

A STUDY OF THE ENVIRONMENTAL BENEFITS OF  
PROPOSED BATEA AND NSPS EFFLUENT LIMITATIONS  
FOR THE OFFSHORE SEGMENT OF THE OIL AND GAS  
EXTRACTION POINT SOURCE CATEGORY



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ENVIRONMENTAL PROTECTION AGENCY  
OFFICE OF WATER PLANNING AND STANDARDS  
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## PREFACE

The attached draft document is a contractor's study prepared for the Office of Analysis and Evaluation of the Environmental Protection Agency (EPA). The purpose of the study is to discuss the environmental benefits which could result from the application of Best Available Technology Economically Achievable (BATEA) effluent limitations and New Source Performance Standards (NSPS) to be established under sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended for the Offshore segment of the Oil and Gas Extraction point source category.

This study supplements the technical study (EPA Development Document) and economic study (EPA Economic Impact Analysis) supporting the issuance of proposed regulations under sections 304(b) and 306. The Development Document surveys existing and potential waste treatment control methods and technology within particular industrial point source categories and supports proposal of certain effluent limitation guidelines and standards of performance based upon an analysis of the feasibility of these guidelines and standards in accordance with the requirements of sections 304(b) and 306 of the Act. Presented in the Development Document are the investment and operating costs associated with the various alternative control and treatment technologies. The Economic Impact Analysis provides further analysis by estimating the broader economic effects which might result from the required application of various control methods and technologies. The Economic Impact Analysis investigates the effect of alternative approaches in terms of product price increases, effects upon production and employment, the continued viability of affected wells, effects upon foreign trade and other competitive effects. The attached document supplements this analysis by attempting to examine the environmental benefits which would result from the implementation of the guidelines and standards. This study investigates the effects of produced water (the brine produced in the wells along with the oil and gas) on marine and estuarine biota, and on human beings. This study does not purport to be an analysis to balance the costs of implementing the BATEA and NSPS regulations with the benefits of these regulations nor does the study address any benefits other than those direct environmental benefits mentioned above.

This study has been prepared with the supervision and review of the Office of Water Planning and Standards of the EPA. This report was submitted in partial fulfillment of

Contract No. 68-01-4177 by Energy Resources Company Inc. This report reflects work completed as of April 1977. This study was undertaken in a spirit of cooperation with concerned parties whose position was that these limitations and standards would do little to benefit the environment. This report in no way signals a departure from the Agency policy of developing technology based standards nor does it in any way reflect a change in the Agency determination that this type of study is not required as part of its rulemaking procedure.

This draft report is not an official EPA publication. The study will be considered along with the information contained in the Development Document and Economic Impact Analysis and any comments received by EPA on these documents before or during proposed rulemaking proceedings necessary to establish final regulations. Prior to final promulgation of regulations, the accompanying study shall have standing in any EPA proceeding or court proceeding only to the extent that it represents the views of the contractor who studied the subject industry. It cannot be cited, referenced, or represented in any respect in any such proceeding as a statement of EPA's views regarding the subject industry.

## SUMMARY

The purpose of this study is to attempt to examine the environmental benefits which would result from the implementation of the Best Available Technology Economically Achievable (BATEA) and New Source Effluent Limitations for the offshore segment of the oil and gas extraction industry, published by the Effluent Guidelines Division of the Office of Water and Hazardous Materials, U.S. Environmental Protection Agency (EPA).<sup>1</sup> The major concern of these effluent limitations is with the produced water (the brine produced in the wells along with the oil or gas) that is discharged into receiving waters after separation of oil or gas from the brine has been effected by separation devices on the production platforms. Produced oilfield brines contain substances, such as oil hydrocarbons and trace metals, with toxic effects on marine and estuarine biota, and on human beings.

The BATEA and New Source regulations prohibit the discharge of produced water into near offshore waters and restrict the oil hydrocarbon content of produced water discharged into far offshore waters. Regulations similar to the near offshore regulations are being considered for onshore coastal waters (e.g., coastal bays and inlets). The BATEA regulations for near offshore waters have been the subject of considerable criticism by the oil industry. The oil industry has claimed that the discharge of produced water has only an insignificant impact on the coastal environment, and hence, the considerable costs that would be involved in implementing the no-discharge limitation are unjustified in terms of the benefits that can be expected to result. In order to assess the merits of this claim, the EPA has supported this study, whose objective is to attempt to evaluate the benefits that may be expected to result from implementation of the effluent regulations.

The methodology adopted in this study was to assess expected benefits of the effluent regulations at four specific sites: two in onshore coastal waters, and one each in near and far offshore waters. Benefits were measured in terms of the reduced levels of brine-related impacts which could be expected to result from the BATEA regulations.

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<sup>1</sup>U.S. Environmental Protection Agency, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Segment of the Oil and Gas Extraction Point Source Category, 1975.

Impacts were evaluated in terms of (1) the area of an "unsafe zone" surrounding the point of discharge (i.e., the area that was predicted to be subjected to brine contaminants at concentration levels known to have toxic effects on marine biota, or to present a potential human health threat because of the bioaccumulation of contaminants in the tissues of marine organisms used for food); (2) the relative size of the unsafe zone compared to the size of the receiving waterbody; and (3) the biological productivity of the impacted zone. The major conclusions of this study follow.

- Toxic Substances in Produced Water

Produced brines contain a variety of substances known to have lethal and sublethal toxic effects on marine and estuarine organisms. These toxic constituents include oil hydrocarbons, trace metals (including arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc), phenol, and cyanide. Some of these toxicants have been measured in produced waters at concentrations up to several orders of magnitude higher than toxicologically safe levels. In addition to their effect on marine organisms, some of the brine components (particularly mercury and the polynuclear aromatic hydrocarbon benz[a]pyrene) are known to be bioaccumulated in shellfish which may be used for human consumption, and so present a potential human health threat.

- Treatment Methods

Current methods used for separating oil hydrocarbons from produced water have little, if any, effect on levels of dissolved contaminants. These include the dissolved aromatic hydrocarbons which are among the most toxic hydrocarbon components of brines, and the trace metals.

- Benefits for Onshore Coastal Waters

The benefits which would be achieved if the proposed near offshore BATEA regulations are extended to apply to discharges in onshore coastal waters are highly site specific. Small, enclosed, shallow, and biologically productive bays with large brine discharges will probably stand to benefit considerably. The benefits to be achieved by prohibiting small discharges of produced water into larger and deeper coastal embayments with adequate tidal and freshwater mixing are likely to be correspondingly small.

- Near Offshore Benefits

In near offshore Gulf of Mexico waters, the analysis performed for a single site is insufficient to serve as a complete basis for estimating regional impacts. In order to extrapolate from impact at a single platform to regional impacts, data on platform locations and discharge rates throughout the region are needed. The benefits to be achieved by prohibiting the discharge of produced waters into near offshore waters will depend critically on the density of production platforms and rates of discharge in a particular region. In areas where platforms are highly concentrated, aggregate discharge levels are likely to be large, and impact zones may overlap. In such areas significant benefits could probably be achieved. In areas with low platform densities and only small rates of brine discharge the benefits are likely to be less pronounced. The analysis performed in this study should, therefore, be supplemented by the assembly of a data base providing information on the location and discharge rates of production platforms in near offshore Gulf of Mexico waters.

- Far Offshore Benefits

In far offshore Gulf of Mexico waters, the major conclusion to be drawn from this study is that there would probably be little reduction in impacts resulting from the imposition of BATEA regulations over and above those already achieved by the BPCTCA restrictions. The more stringent treatment requirements imposed on far offshore platforms by the BATEA requirements will do little to remove the dissolved hydrocarbons and trace metals which are responsible for much of the toxic impact of oilfield brines.

These conclusions are documented and amplified in the main body of this report. The individual chapters of the report are summarized in the remainder of this section.

- Chapter One: Introduction

Oil extracted at offshore oil production platforms is found to be mixed with a saline solution which, when separated from the oil, is known as produced water or oilfield brine. After separation from the oil, this brine is frequently discharged into the estuary, bay, or open ocean in which the platform is located. Oilfield brines are generally highly saline -- much more so than seawater -- and contain a variety of components known to be toxic to marine



and coastal life, including oil hydrocarbons, phenols, cyanide, arsenic, silver, nickel, chromium, copper, lead, mercury, and cadmium. Since brine constituents have a demonstrated toxicity to marine life, and since they may be bioaccumulated by marine organisms destined for human consumption, their discharge into the ocean is a source of concern for environmental policy makers. In response to this concern, the U.S. Environmental Protection Agency (EPA) has published a set of effluent limitations for the offshore segment of the oil and gas extraction industry in order to prevent any adverse effects which may be associated with brine discharge. These guidelines include Best Practicable Control Technology Currently Available (BPCTCA) regulations which take effect in July 1977 and Best Available Technology Economically Achievable (BATEA) and New Source regulations which take effect for existing sources in June 1983. The 1983 regulations require zero produced water discharge in near offshore waters. Similar regulations are being considered for oil production in onshore waters inside the coastal baseline (a legal demarcation line constructed as a "smoothed" version of the actual coast. Inland bays such as Barataria Bay, which contains significant oil production activity, are inside this demarcation line). Less stringent BATEA requirements are imposed on far offshore oil platforms (i.e., those lying outside of the 3-mile limit). The far offshore regulations require only reduced, rather than zero, oil discharge. Since the expense of implementing the BATEA regulations is expected to be great, it is important to assess the level of benefits which could be achieved by their implementation. The analysis in this report is addressed to that issue.

## ● Chapter Two: Project Methodology

An approach was developed for analyzing the environmental impacts of brine discharges in a site specific fashion. For each site a "zone of impact" is defined inside of which particular levels of adverse effects can be expected to occur. The site can then be characterized by the area of the zone of impact, by the percent of the receiving waterbody which it covers (in the case of an enclosed waterbody such as Hackberry Bay), and by the ecological importance of the area being impacted. Two classes of adverse effects are considered: toxic impacts on marine communities (fish, benthos, plankton), and potential toxic impacts on humans as a result of the bioaccumulation of brine constituents in food organisms. Specific brine components considered in the analysis are oil hydrocarbons, cadmium, silver, copper, chromium, mercury, lead, nickel, arsenic, zinc, cyanide, and phenol.

The analysis contains four principal steps: (1) data are collected on the concentrations of particular pollutants in oilfield brines and of the volumes of brine discharged at each site; (2) a computer dispersion model is used to predict the quasi-steady state concentrations of each of these constituents in the vicinity of the production platform; (3) the nature and level of impacts associated with various concentrations of each contaminants are determined, and "safe" concentrations are estimated; and (4) the areas of impact zones are determined.

The report focuses on four oil production sites: two onshore (Hackberry Bay, Louisiana, and Cook Inlet, Alaska), one near offshore (Grand Isle), and one far offshore (in the Gulf of Mexico).

- Chapter Three: Composition of Oilfield Brines

Oilfield brines contain trace metals, oil-derived hydrocarbons, and a number of other toxicants including ammonia and cyanide. The brines are also highly saline. Although some studies have been done on the trace metal composition of oilfield brines, little is known about the specific hydrocarbon components. In general, these hydrocarbons cannot be expected to occur in the same relative concentrations at which they occur in crude oil, since the more water-soluble components will be preferentially concentrated in the oilfield brines. In particular, the brines will be relatively enriched in aromatic hydrocarbons. This is significant since the aromatic components of crude oil are those which create the most severe toxicity problems. Some inference relating to the hydrocarbon composition of oilfield brines can be made by analogy with data on the composition of the so-called water-soluble fraction of crude oil.

Concentrations of trace metals in produced water vary considerably from region to region and even from site to site within the same region. Some of the metals have been measured at concentrations up to several orders of magnitude higher than toxicologically safe levels.

A number of treatment processes are available for reducing the levels of oil contamination in produced waters, but these generally only reduce the levels of suspended contaminants in the brine. As a result, they have little or no effect on trace metal levels or on dissolved hydrocarbon concentrations. One treatment process, gas flotation, may

result in oxidation of some of the dissolved hydrocarbon components, but it will be predominantly the non-aromatic components which will be affected by this process.

#### ● Chapter Four: Dispersion Modeling

A plume of produced water discharged from an offshore oil platform will disperse under the influence of three principal forces: advection (movement with the prevailing current), diffusion ("spreading" of the plume due to spatial inhomogeneities in the current field), and decay (loss of brine constituents due to sedimentation, adsorption, or biodegradation). Advection will be influenced principally by current velocity and direction; in general, there will be two current components, a "steady" component (due in an estuary, for example, to the continuous influx of fresh-water) and a periodically varying tidal component. The diffusion of a plume can be characterized by a set of three diffusion coefficients (one for each of three mutually perpendicular directions) whose magnitude in general will depend both on the scale (size) of the pollutant plume and on site specific dispersion characteristics.

The dispersion of brine under the influence of these three forces can be modelled by a set of differential equations and associated boundary conditions as described in detail in Appendix B. These in turn can be solved numerically by a computer program which predicts quasi-steady state concentration distributions through a tidal cycle. Such a program was used in this project to predict tidally averaged pollutant concentrations and to locate a series of isopleths, or lines of equal predicted pollutant concentration.

Isopleths were plotted for several concentrations at each site, and the areas they enclosed were measured by planimetry. Area versus concentration curves (showing the total area at each site over which the pollutant concentration is greater than or equal to a particular value) were then drawn for each site. Several model runs were made for each site, using several sets of plausible values for input parameters for which precise quantitative data were not available (the computer model requires a number of input parameters, including volume of brine discharged, current velocities and directions, magnitude of various diffusion coefficients, and water depth at the discharge point). For each site best, worst, and base case area versus concentration curves were then defined.

- Chapter Five: Results of Calculations with Dispersion Model

Each of the input parameters required by the model is described in this chapter, and their qualitative effect on final pollutant concentrations are discussed. The determination of precise values for some of these parameters would require extensive field studies at each site, so some estimates were based on previous empirical and theoretical work. The rationale for the base values and ranges used for the input parameters are discussed.

In general, predicted brine concentrations showed a high degree of site specific variability.

- Chapter Six: Methodology for Impact Assessment

The toxicological data on the effects of oilfield brine components were reviewed, and used to make estimates of "safe" levels of brine constituents. Safe levels were defined which would prevent significant toxic impacts on marine communities and prevent the bioaccumulation of brine constituents to dangerous levels by human food organisms. A number of factors which may modify the toxicity of brine components in the marine environment, including adsorption, sedimentation, biodegradation, complexation, synergistic or antagonistic interactions with other pollutants, and interactions with the effects of other environmental stresses, are discussed. Because of the lack of sufficient data, these factors are not used in the quantitative analysis. The chapter also discusses the available field data on ecological impacts in areas surrounding offshore oil production platforms.

- Chapter Seven: Impact Analysis

Using data on safe levels in conjunction with data on levels of each constituent in the discharged brine, a Necessary Dilution Factor (NDF) was calculated separately for each constituent (this was the dilution necessary to reduce the concentration of the constituent to its "safe" level). An analysis which assumed purely additive (i.e., neither synergistic nor antagonistic) interactions between the toxic effects of different brine constituents was also used to define an overall safe level for brine itself, and the necessary dilution factor implied by it. Area versus concentration curves for each site were then used to determine the area over which the actual brine dilution would be

less than or equal to its NDF. This was used as an estimate of the impacted area for each site. Qualitative ecological descriptions of each site were also used in a discussion of the relative ecological and economic importance of the areas being impacted.

The areas of the impact zones are highly site specific, and depend to a significant extent on site specific dispersion patterns. The severest impacts would probably be felt in relatively small, enclosed, and highly fertile regions such as Hackberry Bay, and significant benefits would probably result from the imposition of no-discharge requirements in these areas. Smaller benefits would probably result at sites such as mid Cook Inlet, where the impacted area is relatively small, where there are no significant fisheries or shellfish beds, and which is relatively nonproductive due to high levels of tidal bottom scouring and the extremely high turbidity naturally found in that area (these comments do not apply to other areas of Cook Inlet, such as the highly fertile Lower Inlet).

Some field studies have been conducted in the vicinity of offshore oil production platforms. With some exceptions, the qualitative findings of these studies agree with the predictions of our analysis, but the available quantitative data is generally inadequate to accurately assess many aspects of the model. Particularly, field studies frequently do not include the current and brine discharge information which is necessary to meaningfully interpret field impact data. It is recommended that an extensive program of field data collection be initiated in order to provide further input data for this type of analysis and to validate some of its conclusions.

- Chapter Eight: Conclusions

In this chapter, the major conclusions of the report are summarized.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 The Nature of the Problem: Summary

Crude oil extracted from natural geological reservoirs at offshore oil production platforms is generally found to be mixed with a saline solution known as oilfield brine. This brine is separated from the crude oil at the production platform, and the "produced water" thus formed is then generally discharged into the estuary, bay, or open sea in which the platform is located. Oilfield brines are generally highly saline -- frequently much more so than seawater -- and contain a variety of components known to be toxic to marine and estuarine life. These components can be divided into two broad classes: trace heavy metals and oil-derived hydrocarbons, although other types of contaminants, including the cyanide ion, are also known to be present (Table 1-1).

TABLE 1-1

#### CONTAMINANTS CONSIDERED IN THE STUDY

ORGANICS	TRACE METALS	OTHER TOXICANTS
Oil Hydrocarbons Phenol	Arsenic Cadmium Chromium Copper Lead Mercury Nickel Silver Zinc	Cyanide

Since brine components have a demonstrated toxicity to marine and estuarine life, and since they may be bioaccumulated by marine organisms destined for human consumption, their discharge into the ocean is a source of concern for environmental policy makers.

In response to this concern, the U.S. Environmental Protection Agency (EPA) has published a set of effluent limitations for the offshore oil extraction industry designed to prevent adverse ecological impacts resulting from brine discharges. These guidelines include Best Practicable Control Technology Currently Available (BPCTCA) regulations, Best Available Technology Economically Achievable (BATEA) regulations, and New Sources Performance Standards. The BPCTCA and BATEA regulations apply to existing sources and take effect in July 1977 and July 1983 respectively. The proposed New Sources Performance Standards for the offshore oil and gas extraction point source category are identical with the BATEA regulations and are applicable to new sources, construction of which is commenced after the promulgation of the regulations for the offshore oil and gas extraction category. These effluent limitations are described in the following section.

Since the 1983 BATEA regulations for the offshore oil and gas extraction point source category are considerably more stringent than the BPCTCA regulations, it is important to assess the level of potential ecological and health benefits which could be achieved by their implementation. The analysis described in this report is addressed to this issue. It attempts to estimate the ecological effects of brine discharge from offshore and onshore oil production platforms, and therefore the ecological benefits which would result from reinjection of brines.

## 1.2 Policy Background: The Effluent Regulations

The Effluent Guidelines Division of the Office of Water and Hazardous Materials of the U.S. Environmental Protection Agency has published interim final effluent limitations and proposed new sources performance standards for the offshore<sup>1</sup> segment of the oil and gas extraction point source category.

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<sup>1</sup>U.S. Environmental Protection Agency, Effluent Guidelines Division, Office of Waste and Hazardous Materials, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Segment of the Oil and Gas Extraction Point Source Category, September 1975.

These effluent limitations are given in Tables 1-2 and 1-3. The limitations given in Table 1-2 are based on BPCTCA and are to be met no later than July 1, 1977. The more exacting limitations given in Table 1-3 are based on BATEA and are to be met no later than July 1, 1983.

The major concern of the effluent limitations is with the potential pollutants contained in the produced water (the brine produced in the wells along with the oil and gas) that is discharged after separation of oil or gas from the water has been effected by the separators on the production platforms. These include oil hydrocarbons, phenols, heavy metals, cyanide, chlorides, BOD, COD, and suspended solids. Of these potential pollutants only oil is directly regulated by the proposed effluent limitations.

The BPCTCA limitations restrict the residual concentration of oil in produced water discharged into open waters to be no greater than 72 mg/l for any one day, and to be no greater than an average of 48 mg/l for any period of 30 consecutive days. The BPCTCA limitations apply uniformly in both near offshore (within the 3-mile limit) and far offshore (outside the 3-mile limit) waters. The BATEA limitations<sup>2</sup> distinguish between near offshore and far offshore waters.

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<sup>2</sup>The coastal waters of the United States are divided into two separate regions, onshore and offshore, by a legal demarcation line known as the coastal baseline. This baseline is used as a reference line for the calculation of the 3-mile line and other coastline-based demarcation lines, and essentially represents a "smoothed" version of the U.S. coastline. Bays or inlets whose closure at the coast is less than 24 miles are inside this reference line, which is drawn across the mouth of such waterbodies. All coastal waters inside the line are known as onshore waters. Included in the onshore classification are areas such as Louisiana's Barataria Bay region, and part of Alaska's Cook Inlet, both of which contain significant oil production activities. The offshore production areas outside the baseline are further subdivided into near offshore sites (inside the 3-mile limit) and far offshore sites (outside the 3-mile limit). Regulations similar to those which apply to brine discharges from offshore platforms are being considered for onshore platforms, so they too will be considered in this report. Figure 1-1 shows the rationale for the construction of the baseline. Figure 1-2 shows the location of the baseline in Cook Inlet. The baseline in the Louisiana coast section of the Gulf of Mexico lies along the string of barrier islands separating open Gulf waters from enclosed coastal bays.



TABLE 1-2  
OFFSHORE SEGMENT - OIL AND GAS EXTRACTION INDUSTRY  
EFFLUENT LIMITATIONS - BPCTCA

SUBCATEGORY	WATER SOURCE	POLLUTANT PARAMETER - EFFLUENT LIMITATIONS		
		OIL & GREASE - mg/l		RESIDUAL CHLORINE mg/l
		MAXIMUM FOR ANY ONE DAY	AVERAGE OF DAILY VALUES FOR 30 CONSECUTIVE DAYS SHALL NOT EXCEED	
Near Offshore	produced water	72	48	N/A
	deck drainage	72	48	N/A
	drilling muds	a	a	N/A
	drill cuttings	a	a	N/A
	well treatment	a	a	N/A
	sanitary M10 <sup>c</sup>	N/A	N/A	greater than 1 <sup>b</sup>
	M9IM <sup>c</sup>	N/A	N/A	N/A
	domestic	N/A	N/A	N/A
Far Offshore	produced sand	a	a	N/A
	produced water	72	48	N/A
	deck drainage	72	48	N/A
	drilling muds	a	a	N/A
	drill cuttings	a	a	N/A
	well treatment	a	a	N/A
	sanitary M10 <sup>c</sup>	N/A	N/A	greater than 1 <sup>b</sup>
	M9IM <sup>c</sup>	N/A	N/A	N/A
	domestic	N/A	N/A	N/A
	produced sand	a	a	N/A

<sup>a</sup>No discharge of free oil to the surface waters.

<sup>b</sup>There shall be no floating solids as a result of the discharge of these materials.

<sup>c</sup>Minimum of 1 mg/l and maintained as close to this concentration as possible.

TABLE 1-3

OFFSHORE SEGMENT - OIL AND GAS EXTRACTION INDUSTRY  
EFFLUENT LIMITATIONS - BATEA AND NEW SOURCE

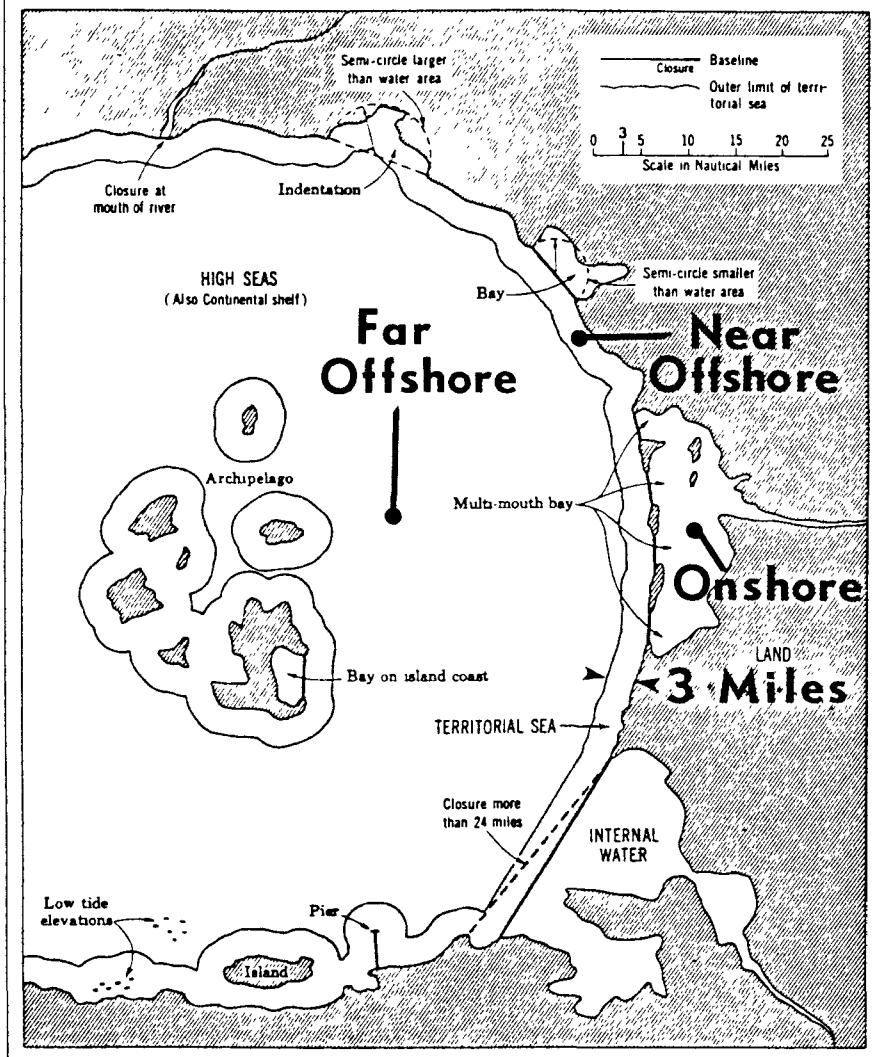
SUBCATEGORY	WATER SOURCE	POLLUTANT PARAMETER - EFFLUENT LIMITATIONS		
		OIL & GREASE - mg/l		RESIDUAL CHLORINE mg/l
		MAXIMUM FOR ANY ONE DAY	AVERAGE OF DAILY VALUES FOR 30 CONSECUTIVE DAYS SHALL NOT EXCEED	
Near Offshore	produced water	No Discharge		
	deck drainage	72	48	N/A
	drilling muds	a	a	N/A
	drill cuttings	a	a	N/A
	well treatment	a	a	N/A
	sanitary M10	N/A	N/A	greater than 1 <sup>b</sup>
	M9IM <sup>c</sup>	N/A	N/A	N/A
	domestic <sup>c</sup>	N/A	N/A	N/A
Far Offshore	produced sand	a	a	N/A
	produced water	52	30	N/A
	deck drainage	52	30	N/A
	drilling muds	a	a	N/A
	drill cuttings	a	a	N/A
	well treatment	a	a	N/A
	sanitary M10	N/A	N/A	greater than 1 <sup>b</sup>
	M9IM <sup>c</sup>	N/A	N/A	N/A
	produced sand	a	a	N/A

<sup>a</sup>No discharge of free oil to the surface waters.

<sup>b</sup>Minimum of 1 mg/l and maintained as close to this concentration as possible.

<sup>c</sup>There shall be no floating solids as a result of the discharge of these materials.

# THE BASELINE FROM WHICH THE TERRITORIAL SEA IS MEASURED



COURTESY U. S. DEPARTMENT OF STATE

Figure 1-1. The baseline dividing onshore and offshore regions of the coastal sea. (J. Leslie Goodier, U.S. Federal and Seacoast State Offshore Mining Laws (Washington, D.C.: Nautilus Press, 1972).)

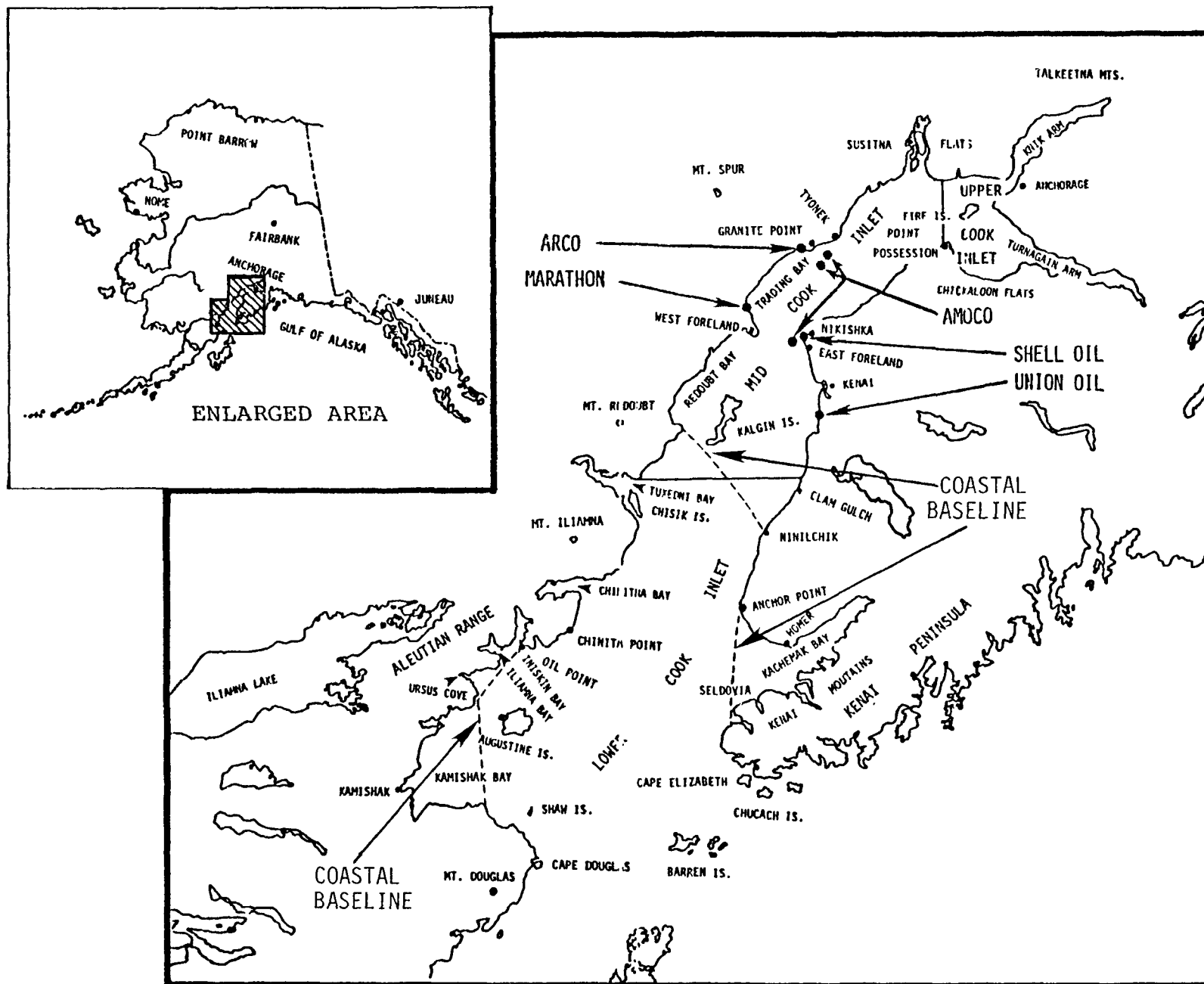


Figure 1-2. Location of the coastal baseline in Cook Inlet.

For far offshore waters the BATEA limitations restrict the residual concentration of oil in discharged produced water to be no greater than 52 mg/l for any one day, and to be no greater than an average of 30 mg/l for any period of 30 consecutive days. For near offshore waters the BATEA limitations prohibit the discharge of produced water. This generally means that produced water from near offshore platforms must be reinjected.

Although only oil, among the various above-mentioned potential pollutants contained in the discharged produced water (see Table 1-1), is directly regulated by the proposed effluent limitations, the other pollutants are indirectly regulated. If, under the BATEA limitations, produced water in the near offshore is reinjected to meet the zero discharge limitation on oil, then any and all contaminants that may be present in the produced water are simultaneously disposed of.

The major purpose of the effluent limitations is, of course, to protect the marine and coastal environment against degradation resulting from the discharge of produced water associated with routine offshore oil and gas production operations. As mandated by the law, the actual effluent limitation levels, given in Tables 1-2 and 1-3, were based primarily upon technological considerations and not on a detailed knowledge of the environmental damage that might be expected to result from the discharge of produced water containing a specified concentration of oil and other pollutants.

The project described in this report deals with the estimation of these impacts and benefits. Since the BPCTCA limitations are already widely in effect, the project focuses on the impacts and benefits of BATEA limitations as compared to the BPCTCA limitations.

## CHAPTER TWO

### PROJECT METHODOLOGY

#### 2.1 General Outline

The starting point in developing a methodology for assessing the benefits that may be expected to result from a particular set of effluent limitations is the realization that the benefits must be evaluated with reference to a baseline. The basic assumptions underlying the establishment of a set of effluent limitations are (1) that a substance is being discharged, or will be discharged, into the environment at a rate that results, or is likely to result, in adverse effects on the environment; and (2) that restricting the discharge of the substance to the level specified by the effluent limitations is likely to result in a significant reduction in the harmful effects, actual or potential. The benefits associated with a set of effluent limitations are then the reduction in adverse effects brought about, or expected to be brought about, by the effluent limitations. The assessment of the benefits expected to result from a set of effluent limitations must accordingly be based on a comparison; namely, a comparison of the state of the environment if the effluent limitations under examination are not in effect (the baseline) with the state of the environment if the effluent limitations are in effect. In this study, since the objective is to assess the benefits expected to ensue from the BATEA limitations over and above those provided by the BPCTCA limitations, the baseline is the state of the environment as impacted by the BPCTCA level of discharge. Therefore, the assessment of BATEA benefits must be based on a procedure for evaluating the environmental impacts of brine discharge under the BPCTCA regulations.

The assessment of the environmental impact of oil and other pollutants contained in produced water discharged at a given site can be divided into five major components. The first component (termed Inputs) is concerned with the characterization of the produced water at the site, and the concentrations of the pollutants contained in the produced water. The second component (Fates) is concerned with what happens to the oil and other contaminants once they are discharged: the physical and chemical processes (transport, diffusion, sedimentation, etc.) undergone, the extent to which oil hydrocarbons are degraded by microorganisms, and the resulting concentration distributions of the pollutants

in the waters surrounding the discharge location. The third component (Toxicology) is concerned with the toxic (lethal and sublethal) effects of the specified concentration levels of the discharged contaminants, and with the bioaccumulation of toxic brine constituents by organisms. The fourth component (Ecological Characterization) is concerned with the biota at the given discharge site: the dominant species present, their habitats and life cycles. The fifth and last component (Impacts) is concerned with the impacts that the discharged produced water can be expected to have on the biota characterized in the Ecological Characterization, taking into account the contaminant concentration distributions determined in the Fates component, and the knowledge of toxic effects and bioaccumulation developed in the Toxicology component of the procedure.

Given this five-component scheme for assessing the impact of the discharge of produced water, the methodology for assessing the benefits that may be expected to result from a particular set of effluent limitations is basically as follows (see Figure 2-1):

STEP 1: Choose site for impact assessment.

STEP 2: Estimate baseline (BPCTCA) level of discharge of oil and other contaminants utilizing information regarding production at the site under consideration provided in the Inputs component.

STEP 3: Estimate expected impacts due to baseline discharge level. (This is done by proceeding through the Fates, Toxicology, Ecological Characterization, and Impacts components of the procedure for assessing impacts outlined above.)

STEP 4: Paralleling Step 2, estimate the level of discharge of contaminants given the set of effluent regulations (BATEA) under examination, again in conjunction with the characterization of production at the given site provided in the Inputs component.

STEP 5: Estimate the environmental impact expected to result from the BATEA level of contaminant discharge, as in Step 3.

STEP 6: Evaluate the difference in the impacts estimated in Steps 5 and 3 to give a measure of the extent to which the BATEA regulations reduce the BPCTCA level of adverse environmental impacts.

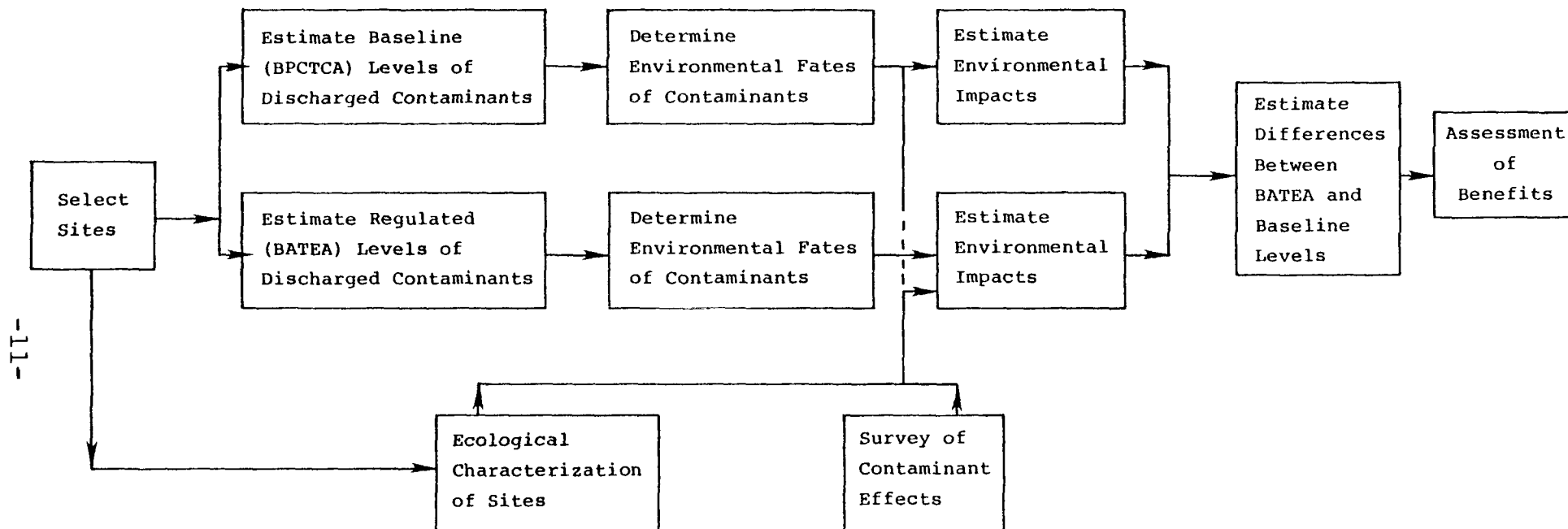


Figure 2-1. Flowchart of procedure for assessing benefits of proposed offshore oil and gas effluent regulations.



## 2.2 Details of Project Methodology

### 2.2.1 Choice of Contaminants

The contaminants chosen for quantitative impact evaluation in this study are listed in Table 2-1. These substances were selected as being those of most concern from tables of pollutants in produced water given in the EPA Development Document. In addition to the 12 substances listed in Table 2-1, hypersalinity was also examined but in a qualitative manner only, because of a lack of data relating specified salinity levels to toxic effects, and also because a relatively small dilution is sufficient to bring a strongly hypersaline effluent down to levels close to that of seawater. Two constituents were also chosen for examination on the basis of possible human health effects if ingested in seafood: mercury and the petroleum hydrocarbon benz[a]pyrene, a potent carcinogen.

TABLE 2-1

#### CONTAMINANTS CONSIDERED IN THE STUDY

ORGANICS	TRACE METALS	OTHER TOXICANTS
Oil Hydrocarbons Phenol	Arsenic Cadmium Chromium Copper Lead Mercury Nickel Silver Zinc	Cyanide

### 2.2.2 Site Selection

Separate impact assessments were made at four sites chosen for reasons of data availability, the presence of production platforms discharging considerable volumes of produced water, and representativeness; and in order to include sites from each of the three location categories: onshore, near offshore, and far offshore waters. The two

onshore coastal sites chosen were in Hackberry Bay, Louisiana, and in Cook Inlet, Alaska. A near offshore site was chosen in the Gulf of Mexico off of Grand Isle, Louisiana, and a far offshore site was chosen in the Ship Shoal oil field 20 miles from the Louisiana coastline. The approximate<sup>1</sup> locations of these sites are shown in Figures 2-2 and 2-3.

Since the sites chosen differ considerably in their characteristics, they may also be expected to differ in the magnitude of the impacts observed at them. For this reason, the analysis is necessarily site specific, taking into account important local features at each of the four sites which might be important in affecting the magnitude of brine-related impacts. The important site specific features which are included in the analysis are listed in Table 2-2.

TABLE 2-2

IMPORTANT SITE SPECIFIC FEATURES OF THE ANALYSIS

- 
- Discharge rate of produced water
  - Composition of produced water
  - Currents (tidal, freshwater, drift)
  - Depth of water
  - Diffusion coefficients
  - Biota at site
- 

2.2.3 Characterization of Produced Water

Data on the rate at which produced water is discharged at a given site are available from different sources depending on the site. For onshore and near offshore coastal waters in Louisiana, discharge information was obtained from the Louisiana Department of Conservation offices in Baton Rouge and Houma. Far offshore Gulf of Mexico discharge data were obtained from the U.S. Geological Survey in Metairie, Louisiana. Cook Inlet discharge data were obtained from the

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<sup>1</sup>Information on the ownership, exact location, and discharge rates of the platforms studied is provided in Appendix D.

