ENSURING THE MOST APPROPRIATE OIL SPILL TREATMENT PRODUCTS ARE AVAILABLE – A REVIEW OF TOXICITY TESTING AND APPROVAL ISSUES IN THE UK

Mark F. Kirby, Bryony Devoy and Robin J. Law
Centre for Environment Fisheries and Aquaculture Science (Cefas)
Burnham Laboratory, Remembrance Avenue
Burnham-on-Crouch, Essex, CM0 8HA, United Kingdom

ABSTRACT

Oil spill treatment products in the UK are a key option in response scenarios. It is recognised that their appropriate usage can significantly reduce net environmental impact. However, the approval process for products in the UK is strictly regulated and all must undergo an approval process before they can be used in UK marine waters. This requires the product to pass both efficacy and toxicity assessments. The toxicity assessment comprises a 'Sea' and 'Rocky Shore' test and is primarily based on a toxicity comparison between mechanically dispersed oil (untreated) and oil under the same conditions but treated with the product. The premise being that the addition of product should not significantly increase the toxicity of the oil alone..

The current toxicity and efficiency testing protocols have been in place for 30 years and the last review of the scheme took place in 1993. The UK Department of Environment, Food and Rural Affairs (Defra) are the regulatory body and have launched another review of the scheme during 2007 to establish whether the process continues to provide the most appropriate means of ensuring that safe and effective products are available to UK responders.

The review will take the form of a wide ranging public consultation. Particular issues that are being considered include; the continued requirement for products to pass both toxicity assessments; the need to test dispersants as a type 2 (water-diluted) or type 3 (neat) separately; the need to approve products for specific use against different oil types, especially heavier fuel and weathered oils; the need to take into account the fact that many modern dispersants are effective at lower product:oil ratios than used in the current test process; the performance of products under different conditions of salinity and/or temperature; the need for specific test development for other product types (e.g. surface cleaners) or to make the process more efficient (e.g. combined efficacy and toxicity test).

The UK Government wishes to ensure that responders have the option of selecting the best product for tackling each oil spill scenario providing that environmental protection is not compromised. It is intended that the outcome of the review will be to facilitate this even more so than at present. This paper will describe the background to the issues being considered in the review, why they may be significant and will give a preliminary overview of initial conclusions.

INTRODUCTION

The use of oil spill treatment products is considered a key element in the treatment and mitigation of oil spills in the UK. It is recognised that, if used correctly and responsibly, the use of oil spill treatments products (particularly dispersants) can reduce environmental damage. The benefits might include protection of sea surface biota such as sea birds and a reduction in potential damage to important coastal and shoreline environments. These benefits have been realised following large incidents such as the Sea Empress spill in Milford Haven, UK in 1996 (Law and Kelly, 2004).

However, while recognising these benefits the UK government has taken a strong line in the testing and approval of products and only those that pass strict criteria are approved for use in UK waters. To this end a testing and approval scheme was developed to enable the assessment and approval of products designed for the treatment of oil spills in the marine environment. This approval process began operating in the late 1970's and involved a combined assessment of efficacy and toxicity. The UK Department for environment, food and rural affairs (Defra) are the current regulators of the scheme, under the Food and Environment Protection Act (FEPA - 1985), and issue approvals for all products to be used for the treatment of oil on the surface of the sea. From the point of view of environmental protection the crucial part of the assessment is toxicity testing, which ensures that only products that are environmentally acceptable gain approval. The standard toxicity testing procedures used in the scheme were developed and amended by Cefas (Blackman *et al.* 1978; Kirby *et al.* 1996) and comprise of two distinct assessments, the Sea Test and the Rocky Shore Test.

SEA TEST

Briefly, the Sea Test involves the exposure of shrimp to either mechanically or chemically dispersed oil (Kuwait crude oil) in 18 litre cylindrical tanks (20 shrimps per tank). 18ml (1000 ppm) of oil is added and dispersion is facilitated by a propeller mounted within a central column and driven via a magnetic coupling to a pneumatic motor. Shrimp are exposed to the dispersed oil for 100 minutes before being removed to recovery tanks of clean flowing seawater for 24 hr. There are 5 replicate tanks for each treatment. After the recovery period mortalities are determined and statistical comparisons are made between the results gained by mechanical and chemical dispersion. The premise of the test is that products will be deemed to fail (and therefore not be eligible for a UK approval) if the toxicity of treatment oil under these conditions is significantly greater than the toxicity of the oil alone. Figure 1 shows the Sea Test rig set up and figure 2 displays a Sea Test in progress clearly showing different levels of oil dispersion within the tanks.

