Natural dispersion of heavy oil products and weathered crude oils

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Abstract: The purpose of the work reported here has been to produce data on natural entrainment or dispersion of oil into the water column, from which an improved numerical algorithm for natural dispersion could eventually be developed. Weathering and entrainment experiments were carried out for 6 oil types, ranging from a light paraffinic to a heavy fuel oil (IFO 380). Entrainment events were simulated using an overhead trough, calibrated to breaking waves in an experimental weathering flume. Droplet size distributions were recorded by high speed photography. Auxiliary data from a laser-diffraction instrument were used to investigate the distribution of droplet sizes below the 100 um limit of the photographic method. The lognormal function provided a very good fit to the data. Maximum energy levels achievable with the experimental setup proved insufficient to produce entrainment for the heaviest crudes and petroleum products, thus reducing the amount of data available for analysis. In addition, even the heaviest oils did not achieve densities exceeding seawater during the 14-day experimental period, such that sinking of oil was not observed. To the extent that entrainment could be induced with the heavier oils, the entrained forms tended to be primarily large (> 10 mm) but irregular bits and pieces, rather than nearly spherical droplets. These irregular oil/emulsion particles tended to return rapidly to the water surface. Rise velocities of these larger emulsion globules were also measured and recorded. The results of this study will be used to develop an improved algorithm for natural dispersion of oil spilled at sea.

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Introduction

Natural dispersion of oil spilled at sea is a key process in determining the expected lifetime on the sea surface of a specific crude oil or petroleum product. How long the oil will remain on the sea surface is a key issue in evaluating alternative oil spill response strategies, determining the probability of impacting coastlines, and in estimating potential effects on sea birds and marine mammals in the path of the slick. For low-viscosity fresh oils, breaking waves tend to produce oil droplets in the water column, with increased energy, lower viscosity, and lower interfacial tension being associated with smaller droplet sizes. High energy input at this stage, as with a passing storm, may disperse the entire slick into the water column, such that only very thin oil sheens are seen after the storm passes.

For oil remaining on the sea surface and weathering, the viscosity increases due to evaporation and emulsification, and changes in the rheology become more important in determining the eventual fate of the oil. To the extent that the oil forms a plastic-elastic non-Newtonian emulsion, natural (or chemical) dispersion in the usual sense may not occur. In quiet weather such oils may be very nearly neutrally buoyant, and float at the water surface, and may be as much as 50 cm thick (ref. experience with Erika and Prestige fuel oil spills in Europe). In heavier weather, such oils will be more or less constantly over-washed, and driven subsurface in large patches or "carpets". These will eventually be torn apart into smaller and smaller pieces if enough energy is present, or may sink due to incorporation of organic or inorganic particles in the water column, or through interactions with bottom sediments in shallower waters.

The purpose of the work reported here has been to produce data on natural entrainment or dispersion of oil into the water column, from which an improved numerical algorithm for natural dispersion could be developed.

Methods

SINTEF has for the past 15 years used a saltwater meso-scale flume (*Figure 1*), in conjunction with laboratory scale and full field scale studies to characterize the weathering properties of oils spilled at sea (e.g. Daling and Strøm, 1999). In the present work the standard weathering methodology was augmented through the addition of an overhead trough of water to simulate the effect of breaking waves of different heights at discrete time intervals during long term (~ 2 week) oil weathering studies. The purpose was to record the droplet size distributions as a function of weathered state and oil properties.

First the plunging jet as an energy source for natural dispersion was validated against actual breaking waves, to establish the degree of similarity between droplet size distributions created by each process. Discrete single-event breaking wave tests using selected oils, and recording of droplet size distributions as a function of weathered state were carried out in a straight 5-meter long channel (Figure 2). Single breaking waves were created by a wave-maker recessed at one end of the channel. This reproduced the basic strategy of Delvigne and Sweeney (1988), and supplied a basis for calibrating the "plunging jet" methodology to be used during the long-term weathering studies.

Then long-term weathering experiments were carried out in the SINTEF elliptical oil weathering flume, actually a reconfiguration of the straight flume used in the first set of single wave breaking experiments (Figure 1). Using the flume in its elliptical configuration, with a plunging jet of water instead of the single breaking wave, allowed for repeated dispersion/over-washing experiment as the oil weathered over days and weeks.

