil concentration in mesocosm 2 was essentially

due to direct emulsification process (droplets of oil under the sea surface). The natural dispersion of castor oil is subject to the dissolution and the direct emulsification processes but, with a 5 Beaufort Force Scale, the direct emulsification process is prevailing.

Figures 5a and 5b represent the oleic acid concentration (mg/l) in the sea water column for mesocosms 1 and 4 (Figure 5). For both, concentrations were homogeneous at the three depths (5 to 15 mg/l) except for mesocosm 1 at T+48 (60 mg/l). The exposition of mesocosm 1 to the sea surface agitation explains this high level: just after the release, the sea state was rough.

CONCLUSION

This field experiment was designed to characterise the behaviour of a vegetable oil (castor oil) and a derived product of vegetable oil (oleic acid) after their release at sea.

This study confirms that the product behaviour is largely dependent on the weather conditions (sunshine and sea surface state). For vegetable oil, the emulsification process could reach 40% after 48 hours under weather conditions characterised by a level 5 on the Beaufort Force Scale. This trend is linked to an increase of the oil density without changes in the oil viscosity. These results show that the castor oil emulsion is unstable. Concerning the pollutant transfer from the sea surface to the water column, it was equally linked to the sea state and the measured concentrations were significant (approximately 3.5 g/l after 3 hours). Considering the amount of sea water included in the mesocosm (18 m^3) and an average concentration of 2 g/l, it should be possible to estimate that 36 kg of oil (or emulsified oil) were dispersed in the sea water column (70 % of the amount of oil released). It clearly appears that the European Classification (SEBC code, Bonn Agreement 1994), which lists this oil as a persistent floater (Fp), should take into account other parameters, such as the emulsification capacity of the product, rather than only the physical chemical parameters. In addition, from operational point of view after an accidental release of a large amount of castor oil, the possibility of using dispersant for treating this type of slick should be considered: no significant evolution of the density during its behaviour at sea and the natural dispersion can be high.

The floater character of the oleic acid was kept during all the experiment: no significant emulsification process was observed and little dispersed oil was detected in the sea water column.

These results are in accordance with the SEBC code which lists oleic acid as a persistent floater (Fp). Consequently, in case of accidental spillage at sea, the responders should consider in first priority the possibility to organise some recovery operations by pumping, trawling or with nets like those which were performed after the *Champion Trader* accident (Golob's Oil Pollution Bulletin, 1998; OSIR, 1998). In second priority, the use of dispersant could be evaluated.

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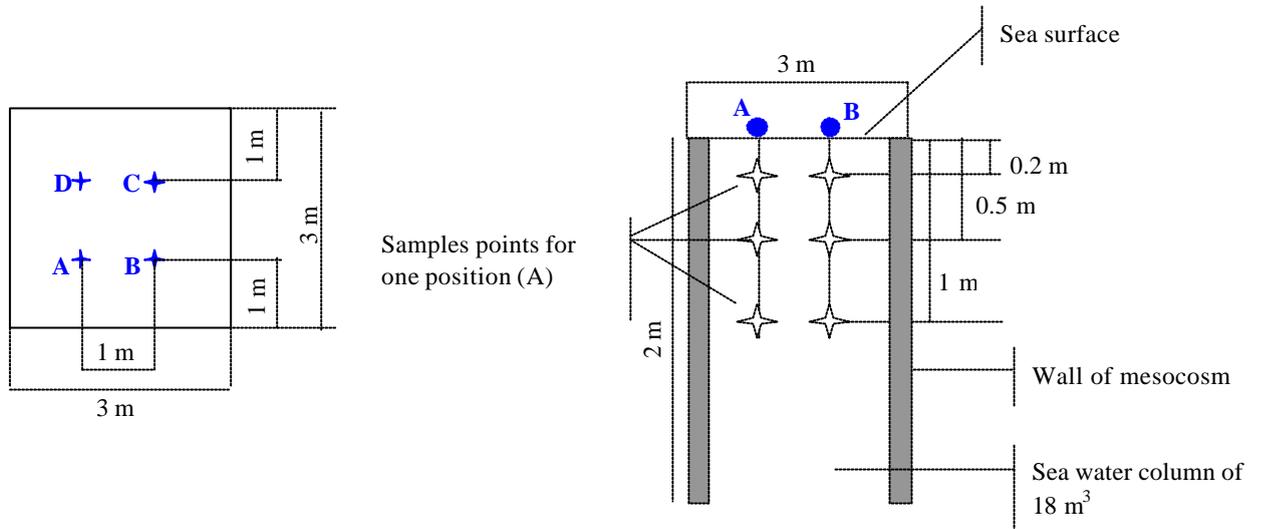
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Figure 1.