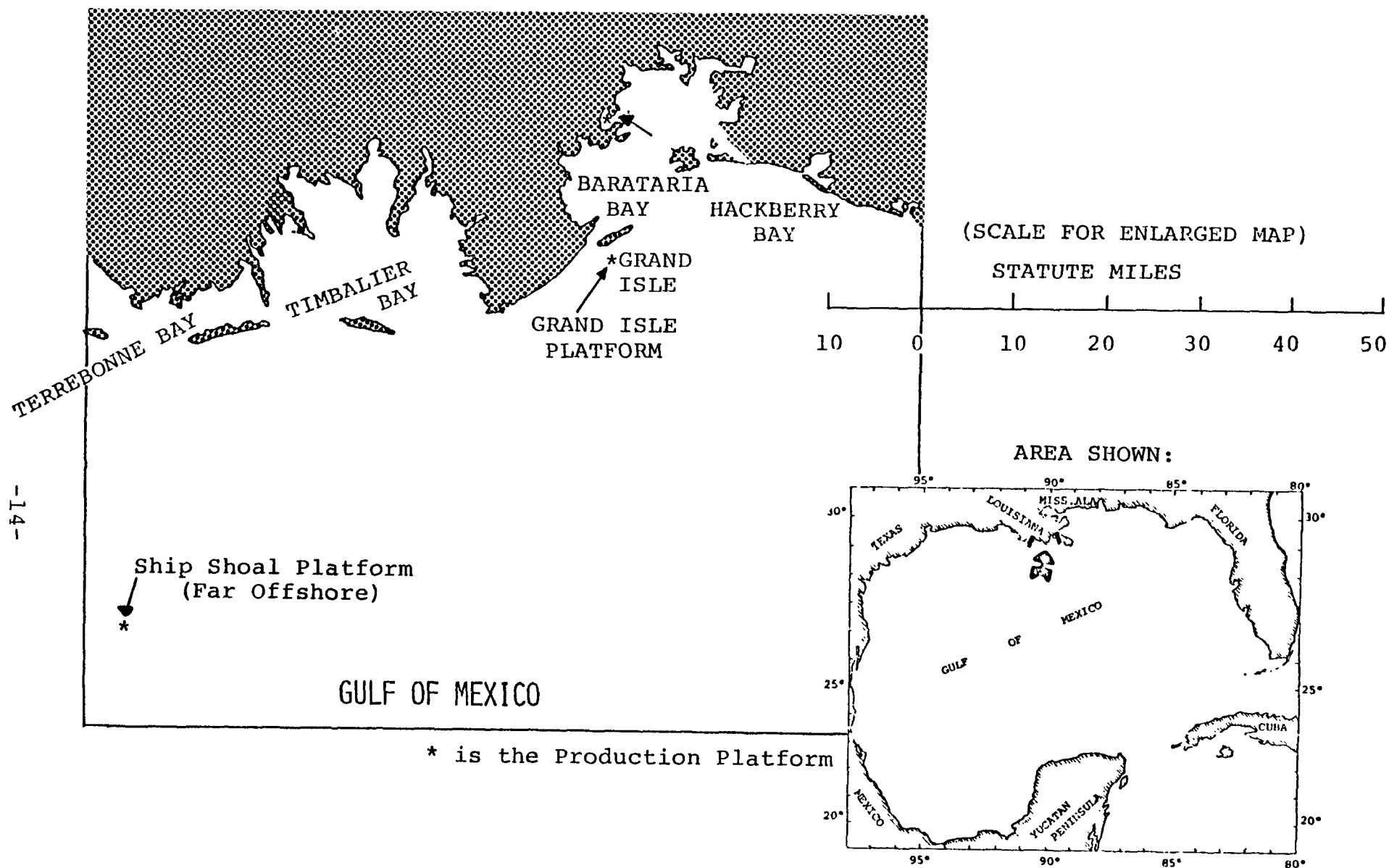


Figure 2-2. Location of Gulf of Mexico production sites.

Figure 2-3. Location of Cook Inlet production sites (ARCO and Marathon platforms were studied in this report).

Water Permits Section, U.S. Environmental Protection Agency in Seattle, Washington, and from U.S. Army Corps of Engineers discharge permit applications.

Available data on the composition of produced water are somewhat sketchy since detailed analyses on brine composition are not performed in general as part of discharge monitoring. A detailed account of the sources used for data on concentrations of contaminants in produced water is given in Chapter Three.

#### 2.2.4 Fates of Contaminants in Discharged Produced Water

Once discharged into the receiving waterbody, the contaminants present in produced water are subjected to a variety of processes which determine their concentration distributions. Such processes include transport by currents, diffusion, dilution, biodegradation, adsorption onto suspended particulates, sedimentation, sediment transport, and chemical transformation. Because little quantitative knowledge is available regarding the processes of adsorption, sedimentation, and chemical transformations in marine waters, these processes were not included in the quantitative estimation of impacts, although they are discussed in the report (see Appendix C).

Quantitative evaluation of contaminant dispersion due to current transport, diffusion, and dilution was accomplished in this study by means of a computerized dispersion model originally developed at the Massachusetts Institute of Technology for predicting the dispersion of thermal discharges. This model uses input data on currents, depth of water, and diffusion coefficients in order to predict the relative dilution of the discharged brines at various points around the production platform. Microbial degradation of oil hydrocarbons can also be incorporated into the model as a decay parameter, but was not used in model runs since little quantitative data on aromatic biodegradation kinetics were available. The outputs of the computer model were used to produce a series of isodilution contours such as the one shown in Figure 2-4. The areas enclosed by each of these isopleths were measured by planimeter and used to plot a curve showing impacted area as a function of concentration.

Since precise quantitative data on inputs to the dispersion model (e.g., the values of the diffusion coefficients) were frequently not available, and since the model itself incorporates certain simplifying assumptions (e.g., constant depth of water), sensitivity analysis was performed. This

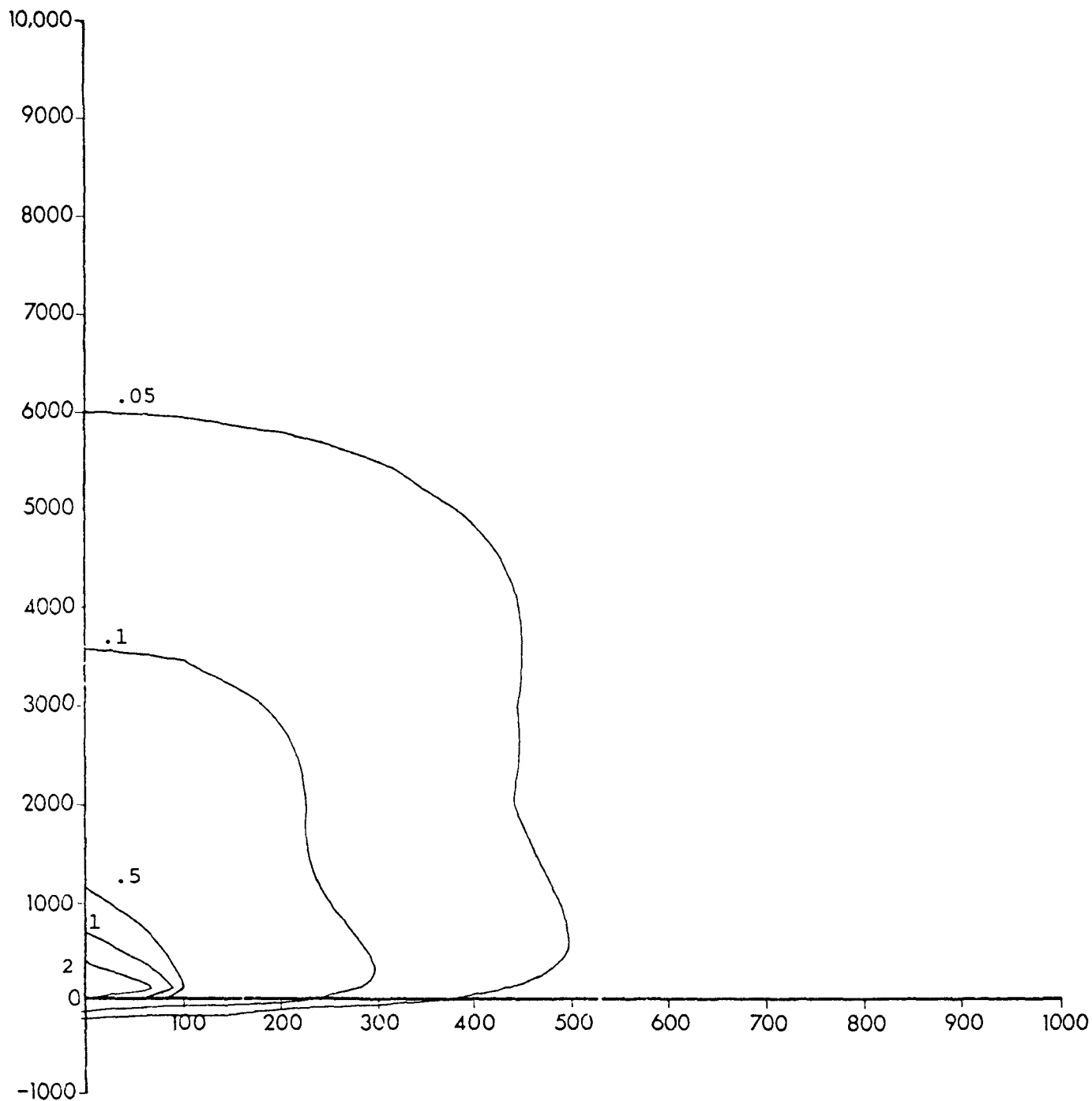


Figure 2-4. A typical set of isodilution contours. Numbers on contours show percent dilution of brines. Distances on axes are in feet. (Near offshore site.)

was done by obtaining model outputs corresponding to a range of input parameter values. The resulting set of concentration/area curves for each site were then used to define a best, worst, and most probable case, based on available knowledge of the input parameters, and on the simplifying model assumptions.

#### 2.2.5 Toxicology

Data from the technical literature were collected on the toxic (lethal and sublethal) effects produced on marine and estuarine organisms by each of the oilfield brine contaminants listed in Table 2-1. The data were organized in tables (see Chapter Six) which facilitate reference to the kind of impact associated with a specified concentration of a given contaminant.

#### 2.2.6 Ecological Characterization of Sites

The detailed assessment of the impact produced by a specified concentration level of a given contaminant on the biota at a site is a highly complicated task. The great majority of studies on toxic effects have been conducted in laboratories under carefully controlled conditions which bear little resemblance to the constantly shifting features of a real environment. Laboratory studies cannot begin to take into account the real world complexity of population dynamics and the web of interconnections of species with their physical and biological environment. To give a simple example, a laboratory study may determine that a particular concentration of a pollutant may cause a 25 percent reduction in the hatching rate of fish eggs of a certain species, but this information is of little value in predicting the impact on an actual field population since eggs may be produced in such large numbers that a 25 percent reduction in egg viability has virtually no effect on the population size. Conversely, a species may be poised in such a delicate competitive balance in its actual field environment that the addition of a certain pollutant concentration may produce a reduction in population numbers which would not be anticipated on the basis of laboratory experiments alone. In view of the great difficulty that would be involved in an attempt to incorporate detailed ecological considerations into the prediction of impact, these indirect effects were not considered in this study. The basic information used was simply a knowledge of the species that are present at a given site and, in the event that the life cycle of a species is divided among different environments, which life stage is spent in the

site under consideration. This information was used to provide an estimate of the economic and ecological importance of the impacted area.

#### 2.2.7 Impacts

The goal of the analysis described in this report is the prediction of the impacts which result from the discharge of oilfield brines. In accordance with what has been said in Section 2.2.4 on the use of a computerized dispersion model to predict concentration distributions, the approach adopted focusses on delineating a set of zones of impact; that is, zones inside of which particular adverse effects are predicted to occur. Each site is characterized in terms of absolute size of the zones of impact for various classes of adverse effects. For enclosed bays, the percentage of the receiving waterbody included in the zones of impact is also taken into account in assessing impact. Two basic classes of impacts are included in the study: toxic (lethal and sublethal) effects on marine and estuarine organisms, and potential human health impacts resulting from the bioaccumulation of toxic brine constituents by organisms which might eventually be used for human consumption.



## CHAPTER THREE

### COMPOSITION OF OILFIELD BRINES

Oilfield brines are generally much more saline than seawater (Mackin, for example, has reported that Louisiana brines have salinities as high as 128 to 131 ppt, as opposed to approximately 30 ppt for seawater<sup>1</sup>). They also contain a number of trace metals in concentrations several orders of magnitude higher than their ambient seawater concentrations. Some data are available on trace metal levels in brines from Louisiana, California, Texas, and Alaska oilfields, but even within individual regions the reported values show a high degree of variability.

Total hydrocarbon content of oilfield brines, measured as total freon-extractable "oil and grease," has been found to be as high as 1,300 mg/l prior to treatment.<sup>2</sup> Little or no data are available on the individual hydrocarbon components of oilfield brines. In general, these hydrocarbons cannot be expected to occur in the same relative concentrations at which they occur in crude oil, since the more water-soluble components will be preferentially concentrated in the oilfield brines. In particular, the brines will be relatively enriched in aromatic hydrocarbons. This is significant since the aromatic components of crude oil are those which create the most significant toxicity problems. Some inference relating to the hydrocarbon composition of oilfield brines can be made by analogy with data on the composition of the so-called water-soluble fraction of crude oil.

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<sup>1</sup>J.G. Mackin, A Review of Significant Papers on Effects of Oil Spills and Oilfield Brine Discharges on Marine Biotic Communities (College Station, Texas: Texas A&M Research Foundation, Project No. 737, February 1973), pp. 4-8.

<sup>2</sup>U.S. Environmental Protection Agency, Effluent Guidelines Division, Office of Waste and Hazardous Materials, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Off-shore Segment of the Oil and Gas Extraction Point Source Category, September 1975, pp. 42-43.

### 3.1 Major Cations and Anions: Salinity

Oilfield brines contain high concentrations of three principal cations -- sodium, magnesium, and calcium -- and one principal anion -- chloride. The high levels of these ions are responsible for the high salinity of brines relative to seawater. The levels of these ions in brines and in seawater are listed in Table 3-1.

### 3.2 Trace Heavy Metals in Oilfield Brines

Metals commonly found in brines are silver, arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc. Data on concentrations of metals in produced waters are scarce. In general, the metals exist in brines at parts per million levels. The limited amount of data which are available give concentrations scattered over a wide range. The inconsistencies in concentration data may represent actual ranges of concentration in different oilfield waters, or they may be the result of the different methods of analysis used in the various studies. Approximate levels of trace metals in oilfield brines are reported in Table 3-2.

As an example of the variability of the composition of oilfield brines even at sites within the same field, and even at different times at the same site, Table 3-3 gives the results of analyses performed on oilfield brines from five sites at Baytown, Texas. Variability is especially noticeable for zinc (from 0.10 to 1.55 ppm), cadmium (from 0.02 to 0.21 ppm), and lead (from 0.20 to 2.00 ppm).

Knowledge of metal content of brines is limited. The ranges presented here are the results of a small sample of oilfield waters. No thorough investigations of the chemical forms or properties of metals in oilfield brines have been performed. This represents a clear limitation to the complete investigation of environmental impacts of brine and disposal, since the impact of the metals contained in the discharged brine will depend on both the concentrations and the forms (oxidation state, etc.) of those metals in the discharge.

#### 3.2.1 Heavy Metals and Other Constituents in Louisiana Produced Waters

Data on produced water content for offshore Louisiana wells were obtained from analyses of effluents from 25

TABLE 3-1  
MAJOR CATIONS AND ANIONS IN OILFIELD BRINES

ION	CONCENTRATIONS IN SEAWATER <sup>a</sup> (mg/l)	TYPICAL BRINE CONCENTRATIONS <sup>b</sup> (mg/l)
Na <sup>+</sup>	10,500	≈ 50,000
Mg <sup>++</sup>	1,350	500-3,000
Ca <sup>++</sup>	400	2,000-8,000
Cl <sup>-</sup>	19,000	50,000-150,000

<sup>a</sup>M.G. Gross, Oceanography: A View of the Earth  
 (Englewood Cliffs, N.J.: Prentice-Hall, 1972).

<sup>b</sup>Gene A. Collins, Geochemistry of Oilfield Waters  
 (New York: Elsevier Scientific Publishing Co., 1975).

TABLE 3-2

TRACE HEAVY METALS IN OILFIELD BRINES

METAL	CONCENTRATION IN SEAWATER <sup>a</sup> (ppb)	CONCENTRATION IN OILFIELD BRINES (ppb)
Arsenic (As)	3.00	1-80, <sup>b</sup> 0-10,000 <sup>c</sup>
Cadmium (Cd)	0.11	<5-675, <sup>b</sup> 0-1 <sup>c</sup>
Chromium (Cr)	0.05	10-230, <sup>b</sup> 1-5 <sup>d</sup>
Copper (Cu)	3.00	<10-380, <sup>b</sup> <500-3,000 <sup>c</sup>
Mercury (Hg)	0.03	0.5-130, <sup>b</sup> 0-150 <sup>c</sup>
Nickel (Ni)	5.40	<10-440, <sup>b</sup> <1-10 <sup>d</sup>
Lead (Pb)	0.03	0-280, <sup>b</sup> 0->100,000 <sup>c</sup>
Silver (Ag)	0.30	<10-100 <sup>b</sup>
Zinc (Zn)	10.00	50-3,200, <sup>b</sup> 0-500,000 <sup>c</sup>

<sup>a</sup>M.G. Gross, Oceanography: A View of the Earth  
(Englewood Cliffs, N.J.: Prentice Hall, 1972).

<sup>b</sup>U.S. Environmental Protection Agency, Effluent Guidelines Division, Office of Waste and Hazardous Materials, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Segment of the Oil and Gas Extraction Point Source Category, September 1975.

<sup>c</sup>Gene A. Collins, Geochemistry of Oilfield Waters  
(New York: Elsevier Scientific Publishing Co., 1975).

<sup>d</sup>G. Rittenhouse et al., "Minor Elements in Oil-Field Waters," Chemical Geology 4 (1969): 189-209.

TABLE 3-3

RESULTS OF ANALYSES OF OILFIELD BRINE DISCHARGED AT BAYTOWN, TEXAS

ITEM	SAMPLE (Concentrations in mg/l)								
	1	2	3	4	5	6	7	8	9
As	--*	<0.50	--	<0.50	--	<0.50	<0.50	<0.50	<0.50
Cd	0.21	0.25	0.08	0.24	0.21	0.08	0.08	<0.01	0.02
Cu	0.12	0.12	0.05	0.10	0.12	0.04	0.07	0.1	0.55
Cr	0.10	0.10	0.05	<0.05	0.15	0.05	0.10	0.25	0.4
Pb	1.80	2.00	0.90	2.05	1.75	0.85	0.70	0.20	0.35
Ni	1.70	1.70	0.90	1.60	1.80	0.60	0.60	1.0	2.2
Hg	0.0001	<0.0001	<0.0001	0.0001	0.0002	0.0001	<0.0002	<0.0001	<0.0001
Ag	0.14	0.14	0.05	0.10	0.11	0.02	0.03	<0.01	<0.01
Zn	1.55	1.36	0.67	0.68	1.32	0.26	0.13	0.10	0.17
Cl <sup>-</sup>	52,200	49,800	54,700	48,500	19,400	13,900	60,800	25,500	63,800
NH <sub>4</sub> <sup>+</sup>	35	1	25	25	25	25	35	0	0
Oil & Grease	4	6	8	8	8	5	10	13	2
Bio Assay (fish kill time in minutes)	10	14	15	21	No kill	No kill	8	65	10

- Sample 1: Gulf Oil Corp., Goose Creek Field, Permit Application No. 000088, Permit sample point #1, 2/22/72.  
 2: Gulf Oil Corp., Goose Creek Field, Permit Application No. 000088, Permit sample point #1, 3/10/72.  
 3: Gulf Oil Corp., Goose Creek Field, Permit Application No. 000088, Permit sample point #2, South, 2/22/72.  
 4: Gulf Oil Corp., Goose Creek Field, Permit Application No. 000088, Permit sample point #2, South, 3/10/72.  
 5: Gulf Oil Corp., Goose Creek Field, Permit Application No. 000088, Permit sample point #2, North, 2/22/72.  
 6: Gulf Oil Corp., Goose Creek Field, Permit Application No. 000088, Permit sample point #2, North, 3/10/72.  
 7: Texaco, Goose Creek Field, Permit No. C.O.E. #000156, Main outfall, 3/21/72.  
 8: Texaco, Goose Creek Field, Permit No. C.O.E. #000156, Main outfall, 5/10/72.  
 9: Texaco, Goose Creek Field, Permit No. C.O.E. #000157, Skinner tank bottoms, 5/10/72.

Analyses performed by the Harris County Pollution Control Department, 107 North Munger, Pasadena, Texas.

\*Blank indicates no analysis performed.

offshore platforms.<sup>3</sup> Unfortunately, the data do not cover all the parameters of interest. Table 3-4 presents the concentrations of parameters measured, with seawater concentrations and chemical forms of the elements of interest. The concentrations of calcium, sodium and chloride ions are all higher in the brine than in seawater. Cadmium and mercury are the only metals for which concentrations were determined. Cadmium, at levels up to 1.68 ppm, is about 15,000 times as concentrated in the brine as in seawater. Mercury levels were determined to be less than 0.0005 ppm, the limit of detection of the analytical method used.

### 3.2.2 Heavy Metals and Other Constituents in Alaska Produced Waters

Concentrations of brine constituents for Cook Inlet, Alaska were obtained from Army Corps of Engineers Waste Water Discharge Permit Application forms submitted by the oil industry to the Corps of Engineers, and later to the EPA. The numbers shown in Table 3-4 are averages of numbers from four separate permit applications, three for onshore facilities treating production from offshore platforms, and one for an onshore facility treating waters from an onshore gas field. All four facilities discharge to Cook Inlet.

Most major nonmetal ions are less concentrated in these waters than in seawater, possibly indicating the occurrence of freshwater flushing of petroleum formations in the area. The metals are more concentrated in the brines than in the seawater. Arsenic, at 1.404 ppm, is 470 times as concentrated as in seawater; cadmium, at 0.081 ppm, is 736 times as concentrated. Levels of chromium and lead are 2,000 and 1,300 times higher, respectively, than corresponding seawater levels. Concentration factors for the other metals are shown in Table 3-4.

### 3.3 Hydrocarbons in Oilfield Brines

The relative proportions of various hydrocarbons in oilfield brines are probably not representative of the proportions found in the parent crude oil. Those hydrocarbons which are most soluble in water -- for example the

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<sup>3</sup>U.S. Environmental Protection Agency, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards, 1975.

TABLE 3-4  
PRODUCED WATER CONSTITUENTS

PARAMETER	SEAWATER <sup>a</sup>		BRINES							WATER QUALITY CRITERIA LIMITS <sup>f</sup>	
	FORM	PPM	FORM <sup>b</sup>	LOUISIANA <sup>c</sup> (mg/l)	ALASKA <sup>d</sup> (mg/l)	CALIFORNIA <sup>c</sup> (mg/l)	TEXAS <sup>c</sup> (mg/l)	LA. CONCENT. RATIO <sup>e</sup>	AK. CONCENT. RATIO <sup>e</sup>	MAXIMUM ACCEPTABLE CONCENTRATIONS (mg/l)	MINIMUM RISK THRESHOLD (mg/l)
Ag	AgCl <sub>2</sub> <sup>--</sup>	.0003			<.010	.03	<.01-.10		<3.3	.005	.001
As	AsO <sub>4</sub> H <sup>--</sup>	.003	HAso <sub>2</sub> <sup>-</sup> , H <sub>2</sub> AsO <sub>4</sub> <sup>--</sup>		<1-1.404	.001-.08	<.01-<.02		<333-468	.05	.01
Cd	Cd <sup>++</sup>	.00011	CdSO <sub>4</sub> , CdCl <sub>2</sub>	<.005-.675	.081	.02-.18	<.02-.193	<45-6136	736	.01 <sup>h</sup>	.0002
CH				<.01-.01		0-.004				.01	.005
Cr	CrO <sub>4</sub> , Cr <sup>3+</sup>	.00005			<.01-.10	.02-.04	<.01-.23		<200-<2000	.1	.05 <sup>i</sup>
Cu	Cu <sup>++</sup>	.003	Org. Acid Salt		.086	.05-.116	<.01-.38		28.7	.05 <sup>h</sup>	.01
Hg	HgCl <sub>2</sub> , HgCl <sub>4</sub> <sup>--</sup>	.00003		<.0005	<.002-<.010	.0005-.002	<.0001-.13	<16.7	<4-<20	.0001	
Ni	Ni <sup>++</sup>	.0054			.005-.430	.1-.29	<.01-.44		.9-79.6	.1	.002
Pb	Pb <sup>++</sup> , PbCl <sup>+</sup>	.00003	Pb(HCO <sub>3</sub> ) <sub>2</sub>		<.01-.39	0-.28	<.01-.22		<33.3-1300	.05	.01
Zn	Zn <sup>++</sup>	.01	ZnCl <sub>2</sub> , ZnSO <sub>4</sub>		.277	.05-3.2	1- 27		27.7	1 <sup>h</sup>	.02
Ca	Ca <sup>++</sup>	400		2,473 <sup>g</sup>	3,725			6.2	9.3		
Mg	Mg <sup>++</sup>	1,350	Mg <sup>++</sup>	747 <sup>g</sup>	145.8			.55	.11		
Na	Na <sup>+</sup>	10,500	Na <sup>+</sup>	44,607 <sup>g</sup>	7.650			4.2	.73		
Cl	Cl <sup>-</sup>	19,000	Cl <sup>-</sup>	61,000 <sup>g</sup>	13,953	17,230-21,000	42,000-62,000	3.2	.73		
Oil & Grease				202 <sup>g</sup>	36	56-359					
Phenols					3.100	.35-2.1	5.3				
BOD					683	370-1,920	126-342				
COD					1,671	400-3,000	182-582				
Total Solids		34,325		110,200	23,842			3.2	.69		
TDS				110,000	23,482	21,700-40,400	806-169,000				
TSS				73	99	1-60	12-656				
TOC				413							

NOTE: Footnotes are on the following page.

FOOTNOTES TO TABLE 3-4

<sup>a</sup>M.G. Gross, Oceanography: A View of the Earth (Englewood Cliffs, N.J.: Prentice-Hall, 1972).

<sup>b</sup>Gene A. Collins, Geochemistry of Oilfield Waters (New York: Elsevier Scientific Publishing Co., 1975).

<sup>c</sup>U.S. Environmental Protection Agency, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Segment of the Oil and Gas Extraction Point Source Category, 1975.

<sup>d</sup>Values are averages of values from four permit application forms submitted to U.S. Army Corps of Engineers. See text.

<sup>e</sup>Concentration Ratio = (mg/l Brine)/(mg/l Seawater).

<sup>f</sup>Water Quality Criteria Limits, October 1973, from Environmental Studies Board, U.S. Environmental Protection Agency - Water Quality Criteria 1973, 1973.

<sup>g</sup>Gene A. Collins, "Geochemistry of Some Petroleum Associated Waters from Louisiana," U.S. Bur. Min. Rep. Invest., No. 7326, 1970.

<sup>h</sup>Synergistic effects have been observed when cadmium, copper, and zinc are present simultaneously. Under those conditions Maximum Acceptable Concentrations should be reduced by an order of magnitude.

<sup>i</sup>When oysters are present the Maximum Acceptable Concentration should be reduced to 0.01 mg/l.



aromatic hydrocarbon components -- would be preferentially concentrated in the brines, since the brines essentially consist of a water extract of crude oil. Little or no data are available on the quantities of specific hydrocarbon components in oilfield brines, but these quantities can be estimated on the basis of composition data on artificial "water-soluble fractions" of crude oil.

Anderson et al.<sup>4</sup> prepared water-soluble fractions and oil-water dispersions of two crude oils, and analyzed the water from these two preparations for specific hydrocarbon content. The water-soluble fraction (WSF) was prepared by mixing oil and 20 ppt salinity seawater gently for 20 hours at 20° C, and then allowing the mixture to separate for 1 to 6 hours. The water was then analyzed for hydrocarbon content. The results of the analysis are shown in Tables 3-5 and 3-6. The water-soluble fractions of South Louisiana crude and Kuwait crude contained 23.76 and 21.65 ppm of hydrocarbons, respectively. As shown in Table 3-6, a large percentage of the hydrocarbons contained in water-soluble fractions from both crudes is composed of aromatics -- in particular the low molecular weight aromatics. The relative abundance of aromatics versus n-paraffins in the water-soluble fractions, as compared to the original crude, is a result of the greater solubility of the aromatic compounds. Table 3-6 shows Aromatic Enrichment Factors (AEF) for the WSF's of the ratio of the concentration of aromatics to n-paraffins in the WSF divided by the same ratio for the whole oil. The AEF is an indication of the degree to which aromatics are enriched in the WSF as compared to the whole crude. The AEF of 125 for Kuwait crude makes it clear that solubility is a key factor in determining the composition of the hydrocarbon content of oilfield waters.

The results obtained by Anderson et al. with oil-water dispersions (OWD) were similar.<sup>5</sup> The OWD's were prepared by mixing oil and 20 ppt seawater violently for 5 minutes, and allowing only 30 to 60 minutes for separation. Analysis of the water fraction of the mixtures yielded the results shown in the "initial" columns of Table 3-7. When a 10,000 ppm

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<sup>4</sup>J.W. Anderson et al., "Characteristics of Dispersions and Water-Soluble Extracts of Crude and Refined Oils and Their Toxicity to Estuarine Crustaceans and Fish," Marine Biology 27 (1974): 15-88.

<sup>5</sup>Oil-water dispersions can be used to model the hydrocarbon content of brines with high levels of suspended oil contamination (e.g., untreated brines).

TABLE 3-5

HYDROCARBON CONCENTRATIONS  
OF CRUDE OIL WATER-SOLUBLE FRACTIONS

COMPOUND	<u>SOUTH LOUISIANA</u>	<u>KUWAIT</u>
	CRUDE OIL	CRUDE OIL
<u>ALKANES</u>		
Ethane	0.54	0.23
Propane	3.01	3.30
Butane	2.36	3.66
Isobutane	1.69	0.90
Pentane	0.49	1.31
Isopentane	0.70	0.98
Cyclopentane + 2-Methylpentane	0.38	0.59
Methylcyclopentane	0.23	0.19
Hexane	0.09	0.29
Methylcyclohexane	0.22	0.08
Heptane	0.06	0.09
C <sub>16</sub> n-Paraffin	0.012	0.0006
C <sub>17</sub> n-Paraffin	0.009	0.0008
TOTAL C <sub>12</sub> -C <sub>24</sub> n-paraffins	0.089	0.004
<u>AROMATICS</u>		
Benzene	6.75	3.36
Toluene	4.13	3.62
Ethylbenzene + m-, p-Xylenes	1.56	1.58
o-Xylene	0.40	0.67
Trimethylbenzenes	0.76	0.73

Source: J.W. Anderson et al., "Characteristics of Dispersions and Water-Soluble Extracts of Crude and Refined Oils and Their Toxicity to Estuarine Crustaceans and Fish," Marine Biology 27 (1974): 15-88.

TABLE 3-5 (CONT.)

COMPOUND	<u>SOUTH LOUISIANA</u>	<u>KUWAIT</u>
	CRUDE OIL	CRUDE OIL
<u>AROMATICS (CONT.)</u>		
Naphthalene	0.12	0.02
1-Methylnaphthalene	0.06	0.02
2-Methylnaphthalene	0.05	0.008
Dimethylnaphthalenes	0.06	0.02
Trimethylnaphthalenes	0.008	0.003
Biphenyl	0.001	0.001
Methylbiphenyls	0.001	0.001
Dimethylbiphenyls	0.001	0.001
Fluorene	0.001	0.001
Methylfluorenes	0.001	0.001
Dimethylfluorenes	0.001	0.001
Dibenzothiophene	0.001	0.001
Phenanthrene	0.001	0.001
Methylphenanthrenes	0.002	0.001
Dimethylphenanthrenes	0.001	0.001
TOTAL SATURATES	9.86	11.62
TOTAL AROMATICS	13.90	10.03
TOTAL DISSOLVED HYDROCARBONS MEASURED	23.76	21.65

TABLE 3-6

AROMATIC AND n-PARAFFIN CONTENT OF  
SOUTH LOUISIANA AND KUWAIT CRUDE OILS AND  
THEIR WATER-SOLUBLE FRACTIONS (WSF) AND  
CALCULATED AROMATIC-ENRICHMENT FACTORS (AEF)

OIL	<u>AROMATICS</u>		<u>n-PARAFFINS</u>		<u>AROMATICS/ n-PARAFFINS</u>		AEF
	Oil (%)	WSF (ppm)	Oil (%)	WSF (ppm)	Oil	WSF	
South Louisiana	0.94	0.305	3.98	0.089	0.24	3.43	14.29
Kuwait	0.60	0.075	4.00	0.004	0.15	18.75	125.00

NOTE:  $AEF = \frac{(\text{Aromatics/n-paraffins})_{\text{WSF}}}{(\text{Aromatics/n-paraffins})_{\text{Oil}}}$

Source: J.W. Anderson et al., "Characteristics of Dispersions and Water-Soluble Extracts of Crude and Refined Oils and Their Toxicity to Estuarine Crustaceans and Fish," Marine Biology 27 (1974): 15-88.

TABLE 3-7

HYDROCARBON COMPOSITION OF AQUEOUS PHASE OF  
1,000 ppm OF OIL-IN-WATER DISPERSIONS (OWD)  
AND EFFECTS OF 24-HOUR AERATION

HYDROCARBON	<u>KUWAIT</u>		<u>SOUTH LOUISIANA</u>	
	INITIAL	FINAL	INITIAL	FINAL
C <sub>12</sub> -C <sub>24</sub> n-paraffins	1,320	71	1,988	64
Tri-and tetra- methylbenzenes	260	70	135	99
Naphthalene	19	15	64	53
1-Methylnaphthalene	12	1	40	24
2-Methylnaphthalene	16	17	46	25
Dimethylnaphthalenes	33	4	108	32
Trimethylnaphthalenes	19	3	56	6
Phenanthrene	2	2	34	2
Methylphenanthrenes	2	2	20	2
TOTAL N-PARAFFINS	1,320	71	1,988	64
PERCENT DECREASE		95%		97%
TOTAL AROMATICS	359	110	506	241
PERCENT DECREASE		69%		52%
TOTAL HYDROCARBONS MEASURED	1,679	181	2,494	305
PERCENT DECREASE		89%		88%

Note: All concentrations expressed in ppb.

Source: J.W. Anderson et al., "Characteristics of Dispersions and Water-Soluble Extracts of Crude and Refined Oils and Their Toxicity to Estuarine Crustaceans and Fish," Marine Biology 27 (1974): 15-18.

OWD prepared from South Louisiana crude was aerated after mixing for 1 to 72 hours, hydrocarbon concentration dropped off from an initial 60 ppm to 4.7 ppm at 24 hours, and remained stable for the rest of the aeration period. Eighty to 90 percent of the initial hydrocarbon burden was lost in the first 24 hours. There was a 95 percent decrease in n-paraffins, and 69 percent decrease in aromatics in a 1,000 ppm OWD of Kuwait crude due to aeration (Table 3-7). A 1,000 ppm OWD of South Louisiana crude lost 97 percent of its n-paraffins and 52 percent of its aromatics as a result of the aeration. The aeration of oil-water dispersions appears to remove the bulk of the n-paraffins present, leaving a greater proportion of aromatics in the aerated OWD than in the original crude.

Aromatics are much more soluble than other oil fractions. They enter solutions more readily, and are retained in solution in both water-oil dispersions and oil-water solutions. Furthermore, most treatment processes which are used for brines prior to their discharge (see following section) will preferentially remove non-aromatic hydrocarbon components. The majority of these processes only remove suspended contamination, and so leave behind the dissolved, and predominantly aromatic, hydrocarbons. Treatment by gas flotation probably serves to oxidize a significant portion of brine hydrocarbons, but the aromatics are relatively resistant to oxidation compared to the non-aromatic oil hydrocarbons (see Table 3-7).

The factors considered here, then, point to the conclusion that aromatics, both mono- and polycyclic, are the hydrocarbons expected to be present in appreciable quantities in the produced water both before and after treatment. These are the compounds that must be considered then in the analysis of possible adverse environmental effects of the discharge of produced waters into the marine environment.

### 3.4 Treatment Processes for Oilfield Brines

Oilfield brines are frequently subjected to primary or secondary treatment processes prior to being discharged into the ocean. These processes can significantly affect some, but not all, of the pollutant content of the brine.

The combined oil and water first go through primary separation processes, which yield relatively pure oil and contaminated water. This water is then treated more extensively to bring oil and grease levels down to an acceptable

level. Several methods are used for this treatment. The simplest method is gravity separation. Production waters are allowed to sit in tanks or settling ponds for a time to allow the lower density oil to rise to the surface, where it can be skimmed off. Some of the suspended particles settle to the bottom of the tank or pit during this process.

Parallel plate coalescers are based on the principle of gravity separation. They are equipped with a series of slanted plates which collect rising oil droplets and channel them to the top of the separators. Similarly, suspended particles sink until coming in contact with a plate, then slide down the plate to be collected in the bottom of the separator.

Filter systems operate by filtering the brine through either a fibrous medium such as fiberglass or a loose medium such as sand, thereby removing oil droplets and suspended particulates.

The gas flotation method of oil-water separation is slightly more sophisticated than the other techniques. Air is bubbled through the untreated water. As the bubbles rise to the surface, they collect oil droplets in their path, and carry them to the surface where they can be skimmed off.

Chemicals are often used in conjunction with other methods to enhance the effectiveness of those methods. Surfactants are used to break up oil-water emulsions. Coagulants promote aggregation of suspended materials, and thus enhance their natural tendencies to rise or to sink. Polyelectrolytes are used to facilitate the removal of colloidal and extremely fine suspended particles.

The results of an Environmental Protection Agency survey of oil and grease content of produced waters after treatment by various methods are shown in Table 3-8. According to this study, loose media filters and gas flotation processors yield lower oil and grease levels than the other commonly used methods.

These treatment processes will generally not affect trace metal levels in brines. It is also clear that all of these separation methods are directed at the removal of suspended oil droplets and particles. None of the methods remove dissolved hydrocarbons from solutions. Therefore, most of the oil and grease which remains in the produced water after treatment is composed of soluble hydrocarbons.

TABLE 3-8

PERFORMANCE OF TREATMENT SYSTEMSLOUISIANA COASTAL

TYPE TREATMENT SYSTEM	OIL & GREASE (mg/l)	NUMBER OF SAMPLES
Gas Floatation	27	27
Parallel Plate Coalescers	48	31
Filters		
Loose Media	21	15
Fibrous Media	38	7
Gravity Separation		
Pits	35	31
Tanks	42	48

Source: U.S. Environmental Protection Agency, Effluent Guidelines Division, Office of Waste and Hazardous Materials, Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Segment of the Oil and Gas Extraction Point Source Category, September 1975, p. 81.



On the basis of this fact and of several other considerations, the decision was made in this study to restrict attention to the dissolved portion of the oil hydrocarbons in the produced water and to omit a detailed and separate treatment of the impacts of the emulsified portion of the hydrocarbons. The reasons for emphasizing the dissolved portion can be summarized as follows:

1. As has been discussed above in this section, standard treatment methods are capable of removing a considerable part of the emulsified portion of the hydrocarbons in produced water but are ineffective in removing the dissolved portion.
2. The dissolved part of the hydrocarbons is, as discussed in Section 3.3, especially rich in aromatic hydrocarbons. It is precisely the dissolved aromatic hydrocarbons that are also the most toxic to marine organisms.<sup>6</sup>
3. There is evidence<sup>7</sup> that bacteria are more effective in degrading emulsified oil than they are in degrading dissolved oil, since emulsified oil provides a more substantial substrate for bacterial colonization. Dissolved hydrocarbons may therefore be expected to persist longer in marine environments.

Thus the dissolved aromatics not only comprise the largest part of hydrocarbons remaining after effective treatment of produced water, but they are the most toxic, and may be the most persistent as well. Since the impacts of the hydrocarbons in produced water can therefore be expected to be

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<sup>6</sup>Stephen F. Moore, "Towards a Model of the Effects of Oil on Marine Organisms," in National Academy of Sciences, Background Papers for a Workshop on Inputs, Fates, and Effects of Petroleum in the Marine Environment, Vol. II, 1973.

<sup>7</sup>National Academy of Sciences, Petroleum in the Marine Environment, 1975, p. 59; P.J. Kinney, D.K. Button, and D.M. Schell, "Kinetics of Dissipation and Biodegradation of Crude Oil in Alaska's Cook Inlet," in Proceedings Joint Conference on Prevention and Control of Oil Spills, American Petroleum Institute, 1969; and C.E. Zobell, "Microbial Modification of Crude Oil in the Sea," in Proceedings Joint Conference on Prevention and Control of Oil Spills, American Petroleum Institute, 1969.

dominated by the dissolved aromatics, it was felt that the emulsified part could be neglected without significantly affecting the conclusions of this study. It should also be noted that the computer dispersion model, described in detail in Chapter Four and Appendix B, used to calculate the concentration distributions of produced water constituents in the receiving waters, is restricted to working with dissolved substances only. Adequate treatment of the dispersion of the emulsified portion of the hydrocarbons would involve a modeling effort additional to the one used as the basis for this study.

## CHAPTER FOUR

### DISPERSION MODELING

#### 4.1 Introduction

Oilfield brines, once discharged into a receiving waterbody, are subject to the processes of transport, diffusion and dilution which determine the distributions through time and space of pollutant concentrations. Since the impact exerted on the marine environment by the brine discharge depends in large part on the concentration distributions of the discharged contaminants in the receiving waterbody, it is of great importance to understand and predict the physical dispersion processes which determine these distribution patterns. The heart of the analysis described in this report is a set of dispersion models which are used to predict the quasi-steady state distributions of brine concentrations resulting from the combined influence of natural decay processes, steady and tidal current flow, and diffusion.

Two types of models are discussed in this chapter. The simplest type of calculation, a tidal prism flushing model, is discussed in Section 4.2. This model is useful for giving the average concentration of a pollutant in a small bay area but cannot give any information regarding concentration contours. In this analysis, this simple tidal prism calculation is used to set a "background" concentration of brine levels in small enclosed bays such as Hackberry Bay. The more detailed diffusion model used in this report is discussed in Section 4.3. It should be emphasized that the discussion given the model in this chapter is only cursory, and designed to highlight the physical assumptions upon which the model is based. A more detailed discussion of the model, including a description of the differential equations which are used to represent physical dispersion processes, is presented in Appendix B to this report. The model used in this analysis is capable of incorporating three-dimensional diffusion as well as the time varying tidal currents which play a key role in estuarine dispersion.

#### 4.2 Simple Tidal Flushing Calculations for Shallow, Enclosed Bays

Pollutants introduced into an estuary are flushed out over a period of time by the combined actions of seaward river flow and mixing at high tides followed by tidal

outflow. The residence time of estuarine pollutants is dependent on the overall rate at which this flushing occurs. Therefore, one important indicator of the ability of an estuary to rid itself of pollutant discharges -- especially if they are conservative<sup>1</sup> -- is the flushing time, or the length of time required for the river flow and tides to flush an amount of water equal to the low tide volume of the estuary. For very large estuaries or those which have complicated geometries, the flushing time is quite difficult to compute; however, for small estuaries a relatively simple method has been developed to make reasonable estimates of the length of time, measured in units of tidal periods, needed to replace the estuary volume.

Such calculations are useful for two reasons. First, they can be used to gain a rough idea of the length of time it takes an estuary to rid itself of oilfield brine pollutants dissolved in the water column. Second, in the case of continuous discharges, they can be used to determine the steady state concentrations of those pollutants. The tidal flushing calculations described below in this section can be used to supplement the predictions of the more sophisticated computer model in small, enclosed bays by supplying order-of-magnitude estimates of the average background levels of discharged pollutants. These estimates are not only useful in their own right but can also serve as checks on the reasonableness of the results obtained from the computer model.