Finally, statistical analysis of the resulting datasets was carried out to identify probability distributions and supply a dataset to eventually produce a functional relationship among the measured parameters characterizing the weathered oils and the observed droplet/particle size distributions. Oil droplet size distributions were measured using primarily high resolution, high speed photography with a Canon EOS 20D camera recording at 5 frames per second, with an image size of 3504 x 2336 pixels and a shutter speed of 1/1000 second. This methodology covers droplet sizes down to about 100 μm. A laser-diffraction instrument (Sequoia LISST-100X) was used to investigate *in-situ* droplet concentration measurements in the 2.5 – 500 μm size range, at concentrations from 5 – 750 μL/L.

Figure 1 Meso-scale flume at SINTEF for long-term weathering studies of oils and petroleum products.

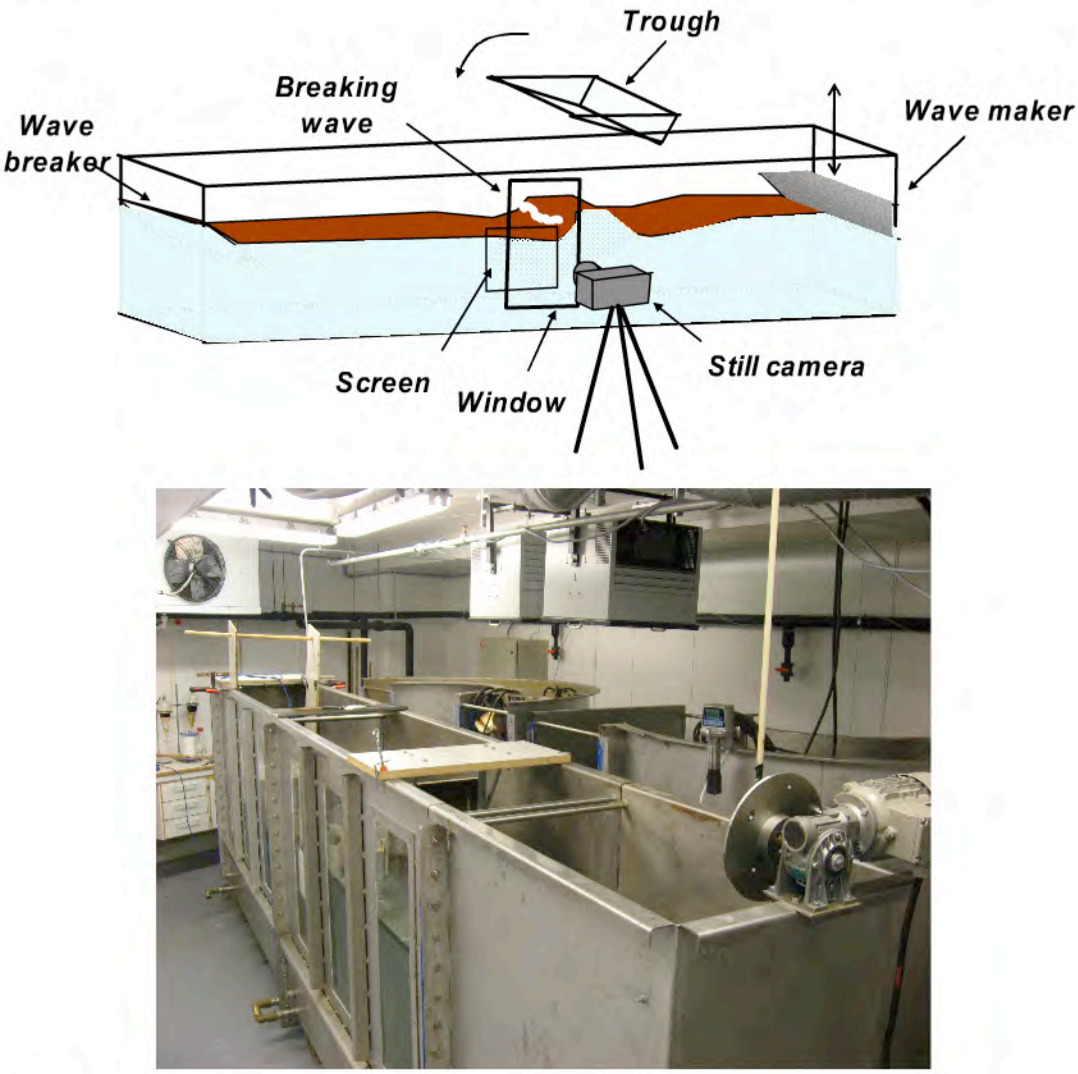


Figure 2. Sketch and photograph of the setup for the breaking wave experiments. In the photograph, the semi-circular ends of the flume in its elliptical configuration can be seen to the right of the straight flume section in the foreground.

