Qatar Univ. Sci. Bull. (1987) 7: 379-391

INHIBITION EFFECT OF FOUR OIL DISPERSANTS ON PRIMARY PRODUCTIVITY IN QATAR WATER (ARABIAN GULF)

By

MOHAMED A. IBRAHIM and MOHAMED I. EL SAMRA
Marine Sciences Department, University of Qatar
Doha, State of Qatar

Key words : Arabian Gulf, oil dispersants, primary productivity, oil pollution, marine pollution.

ABSTRACT

Four major oil dispersant mixtures in seawater were used to depict their in-situ inhibition ratio to productivity rate of natural phytophankton populations in Qatar water – Arabian Gulf – during the spring season of 1986. Results revealed that the highest gross production rate was attained in March (82 mg C m^{-3} h^{-1}), while the highest net production rate was in February (56 mg C m^{-3} h^{-1}). The ratios between the net and gross production-rates were 83.60%, 57.30% and 38.95% for the months of February, March and April respectively. The 50% relative inhibition in gross production rate due to dispersant mixtures ranged between 73–450 ppm and their threshold inhibition effect appeared between 2–57 ppm indicating their adverse effect on the marine ecosystem if misused or misplaced away from the slick area.

INTRODUCTION

Chemical oil dispersants are used routinely for marine oil spill clean up operations. However, reseach revealed that they have adverse effects on the marine ecosystem (Ukeles, 1965; Lewis, 1971; Ballen *et al.*, 1972; Mommaerts, 1976; Bleakley *et al.*, 1974; Wilson, 1976; Czyzewska, 1976; Ordzie and Garofalo, 1981 and El-Samra *et al.*, 1987). Historically, priority has been given to acute toxicity of pollutants to individual fish with little attention given to sub-lethal stress on the entire community.

In the marine ecosystem, phytoplankton represents a large portion of the total basic food supply. Thus, studies on these populations could give information about the impact of such pollutants on the main producers in the marine ecosystem. Even though, information about the effect of oil dispersants upon planktonic organisms is much sparcer than for nekton and benthos.

The marine Sciences Department of the University of Qatar has been executing a programme intended for in−situ assessment of oil and oil dispersants impact, under the prevailing environmental conditions, to circumvent some of the problems of uncertainty in Qatar water. This is frequently subjected to oil spills either during exploration and production of oil within the country and/or during spills originating offshore through oil industry, transportation and the act of war in the area. Reseach is underway to determine the impacts on fish larvae, economic invertebrates and the basic food chain in the mentioned water.

The present paper is intended to assess (in−situ) the impact of oil dispersants on the primary production rate of the natural phytoplankton population during the spring season in the study area. The spatial composition of the planktonic organisms has been delt with else where (Dorgham and Muftah, 1986).

MATERIALS AND METHODS

The study area is located some 25−30 km south of Doha, the capital, on the eastern side of Qatar (Fig. 1). The current pattern of this side as a whole is very complicated due to irregular bathymetry (Sivasubramaniam and Ibrahim, 1982). The most conspicuous trend in current direction in the study area is a surface current moving almost parallel to the shore from North to South.

Temperature was recorded in the field to the nearest 0.5°C. Salinity was determined by a high−range hand refractometer. Net production rate was determined according to the Winkler's dissolved oxygen method.

Four oil dispersants namely, Exxon OSD 9217, Servo CD 2000, Shell Concentrate and Shell LTX, as currently stocked in Qatar General Petroleum Company offshore for application against oil spills in Qatar water, were used to depict the effect of such dispersants on the phytoplankton productivity under the prevailing environmental conditions of the Qatar water during the months of February, March and April, 1986.

From each of the above mentioned dispersants; a series of successively increasing so called concentrations (the row dispersant liquid was considered as 100% concentration), covering the range from 50 to 500 ppm at 50 ppm intervals of dipersant in seawater by volume, was prepared as described below.

