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INVESTIGATIONS INTO THE TOXICITY OF COREXIT - A NEW OIL DISPERSANT

by

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INTRODUCTION

In view of the high degree of toxicity (Smith 1968, Simpson,1968) of BP 1002, Gamlen Oil Spill Remover, Dasic Slickgone and other "detergents" used in Cornwall to combat pollution from Torrey Canyon oil, it was considered desirable to investigate the toxicity of a compound marketed as an oil dispersant under the brand name "Corexit 7664", claimed by the manufacturers to be non-toxic to marine fauna. It is produced by the Standard Oil Company of New Jersey and marketed in the U.K. by the Esso Petroleum Company. It is stated by the manufacturers to be a non-ionic surfactant, soluble in fresh water, 5% NaCL solution and isopropanol, and dispersible in fuel and crude oils. It contains no organic halides or heavy metals and its physical properties are given as follows:-

Specific gravity @ 60°F	1.004
Density, lbs/gal @ 60°F	8.36
Flash point, T.O.C., °F	90
Pour Point, °F	-5
Viscosity:	
SSU @ 100°F	186
CS @ 32°F	588
CS @ 0°F	2444

The recommended working dilution is 1 part Corexit to 10 parts oil, although it is said to be effective even at 1 part per 100 parts of oil. From the biological standpoint the most important part of the manufacturers' information sheet is the claim that "Corexit 7664 is non-toxic to marine fauna ..... the mortality rate of shrimps and fish exposed to Corexit at 10,000 parts per million was not significantly different from that of untreated seawater".

The investigations reported in this paper were made in two experiments. In the first, the toxic effects of straight dilutions of Corexit in seawater were assessed. In the second, the toxicity of Corexit-dispersed crude oil was compared with that of crude oil alone, with an attempt to imitate conditions at low tide on a polluted beach. The first experiment was carried out in Bantry, Co. Cork, using material collected locally. The second experiment was carried out in the laboratory of the Fisheries Division, Department of Agriculture and Fisheries, and the material was collected at Sandycove, eight miles south of Dublin.

I. TOXICITY OF COREXIT AT VARIOUS CONCENTRATIONS.

MATERIALS AND METHOD:

Four tanks (circular polythene basins of 35.5 cm diameter) of clean seawater were set up containing -

12 *Patella vulgata* (Limpet)
12 *Littorina littorea* (Periwinkle)
11 *Gibbula umbilicalis* (Topshell)
1 small stone with *Balanus balanoides* (Barnacles) attached
1 small frond each of *Fucus vesiculosus*
Ascophyllum nodosum
Enteromorpha clathrata
Polysiphonia fastigiata

The tanks were left for 12 hours overnight with aeration.

The following morning all the animals and plants were healthy, and the water clear. The water was drained from all four tanks and dilutions of Corexit substituted in three of them as follows:-

Tank 1 10,000 parts per million
Tank 2 1,000 p.p.m.
Tank 3 100 p.p.m.
Tank 4 clean seawater.

Each tank contained 5 litres, which gave a surface 33 cm in diameter or 855 sq.cm. in area. Aeration was by a Hy-flo model C pump (4 outlets) with one cubical porous block of side 2.5 cm. in each tank. In tanks 1 and 2 deep foam covered the surface almost immediately after the detergent solution had been poured in; tank 3 foamed slightly but only over about $\frac{1}{4}$ of the total surface area.

RESULTS.

AFTER 6 HOURS: The surface of tank 1 was still completely covered by foam, but only $\frac{1}{4}$ of the surface of tank 2 was covered and there was none on tank 3. The condition of the animals was already noticeably varied between tanks. The algae in all the tanks appeared healthy and the barnacles were functioning normally.

Tank 1. Five limpets could be lifted off without resistance. The foot response was barely perceptible. All the topshells and eight periwinkles were easily knocked off the substratum and showed a sluggish closing response, but two small amphipods which had been brought in on the algae were swimming strongly. When the foam on the surface had died down after the aerator had been switched off for the examination, a distinct scum was visible.