Crude oils can be characterized in four categories: asphaltenic, naphthenic, paraffinic and waxy. The oils tested were selected to represent different categories of oils. In addition to the crudes, two heavy fuel oils (IF180 and IF380) were also tested (Table 1.)

Table 1 Oils used in the flume experiments

SINTEF ID		Oil type	Viscosity (cP, 13 °C)	Density (kg/m^3)
2007-0287	Crude Oil T	Naphthenic	113	0.900
2007-0260	Crude Oil N	Waxy	434	0.860
2006-1125	IFO 380	Heavy fuel oil	10100	0.963
2006-1060	Crude Oil G	Asphaltenic	614	0.941
2000-0594	IF180	Heavy fuel oil	5500	0.956
2007-0361	North Slope	Paraffinic	9	0.852

The meso-scale flume basin (Singsaas *et al.*, 1993) located at SINTEF is routinely used to study the weathering processes simultaneously. This methodology allows for the interactions among weathering processes to take place in a relatively realistic fashion, but under controlled conditions. Approximately 5 m^3 seawater circulates in the 10 meter long flume. The flume is located in a climate-controlled room (+20°C to – 20°C). Two fans placed in a covered wind-tunnel allow various wind speeds.

An oil sample (typically 9 L) was carefully released on the water surface. Surface oil/emulsion and water samples were taken frequently in the first hours of the experiment and at increasing intervals as changes in oil properties slowed down at longer weathering times. Samples of the surface oil/emulsion were taken with an aluminum tray and transferred to a 0.5 L separating funnel. After settling for 10 minutes in the climate room, free water was drained off.

Physical properties determined for all emulsion samples during the experiment included viscosity, water content, evaporative loss, and density. Yield stress, chemical characterisation (SARA analysis), FT-IR (Fourier Transform IR-spectroscopy), and GC-FID (Gas chromatography coupled with Flame Ionisation Detector) were also carried out on a limited number of samples.

The planned sampling schedule is given in **Error! Reference source not found.**. The plan was followed in the early stages of the experiments. As sampling intervals increased to several days, sampling have been adjusted to fit working hours. Some experiments have also been ended earlier than 14 days.

Plunging jet experiments were conducted at specific time intervals during the regular oil weathering tests, the first about one hour after test initiation. The wave generator in the weathering flume was shut down some minutes prior to the experiments to allow resurfacing of dispersed oil droplets, and the oil was confined behind a barrier inserted downstream of the test section to obtain a homogeneous oil slick below the plunging water jet.

All experiments were conducted with the plunging jet apparatus described previously in conjunction with the initial calibration experiments. The experimental conditions were varied from one test to the next, partly with the aim of obtaining a picture of the droplet cloud with sufficient quality for the subsequent digital image processing. The flume tests were conducted at two different water temperatures (5 and 13 °C). Most tests were conducted with artificial sunlight, but a few tests were made without solar exposure.

Results

Calibration experiments

The plunging jet test has been developed for use in oil droplet breakup tests to be performed in situ during long term weathering studies in SINTEF's weathering flume. The object of the calibration study was to establish a relationship between oil droplet breakup in these tests and in breaking wave tests. Calibration of the plunging jet to the breaking wave was carried out with moderately weathered Crude Oil T (150oC+) to avoid unwanted changes in the oil properties due to evaporation during the experiments. One set of experiments was made with water-free oil, while another set was made with a 50 % water-in-oil emulsion made up of the same oil. In all experiments, the water surface of the straight flume was covered with a 2 mm thick layer of oil or emulsion.
The wave generator was adjusted to produce two subsequent waves with a frequency of 65 cycles per second and 10 cm amplitude. With this setup, the first wave passed without breaking, while the second wave formed a spilling breaker in front of the observation window.

