

# THE CONCENTRATIONS OF OIL IN SEA WATER RESULTING FROM NATURAL AND CHEMICALLY INDUCED DISPERSION OF OIL SLICKS

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## ABSTRACT

Results are presented on the factors relating to the dissipation of oil spills at sea, including evaporation, emulsion formation, spreading, and natural dispersion into the water column.

For Ekofisk oil, 20% evaporates in about 7.5 hours and, while emulsion formation is as rapid as for Kuwait crude, the resulting viscosity is low and insufficient to allow interference with the natural spreading and dispersion rates. Spreading has two components. One is controlled by surface tension-viscous drag forces and the other is wind-induced. Together they contribute to the two dimensional dissipation of the oil so that subsequent oil concentrations in the sea are of necessity, low. These concentrations were measured for naturally dispersing and chemically dispersed slicks. The chemically-dispersed slicks were of two kinds. One was previously weathered for three hours, the other was of controlled thickness and was dispersed immediately upon being laid. Resulting concentrations of oil in the sea are low and of short duration compared with those required to give observable effects in laboratory toxicity studies.

No significant deleterious effects were found to result from the dispersion of oil slicks at sea using low toxicity dispersant chemicals; also it was noted that, in any case, substantial quantities of oil can be expected to enter the sea before oil recovery operations can be mounted.

## INTRODUCTION

The United Kingdom response capability for oil spill clearance is based on the use of modern low toxicity dispersants. Procedures have been worked out and the necessary equipment developed for operations on beaches, in sheltered waters, and on the open sea. Adsorbents and other mechanical oil recovery devices can be useful in sheltered waters and efforts are currently being made to extend their use to the open sea situation. At the present time, however, in the absence of clearly-proven recovery devices, the dispersant approach is considered the only valid one for open sea use around our coasts.

This paper presents results obtained from experiments carried out at sea on the natural and chemically-induced dispersion of oil slicks. The aim was to determine the resultant concentrations of oil in the water column below the area affected by the slick. The spreading and bodily movement of the oil were studied because these phenomena extend the area of sea surface covered by oil and hence the volume of sea which will be affected by the slick. The greater the area of sea affected the smaller will be the resultant concentrations of oil in the sea. Evaporation of volatile fractions will prevent these fractions from entering the sea water and the extent to which this occurs is also assessed. Again the formation of water-in-oil emulsion which increases the viscosity of slicks will tend to limit spreading and possibly

evaporation which could lead to greater concentrations, because a smaller area is affected. Alternatively, the rate of natural dispersion into the sea could simply be reduced by increase in slick viscosity so that no sensible increase in concentration would result.

Such considerations are the subject of an extended study presently underway at Warren Spring Laboratory. The results presented here were obtained with Ekofisk and Kuwait crude oils; while of a preliminary nature, they nonetheless quantify the concentrations to be expected from both natural and chemically-induced dispersion of such oil slicks. These concentrations are compared with those required to give observable results in laboratory tests of oil toxicity.

## Experimental

Experiments were conducted in the North Sea in areas chosen after consultation with the Nature Conservancy Council and U.K. Fisheries Departments as being acceptable from the fishery and wildlife point of view. Two methods of releasing oil onto the sea surface were employed depending upon the processes studied. Natural processes leading to the dissipation of oil were investigated by releasing 0.5 ton amounts of crude oil and observing the behaviour of the resulting slicks as they weathered naturally. Chemical dispersal processes were also examined by treatment of oil slicks which had been allowed to weather naturally. In addition, some slicks were discharged and treated with chemical under controlled conditions.

In order to obtain movement and spreading data for oil it was decided to release it instantaneously. This was achieved by containing the oil in a polythene sleeve 4 m in diameter supported by a cylindrical frame. A derrick on the discharge vessel was used to suspend the frame in the sea so as to give 0.5 m of freeboard. The sleeve was weighted at the bottom to ensure that it hung vertically in the water. About 0.5 tons of Ekofisk crude oil was pumped onto the sea surface within the confines of the sleeve. To effect release of the oil, the frame and sleeve were raised above the sea surface by the derrick. The vessel then moved slowly astern to avoid mixing the oil into the sea water.