The simplest version of the method to be discussed is based on the fairly crude assumption that the total volume of water entering the estuary between low and high tides (incoming river water plus incoming seawater) becomes thoroughly mixed with the low tide volume before the ebb tide begins. On the basis of this assumption, the fraction of the low tide estuary volume ("old water") flowing seaward during the ebb tide can be computed. In particular, if  $V$  is the low tide volume of the estuary and  $P$  is the volume entering between low and high tides (called the tidal prism), then  $V + P$  is the volume of the estuary at high tide. Since the tidal prism  $P$  is carried away on the next ebb flow and since the total high tide volume is assumed to be thoroughly mixed, the fraction of the volume  $V$  of old water carried away per tidal period is  $P/(V + P)$ . The

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<sup>1</sup>A pollutant discharge is conservative if the pollutants do not decay with time; i.e., if total pollutant mass is conserved.

number T of tidal periods needed to flush out all of the old water is just the inverse of this fraction:

$$T = \frac{V + P}{P}$$

This number is a first estimate of the flushing time.<sup>2</sup>

As ought to be expected, this simple-minded method generally yields shorter-than-realistic flushing times for most types of estuaries.<sup>3</sup> For most real estuaries, complete mixing during high tide does not occur, and the ebb tide does not always carry waters near the head of the estuary all the way past the mouth and into the open sea.

Despite this drawback, the approach leads to an equation relating the low-tide, steady-state concentration of a given contaminant to the amount of pollutant discharged into an estuary. For simplicity it can be assumed that all of the discharge occurs between low tide and the following high tide. Let the concentration of the contaminant at low tide (ambient concentration) be  $C_L$  and its concentration in the discharge stream be  $C_D$  in a total volume  $V_D$  of discharge in one tidal cycle. A simple calculation (Figure 4-1) then yields:

$$C_L = C_D \frac{V_D}{P} \quad (4-1)$$

Hackberry Bay, 29°4', 90°15' (see Figure 4-2) in the northwest corner of Barataria Bay, Louisiana, provides a good example of the kind of bay for which this approach can be useful. It harbors Texaco's Bay de Chene oilfield, the site of the largest brine discharge ( $V_D = 9,747 \text{ m}^3$  per tidal period) in Barataria Bay. The average tidal height in Barataria Bay<sup>4</sup> is 0.3 m; if we assume this datum for Hackberry

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<sup>2</sup>F.F. Wright, Estuarine Oceanography, Council Education in the Geological Sciences Publication No. 18 (New York: McGraw-Hill Inc., 1974), pp. 28-33; and K.R. Dyer, Estuaries: A Physical Introduction (London: John Wiley and Sons, 1973), pp. 109-114.

<sup>3</sup>Dyer, Estuaries: A Physical Introduction.

<sup>4</sup>Barney Barrett, Cooperative Gulf of Mexico Estuarine Inventory and Study, Louisiana, Phase II Hydrology and Phase III Sedimentology (New Orleans: Louisiana Wildlife and Fisheries Commission, 1971), p. 55.

(A) Low Tide

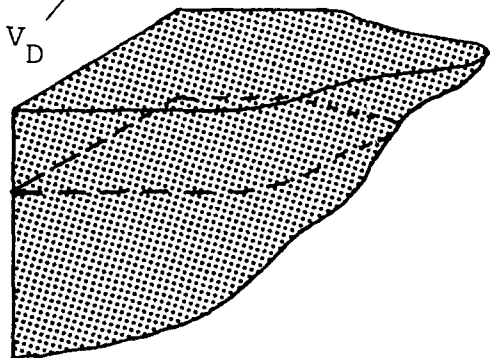
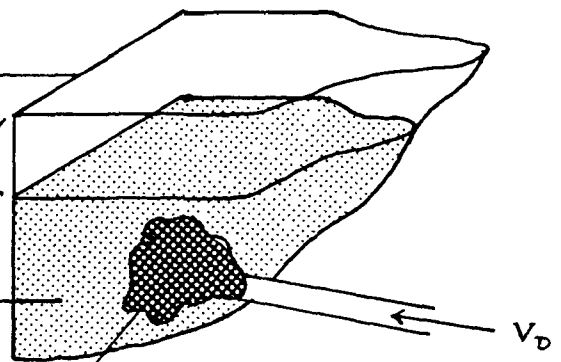
$$\begin{aligned} \text{TOTAL VOL} &= V + P \\ \text{TOTAL AMT OF POLLUTANT} &= V_D C_D + V C_L \end{aligned}$$

high tide volume of bay

water entering between low and high tide (tidal prism; vol = P)

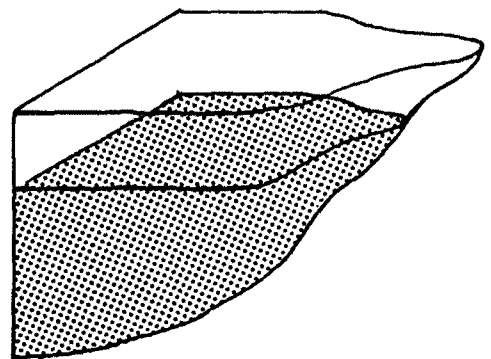
low tide vol. of bay (V) (ambient concentration of pollutant =  $C_L$ )

discharge introduces vol  $V_D$  of effluent ( $V_D \ll V+P$ ) (conc. of pollutant =  $C_D$ )



(B) High Tide  
Bay Becomes Well-Mixed

$$\begin{aligned} \text{New conc. of Pollutant} &= \frac{\text{Amount of Pollutant}}{\text{Volume of Bay}} \\ &= \frac{V_D C_D + V C_L}{V + P} \end{aligned}$$



(C) Low Tide  
Volume P Carried Out of Bay

$$\begin{aligned} \text{Amount of Pollutant Lost} &= (\text{conc.})(\text{vol.}) \\ &= P \frac{V_D C_D + V C_L}{V + P} \end{aligned}$$

Steady State Assumption: Amount of Pollutant Introduced in One Tidal Cycle = Amount Lost During One Tidal Cycle

Therefore:

$$V_D C_D = P \frac{V_D C_D + V C_L}{V + P}$$

Solving for  $C_L$  (steady state concentration)

$$C_L = \frac{C_D V_D}{P}$$

Figure 4-1. Tidal flushing calculation.



Figure 4-2. Location of Hackberry Bay study area.

Bay our estimate of  $C_L$  is likely to be slightly low, since the smaller bay probably experiences less extreme tides than the larger one. This tide height multiplied by the surface area of Hackberry Bay of  $1.77 \times 10^7$  square meters<sup>5</sup> gives  $P = 5.33 \times 10^6 \text{ m}^3$ ; if the tide height is 0.1 m,  $P = 1.78 \times 10^6$ . By (4-1), assuming 0.3 m tides gives

$$C_L = 1.8 \times 10^{-3} \quad C_D = 0.18\% C_D$$

Assuming 0.1 m tides gives

$$C_L = 5.5 \times 10^{-3} \quad C_D = 0.55\% C_D$$

It is important to emphasize that these results have considerable limitations. To begin with, the methodology is based on the assumption that complete mixing occurs during the flood tide, an approximation which can be used reasonably only for relatively small, shallow bays like the Hackberry Bay. Thus no attempt is made to reproduce the concentration isopleths, in direct contrast to the computer model. The implicit assumption that the surface area of a natural body of water remains constant over a tidal cycle introduces yet another source of error. Another underlying assumption in these calculations is that the concentrations of pollutants are at a steady state. While this may be true over short time intervals or in a time-averaged sense, seasonal and even weekly variations in the tides and river inflow may cause significant discrepancies between the computed concentrations and observed values of background concentrations. The method is valid as a means of arriving at an order of magnitude approximation to the average background concentrations of contaminants in relatively small, shallow estuarine bays.

#### 4.3 Description of the Dispersion Model

The rough tidal prism calculations described in the previous section are only applicable to enclosed areas such as Hackberry Bay, and even then only indicate one summary statistic: the well-mixed "background" concentration of a continuously discharged pollutant flushed by tidal mixing.

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<sup>5</sup>Barney Barrett, Water Measurements of Coastal Louisiana (New Orleans: Louisiana Wildlife and Fisheries Commission, Division of Oysters, Water Bottom and Seafood, 1970).



A much more detailed analysis is, of course, necessary to predict detailed concentration distributions for the pollutant as it disperses under the influence of currents and diffusion forces. A very useful approach to the problem of predicting pollutant concentrations in the receiving waterbody is to apply the fluid dynamics to modeling the actual diffusion process responsible for the dispersion of concentrated effluents. This kind of analysis yields concentration distributions instead of averages. The mathematical background of such an analysis is developed in detail in Appendix B, and has been implemented as a computer program which was used for this project.<sup>6</sup> This section will describe the physical assumptions relating to pollutant dispersion upon which the model is based. Readers interested in further information on the nature of the model should consult Appendix B.

There is an interest in analyzing the movement of pollutants in a current field. An important factor influencing the nature of pollutant movement in such a field is the relationship between the scale of the pollutant concentration distribution and the curvature of the streamlines, or directions of fluid flow.

If the scale is small compared to the streamline curvature, i.e., if the pollution stream is small compared to the distance over which the current remains relatively uniform, then the current will not disperse the pollutants very much. Rather, it will tend to carry them more or less intact along the overall direction of flow. This situation, illustrated in Figure 4-3, is often described by saying that the characteristic eddy of the current is much larger than the pollutant stream, and the resulting transport is called advection.

On the other hand, if the characteristic eddy is smaller than the pollutant stream, the pollutants will be subject to several different directions of flow over any small period of time. The resulting transport pattern, illustrated in Figure 4-4, tends to disperse the pollutant

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<sup>6</sup>The dispersion model used for this project was developed at the Massachusetts Institute of Technology by E. Adams and K.D. Stolzenbach. See E.E. Adams et al., Near and Far Field Analysis of Buoyant Surface Discharges into Large Bodies of Water, Ralph Parsons Lab, for Water Resources, Report No. 205 (Cambridge, Mass.: Massachusetts Institute of Technology, 1975).

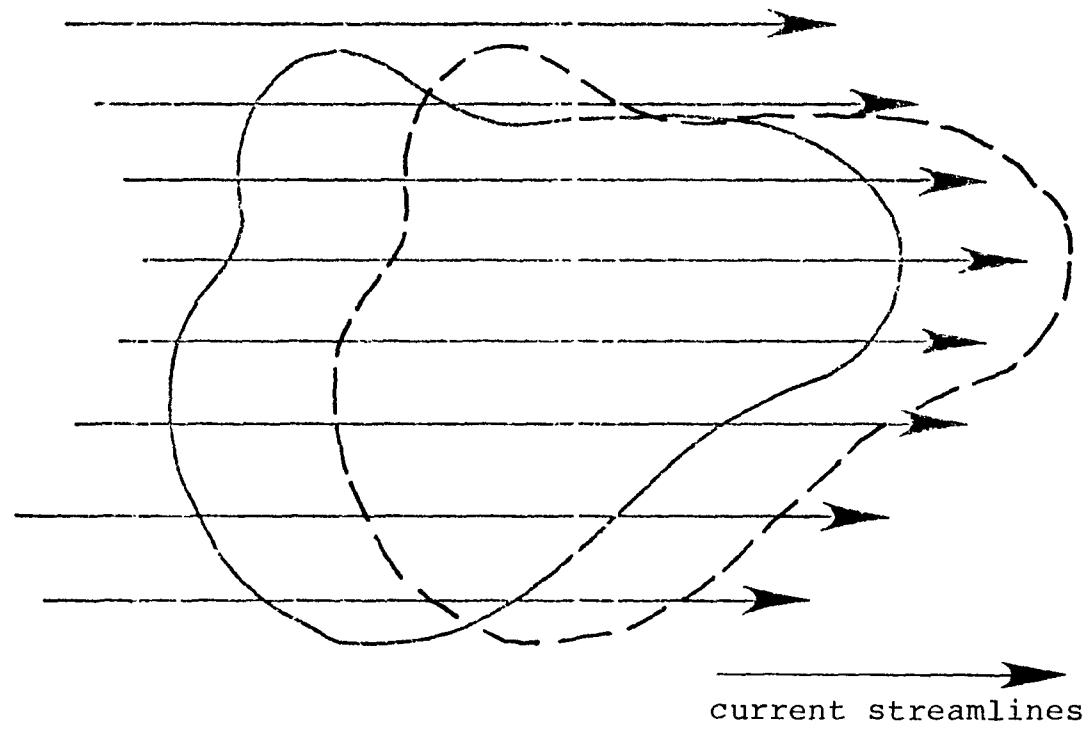


Figure 4-3. Advection due to uniform, steady flow.

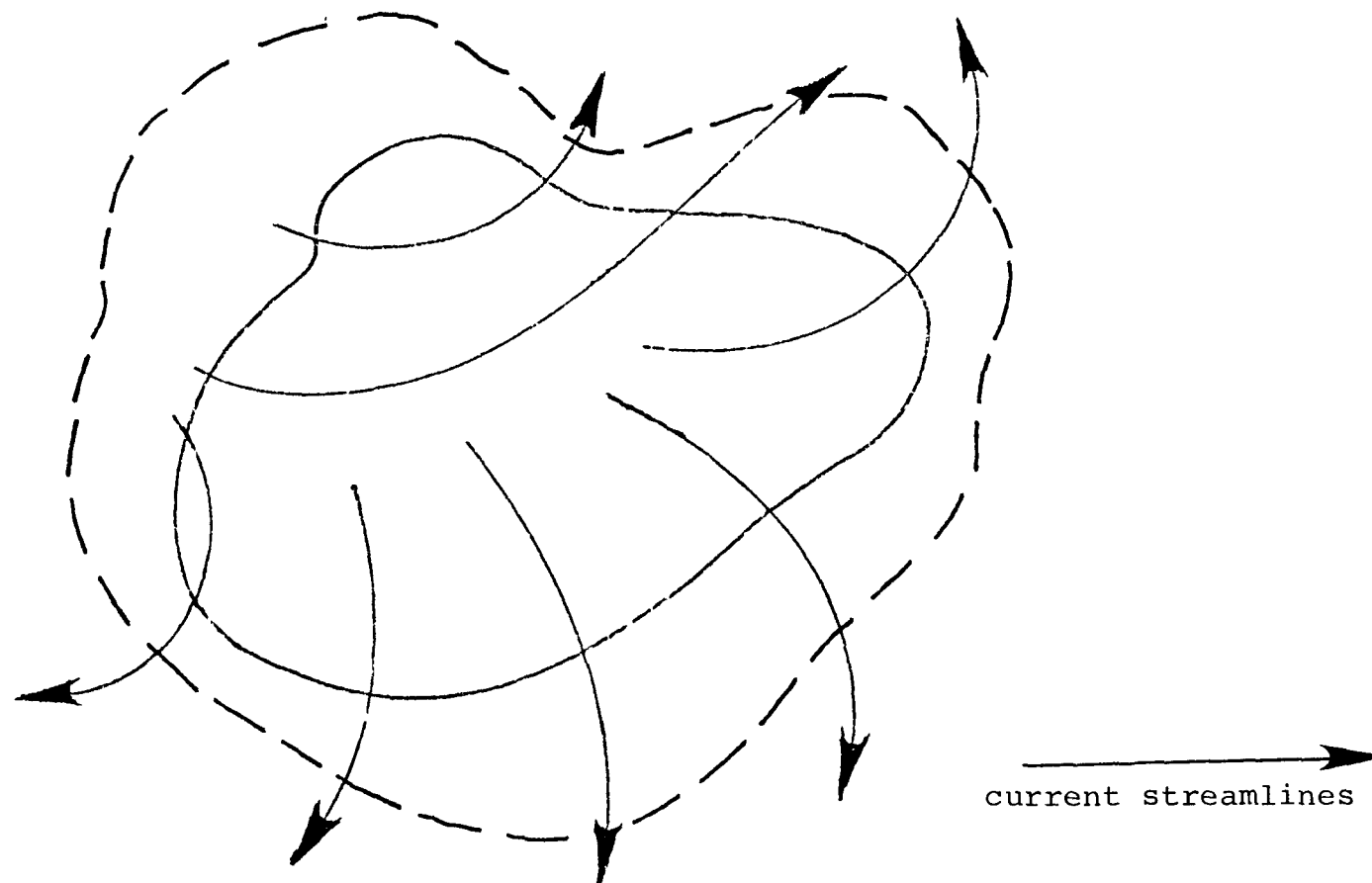


Figure 4-4. Diffusion due to turbulent flow.

parcel. This situation is often described by saying that turbulent flow causes more pronounced diffusion of the pollutant stream. (The reason for the adjectives "more pronounced" is that diffusion also occurs on a molecular scale, independent of any observable fluid flow. The component of diffusion attributable to turbulence is usually called "eddy diffusion.")

There is an interest, then, in the extent to which diffusive and advective forces will influence the movement of pollutants. The extent to which the pollutant distribution is "spread out" in any particular direction (say the y direction) can be described by the variance of this distribution.<sup>7</sup>

If the diffusion processes operate, this variance will be taken as a measure of the rate of diffusion, so that a very large part of the task of characterizing a diffusion process is accomplished by defining a diffusion coefficient E in terms of the time rate of change in the variance (spatial spreading) of the pollutant stream.<sup>8</sup>

The analysis is complicated by the experimental fact that the spreading rate, E, of pollutant streams in natural waters increases as the diffusion process progresses. In other words, as the scale of the pollutant stream increases because of diffusion, the rate at which further diffusion occurs also increases, causing increasingly rapid dispersal. This observation can be explained in terms of the turbulent effects discussed above. When a pollutant stream is small

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<sup>7</sup>Mathematically, the variance in the y direction is given by:

$$\sigma^2 = \int_{-\infty}^{\infty} y^2 c(x,y,z) dy$$

where  $c(x,y,z)$  is the spatial concentration distribution.

<sup>8</sup>E is defined as:

$$E = \frac{1}{2} \frac{d}{dt} (\sigma^2)$$

See Frank D. Masch, "Mixing and Dispersion of Wastes by Wind and Wave Action," in Advances in Water Pollution Research, ed. by E.A. Pearson (Oxford: Pergamon Press, 1964), p. 146.

in scale, only currents with comparatively small characteristic eddies can be considered turbulent with respect to the stream. Two representative pollutant particles will therefore tend to have very similar trajectories because of their proximity to each other, so that they will not be separated quickly at this small scale. As the scale increases, the degree to which the motion of two representative pollutant particles are correlated diminishes, resulting in a more rapid overall rate of separation.<sup>9</sup> Therefore, the eddy diffusion coefficient  $E$  is a function of the scale (i.e., the largest dimension)  $\sigma$  of the parcel formed by the pollutant stream. Empirical studies have found that a reasonably accurate expression for the dependence of  $E$  on  $\sigma$  is frequently given by a power law such as:

$$E = \alpha \sigma^{4/3} \quad (4-2)$$

where  $\alpha$  is an empirically determined constant.<sup>10</sup> This relation is generally known as the "four-thirds law".

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<sup>9</sup>Henry Stommel, "Horizontal Diffusion Due to Ocean Turbulence," Journal of Marine Research 8 (1949): 199-225.

<sup>10</sup>It is important to realize that eddy diffusion, as described by (4-2), is nothing more than a sort of statistical construct devised to alleviate the difficulties encountered in solving differential equations for complicated velocity fields. Analysis at the microscopic scale would involve a set of equations of motion tracing the path of each minute parcel of the pollutant as it moved through a current field, which varied both spatially and temporally in a complicated and irregular way. Such problems are hopelessly intractable. The saner approach normally taken for eddy diffusion is to view the background current field from a macroscopic standpoint, taking into explicit account only the major features of speed and direction of the flow. So that the important dispersing effect of the irregular details (turbulence) of the current fields is not thereby ignored, it is modeled by lumping all of the eddy-diffusive flow characteristics into a single factor representing, in a sense, their aggregate effect on the pollutant stream. This factor is the non-molecular diffusion coefficient  $E$  described by (4-2). The justification for the form of such a simplifying assumption must be provided by actual empirical studies verifying that the hypothetical law accurately models the measurable behavior of dispersing pollutant particles in real bodies of water.

There remains considerable controversy over the accuracy with which eddy diffusion coefficients can be evaluated. It is likely that different flow and depth regimes are best characterized by different diffusion laws. The 4/3 law in (4-2) best fits data for ocean regimes as summarized by Pearson<sup>11</sup> and has been used in many investigations of ocean diffusion. The model used for this report incorporates a more general form of the diffusion coefficients (diffusion must be described by three coefficients, one for each mutually perpendicular direction) to take into account cases in which the 4/3 law may not be valid (an example is Hackberry Bay -- see Chapter Five). The horizontal diffusion coefficients are assumed to be of the following form:

$$E = A\sigma^n \quad \sigma < \sigma_c \quad (4-3)$$

$$E = A\sigma_c^n \quad \sigma > \sigma_c \quad (4-4)$$

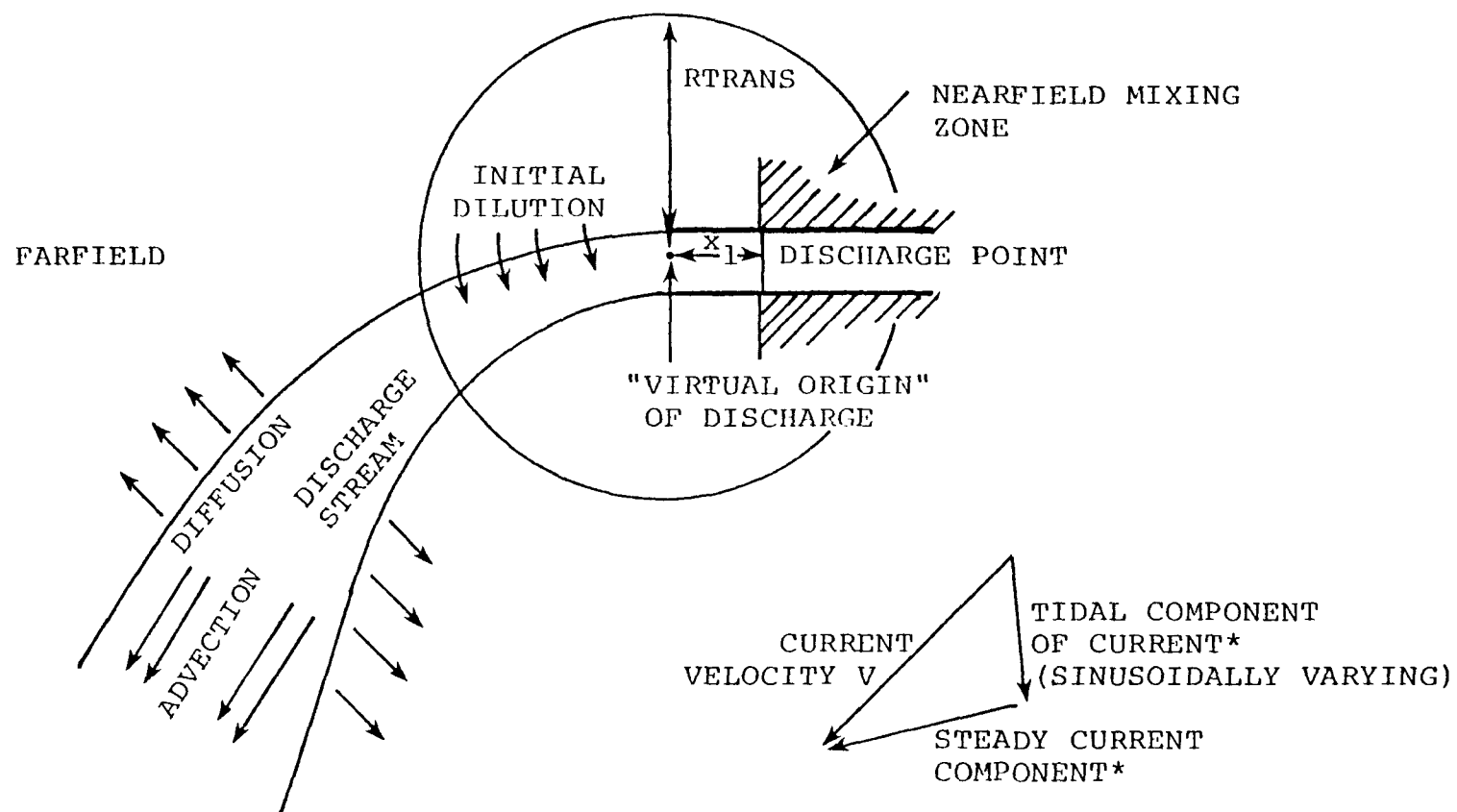
where A is constant,  $\sigma$  is the scale of the pollution distribution, and  $\sigma_c$  is some limiting scale. The form of the equations suggest that over a certain range of length scales ( $\sigma < \sigma_c$ ), pollution patches undergo "accelerated diffusion" due to current shear effects, while for large length scales ( $\sigma > \sigma_c$ ) diffusion is more accurately (or conservatively in the absence of data) described by constant diffusion coefficients. Based on empirical results, vertical diffusion in the model does not depend on scale, but instead has a value which varies only with depth, and is constant at any given depth.

The model described in Appendix B was used to predict the quasi-steady state<sup>12</sup> distributions of pollutant concentrations in the neighborhood of a brine discharge point. The nature of the system being analyzed is summarized in Figure 4-5. Pollutant is discharged from an orifice in a particular direction. For a small time it moves under the

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<sup>11</sup>N.H. Pearson, An Investigation of the Efficacy of Submarine Outfall Disposal of Sewage and Sludge, State Water Pollution Control Board Publication No. 14, Sacramento, California, 1956.

<sup>12</sup>The distributions are quasi-steady state in that although they vary through the course of the tidal cycle, the distribution at any particular time in a cycle is the same as that at the equivalent time in the next cycle.



\* CURRENTS ARE ASSUMED TO BE SPATIALLY HOMOGENEOUS

Figure 4-5. Dispersion of brine discharges.

influence both of its discharge momentum and of an external current, but outside of a relatively small nearfield mixing zone it is pushed along primarily by the current. Once beyond a characteristic distance RTRANS from its source the pollutant moves under the influence only of current, decay, and diffusion forces. The current is the vector sum of a steady current component (due, for example, to freshwater flow in an estuary or drift current in the ocean) and a sinusoidally varying tidal component. The pollutant plume absorbs some water in the nearfield mixing zone (inside RTRANS), so another important input parameter to the model is the initial dilution, which can be predicted roughly on the basis of previous empirical work (see Chapter Five).

The dispersion of pollutants after their discharge is assumed to be influenced primarily by three forces: advective transport by currents, diffusion (described by a set of diffusion coefficients for the x, y, and z directions), and decay (see Figure 4-6).

The movement of the pollutant under the influence of these three forces can be modeled by a set of differential equations and associated boundary conditions as described in Appendix B. These in turn are solved numerically by a computer program which predicts quasi-steady state pollutant distributions and then averages them over an entire tidal cycle to produce a matrix showing the spatial distributions of average pollutant concentrations near the discharge site. The program then uses this concentration matrix to calculate the positions of a series of isopleths, or lines of equal pollutant concentration (or equivalently, lines of equal brine dilution).

The model used is also able to simulate the presence of a single straight shoreline. When the discharge is located near a straight shoreline, two constraints are imposed. First, the currents are assumed to flow parallel to the shoreline to prevent advection of the pollutant mass across the boundary. Secondly, to prevent effective diffusion across the boundary, an image source corresponding to each real source is assumed to be located on the opposite side of the shoreline.

#### 4.4 Summary of Model Parameters

The model described in this chapter requires the specifications of the following parameters:



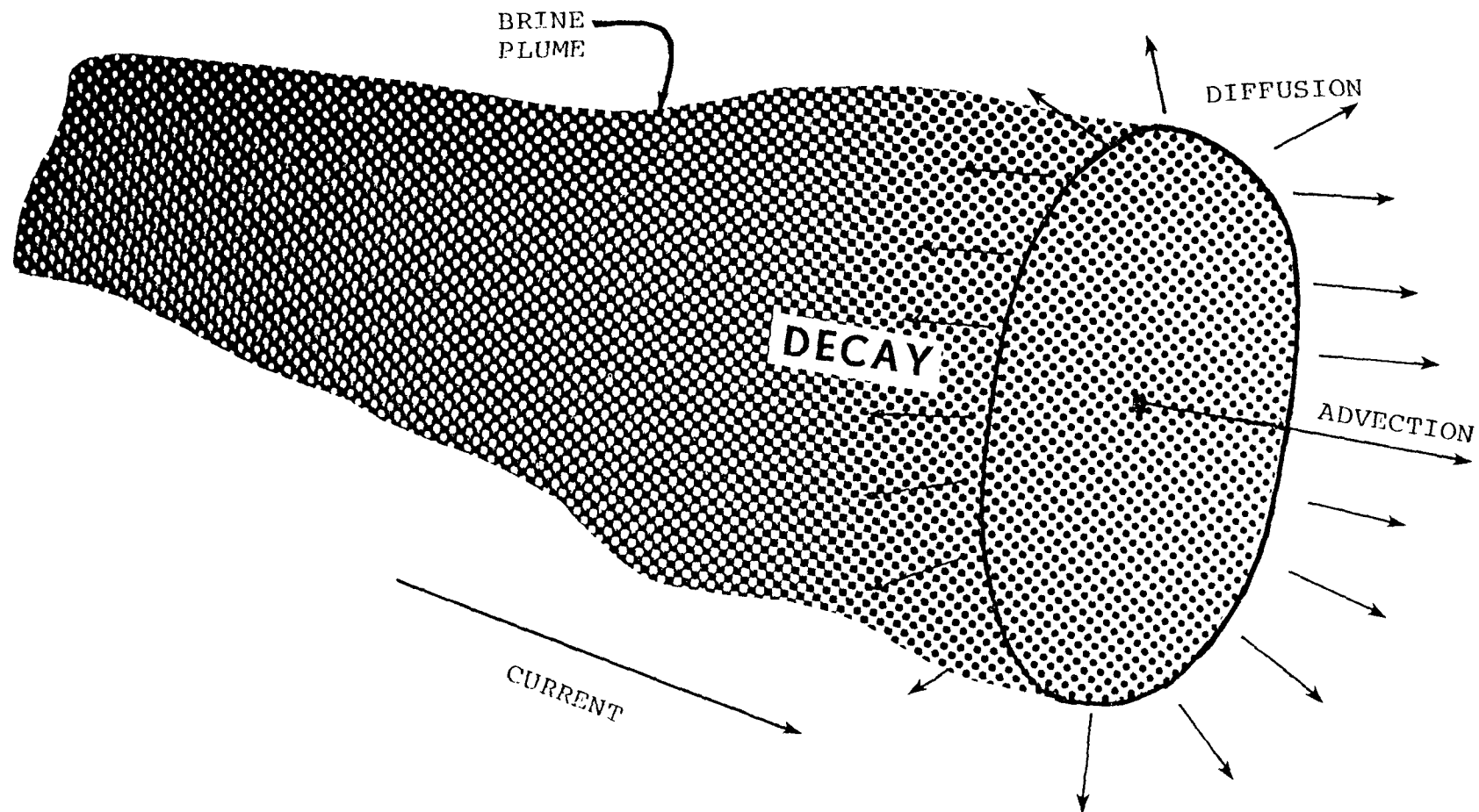


Figure 4-6. Forces affecting brine dispersion.

$Q_o$  = initial brine discharge flow  
(ft<sup>3</sup>/sec)  
 $\Delta c_o$  = initial discharge excess concentration (= 100 percent)  
 $D$  = initial dilution (in near field)  
 $x_1$  = initial fixed mixing distance (see Figure 4-5)  
 $H_2$  = initial depth of source  
 $RTRANS$  = initial variable mixing distance (see Figure 4-5)  
 $H$  = total water depth (assumed to be constant)  
 $XSHORE$  = distance to shoreline (if applicable)  
 $k_d, k_s, k_b$  = internal, surface, and bottom decay coefficients  
 $E_z$  = vertical diffusion coefficient  
 $A_x, A_y, n_x, n_y, \sigma_{xc}, \sigma_{yc}$  = parameters describing the horizontal diffusion coefficients<sup>13</sup>  
 $U_1, V_1$  = components of amplitude of tidal current  
 $U_o, V_o$  = components of steady current velocity

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<sup>13</sup>The horizontal diffusion coefficients ( $E_y$  and  $E_x$ ) are given by:

$$\begin{array}{ll}
 E_x = A_x \sigma_x^{n_x} & (\sigma_x < \sigma_{xc}) \\
 E_y = A_y \sigma_y^{n_y} & (\sigma_y < \sigma_{yc}) \\
 E_x = A_x \sigma_{xc}^{n_x} & (\sigma_x > \sigma_{xc}) \\
 E_y = A_y \sigma_{yc}^{n_y} & (\sigma_y > \sigma_{yc})
 \end{array}$$

## CHAPTER FIVE

### RESULTS OF CALCULATIONS WITH DISPERSION MODEL

#### 5.1 Introduction

In this chapter the results of the calculations performed to estimate the physical dispersion of discharged brines are presented. The calculations were made using the computer dispersion model described in Chapter Four. For each of the four site areas -- Hackberry Bay, Louisiana; Cook Inlet, Alaska; near offshore Gulf of Mexico (Grand Isle, Louisiana); and far offshore Gulf of Mexico -- a series of computer runs was made to predict the patterns of concentration resulting from brine discharges. The key variables incorporated in the model influencing the concentration contours are (1) rate of discharge, (2) depth of water, (3) initial mixing dilution, (4) currents in the receiving waterbody, and (5) diffusion coefficients. The results of the computations are given in the form of plots of normalized concentration contours (isopleths) and plots of the areas enclosed by the concentration contours.

Section 5.2 discusses the calculation methodology, and Sections 5.3, 5.4, 5.5 and 5.6 present the computed results for Hackberry Bay, Cook Inlet, near offshore Gulf of Mexico, and far offshore Gulf of Mexico, respectively.

#### 5.2 Calculation Methodology

The dispersion model described in Chapter Four, Section 4.3, was used to calculate concentration distributions for four sites: Hackberry Bay, Louisiana; Cook Inlet, Alaska; near offshore Gulf of Mexico waters (Grand Isle, Louisiana); and far offshore Gulf of Mexico. The input parameters to the dispersion model have been summarized in Chapter Four and will be given here as well for convenience:

$Q_0$	=	rate of brine discharge
$\Delta c_0$	=	excess concentration (compared with ambient level) of contaminants in discharged brine
RTRANS	=	initial mixing distance (length of near and intermediate mixing zones: the zones in which initial discharge velocity of effluent

plays an important role; in addition to currents, in determining the movement of the effluent)

- D = initial dilution of discharge resulting from mixing of discharge with receiving waters in near and intermediate mixing zones
- H = total water depth (assumed constant)
- H2 = depth of source at beginning of far mixing field (zone in which effluent can be considered to be moved passively by currents and diffusion forces)
- XSHORE = distance to shoreline if applicable (the model can incorporate the effects of only one straight shoreline)
- $E_x, E_y$  = horizontal diffusion coefficients; these are given in terms of  $A_x, A_y, n_x, n_y, \sigma_{xc}$ , and  $\sigma_{yc}$  (see Equations 4-3 and 4-4)
- $U_0, U_1, V_0, V_1$  = current parameters. The current is assumed to be spatially homogenous. Given an x-y cartesian coordinate system chosen on the basis of site geography,  $U_0$  and  $V_0$  are the non-time-varying current components in the x and y direction respectively, and  $U_1$  and  $V_1$  are the amplitudes of sinusoidally varying current components in the x and y direction. The total currents in the x and y direction respectively,  $U(t)$  and  $V(t)$ , are given by

$$U(t) = U_0 + U_1 \sin (2\pi t/T)$$

$$V(t) = V_0 + V_1 \cos (2\pi t/T)$$

where T is the tidal period.

For each set of input parameters, the output of the computer dispersion model is a set of predicted concentration values averaged over a tidal cycle, at points on a cartesian grid whose origin corresponds to the discharge point. In the computations performed, the initial excess concentration,  $\Delta c_0$ , was always set equal to 100.00 so that the output concentration values can be interpreted as indicating percent dilution of the discharged produced water itself, or percent dilution of the initial concentration of any contaminant contained in the discharged brine. A value of 1.00, for

example, at a certain point means that the contaminant concentrations at this point are predicted to be 1 percent of their level in the discharged brine at the point of discharge. The actual concentration of a particular brine constituent can then be found simply by multiplying its concentration in the produced water (as known from laboratory analyses) by the dilution percentage given by the computer program.

The basic computer output, an array of concentration factors or dilution percentages, can be converted to a form which is much more accessible to analysis and interpretation by connecting points with the same concentration values. The curves thus formed are called concentration isopleths or contours (or more accurately, concentration factor isopleths, because of the normalized value of 100.00 used for  $\Delta c_0$ ) and were obtained by estimating concentrations between output grid points using linear interpolation. Since a principal aim of the study is to assess the impact of pollutants discharged into the marine environment, and since impact depends in large part on the size of the areas subjected to particular levels of concentration, the areas enclosed by the concentration isopleths were calculated, by use of a planimeter, to give estimates of the areas of the receiving waterbodies for which concentrations can be expected to be equal to or greater than any particular level.

As an example, Figure 5-1 shows a set of concentration isopleths obtained from one of the near offshore Gulf of Mexico calculations. The origin of the coordinate system is the location of the discharge. The concentration distribution is symmetrical with respect to the y-axis so that only one-half of the pattern is shown. Points between the y-axis and the 2 percent isopleth have contaminant concentrations greater than 2 percent of their concentration in the discharge, points between the 2 percent isopleth and the 1 percent isopleth have concentrations between 2 percent and 1 percent of the discharge concentrations, and so on. The decrease of concentration with increasing distance from the source is shown by the location of the isopleths for smaller concentrations at greater distances from the origin. A plot of the areas enclosed by the concentration isopleths in Figure 5-1 is shown in Figure 5-2. The area of  $184 \times 10^4$  square feet corresponding to a concentration level of 0.1 percent, for example, is obtained by measuring (by planimeter) the area enclosed between the 0.1 percent isopleth and the y-axis in Figure 5-1 (and doubling this value to incorporate the symmetry of the concentration distribution). This area is shaded in Figure 5-1. Similarly, values for the areas enclosed by the other concentration isopleths are measured,

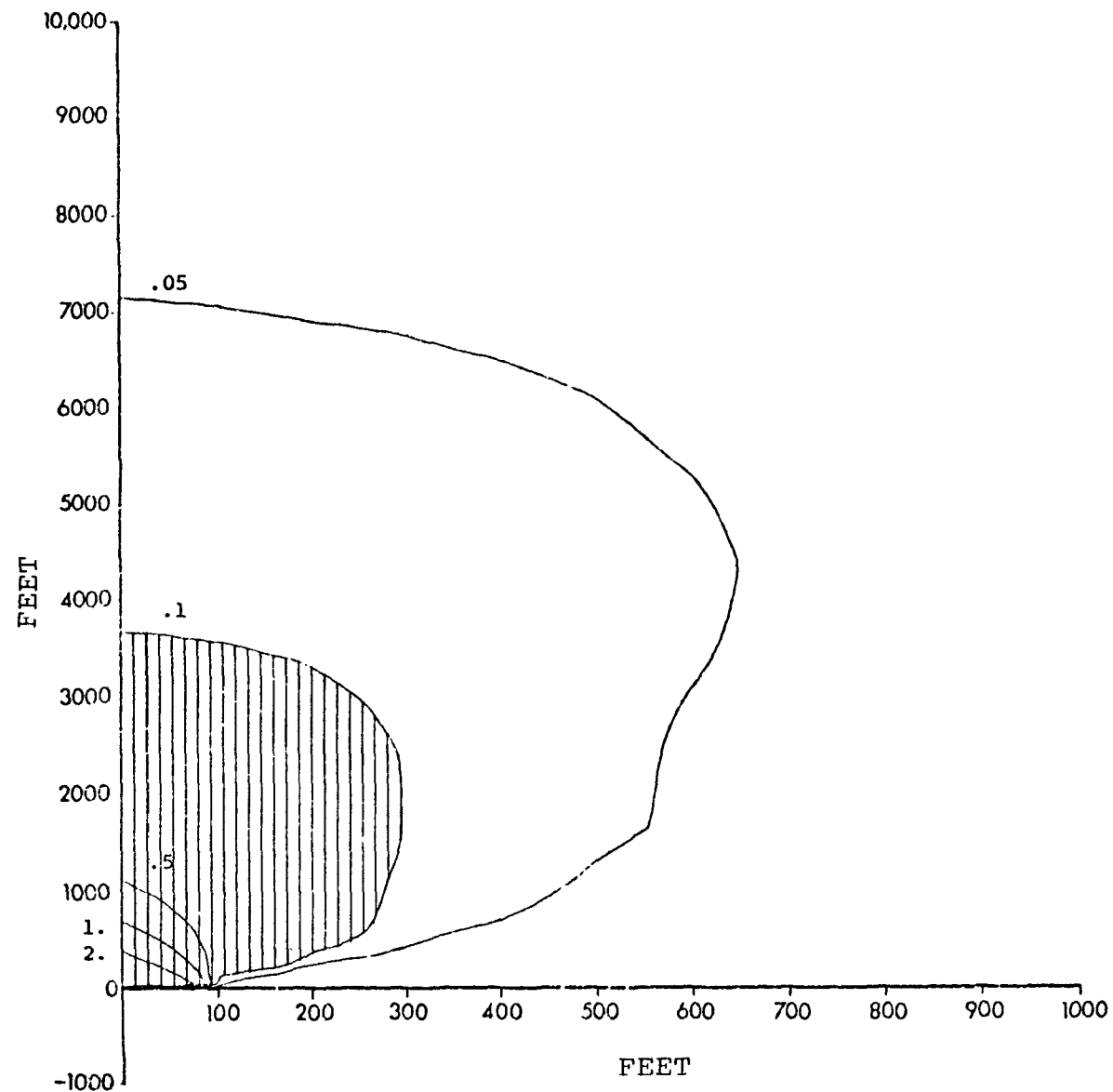


Figure 5-1. Isopleths for near offshore site. Concentrations are in percent, and distances in feet. Shaded area shows region in which brine concentration is 0.1 percent or greater.