In order to determine the correspondence between the given wave amplitude and the free fall height in the plunging jet experiments, the water tray was mounted at different heights above the surface of the flume. In the experiments with water free Crude Oil T, two free fall heights were tested, 5 cm and 15 cm, while in the experiments with a 50 % water-in-oil emulsion, three heights were tested: 5 cm, 15 cm and 23 cm.

The droplet size distribution parameters determined in the various experiments are summarized in Figure 3.

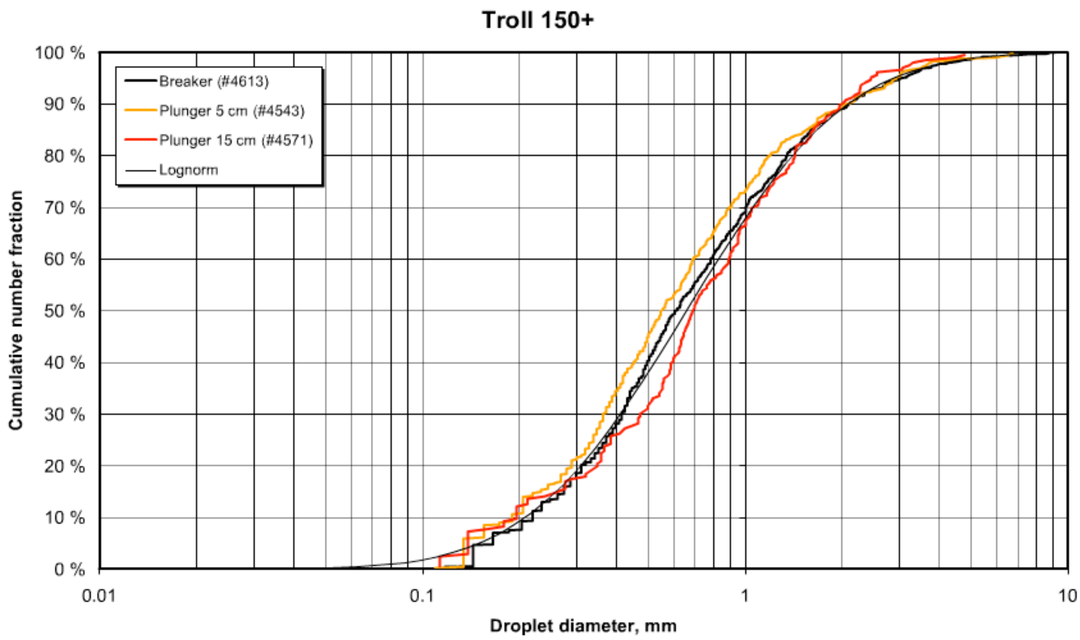


Figure 3. Plot of droplet size distributions obtained in the Crude Oil T 150°C+ experiments.

The resulting median droplet sizes are compared in Figure 4. In general, the experiments demonstrated that the plunging jet tests will generate droplet size distributions with the same character as obtained in the breaking wave tests – i.e. in both types of test, the droplet size distributions resembled log-normal distributions. Taking into account the experimental uncertainties, we conclude that droplet breakup experiments with plunging jets with 10 cm free fall height will produce droplet size distributions corresponding closely to those produced by breaking waves with about 10 cm amplitude.