ROCKY SHORE TEST

The Cefas Rocky Shore Test is a second toxicity test assessment that oil spill treatment products have to undertake to gain approval for use in UK waters. Along with the Sea Test it is currently a compulsory requirement that products pass the Rocky shore test for approval to be granted.

Briefly, the Rocky Shore Test involves the introduction of limpets onto Perspex plates (20 limpets per plate) (Figure 3) on which they are exposed to oil or dispersant at a dose of 0.8 ml of oil/dispersant per limpet (0.4 l m^{-2} equivalent under these test conditions). The limpets are left in air exposed to the dispersant/oil for 6 hours prior to being rinsed with clean seawater and the plates being placed horizontally in tanks of clean flowing seawater. The mortality of the limpets are monitored over a further 72 hours during which tanks are drained daily and the limpets left in air for a period of 6 hours to simulate a tidal cycle. After this period mortalities are statistically compared between five treatment (dispersant only) and five control (oil only) exposures. The premise of the test is that products will be deemed to fail (and therefore not be eligible for a UK approval) if the mortality observed in the product exposures significantly exceeds that gained with the oil alone.

REVIEW AND IMPROVEMENT

Essential as regulatory approval schemes are considered to be, it remains critical that their basis and mechanisms are reviewed regularly to ensure that they are taking account of new developments and that they remain fit for purpose. Defra, the UK regulator, have been aware of this need and conducted an original review of the use and approval of dispersants in 1993 (Rycroft et al. 1994). This made a number of recommendations but the most significant was that all approved products should be made to pass both the Sea and the Rocky Shore Test assessments before being granted an approval. Previously, products which failed the Rocky Shore test could be approved for offshore use only. This decision was based on the application of the precautionary principle, to avoid products designed for use offshore from being applied on coasts and *vice-versa*. There was no direct scientific justification for the decision as it was considered that, if used correctly, products designed for use 'at sea' could still be used safely away from shorelines.

The UK government are in the process of conducting a second scheme review which is looking in much more detail at whether the testing methods and approval processes are appropriate for modern products and take into account any significant operational considerations. While not complete at the time of writing this paper, the following does give an overview of some of the main issues.

SPECIFIC ISSUES

Sea and Rocky Shore Test Assessment?

As already mentioned the need for products to pass both toxicity test procedures is being reassessed. The original requirement, brought in over 10 years ago, had the required effect in that it resulted in an approved list that consisted of products that could be used safely in all marine environments. However, this also meant that manufacturers had to produce products that could pass both tests and therefore this somewhat stifled the development of specialist products for use in offshore or near-shore scenarios, and removed from the list some products that were particularly effective when treating heavy oils. Concerns have been raised that the general reduction in the number of products approved for use in the UK and the lack of 'specialist' products has limited the product options for responders.

This issue is being carefully assessed and it seems likely that a strong case will be made for removing the need for products to pass both test assessments for certain products (e.g. those developed to treat offshore spills of heavy fuel oil). If so, it is anticipated that this could result in greater freedom for manufacturers to develop more specialised products that will ultimately give a wider choice for responders.

Type 2 vs Type 3 testing

The majority of modern dispersants can be used as a type 2 (water diluted concentrate) or a type 3 (concentrate used neat) product. As such they are designated type 2/3 dispersants. In the current testing protocols it is stipulated that type 2/3 dispersants only have to pass toxicity assessments as a type 2 dispersant to get approval as a type 2/3. This was introduced on the basis that early products appeared to show less efficacy differentiation whether applied as a Type 2 or 3. However, we now have limited evidence to suggest that results from the standard Sea tests can differ depending on whether the product is applied as a type 2 or 3. Furthermore, in the majority of cases it is apparent that the toxicity increase is greater when tested as a type 3 (Figure 4). The majority of dispersants in any large scale response are used in the undiluted Type 3 mode (from aircraft) and there is some concern that products are approved for use as a type 3 product although their approval was given on the basis of testing as a type 2 product.

It is uncertain how significant this is and certainly most Type 3 uses will be offshore where there is a high potential for dilution. Nevertheless the review will be considering the need to separate the testing of Type 2 and 3 products.