Tank 2. Two limpets could be lifted off without resistance. The foot response was sluggish but not as weak as the five in tank 1. All the other animals appeared to be normal. One periwinkle and one topshell which had climbed up the wall of the tank were re-immersed. A slight scum was visible on the water surface, but it was not as heavy as that of tank 1. Water temperature: 17.5^{0}C.

Tank 3. One limpet was upside down beside the stone, off which it had evidently fallen. It was put right-way up and was firmly attached two hours later. All the other animals and plants appeared to be normal.

Tank 4. All normal. Molluscs firm on substratum. Water temperature 17.5^{0}C.

AFTER 12 HOURS: Foam still covered tank 1, but not so deeply as before. Large bubbles covered $\frac{1}{4}$ of tank 2.

Tank 1. Nine limpets removable with a weak foot response. All the topshells were still withdrawn and not adhering to the substratum. Eight periwinkles were withdrawn or easily dislodged. The water was scummy and cloudy.

Tank 2. Four limpets removable, foot response sluggish. Two periwinkles and one topshell had to be replaced underwater from the tank wall; all appeared healthy. The water was scummy and slightly cloudy, temperature 17.0°C.

Tank 3. All appeared healthy, including the limpet previously upside down. Water clear.

Tank 4. All normal, water clear, temperature 17°C. All the algae and barnacles were healthy.

AFTER 24 HOURS. Foam half covered the surface of tank 1 and there were large bubbles over $\frac{1}{4}$ of tank 2. All the barnacles were functioning normally. The algae were examined with the naked eye and under the microscope but no damage was apparent.

Tank 1. Eleven limpets removable, no adhesion. When they were left upside down in the tank after removal, the head and tentacles half emerged but did not move about. All the topshells and all the periwinkles were contracted. One amphipod was seen to be still swimming strongly. The water was very scummy and cloudy which made examination difficult.

Tank 2. Six limpets removable, slight adhesion (i.e. about as strongly as the removable limpets in any of the tanks at the 6-hour and 12-hour stages). When they were left upside down in the tank the head and tentacles half emerged and moved about slowly. All the topshells and periwinkles appeared healthy; one periwinkle was on the tank wall above water. The water was scummy and cloudy, temperature 16.0°C.

Tank 3. All normal, water clear.

Tank 4. One limpet easily removed, foot response normal with muscle flexing and extending. All else normal, water clear, temperature 16.0°C.

The eleven limpets from tank 1 were rinsed in clean seawater and placed in a clean aerated tank. After $5\frac{1}{2}$ hours there was still no adhesion to the substratum and the foot and tentacle response barely perceptible.

These results are summarised in Tables 1 and 2

TABLE 1. Condition of organisms, % affected by detergent

	Concentration of Corexit 7664			
	10,000 p.p.m.	1,000 p.p.m.	100 p.p.m.	0 (Control)
6 hours				
Patella vulgara	42	17	0	0
Gibbula umbilicalis	100	0	0	0
Littorina littorea	67	0	0	0
Balanus balanoides	0	0	0	0
Algae	0	0	0	0
12 hours				
Patella vulgata	75	25	0	0
Gibbula umbilicalis	100	0	0	0
Littorina littorea	67	0	0	0
Balanus balanoides	0	0	0	0
Algae	0	0	0	0
24 hours				
Patella vulgata	92	50	0	0
Gibbula umbilicalis	100	0	0	0
Littorina littorea	100	0	0	0
Balanus balanoides	0	0	0	0
Algae	0	0	0	0

TABLE 2. Water condition

	Concentration of Corexit 7664			
	10,000 p.p.m.	1,000 p.p.m.	100 p.p.m.	0 (Control)
6 hours				
Foam Cover %	100	25	0	0
Scum	Present	Present	Absent	Absent
Clarity	Clear	Clear	Clear	Clear
T°F	-	17.5°C	-	17.5°C
12 hours				
Foam cover%	100	25*	0	0
Scum	Present	Present	Absent	Absent
Clarity	Cloudy	Cloudy	Clear	Clear
T°F	-	17.0°C	-	17.0°C
24 hours				
Foam cover%	50	25*	0	0
Scum	Heavy	Present	Absent	Absent
Clarity	v.cloudy	Cloudy	Clear	Clear
T°F	-	16°C	-	16°C

* Large bubbles

11. TOXICITIES OF DISPERSED AND UNTREATED CRUDE OIL.

MATERIALS AND METHOD:

Three similar tanks were set up, each with a stop-cock fitted low down in the side so that the water could be drained off. Each tank contained -

12 *Patella vulgata*
10 *Littorina littorea*
8 *L. littoralis*
1 stone with *Balanus balanoides* attached
5 litres fresh sea water.

