

FOREWORD

Marine contamination by petroleum, whether by natural seepage or by spills from ships at sea, by accidents in harbour or at offshore installations or by atmospheric or terrigenous input is by no means a new or rare phenomenon. In recent years however, the problems have been highlighted not only by the increased utilisation and marine transport of oil but also by a number of spectacular accidents which have raised questions about possible effects on the ecosystem. A number of detailed studies have been carried out in an attempt to answer these questions. The demands for such knowledge have been further increased by the various questions raised as a result of expansion of offshore exploration and exploitation for oil, particularly in environments hostile to these operations, in regions as far apart as the northern North Sea and the coast of Alaska.

Consequently, diverse aspects of the problem are being studied in several parts of the world by chemists and biologists who are often asking the same questions but using different approaches and sometimes producing conflicting views. Against this background, it seemed timely therefore to bring together a group of scientists from university, industry and government, actively engaged in such work, to examine and discuss common problems relevant to petroleum hydrocarbon contamination of the marine ecosystem and so a Work-

shop was sponsored by the International Council for the Exploration of the Sea, and held in Scotland at Aberdeen in September 1975.

The Workshop considered methodology, occurrence and fate in the environment, and effects on the ecosystem of petroleum hydrocarbons in the sea. Most of the papers presented and updated where necessary, are brought together in the present volume together with an edited version of the recorded discussion that followed each session. Of necessity, the reportage of the discussion is very brief although the proportion of time available for discussion compared favourably with that set aside for formal presentation of the papers. In preparing the discussion reports, the editors were assisted in particular by Dr R. Hardy, Dr R. Johnston, Mr P. R. Mackie and Dr I. C. White, and by comments from several contributors.

No attempt was made to produce specific recommendations but a study of the papers in this volume does give a clear indication of several lines of research which must be followed up before an adequate understanding can be reached of the effects of petroleum in the sea and it is evident that widespread monitoring operations will be fully effective only when the basis of our knowledge has been thus extended.

A list of participants to the workshop may be found in Appendix I.

A. D. MCINTYRE
K. J. WHITTLE

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THE NATURAL AND CHEMICAL DISPERSION OF OIL IN THE SEA

D. CORMACK and J. A. NICHOLS

Department of Industry, Warren Spring Laboratory, P.O.Box 20, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2BX, U.K.

The contribution of dispersion to the natural fate of oil slicks at sea is considered in relation to wind and wave conditions. Data are presented on the concentrations of dispersed hydrocarbons at various depths beneath crude oil and refined oil slicks. Estimates are given of the maximum amount of oil likely to be dispersed naturally. The role of chemicals to enhance oil dispersion is discussed and the equipment used in the U. K. to treat oil slicks at sea is described. Data are presented, showing the rapid rate of dilution of chemically dispersed oil to background levels under relatively calm sea conditions.

INTRODUCTION

Natural surface-active components of crude oil tend to promote water-in-oil rather than oil-in-water dispersions, but under open sea conditions, the latter may be a significant parameter governing the ultimate fate of oil slicks.

A working party set up by the U.K. Ministry of Defence (Navy) conducted trials on the open sea in 1970-71 to examine this and other factors contributing to the fate of oil at sea. One hundred tonne quantities of Kuwait crude oil (s.g. 0.87) were discharged onto the sea, and subsurface water samples were taken from underneath the slicks at various depths over a period of 24 hours. The samples were found to have oil contents ranging from 0.01-0.02 µg/ml with some as high as 0.4 µg/ml. Taking 0.1 µg/ml as an approximate average value for the top five metres of water over the area covered by the slick, they estimated that some five per cent of the oil was removed from the surface. (Anon. 1973).

Following the Arrow incident in which some 6000 tonnes of Bunker C fuel oil (s.g. 0.97) were spilt, Forrester (1971) investigated its physical dispersion in terms of particle size distribution and diffusion through the water. The size of particles ranged from 5 to 100 µm. Oil was detected at depths down to 80 m and, as would be expected, the greater the depth, the smaller the particles.