The position of the slick and the extent to which it spread was observed from a survey ship which circuted the slick continuously whilst plotting its course by means of a Decca Navigator (accurate to within 50 meters). A subsurface float was launched into the sea to provide continuous current velocity data. The movement of this float had previously been verified in terms of known tidal velocities. The position of this float (an observable mast was fitted) was measured relative to the vessel using a Barr and Stroud optical range finder type FT37 in conjunction with a bearing compass. The position of the ship was known from the Decca Navigator, and therefore the position of the float could be plotted on the Decca chart as a function of time,

giving the velocity of the current. A surface drift card consisting of card board  $1\text{m}^2 \times 1.2\text{mm}$  thick, sealed in 0.25 mm polythene sheet was also launched to determine the extent to which such a card could be used to simulate oil slick movement.

Local wind speed and direction was monitored throughout the experiment using a cup-wheel anemometer and direction indicator mounted on the observation vessel. Oil samples were taken from the slick at regular intervals using a small inflatable rubber dinghy. Surface layers were scooped up with an open neck jar and the contents transferred to separating funnels to enable the free water to be run off. The oil, or water-in-oil emulsion, was then placed in sealed glass containers.

Subsurface water samples were obtained at depths varying from 2 to 15 meters using Knudsen marine sampling bottles. These bottles, constructed from stainless steel are fitted with spring loaded caps which are closed at the sampling depth by sending a messenger down the supporting wire. The open bottles were clamped onto 4 mm diameter steel wire rope and lowered over the side of the dinghy into clear water, to depths greater than those for which samples were to be taken. The dinghy was then maneuvered into the slick and at the chosen position the bottles were raised to the required sampling depth and the messenger was sent down the wire to effect closure. The dinghy returned to clear water before the bottles were taken on board. The contents of the bottles were transferred to glass Kilner jars which were sealed and returned to the laboratory for analysis.

Oil samples were subjected to water content determination using the method of Dean and Stark. Samples were heated under reflux with toluene and the resulting water/toluene azeotrope allowed to distill into a graduated receiver where the water separated to form the lower layer. The oil fractions were then recovered by distilling the toluene under nitrogen at reduced pressure. The recovered oils were subjected to gas liquid chromatographic analysis using a Pye 104 gas chromatograph equipped with dual flame ionisation detectors and 1 meter, 0.5 cm O.D. columns packed with chromosorb G 80-100 mesh acid washed, dimethyl dichloro silane treated and coated with 10% by weight silicone gum OVI. The oven was temperature-programmed at 5 degrees per minute from 75 to 300°C.

The water samples were analysed for oil content by fluorescence spectroscopy. The volume of each sample was measured before being extracted with a total of 25 ml of spectroscopic grade cyclohexane. The extracts were dried with anhydrous sodium sulphate and the fluorescent emission intensity at 395 nm was measured using a Farrand spectrofluorimeter at an excitation wavelength of 340 nm.

Subsequently, a second 0.5 ton slick of Ekofisk crude oil was released and after a period of three hours the oil was dispersed with a low toxicity dispersant chemical using spraying equipment developed by WSL.<sup>2</sup> The equipment, which is suitable for installing on tugs and other sea going craft, is widely used in the U.K. The main feature of the equipment is the method of agitating the oil and dispersant by utilising the power of the spraying vessel when moving. Two sets of three wooden surface breaker boards are towed in line abreast some six meters behind the dispersant spraying booms which are located on each side of the vessel. These units, when towed at speeds varying from 4 to 10 knots, harrow the water surface, mixing the treated oil into the upper 25 cm of water.

As the oil slick was dispersed, samples of water (30 cm depth) were taken from a rubber dinghy following in the wake of the spraying vessel. The samples were returned to the laboratory in sealed containers and analysed for oil content as before.

Further experiments were conducted to determine the rate of dilution of chemically-dispersed oil under practical conditions at sea. The apparatus used was designed previously by WSL for routine dispersant efficiency testing. It has not been published however so a brief description is given here in relation to the present work.

In order to ensure that all the oil was treated, the slick was laid immediately ahead of the dispersant spray. This was achieved by spraying Kuwait crude oil at a rate of 10 gallons per minute from a wide angle flat jet nozzle mounted on a boom projecting about three meters from the side of the spraying vessel. The position of the nozzle was adjusted so that as the vessel traveled in a straight line at a speed of 4 knots, a uniform slick of oil of known width and thickness was deposited onto the sea surface.

Dispersant was sprayed from a second nozzle positioned behind the oil nozzle and at such a height above the sea surface that the dispersant spray covered all of the oil. The experiments were conducted using the surface breaker boards to agitate the oil/dispersant mixture. After several minutes, spraying was stopped and water samples were taken at a depth of 1 meter below the surface for as long as dispersed oil was visible in the water. These samples were also analysed for oil content.

