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ESTIMATE OF MAXIMUM LEVEL OF OIL INNOCUOUS TO MARINE BIOTA AS INFERRED FROM LITERATURE REVIEW

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under contract to:  
U.S. Coast Guard Research and Development Center  
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Final Task Report

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16. Abstract The objective of this study was to derive an estimate of the maximum level of oil which can be considered harmless to the marine biological community based on the current state-of-the-art as determined through review and interpretation of the literature. It was found that the pelagic copepod, <u>Acartia tonsa</u> is the most oil-sensitive of the organisms for which there are toxicity data available. The literature review also revealed that Nigerian crude was the most toxic of five crude oils which had been tested against <u>Acartia</u> . The 96-hr. TL <sub>m</sub> (median tolerance level) of Nigerian crude for the subject organism was reported to be 0.55 mg/l. Obviously, a concentration which causes no biological harm would have to be less than 0.55 mg/l. In accordance with accepted practice, 0.01 of the TL <sub>m</sub> value or 0.0055 mg/l (5.5 µg/l) should be safe for <u>Acartia tonsa</u> . Therefore, an oil concentration of 5.5 µg/l should also be safe for all other members of the marine ecosystem. Overall nearly 2,000 individual articles relating to oil pollution were examined. One hundred and thirty-five of the most germane of these articles are listed as references. ↑				
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### METRIC CONVERSION FACTORS

#### Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
<b>LENGTH</b>				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
<b>AREA</b>				
in <sup>2</sup>	square inches	6.5	square centimeters	cm <sup>2</sup>
ft <sup>2</sup>	square feet	0.09	square meters	m <sup>2</sup>
yd <sup>2</sup>	square yards	0.8	square meters	m <sup>2</sup>
mi <sup>2</sup>	square miles	2.6	square kilometers	km <sup>2</sup>
	acres	0.4	hectares	ha
<b>MASS (weight)</b>				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons	0.9	tonnes	t
	(2000 lb)			
<b>VOLUME</b>				
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft <sup>3</sup>	cubic feet	0.03	cubic meters	m <sup>3</sup>
yd <sup>3</sup>	cubic yards	0.76	cubic meters	m <sup>3</sup>
<b>TEMPERATURE (exact)</b>				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

#### Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
<b>LENGTH</b>				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
<b>AREA</b>				
cm <sup>2</sup>	square centimeters	0.16	square inches	in <sup>2</sup>
m <sup>2</sup>	square meters	1.2	square yards	yd <sup>2</sup>
m <sup>2</sup>	square meters	0.4	square miles	mi <sup>2</sup>
ha	hectares (10,000 m <sup>2</sup> )	2.5	acres	
<b>MASS (weight)</b>				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
<b>VOLUME</b>				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m <sup>3</sup>	cubic meters	35	cubic feet	ft <sup>3</sup>
m <sup>3</sup>	cubic meters	1.3	cubic yards	yd <sup>3</sup>
<b>TEMPERATURE (exact)</b>				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

\*1 in = 2.54 centimeters. For other exact conversions and more details, see *Units, Weights, and Measures*, Price 92-25, 30 (GPO: 1976, Publ. 286).

## PREFACE

The following report represents the results of one of ten separate tasks on Contract No. DOT-CG-81-76-1476.<sup>1</sup> The objective of this particular task was to derive an estimate of the maximum level of oil which can be considered harmless to the biological community based on the current state-of-the-art as determined through review and interpretation of the available literature.

To accomplish this task, the available literature was accumulated and screened for opinions relating to levels of oil which might be considered harmless to the biological community, as well as for data to document quantitatively the toxicity of various oils to marine organisms. Only those papers which contained data relating to the degree of toxicity of specific oils or to specific components of oils were found to be useful to this task.

Once the relevant papers were identified, they were categorized according to groups (mollusks, fish, plankton, etc.). Subsequently, by a process of elimination, the organism from each trophic level with the lowest  $TL_m$  (median tolerance level) for oil or oil products was identified. Where possible, data from studies relating the toxicity of specific components of oils, such as the water soluble fractions, were translated into amounts of whole crude oil.