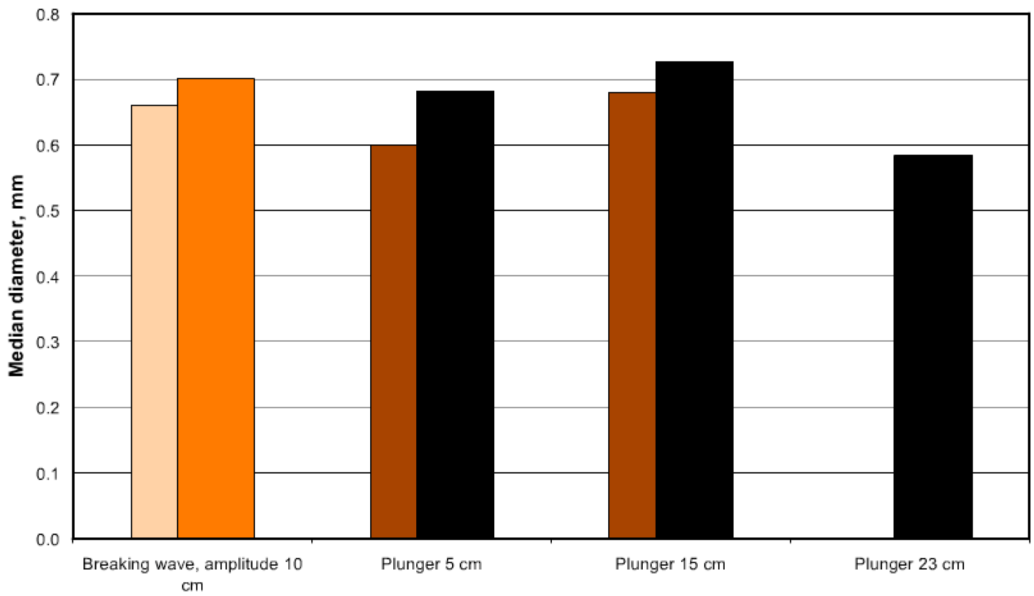


Figure 4. Comparison of median droplet sizes observed in the calibration experiments. Results from the water-free oil (lighter colors) are shown behind the results from the 50 % water in oil emulsion (darker colors)

Resurfacing rates for submerged oil

Observations from actual spills suggest that highly weathered oils can submerge, at least temporarily, below the sea surface. Submersion time is expected to be determined primarily by oil density and sea state. Water-in-oil emulsions have higher density than the parent oil and may tend to submerge more easily. However, as long as density of the parent oil is below the density of the ambient sea water (i.e. buoyant), emulsions formed with the same sea water will also be buoyant, but closer to neutral, unless sediment material becomes embedded in the oil.

In the weathering flume tests, lumps of emulsion were observed to form when a slick of weathered water-in-oil emulsion passed the breaking wave in the flume. Some simple tests were performed in order to investigate the potential for submersion of these lumps. The tests were performed by isolating a lump of emulsion formed, and displacing it to the bottom of the tank inside an inverted cup. By turning the cup right side up, the lump could be released, and its rise velocity recorded by video. Rise time and height were extracted from the video, and the rise velocity was calculated. The vales ranged between 12 and 13 cm/s for all such tests.

Measurement of small droplet (< 400 um) size distributions

Data were obtained with the LISST positioned in the flume, opposite the side at which the breaking wave occurred, at a depth of approximately 80 cm. The distance between the breaking wave and the measuring position represents about 45 seconds in circulation time, such that larger droplets would in general resurface before reaching the LISST. The measurements give an indication of the extent to which smaller droplets accumulate in the water column, representing a balance between entrainment of new droplets in the smaller size range, and eventual resurfacing (*Figure 5*). This figure shows the increase in concentration associated with droplets less than about 400 μm um in diameter, reaching a maximum at about 4 hours, and decreasing thereafter, reflecting the fact that smaller droplets are no longer created as the viscosity of the emulsion increases, at least at the energy levels available in these experiments. At about 4 hours the resurfacing of droplets starts to occur more rapidly than the introduction of new droplets through dispersion.