A spillage of Arabian light crude (s.g. 0.85) into shallow, turbulent water in Saudi Arabia, (Spooner, 1970) resulted in dispersed oil concentrations of 50 µg/ml.

NON-PERSISTENT OILS

In 1973 Warren Spring Laboratory investigated the fate of non-persistent oils, defined as those petroleum

products obtained from crude oil in the refinery processes and having boiling points in the range 30 to 380°C. Attempts were made to determine the relative contributions of evaporation and dispersion to the removal of the oil from the surface of the open sea. Fourteen-tonne slicks of leaded gasoline (boiling point 30-205°C s.g. 0.72) and heavy gas oil (boiling point 200-360°C s.g. 0.85) were laid and subsurface water samples were taken in the contaminated area.

Knudsen marine sampling bottles were used to obtain water samples. 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 3/16 inch diameter galvanised steel wire rope and lowered over the bow of the sampling vessel into clear water to depths greater than those from which samples were to be taken. The vessel was gently manoeuvred into the slick and at the chosen position the bottles were raised so that the uppermost one was 1.5 m below the surface and the messenger was then sent down the wire to effect closure. The bottles were lowered to a greater depth while the vessel manoeuvred astern into clear water, and were then taken on board. The contents of each bottle were transferred to Kilner jars which were sealed and returned to the laboratory for analysis.

The volume of each sample was measured before extraction with a total of 25 ml of spectroscopic-grade cyclohexane. The extracts were dried with sodium sulphate and the fluorescent emission intensity was measured using a Farrand spectrofluorimeter. For the leaded petrol the excitation wavelength used was 270 nm and the emission wavelength 283 nm. An excitation wavelength of 298 nm and emission wavelength of 329 nm were used for the gas oil.

For the duration of the trial, the windspeed was 15

Table 25. Change of oil content with depth

Depth, m	Concentration of gas oil, $\mu\text{g/ml}$
1.5	0.46
4.5	0.40
7.5	0.35
10.5	0.23

knots gusting to 20 knots. Wave heights were 1–1.5 m with a swell up to 7 m corresponding to a sea state of 4–5 on the Beaufort Scale. The leaded petrol slick was visible on the sea surface for about one hour and only one subsurface sample, taken immediately after the petrol was discharged, contained a measureable amount of hydrocarbon. This was probably due to initial mixing which took place during the discharge. The gas oil slick was somewhat more persistent and lasted for about three hours. Dispersion appeared to be a significant process contributing to the removal of the oil from the surface. Shortly after discharge the concentration of oil in the water at a depth of 1.5 m below the surface was 1.52 $\mu\text{g/ml}$, dropping to 0.46 $\mu\text{g/ml}$ after 90 minutes. The initial high value was again probably due to mixing during the discharge.

Table 25 shows the decrease in oil content with depth under the centre of the slick 90 minutes after being laid. There is a linear relationship between concentration and depth which may be extrapolated to background concentration (0.01 $\mu\text{g/ml}$) at 17.5 m depth. At the time of sampling the size of the slick was estimated from the air to be about 1000 m by 600 m.

Using this area, and taking 0.29 $\mu\text{g/ml}$ as the average concentration of gas oil in the upper 17.5 m of water, it is estimated that 3.0 m³ (18 %) of the oil was dispersed into the water column.

NORTH SEA CRUDE OIL

During recent oil recovery trials in the North Sea, the opportunity was taken to investigate the fate of a slick of North Sea crude oil. In order to obtain spreading data it was considered necessary to release all the oil instantaneously. To achieve this the oil was contained in a polythene sleeve supported by a cylindrical frame. A derrick on the discharge vessel was used to suspend the frame in the water to give 0.5 m of free-board.