Using the above procedures, the minimum amount of oil which has been shown to have any harmful effect on a member of the biological community (marine) was identified. This  $TL_m$  value was then multiplied by 0.01 to obtain an estimation of the maximum amount of oil which could be considered harmless to members of the marine ecosystem. Although this estimation is purely arbitrary on the part of the writers, insofar as possible it reflects the consensus of the scientific community.

It should be emphasized that the estimate of maximum harmless level of oil presented in this report does not take into consideration the problem of permanent harm versus reversible harm. It also does not address the question of bio-availability of the oil or oil components. In addition, the publication of new data may require future re-evaluation of this estimate.

Major contributions to this report were made by Dr. C. D. Minchew and are hereby acknowledged with gratitude. The technical assistance of Chris Behr and Ruth Thompson is gratefully acknowledged. The assistance of Mrs. Carol Sprayberry in preparing this report is gratefully acknowledged.

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<sup>1</sup>Contract title: "A Scientific Study to Develop One or More Practical Methods for the Accurate Assessment of an Oil Spill Cleanup"

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## INTRODUCTION

While the objective of this report seems rather straightforward, the issues involved are highly complex and poorly understood. In the first place, crude oil can only be defined in the broadest of terms. Simplistically, petroleum is defined as "an oily flammable bituminous liquid that occurs in many places in the upper strata of the earth either in seepages or in reservoir formations" (1). "Crude oil" or "crude petroleum" refers to the fact that it is "petroleum as it occurs naturally as it comes from an oil well or after extraneous substances (such as entrained water, gas, and minerals) have been removed" (1). Chemically it is a complex mixture of hydrocarbons which contains small amounts of other substances such as oxygen, nitrogen or sulfur containing compounds, resinous compounds, asphaltic compounds and metallic compounds. Even in their natural state, crude oils vary widely in chemical and physical characteristics, and when they are released into the environment they undergo continuous change. For example, when crude oil is released onto the surface of a body of water, some constituents volatilize, some dissolve in the water column, some undergo oxidation and photochemical changes, and some are biologically degraded or transformed. In essence then, crude oil must be viewed as more of a concept or a state-of-affairs than as a chemically definable entity. There is considerable variation in the methodology employed in estimating the concentration of oil in environmental samples; consequently, even more confusion is generated in terms of the amount of oil causing a given effect.

The second major issue involved in meeting the objective of this report is an understanding of the term "harmless." By definition "harmless" means innocuous or free of or lacking the capacity or intent to injure or damage (1). As used in the objective, the term refers to the level of oil which can be considered innocuous to the biological community. In this respect it must be realized that the level of oil which is harmful to one member of the community may be innocuous to others or even stimulatory to still others. Therefore, change is not synonymous with harm. Furthermore, some effects are temporary, and the organism returns to normal as soon as the concentration of oil drops below that causing the effect.

From a realistic standpoint, a locally damaging spill may have very little impact on the overall system, and judgments in this respect are subject to considerable personal bias.

The literature on the subject of oil pollution is voluminous and ranges from legal ramifications of oil spills to the origin of petroleum. Overall, nearly 2000 individual articles relating to oil pollution were examined in the course of completing this report. Generally speaking, papers germane to this report can be categorized as (a) reports on accidental oil spills in the environment or (b) laboratory investigations of the effects of oil or components of oil on specific target organisms.

#### REPORTS ON SPILLS IN THE ENVIRONMENT

Over 250 reports on field investigations following oil spills were evaluated in this study. From the scientific standpoint, these reports are lacking for a number of reasons, including the absence of pre-spill data and inadequate sampling. Often, different investigators drew entirely different conclusions from the same data. The report by Mackin (2) clearly illustrates this point.