Each tank was aerated as before and left for 18 hours.

Meanwhile 900 ml. Middle East crude oil (60% Kuwait, 40% Iraq) was poured into a crystallising dish 14.5 cms. in diameter and stirred mechanically for 18 hours. This was an attempt to approach the conditions of an actual oil spill at sea, in which most of the more volatile fractions would have been lost by the time the oil reached the shore.

At the start of the experimental treatment following the acclimatisation period the animals were examined and anything not firmly adhering to the substratum was removed. This resulted in the loss of one *L. littoralis* each from Tank 1 and Tank 2, and five *L. littoralis* from Tank 3. The water temperature was 18°C. The aeration was switched off and the crude oil, which had been reduced to 800 ml. was divided into two portions.

Tank 1. 400 ml crude oil was poured on to the surface and 40 ml Corexit was added in a thin stream from a 100 ml. graduated cylinder, moving over the entire surface. The surface layers were agitated for abour 30 seconds with the mechanical stirrer and the tank was drained.

Tank 2. 400 ml. crude oil was poured on to the surface and agitation carried out with the mechanical stirrer (before agitating Tank 1, to avoid Corexit contamination). The tank was then drained.

Tank 3. Tank drained.

RESULTS:

AFTER 2 HOURS

Air temperature in the tanks 19°C.

Tank 1. Two limpets were "standing up" and were removable. All the *L. littorea* and six *L. littoralis* were upturned or removable. The only *L. littoralis* that was healthy was on top of the stone.

Tank 2. Four limpets were removable and six *L. littorea* and two *L. littoralis* were upturned or removable.

Tank 3. Everything firmly attached.

AFTER 7 HOURS:

Air temperature in the tanks 19°C.

Tank 1. Six limpets removable. All the L. Littorea and all the L. littoralis were upturned or removable. The L. littorea mostly remained half out of the shell, while the L. littoralis were well contracted.

Tank 2. Eight limpets removable. Eight L. littorea and five L. littoralis were upturned or removable.

Tank 3. One limpet removable. All the L. littorea and L. littoralis were firmly attached.

Five litres of clean sea water were poured down the sides of each tank, and the aeration was renewed.

AFTER 6 HOURS UNDERWATER.

Water temperature 18.5°C. The aeration was switched off and the tanks were drained.

Tank 1. Seven limpets removable (6 dead and 1 moribund, i.e. barely perceptible foot response on prodding). All the L. littorea were removable, and were either completely contracted or showing a very sluggish closing response. All the L. littoralis were removable and all were closed. The barnacles remained open but they closed when touched.

Tank 2. Six limpets removable (3 dead and 3 moribund). Seven L. littorea were removable, three completely closed but four oper and capable of closing when touched. Two L. littoralis were removable and open, but also able to contract. The barnacles were open but closed when touched.

Tank 3. Everything normal, including the limpet that had been removable before.

AFTER 8 HOURS

Air temperature in tanks 18°C.

Tank 1. Nine limpets removable, all dead. All the L. littorea and L. littoralis were upturned or removable. The barnacles behaved as before.

Tank 2. Eight limpets removable (6 dead and 2 moribund). All the L. littorea and 4 L. littoralis were removable or upturned. The barnacles behaved as before.

Tank 3. Two limpets removable. All the L. littorea and L. littoralis were firmly attached.

Five litres of clean sea water were poured in to each tank and the aeration was renewed.

AFTER 5 HOURS UNDERWATER

Water temperature 19°C. The aeration was switched off and the tanks drained.