Different oils

It is recognised that significant marine oil spills are increasingly likely to involve heavy and very heavy fuel oils, which can be carried in the 1000's of tonnes by large ocean-going vessels as bunker fuels alone. Furthermore, the volume of heavy and residual fuel oils transported through UK waters from Russia and the former Soviet Union states continues to grow and the increased risk of spills of heavy fuel oils has been recognised following recent incidents involving the product tankers *Prestige* and *Erika*.

The need to ensure that there are products available specifically approved for use on heavier oils has been one of the most high profile debates in the current scheme review and it seems likely that a new category of approval will be introduced to approve dispersants for use against these types of oil.

Any new approval will be based on a product passing appropriate efficacy and toxicity tests using a representative heavy oil but the appropriate pass/fail levels will need to be established.

Product:oil ratios

In the current UK Sea Test all dispersant products are tested at a dispersant:oil ratio of 1:10. This is a higher ratio than most manufacturers recommended application rates (1:20 – 1:30) but allows for a safety margin in the event that excess dispersant is applied during a real incident. Nevertheless, claims are made by the manufacturers of modern dispersants that they are highly efficacious and can work effectively at oil:dispersant ratios as low as 1:100 and, therefore, the 1:10 test ratio is too stringent.

Preliminary evidence (Figure 5) using 3 different dispersants at a range of dispersant:oil ratios in the Sea Test shows a reduction in total mortality at lower ratios. In cases the change in mortality would have been enough to affect whether a product passed or failed the approval process. This implies that, providing a product could demonstrate proven efficacy at lower ratios, certain efficacious products could be approved with ratio use limitations. The review is looking at this aspect carefully but it seems unlikely that lower ratios will be incorporated while there remain uncertainties about how dose ratios could be operationally controlled and concerns about possible over application. It is possible that the current tests could be modified such that a dilution element is introduced during the test exposure period (100 minutes) so that dispersed oil concentrations reduce quicker over the exposure period for more efficacious products.

Physical conditions

It is known that certain physical conditions can have a significant impact on dispersant efficacy and hence toxicity. The UK tests are based on standard conditions of 15ºC and 30-35‰. This is representative of most offshore summer conditions in the UK but the question has been raised regarding whether products should be tested under differing physical conditions to ascertain their effectiveness and environmental acceptability in spill scenarios in other waters.

In general it is well appreciated that increases in temperature tend to result in higher levels of toxicity for most pollutants with most test species. Preliminary data proves this also to be true with the toxicity of Kuwait crude oil under Sea Test conditions (Figure 6). This relationship has also been seen in assessments of toxicity in dispersants (Georges-Ares and Clark, 2000). However, it also needs to be considered that oil viscosity generally reduces with increased temperature (Wei *et al,* 2005) and therefore a greater range of oils may be amenable to dispersion under these conditions. Converse to that is that fact that one would expect the oil to weather faster at higher water temperatures and therefore the window of opportunity for successful dispersant treatment might be reduced. The impact of temperature on dispersant effectiveness is complex, leading Chandrasekar *et al* (2006) to conclude that dispersant efficiency does not follow a general trend with increase in temperature, and is different for each oil, depending on its properties.

Salinity is a very significant factor in the effectiveness of dispersants. All the major commercially available dispersants have been formulated for use in normal marine salinities of 30 ‰+ and it has been well documented that effectiveness of dispersants generally decreases at lower salinities (Blondina, *et al.* 1999; Chandrasekar *et al.* 2006). The reason for this is not fully understood. However, the effectiveness of a dispersant is, in part, a function of how much of the surfactant component of the formulation is available to interact and mix with the oil and thus reduce the oil-water interfacial surface tension. As salinity decreases the surfactant effectively becomes more soluble and thus less is available to interact with the oil. Sterling et al. (2004) discovered only a limited influence on dispersant effectiveness by changes in salinity when the oil and dispersant were pre-mixed, and no significant impact was noted with respect to droplet size or subsequent coalescence kinetics under these conditions. The evidence suggests that the salinity effect on dispersant effectiveness is therefore primarily due to how this affects solubility which is not such an issue when the oil and dispersant are pre-mixed. Pre-mixing is not an option during real response scenarios so some research has been conducted to take this into account by increasing the salt content (by addition of calcium chloride) of the dispersant formulation (Georges-Ares et al. 2001) and thus reducing its initial solubility on application. Toxicity is closely related to the solubility and bioavailability of toxic oil components (e.g. polycyclic aromatic hydrocarbons – PAH). Solubility is much greater at lower salinities therefore the potential for toxicological impact of oil spills is, in general, lower in high salinity environments. This effect is demonstrated for dispersed oil toxicity under Sea Test conditions (Figure 7). This increased solubility holds true for oil components whether dispersants are used or not but is enhanced by the use of dispersants (Ramachandran *et al, in press*) almost certainly as a result of decreased droplet size which is also know to increase toxicity (Norton and Franklin, 1980). Therefore, high salinity environments could result in increased dispersion but lower solubility of toxic components (Riazi and Al-Enezi, 1999) the combined impacts of which are a complex issue to extrapolate to the environment.