The 4 samples points inside a mesocosm (A, B, C et D).
 Top sight

The 3 depths at 2 samples points (A and B).
 Aside view

Figure 2.

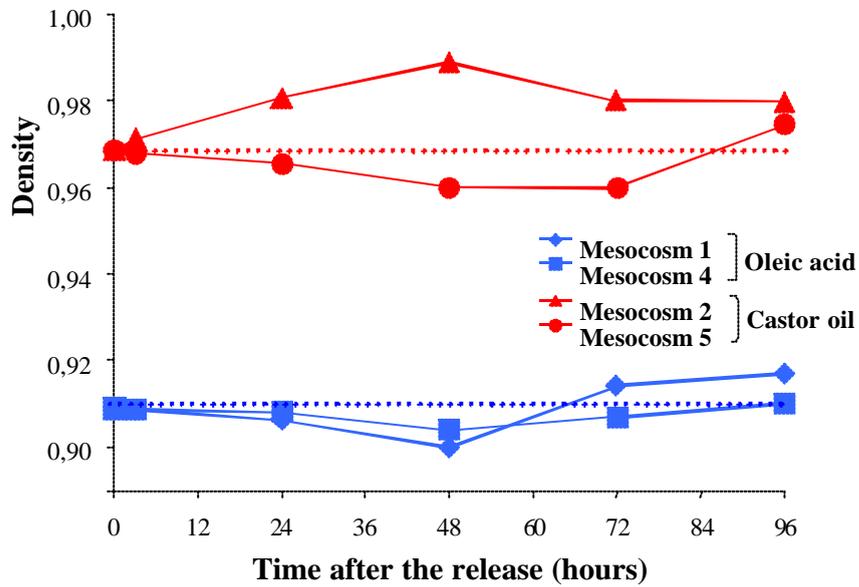


Figure 3.