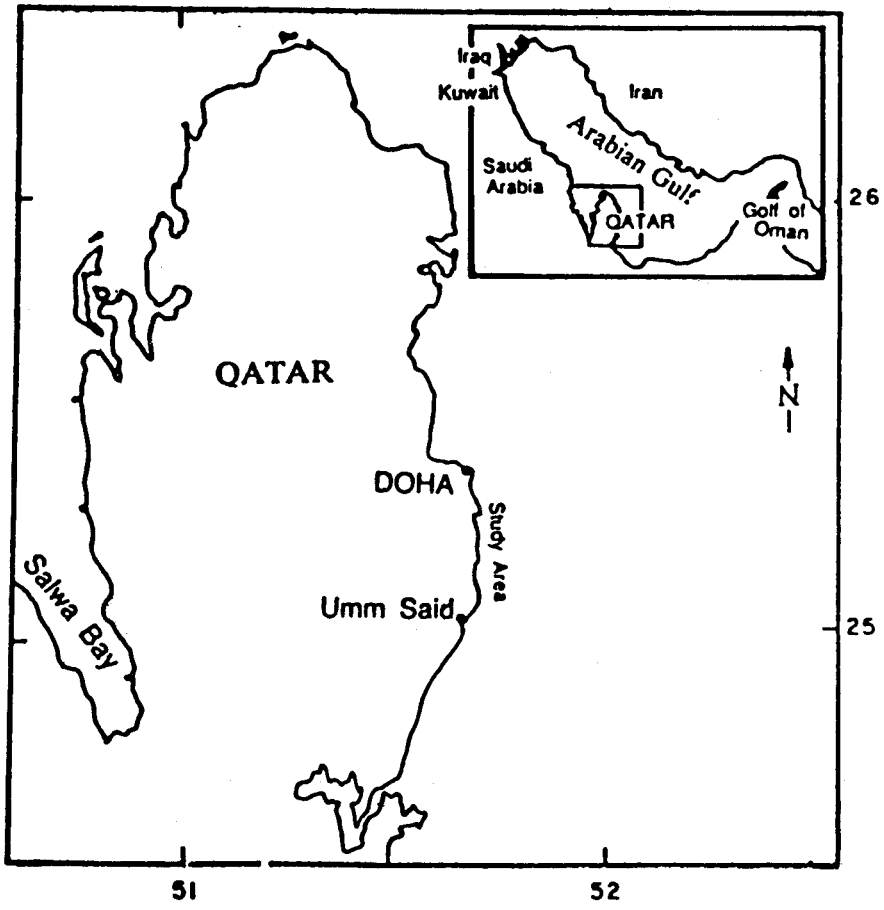

Fig. 1 : Location map of the study area on the eastern side of Qatar in the Arabian Gulf.

The internal volume of each BOD bottle was estimated by filling it with water, stoppering always with the same stopper to tightness, removing the stopper to mark the water level around the bottle's neck and then measuring the water content to the nearest millilitre.

Into each empty, acid washed and marked BOD bottle; a calculated volume of one of the dispersants – to give the required concentration in the particular series relative to the BOD internal volume – was micropipetted. The number of

bottles of any one concentration was 4 light, 3 dark and 3 indescriminate bottles (to be used for initial dissolved oxygen content estimate). The same was done for the complete series of a particular dispersant and likewise for the rest of the four dispersants. Meanwhile, 20 light, 10 dark and 5 indescriminate BOD bottles with no dispersants added were used as control group for estimating the production rate.

Surface water sample from the study area was filtered through a standard zooplankton net to remove bulky substances then syphoned into each BOD bottle close to its bottom through a narrow rubber tube. The outlet portion of the tube (ca. 15 cm) was discarded and replaced after each one filling to avoid contamination with dispersant from one BOD bottle to the other. Syphoning was halted when the water level in the BOD bottle reached the pre-set mark at the bottle's neck to avoid over flow of the water sample containing the dispersant. The BOD bottle was then stopped and shaked well by hand to assure thorough mixing of the dispersant in the bottle.

To assess the interference of the dispersants on the dissolved oxygen measurements and the oxygen uptake due to dispersant mixture degradation, when performing the net production rate calculations, a portion of the water sample was millipore-filtered through 0.47 mm filter paper to remove the planktonic organisms. Then the filtered water was used to fill another group of BOD bottles (Group B) in the same way as described.

Except for the initial dissolved oxygen content bottles, all other BOD bottles were suspended in-situ from ropes in the form of trains at an average depth of about one metre checked hourly in relation to tidal level. At the onset of the experimental timing, the initial dissolved oxygen content bottles were treated to fix the dissolved oxygen content according to Winkler's method. The trains of BOD bottles were incubated for about 6-8 hours during the local apparent noon in the area, then the final dissolved oxygen contents of all the bottles were measured. Production rate was estimated according to Strickland and Parsons (1972).