This short review suggests that the issue of temperature and salinity is a complex one and is unlikely to be able to be introduced into any statutory testing process and therefore the review is unlikely to recommend changes to the testing requirements in this respect. However, it does highlight the fact that oil treatment products used in areas of high temperature/salinity (e.g. the Arabian Gulf) or low temperature/salinity (e.g. the Baltic Sea) may need to be assessed under specific test conditions in order to obtain the best list of approved products (Chapman *et al*. 2007).

Combined toxicity/efficacy

Currently the UK scheme uses distinct and separate assessments for toxicity and efficacy. This approach has worked well and therefore is seems unlikely that it will change substantially. It has, however, been acknowledged that the various efficacy tests used globally tend to provide a similar ranking of products and therefore it will be considered whether efficacy results generated by other established methods can be used to support approval applications in the UK.

The rationale underpinning the toxicity assessment in the UK is, however, quite distinct and heavily based on how a product application affects the toxicity of the oil rather than any assessment of the inherent toxicity of the product itself. The review has shown strong continued support for this approach and the protection it affords.

The relationship between efficacy and toxicity is not straightforward and is still not well understood. While we continue to assess these elements in isolation the statutory test process (which provides the greatest bulk of information in the UK) will not inform this debate further. As such some consideration has been given to the introduction of a combined efficacy/toxicity testing procedure. The current Sea Test toxicity assessment incorporates an environment with a standard and reproducible mixing/energy regime from which an efficacy assessment could easily be derived. This would allow the direct comparison of efficacy and toxicity from the same test. However, while current standard guidelines are considered sufficient it seems unlikely that the review will support such a change to the test procedures.

Products other than dispersants

The current Sea and Rocky Shore test procedures were designed specifically with the assessment of oil dispersants in mind and have been used or modified for the assessment of other products as required. In general this has worked well, with the tests being fully suitable for the assessment of other types of products designed to be applied to oil directly on the sea surface (e.g. sorbents etc.). Of the currently recognised categories of product covered by the UK approval scheme it has been raised that the current test procedures are most unsuitable for the assessment of surface cleaners which are not designed for direct application on oil slicks.

A specific testing approach has been developed by Cefas to address the assessment of surface cleaners. In essence this requires the development of a standard procedure for the oiling and weathering of surfaces followed by a test procedure that will allow for the surface to be treated with a given technique or product and all the run-off collected. The subsequent assessment will then be based on three pillars: i) *Efficacy* – Determination of the success of oil removal from the surface via chemical analysis; ii) *Oil Recoverability* – Volumetric determination of the oil floating in the run-off tank; and, iii) *Toxicity* – Toxicological assessment of the run-off water from the treatment. These three elements will enable an assessment of efficiency vs potential impact for a given coastal environment for a given approach.

While relatively few surface cleaners are being provided for approval it is unlikely that the development of a new test procedure will be supported by the review. However, it is known that a variety of commercial surface cleaners (from domestic detergents to garage forecourt cleaners) are being used regularly by recreational and small users in ports and marinas which are not covered by the scheme. Efforts to bring the need to use environmentally acceptable products to the attention of recreational users may result in things changing in the future.

DISCUSSION AND CONCLUSIONS

The government conducted review of the scheme was driven by an increased awareness that there were a number of issues that were limiting the 'fit for purpose' nature of the scheme. These concerns had been raised by scientists, manufacturers, conservationists and responders and the review was designed as a wide consultation that would offer all the opportunity to comment on a broad range of issues.

It is hoped that the review recommendations will allow the approval scheme to become more flexible and responsive to the needs of the manufacturers and responders while fully addressing the needs and concerns of the conservationists and regulators. Presently the scheme applies stringent testing for both efficacy and toxicity using limited oil types and conditions which results in an approved product list that can be applied to all oils and under all conditions (subject to permission). There is no differentiation in the approvals that would allow a responder to make a choice of the most appropriate product for a given scenario based on scientific assessment. It is hoped that the revised scheme will partially address this while not overcomplicating the process or providing excessive financial burdens on the applicants.