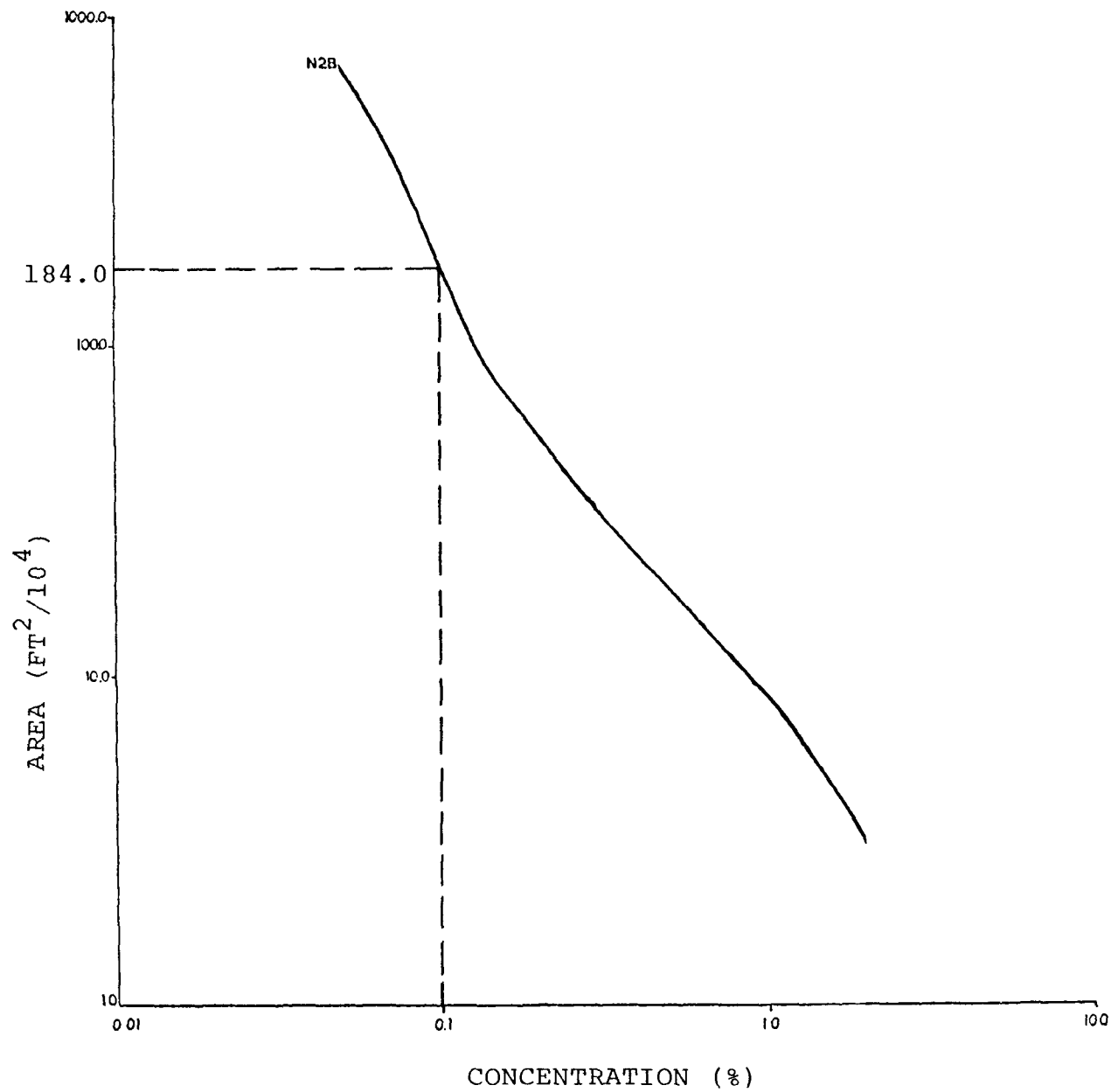


Figure 5-2. Area/concentration curve for same site as used in Figure 5-1. Dotted lines show that brine concentration is  $\geq 0.1$  percent over  $184 \times 10^4 \text{ ft}^2$  (shaded area in Figure 5-1).

the areas plotted versus the corresponding concentrations, and the resulting set of five points connected to give the curve shown in Figure 5-2.

In general, the values of the input parameters are not known exactly. In the absence of detailed field measurements at the discharge sites, values for the diffusion coefficients, currents, and initial mixing depth all have to be estimated using whatever information and knowledge is available. Details on how these parameter values were estimated are given below in Sections 5.3 through 5.6. In addition, certain simplifying assumptions are built into the model (as indeed they are in any model) such as, for example, the assumption here of spatially homogeneous currents. It is, therefore, important to perform sensitivity analyses consisting of a series of computer runs in which input parameters are given a range of values to allow for the degree of uncertainty with which they are known, or to allow for simplifying model assumptions. The concentration factor isopleths for each such calculation can be plotted and compared with the isopleths of calculations performed with different choices of the input parameter values. In this study impacts are measured in terms of receiving waterbody areas that are subjected to particular levels of contaminant concentrations. Hence, comparison of the computer outputs for different sensitivity analyses are most easily performed by plotting the area versus concentration curves, one for each sensitivity analysis, together on one graph. An example of this is shown in Figure 5-3. The base case is the curve corresponding to the set of input parameters regarded as the most probable. A "best" (least impacted area) and "worst" (greatest impacted area) case can be constructed as shown in Figure 5-3 by forming the two envelopes of the set of area/concentration curves. These do not, in general, correspond to any one set of input parameters but are best and worst in the collective sense that particular points on these curves correspond to some choice of possible input parameter values.

Although the dependence of the distribution of concentration factors on the input parameters is not a simple one (as is evidenced by the involved structure of the dispersion model), it may be useful here to indicate in qualitative terms the influence of the input parameters on the output distribution of concentrations (see Table 5-1). Concentrations naturally vary directly with the rate of brine discharge,  $Q_0$ . The greater  $Q_0$ , the greater will be the value of the concentration at a given point if all other parameters are held constant. The variation of concentration with  $Q_0$  is, however, not linear as demonstrated by the fact that in the



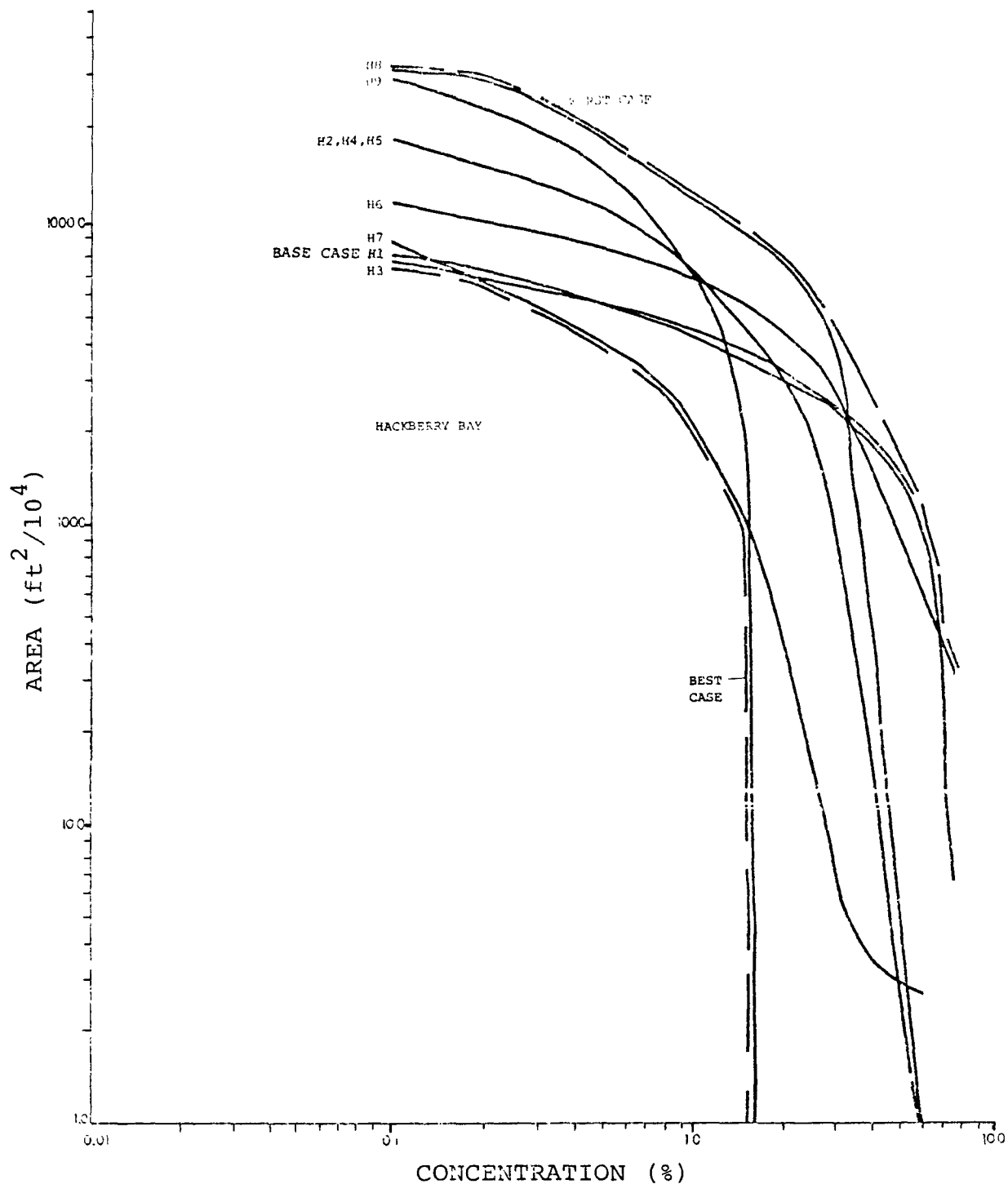


Figure 5-3. Plots of area/concentration curves for sensitivity analyses performed for Hackberry Bay site. Base Case assumes most probable values of input parameters; for other cases, input parameters are individually varied over their range of plausible values.

TABLE 5-1

QUALITATIVE INFLUENCE OF INPUT PARAMETERS  
ON CONCENTRATION DISTRIBUTION

PARAMETER	EFFECT
$Q_0$ = discharge rate	Larger discharge rate results in larger concentrations.
$\Delta c_0$ = excess contaminant concentration	Set equal to normalized value 100.00 for all computations.
RTRANS = radius of initial mixing zone	No effect on shape of pattern.
D = initial mixing dilution	Most strongly influences concentrations close to source. Larger values of D result in smaller concentration values.
H = total water depth H2 = thickness of pollutant plume layer	Larger values of H and H2 result in larger initial mixing dilution.
$U_0, V_0$ = steady current	Steady currents remove pollutant from vicinity of discharge. Larger values result in more rapid rate of pollutant dilution.
$U_1, V_1$ = tidal current components	Tidal currents produce periodic circulation of pollutants but no net removal. Larger values result in larger effluent dilutions because mixing occurs over a larger area.
$E_x, E_y$ = diffusion coefficients	Larger values of coefficients result in more rapid rate of pollutant diffusion. Shape of pollutant plume strongly influenced by diffusion in direction transverse to principal current flow.

receiving waters the effluent discharge contaminant concentrations cannot be larger than they are in the effluent itself, no matter how great the effluent discharge rate is. The parameter  $\Delta c_0$ , the excess concentration of a contaminant in the discharged brine, does not directly influence the computed concentrations here since, as mentioned above, it is set equal to a normalized value of 100.00 for all computations. The output values of the computer program are thus percentage concentrations of the discharged produced water. Data on the actual concentrations of particular contaminants in the receiving water can be obtained by multiplying the concentration of a brine constituent in produced water by the percent dilution of the produced water as given by the computer program.

The parameter RTRANS, as used here, influences only the location of the effective far field source (see Figure 4-5). It serves to indicate that the concentration distributions are computed starting from an effective origin whose distance from the actual point of discharge varies with the initial effluent discharge velocity. In all computations performed in this study RTRANS is small and has an insignificant effect on the output concentration distribution, producing only a slight displacement of the concentration distribution away from the actual point of discharge.

The parameter D, the initial dilution of the discharge resulting from mixing in the near and intermediate mixing zones,<sup>1</sup> has a marked influence on concentrations at points relatively close to the discharge point, but its influence tends to diminish with increasing distance from the discharge point. For distances close to the discharge point, the greater the value of D the smaller are the resulting receiving water concentrations. The parameters H and H2, total depth of water and initial mixing depth, respectively, are used in computing D. In general, the greater the water depth the greater will be the dilution of the discharged brine. Because of the fact that produced water is generally more saline, and therefore denser than seawater, the discharge will tend to form a layer at the bottom of the water column. The thickness of this layer is H2 and it is generally proportional to the total depth of water. Larger values of H and H2 are reflected in larger values of the initial mixing dilution D.

The current parameters, as might be expected, have an important influence on the concentration distribution. The

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<sup>1</sup>These are the zones in which the initial discharge momentum of the brine still affects its movement.

steady current components,<sup>2</sup>  $U_0$  and  $V_0$ , control the net movement of the discharge away from the discharge point. The greater  $U_0$  and  $V_0$ , the more rapidly the effluent will be carried away from the discharge point and hence the faster that concentrations will decrease with increasing distance from the source location. The tidal current components,  $U_1$  and  $V_1$ , do not produce any net movement of effluent. In fact, if there were no steady current components, the tidal current components alone would result in a periodic circulation of effluent but no net movement, with the result that concentrations would tend to increase with time. The magnitude of the tidal current parameters influences the size of the region in which the discharge is circulated (the tidal excursion). The larger the tidal current the more mixing of the discharge with receiving waters can occur in each tidal cycle, and hence the more rapidly concentrations will tend to decrease farther from the source.

The diffusion coefficients control the rate at which the discharge plume spreads out in the receiving waters. The greater the diffusion coefficients, the more rapidly diffusion occurs. In open waters diffusion has been found to increase with the scale of the diffusing patch (this is discussed in more detail in Appendix B) so that the rate of diffusion increases with increasing distance from the source. There is also an interplay between the diffusion coefficients and the shape of the discharge plume. If currents are assumed to flow along one axis only (the longitudinal or y axis) the smaller the transverse diffusion coefficient,  $E_x$ , the more long and narrow the plume tends to be. Conversely, large values of  $E_x$  result in a more rapid diffusion of effluent in the transverse direction with the result that the plume tends to be wider and shorter. The influence of the transverse diffusion coefficient on plume shape is a direct consequence of the law of conservation of mass. Since the quantity of discharged contaminant is fixed by the discharge rate, it follows that if more contaminant spreads out in the transverse direction then less contaminant is available at large distances in the longitudinal direction, and conversely.

The above remarks on the influence of the input parameters are rough and qualitative only, but they do serve to give some insight into the kinds of changes in the concentration distributions that can be expected to accompany changes in the values of the input parameters.

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<sup>2</sup>Current components in the x and y direction are represented by U and V, respectively.

### 5.3 Hackberry Bay, Louisiana

Table 5-2 lists the various sets of input parameters which were used in computer calculations of concentration factors at the Hackberry Bay site. Case H1 can be considered the base (most probable) case; H2 and H3 examine the effect of varying the horizontal diffusion coefficients; in H4 and H5 the initial dilution is varied; in H6 the tidal velocity is varied; in H7 and H8 the nontidal current component is varied; and in H9 a rotational current component<sup>3</sup> is introduced.

Table 5-3 gives for each input parameter its base case value, the range within which it was varied, and comments about the choice of values. For all calculations  $Q_0$  was set equal to 3.98 cubic feet per second, the average rate of oilfield brine disposal from the Bay de Chene oil field in Hackberry Bay (see Appendix D). On the basis of what was known about the mode of disposal (release of effluent into a large cylinder extending below the surface of the water) RTRANS was set equal to 1 foot. The value of RTRANS is in any event unimportant for the purpose of this study since it influences only a small zone immediately adjacent to the point of disposal. In all calculations XSHORE was set equal to infinity and the effect of the shoreline was incorporated by computing a background concentration level of the order of 0.1 percent (see Chapter Four, Section 4.2) and using the computer model to predict concentration factors only down to this level of dilution. The base case value of  $D$  equal to 2 is a conservative minimum as any form of discharge is likely to achieve at least this level of initial dilution. The base case value of  $H$  of 3 feet was obtained by calculating the mean low water depth of Hackberry Bay to be 2.4 feet on the basis of known volume and surface area,<sup>4</sup> and adding to this an amount equal to one-half the average tidal range of approximately 1 foot.<sup>5</sup>

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<sup>3</sup>If there are nonzero tidal current components in both the  $x$  and  $y$  directions, then the tidal current vector will rotate through an ellipse during each tidal period.

<sup>4</sup>Barney Barrett, Water Measurements of Coastal Louisiana, (New Orleans: Louisiana Wildlife and Fisheries Commission, Division of Oysters, Water Bottoms and Seafoods, 1970), p. 97.

<sup>5</sup>Barney Barrett, Cooperative Gulf of Mexico Estuarine Inventory and Study, Phase II, Hydrology and Phase III, Sedimentology (New Orleans: Louisiana Wildlife and Fisheries Commission, 1971), p. 55.

TABLE 5-2

LISTING OF COMPUTER CALCULATIONS PERFORMED  
FOR THE HACKBERRY BAY SITE

CALCULATION	$Q_0$ (ft <sup>3</sup> /sec)	D	RTRANS (ft)	H	H2 (ft)	$E_x$ (ft <sup>2</sup> /sec)	$E_y$ (ft <sup>2</sup> /sec)	$U_0$ (ft/sec)	$U_1$ (ft/sec)	$V_0$ (ft/sec)	$V_1$ (ft/sec)	COMMENTS
H1	3.98	2	1	3	3	0.1	1.0	0	0	0.035	0.22	Base Case
H2	3.98	2	1	3	3	1.0	1.0	0	0	0.035	0.22	Variation of Diffusion Coefficients
H3	3.98	2	1	3	3	0.1	0.1	0	0	0.035	0.22	
H4	3.98	5	1	3	3	1.0	1.0	0	0	0.035	0.22	Variation of Initial Mixing Dilution, D
H5	3.98	10	1	3	3	1.0	1.0	0	0	0.035	0.22	
H6	3.98	2	1	2.5	2.5	1.0	1.0	0	0	0.035	0.065	Variation of Tidal Velocity, $V_1$
H7	3.98	2	1	3	3	1.0	1.0	0	0	0.1	0.22	Variation of Steady (Fresh Water) Velocity, $V_0$
H8	3.98	2	1	3	3	1.0	1.0	0	0	0.01	0.22	
H9	3.98	2	1	3	3	1.0	1.0	0	0.05	0.035	0.22	Rotational Velocity Component, $V_1$

TABLE 5-3

PARAMETER VALUES FOR HACKBERRY BAY CALCULATIONS

PARAMETER	VALUES		COMMENTS
	BASE CASE	RANGE	
$Q_0$	3.98 ft <sup>3</sup> /sec	--	Based on discharge data.
RTRANS	1 ft	--	Conservatively small. Insignificant effect on concentration distribution.
D	2	2-10	Two is conservative minimum.
H	3 ft	2.5-3 ft	Real mean depth. Varies with tidal height.
H2	3 ft	2.5-3 ft	Realistic value considering shallow water depth. Complete mixing assumed.
$V_0$	0.035 ft/sec	0.01-0.1 ft/sec	Based on net flow values.
$V_1$	0.22 ft/sec	0.065-0.22 ft/sec	Consistent with tidal volumes.
$U_0$	0	--	Reasonable and conservative assumption in absence of detailed current data.
$U_1$	0	0.05	Arbitrarily assumed to examine sensitivity to rotational velocity component.
XSHORE	$\infty$	--	Account for boundaries by computing background concentration with tidal flushing calculation.
$E_x$	0.1 ft <sup>2</sup> /sec	0.1-1.0 ft <sup>2</sup> /sec	Values of $E_x/H_{u*}$ and $E_y/H_{u*}$ consistent with Fischer. <sup>a</sup>
$E_y$	1.0 ft <sup>2</sup> /sec	0.1-1.0 ft <sup>2</sup> /sec	
$E_z$	0	--	
			Complete mixing in water column assumed.

<sup>a</sup>Hugo B. Fischer, "Longitudinal Dispersion and Turbulent Mixing in Open-Channel Flow," Annual Review of Fluid Mechanics, Vol. V, ed. by Van Dyke (Palo Alto: Annual Reviews, Inc., 1973).

A simplified current scheme was adopted in the calculations in which tidal and nontidal (i.e., freshwater) currents were assumed to flow along the y-axis. Values for these current velocity components were then estimated on the basis of tidal volume information<sup>6</sup> using the somewhat involved calculations described in Appendix E.

Values for the diffusion coefficients were estimated by combining values of depth and current velocities with values given by Fischer<sup>7</sup> for the dimensionless quantity  $E/Hu_*$  where  $u_*$  is the friction velocity. This procedure is discussed in more detail in Appendix E.

The concentration factor isopleths for the calculations H1 through H9 enumerated in Table 5-2 are shown in Figures 5-7a through 5-7i, respectively, and plots of areas enclosed by the isopleths versus dilution level are given in Figure 5-3 (above). The concentration factor isopleths are symmetric with respect to the y axis.

#### 5.4 Cook Inlet, Alaska

Table 5-4 presents a listing of the sets of input parameters for which computer calculations were performed to predict concentration factors for the Cook Inlet oilfield area, and Table 5-5 gives for each parameter its base value, range when varied, and comments about choice of values.

Of the seven known sources of brine discharge into Cook Inlet waters (see Appendix D), two were selected for computations: the Trading Bay Production Facility with an average daily discharge of 12,500 barrels brine (0.81 cubic feet per second), and the Granite Point Production Facility with an average discharge of 5,000 barrels brine per day (0.32 cubic feet per second). Both of these are onshore facilities which discharge brine into Cook Inlet close to the shore. These facilities were selected on the grounds that the impacted areas for these facilities would be considerably larger than those corresponding to offshore platforms discharging produced water into the much deeper waters of Cook Inlet far from the shoreline.

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<sup>6</sup>Barrett, Cooperative Gulf of Mexico Estuarine Inventory and Study, p. 57.

<sup>7</sup>Hugo B. Fischer, "Longitudinal Dispersion and Turbulent Mixing in Open-Channel Flow," Annual Review of Fluid Mechanics, Vol. V, ed. by Van Dyke (Palo Alto: Annual Reviews Inc., 1973).



TABLE 5-4

LISTING OF COMPUTER CALCULATIONS  
PERFORMED FOR COOK INLET, ALASKA

CALCULATION	$Q_0$ (ft <sup>3</sup> /sec)	D	RTRANS	H (ft)	H2 (ft)	$E_x$			$E_y$ (ft <sup>2</sup> /sec)	$U_0$ (ft/sec)	$U_1$ (ft/sec)	$V_0$ (ft/sec)	$V_1$ (ft/sec)	COMMENTS
						$A_x$	$n_x$	$\sigma_{xc}$						
C1	0.81	2	1	8	8	0.005	4/3	250	1,250	0	0	0.014	n.a.	Trading bay production facility. Variation of tidally averaged diffusion coefficient, $E_y$ .
C2	0.81	2	1	8	8	0.005	4/3	250	7,500	0	0	0.014	n.a.	
C3	0.81	2	1	8	8	0.005	4/3	250	250	0	0	0.014	n.a.	
C4	0.32	2	1	8	8	0.005	4/3	50	1,250	0	0	0.014	n.a.	Granite point production facility. Variation of $E_y$ .
C5	0.32	2	1	8	8	0.005	4/3	50	250	0	0	0.014	n.a.	

TABLE 5-5

PARAMETER VALUES FOR COOK INLET CALCULATIONS

PARAMETER	VALUES		RANGE	COMMENTS
	BASE CASE			
$Q_0$	0.81, 0.32		--	Based on discharge data.
RTRANS	1	}	--	Conservative minimum value.
D	2			
H	8	}	--	Based on actual water depth. Total mixing assumed.
$H_2$	8			
$V_0$	0.014		--	Estimated from freshwater flow data.
$V_1$	--		--	Not input parameter. Maximum observed value of 6.4 ft/sec used in computing base case value of $E_y$ .
$U_0$	0		--	{ Currents assumed to be along shore only.
$U_1$	0		--	
$E_x$ { $A_x$ $n_x$ $\sigma_{xc}$	0.005		--	{ "4/3" diffusion law in direction perpendicular to shoreline. Eddy size bounded by distance to shore.
	4/3		--	
	250, 50 ft		--	
$E_y$	1,250 ft <sup>2</sup> /sec	250-7,500 ft <sup>2</sup> /sec		Estimated by tidally averaged computation.
$E_z$	--		--	No vertical diffusion. Uniform mixing assumed.

The extremely fast tidal currents in Cook Inlet (see Appendix A) with speeds up to 6.5 feet per second in the region of the oil fields, and the consequently large tidal excursions, result in a situation in which discharged contaminants tend to be sloshed back and forth over large distances for a considerable length of time. The contaminants are moved seaward only gradually by the relatively small freshwater flow. In the computer model, concentrations are calculated by summing over the contributions of a series of contaminant "puffs" released at discrete time intervals. To calculate a steady state concentration distribution, the model must follow the course of the discharge puffs over the period of time that the initial puff in the series remains in the zone of interest. It follows that in the case of Cook Inlet with its long flushing times, a lengthy computation is required if the model is to incorporate tidal currents directly. In order to circumvent this problem, it was decided to account for the effects of the tidal currents by incorporating them into the alongshore diffusion coefficient,  $E_y$ . The procedure for doing this is given in Appendix E along with the associated calculation required to estimate  $V_0$ , the downstream freshwater flow velocity.

The concentration factor isopleths for the calculations C1 through C5 enumerated in Table 5-4 are shown in Figures 5-8a through 5-8e respectively, and area vs. dilution plots are given in Figure 5-4.

### 5.5 Near Offshore Gulf Waters

For Gulf of Mexico waters offshore from the barrier islands and within the 3-mile limit, a site was selected in Block 16 of the Grand Isle oilfield area offshore of Grand Isle, Louisiana. Table 5-6 presents a listing of the various sets of input parameters for which calculations were performed, and Table 5-7 gives base values, ranges when varied, and comments about choice of values for each parameter.

The value of  $Q_0 = 1$  cubic foot per second used for the base case (approximately 15,000 barrels produced water discharged per day) is somewhat higher than the figure obtained from the Louisiana Department of Conservation in Houma, Louisiana, for 1975 produced water discharge in Block 16 (approximately 9,000 barrels produced water discharged per day). However, an average brine discharge of 15,000 barrels is known to occur in offshore waters (as can be seen from USGS records for far offshore Gulf of Mexico brine discharges), and since only one near offshore site was considered in this study it was decided that potential benefits

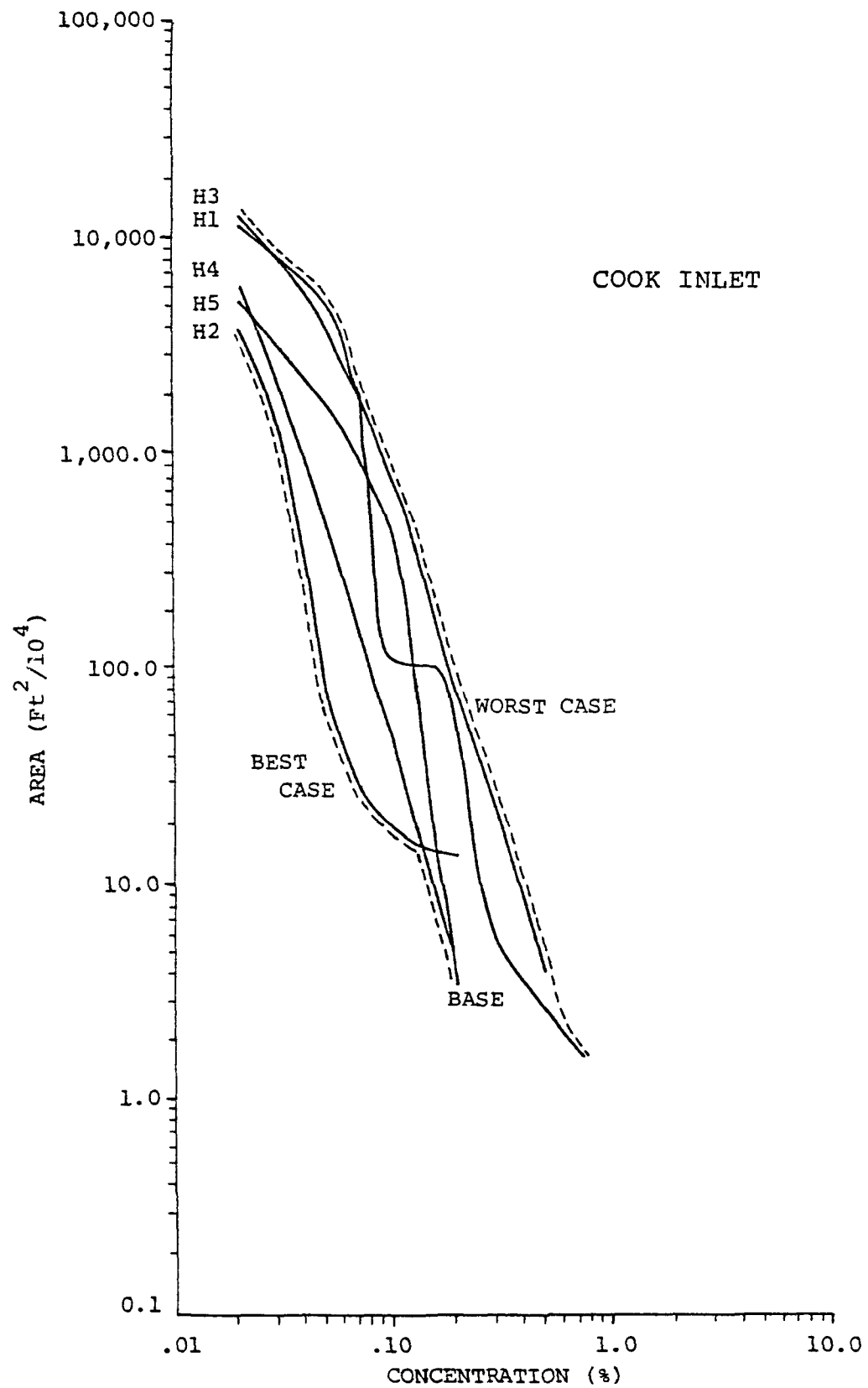


Figure 5-4. Area/concentration curves for Cook Inlet.

TABLE 5-6

LISTING OF COMPUTER CALCULATIONS PERFORMED  
FOR THE NEAR OFFSHORE GULF OF MEXICO SITE

CALCULATION	$Q_0$	D	RTRANS	XSHORE	H <sub>1</sub>	H <sub>2</sub>	$E_x$			$E_y$			$U_0$	$U_1$	$V_0$	$V_1$	COMMENTS
	(ft <sup>3</sup> /sec)		(ft)	(ft)	(ft)	(ft)	$A_x$	$n_x$	$\sigma_{xc}$	$A_y$	$n_y$	$\sigma_{yr}$	(ft/sec)	(ft/sec)	(ft/sec)	(ft/sec)	
N1A	1	25	20	15,000	33	5.5	.00524	4/3	7,500	.00524	4/3	$\infty$	0	0	.37	.25	Base Case: XSHORE=3 miles
N1B	1	10	20	15,000	33	5.5	.00524	4/3	7,500	.00524	4/3	$\infty$	0	0	.37	.25	Variation of D
N1C	1	25	20	15,000	33	5.5	.00524	4/3	7,500	.00524	4/3	$\infty$	0	0	.18	.12	Variation of Current Velocity
N1D	.5	25	20	15,000	33	5.5	.00524	4/3	7,500	.00524	4/3	$\infty$	0	0	.37	.25	Variation of $Q_0$
N1E	1	25	20	15,000	33	5.5	.002	4/3	7,500	.002	4/3	$\infty$	0	0	.37	.25	Variation of $A_x$ , $A_y$
N2A	1	5	20	2,500	15	3.5	.00524	4/3	1,250	.00524	4/3	$\infty$	0	0	.37	.25	Base Case: XSHORE=1/2 mile
N2B	1	5	20	2,500	15	3.5	.00524	4/3	1,250	.00524	4/3	$\infty$	0	0	.18	.12	Variation of Current Velocity
N2C	1	5	20	2,500	15	3.5	.002	4/3	1,250	.002	4/3	$\infty$	0	0	.37	.25	Variation of $A_x$ , $A_y$

TABLE 5-7

PARAMETER VALUES FOR NEAR OFFSHORE  
GULF OF MEXICO CALCULATIONS

PARAMETER	BASE CASE	RANGE	COMMENTS
$Q_0$ (ft <sup>3</sup> /sec)	1	.5-1	Value of 1 chosen to given conservative estimate.
D	25	5-25	Value of D computed using EPA plume theory. <sup>a</sup> Results not sensitive to varying D by factor of 2.
XSHORE (ft)	15,000	2,500-15,000	15,000 is actual distance to shore. 2,500 used to test sensitivity of results to variation of XSHORE.
H (ft)	33	15-33	Actual depth at site. 15 is approximate depth at XSHORE = 1/2 mile.
H2 (ft)	5.5	3.5-5.5	$H2 = 1/6H^b$
$E_x \begin{cases} A_x \\ n_x \\ \sigma_{xc} \end{cases}$	.00524 4/3 7,500	.002-.00524  1,250-7,500	"4/3" diffusion law for horizontal diffusion in ocean waters. <sup>c</sup> Scale limited by distance to shore. Value of .002 for $A_x$ and $A_y$
$E_y \begin{cases} A_y \\ n_y \\ \sigma_{yc} \end{cases}$	.00524 4/3 $\infty$	.002-.00524  	conservative estimate consistent with published data. <sup>d</sup> Results insensitive to $E_y$ .
$U_o$ (ft/sec)	0		Transverse (onshore) currents set equal to zero. Conservative assumption.
$U_1$ (ft/sec)	0		
$V_o$ (ft/sec)	.37	.18-.37	Base Case values consistent with published studies. <sup>e,f</sup> Lower values used to obtain more conservative estimates.
$V_1$ (ft/sec)	.25	.12-.25	

Note: See references on following page.

REFERENCES FOR TABLE 5-7

<sup>a</sup>M.A. Shirazi and L.R. Davis, Workshop of Thermal Plume Prediction, Volume 1: Submerged Discharge, EPA-R2-72-005a (Corvallis, Oregon: National Environmental Research Center, U.S. Environmental Protection Agency, August 1972).

<sup>b</sup>G. Abraham, Jet Diffusion in Stagnant Ambient Fluid, Delft Hydraulics Laboratory, Publication No. 29, 1963.

<sup>c</sup>N. Brooks, "Diffusion of Sewage Effluent in an Ocean-Current," in Proceedings of the First International Conference on Waste Disposal in the Marine Environment, University of California, Berkeley, July 22-25, 1959, ed. by E.A. Pearson (Oxford: Pergamon Press, 1960).

<sup>d</sup>R. Koh and L. Fan, Mathematical Models for the Prediction of Temperature Distributions Resulting from the Discharge of Heated Water into Large Bodies of Water, for the U.S. Environmental Protection Agency, Water Quality Office, Water Pollution Control Research Series Report 16130 DWO 10/70, October 1970.

<sup>e</sup>P. Oetking et al., Currents on the Nearshore Continental Shelf of South Central Louisiana, Report No. 17, Offshore Ecology Investigation, Gulf Universities Research Consortium, May 1, 1974.

<sup>f</sup>Louisiana Offshore Oil Port Environmental Baseline Study, Volume II, Technical Appendices 1-5 (New Orleans: LOOP, Inc.).

of the EPA regulations could be more usefully estimated by choosing a relatively high value for the rate of discharge. A sensitivity run was made with the value of  $Q_0$  equal to 0.5 cubic feet per second so that the impact associated with a rate of discharge more closely approximating the actual Block 16 discharge rate could be estimated. Several computations were made with a value of XSHORE (i.e., distance to shore) of 0.5 miles instead of the actual distance of 3 miles offshore of Block 16. The results of these computations can be used to indicate the predicted impacts of discharge from platforms located one-half mile offshore.

Data on the depth of water,  $H$ , was obtained from the NOAA National Ocean Survey 1:80,000 scale map of Barataria Bay and approaches. The values for the thickness of the initial mixing layer  $H_2$  were obtained from  $H$  by using the relation  $H_2 = H/6$ . The source for this relationship is Abraham<sup>8</sup> who gives a range for  $H_2$  of from  $H/12$  to  $H/6$ . The larger value of  $H_2$  (i.e.,  $H_2 = H/6$ ) was used in the computations since vertical diffusion was not explicitly incorporated into the computations, and the assumption of a thick mixing layer without vertical diffusion is roughly equivalent to assuming a thin initial mixing layer with vertical diffusion.

The values of  $D$  were computed on the basis of values of  $H$ ,  $H_2$ , and  $Q_0$  using charts given in the EPA Workbook of Thermal Plume Prediction<sup>9</sup> (see Appendix E). Diffusion coefficients were computed using the "4/3" diffusion law discussed in Appendix B. The base case value of  $A_x = A_y = 0.00524$  is taken from Brooks.<sup>10</sup> The sensitivity test value of  $A_x = A_y = 0.002$  is consistent with a range of 0.001 to 0.06 reported by Koh and Fan.<sup>11</sup>

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<sup>8</sup>G. Abraham, Jet Diffusion in Stagnant Ambient Fluid, Delft Hydraulics Laboratory Publication No. 29, 1963.

<sup>9</sup>M.A. Shirazi and L.R. Davis, Workbook of Thermal Plume Prediction, Volume 1: Submerged Discharge, EPA-R2-72-005a (Corvallis, Oregon: National Environmental Research Center, U.S. Environmental Protection Agency, August 1972).

<sup>10</sup>N. Brooks, "Diffusion of Sewage Effluent in an Ocean-Current," in Proceedings of the First International Conference on Waste Disposal in the Marine Environment, University of California, Berkeley, July 1959, ed. by E.A. Pearson (Oxford: Pergamon Press, 1960).

<sup>11</sup>R. Koh and L. Fan, Mathematical Models for the Prediction of Temperature Distributions Resulting from the Discharge of Heated Water into Large Bodies of Water, for the U.S. Environmental Protection Agency, Water Quality Office, Water Pollution Control Research Series Report 16130 DWO 10/70, October 1970.



The base case drift current velocity of 0.37 feet per second was obtained from the GURC study.<sup>12</sup> The tidal current velocity value of 0.25 feet per second is in accord with studies of the tidal current made for the proposed Louisiana Offshore Oil Port (LOOP).<sup>13</sup> The assumption that all currents are in the alongshore direction ( $U_0=U_1=0$ ) is a conservative one since the tidal current component then transports the discharge back and forth in the same line.

The concentration factor isopleths for the calculations N1A through N2C listed in Table 5-6 are shown in Figures 5-9a through 5-9h, respectively, and plots of the areas enclosed by the isopleths are given in Figure 5-5.

#### 5.6 Far Offshore Gulf of Mexico Waters

For Gulf of Mexico waters beyond the 3-mile limit, a site was selected in Block 108 of the Ship Shoal oilfield area. Block 108 is located approximately 27 miles offshore with a depth of water of only 20 feet.<sup>14</sup> Table 5-8 presents a list of the various sets of input parameters for which calculations were performed to obtain concentration factors for far offshore Gulf waters, and Table 5-9 gives for each input parameter its base case value, other values used, and comments about choice of these values.

As in the case of the near offshore calculations, a value of  $Q_0$  = one cubic foot per second (15,000 barrels per day) was used. This value is reasonable considering that the average 1975 produced water discharge rates of Chevron platforms S-93 and S-94 in Block 108 were 9,000 and 12,000 barrels per day, respectively. Values of the mixing layer thickness,  $H_2$ , the initial dilution,  $D$ , and the diffusion coefficients were obtained as described in Section 5.5. Estimates of the current magnitudes were obtained from the

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<sup>12</sup>P. Oetking et al., Currents on the Nearshore Continental Shelf of South Central Louisiana, Report No. 7, Offshore Ecology Investigation, Gulf Universities Research Consortium, May 1, 1974.

<sup>13</sup>Louisiana Offshore Oil Port Environmental Baseline Study, Volume II, Technical Appendices 1-5 (New Orleans: LOOP, Inc.).

<sup>14</sup>Transcontinental Gas Pipe Line Corporation Map of South Louisiana and Louisiana Continental Shelf Showing Natural Gas Pipe Lines, Transcontinental Gas Pipeline Corporation, 1974.

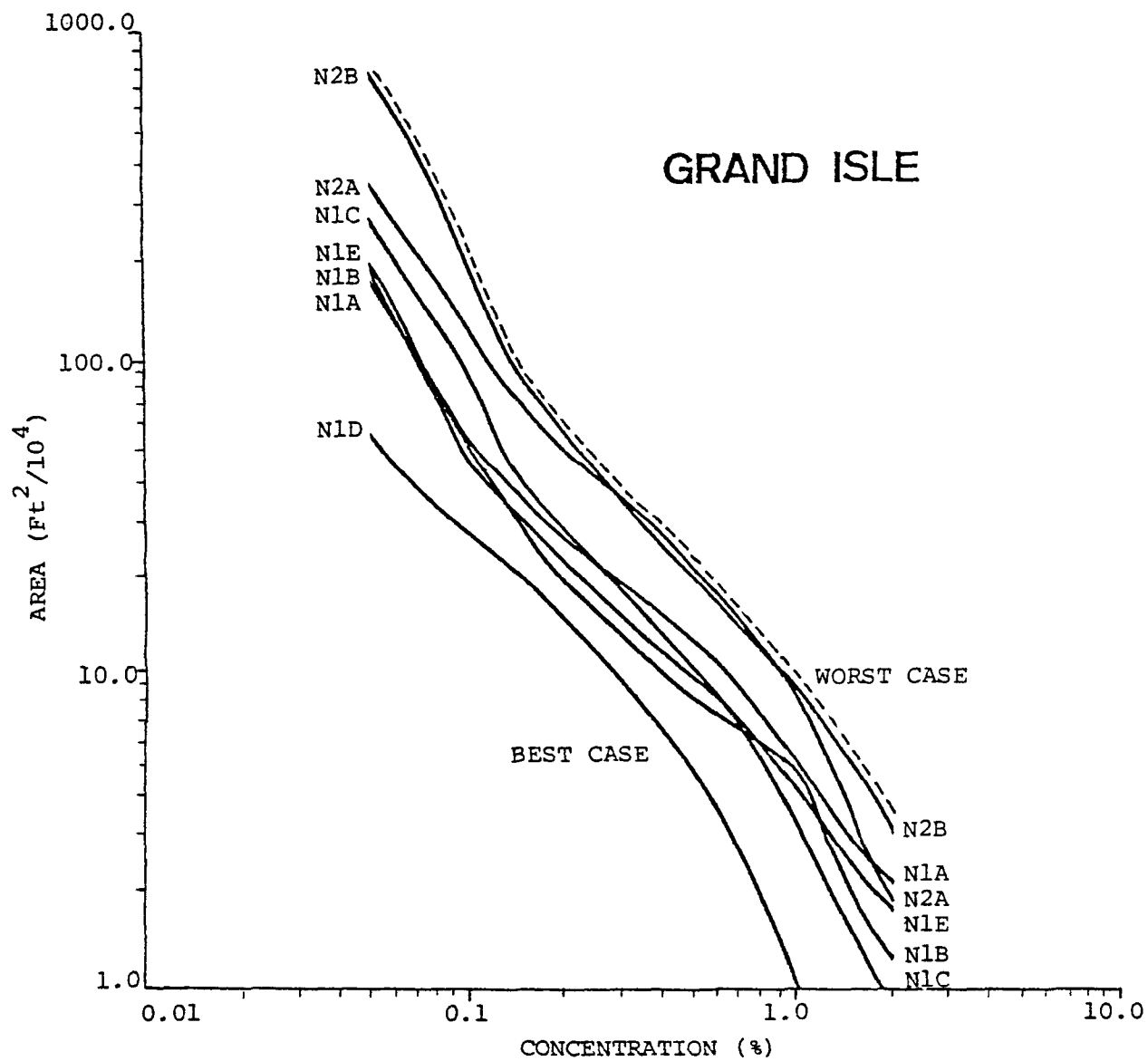


Figure 5-5. Area/concentration curve for Grand Isle site in near offshore Gulf of Mexico.