## RESULTS

### Natural processes

**Evaporation.** Evaporation causes major changes to the physical nature of crude oil spilt at sea, particularly during the early stages. The rate of evaporation will be largely dependent on the vapour pressure of the oil at ambient temperature, but other factors will play a significant role—in particular, wind speed and sea state. Spreading would be expected to increase evaporation rate, but spreading may be checked to some extent by emulsification of the oil. Table 1 summarises the distillation characteristics of Ekofisk crude oil; notably that some 53% by weight of the oil boils below 350°C. Evaporation would therefore be expected to be quite rapid.

During the period of the trial, the sea temperature remained steady at around 11.6°C and the average air temperature was 18°C. The average wind speed was 12 knots gusting to 18 knots with a sea state of 3-4 on the Beaufort Scale. Table 2 shows the amounts of oil lost by evaporation over a 7.5 hour period. Oil samples were taken from the main body of the slick and were found to be heavily emulsified with water.

The surrounding thin film of oil which might have lost a greater proportion of volatiles was not sampled. After 3 hours most of the light ends were lost, there being no evidence of any hydrocarbons below C9. After 7.5 hours, all hydrocarbons up to C11 were lost and the amounts of C12 and C13 hydrocarbons were considerably depleted, total losses due to evaporation being about 20%. Thus, the emulsification which did occur (see next section) appears not to have seriously affected the rate of evaporation loss.

Table 1. Distillation characteristics of Ekofisk crude oil

Boiling range °C	Percentage wt.
5-100	7.0
100-160	11.1
160-250	15.1
250-350	19
350	46.5

Table 2. Evaporative losses for Ekofisk crude oil with time

Time hours after spill	Percentage wt. Loss
0.5	7
3.0	11.5
7.5	21

**Emulsification.** One of the major processes which leads to the persistence of crude oil on the surface of the sea is the formation of water-in-oil emulsions. The ease of formation and stability of these emulsions can vary according to the nature of the oil. Kuwait crude is known to be capable of producing very stable emulsions often referred to as "chocolate mousse." Stabilisation appears to be due to the components in the non-volatile residues from crudes, in particular asphaltenes. Ekofisk crude has a relatively low asphaltene content (0.03% by weight) compared with Kuwait crude (1.45% by weight), and one would therefore expect it to be less likely to form a stable emulsion. Table 3 gives the water content of the oil with time over a seven hour period.

Some 72% by volume of water was absorbed in the first 80 minutes, after which a slower rate of absorption was observed; a maximum water content of 83% being achieved in 7½ hours. These absorption rates will of course be dependent to a large extent on the degree of surface agitation afforded by wind and waves. The final emulsion was fluid in character and had a viscosity of 1,000 centipoise at shear rate of  $10\text{s}^{-1}$  compared with 3,600 centipoise for a Kuwait crude oil emulsion of similar water content.

The central slick of emulsion rapidly broke up into patches of about 1-5 cm diameter and, after some 21 hours, these were further broken down into small flecks 5-10 mm diameter interspersed with an iridescent sheen. In

**Table 3. Percentage water absorbed by Ekofisk crude oil with time on sea surface**

Time hours	Percentage water absorbed V/V
0.5	35
1.3	72
3.0	77
3.8	79
7.4	83

contrast, Kuwait (e.g., *Torrey Canyon*) emulsions are much more persistent. It would appear that while Ekofisk oil will take up just as much water as Kuwait oil, the resulting emulsion does not interfere with dissipation processes to the same extent.

**Movement.** The size of the Ekofisk slick as plotted on the Decca chart as a function of time is shown in Figure 1. The courses taken by the surface drift card and the subsurface float are also shown. During the period of observation, the wind blew from southeast-by-east (170°) at about 12 knots and the current, as indicated by the subsurface float was in the direction east-northeast (66°) at a rate of about 1 knot in agreement with published data for the area. The surface drift card tended to move with the centre of the slick.

The measured drift, current and wind velocities are given in Table 4. Vector triangles constructed from the observed drift and current enable the wind contribution to be calculated (Figure 2). The effective wind vector so calculated is 2.8% of the actual wind vector for the downwind edge of the slick and 1.0% for the drift card. These values are somewhat lower than those previously reported for oil slicks and drift cards.

However, the effective wind vector, whatever its exact magnitude (1-4%) is only one contributor to the movement of the oil and the current vector must also be considered. The oil moves as a vector sum of the whole current vector and the effective wind vector. It should also be noted that the "spreading" of the oil is greater in the wind direction than at right angles to it.