The whole procedure and analysis mentioned above were repeated three times each in February, March and April, 1986 to obtain an average of the production rate of the so-called spring season in the area.

RESULTS AND DISCUSSION

Frequent occurence of Shamal winds during the study period contributed to high turbidity and mixing of the shallow water. The wave height was generally around one foot and the tidal variation was in the range of 1.6 metres and the current speed was around 10–20 cm/sec. As a result, large streches of the tidal flats are temporarily exposed. The water temperature varied from a mean of 21.5°C in February, 26.0°C in March to29.5°C in April, later it reached 36.0°C in August/September. The corresponding salinities were 44, 44 and 45‰, while the dissolved oxygen contents were 4.57, 5.44 and 4.13 ml/1 respectively, as shown in table (1).

Table 1

Some environmental parameters in Qatar water during the months of February, March and April, 1986.

Parameters	Feb.	March	April	Average
Water temperature°C:				
Range	20–23	24–28	27–32	20–32
Mean	21.5	26.0	29.5	25.5
Dissolved oxygen (ml/l)	4.57	5.44	4.13	4.71
Salinity ‰	43	44	45	44
pH	8.20	8.20	8.30	8.25

Emara *et al.*, (1984) estimated that ammonia concentration ranges between 0.38 – 4.0 mg N/1, nitrate 0.7 – 2.8 μg N/1 and copper 1.7 – 6.7 μg/1. Al Kholy and Soloviov (1978) estimated that the plankton biomass in the eastern waters of Qatar ranges between 200–500 mg/m^3. Dorgham and Muftah (1986) recorded a total number of 390 plankton taxa including 225 diatoms, 152 dinoflagellate, 2 siliocoflagellate and 11 blue green algae species in this water. Hsiao et al (1978) indicated that the effects of an oil dispersant on primary production rate varied with environmental conditions and species composition of each sample among other things. Hence, no attempt was made to identify or quantify the plankton populations in the present study down to the species, since it was delt with elsewhere (Dorgham and Muftah, 1986), and it was

intended merely to get an in–situ average of the primary production rate of the control BOD bottles to compare it with that under the stressed condition due to dispersant mixture.

Due to hourly variations in the environmental conditions such as light intensity (due to clouds), and turbidity (due to wind and wave action), the data obtained was subjected to statistical analysis to test for significant differences in the dissolved oxygen concentration among the BOD bottles before performing productivity calculations. Statistics in Table (2) indicate the presence of such differences at the 95% level under the prevailing environmental conditions during the study period.

Table 2

Statistics of comparing the mean rate of change of dissolved oxygen in light (L), dark (D) and initial (I) experimental BOD bottles. Where t' and $t_{0.05}$ are the calculated and tabulated student "t" value as based on Snedecor et al, 1967 for comparison of the means of two independent samples.

BOD Bottle Type	February		March		April	
	t'	$t_{0.05}$	t'	$t_{0.05}$	t'	$t_{0.05}$
L vs D	9.50	2.20	4.04	3.65	9.80	2.24
L vs I	7.50	2.44	3.16	2.19	5.77	2.59
I vs D	1.58	0.91	2.34	0.43	3.00	2.57

The estimated primary production rates are shown in Table (3). Results indicate that the highest gross production rate was attained in March (82 mg C m^{-3} h^{-1}), while the highest net production rate was attained in February (56 mg C m^{-3} h^{-1}) and the ratios between the net and gross production rates were 83.60%, 57.30% and 38.95% for the months of February, March and April respectively.

The gross and net primary production rate are calculated according to Strickland and Parsons, 1972 by the equations 1 and 2 respectively. V_L, V_D and V_I are the thiosulfate titrations of the light, dark and initial BOD bottles respectively, f is the calibration factor, 605 is the conversion factor, N is the number of hours of incubation and PQ is the photosynthetic quotient.

$$\text{Gross primary production rate (mg C/m}^3\text{/hr)} = \frac{605\ (f)\ (V_L - V_D)}{N\ .\ PQ} \quad (1)$$

$$\text{Net primary production rate (mg C/m}^3\text{/hr)} = \frac{605\ (f)\ (V_L - V_I)}{N\ .\ PQ} \quad (2)$$

Table 3

Estimated primary production rate in Qatar water at 95% confidence limit during the months; February, March and April, 1986, (mgC/m^3/h).