TABLE 5-8

LISTING OF COMPUTER CALCULATIONS PERFORMED  
FOR THE FAR OFFSHORE GULF OF MEXICO SITE

CALCULATION	Q <sub>0</sub>	D	RTRANS	XSHORE (ft)	H (ft)	H2 (ft)	E <sub>x</sub>			E <sub>y</sub>			U <sub>0</sub>	U <sub>1</sub>	V <sub>0</sub>	V <sub>1</sub>	COMMENTS
							A <sub>x</sub>	n <sub>x</sub>	σ <sub>xc</sub>	A <sub>y</sub>	n <sub>y</sub>	σ <sub>yc</sub>					
F <sub>1</sub>	1	11	20	∞	20	3.3	.00524	4/3	∞	.00524	4/3	∞	0	0	.37	.37	Base Case
F <sub>2</sub>	1	11	20	∞	20	3.3	.00524	4/3	∞	.00524	4/3	∞	0	0	.18	.18	Current Sensitivity
F <sub>3</sub>	1	11	20	∞	20	3.3	.002	4/3	∞	.002	4/3	∞	0	0	.37	.37	Diffusion Coefficient Sensitivity
F <sub>4</sub>	1	5	20	∞	20	3.3	.00524	4/3	∞	.00524	4/1	∞	0	0	.37	.37	Initial Dilution Sensitivity

TABLE 5-9

PARAMETER VALUES FOR FAR OFFSHORE  
GULF OF MEXICO CALCULATIONS

PARAMETER	BASE CASE	RANGE	COMMENTS
$Q_o$ (ft <sup>3</sup> /sec)	1		Value of 1 consistent with discharge data.
D	11	5-11	Computed using EPA plume theory. <sup>a</sup>
H	20		Actual depth of water in block 10S, ship shoal oilfield area.
H2	3.3		$H2 = H/6^b$ .
$E_x, E_y$ $\left\{ \begin{array}{l} A_x, A_y \\ n_x, n_y \\ \sigma_{xc}, \sigma_{yc} \end{array} \right.$	.00524 4/3 $\infty$	.002	"4/3" diffusion law for horizontal diffusion in ocean waters. <sup>c</sup> Value of .002 for $A_x, A_y$ conservative estimate consistent with published data. <sup>d</sup>
$U_0$	0		Transverse currents set equal to zero.
$U_1$	0		Conservative assumption.
$V_0$	.37	.18-.37	Base case values consistent with published study. <sup>e</sup> Lower
$V_1$	.37	.18-.37	values used to obtain more conservative estimate.

Note: References a-e are identical to references a-e in Table 5-7.

GURC Study report.<sup>15</sup> The conservative assumption was made that both drift and tidal currents flow along the same axis.

The concentration factor isopleths for the calculations F1 through F4 listed in Table 5-8 are shown in Figures 5-10a through 5-10d, respectively, and plots of the areas enclosed by these isopleths are given in Figure 5-6.

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<sup>15</sup>Oetking et al., Currents on Nearshore Continental Shelf of South Central Louisiana.

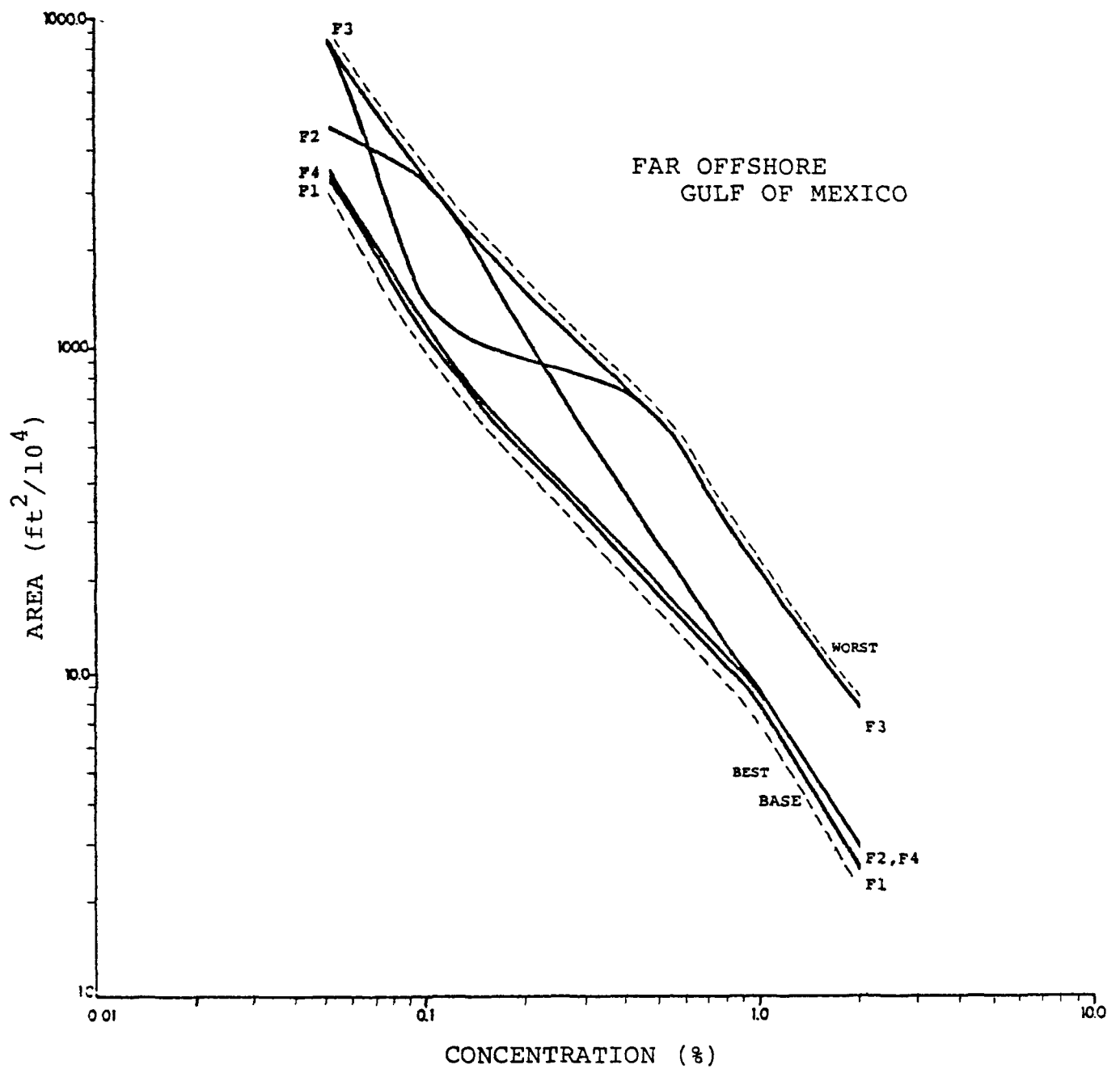


Figure 5-6. Area/concentration curves for far offshore Gulf of Mexico site.

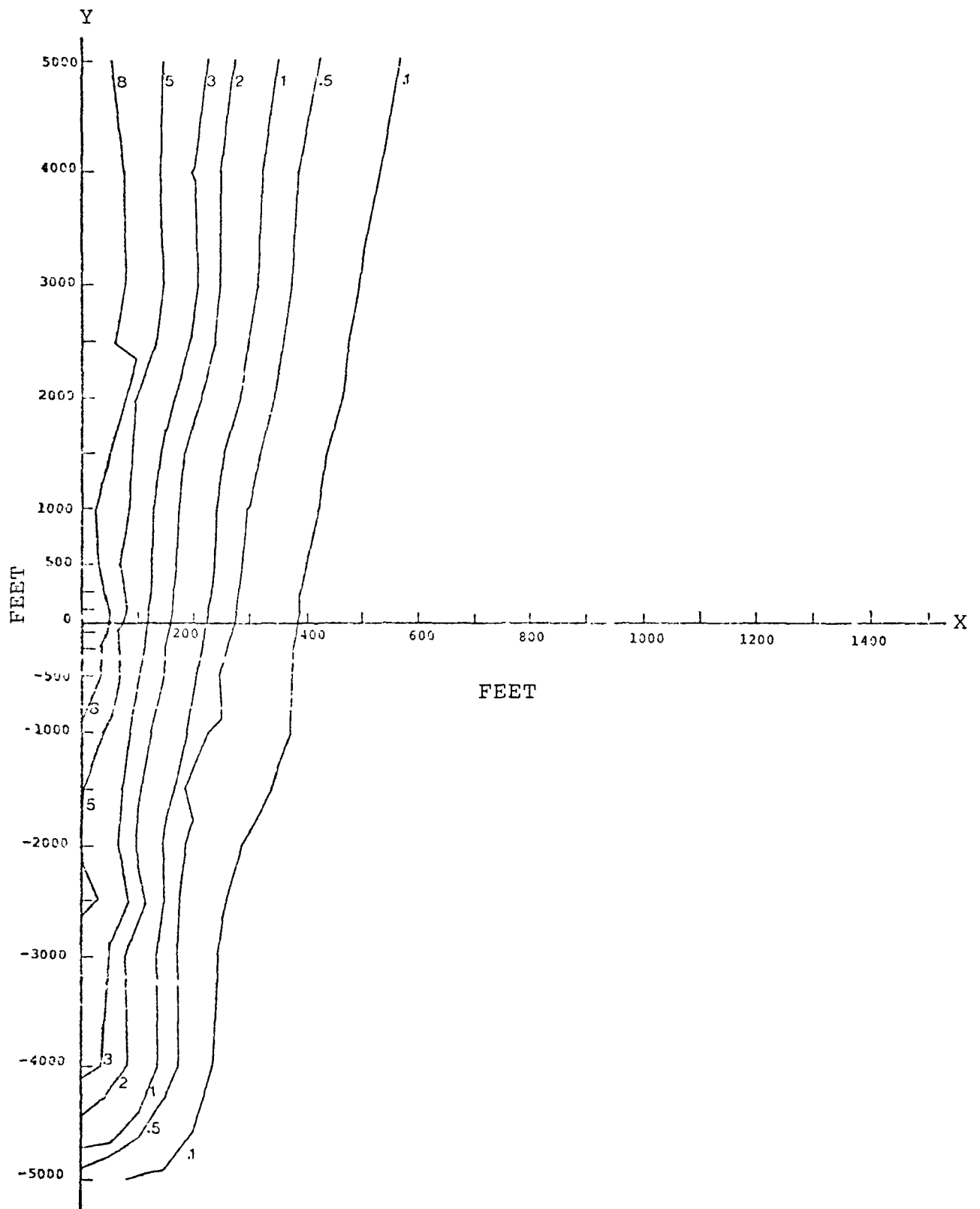


Figure 5-7a. Percent dilution isopleths, Hackberry Bay, La.  
H1: Base case.

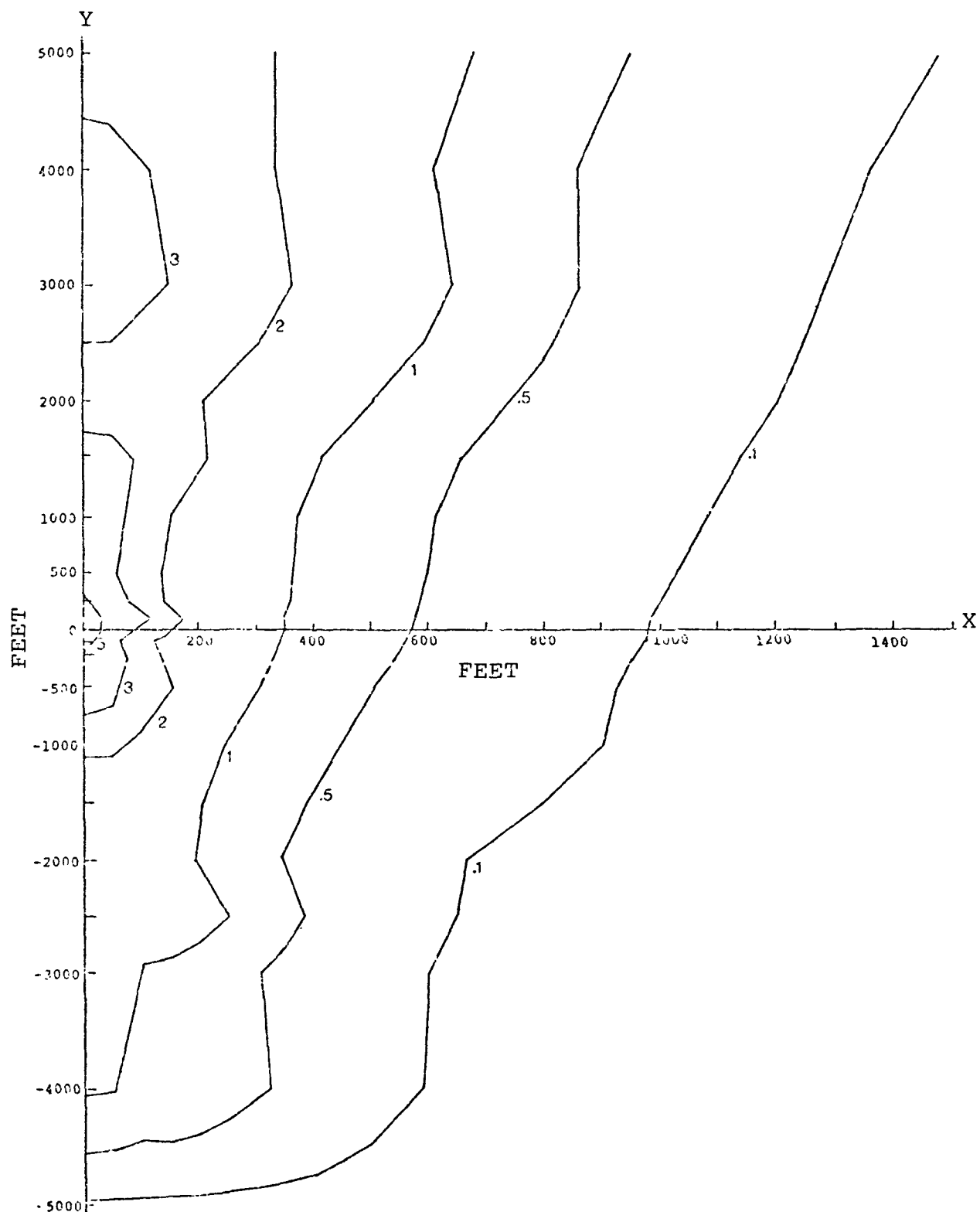


Figure 5-7b. Percent dilution isopleths, Hackberry Bay, La.  
H2: Diffusion coefficient sensitivity,  $E_x = E_y = 1.0$



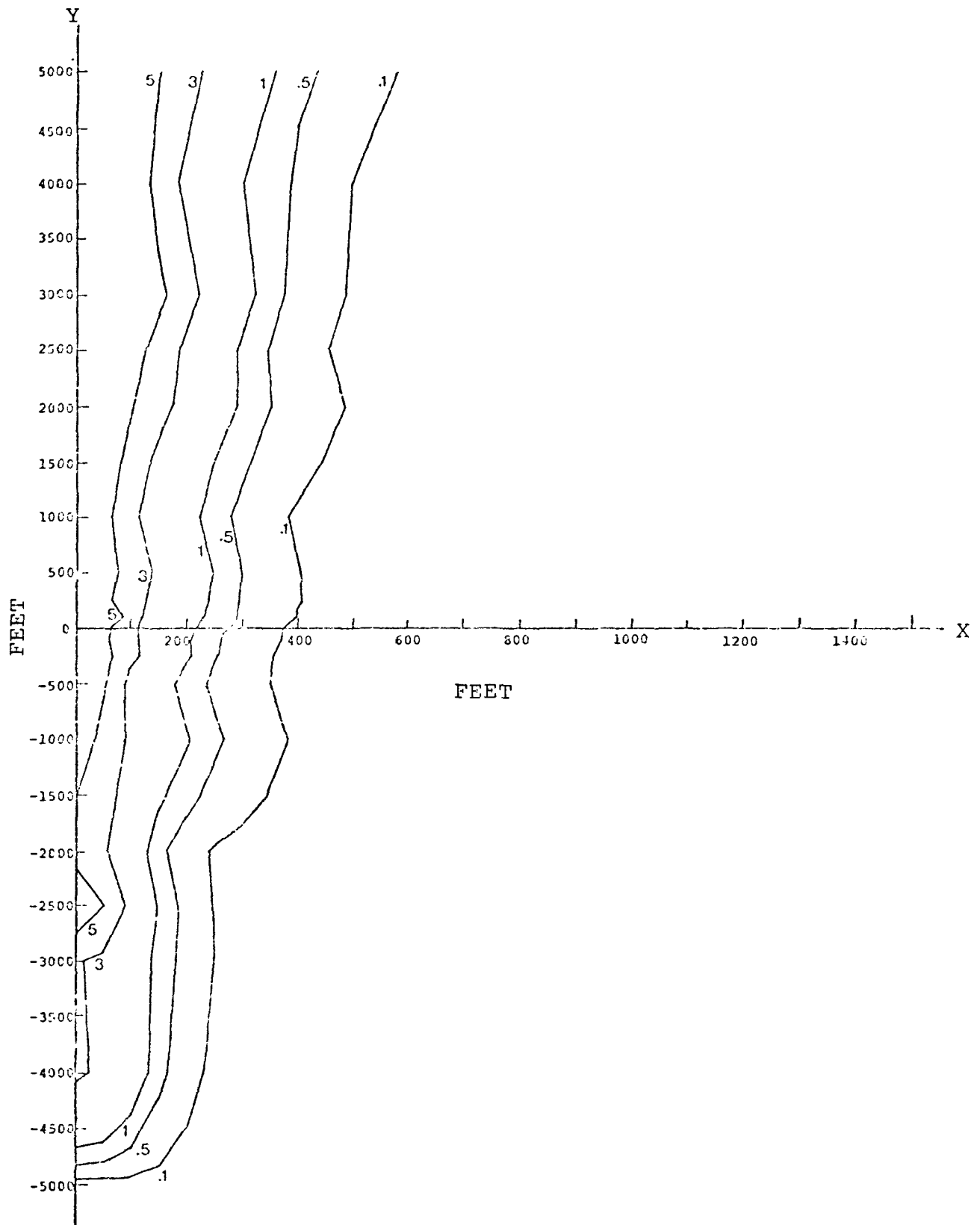


Figure 5-7c. Percent diffusion isopleths, Hackberry Bay, La.  
H3: Diffusion coefficient sensitivity,  $E_x = E_y = 1.0$

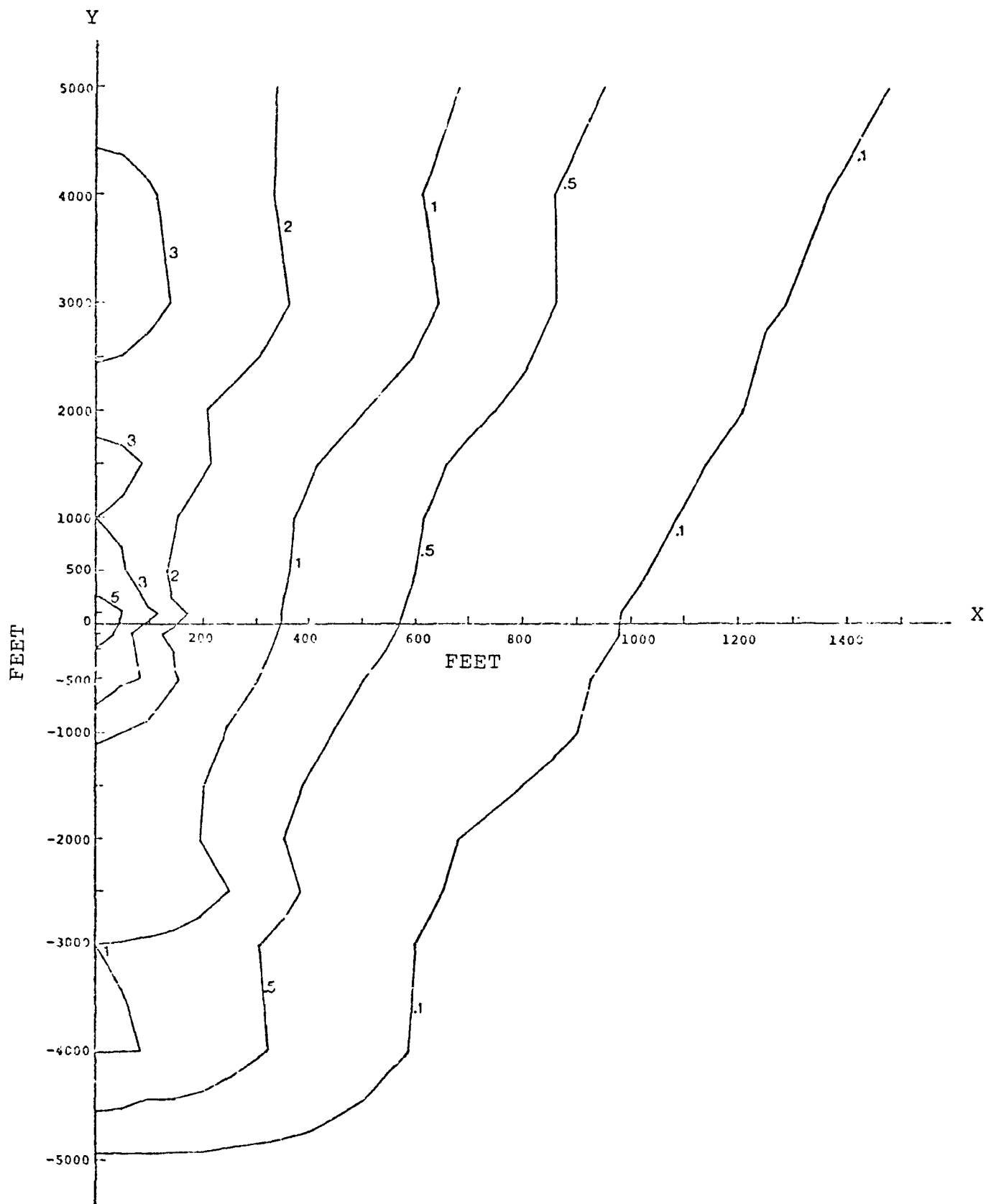


Figure 5-7d. Percent dilution isopleths, Hackberry Bay, La.  
H4: Initial dilution sensitivity,  $D=5, (E_x=1.0)$

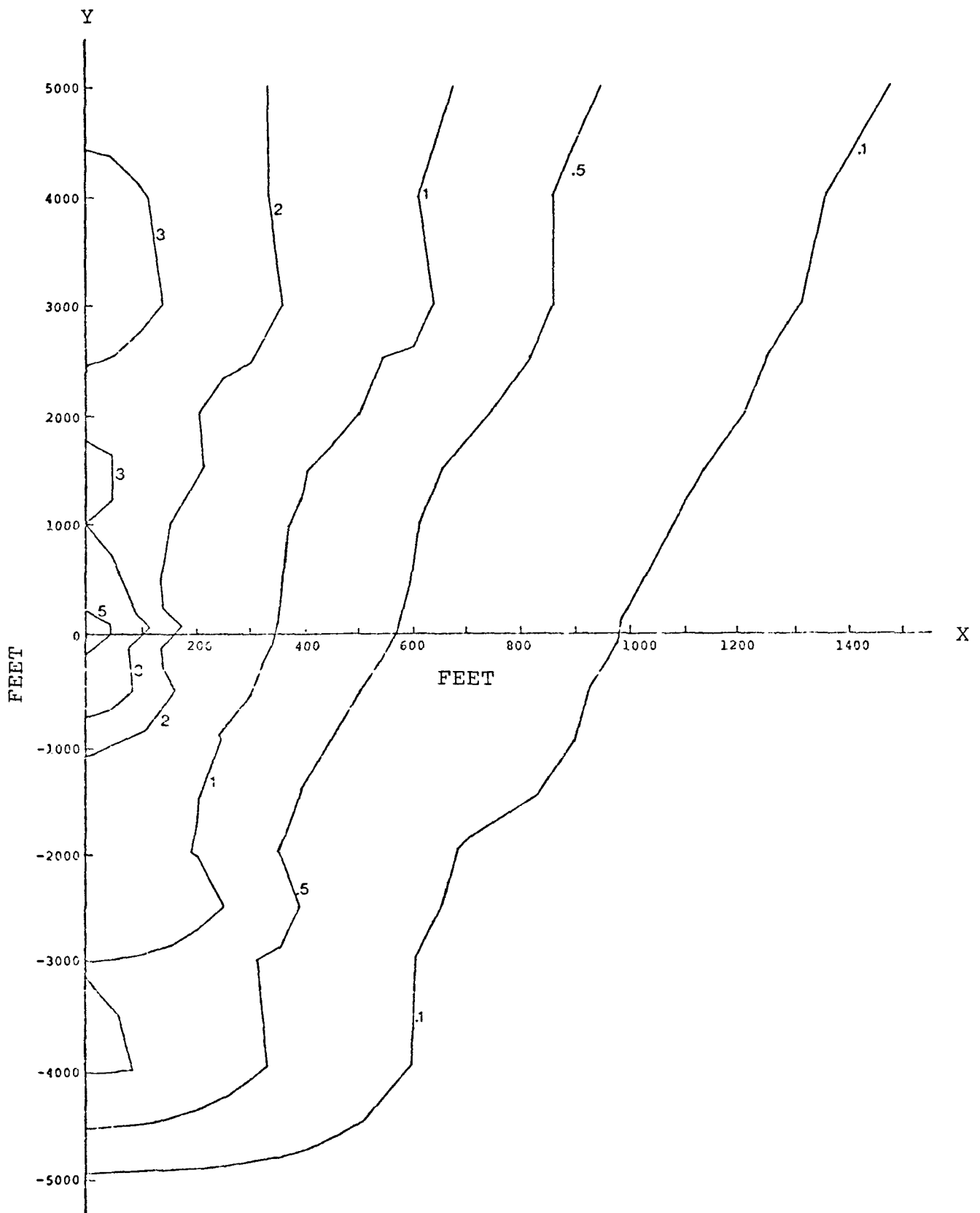


Figure 5-7e. Percent dilution isopleths, Hackberry Bay, La.  
H5: Initial dilution sensitivity,  $D=10$ , ( $E_x=1.0$ )

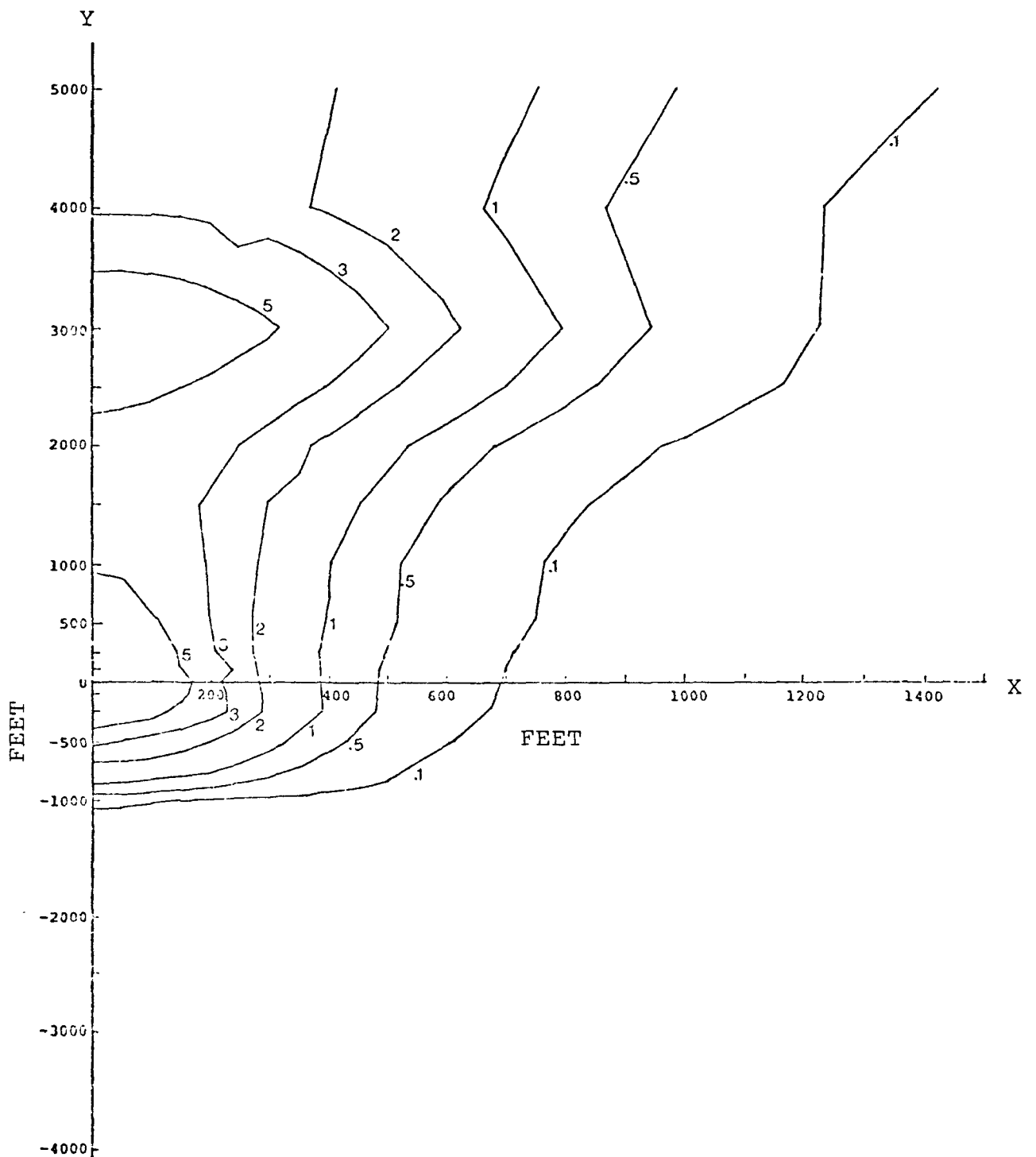


Figure 5-7f. Percent dilution isopleths, Hackberry Bay, La.  
H6: Tidal velocity sensitivity,  $V_1=0.065$ , ( $E_x=1.0$ )

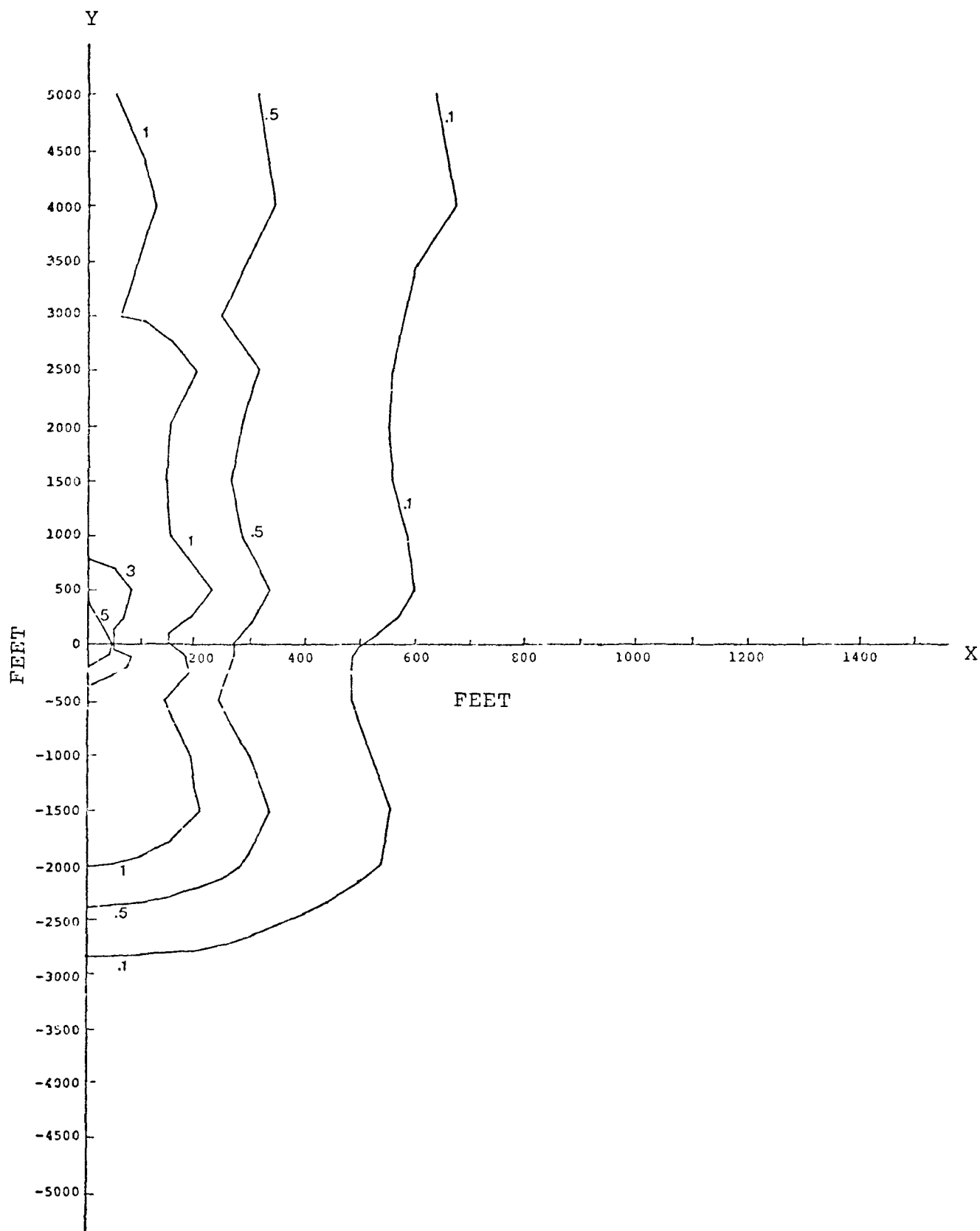


Figure 5-7g. Percent dilution isopleths Hackberry Bay, La.  
H7: Freshwater current velocity sensitivity,  $V_o=0.1$  ( $E_x=1.0$ )

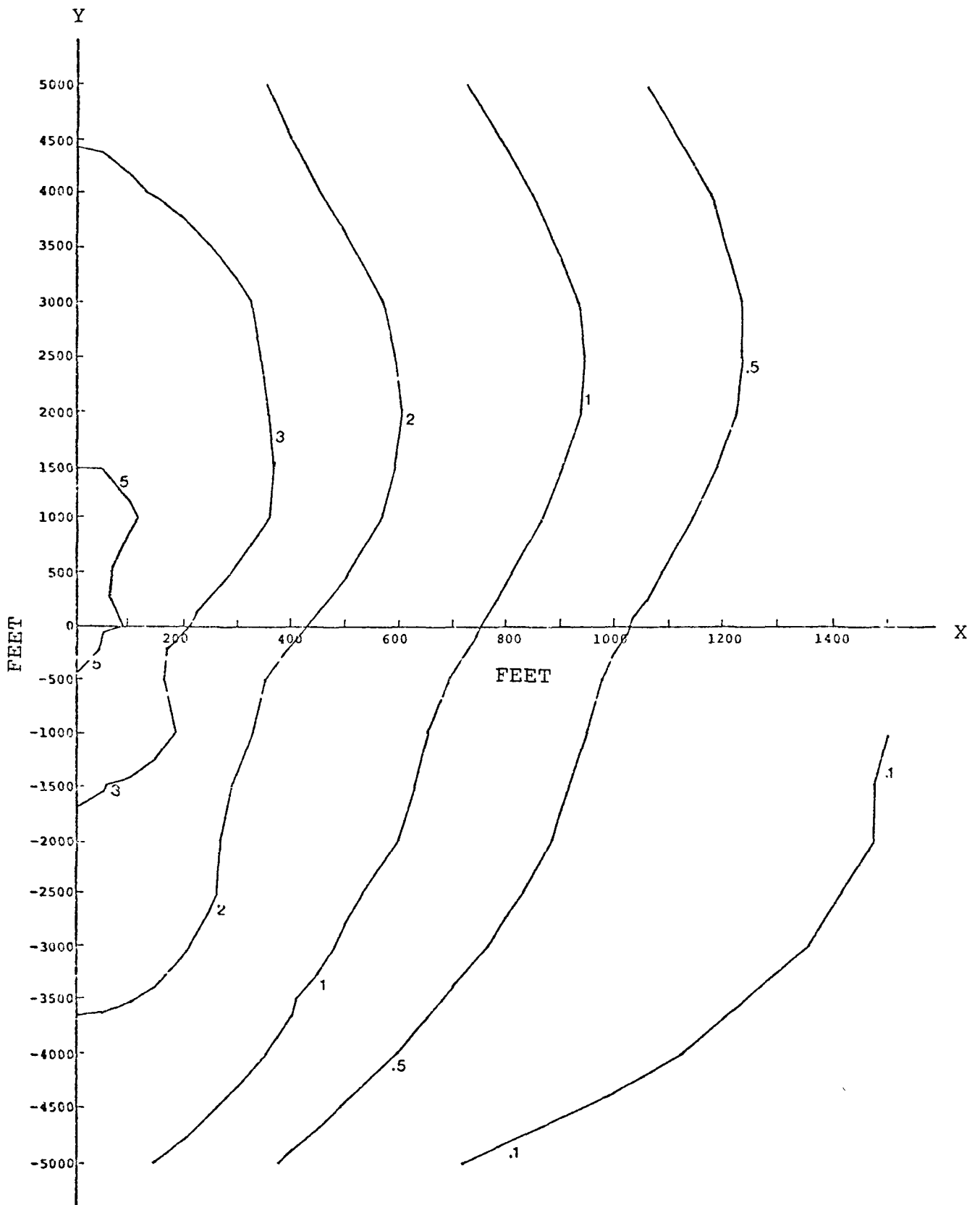


Figure 5-7h. Percent dilution isopleths, Hackberry Bay, La.  
H8: Freshwater current velocity sensitivity,  $V_o=0.01$  ( $E_x=1.0$ )

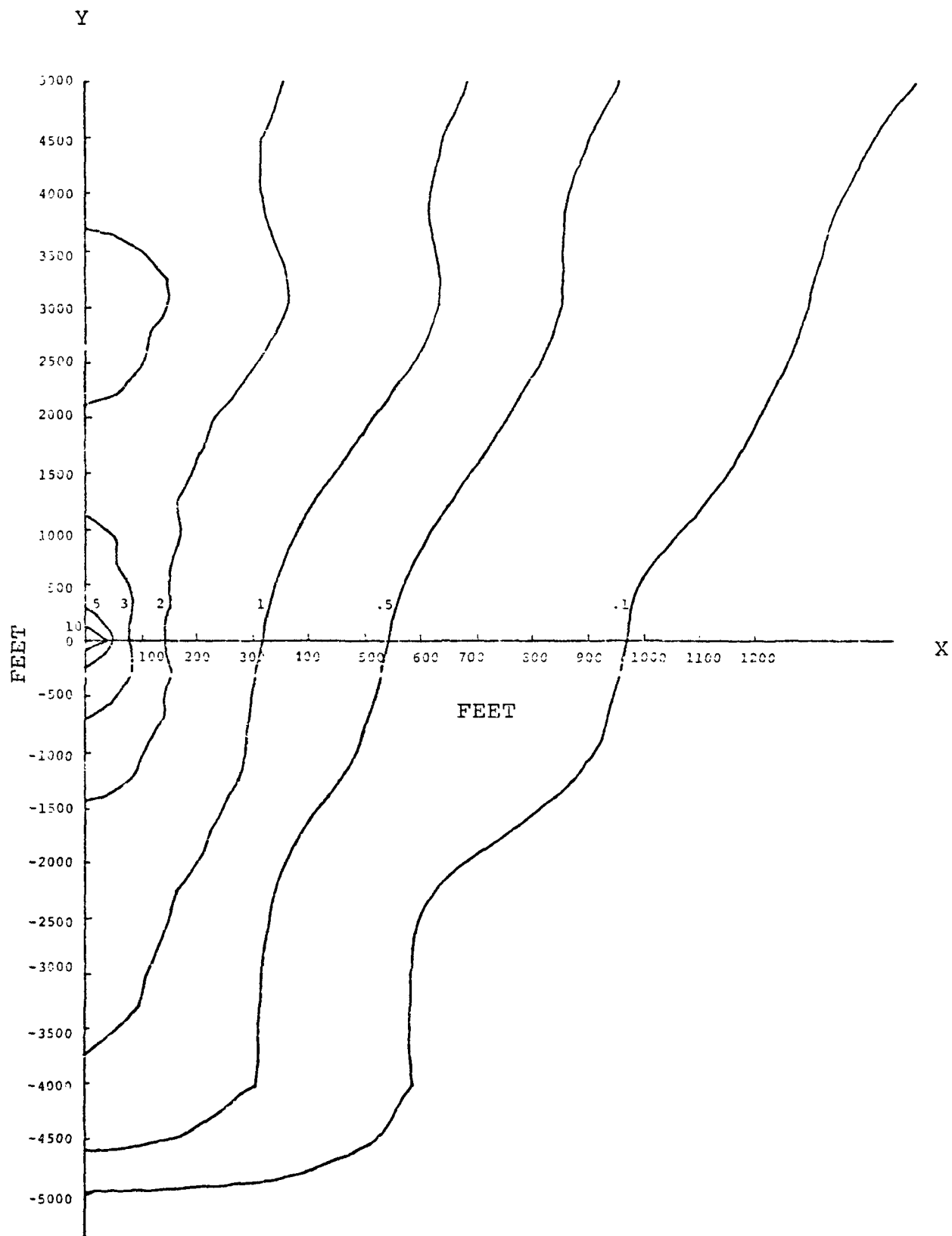


Figure 5-7i. Percent dilution isopleths, Hackberry Bay, La.  
H9: Rotational tidal current sensitivity,  $U_1=0.05$  ( $E_x=1.0$ )

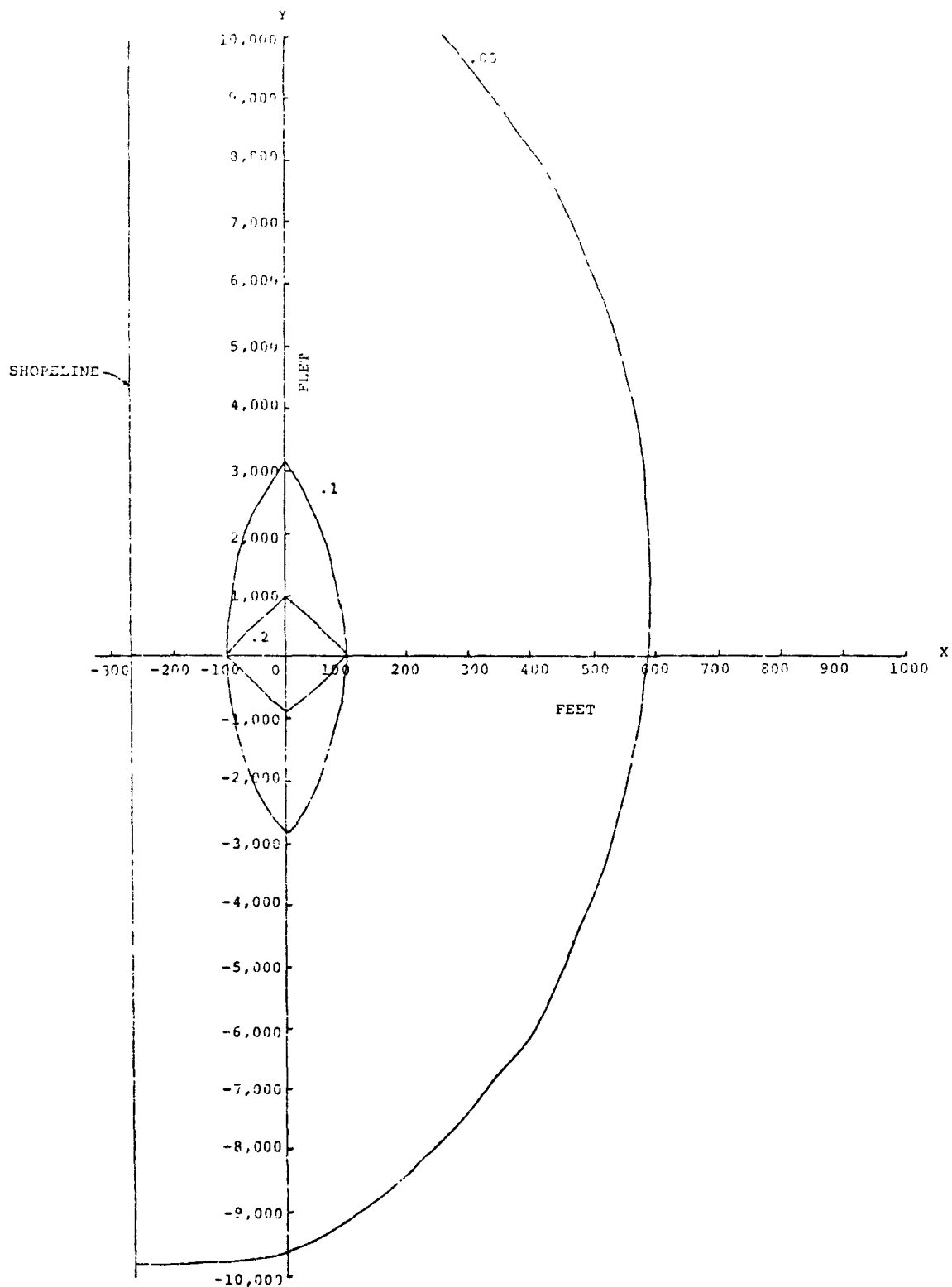


Figure 5-8a. Percent dilution isopleths, Trading Bay Facility, Cook Inlet, Alaska.  
 C1: Base Case,  $E_y = 1250$ .