At the time of writing this paper the consultation process has been completed but the final recommendations have not been agreed or implemented. By the time of the International Oil Spill Conference in 2008 it is anticipated that many of the above issues, with respect to the UK approval process, will have been resolved.

BIOGRAPHY

Mark Kirby is a senior ecotoxicologist working in the United Kingdom for the Centre for Environment, Fisheries and Aquaculture Science (Cefas). He has over 15 years experience investigating the environmental impacts of the oil industry and is a key advisor to UK government and industry on the effects of oil/chemical spills in the marine environment and of their subsequent treatment (e.g. oil spill dispersants). Mark oversees the regulatory toxicity assessment of oil spill treatment products in UK waters. He is first author of over 15 scientific papers and numerous reports in the field and continues to conduct associated environmental research.

REFERENCES

Blackman, R.A.A., Franklin, F.L., Norton, M.G., Wilson, K.W. (1978). New procedures for the toxicity testing of oil slick dispersants in the United Kingdom. Marine Pollution Bulletin, 9, 234-238.

Blondina, G.J., Singer, M.M., Lee, I., Ouano, M.T., Hodgins, M., Tjeerdema, R.S., Sowby, M.S. 1999. Influence of Salinity on Petroleum Accommodation by Dispersants. Spill Science & Technology Bulletin 5 (2), 127-134.

Chandrasekar, S., Sorial, G.A., Weaver, J.W. 2006. Dispersant effectiveness on oil spills – impact of salinity. ICES Journal of Marine Science 63, 1418-1430.

Chapman, H., Purnell, K., Law, R.J., Kirby, M.F. (2007). The use of chemical dispersants to combat oil spills at sea: A review of practice and research needs in Europe. Marine Pollution Bulletin, 54, 827-838.

FEPA, 1985. The Food and Environment Protection Act 1985. Her Majesty's Stationery Office, London, UK. 38pp.

George-Ares, A., Clark, J.R. 2000. Aquatic toxicity of two Corexit® dispersants Chemosphere 40 (8), 897-906.

George-Ares, A., Lessard, R.R., Becker, K.W., Canevari, G.P., Fiocco, R.J. 2001. Modification of the dispersant Corexit 9500 for use in freshwater. Proceedings: International Oil Spill Conference 2001, Tampa, Florida, March 26-29, 2001, 1209-1211.

Kirby, M.F., Matthiessen, P., Rycroft, R. 1996. Procedures for the Approval of Oil Spill Treatment Products in the UK. DFR Fisheries Research Technical Report Series, Lowestoft,(102): ISSN 0308-5589: 19pp

Law, R.J., Kelly, C.A. (2004). The impact of the *'Sea Empress'* oil spill. Aquatib Living Resources, 17, 389-394.

Norton, M.G., Franklin, F.L. 1980. Research into toxicity evaluation and control criteria of oil dispersants. MAFF DFR Fisheries Research Technical report No. 57, Lowestoft, 20pp.

Ramachandran, S.D., Sweezey, M.J., Hodson, P.V., Boudreau, M., Courtenay, S.C., Lee, K., King, T., Dixon, J.A. 2006. Influence of salinity and fish species on PAH uptake from dispersed crude oil. Marine Pollution Bulletin 52 (10), 1182-1189.

Riazi, M.R., Al-Enezi, G.A. 1999. Modelling of the rate of oil spill disappearance from seawater for Kuwaiti crude and its products. Chemical Engineering Journal 73 (2), 161-172.

Rycroft, R.J., Matthiessen, P., Portmann, J.E. (1994). MAFF review of the UK oil dispersant testing and approval scheme. Directorate of Fisheries Research publication, Lowestoft, United Kingdom, 89 pp.

Sterling, M.C., Bonner, J.S., Ernest, A.N.S., Page, C.A., Autenrieth, R.L. 2004. Chemical dispersant effectiveness testing: influence of droplet coalescence. Marine Pollution Bulletin 48 (9-10), 969-977.

Wei, Q.F., Mather, R.R., Fotheringham, A.F. 2005. Oil removal from used sorbents using a biosurfactant. Bioresource Technology 96 (3), 331-334.

FIGURES

FIGURE 1. THE STATUTORY SEA TEST RIG SET-UP AS USED FOR THE TOXICITY ASSESSMENT OF OIL SPILL TREATMENT PRODUCTS IN THE UNITED KINGDOM.