Primary Production	Feb.	Mar.	Apr.	Average
Gross Production Rate:				
Mean	67	82	59	69
Upper Limit	81	156	76	98
Lower Limit	52	8	43	40
Net Production Rate:				
Mean	56	47	37	46
Upper Limit	72	80	54	62
Lower Limit	39	14	20	31

In the absence of concrete evidence of how the dispersants interfere with the Winkler's method, the authors are of the opinion that such interference error will be cancelled through calculations.

On a second thought, the oxygen content of the V_I bottles of both the control and the dispersant's mixture–containing sets were fixed at the start of each incubation interval, i.e. they are not subjected to the same conditions as the light bottles. This situation could introduce a source of interference error that may vary with dispersant's mixtures – when comparing the various net primary productivity. Another source of error may arise when estimating the net productivity from the observations that, group (B) BOD bottles were lower in their initial oxygen content than the other bottles. This is due to low atmospheric pressure exerted by vaccum filtration, when preparing the water sample of group (B) bottles. Hence, only the gross primary production rates under the stress condition by dispersants were calculated to compare them with the control BOD bottles.

The percent relative inhibition in gross primary productivity is given by equation 3 as follows:

$$\% \text{ Relative Inhibition} = \frac{\text{Mean gross primary productivity of dispersant mix. X100}}{\text{Mean gross primary productivity of control experiment}} \quad (3)$$

Reference to Table (3) and performing regression analysis between percent relative inhibition of each dispersant mixture and its concentration, the best fit was obtained by a logarithmic equation.

The relationships between percent inhibition in gross primary production rates due to the dispersant mixtures of Exxon OSD 9217, Servo CD 2000, Shell concentrate and Shell LTX relative to the controlled bottles with no dispersants, are given by formulae 4–6 respectively, and are shown in (Fig.2), where (Y_i) is the percent relative inhibition and (X_i) is the dispersant mixture in seawater in ppm.

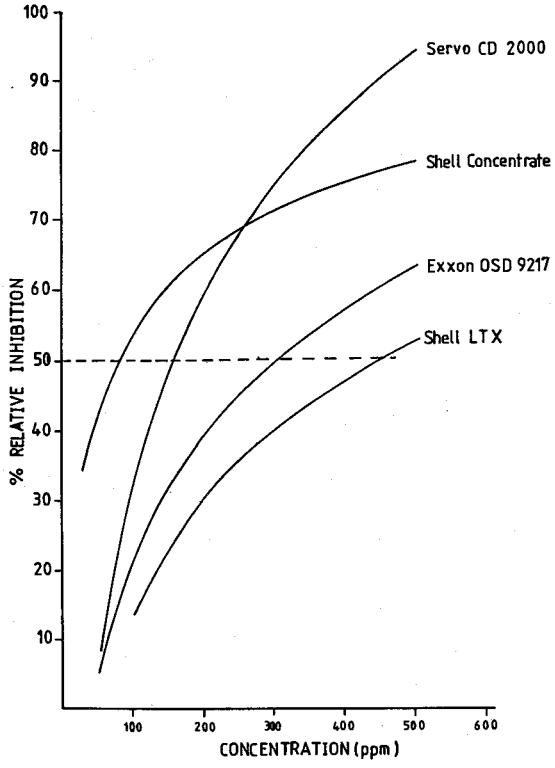

Fig. 2 : % Relative inhibition in gross primary production rate due to four oil dispersant mixtures in Qatar water.

$$Y_i = -\ 93.51 + 57.88 \log (X_i) \quad \ldots\ldots (4)$$

$$Y_i = -\ 138.85 + 86.26 \log (X_i) \quad \ldots\ldots (5)$$

$$Y_i = -\ 11.81 + 33.23 \log (X_i) \quad \ldots\ldots (6)$$

$$Y_i = -\ 97.98 + 55.78 \log (X_i) \quad \ldots\ldots (7)$$

Statistics of the analysis of variance of the % relative inhibition in the gross primary production rate due to the four dispersant mixtures used are presented in Table (4).

Table 4

Analysis of variance of the % relative inhibition in gross primary production rate due to the four dispersant mixtures concentrations.