The sleeve was weighted at the bottom to ensure that it hung vertically in the water. About half a tonne of crude oil was pumped onto the water within the confines of the sleeve. To effect release of the oil, the frame and sleeve were raised above the sea surface with the derrick. The vessel then moved slowly astern to avoid mixing the oil. The resulting slick, which was semi-

Table 26. Effect of time on oil concentrations in water samples

Time after spill, hours	Depth, m	Oil concentration under edge of slick, $\mu\text{g/ml}$	Oil concentration under centre of slick, $\mu\text{g/ml}$
0.5	2	2.49	2.03
1.5	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

circular in shape, spread rapidly down-wind. Subsurface water samples were taken at intervals using the same technique as above.

In the 24-hour period that the slick was monitored, the average windspeed was 12 knots, gusting to 18 knots and the sea state was 3–4 on the Beaufort Scale. The oil took up considerable amounts of water in the first two hours, after which time, patches of water-in-oil emulsion 30–50 cm in diameter began to break away from the centre of the slick.

After eight hours these patches had broken down further to about 1–5 cm diameter. By 21 hours, the majority of oil visible on the sea surface consisted of small flecks of water-in-oil emulsion, 5–10 mm diameter interspersed with a silvery sheen. Table 26 shows the concentrations of oil found beneath the slick at depths ranging from 2 to 15 m. These results give a flexed linear relationship showing a comparatively rapid decrease in concentration down to 5 m depth followed by a slower decrease to background at around 20 m.

The slick 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 $\mu\text{g/ml}$ for the top 5 m of water under the slick, the amount of oil dispersed is 0.21 tons, i.e. 42 % of the amount discharged.

CHEMICAL DISPERSION

The most satisfactory method of dealing with oil slicks which are threatening coastal amenity areas is to enhance dispersion of the oil by the use of suitable emulsifying chemicals. The application of these materials results in a reduction in interfacial tension between oil and water, which promotes droplet formation. In addition, the surface-active molecules present in the

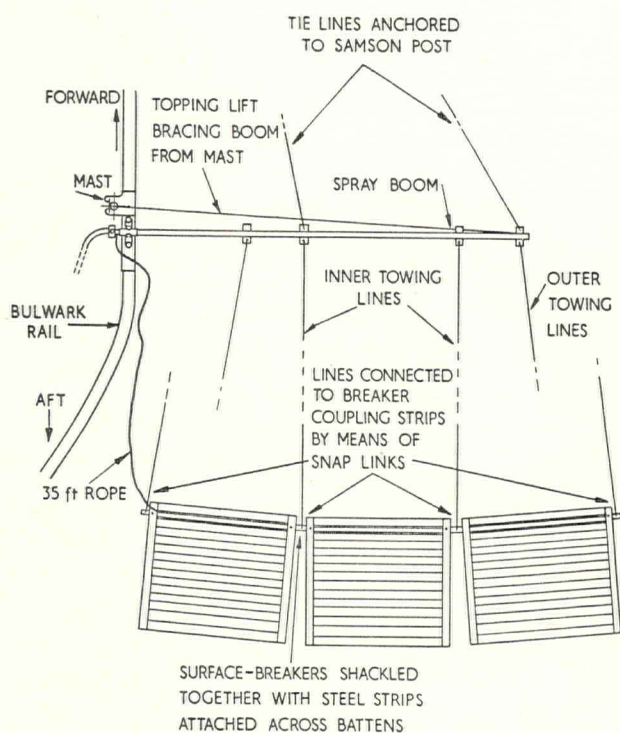


Figure 68. Arrangement of spray boom and surface-breakers (shown with boom fitted on starboard side).

chemical become located at the oil/water interface and prevent coalescence of the droplets once they are formed.

The technique of dispersing oil slicks at sea consists of spraying the chemical on to the floating oil, allowing a few seconds for penetration and then mixing the treated oil with the upper layers of the sea with sufficient energy to form a stable dispersion. In 1971, Warren Spring Laboratory developed spraying equipment suitable for installing on tugs and other sea-going craft. The main feature of the equipment is the method of agitating the oil and dispersant by utilising the power of the vessel when moving. Two sets of three wooden surface-breaker boards are towed line abreast some six metres behind the dispersant spraying booms which are located on each side of the vessel as shown in Figure 68.