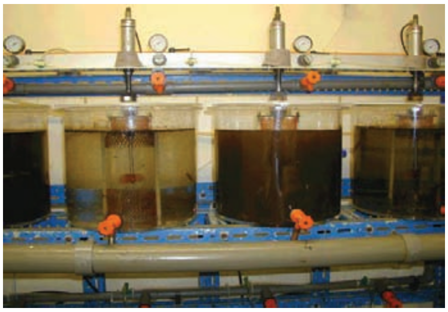

FIGURE 2. A STANDARD SEA TEST IN PROCESS. THE DIFFERENCE CAN CLEARLY BE NOTED BETWEEN MECHANICALLY DISPERSED OIL (LEFT) AND CHEMICALLY DISPERSED OIL (RIGHT).

FIGURE 3. THE COMMON LIMPET (*PATELLA VULGATA*) IS USED IN THE STANDARD ROCKY SHORE TEST. HERE THE TEST ORGANISMS ARE SEEN ON THE PERSPEX PLATE PRIOR TO OIL OR PRODUCT TREATMENT.

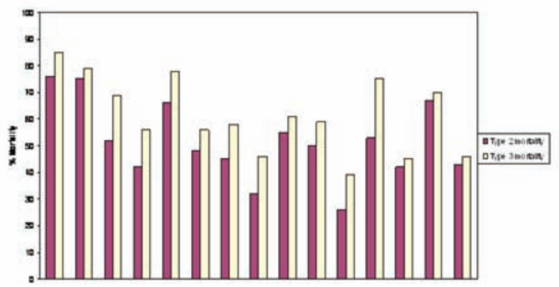

FIGURE 4. A SELECTION OF COMPARITIVE BROWN SHRIMP (*CRANGON CRANGON*) MORTALITY RESULTS OBTAINED DURING SEA TEST EXPOSURES WHEN A DISPERSANT IS APPLIED AS EITHER A TYPE 2 OR A TYPE 3 PRODUCT.

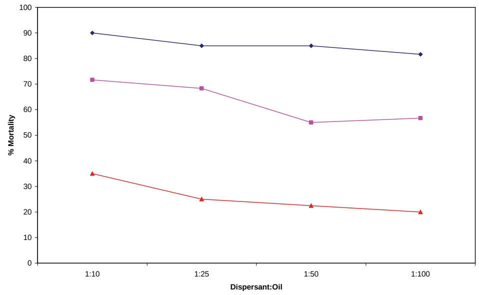

FIGURE 5. MORTALITIES OF BROWN SHRIMP (*CRANGON CRANGON*) DURING A STANDARD SEA TEST WHEN THREE SELECTED DISPERSANTS ARE APPLIED AT REDUCING PRODUCT:OIL RATIOS.

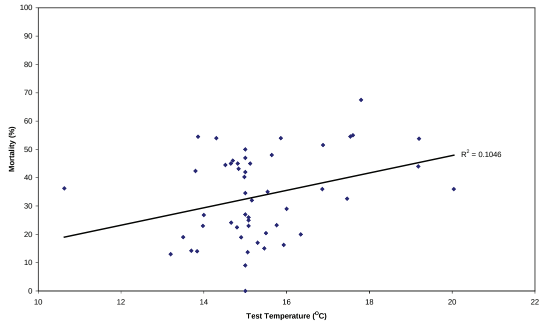

FIGURE 6. THE RELATIONSHIP BETWEEN TEST TEMPERATURE AND FINAL MORTALITY LEVELS OF BROWN SHRIMP (*CRANGON CRANGON*) EXPOSED TO KUWAIT CRUDE OIL DURING THE STANDARD SEA TEST.

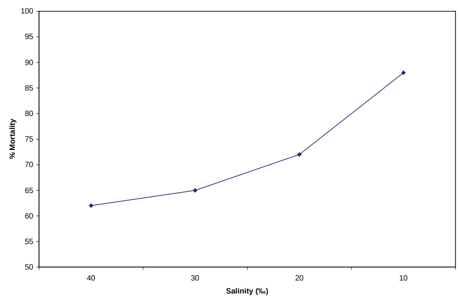

FIGURE 7. THE MORTALITY OF BROWN SHRIMP (*CRANGON CRANGON*) WHEN EXPOSED TO CHEMICALLY DISPERSED KUWAIT CRUDE OIL IN VARYING SALINITY CONDITIONS.