Source of Variance	Sos	D.f.	M.ss.
Between-treatments	7791.63	3	2597.2
Residual	13510.49	36	375.3
Total	21302.12	39	2972.5

The results of the analysis of variance revealed a significant inhibition ratio by the different dispersants due to a calculated (F) ratio of 6.92 compared to a tabulated (F) of 2.75 at 0.05 probability level. The threshold inhibition concentrations of the four mentioned dispersants are 41, 41, 2 and 57 ppm respectively (Table 5).

Among the incentives for dispersing oil in the water are; the rate of oil biodegradation is increased because of the increased surface-to-volume ratio, the adhering of oil to most surfaces is reduced and the formation of tar-like residue is prevented. Among the disadvantages, on the other hand, are; the toxic effects of most dispersants on aquatic organisms, the increased surface - to - volume ratio increases the toxicity of the oil to aquatic organisms and the lack of knowledge concerning the fate of oil once it has been dispersed (Anonymous, 1973).

Table 5
Threshold dispersant mixture concentrations (ppm/v. in seawater) inhibiting primary productivity in Qatar water as well as Median concentrations causing 50% relative inhibition to production rate.

Concentration Effect	Dispersant			
	Exxon OSD 9217	Servo CD 2000	Shell Conc.	Shell LTX
Threshold concentration	41	41	2	57
50% relative inhibition concentration:				
Median	302	155	73	450
Upper Limit	315	227	83	497
Lower Limit	280	106	64	407

Authorities abroad issued some restrictions on the use of dispersants. Among the restrictions by Environment Canada are; avoiding the uses of dispersants in any water containing major fish populations or large breeding or migration areas for species of fish or other aquatic life and on oil that has been deposited on sandy beaches or on shorelines with important flora and fauna. Such restrictions are not applied, yet, in the Gulf area. Observations showed generous application of dispersants in the mentioned area. This behaviour, if persisted, may cause delaterious effect on the marine ecosystem of the Gulf in the future.

CONCLUSION

Oil dispersants applied to slicks in Qatar water proved to cause mortality among marine animals in the intertidal zone (Sivasupramaniam and Ibrahim, 1984). The 72−h. LC_{50} of four oil dispersants to fry *Liza macrolepis* in Qatar water ranged between 27−244 ppm (El Samra *et al*, 1987). Hydrocarbon can change development and alter behaviour and physiology in planktonic

organisms (Davenport, 1982). Nitrogen generation by microfauna was severely inhibited by dispersant mixtures (Hartly *et al.*, 1982). 50% inhibition in gross primary production rate was attained by concentration of 73–450 ppm of the four dispersants used in the present work which indicates that these dispersants fall into the moderately toxic category as applied for Crangon crangon (Sprague, 1970). Meanwhile, their threshold inhibition effect on primary production appears between 2 and 57 ppm, which indicates their adverse effect on marine ecosytem if misused or applied away from slicks or applied in more quantity than the situation requires.

REFERENCES

Al-Kholy, A.R. and **B. Soloviov, 1978.** Fisheries in Kuwait. Ministry of Public Works, Kuwait.

Anonymous, 1973. Guidelines on the use and acceptability of oil spill dispersants. Environmental Emergency Branch, Environ. Can. Rep. EPS–1–EE–73–1. pp. 54.

Ballen, G., D.J. Reish and **J.P. Foret, 1972.** The sublethal effects of a detergent on the reproduction, development and settlement in the polychaetous annalid Capitella capitata. Mar. Biol. 14 (3): 183–188.

Breakley, R.J. and **P.J.S. Boaden, 1974.** Effects of an oil spill remover on beach meiofauna. Ann. Intst. Ocean. Paris. 50(1): 51–58.

Czyzewska, K. 1976. The effect of detergents on larval development of a crab. Mar. Pollut. Bull. 7(6): 108–112.

Davenport, J. 1982. Oil and planktonic ecosystems. Phil. Trans. R. Soc. London, Ser. B. 297, (1087), 369–384.

Dorgham, M.M. and **A. Muftah, 1986.** Plankton studies in the Arabian Gulf. I – Preliminary list of phytoplankton species in Qatari waters. Arab Gulf Journal of Scientific Reseach. 4(2): 421–436.

El Samra, M.I., M.A. Ibrahim, I.F. Ahmed, and **S.M. Awartani, 1987.** Acute toxicity of some oil dispersants to mullet fry Liza macrolepis of the Arabian Gulf. Qatar Univ. Sci. Bull. Vol. 6.