**Spreading.** Models have been suggested for predicting spreading rates for oil slicks at sea. Perhaps the best known is due to Blokker<sup>1</sup> whose model assumes that the instantaneous rate of spreading is proportional to the prevailing slick thickness. A more detailed treatment due to Fay<sup>3</sup> is also available in which three distinct spreading phases are identified:

1. an initial phase in which spreading is caused by gravity and controlled by inertial resistance forces
2. an intermediate phase in which gravity and viscous drag forces predominate
3. a final phase controlled by surface tension and viscous drag forces

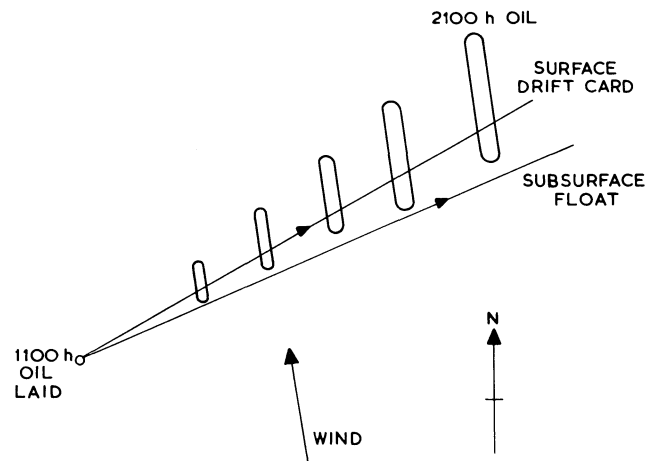


Figure 1. Chart showing drift positions of oil, drift card, and subsurface float

**Table 4. Drift data**

Object	Average wind direction degrees	Average wind speed knots	Average direction object degrees	Average speed object knots
Subsurface Float	170	12.7	066°	1.1
Surface Drift Card	170	12.7	060°	1.1
Downwind edge of slick	170	12.7	050°	1.2

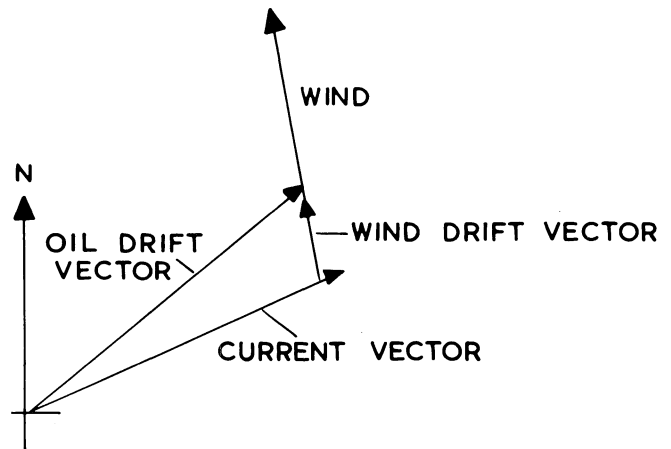


Figure 2. Velocity vector triangle for downwind edge of oil slick

It can be shown that Blokker's treatment is essentially the same as phase 1 of Fay's. However, it seems unlikely that this type of gravity spreading will be encountered in practice except in the case of massive instantaneous discharges. For small spills such as the one in this experiment, phase 3 spreading would be expected to come into play almost immediately. Table 5 gives the major and minor dimensions of the slick with time.

This data is plotted in Figure 3 and gives good agreement using Fay's equation for phase 3 spreading:

$$l = K \left\{ \frac{\sigma^2 t^3}{e^2 v} \right\}^{1/4}$$

- where l = slick dimension
- σ = spreading coefficient
- e = density of water
- v = kinematic coefficient of viscosity
- t = time
- K = constant

Where K = 1 for the minor axis and 10 for the major axis. It is suggested that the high rate of spreading of the major axis is due to wind assistance, whereas the minor axis is the true spreading rate.

It is not clear what the effect of different wind speeds would have on the value of K, but Fay plotted spreading data for a number of accidental spillages, all of which were found to lie on or below the line

$$l = 10 \left\{ \frac{\sigma^2 t^3}{e^2 v} \right\}^{1/4}$$

This further confirms the view that for most types of oil spill, the ultimate extent of spreading can be predicted using the surface tension-viscous drag model.