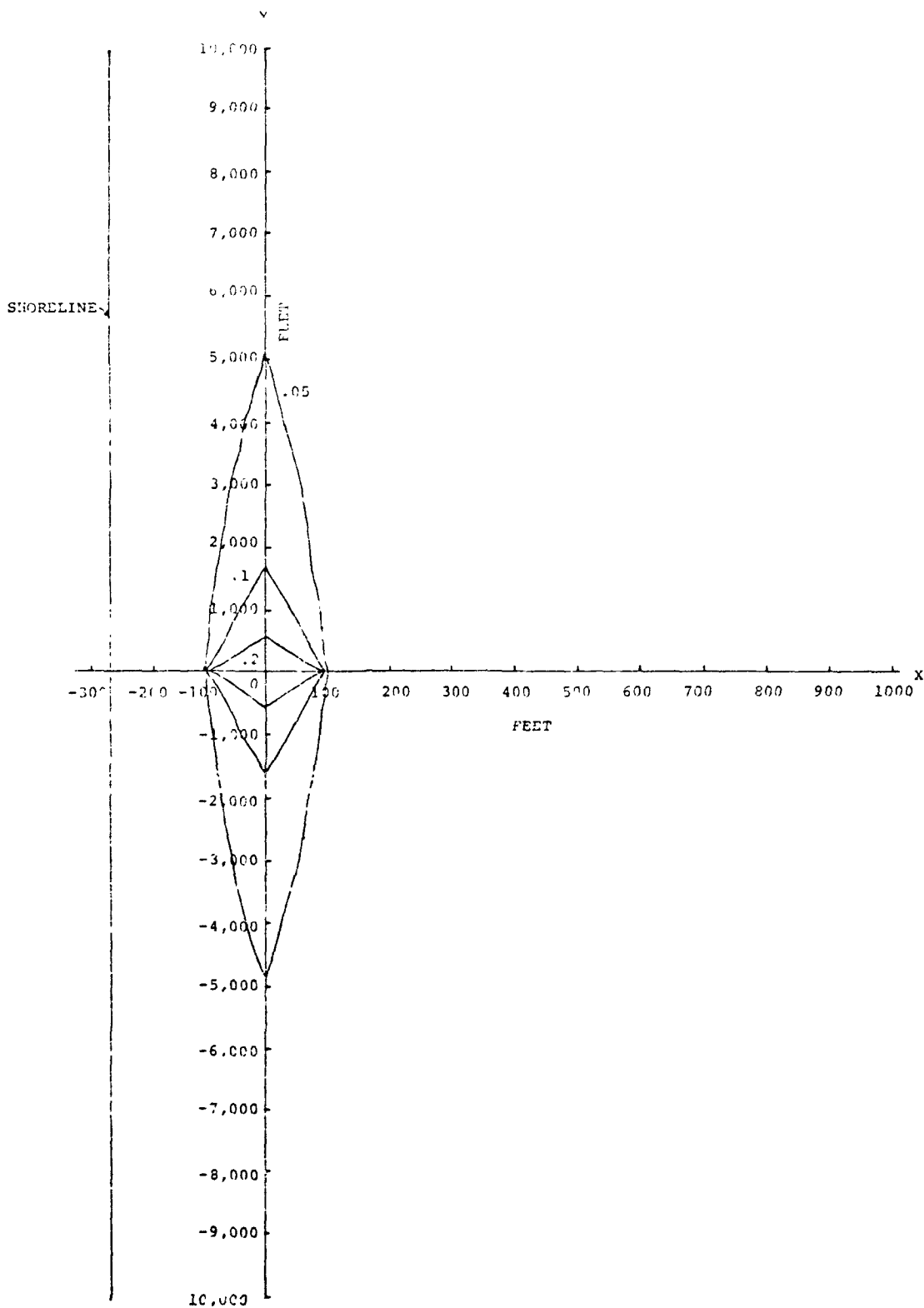


Figure 5-8b. Percent dilution isopleths, Trading Bay Facility, Cook Inlet, Alaska.  
 C2: Diffusion coefficient sensitivity,  $E_y = 7500$ .

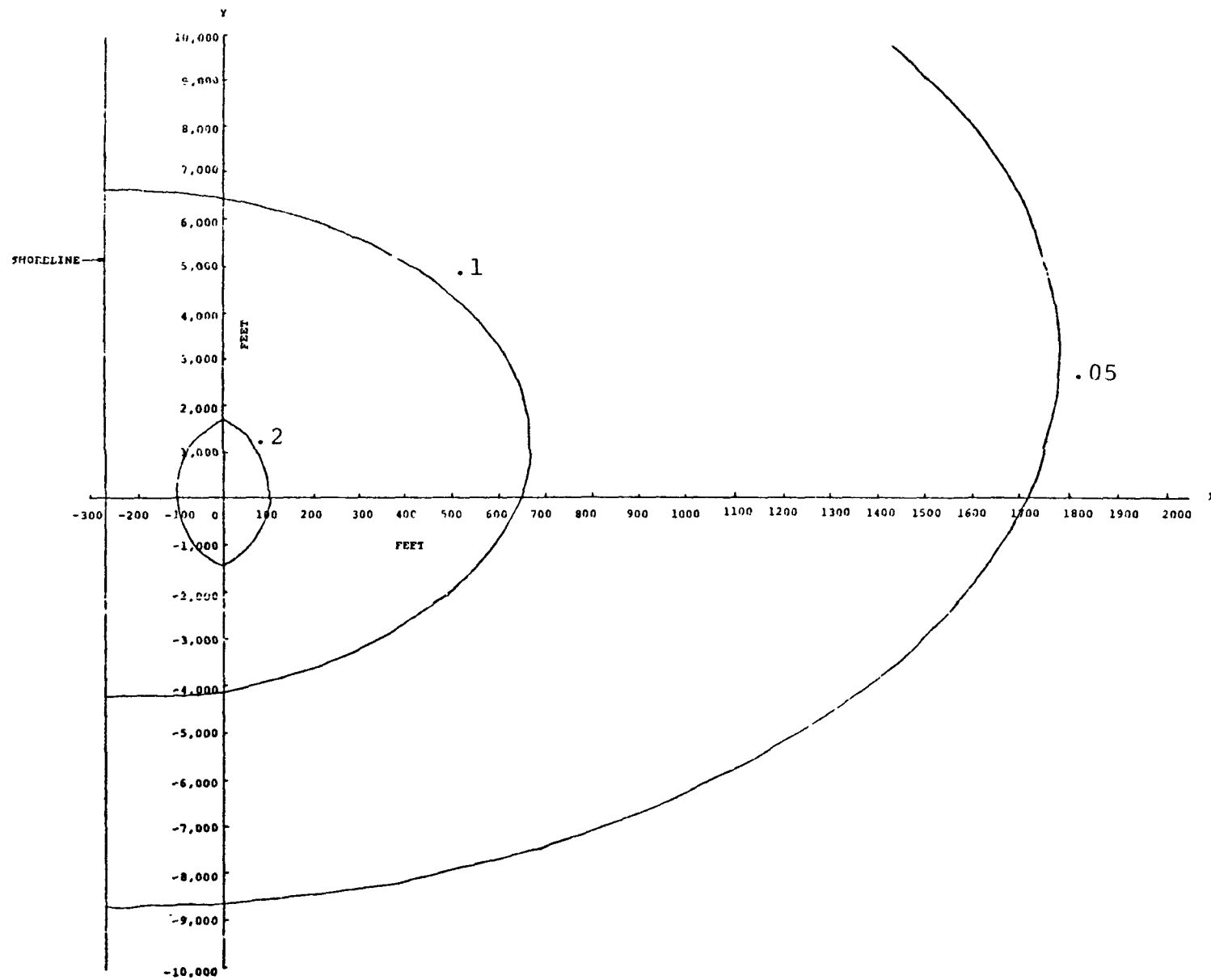


Figure 5-8c. Percent dilution isopleths, Trading Bay Facility, Alaska.  
 C3: Diffusion coefficient sensitivity,  $E_y = 250$ .

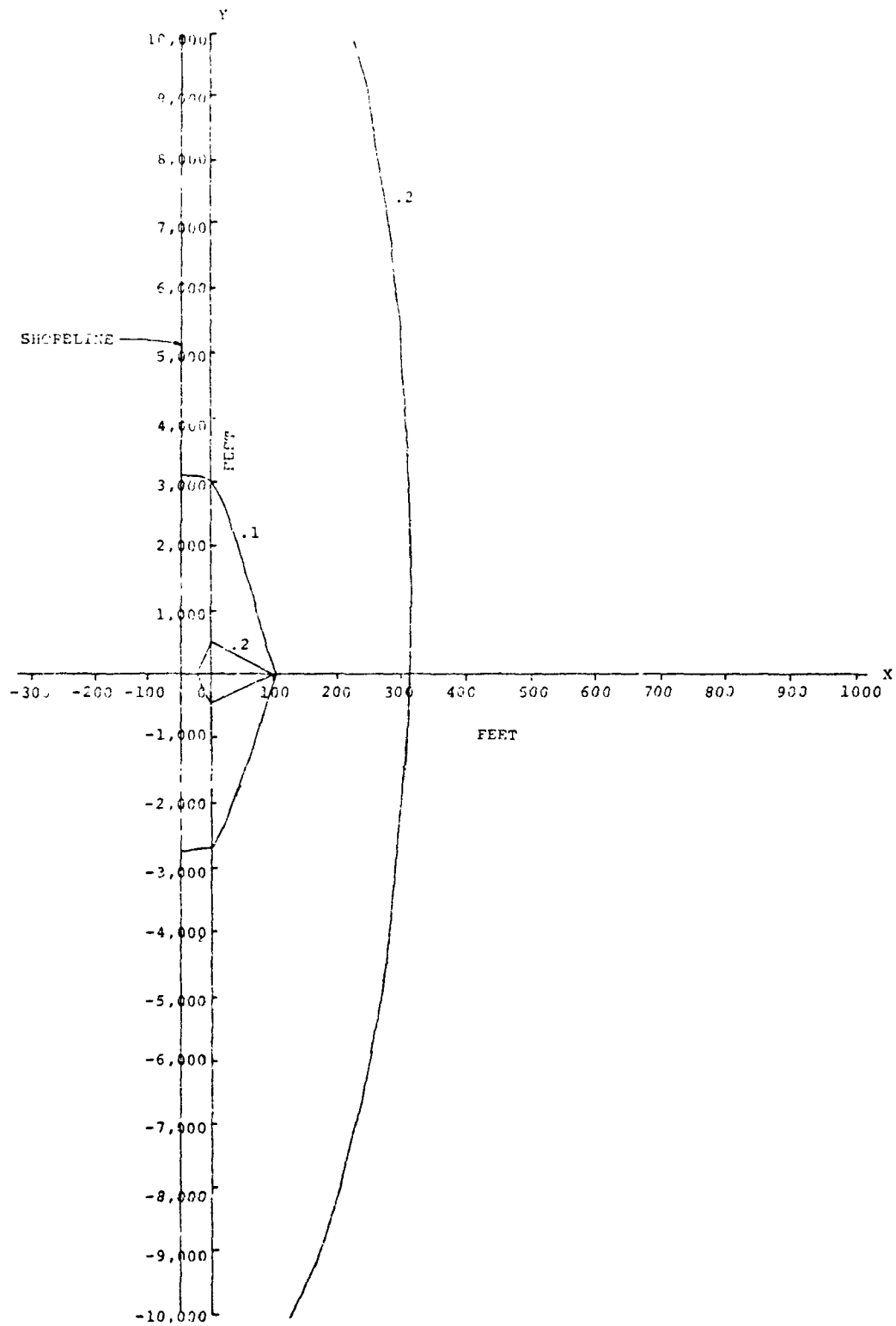


Figure 5-8d. Percent dilution isopleths, Granite Point Facility, Cook Inlet, Alaska.  
 C4: Base Case,  $E_y = 1250$ .

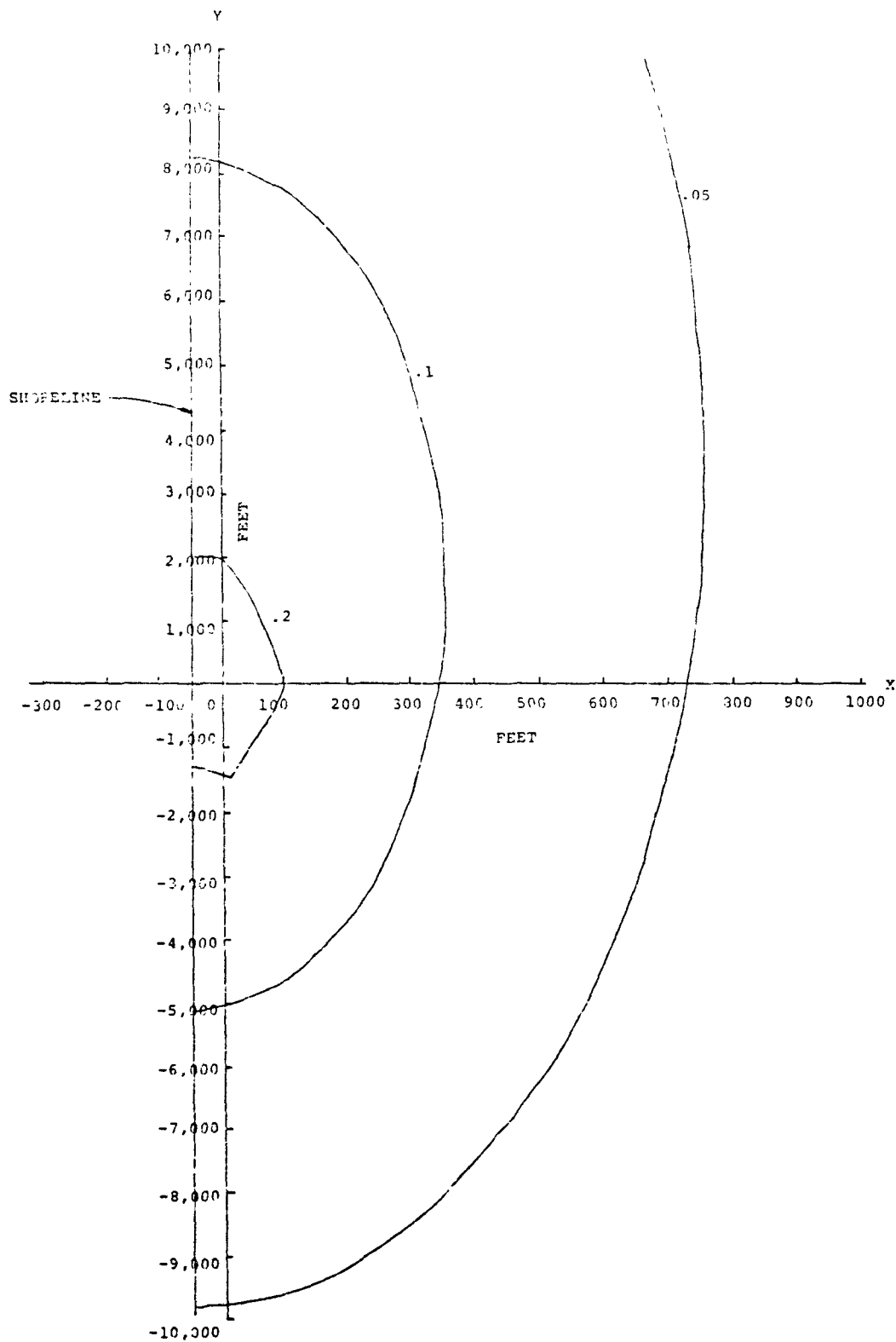


Figure 5-8e. Percent dilution isopleths, Granite Point Facility, Cook Inlet, Alaska.  
 C5: Diffusion coefficient sensitivity,  $E_y = 250$ .

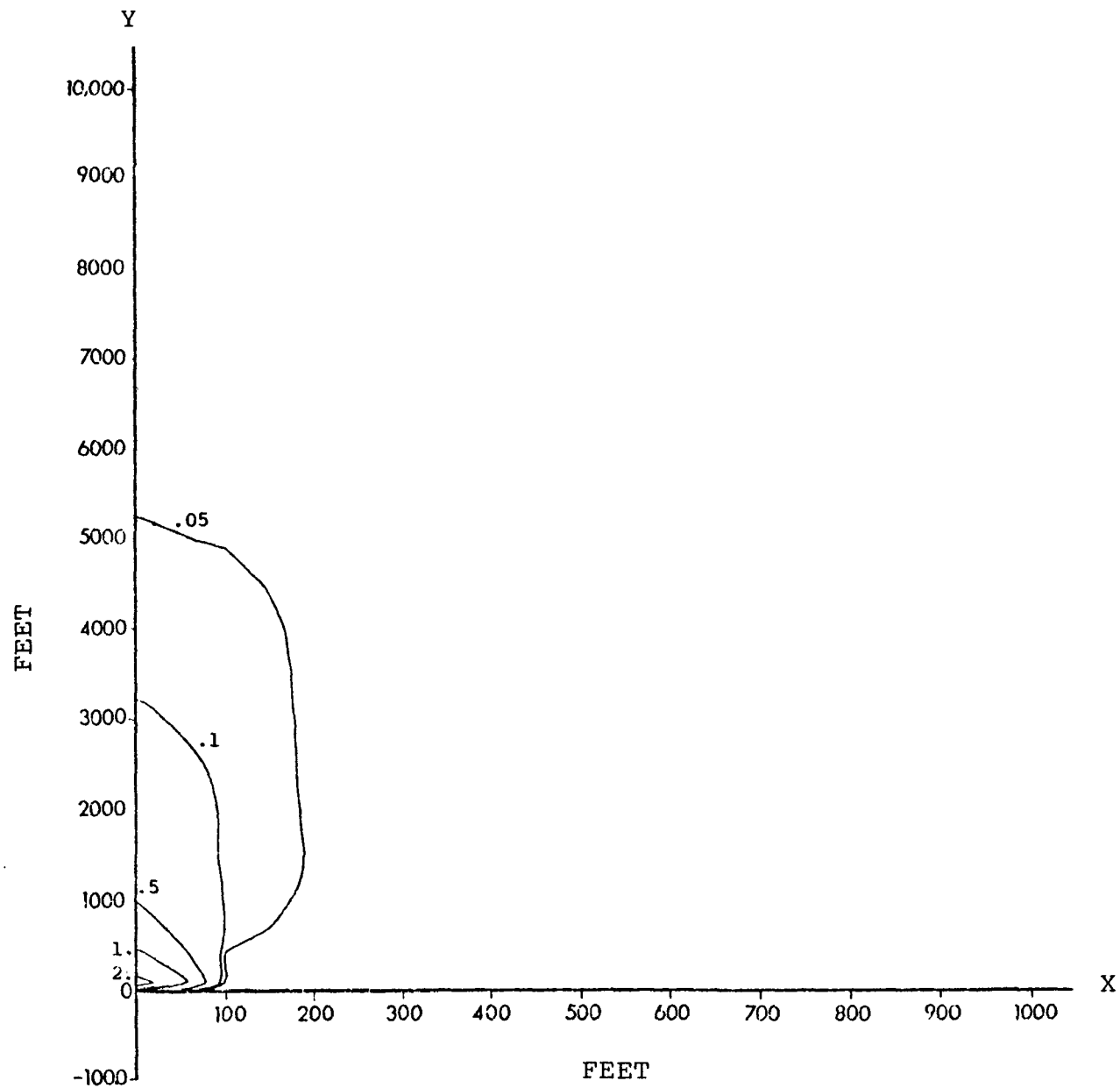


Figure 5-9a. Near offshore dilution percentage isopleths.  
N1A: Base case, XSHORE=3 miles.

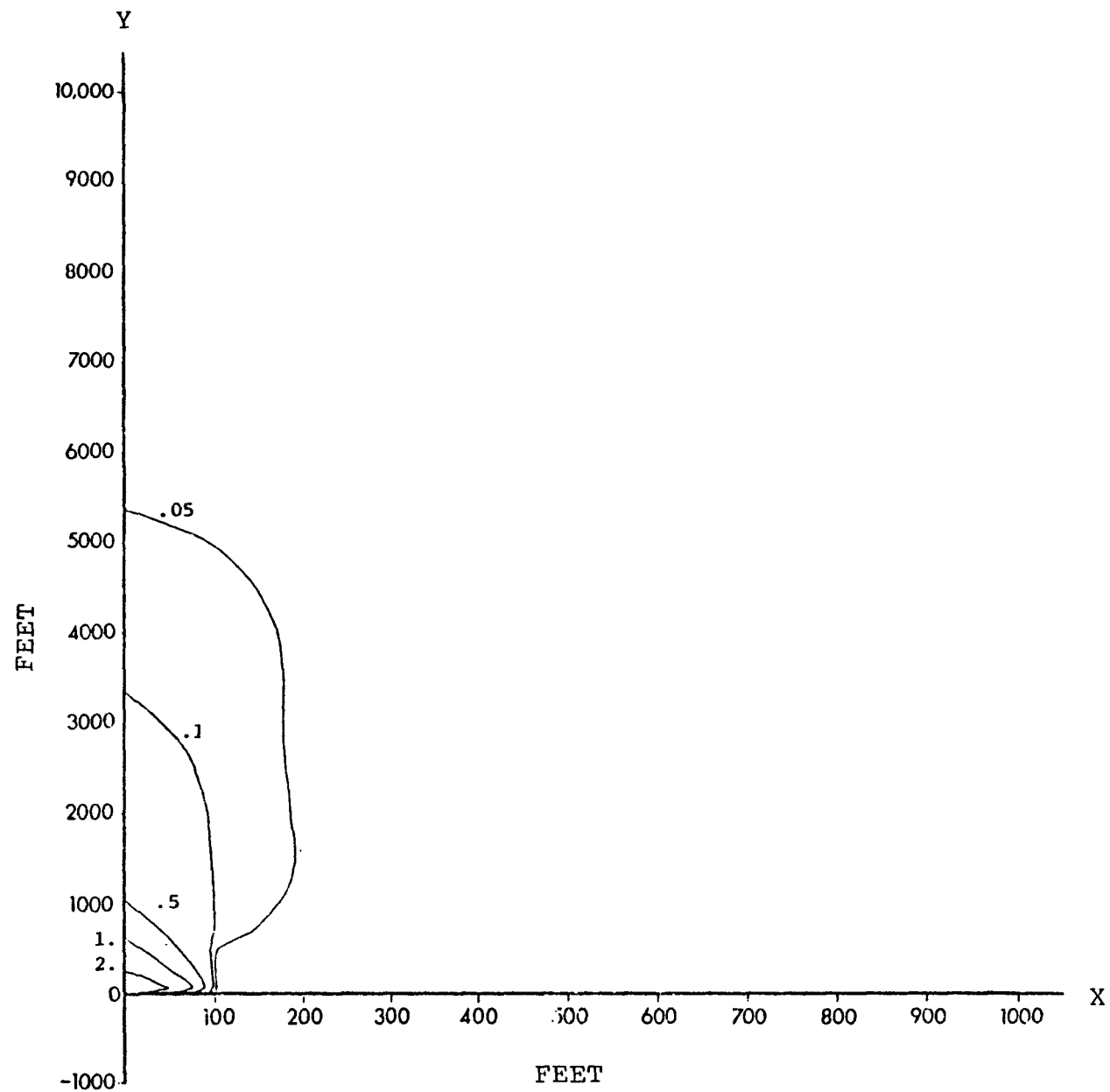


Figure 5-9b. Near offshore dilution percentage isopleths.  
N1B: Dilution sensitivity, D=10 (XSHORE=3 miles)

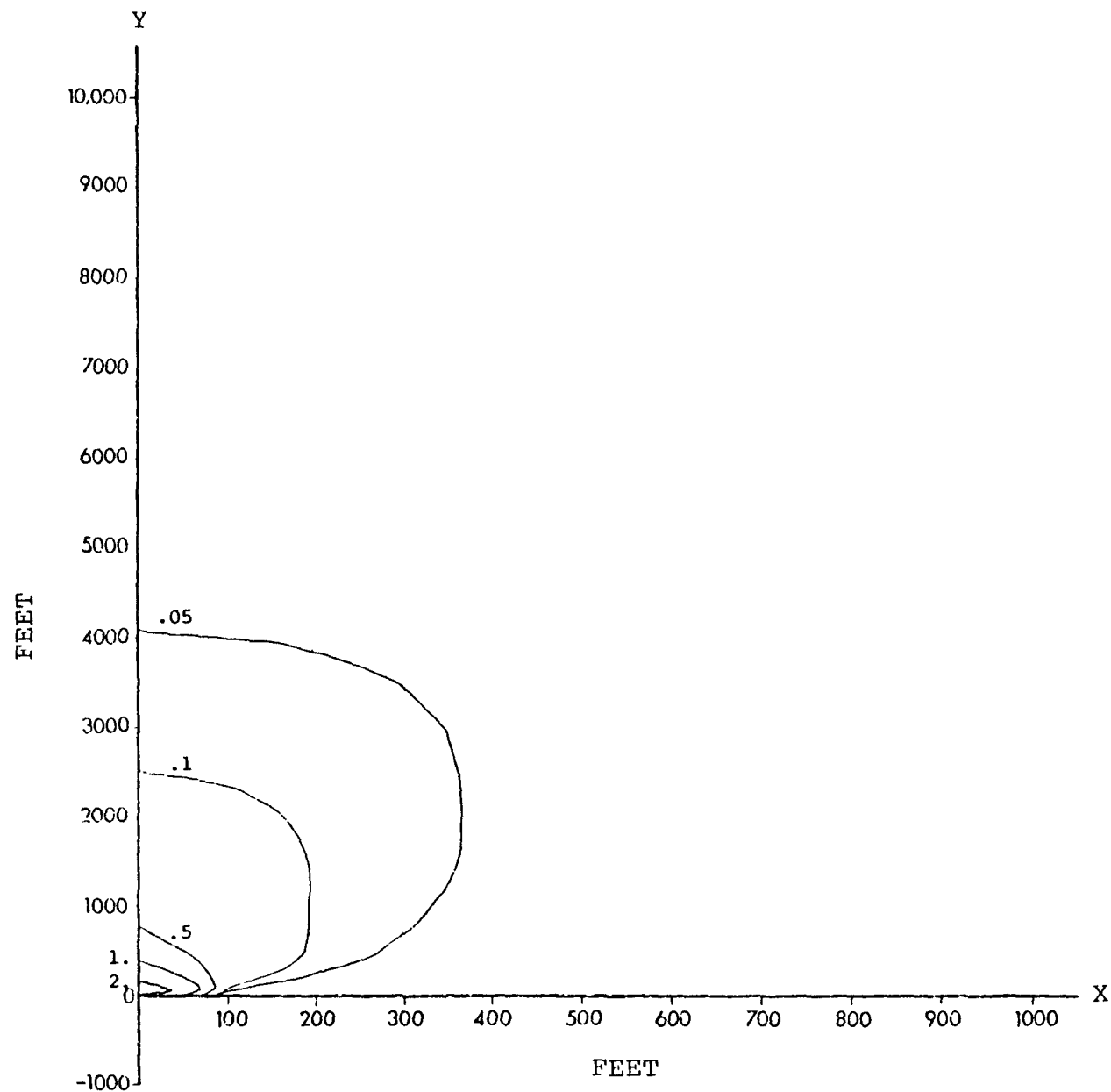


Figure 5-9c. Near offshore dilution percentage isopleths.  
NLC: Current velocity sensitivity,  $V_0=.18$ ,  $V_1=.12$  (XSHORE=3 miles)

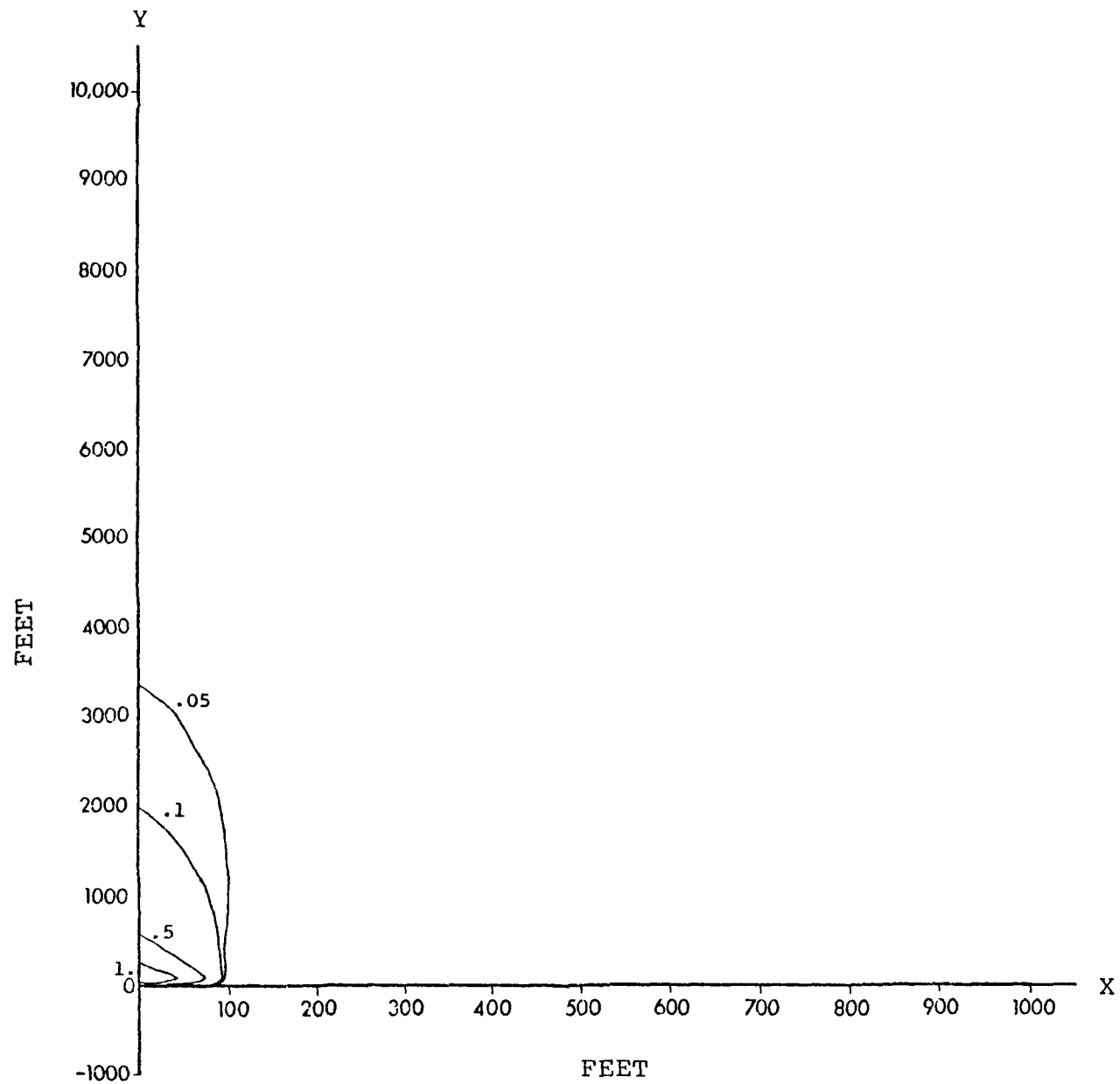


Figure 5-9d. Near offshore dilution percentage isolpleths.  
N1D: Discharge rate sensitivity,  $Q_0 = .05$  (XSHORE=3 miles)



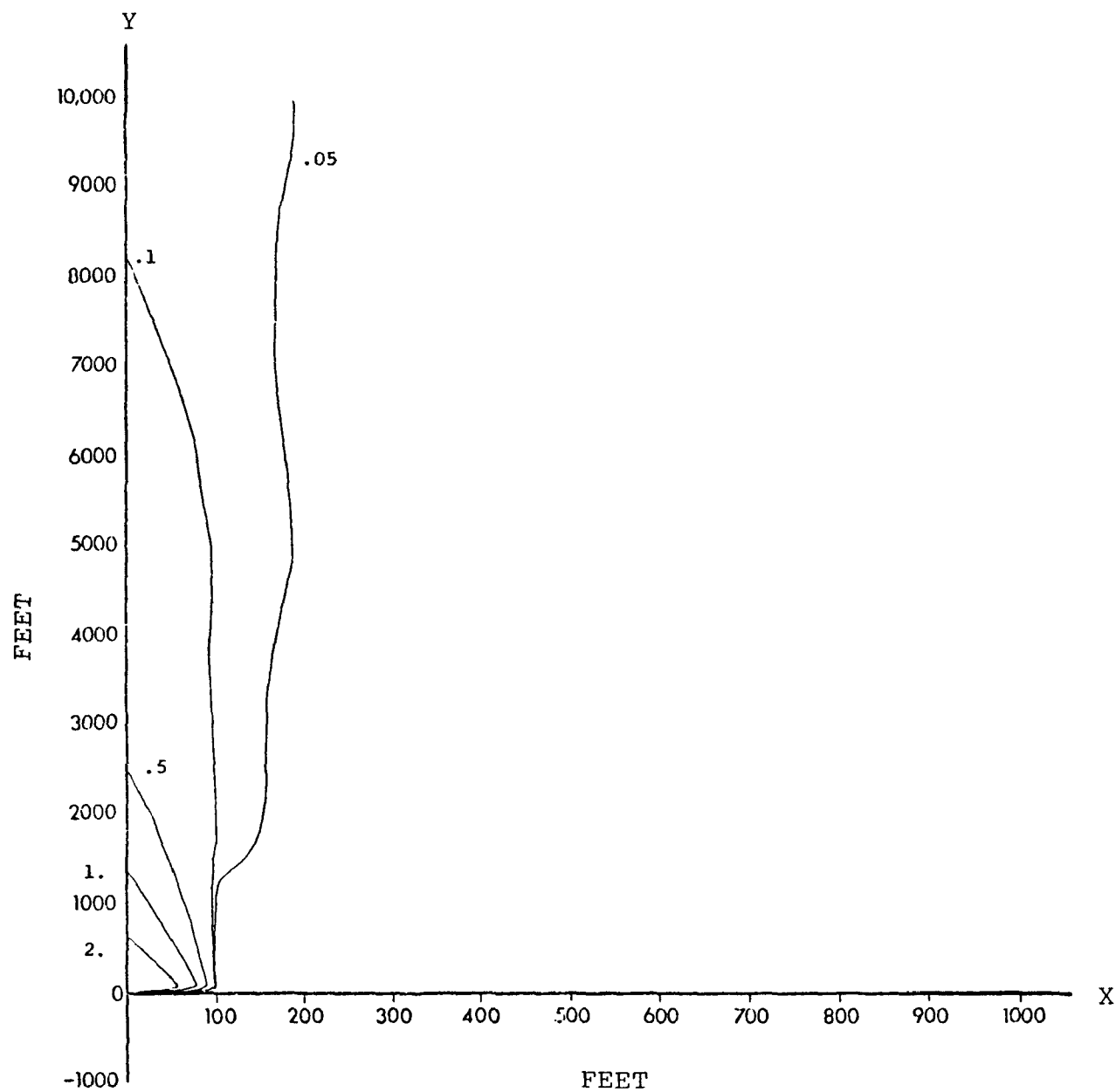


Figure 5-9e. Near offshore dilution percentage isopleths.  
N1E: Diffusion coefficient sensitivity,  $A_x = A_y = 0.002$  (XSHORE=3 miles)

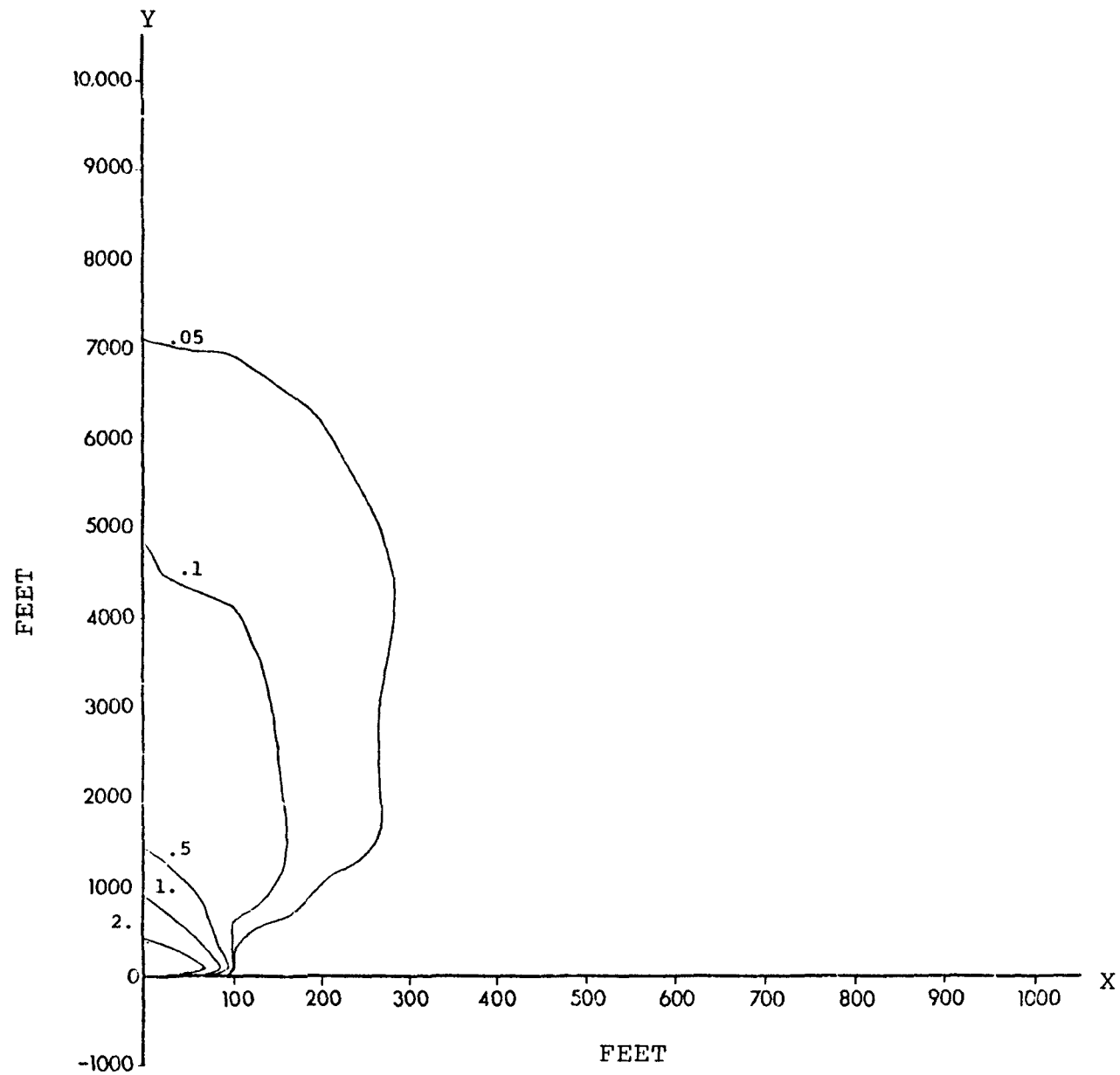


Figure 5-9f. Near offshore dilution percentage isopleths.  
N2A: Base case, XSHORE= $\frac{1}{2}$  mile.