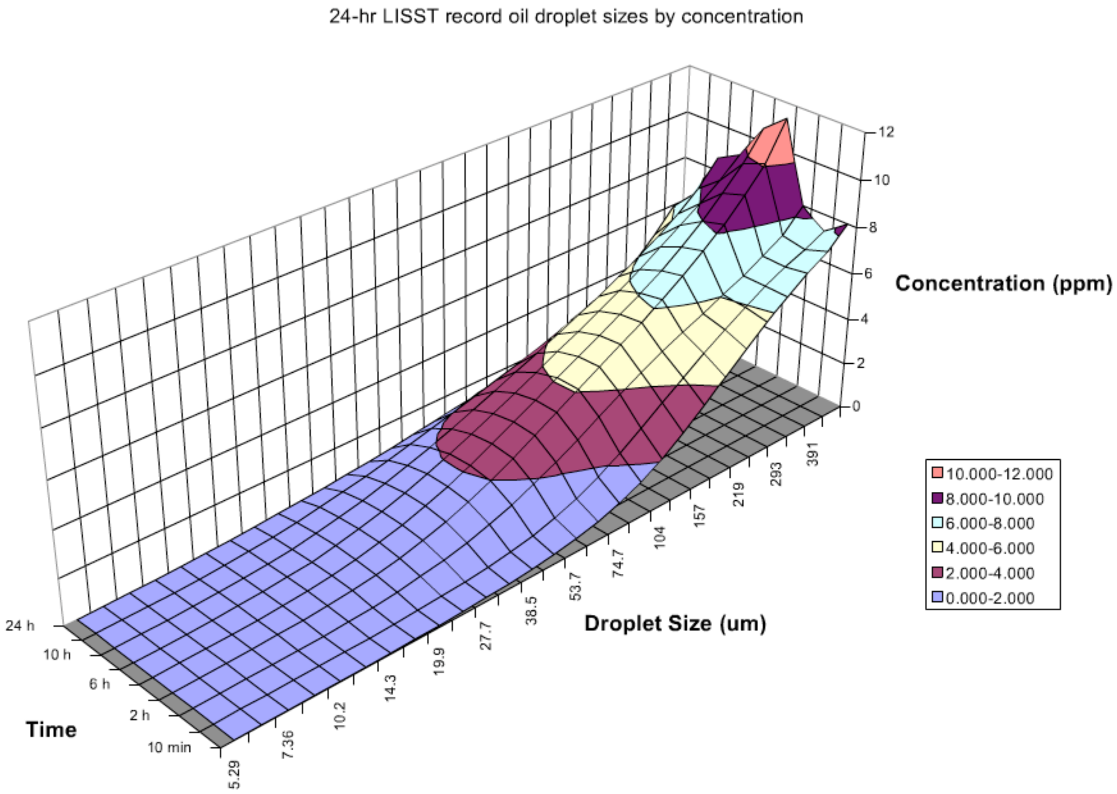


Figure 5 Changes in droplet size distributions over time during a 24-hour recording session with the LISST in situ. Maximum concentrations are recorded after 4 hours, after which time concentrations associated with droplets in the range 50 – 250 um are reduced.

Plunging jet experiments

Plunging jet experiments were conducted at intervals during the regular oil weathering tests, the first about one hour after test initiation.

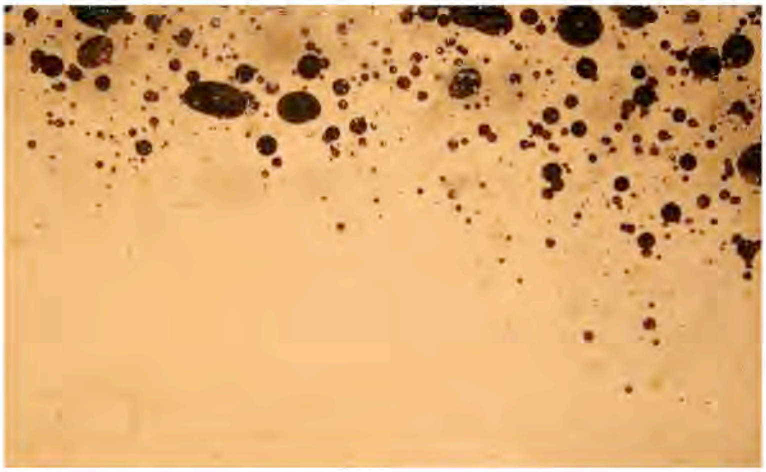
The film thickness of the confined oil layer differed from one experiment to the next since water-in-oil emulsions with densities approaching the density of sea water tend to form thicker oil layers than more buoyant water-free oil. The free fall height had to be increased from time to time to compensate for the increasing resistance to break-up of the oil film caused by increased viscosity and film thickness.

In the weathering tests with heavy fuel oils, IFO 180 and IFO 380, we were unable to obtain droplet cloud pictures for digital processing. In these cases, the plunging water jet resulted in large irregular oil globules with very brief submersion times, or more often the jet was unable to break through the oil layer at all. In general, we found that the energy level of the entrainment method used here was sufficient for cases with oil/emulsion viscosities below about 10 000 mPas. A higher energy methodology will be necessary for higher viscosities and thick emulsion layers.

The median droplet diameter and the logarithmic standard deviation were obtained from automated droplet counts performed by digital analysis of pictures selected from a sequence of pictures recorded at a rate of 5 per second. The pictures to be analyzed were selected by visual inspection of the series obtained in the experiment. A picture judged as the best suited for digital analysis was selected, and, in order to check that this picture was representative, two additional pictures were selected two frames before and after the best selection. A comparison among three such pictures is shown in Figure 6. Figure 7 shows the droplet number distribution obtained by combining the three data sets.