Some of the reports are most informative in regard to acute effects of oil in the environment, but no data are available on the concentration of oil causing the effect. In other cases, where estimates have been made on the concentration of oil in the sediments, the lack of pre-spill data negates the value of the reports as they relate to the objective of this report. The data from major oil spills may be valuable from the standpoint of overall observations on effect and recovery, but cannot be employed to derive rigidly quantitative dimensions on the amount of oil causing an effect. For example, it is impossible to differentiate between effects caused by residual low levels of oil in the system and effects caused by shifts in the ecology resulting from the impact of the initial spill. Under these circumstances, the reports on field investigations following oil spills were found to be useless in regard to the objective of this report.

#### REPORTS ON LABORATORY STUDIES

On the other hand, some of the laboratory investigations quantitate the amount of oil causing an effect, but considerable caution must be exercised in extrapolating from their results to the environment. Other reports are concerned with the effect of certain fractions of oil or specific compounds (e.g. naphthalene). These laboratory studies cover a wide range of organisms and address both lethal and non-lethal effects.

### Lethal Effects of Oil

Figures on lethality are normally reported as LD<sub>50</sub> values, LC<sub>50</sub> values or TL<sub>m</sub> values where: LD refers to the lethal dose (the subscript number refers to the percent of the population killed at the dose), LC refers to lethal concentration (the subscript number refers to the percent of the population killed at that concentration), and TL<sub>m</sub> refers to the tolerance level at which 50% (subscript m = median) of the population survives. In all cases the subscript descriptor may be changed to reflect the percentage of the population killed (LD and LC values) or the percentage of the population surviving (TL values). The term TL, as used in Standard Methods (3), is very broad in its application and can be used to express the lethal level of a toxic agent such as temperature and pH as well as to express the lethal concentration of a toxic agent such as oil or pesticides. For this reason, it can be substituted for LC<sub>50</sub> when reference is made to a toxic concentration. The term LC<sub>50</sub> cannot be substituted for the term TL<sub>m</sub> when reference is made to the lethal level of a toxic agent such as temperature and pH. The term LD<sub>50</sub>, as used in most reports citing aquatic bioassay results, may also be replaced by the term TL<sub>m</sub> because it has generally been used to refer to a certain concentration of a toxic substance in water. This usage is not appropriate, however, since technically, dose refers to a measured quantity administered directly to a test organism. Consequently, the term LD<sub>50</sub>, though encountered in earlier papers, is currently not recommended for reporting aquatic bioassay data.

The objective of this report, as stated above, is to determine, via the literature, the maximum level of oil which can be considered harmless to the biological community. Therefore, the following are references to the smallest amounts of oil reported to be lethal to representatives of various groups.

For the mummichog (Fundulus heteroclitus), the TL<sub>100</sub> value (amount of oil at which 100% of the test organisms survived) was 12 ml/l for exposure times up to 96 hrs. The TL<sub>0</sub> value was 36 ml/l for exposure times as short as 24 hrs (4). Assuming a specific gravity of 0.7 for the oil, this means that a dose of 8400 mg/l (ppm) would not be lethal to this fish.

With pink salmon fry (Oncorhynchus gorbuscha), the lethality of Prudhoe Bay crude oil varied with season and the lowest 96-hr TL<sub>m</sub> value reported was 110 mg/l (5).

Other reports give 96-hr TL<sub>m</sub> values as low as 1.9 mg/l of Bunker C for the tidewater silverside (Menidia beryllina) (6). In some cases there is a

tremendous difference between the  $TL_m$  values for whole crude oil versus the water-soluble fraction of the crude oil. For example, the 96-hr  $TL_m$  value for whole South Louisiana crude was 3,700 mg/l but only 5.5 mg/l for its water-soluble fraction (Menidia beryllina as the test organism) (6).

The 48-hr  $TL_m$  values for the shrimp-like crustacean, Mysidopsis almyra, ranged from a high of 37.5 mg/l for South Louisiana crude to a low of 0.9 mg/l for Bunker C. The 96-hr  $TL_m$  using Bunker C was 2.6 mg/l for the palaemonid shrimp (Palaemonetes pugio) and 1.9 mg/l for postlarvae of the penaeid shrimp (Panaeus aztecus) (6).