Table 3 Condition of organisms, % affected by treatment

Time and species	Corexit and oil	Oil	Control
2 hours after draining			
Patella vulgata	17	33	0
L. littorea	100	60	0
L. littoralis	86	29	0
7 hours after draining			
Patella vulgata	50	66	8
L. littorea	100	80	0
L. littoralis	100	71	0
6 HOURS UNDERWATER			
On draining			
Patella vulgata	58	50	0
L. littorea	100	70	0
L. littoralis	100	29	0
8 hours after draining			
Patella vulgata	75	66	17
L. littorea	100	100	0
L. littoralis	100	57	0
5 HOURS UNDERWATER			
On draining			
Patella vulgata	100*	100*	0
L. littorea	100	80	0
L. littoralis	100	57	0

* See text

Tank 1. Nine limpets removable, but the three apparently healthy ones were forced off the bottom and were found to be dead. All the L. littorea and L. littoralis were removable or upturned. The barnacles behaved as before.

Tank 2. Eight limpets removable (7 dead and 1 moribund), but as in Tank 1 when the four apparently healthy individuals were forcibly lifted, they were found to be dead. Eight L. littorea and four L. littoralis were upturned or removable. The barnacles behaved as before.

Tank 3. All limpets, L. littorea, L. littoralis and barnacles were firmly attached. The barnacles were contracted.

These results are summarised in table 3.

DISCUSSION:

It appears that although untreated crude oil is more toxic than an oil-Corexit mixture to Patella vulgata, the reverse is true for Littorina littorea and L. littoralis. At all times L. littoralis is more resistant than L. littorea, and all three species are capable of recovering from contact with crude oil when covered by a rising tide of clean water. This recovery is not seen following detergent treatment of the oil.

As quoted above, literature from the manufacturers of Corexit stated that the detergent "is non-toxic to marine fauna", a statement apparently based on the survival of "shrimps and fish" at Corexit concentrations of 10,000 p.p.m., and the survival of such crustacea as were observed here seem to bear this out. But unlike other detergents examined by Smith & Simpson, Corexit is more toxic towards molluscs than to crustaceans, and the mollusc species tested in my experiments succumbed to a Corexit concentration of 10,000 p.p.m. However, the concentrations of this detergent which are required to kill experimental animals are still a great deal higher than those of others which have been the subject of toxicity tests. Smith reports that only 5 p.p.m. of BP 1002 were sufficient to kill the majority of Patella vulgata in 24 hours; the corresponding lethal dose for L. littorea was 100 p.p.m. while for the crustaceans tested the lethal concentrations ranged from 2 p.p.m. to 25 p.p.m.

When compared with these figures the toxicity of Corexit even towards molluscs is very low - 50% Patella vulgata died after 24 hours in a concentration of 1,000 p.p.m., and although 50% of this species had become detached after only 7 hours of contact with an oil-Corexit mixture, this was in an equivalent detergent strength of 8,000 p.p.m. in seawater (or stronger, if allowance is made for the possible incomplete dispersal of free Corexit throughout the tank before draining). While the mortality rates for Littorina spp. is higher

than that of Patella vulgata on contact with the oil-detergent mixture, as well as in an ordinary solution of 10,000 p.p.m. Corexit, the concentration required to kill them is still greater than that of BP 1002, for example.

The manufacturers do not claim that Corexit is effective in cleaning an oil-polluted beach, but if it ever were to be used for this purpose it is obvious that locally the concentration of detergent will be many times greater than 10,000 p.p.m. Thus the optimism implied above cannot be considered relevant to this situation. But what can be viewed optimistically are the chances of survival of the littoral fauna on those parts of the shore exposed to detergent patches drifting in from treated areas at sea or from nearby beaches where such treatment has been carried out. Smith found that 2 hours after high water the maximum concentration of detergent immediately offshore from a treated beach was 25 p.p.m. the beach having received 4,000 gallons at low tide. Clearly this concentration would constitute a lethal dose for many species in terms of BP 1002, but it is well below the lethal levels found in the experiments reported here.

Finally it should be pointed out that a firm statement on the acceptability of Corexit from the biological standpoint cannot be made until a representative range of species have been subjected to toxicity tests, particularly the commercially valuable molluscs.

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