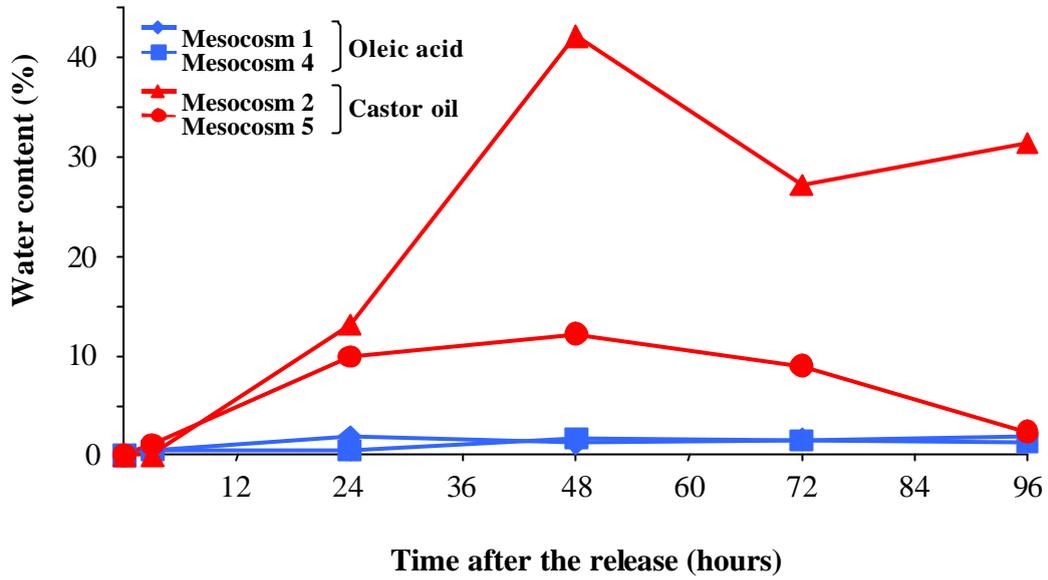


Figure 4

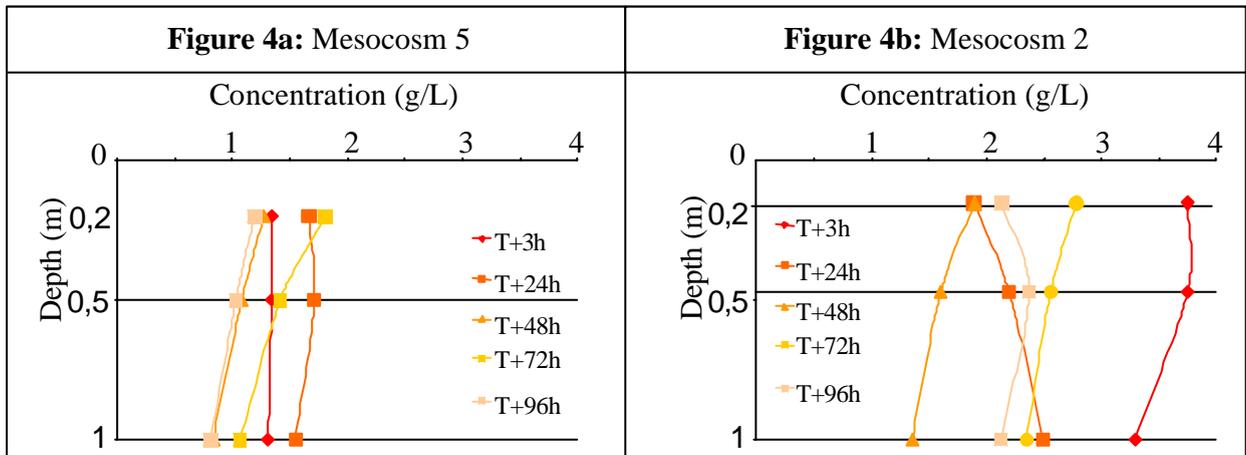


Figure 5.

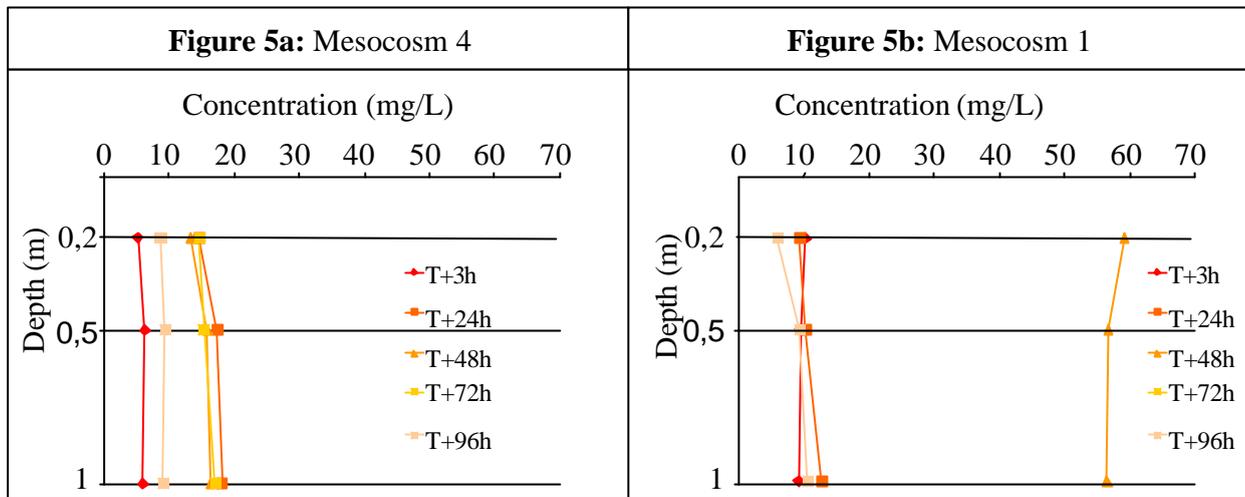


Table 1.

Properties	Castor oil	Oleic acid
CAS	8001-79-4	112-80-1
Melting point, °C	-10	0
Boiling point, °C	313	286
Vapour pressure, mmHg	5	0.016 (121 °C)
Vapour density (air=1)	Negligible	9.7
Density	0.95 g/cm ³	0.8946
Solubility in water	No soluble	No soluble
Viscosity	-	164.20 cP (150 °C)
Refractive index	1.48 (20 °C)	1.46 (11.8 °C)

Table 2.

	T ₀	T _{+3h}	T _{+24h}	T _{+48h}	T _{+72h}	T _{+96h}
Oil released	x					
Slick sampling		x	x	x	x	x
Water column sampling		x	x	x	x	x
Mesocosm clean up						x

Table 3.

Weather conditions	T _{+3h}	T _{+24h}	T _{+48h}	T _{+72h}	T _{+96h}
Sky	Rain	Sunny	Sunny	Sunny	Overcast
Wind (Km/h)	30 to 35	35 to 40	7 to 10	0	13 to 15
Beaufort Force Scale	5 Fresh breeze	6 Strong breeze	2 Light breeze	0 Calm	3 Gentle breeze
Air temperature (°C)	12	14	13	15	13

Picture 1.