Tests employing the tidalpool copepod crustacean, Tigriopus californicus, showed that the concentration of diesel oil had to be less than 87 mg/l to be equal to control values (7).

Of the five crude oils tested against four pelagic copepod species, Nigerian crude was the most toxic. Its 96-hr  $TL_m$  value for Acartia, the most sensitive of the copepods tested, was 0.55 mg/l. With marine phytoplankton the lowest 12-day  $TL_m$  value (9.5 mg/l) was obtained with Empire Mix crude oil using Lithodesmium undulatum as the test organism (8).

Studies using the amphipod crustacean, Gammarus oceanicus, revealed that the toxicity of Venezuelan crude was far greater for juveniles (48-hr  $TL_m = 0.8 \mu\text{l/l}$ ) than it was for adults (48-hr  $TL_m = 550 \mu\text{l/l}$ ) (9). These values translate into 48-hr  $TL_m$  values of 530 mg/l and 0.77 mg/l for the adults and juveniles, respectively.

The water-soluble fraction from light Venezuelan crude was shown to be toxic to larvae of the decapod crustacean (Neopanope texana). The water-soluble fraction was prepared by using 10 ml of oil/liter of water and had an approximate hydrocarbon concentration of 4 mg/l (10).

The lowest 96-hr  $TL_m$  values for the polychaetous annelid, Neanthes arenaceo-dentata was found to be 2.7 mg/l for the water-soluble fraction of Bunker C (11).

#### Non-lethal Effects of Oil

Without addressing the question of whether or not a specific non-lethal effect was harmful to the biological community, the following review of the non-lethal effects and causative concentrations of oil is given.

It has been shown that oil can inhibit phytoplankton photosynthesis but the inhibitory concentration was in excess of 30-50  $\mu\text{g/l}$ . Lower concentrations of oil were stimulatory (12). Oil was also shown to be inhibitory to photosynthesis by kelp, but the amounts of oil required were large (approx. 100 mg/l) compared to the above (13).

Oysters remained tightly closed in oil concentrations of 900  $\mu\text{g}/\text{l}$  (14). Obviously, this could be detrimental to the organism if this continued for a long period of time.

A concentration of oil as low as 1  $\text{mg}/\text{l}$  was reported to have some apparent sublethal effect on the color and behavior of the American lobster (Homarus americanus) (15).

The opercular rate of pink salmon (Oncorhynchus gorbuscha) was shown to be increased in 3 hrs by 2.83  $\text{mg}/\text{l}$  of oil but the rate normalized after 12 hrs (16).

Bacterial chemoreception was shown to be inhibited by the presence of oil. This effect was reversible (17).

#### CONCLUSIONS

The objective of this report is to derive an estimate of the maximum level of oil which can be considered harmless to the biological community. As indicated in this report, a concentration of 0.55  $\text{mg}/\text{l}$  of Nigerian crude oil was reported to be toxic to the copepod, Acartia tonsa (96-hr,  $\text{TL}_m$ ) (8). Obviously, a concentration which causes no biological harm would have to be less than 0.55  $\text{mg}/\text{l}$ . After consultation with numerous investigators, it was concluded that 0.1 - 0.01 of the  $\text{TL}_m$  or  $\text{LD}_{50}$  value would be safe for the subject organism. Therefore, a concentration of 0.0055  $\text{mg}/\text{l}$  or 5.5  $\mu\text{g}/\text{l}$  should be safe for Acartia tonsa. Since Acartia is the most oil-sensitive of the organisms for which toxicity data are available, an oil concentration of 5.5  $\mu\text{g}/\text{l}$  should be safe for all other members of the ecosystem. This concentration of oil is considerably less than that reported to have any non-lethal effect. The lowest concentration of oil reported to be deleterious to any member of the ecosystem was 30-50  $\mu\text{g}/\text{l}$  (possibly inhibitory to phytoplankton photosynthesis) (12).

After a comprehensive review of the literature on oil pollution and consultations with numerous investigators, it is concluded that an oil concentration of 5.5 ppb would be harmless to the biological community.

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