Emara, H.I.; M.I. El-Samra, and **K.Z. El-Deeb, 1985.** Chemical characteristics of seawater in front of Doha City (Qatar). 2nd Sympos. on Port Development in the Arabian Gulf, Kuwait.

Harty, B. and **A. McLachlan, 1982.** Effects of water soluble fractions of crude oil and dispersants on nitrate generation by sandy beach microfauna. Mar. Pollut. Bull. 13(8): 287–291.

Lewis, J.B. 1971. Effect of Crude oil and oil spill dispersant on reef corals. Mar. Pollut. Bull. 2(4): 59–62.

Mommaerts-Billiet, F. 1973. Growth and toxicity tests on the marine nanoplanktonic algae Phatymanas tetrathele G.S. West in the presence of crude oil and emulsifiers. Environ. Pollut. 4: 261–282.

Ordzie, C.J. and **G.C. Garofalo, 1981.** Lethal and sublethal effects of short term doses of Kuwait crude oil and a dispersant Corexit 5927 on bay Scallop. Mar. Environ. 5(3): 195–210.

Sivasubramaniam, K. and **M.A. Ibrahim, 1982.** Common fishes of Qatar. Scientific Atlas of Qatar, Vol. I, Qatar.

Sivasubramaniam, K. and **M.A. Ibrahim, 1984.** Fisheries in Qatar: Past, present and future development possibilities. Sci. Res. Centre, Qatar Univ. Qatar.

Snedecor, G.W. and **W.G. Cochran, 1977.** Statistical methods. Iowa State Univ. Press, Ames, Iowa. pp. 593 (6th Ed.).

Sprague, J.B. and **W.G. Carson, 1970.** Toxicity tests with oil dispersants in connection with oil spill Chedabucto Bay, Nova Scotia. Fish. Res. Bd. Can. Tech Paper No. 201: pp. 30.

Strickland, J.D.H. and **T.R. Parsons, 1972.** Practical handbook of seawater analysis. Bull. Fish. Res. Bd. Can., pp. 167.

Ukeles, R. 1965. Inhibition of unicellular algae by synthetic surface–active agents. J. Phycol. 1 (3): 102–110.

Wilson, K.W. 1976. Effects of oil dispersants on the developing embryos of marine fish. Mar. Biol. 36: 259–268.

التأثير المثبط لأربعة من مشتقات البترول على عملية البناء العضوي الأولية في المياه القطرية (الخليج العربي)

محمد أمين إبراهيم و محمد إبراهيم السمرة

تم هذا البحث في ربيع ١٩٨٦م ضمن سلسلة البحوث التي يقوم بها قسم علوم البحار بجامعة قطر لدراسة تأثير التلوث بالبترول والمشتقات المستخدمة في مكافحته على البيئة البحرية في الخليج العربي بصفة عامة والمياه القطرية بصفة خاصة .

وقد أثبتت قياسات معدل عملية البناء العضوي الأولية أن النسبة بين الإنتاج العضوي الصافي والإنتاج القائم هي كالآتي :-
٨٣,٦٠٪ ، ٥٧,٣٠٪ ، ٣٨,٩٥٪ لشهور فبراير - مارس - إبريل بالترتيب .
وأن أقصى معدل للإنتاج العضوي القائم كان خلال شهر مارس حيث بلغ ٨٥ ملجم كربون / م٣ / ساعة ، بينما أقصى معدل للإنتاج الصافي كان ٥٦ ملجم كربون / م٣ / ساعة وذلك خلال شهر فبراير .

وبدراسة تأثير أربعة من مشتقات البترول المستخدمة في المياه القطرية على الإنتاجية العضوية المشار إليها سابقاً وجد أن تركيزات تتراوح بين ٧٣ - ٤٥٠ جزء في المليون من هذه المشتقات تثبط معدل الإنتاجية بمقدار ٥٠٪ . وأن ظهور تأثير عملية التثبيط يبدأ عند تركيزات تتراوح بين ٢ - ٥٧ جزء في المليون .

مماسبق يتضح التأثير الضار لهذه المشتقات على أساس السلسلة الغذائية في البيئة البحرية عموماً إذا أسيء استخدامها سواء من ناحية التركيزات المناسبة أو استخدامها بعيداً عن موضع التلوث بالبترول .