As Figure 7 indicates, the droplet size distributions obtained from the three frames tended to be virtually identical. In this case the median diameters ranged from 0.57 to 0.61 mm, and standard deviations from 0.36 to 0.38 in $\log_{10}$ units. The median diameter and standard deviation from the combined data was 0.59 mm and 0.37.

The droplet size data obtained from the digital image analyses contains the equivalent diameter of each identified object in the picture, presuming a circular shape, in addition to the length and width of the object in x- and y-directions (Feret's diameters, or maximum and minimum calipers). Most droplets in the medium to small size range are found to be close to circular, but some objects may represent two or more overlapping droplets. In the present study, a roundness criterion corresponding to a Feret's diameter ratio of $0.8 < R < 1.2$ has been used in order to eliminate objects that are formed by overlapping droplets. However, this criterion may also eliminate some of the larger droplets that may have an elongated shape. These droplets are normally few in number, and will not contribute significantly to the overall number distribution parameters.



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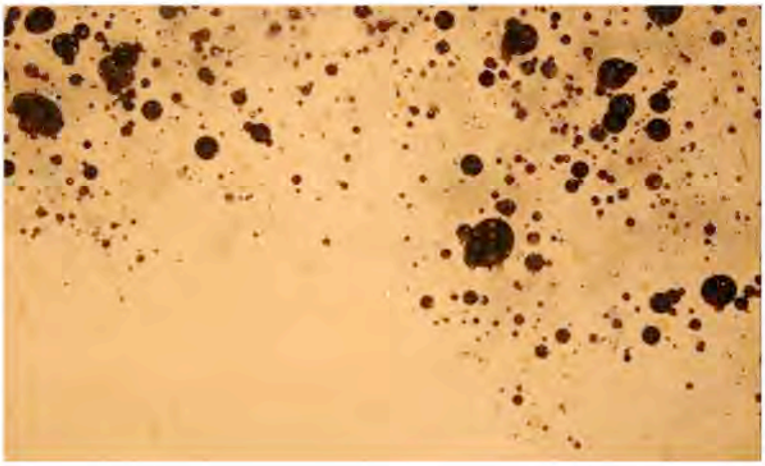

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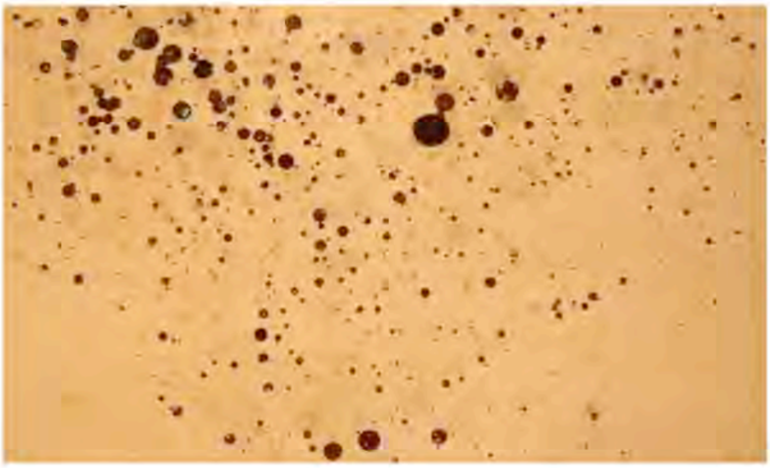

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Figure 6. Examples of pictures from plunging jet experiments with Crude Oil T at 13°C. Pictures of droplet clouds obtained in three subsequent pictures 1 hour after start of the flume test. Picture numbers are given to the right of each picture. Note that the picture sequence is obtained within a time period of only a few seconds .