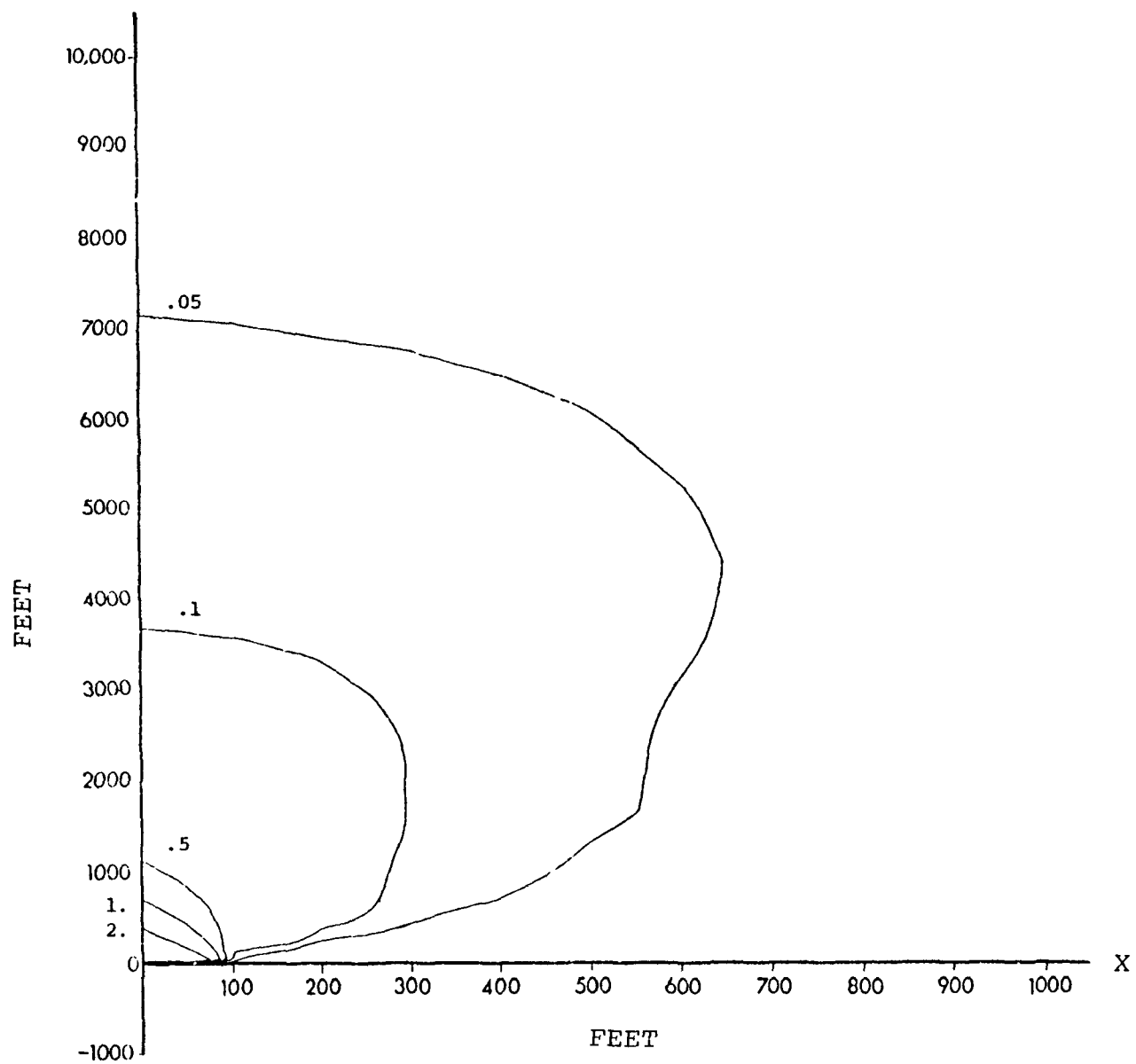


Figure 5-9g. Near offshore dilution percentage isopleths.  
N2B: Current velocity sensitivity,  $V_o = .18$ ,  $V_1 = .12$  (XSHORE =  $\frac{1}{2}$  mile).

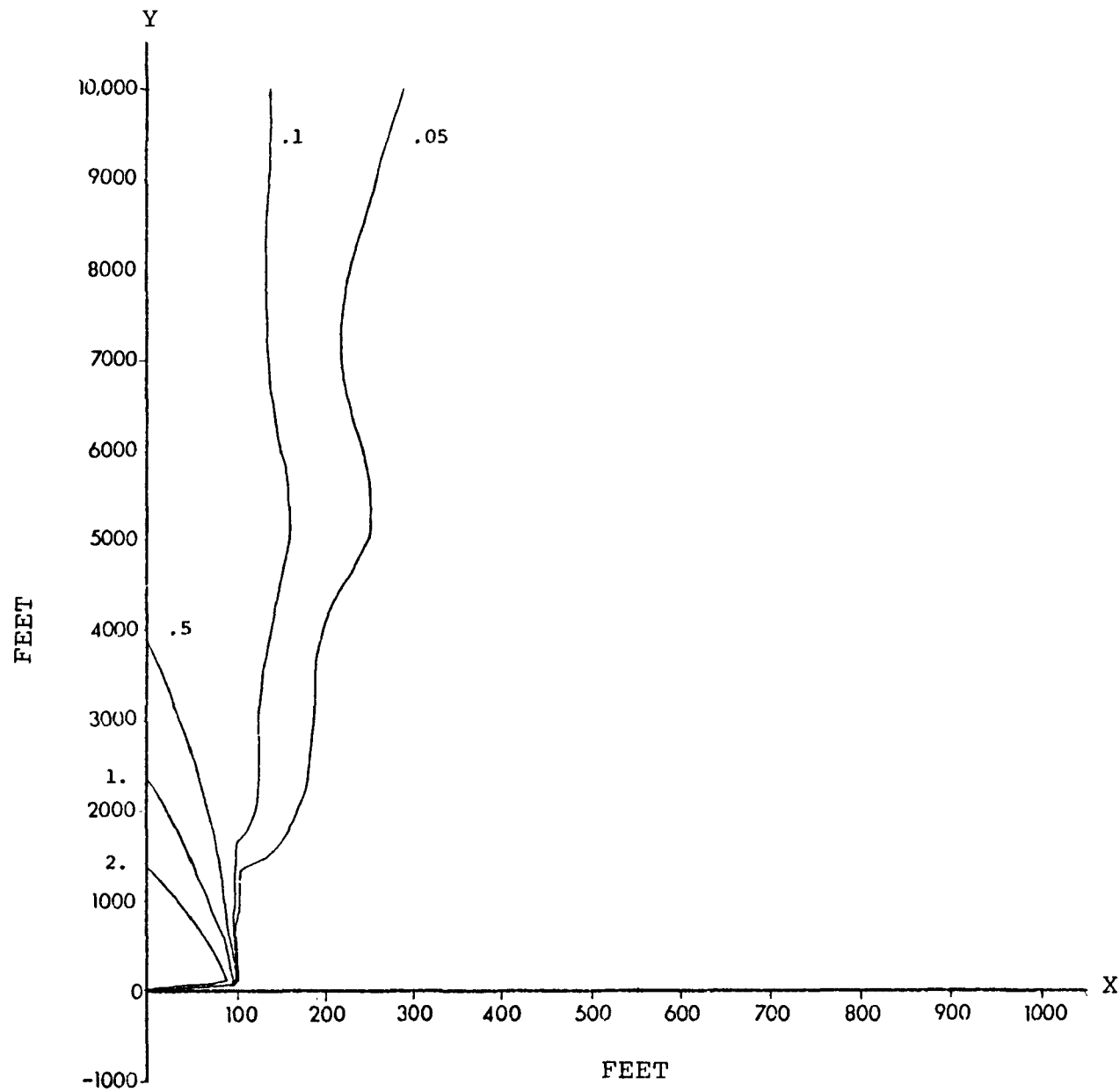


Figure 5-9h. Near offshore dilution percentage isopleths.  
N2C: Diffusion coefficient sensitivity,  $A_x = A_y = 0.002$  (XSHORE =  $\frac{1}{2}$  mile).

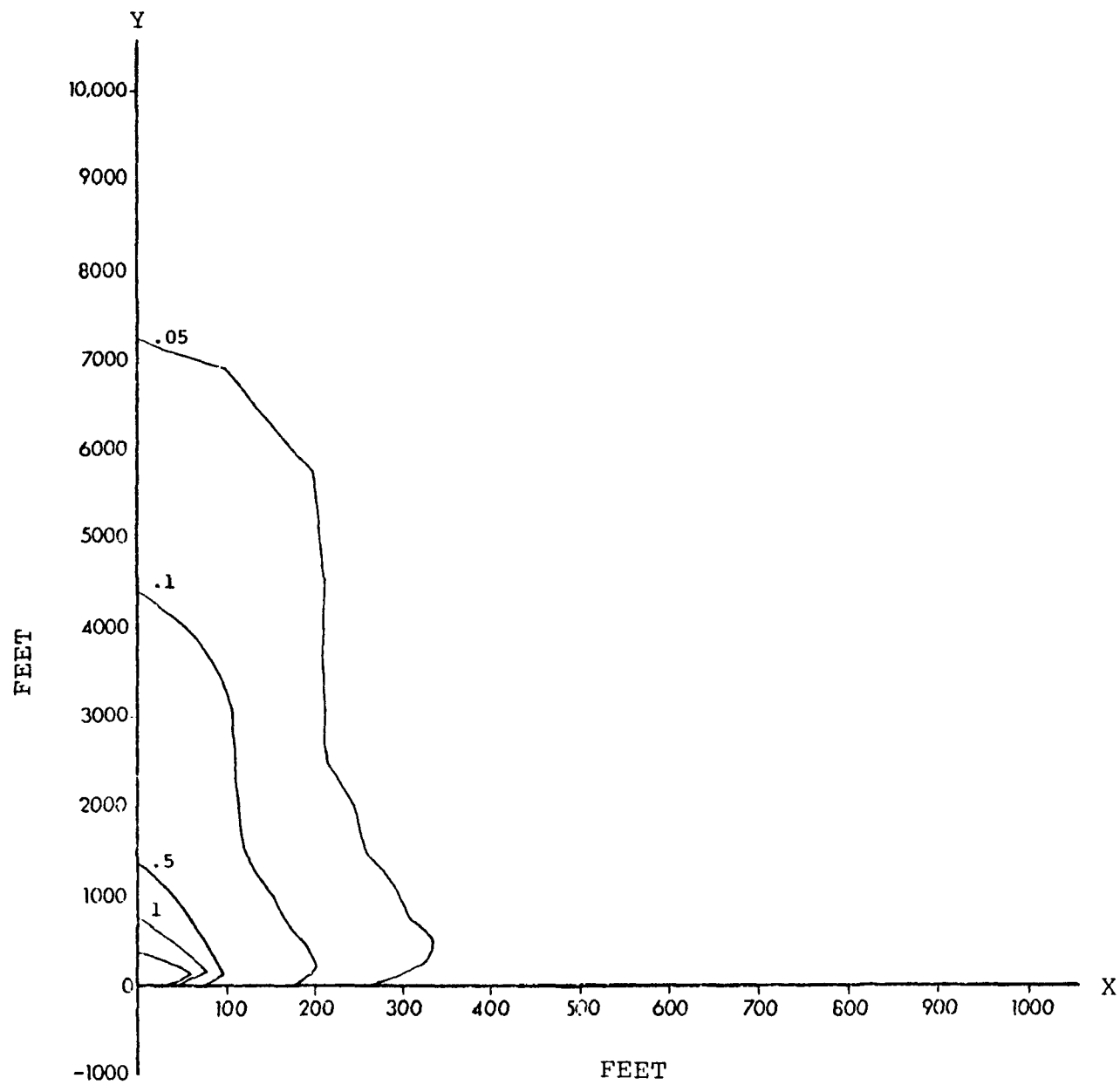


Figure 5-10a. Far offshore dilution percentage isopleths.  
F1: Base case.

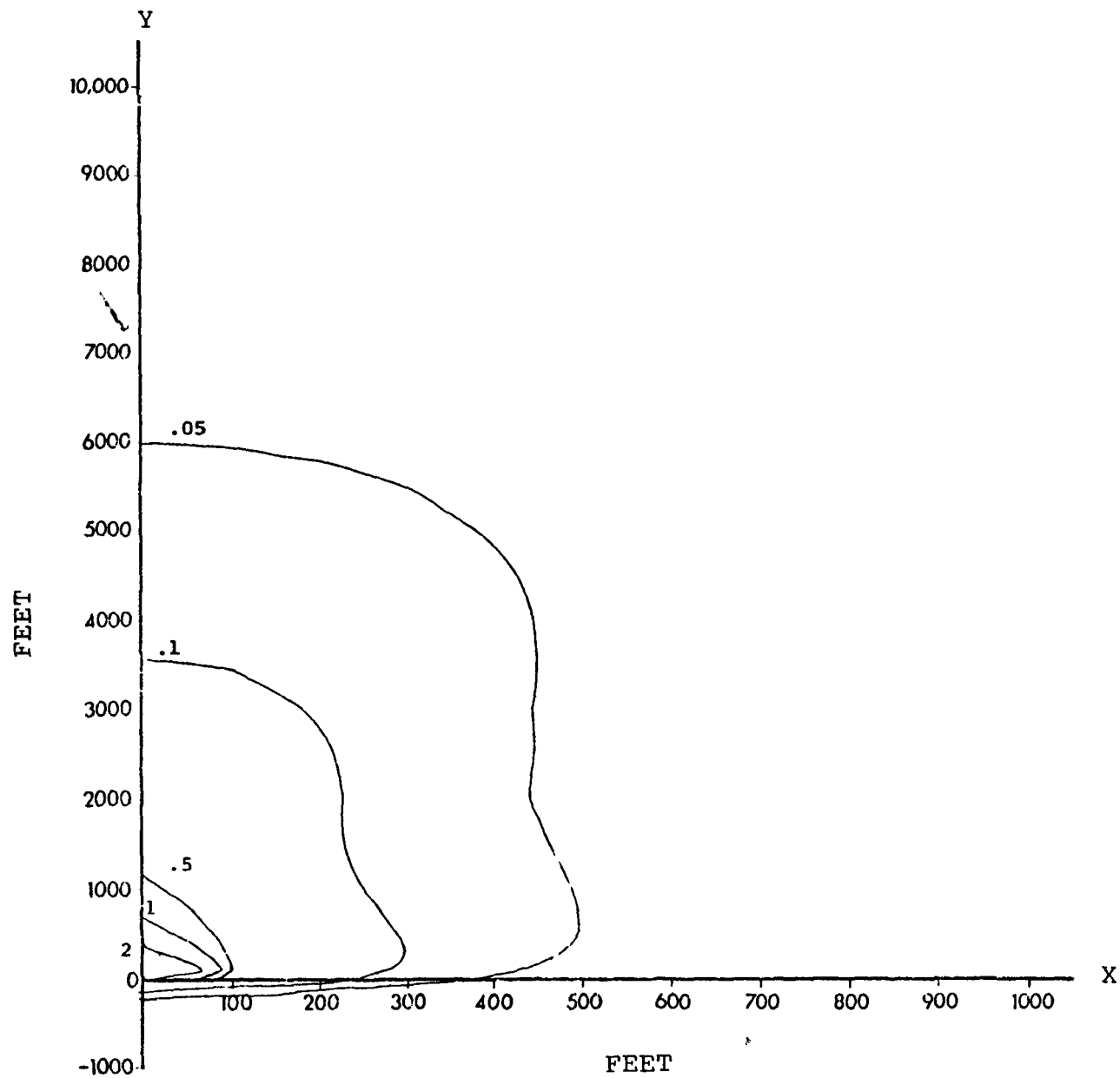


Figure 5-10b. Far offshore dilution percentage isopleths.  
F2: Current velocity sensitivity,  $V_o = V_1 = 0.18$ .

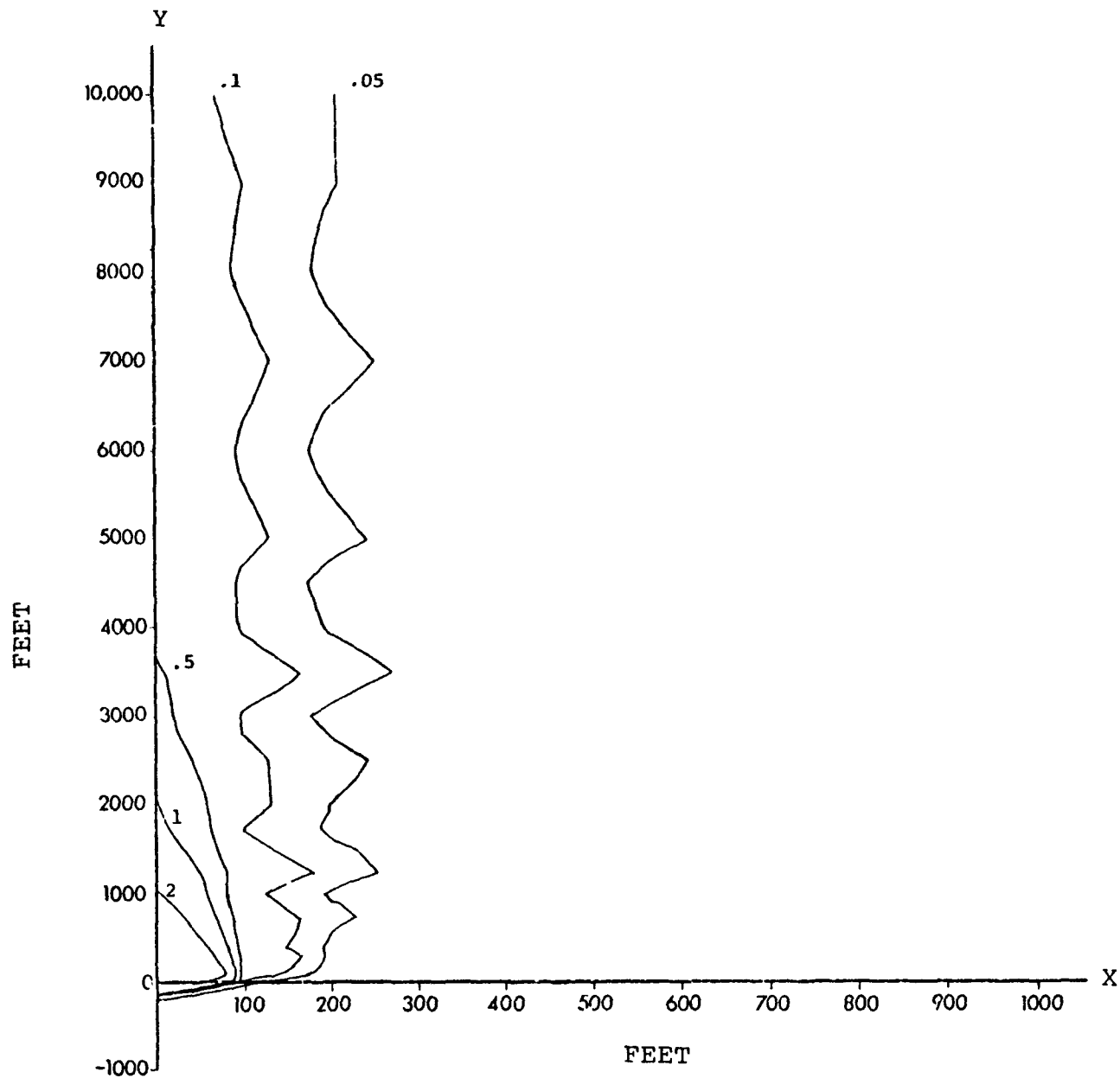


Figure 5-10c. Far offshore dilution percentage isopleths.  
F3: Diffusion coefficient sensitivity,  $A_x = A_y = 0.002$ .

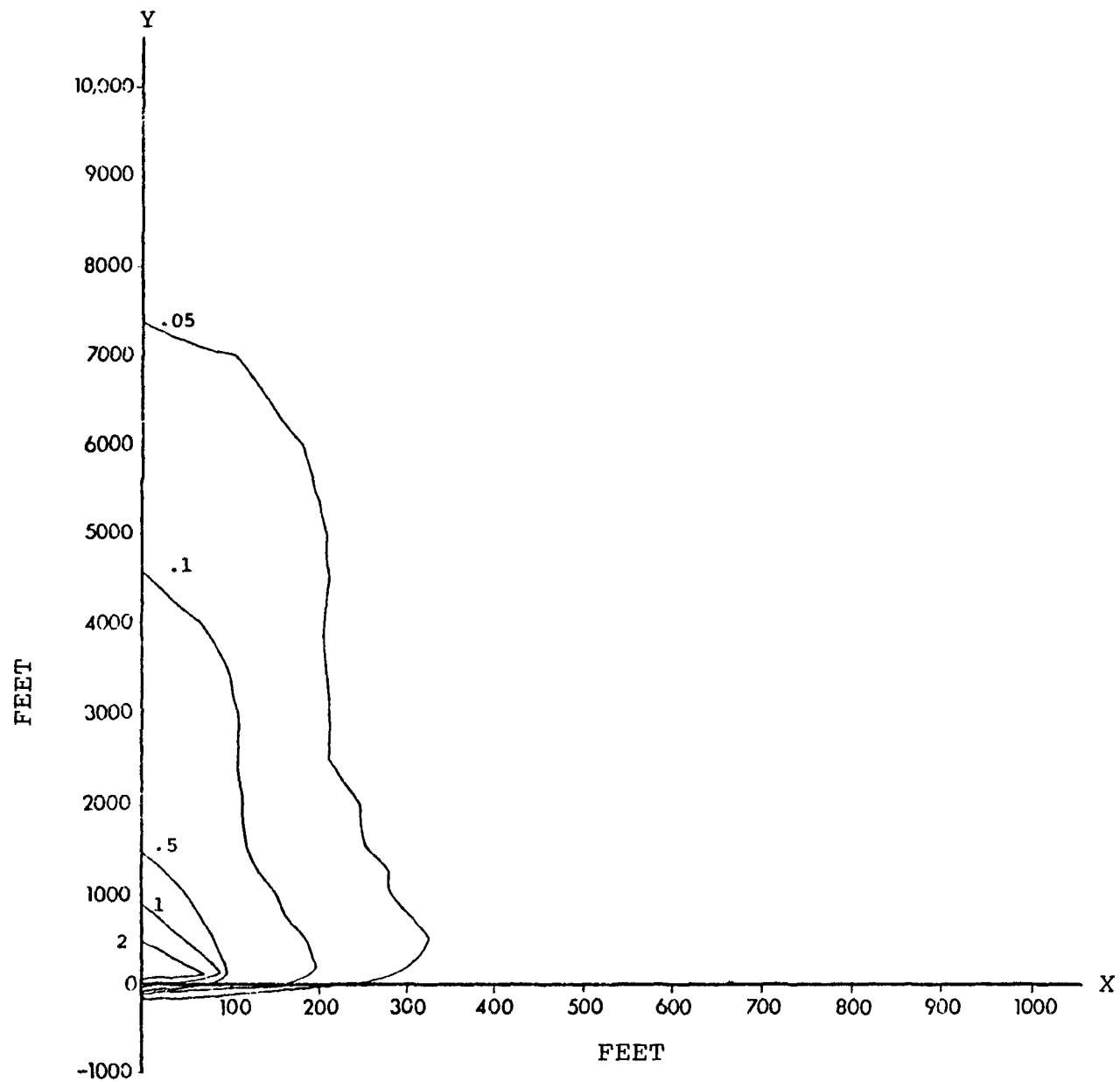


Figure 5-10d. Far offshore dilution percentage isopleths.  
F4: Initial dilution sensitivity,  $D=5$ .



## CHAPTER SIX

### METHODOLOGY FOR IMPACT ASSESSMENT

#### 6.1 Introduction

This chapter is concerned with the data and analytical methods which were used for predicting the toxic impacts which would result from the altered toxicant and salinity distributions in the waters surrounding an offshore oil drilling site as a result of brine discharges. Two classes of brine-related impacts are considered here: toxic effects, including direct mortality and a variety of sublethal effects on resident organisms; and potential human health effects resulting from the consumption of oysters or other organisms which can accumulate in their body tissues high levels of toxic metals and hydrocarbons. Because of the highly variable and nonsystematic nature of the available data on the toxic effects of pollutants, the analysis described here is necessarily only semi-quantitative, and based on simplifying assumptions derived from general toxicological considerations and from recent field studies of biological communities in the vicinity of offshore drilling sites in Louisiana and Texas. It is believed that the approximations which are introduced have at least order-of-magnitude validity; and the results, which are described in a subsequent chapter of the report, should be considered in that light.

The material in this chapter is of two types. The first consists of toxicity data directly used in the impacts analysis of the next chapter, and the second deals with a variety of issues (e.g., synergisms, adaptation responses, etc.) which although not used directly in the analysis due to the lack of quantitative data, are nonetheless secondary considerations which should be kept in mind in interpreting the conclusions reached in this report.

#### 6.2 Methodology

The assessment of impacts, outlined in Figure 6-1, consists basically of delineating a "zone of impact" outside of which only insignificant impacts would be predicted on ecological communities and on contaminant levels in human food organisms. Determining the area of this zone of impact involves three steps:

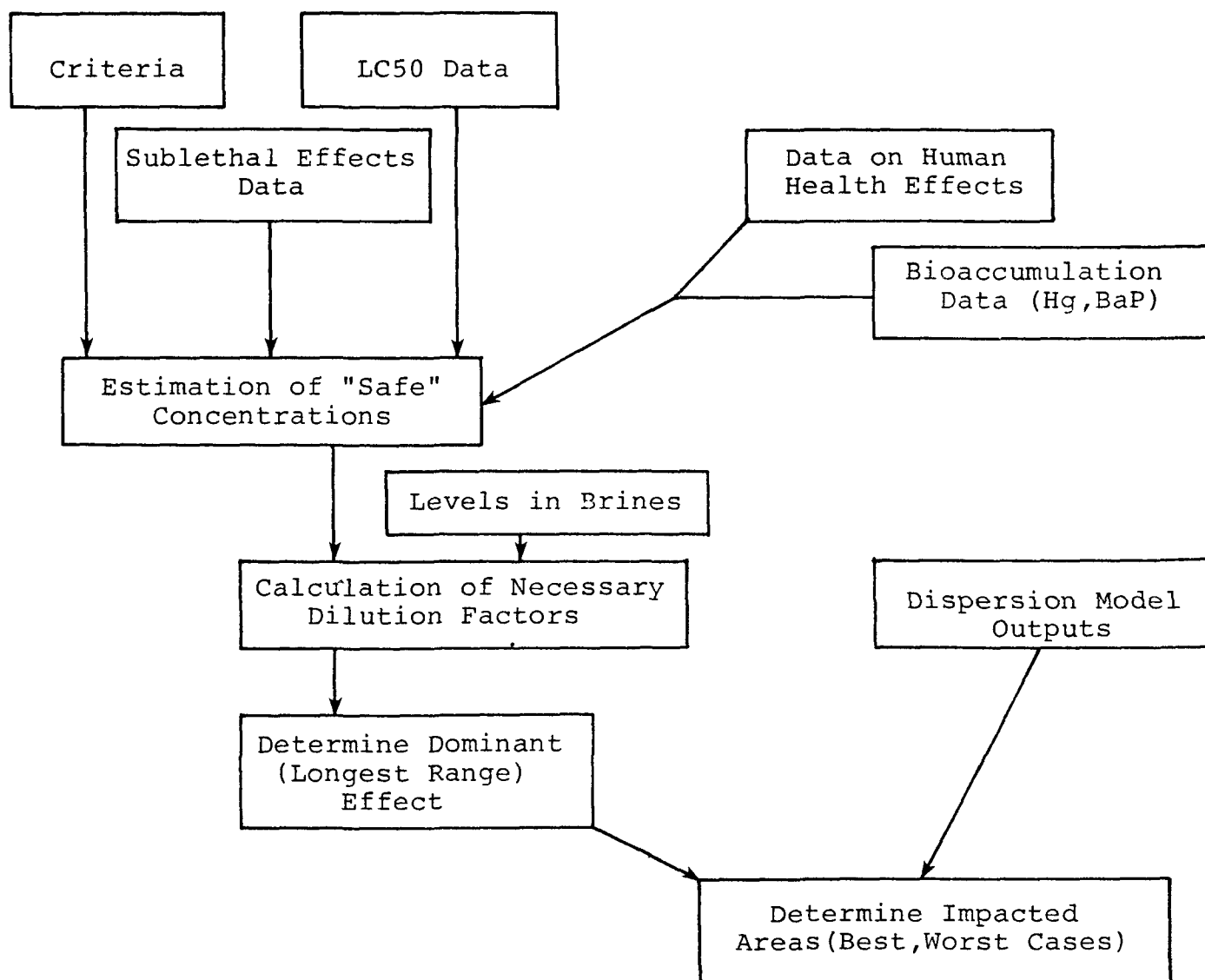


Figure 6-1. Outline of the analysis.

1. For a particular class of impact, a set of "safe" levels must be defined for each toxic contaminant in oilfield brines.
2. The safe levels of each constituent must then be compared with the levels actually found in oilfield brines to produce a Necessary Dilution Factor (NDF) for each constituent; i.e., the dilution necessary to bring that constituent down to a "safe" level.
3. The dispersion model output described in the previous chapter can then be used to determine the area around the production platform in which the dilution of each constituent is less than or equal to its NDF. The maximum area for any of these constituents will then be used as an estimate of total impacted area.

Similar analyses can be done for specific classes of effects which are known to be associated with the pollutants found in oilfield brines. For example, the band between two adjacent isopleths produced by the dispersion model represents a region of predicted pollutant concentration in the range  $x$  to  $x + \Delta x$ , for some particular  $x$ , and the tables of effects given later in this chapter can then be consulted to see if any significant effects have been noted on organisms in that range of concentrations. Thus, the type of effect, and in some cases, the absolute magnitude of the effect (in terms of number of organisms affected) can be estimated for each band. This information is complemented by the calculations of the areas of impacted zones, which provide a useful summary statistic for the whole site.

Three separate estimates of "safe" (no effects) concentrations are made for each brine constituent based upon the toxicological data presented later in this chapter. The first is based on the EPA marine water quality criterion for each constituent (see Table 6-1); a second is based on the minimum concentration at which any adverse effect has been noted in the literature; and a third is based on the use of an application factor of 0.01 in conjunction with 96 hr LC50 data. (The use of an "application factor" of 0.01 together with 96 hr LC50 data in predicting safe levels is supported

TABLE 6-1

EPA WATER QUALITY CRITERIA FOR BRINE CONSTITUENTS

SUBSTANCE	MAXIMUM LEVEL <sup>a</sup> (mg/l)	RECOMMENDED APPLICATION FACTOR <sup>a</sup>
Arsenic	0.05 <sup>b</sup>	0.01 x 96 hr LC50 <sup>b</sup>
Cadmium	0.005 <sup>c</sup>	0.01 x 96 hr LC50 <sup>b</sup>
Chromium	0.1 (0.01 in oyster-producing areas) <sup>b</sup>	0.01 x 96 hr LC50 <sup>b</sup>
Copper	0.05 <sup>b</sup>	0.1 x 96 hr LC50 <sup>c</sup>
Cyanide	0.005 <sup>c</sup>	0.1 x 96 hr LC50 <sup>b</sup>
Lead	0.05 <sup>b</sup>	0.01 x 96 hr LC50 <sup>c</sup>
Mercury	0.0001 <sup>c</sup>	--
Nickel	0.1 <sup>b</sup>	0.01 x 96 hr LC50 <sup>c</sup>
Oil & Grease	--	0.01 x 96 hr LC50 <sup>c</sup>
Silver	0.005 <sup>b</sup>	0.01 x 96 hr LC50 <sup>c</sup>
Zinc	0.1 <sup>b</sup>	0.01 x 96 hr LC50 <sup>b</sup>

<sup>a</sup>Criterion is lower of the numbers in these two columns.

<sup>b</sup>Committee on Water Quality Criteria, Water Quality Criteria 1972, National Academy of Sciences and National Academy of Engineering, 1972.

<sup>c</sup>U.S. Environmental Protection Agency, Quality Criteria for Water, 1976, Washington, D.C.

both in recent EPA water quality criteria documents<sup>1</sup> and in the technical literature.<sup>2</sup> It is believed to represent a margin of safety adequate to protect marine communities from significant acute and chronic deleterious effects. The use of application factors in interpreting lethal concentration data is discussed later in this chapter.)

Accurate numerical estimates of the degree of risk associated with the human consumption of fish or shellfish which have accumulated quantities of trace metals or hydrocarbons are, of course, impossible to obtain, so the following highly qualitative approach is adopted. The analysis will concentrate on a two components of oilfield brines which are known to be bioaccumulated and to pose a significant human health risk: benz[α]pyrene and mercury. For benzpyrene, an important hydrocarbon carcinogen in crude oil, extrapolations from concentrations in water to concentrations in sessile food organisms such as shellfish will be estimated based on available data on the bioaccumulation of aromatic hydrocarbons. Although reliable dose response data for this chemical are not available, the estimated concentration in fish will be considered unacceptable if it exceeds the background level of benzpyrene exposure in other food sources, as estimated in previous studies. Mercury bioaccumulation will be estimated from available data on mercury accumulation rates for various organisms, and the final levels in organisms will be considered unacceptable if they exceed the 0.5 ppm standard currently prevailing in the United States and Canada. Each site can then be characterized by the area of its "unacceptable" or "unsafe" region.

Two important assumptions of the impact analysis are:

1. That there is no significant toxicity modification due to complexation of metal ions, oxidation or reduction, microbial degradation of hydrocarbons, and other environmental interactions (in other words, it is assumed that these effects are small

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<sup>1</sup>For example: "The maximum acceptable concentration of mercury in marine or estuarine waters is 1/100 (0.01) of the 96 hr LC50 value determined using the receiving water in question and the most important sensitive species in the locality as the test organism." U.S. Environmental Protection Agency, Water Quality Criteria, 1973, p. 275. Similar criteria are set for other metals.

<sup>2</sup>See the data reviewed in J.B. Sprague, "Measurement of Pollutant Toxicity to Fish--III. Sublethal Effects and 'Safe' Concentration," Water Research 5 (1971): 257.

in magnitude compared with concentration effects which depend only on the rate of dilution of the brine).

2. That the effects of the pollutants are purely additive, and do not depend in a synergistic or antagonistic fashion on the levels of other pollutants. In general, this second assumption is not valid, since synergisms have been noted for trace metals, but it has been shown to hold for at least some pollutants at low concentrations (on the order of only a few tenths of their LC50's).<sup>3</sup>

These assumptions are made necessary by the absence of quantitative data on the extent to which environmental interactions or synergisms with other pollutants will effect toxicity at a particular site.

### 6.3 Toxicity Data

#### 6.3.1 Introduction

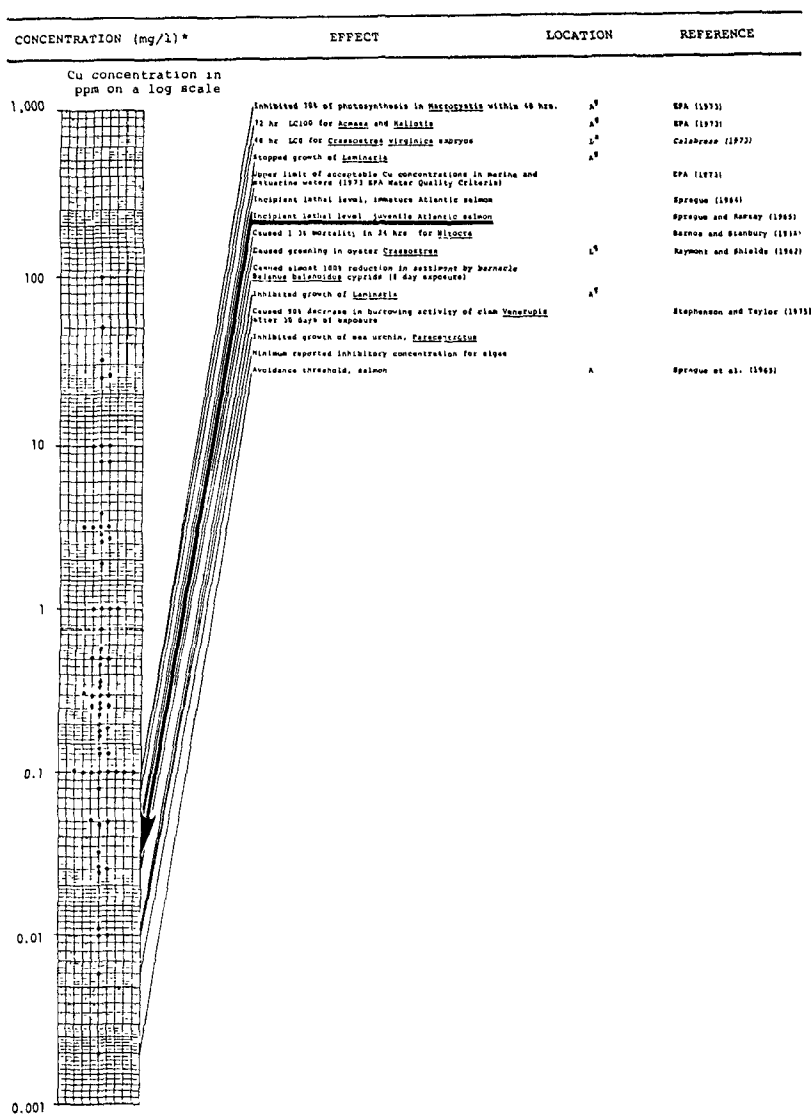
Tables 6-2 through 6-12 summarize currently available data on the toxicity of crude oil, phenol, and trace metals (silver, copper, mercury, cadmium, chromium, zinc, nickel, arsenic, and lead) to organisms in marine and estuarine environments. (See Figure 6-2 for an explanation of the format of these tables.) In addition, supplementary data are presented in Table 6-13 relating to the toxicity of specific crude oil fractions and components. This section will deal briefly with some of the factors which must be taken into account in interpreting and applying the data contained in these tables.

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<sup>3</sup>See, for example, J.B. Sprague and Ramsay, "Lethal Levels of Mixed Copper-Zinc Solutions for Juvenile Salmon," Journal of the Fisheries Research Board of Canada 22(2) (1965): 425-432, who found an additive interaction between copper and zinc for the juvenile Atlantic salmon in the range of one toxic unit, and a superadditive interaction only at much higher levels.

Typical Data Point: 0.32 ppm - Incipient lethal level of copper for juvenile Atlantic salmon (J.B. Sprague and B.A. Ramsay, Journal of the Fisheries Research Board of Canada 22/2) (1965): 425-432)

is entered in Table 6-3 as follows:



\*1 mg/l = 1 ppm

Tables use the approximation 1 ppm  $\approx$  1 mg/l. Location code indicates whether tested species is found in Alaska (A) or Louisiana (L) waters. Superscript s indicates that test species is found in location; superscript g indicates that other species of the same genus as the test species are found in the location.

Figure 6-2. Explanation of toxicity tables.