**Table 5. Dimensions of Ekofisk crude oil slick with time**

Time hours	Major dimension metres	Minor dimension metres
1.0	—	28
1.25	533	—
2.84	1778	—
3.40	—	91
4.25	—	270
4.33	3467	—
5.25	3556	—
6.84	3823	—
10.17	5334	—

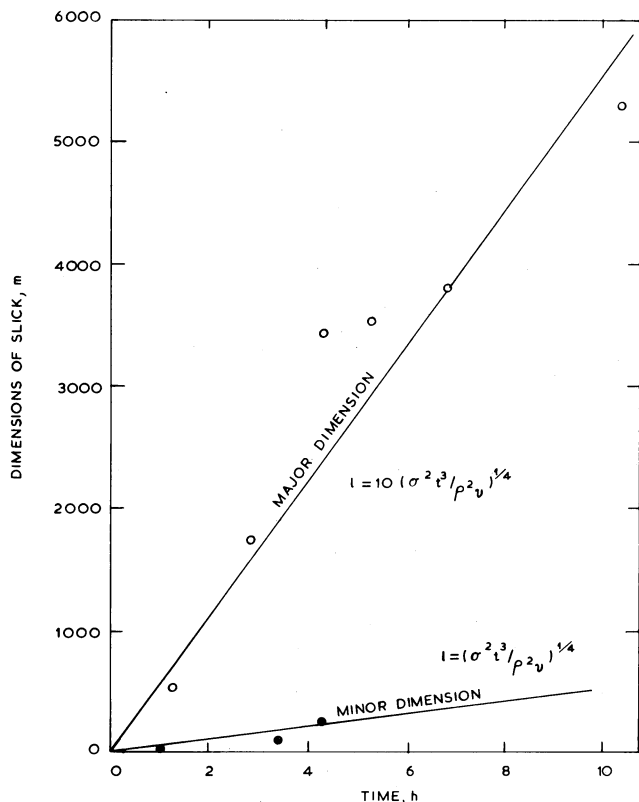


Figure 3. Measured dimensions of Ekofisk crude oil slick with time

**Dispersion.** Table 6 shows the concentrations of oil measured beneath the main slick at depths ranging from 2 to 15 meters. These results give a flexed linear relationship, showing a comparatively rapid decrease in concentration down to 5 meters depth followed by a slower decrease to background at 20 meters. The central cone of water in oil emulsion, under which samples were taken, was estimated to be some 2.3 km long and 30 m wide eight hours after being laid. Taking an average concentration of 1.42 ppm for the top 5 m of water under this part of the slick, the amount of oil dispersed is 0.21 tons (i.e., 42% of the total amount discharged). This estimate may be considered to be somewhat conservative, bearing in mind that the central cone was surrounded by a thin film, (less than 0.3  $\mu\text{m}$ ) extending over a much larger area (1.6 km<sup>2</sup>).

### Chemical dispersion

During this experiment with Ekofisk oil winds were very light, 1–3 knots corresponding to a sea state of 1 on the Beaufort Scale. Detailed spreading

data for the slick was not obtained but applying the phase 3 equation of Fay and assuming that  $K = 1$  in the absence of wind, the slick would be expected to cover an area of 20,000 m<sup>2</sup> after three hours. Furthermore, the calm conditions prevented the oil from emulsifying with water so that it is reasonable to assume that spreading was fairly uniform, giving an average film thickness of 27  $\mu\text{m}$ . If this oil were completely dispersed into the top 30 cm of sea water, the maximum concentration of oil would be 75 ppm. The average concentration of oil found in the top 30 cm was considerably below this, the maximum concentration being 18 ppm. Further experiments were carried out with Kuwait crude oil at experimentally controlled slick thickness, using the fan jet nozzle arrangement previously described, to determine the rate at which chemically-dispersed oil is diluted. Here, slicks of thickness up to 1 mm were produced so as to give initial high concentrations of oil in water. Maximum possible concentration in the top 1 m for a 1 mm slick would be 1,200 ppm. Wind speeds on this occasion were of the order of 8–10 knots, with a sea state of 2–3. The observed concentrations of oil in the water samples (1 meter depth) are given in Table 7. After about 30 minutes, sampling became difficult since the dispersed oil was no longer visible to the naked eye. However, the results illustrate that even under moderate sea conditions oil concentrations fall rapidly to very low levels.