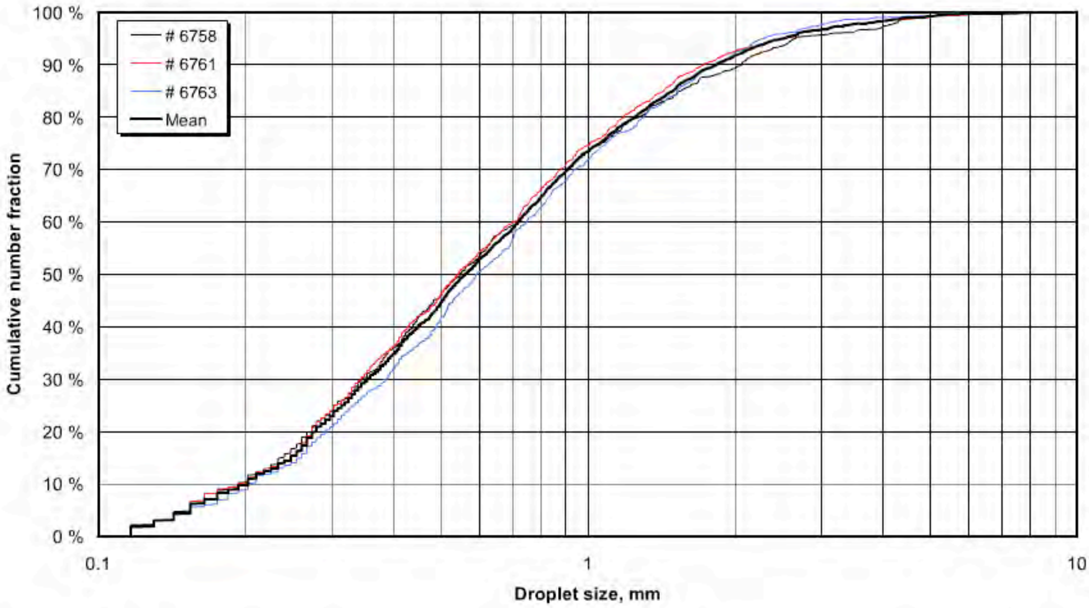

Figure 7. Droplet number distribution obtained from the three subsequent picture frames shown in Figure 6. The thick black line shows the distribution obtained from a combination of the three data sets.

Conclusions

Long term weathering experiments

- The weathering flume tests covered a wide range in oil types, from a light oil/condensate, via medium and heavy crude oils, to heavy fuel oils. However, after 14 days exposure in the weathering flume, the residues of the various oils were found to be quite similar in terms of density, with viscosity varying inversely with water content..

- None of the tested oils reached densities exceeding the density of the sea water in the flume, so the water-in-oil emulsions were buoyant in sea water throughout the 14 day duration of the experiments.
- Exposure to artificial sunlight was found to cause a significant increase in the viscosity of water-in-oil emulsions, compared to tests without solar exposure. This effect appears to be due to changes in the chemistry of the oil caused by photo-oxidation. Evaporative losses and water uptake were found to be practically identical with and without solar exposure. Moreover, different chemical analyses which were performed to detect possible changes in the chemical makeup of the oil related to photo-oxidation did not show any significant formation of polar components or other functional groups.
- The various oil properties determined during the long term flume experiments were found to correspond well with predicted oil properties for the whole 14 day duration. This conclusion is based on results from two of the tested oils (Crude Oil N and Crude Oil T), for which oil weathering predictions were available with SINTEF's oil weathering model (SINTEF OWM).

Natural dispersion experiments with plunging jet

- Droplet break-up could be obtained with the plunging jet until about 2 days after start of the weathering tests, or as long the viscosity did not exceed about 10 000 mPas. In order to reach this limit, the free fall height of the jet was increased to overcome the increasing resistance to breakup caused by the increasing viscosity and yield stress, and thickness of the oil layer. Above this limit, breakup could not be accomplished with the physical limitations of the available apparatus. For the heaviest oils used in the study, no droplet breakup data could be produced using the methodology applied here.
- The droplet size distributions obtained from the successful experiments showed a close fit to log-normal number distributions. The results from each test could therefore be expressed in terms of two distribution parameters, the mean logarithmic droplet diameter and the logarithmic standard deviation.
- Both parameters were found to vary within relatively narrow ranges, but trends were found in the data that indicate that the median droplet size correlates with fall height, film thickness and oil viscosity, while no clear trends were found for the logarithmic standard deviation.

The calibration study performed prior to the flume tests indicated that a one-to-one relation exists between the free fall height in the plunging jet tests and the amplitude of the breaking wave (half the wave height). The droplet size distribution data obtained from these experiments may thus be used to derive correlations for prediction of initial droplet size distributions generated in breaking wave events.

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