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. Provided there is reasonable sea movement, the oil droplets diffuse rapidly into the water column and do not recontaminate the surface. Although concentrations of oil in the upper layer will be quite high immediately after spraying, dilution into the surrounding water should be rapid.

In 1973 Warren Spring Laboratory collaborated with the Ministry of Agriculture, Fisheries and Food to de-

termine the rate of dilution of chemically dispersed oil under field conditions. Approximately 230 litres of Kuwait crude oil were dispersed with the dispersant BP1002 using the Warren Spring Laboratory-designed spraying equipment. In order to ensure that all of the oil was treated, the slick was laid immediately ahead of the dispersant spray boom. This was achieved by spraying the oil at a rate of 45 litres/minute from a wide-angle flat-jet nozzle mounted on a boom projecting about three metres from the side of the spray vessel and ahead of the dispersant spray boom. The position of the nozzle was adjusted so that as the vessel travelled in a straight line at a speed of four knots, a uniform carpet of oil, some 0.3 m wide and 1 mm thick was deposited onto the surface of the sea. At the same time the dispersant was sprayed on the oil at a rate of 45 litres/minute. The width of the spray pattern was about one metre and therefore sufficient to cover the oil. The application rate of dispersant to oil is therefore approximately 1:3 by volume in agreement with the usual application rate for the treatment of real slicks at sea. The quantity of oil dispersed per unit volume of sea water is, however, approximately 5 times greater than can be achieved by the standard WSL spray set in a single pass. After five minutes, spraying was stopped and water samples were taken at a depth of one metre below the surface for as long as the dispersed oil slick was visible. Two further runs were made in different locations. The oil contents of the water samples were determined by the spectrofluorimetric method already described. In practice, oil is initially dispersed into the surface layers of the sea by means of the breaker boards. If such oil were maintained in this layer, say 0.3 m deep, the concentration would be 500 µg/ml. The ex-

Table 27. Concentrations of dispersed Kuwait crude oil

Time after spill, min.	Concentration of Kuwait crude oil in µg/ml 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	0.80		1.35
50		1.9	
80			1.50
100		0.80	

periments were carried out in the Solent, in very light sea conditions. Windspeeds were of the order of 8-10 knots with a sea state of 2-3. The concentrations of oil found in the water samples are given in Table 27.

After about 30 minutes, the dispersed oil became difficult to trace from the observer boat. Nevertheless, the results serve to illustrate that under tidal conditions, dispersed oil rapidly diffuses throughout the water.

However it should be borne in mind that dilution of dispersed oil from an extensive oil slick may not be as great as for the experimental slick studied here.

CONCLUSIONS

Experiments on the fate of oil slicks at sea suggest that natural physical dispersion of the oil into the upper layers may account for the removal of up to 40% of the oil from the surface in the first 8 hours without the development of high concentrations in the water. In the case of light crude oils and volatile crude oil products, dispersion and evaporation may result in the complete removal of oil from the surface of the sea.

More persistent crude oils and fuel oils may require

the use of dispersant chemicals when coastal areas are threatened. Provided these chemicals are applied correctly with suitable equipment, oil slicks can be effectively dispersed to prevent the oiling of birds, intertidal marine life and amenity beaches. Initial concentrations in the upper 0.3 m of water are expected to be higher than for natural dispersion, which is slower. Indications are however that dilution into the body of the sea is significant and the initial surface concentrations are not maintained for any length of time.

These preliminary studies are currently being extended to obtain more detailed information on the results of natural and chemical dispersion of oil in the sea.

REFERENCES

- Anon. 1973. The fate of oil spilt at sea. Report by a Ministry of Defence Working Party. St. Mary Cray; Defence Research Information Centre, 57 pp.
- Forrester, W. D. 1971. Distribution of suspended oil particles following the grounding of the tanker "Arrow". *J. Mar. Res.*, 29, 151-70.
- Spooner, M. F. 1970. Oil spill at Tarut Bay, Saudi Arabia. *Mar. Poll. Bull.* 1, 166-67.