**Table 6. Oil concentrations beneath the main slick with time**

Time after spill, hours	Depth metres	Oil Concentration under edge of main slick ppm	Oil Concentration under centre of main slick ppm
½	2	2.49	2.03
1½	2	2.22	0.85
3	2	1.15	0.79
4	2	0.94	3.95
8	2	1.88	1.63
8	5	0.17	0.19
8	10	0.10	0.07
8	15	0.08	0.07
11	5	0.02	0.04
11	10	0.02	0.02
11	15	0.02	0.03
21	2	0.59	1.49

**Table 7. Concentrations of Kuwait crude oil in water with time**

Time after spill, minutes	Concentration of Kuwait crude oil in ppm in the upper metre of water		
	Run 1	Run 2	Run 3
0	34.4	24.2	0.85
1		15.8	
2	47.8		8.7
2.5		12.2	
5		9.4	
7	17.8		3.5
10		5.2	
15			1.7
18	1.9		
25		4.2	
40	0.8		1.35
50		1.9	
80			1.5
100	2.2	0.8	

**Environmental impact of naturally and chemically dispersed oil**

The above data showing the maximum concentrations which arise from the chemical dispersion of slicks and the rate at which the oil is diluted serve to put toxicity data into perspective. Table 8 shows estimated continuous concentrations of oil components likely to produce mortality for different classes of organisms.<sup>4</sup> If, as is normally assumed, these components are the smaller aromatic hydrocarbons, then the known composition of Ekofisk and Kuwait crude oils enables the corresponding lethal concentrations for total oil to be calculated as shown in Table 8. These latter concentrations are seldom reached in respect of single spills on their subsequent treatment but in any case are subject to rapid dilution to safe levels. It should also be borne in mind that most of the toxic aromatic components of crude oil occur in the volatile fractions and consequently may be expected to readily evaporate from a spreading slick.

It may be argued that although persistent high concentrations of oil may be required to produce mortality, much lower levels of soluble fractions may give rise to sub-lethal effects, particularly to surface water organisms such as plankton. Once again, however, chronic long-term concentrations are being considered. There is no reason to believe that such low levels will be significantly more persistent than those for lethal effects in the case of a chemically dispersed slick. However, if oil remains on the surface of the sea for an extended period, low concentrations of oil arising from natural dispersion may persist for the lifetime of the slick.

**CONCLUSIONS**

This paper has been concerned with assessing the likely environmental impact of oil slicks dispersed at sea. It has been shown that evaporative losses are extensive and related in a simple way to the boiling point profile of the oil in question in spite of substantial emulsion formation. Evaporation is probably promoted by the rapid spreading of the oil on the sea surface. This spreading has been shown to follow an equation appropriate for surface tension-viscous drag forces. Spreading and bodily movement of the slick under the action of wind are closely related and it has been shown that this equation can be simply modified to take account of wind induced spreading.

Spreading by surface tension and wind forces results in a substantial two-dimensional dissipation of the oil such that when it is subsequently

carried into the body of the sea, the maximum possible oil concentrations likely to occur there must be low. If dispersants are used, initial surface water concentrations are higher than would occur if the slick dispersed naturally, but these concentrations decrease rapidly.

The duration of sensible oil concentrations is less for chemically dispersed slicks than for naturally dispersing slicks. In the latter case the correspondingly lower concentrations are likely to be present for the duration of the slick. Such concentrations as do occur are very much less and persist for very much shorter times than those required to kill test organisms in the laboratory. With the exception of the small percentage of water soluble components, included in the seawater oil analyses, the composition of the oil in the sea is thought to be the same as for the original oil, less those volatile fractions which have evaporated. Thus, many of the more toxic components probably do not enter the sea at all.

We conclude, therefore, that at sea no significant effects on marine life are likely to occur as a result of dispersing oil slicks. We note also that in the case of Ekofisk and similar oil, at least a substantial fraction of the oil will have naturally dispersed into the sea in any case before a recovery operation could be mounted.

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**Table 8. Estimated concentrations of oil components and crude oils expected to cause mortality to different marine organisms**

Class of Organism	Estimated continuous concentration (ppm) of oil components expected to cause mortality	Estimated continuous concentration (ppm) of Ekofisk crude oil expected to cause mortality	Estimated continuous concentration (ppm) Kuwait crude oil expected to cause mortality
Larvae (all species) some phyto-zoo plankton	1	20	25
Crustaceans (lobsters, crabs etc.). Other invertebrates (worms etc.)	1-10	20-200	25-250
Fish bivalves (oysters, clams etc.)	1-50	200-1000	25-1250
Gastropods (whelks, winkles etc.)	10-100	200-2000	250-2500