TABLE 6-2  
TOXICITY TABLE - COPPER

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
	92 hr. LC50 for <i>Artemia</i>		Corner and Sparrow (1956)
	5 hr. LC50 for <i>Elminius</i>		Corner and Sparrow (1956)
	2 hr. LC50 for <i>Mytilus</i>	A <sup>9</sup>	Wisely and Blick (1967)
	Caused 42.5% mortality in 24 hrs. in <i>Nitocra</i>		Barnes and Stanbury (1948)
	20 min. produced 28.5% reduction in O <sub>2</sub> consumption by <i>Marinogammarus marinus</i>		
	Concentration which produces 50% reduction within 1 hr. of an activity index for <i>Marinogammarus marinus</i>		
	Toxicity threshold for globes and three-spined stickleback		Raymont and Shields (1962)
	Toxicity threshold <i>Elminius</i>		Corner and Sparrow (1956)
	96 hr. TL30 for <i>Fundulus</i>	L <sup>9</sup>	Eisler and Gardner (1973)
	2 h4 LC50 for <i>Bugula</i>		Wisely and Blick (1967)
	96 hrs. of exposure produced 25.4% decrease in catalase levels in surviving <i>Fundulus</i>	L <sup>9</sup>	Jackim (1970)
	As above, 26.8% increase in oxidase levels	L <sup>9</sup>	Jackim (1970)
	As above, 13.7% reduction in acid phosphatase levels	L <sup>9</sup>	Jackim (1970)
	96 hr. TLM <i>Fundulus</i>	L <sup>9</sup>	Jackim (1970)
	Lethal concentration for oyster larvae		Raymont and Shields (1962)
	2 hr. LC50 for <i>Galeolaria</i>		
	2.5 hr. LC50 for <i>Acartia</i>	L <sup>9</sup>	Corner and Sparrow (1956)
	Caused 21.2% mortality in <i>Nitocra</i> in 24 hrs.		Barnes and Stanbury (1948)
	96 hr. TLM for adult oysters		Raymont and Shields (1962)
	11-12 day toxicity threshold for shore crab, <i>Carcinus</i>		
	Chronic exposure of flounder <i>Pseudopleuronectes</i> at this level produces histopathology of gills, kidney, and liver		
	96 hrs. caused 10% mortality in <i>Fundulus</i>	L <sup>9</sup>	Eisler and Gardner (1973)
	100 hr. LC50 for <i>Hereis</i> taken from a highly polluted estuary	L <sup>9</sup>	Bryan and Hummerstone (1971)
	Concentration in Alabama brines		
	2 hr. LC50 for <i>Watersiporia</i>		Wisely and Blick (1967)
	2 hr. LC50 for <i>Spirobus</i>		Wisely and Blick (1967)
	11 day toxicity threshold for small prawn, <i>Leander squilla</i>	L <sup>8</sup>	Raymont and Shields (1962)
	LC0 for oyster larvae		
	6 hr. LC50 <i>Balanus balanoides</i> stage V & VI nauplii	A <sup>9</sup>	Pyefinch and Mott
	2 day LC100 for adult barnacle	A	Raymont and Shields (1962)
	6 hr. LC50 for <i>Balanus balanoides</i> stage V & VI nauplii	A <sup>9</sup>	Pyefinch and Mott
	6 hr. LC52 for barnacle <i>Balanus crenatus</i>	A <sup>8</sup>	Pyefinch and Mott
	Toxicity threshold for <i>Acartia</i>	L <sup>9</sup>	Corner and Sparrow (1956)
	Interpolated 100 hr. LC50 for <i>Hereis</i> from an unpolluted estuary	L <sup>9</sup>	Bryan and Hummerstone (1971)
	Kills colonial bryzoan, <i>Bugula</i>		Raymont and Shields (1962)
	6 hr. LC50 for <i>Balanus crenatus</i> stage IV nauplii	A <sup>8</sup>	Pyefinch and Mott
	6 hr. LC50 for <i>Balanus crenatus</i> stage VI nauplii	A <sup>8</sup>	Pyefinch and Mott
	Caused 11.3% mortality in 24 hrs. in <i>Nitocra</i>		Barnes and Stanbury (1948)
	Reduced O <sub>2</sub> consumption 59% in mud snail <i>Nassarius obsoletus</i>	L <sup>9</sup>	MacInnes and Thurberg
	6 hr. LC50 for <i>Balanus crenatus</i>	A <sup>8</sup>	Pyefinch and Mott
	Prevents growth of <i>Bugula</i>		Raymont and Shields (1962)
	12 day LC50 for <i>Hereis</i>	L <sup>9</sup>	
	Chronic exposure caused gill histopathology in flounder <i>Pseudopleuronectes</i>		
	5 day LC100 for adult barnacle		Raymont and Shields (1962)
	24 hr. LC100 for mussel	A	
	48 hr. LC100 for <i>Crassostrea virginica</i> embryos	L <sup>8</sup>	Calabrese (1973)
	Causes greening of oysters within 3 wks.	L	Raymont and Shields (1962)
	LC50 48 hr. <i>Crassostrea virginica</i>	L <sup>8</sup>	Calabrese (1973)
	Toxicity threshold for plaice		Raymont and Shields (1962)
	Causes in movement behavior of mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	MacInnes and Thurberg
	21 day LC0 for <i>Hereis</i>	L <sup>9</sup>	
	Caused 1-2%/day mortality in <i>Venerupis</i> after 30-40 days of exposure		Stephenson and Taylor (1975)
	Caused 100% mortality in clam <i>Venerupis</i> after 50 days of exposure		Stephenson and Taylor (1975)

\*1 mg/l = 1 ppm

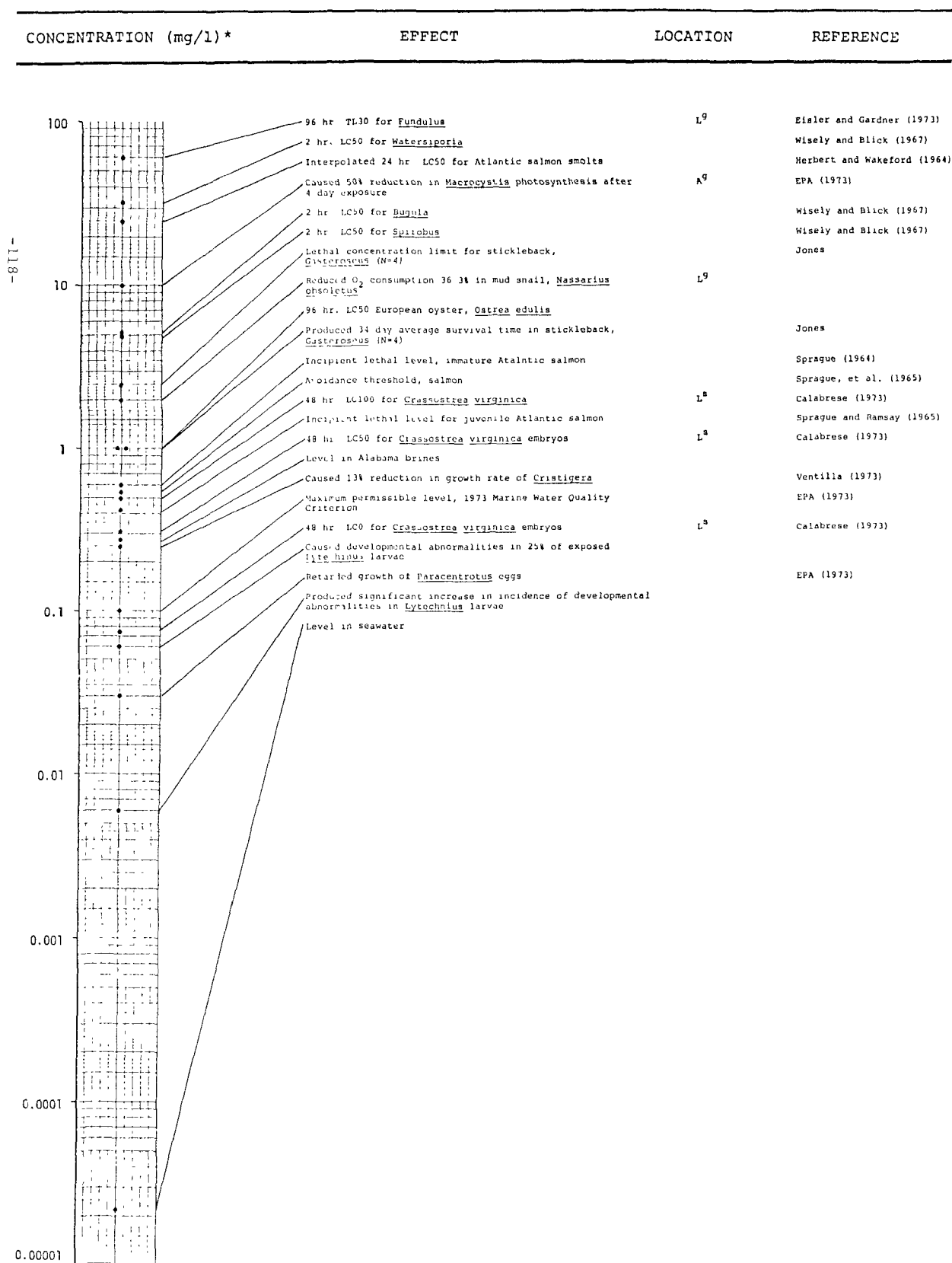


TABLE 6-2 (CONT.)  
TOXICITY TABLE - COPPER

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
	Inhibited 70% of photosynthesis in <u>Macrocyctis</u> within 48 hrs.	A <sup>9</sup>	EPA (1973)
	72 hr. LC100 for <u>Acmsea</u> and <u>Haliotis</u>	A <sup>9</sup>	EPA (1973)
	48 hr. LC0 for <u>Crassostrea virginica</u> embryos	L <sup>8</sup>	Calabrese (1973)
	Stopped growth of <u>Laminaria</u>	A <sup>9</sup>	
	Upper limit of acceptable Cu concentrations in marine and estuarine waters (1973 EPA Water Quality Criteria)		EPA (1973)
	Incipient lethal level, immature Atlantic salmon		Sprague (1964)
	Incipient lethal level, juvenile Atlantic salmon		Sprague and Ramsay (1965)
	Caused 1.34 mortality in 24 hrs. for <u>Nitocra</u>		Barnes and Stanbury (1945)
	Caused greening in oyster <u>Crassostrea</u>	L <sup>9</sup>	Raymont and Shields (1962)
	Caused almost 100% reduction in settlement by barnacle <u>Balanus balanoides</u> cyprids (8 day exposure)		
	Inhibited growth of <u>Laminaria</u>	A <sup>3</sup>	
	Caused 90% decrease in burrowing activity of clam <u>Venerupis</u> after 30 days of exposure		Stephenson and Taylor (1975)
	Inhibited growth of sea urchin, <u>Paracentrotus</u>		
	Minimum reported inhibitory concentration for algae		
	Avoidance threshold, salmon	A	Sprague et al. (1965)

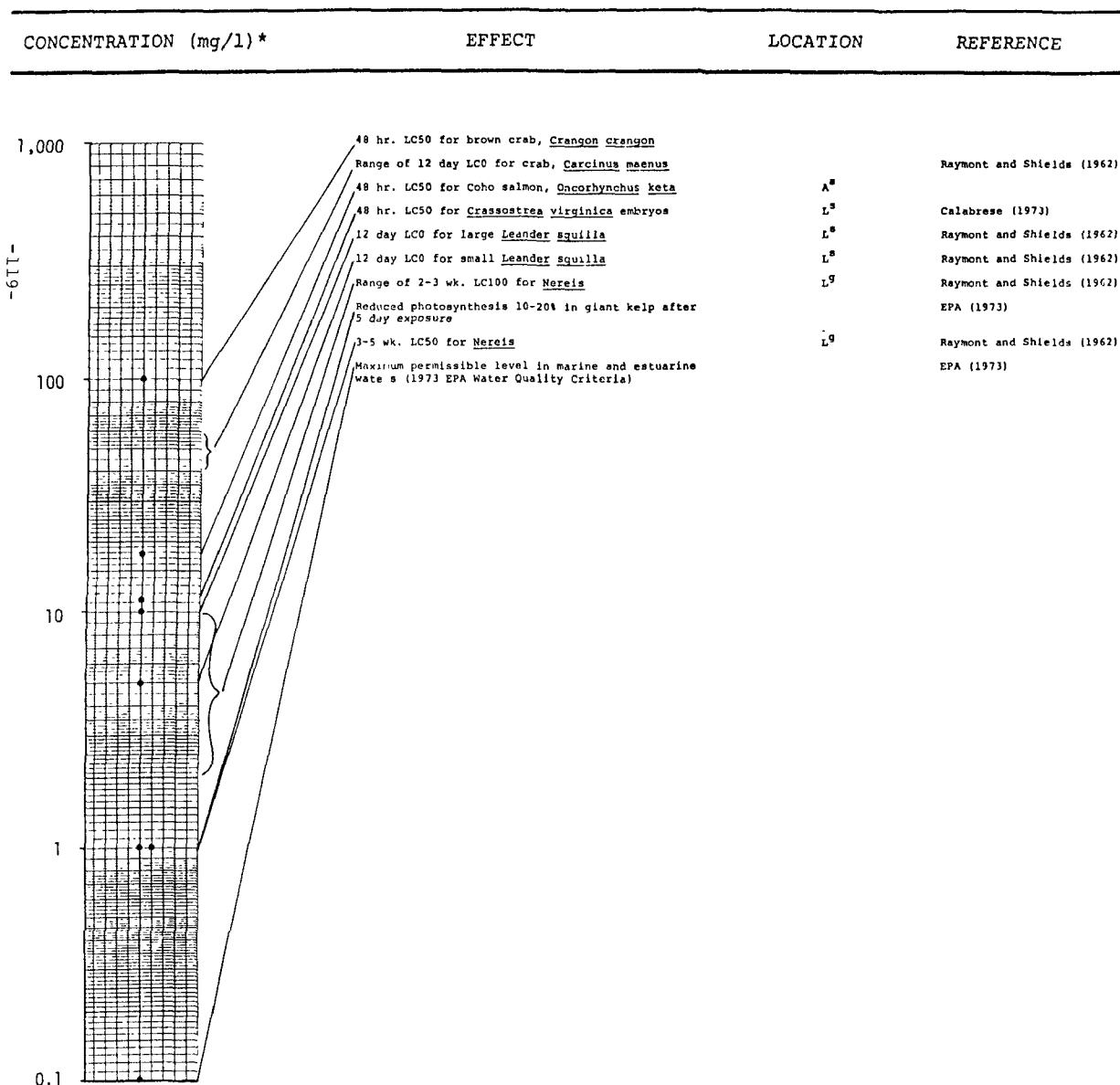
\*1 mg/l = 1 ppm

TABLE 6-3  
TOXICITY TABLE - ZINC



\*1 mg/l = 1 ppm

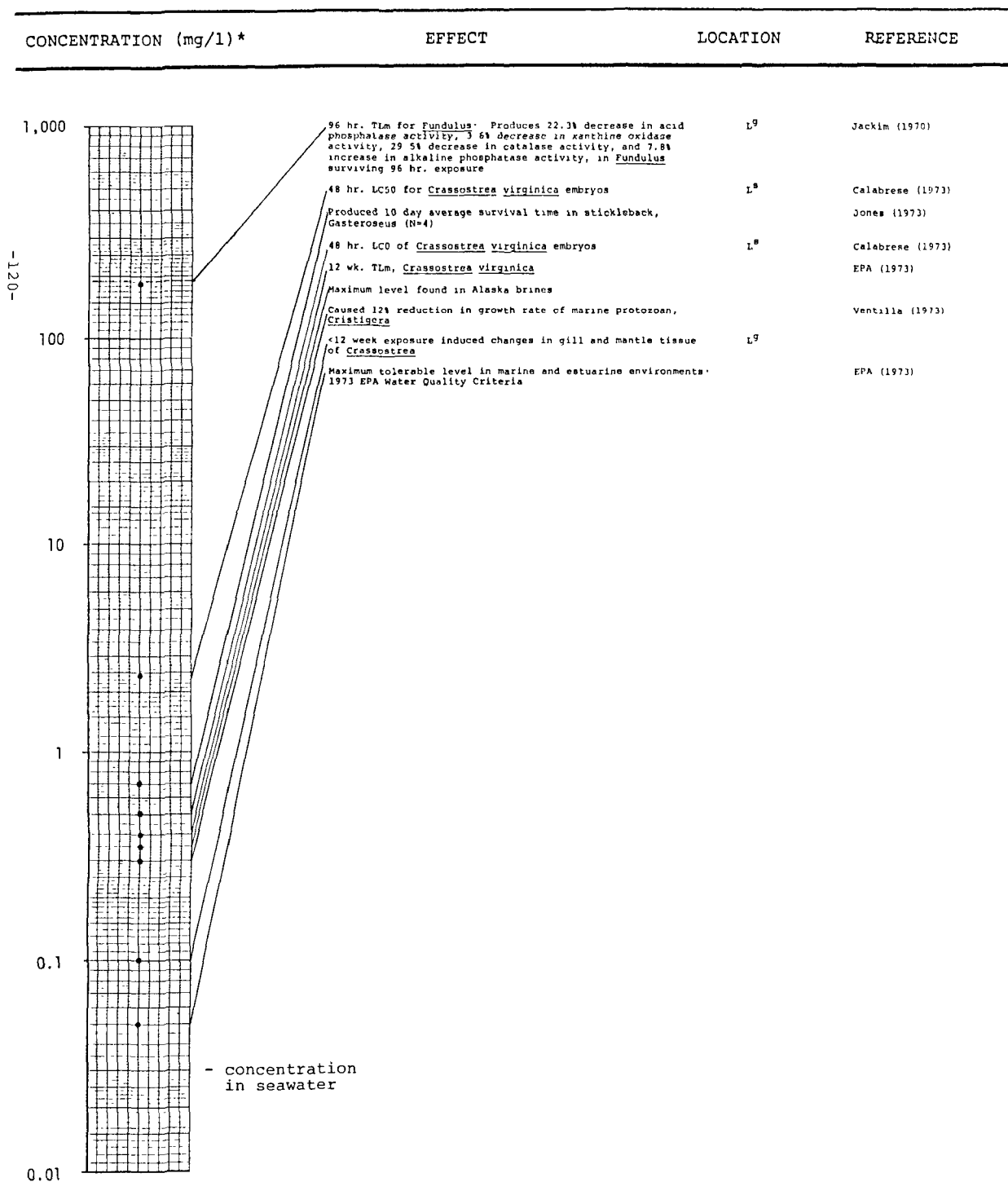
TABLE 6-4  
TOXICITY TABLE - CHROMIUM



\*1 mg/l = 1 ppm

TABLE 6-5

## TOXICITY TABLE - LEAD



\*1 mg/l = 1 ppm

TABLE 6-6

## TOXICITY TABLE - MERCURY

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
1000.0	2.5 hr. LC50 for <i>Artemia</i>		Corner and Sparrow (1956)
	4.5 hr. caused 50% decrease in <i>Artemia</i> larvae respiration		Corner and Sparrow (1956)
	4.5 hr. caused 60% decrease in <i>Artemia</i> larvae motility		Corner and Sparrow (1956)
	2 h4 LC50 for <i>Artemia</i>		Wisely and Blick (1967)
	Produced 4% reduction in O <sub>2</sub> consumption of <i>Marinogammarus</i> <i>marinus</i> (i.e. 50% reduction in an activity index for a population)		Hunter
	2 hr. LC50 for <i>Mytilus</i>	A <sup>9</sup>	Wisely and Blick (1967)
	Caused 44% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
	96 hr. LC50 flatfish <i>Pleuronectes flesus</i>		
	Caused 84% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
100.0	6 hr. LC39 for adult barnacle <i>Balanus crenatus</i>	A <sup>8</sup>	Barnes and Stanbury (1948)
	Caused 78% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
	2 hr. LC50 for <i>Galiolaria</i>		Wisely and Blick (1967)
	48 hr. exposure lethal to barnacles		EPA (1973)
	Reduced fertilizing capacity of steelhead trout spermatazoa (as CH <sub>3</sub> HgCl)	A <sup>8</sup>	
	24 hr. exposure produced 80% mortality in <i>Australorbis</i>		EPA (1973)
	Caused 72% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
	Caused 50% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
	Caused 16.7% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
	Caused 10% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
10.0	6 hr. LC50 for <i>Balanus balanoides</i> stage V and VI nauplii	A <sup>9</sup>	Pyefinch and Mott
	2.5 hr. LC50 for <i>Elminius</i>		Corner and Sparrow (1956)
	6 hr. LC50 for <i>Balanus balanoides</i> stage IV nauplii	A <sup>9</sup>	Pyefinch and Mott
	96 hr. LC50 for <i>Fundulus heteroclitus</i>	L <sup>9</sup>	
	96 hr. exposure ( <i>Fundulus</i> ) caused 19.1% reduction in catalase levels in livers of surviving fish	L <sup>9</sup>	Jackim (1970)
	As above, 31.9% reduction in xanthine oxidase levels	L <sup>9</sup>	Jackim (1970)
	As above, 7.19% reduction in acid phosphatase levels	L <sup>9</sup>	Jackim (1970)
	As above, 8.19% increase in alkaline phosphatase levels	L <sup>9</sup>	Jackim (1970)
1.0	96 hr. TLM for <i>Fundulus</i>		
	48 hr. LC100 for <i>Crassostrea virginica</i>	L <sup>8</sup>	
	Caused extensive ultrastructural cytopathology in <i>Uca pugilator</i> gill filaments within a 28 day exposure period		
	1 day LC50 for larval fiddler crab		
	6 hr. LC50 for <i>Balanus crenatus</i> stage VI nauplii	A <sup>8</sup>	Pyefinch and Mott
	Caused by 1.4% 24 hr. mortality in <i>Nitocra</i>		Barnes and Stanbury (1948)
	2 h4 LD50 for <i>Spirobus</i>		Wisely and Blick (1967)
	24 hr. exposure caused 53% reduction in efficiency of <i>Gambusia</i> in escaping predation by bass <i>Micropterus</i>		Kania and O'Hara (1974)
	2 hr. LC50 for <i>Watersiporia</i>		Wisely and Blick (1967)
0.1	6 hr. LC50 for <i>Balanus balanoides</i> stage III nauplii	A <sup>9</sup>	Pyefinch and Mott
	6 hr. LC50 for <i>Balanus crenatus</i> stage V nauplii	A <sup>8</sup>	Pyefinch and Mott
	6 hr. LC50 for <i>Balanus crenatus</i> stage IV nauplii	A <sup>8</sup>	Pyefinch and Mott
	Caused 100% reduction in settlement by cyprids of barnacle <i>Balanus balanoides</i> (19 day exposure)	A <sup>9</sup>	Pyefinch and Mott
	2.5 hr. h4 LC50 for <i>Acartia</i>	L <sup>9</sup>	Corner and Sparrow (1956)
	24 hr. exposure caused 22.2% reduction in efficiency of <i>Gambusia</i> in escaping predation by <i>Micropterus</i>		Kania and O'Hara (1974)
	Caused teratogenic effect in eggs of pink and sockeye salmon		
	24 hr. exposure caused 33.6% reduction in efficiency of <i>Gambusia</i> in escaping predation by <i>Micropterus</i>		Kania and O'Hara (1974)
0.01	48 hr. LC100 for <i>Crassostrea virginica</i> embryos	L <sup>8</sup>	Calabrese (1973)
	48 hr. LC50 for <i>Crassostrea virginica</i> embryos	L <sup>8</sup>	Calabrese (1973)
	Caused 12% reduction in growth rate of marine protozoan <i>Cristigera</i>		Ventilla (1973)
	Produced developmental deformities in <i>Onchobranchius</i> eggs	A <sup>9</sup>	EPA (1973)
	Maximum permissible level in marine and estuarine waters, 1973 Water Quality Criteria		EPA (1973)
0.001	48 hr. LC0 for <i>Crassostrea virginica</i> embryos	L <sup>8</sup>	Calabrese (1973)

\*1 mg/l = 1 ppm

TABLE 6-7

## SILVER

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
10	Approximately double O <sub>2</sub> consumption in <u>M. tilus</u>	A <sup>g</sup>	
	Reduced O <sub>2</sub> consumption rate 58.8% in mud snail, <u>Nassarius obsoletus</u>	L	
	Caused approximately 14% increase in O <sub>2</sub> consumption of <u>Mercuraria</u> (25 ppt salinity)		
	Caused approximately 15% increase in O <sub>2</sub> consumption of <u>Crassostrea</u> (25 ppt salinity)	L <sup>g</sup>	
	48 hr. LD90 for barnacles	A	EPA (1973)
	Caused alteration in movement behavior of mud snail, <u>Nassarius obsoletus</u>	L <sup>g</sup>	MacInnes and Thurberg
	Caused abnormal development of sea urchin eggs	A	
	Minimum inhibitory concentration for algae		
1	96 hr. exposure caused 32.4% reduction in catalase levels in surviving <u>Fundulus</u>	L <sup>g</sup>	Jackim (1970)
	96 hr. exposure caused 26.9% reduction in xanthine oxidase levels in surviving <u>Fundulus</u>	L <sup>g</sup>	Jackim (1970)
	96 hr. exposure caused 11.6% reduction in alkaline phosphatase levels in surviving <u>Fundulus</u>	L <sup>g</sup>	Jackim (1970)
	96 hr. LC50 for <u>Fundulus</u>	L <sup>g</sup>	Jackim (1970)
	48 hr. LC100 for <u>Crassostrea virginica</u> embryos	L <sup>8</sup>	Calabrese (1973)
	48 hr. LC50 for <u>Crassostrea virginica</u> embryos	L <sup>8</sup>	Calabrese (1973)
	Toxicity threshold for sticklebacks		EPA (1973)
	48 hr. LC0 for <u>Crassostrea virginica</u> embryos	L <sup>8</sup>	Calabrese (1973)
0.1	Slowed development and induced abnormal plutei in embryonic sea urchin, <u>Paracentrotus</u>		
	Inhibits growth of sea urchin, <u>Paracentrotus</u>		
	Caused development abnormalities in sea urchin, <u>Arbacia</u>		EPA (1973)
	Maximum permissible level in marine and estuarine waters. 1973 Water Quality Criteria		EPA (1973)
0.01			
0.001			
0.0001			

\*1 mg/l = 1 ppm

TABLE 6-8

## CADMIUM

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
1,000	48 hr. TL25 mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL25 blue mussel, <i>Mytilus edulis</i>	A <sup>9</sup>	Eisler (1971)
	24 hr. TL25 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL25 blue mussel, <i>Mytilus edulis</i>	A <sup>9</sup>	Eisler (1971)
	48 hr. TL50 blue mussel, <i>Mytilus edulis</i>	A <sup>9</sup>	Eisler (1971)
	24 hr. killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL25 soft shell clam, <i>Mya arenaria</i>		Eisler (1971)
	24 hr. TL50 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL25 sheepshead minnow, <i>Cyprinodon variegatus</i>	L <sup>8</sup>	Eisler (1971)
	24 hr. TL50 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL50 mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL75 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL25 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	24 hr. TL50 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	24 hr. TL50 sheepshead minnow, <i>Cyprinodon variegatus</i>	L <sup>8</sup>	Eisler (1971)
	48 hr. TL75 blue mussel, <i>Mytilus edulis</i>	A <sup>9</sup>	Eisler (1971)
	24 hr. TL75 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL75 mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL25 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL100 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL25 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL25 sheepshead minnow, <i>Cyprinodon variegatus</i>	A <sup>8</sup>	Eisler (1971)
	48 hr. TL25 sheepshead minnow, <i>Cyprinodon variegatus</i>	A <sup>8</sup>	Eisler (1971)
	24 hr. TL75 sheepshead minnow, <i>Cyprinodon variegatus</i>	A <sup>8</sup>	Eisler (1971)
	48 hr. TL50 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	168 hr. TL25 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL50 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL50 soft shell clam, <i>Mya arenaria</i>		Eisler (1971)
	24 hr. TL25 grass shrimp, <i>Palaemonetes vulgaris</i>	L <sup>8</sup>	Eisler (1971)
	96 hr. TL50 sheepshead minnow, <i>Cyprinodon variegatus</i>	L <sup>8</sup>	Eisler (1971)
	48 hr. TL50 sheepshead minnow, <i>Cyprinodon variegatus</i>	L <sup>8</sup>	Eisler (1971)
	In <i>Fundulus</i> , produced intestinal histopathology in 1 hr. and kidney histopathology in 12 hrs. and gill histopathology in 20 hrs.	L <sup>9</sup>	Gardner and Yevich (1970)
	24 hr. TL50 grass shrimp, <i>Palaemonetes vulgaris</i>		Eisler (1971)
	48 hr. TL75 soft shell clam, <i>Mya arenaria</i>		Eisler (1971)
	168 hr. TL50 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL75 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	96 hr. TL75 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	264 hr. TL25 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL25 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL50 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL25 sandworm, <i>Nereis virens</i>		Eisler (1971)
	48 hr. TL25 sandworm, <i>Nereis virens</i>		Eisler (1971)
	48 hr. TL75 sheepshead minnow, <i>Cyprinodon variegatus</i>	L <sup>8</sup>	Eisler (1971)
	48 hr. TL50 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. LC50 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TLm for <i>Fundulus</i> , 96 hr. exposure caused 19.4% reduction in acid phosphatase levels; 10.6% reduction in xanthine oxidase levels, and 17.3% reduction in catalase levels in surviving <i>Fundulus</i>	L <sup>9</sup>	Jackim et al. (1970)
	48 hr. TL50 sandworm, <i>Nereis virens</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL50 blue mussel, <i>Mytilus edulis</i>	A <sup>9</sup>	Eisler (1971)
	24 hr. TL50 sandworm, <i>Nereis virens</i>	L <sup>9</sup>	Eisler (1971)
	264 hr. TL50 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL50 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL75 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	168 hr. TL75 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)

\*1 mg/l = 1 ppm

TABLE 6-8 (CONT.)

## CADMIUM

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
1,000 100 10 1 0.1 0.01 0.001	24 hr. TL75 sandworm, <i>Nereis virens</i>		Eisler (1971)
	24 hr. TL25 starfish, <i>Astarias forbesi</i>		Eisler (1971)
	48 hr. TL75 sandworm, <i>Nereis virens</i>		Eisler (1971)
	96 hr. TL25 sandworm, <i>Nereis virens</i>		Eisler (1971)
	24 hr. TL75 grass shrimp, <i>Palaemonetes vulgaris</i>		Eisler (1971)
	96 hr. TL25 mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL50 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	48 hr. TL25 starfish, <i>Astarias forbesi</i>		Eisler (1971)
	264 hr. TL75 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL25 starfish, <i>Astarias forbesi</i>		Eisler (1971)
	24 hr. TL50 starfish, <i>Astarias forbesi</i>		Eisler (1971)
	96 hr. TL50 for sandworm, <i>Nereis virens</i>		Eisler (1971)
	72 hr. LC100 for <i>Eurypanopeus</i>		Collier et al. (1973)
	TL50 for mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL25 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL4 for <i>Fundulus</i>	L <sup>9</sup>	Eisler and Gardner (1973)
	168 hr. TL100 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL25 grass shrimp, <i>Palaemonetes vulgaris</i>		Eisler (1971)
	96 hr. TL75 sheepshead minnow, <i>Cyprinodon variegatus</i>	L <sup>8</sup>	Eisler (1971)
	96 hr. TL100 mummichog, <i>Fundulus heteroclitus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL25 hermit crab, <i>Pagurus longicarpus</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL25 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	48 hr. TL75 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	96 hr. TL75 blue mussel, <i>Mytilus edulis</i>	A <sup>9</sup>	Eisler (1971)
	Reduced oxygen consumption of <i>Eurypanopeus</i> gill tissue by 36%		Collier et al. (1973)
	96 hr. TL50 for Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL75 mud snail, <i>Nassarius obsoletus</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL50 grass shrimp, <i>Palaemonetes vulgaris</i>		Eisler (1971)
	48 hr. LC50 <i>Crassostrea virginica</i>	L <sup>8</sup>	
	96 hr. TL75 sandworm, <i>Nereis virens</i>		Eisler (1971)
	96 hr. TL75 Atlantic oyster drill, <i>Urosalpinx cinerea</i>	L <sup>9</sup>	Eisler (1971)
	24 hr. TL75 starfish, <i>Astarias forbesi</i>		Eisler (1971)
	96 hr. TL75 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	48 hr. TL75 killifish, <i>Fundulus majalis</i>	L <sup>9</sup>	Eisler (1971)
	96 hr. TL50 green crab, <i>Carcinus maenas</i>		Collier et al. (1973)
	24 hr. TL25 sand shrimp, <i>Crangon septemspinosa</i>	L	Eisler (1971)
	24 hr. TL75 hermit crab, <i>Pagurus longicarpus</i>		Eisler (1971)
	96 hr. TL50 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	Reduced <i>Eurypanopeus</i> gill tissue O <sub>2</sub> consumption by 7.6%		Eisler (1971)
	48 hr. LC50 <i>Crassostrea virginica</i> embryos	L <sup>8</sup>	Calabrese (1973)
	48 hr. TL25 hermit crab, <i>Pagurus longicarpus</i>		Eisler (1971)
	72 hr. LC50 <i>Eurypanopeus</i>		Collier et al. (1973)
	96 hr. TL25 soft shell clam, <i>Mya arenaria</i>		Eisler (1971)
	48 hr. TL75 grass shrimp, <i>Palaemonetes vulgaris</i>		Eisler (1971)
	96 hr. TL25 starfish, <i>Astarias forbesi</i>		Eisler (1971)
	24 hr. TL50 sand shrimp, <i>Crangon septemspinosa</i>	L	Eisler (1971)
	48 hr. TL75 hermit crab, <i>Pagurus longicarpus</i>		Eisler (1971)
	96 hr. TL50 soft shell clam, <i>Mya arenaria</i>		Eisler (1971)
	24 hr. TL75 green crab, <i>Carcinus maenas</i>		Eisler (1971)
	Reduced gill tissue O <sub>2</sub> consumption 20-25% in green crab and rock crab		Collier et al. (1973)
	96 hr. TL75 soft shell clam, <i>Mya arenaria</i>		Eisler (1971)
	24 hr. TL75 sand shrimp, <i>Crangon septemspinosa</i>	L	Eisler (1971)
	48 hr. LC0 <i>Crassostrea virginica</i> embryos	L <sup>8</sup>	Calabrese (1973)
	72 hr. LC0 mud crab, <i>Eurypanopeus</i>		Collier et al. (1973)
	Increased O <sub>2</sub> consumption 32.5% in mud snail <i>Nassarius obsoletus</i>	L <sup>9</sup>	MacInnes and Thurberg

\*1 mg/l = 1 ppm



TABLE 6-8 (CONT.)

## CADMIUM

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
1,000	Caused alteration in movement behavior of mud snail <u>Nassarius obsoletus</u>	L <sup>9</sup>	MacInnes and Thurberg
	48 hr. TL50 starfish, <u>Asterias forbesi</u>		Eisler (1971)
	96 hr. TL25 grass shrimp, <u>Palaemonetes vulgaris</u>		Eisler (1971)
	96 hr. TL50 hermit crab, <u>Pagurus longicarpus</u>		Eisler (1971)
	48 hr. TL25 sand shrimp, <u>Crangon septemspinosa</u>	L	Eisler (1971)
	96 hr. TL50 starfish, <u>Asterias forbesi</u>		Eisler (1971)
	96 hr. TL25 hermit crab, <u>Pagurus longicarpus</u>		Eisler (1971)
	96 hr. TL25 sand shrimp, <u>Crangon septemspinosa</u>	L	Eisler (1971)
	48 hr. TL75 starfish, <u>Asterias forbesi</u>		Eisler (1971)
	96 hr. TL75 starfish, <u>Asterias forbesi</u>		Eisler (1971)
	48 hr. TL50 sand shrimp, <u>Crangon septemspinosa</u>	L	Eisler (1971)
	96 hr. TL50 grass shrimp, <u>Palaemonetes vulgaris</u>		Eisler (1971)
	96 hr. TL50 sand shrimp, <u>Crangon septemspinosa</u>	L	Eisler (1971)
	48 hr. TL75 sand shrimp, <u>Crangon septemspinosa</u>	L	Eisler (1971)
	96 hr. TL75 grass shrimp, <u>Palaemonetes vulgaris</u>		Eisler (1971)
	96 hr. TL75 hermit crab, <u>Pagurus longicarpus</u>		Eisler (1971)
	8 wk. LD50 American oysters		EPA (1973)
	15 wk. LD50 American oysters		EPA (1973)
	Minimum reported inhibitory concentration for algae		
	96 hr. TL75 sand shrimp, <u>Crangon septemspinosa</u>	L	Eisler (1971)
	Maximum acceptable level in marine and estuarine waters (1976 EPA Water Quality Criteria)		EPA (1976)
100			
10			
1			
0.1			
0.01			
0.001			

\*1 mg/l = 1 ppm

TABLE 6-9

TOXICITY TABLE - CRUDE OILS<sup>a</sup>

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
100,000	168 hr. LC50 for <i>Siganus rivulatus</i> (rabbitfish), 41 o/oo salinity, 23° C		Eisler (1973)
	Predation rate and fecundity of <i>Brugia granulata</i> (gastropod drill) reduced by a factor of 3 as a result of 168 hr. exposure		Eisler (1973)
	100% death of <i>Coscinodiscus granii</i> , <i>Limnophora ehrenbergii</i> , <i>Melosira monociliata</i> (diatoms); and of <i>Pseudonitzschia</i> <i>trachoides</i> , <i>Pseudonitzschia trachoides</i> (dinoflagellates)	L <sup>9</sup>	Perkins (1974)
	Phytoplankton death with 5 day exposure		Moore et al. (1974)
10,000	168 hr. LC50 for <i>Siganus rivulatus</i> (rabbitfish), 41 o/oo salinity, 23° C		Eisler (1973)
	96 hr. LC50 for <i>Syngnathus griseolineatus</i> (pipefish)		Eisler (1975)
	48 hr. TLM for <i>Chionoecetes bairdi</i> (tanner crab)	A <sup>8</sup>	Karinen and Rice (1974)
	Pronounced loss of equilibrium in <i>Oncorhynchus nerka</i> (sockeye salmon) smolts within 1 day exposure	A <sup>8</sup>	Sturdevant (1972)
	Avoidance response in <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, fresh water at 7.5° C	A <sup>8</sup>	Rice (1973)
1,000	24 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, sea water at 7.5° C	A <sup>8</sup>	Rice (1973)
	48 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, sea water at 7.5° C	A <sup>8</sup>	Rice (1973)
	Interference with byssal thread formation in <i>Mytilus edulis</i> (mussel)	A <sup>9</sup>	Eisler (1975)
	Loss of equilibrium in codfish		Eisler (1975)
	Immobilization of <i>Palaeomonetes pugio</i> (prawns)		Eisler (1975)
	Delays moulting in <i>Chionoecetes bairdi</i> (tanner crab)	A <sup>8</sup>	Karinen and Rice (1974)
100	24 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, fresh water at 5° C	A <sup>8</sup>	Rice (1973)
	96 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, sea water at 7.5° C	A <sup>8</sup>	Rice (1973)
	48 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, fresh water at 5° C	A <sup>8</sup>	Rice (1973)
	96 hr. TLM for <i>Palaeomonetes pugio</i> (grass shrimp)		
	Lethal to <i>Chlorella autotrophica</i> (green algae)		Pulich et al. (1974)
	24 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, sea water at 11.5° C	A <sup>8</sup>	Rice (1973)
10	72 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, fresh water at 5° C	A <sup>8</sup>	Rice (1973)
	48 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry, sea water at 5° C	A <sup>8</sup>	Rice (1973)
	100% death of <i>Echinometra mathaei</i> and <i>Diadema petosum</i> (sea urchins) with 68 hr. exposure		Eisler (1975)
	72 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry	A <sup>8</sup>	Rice (1973)
	100% death of <i>Chaetoceros curvisetum</i> (diatom), <i>Glenodinium foliaceum</i> , <i>Ceratium hirundinella</i> (dinoflagellates)	L <sup>9</sup>	Perkins (1974)
	No cell division or delayed cell division in <i>Coscinodiscus granii</i> , <i>Melosira monociliata</i> (diatoms)	L <sup>9</sup> , A <sup>9</sup>	Perkins (1974)
1	Emulsions toxic to lobster larvae		Wells (1972)
	100% death of <i>Gadus morhua</i> (cod) eggs		Kuhnhold
	Death of lobster larvae		Wells (1972)
	1 hr. LC50 for <i>Eminius modestus</i> (barnacle), and for <i>Nauplius</i> larvae		Spooner (1968)
	24 hr. exposure toxic to <i>Calanus</i> (copepod)	A <sup>9</sup>	Mironov (1970)
	83.7% fertilization of <i>Crassostrea virginica</i> eggs, 81.9% embryo development, 75.2% larval survival	L <sup>8</sup>	
0.1	24 hr. exposure toxic to <i>Rhodeus sericeus</i> (bitterling)		Malacee (1964)
	No avoidance response by <i>Oncorhynchus gorbuscha</i> (pink salmon) fry in fresh water at 5° C	A <sup>8</sup>	Rice (1973)
	96 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry in fresh water at 5° C	A <sup>8</sup>	Rice (1973)
	48 hr. LC50 for <i>Cyprinodon variegatus</i> (sheepshead minnow)	L <sup>8</sup>	Anderson et al. (1974)
	48 hr. LC50 for <i>Fundulus similis</i>	L <sup>9</sup>	Anderson et al. (1974)
	48 hr. LC50 for <i>Menidia beryllina</i> (silverside)	L <sup>8</sup>	Anderson et al. (1974)
0.01	48 hr. LC for <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)
	<i>Mytilus edulis</i> (mussels) unable to attach properly	A <sup>9</sup>	Moore et al. (1974)
	48 hr. LC50 for <i>Penaeus aztecus</i> (brown shrimp) post larvae	L <sup>8</sup>	Anderson et al. (1974)
0.001	Diminished growth rates in <i>Platymonas tetrahele</i> (flagellate)		Monmaerts-Villiet (1973)

\*1 mg/l = 1 ppm

<sup>a</sup>The data in the hydrocarbon toxicity table relate to observed effects of crude oils on marine organisms. In interpreting these data, it should be kept in mind that the hydrocarbons contained in offshore brines represent a specific fraction of crude oil: specifically, they are highly enriched in the soluble (particularly the aromatic) components of the oil. Although it is hard to make generalizations on the relationship between the chemical composition of crude oil and its toxicity to marine life, Ottway and others have found that toxicity roughly correlates with the content of aromatic hydrocarbons. Supplementary data have therefore been provided in Table 9-10 on the toxicity of specific oil fractions and components to marine organisms.

TABLE 6-9 (CONT.)

## TOXICITY TABLE - CRUDE OILS

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
	Increasing oil content decreased carbon uptake from 0 to 50% in phytoplankton		Gordon and Prouse (1973)
	48 hr. LC50 for <i>Cyprinodon variegatus</i> (sheepshead minnow)	L <sup>g</sup>	Anderson et al. (1974)
	48 hr. LC50 for <i>Fundulus similis</i> <sup>g</sup> and for <i>Menidia beryllina</i> <sup>g</sup> (silverside)	L <sup>g, s</sup>	Anderson et al. (1974)
	48 hr. LC50 for <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)
	24, 48 hr. exposures toxic to <i>Phoxinus phoxinus</i> (minnow)		Malacea et al. (1964)
	48 hr. LC50 for <i>Mysidopsis almyra</i> (mysid)		Anderson et al. (1974)
	<i>Oncorhynchus gorbuscha</i> (pink salmon) eggs resistant	A <sup>s</sup>	Rice et al. (1975)
	<i>Spartina anglica</i> (marsh grass) killed over long periods of time	L <sup>g</sup>	Cowell et al. (1972)
	Fucoid algae replaced barnacles and limpets	A <sup>g</sup>	
	48 hr. TL50 for <i>Penaeus aztecus</i> (brown shrimp) post larvae and for <i>Cyprinodon variegatus</i> (sheepshead minnow)		Anderson et al. (1974)
	48 hr. TL50 for <i>Mysidopsis almyra</i> (mysid)		Anderson et al. (1974)
	48 hr. TL50 for <i>Palaeomonetes pugio</i> (grass shrimp) and <i>Fundulus similis</i>	L <sup>g</sup>	Anderson et al. (1974)
	Avoidance response in <i>Oncorhynchus gorbuscha</i> in sea water at 7.5° C	A <sup>s</sup>	Rice (1973)
	96 hr. TLM of <i>Oncorhynchus gorbuscha</i> (pink salmon) fry in fresh water	A <sup>s</sup>	Rice et al. (1974)
	48 hr. TL50 for <i>Fundulus similis</i>	L <sup>g</sup>	Anderson et al. (1974)
	48 hr. TL50 for <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)
	80% reduction in oxygen production of <i>Enteromorpha intestinalis</i>	A <sup>s</sup>	Shiels (1973)
	Composition of phytoplankton population altered		Shiels (1973)
	50% inhibition of <i>Pseudomonas</i> sp. chemotaxis		Walsh and Mitchell (1973)
	No noticeable effect on <i>Homarus americanus</i> (lobster)		Atena and Stein (1974)
	Interference with chemosensory and feeding behavior of <i>Homarus americanus</i>		Atena and Stein (1974)
	Increase in photosynthesis of <i>Pecus distichus</i>	A <sup>g</sup>	Shiels (1973)
	95% reduction in photosynthesis of <i>Enteromorpha intestinalis</i>	A <sup>s</sup>	Shiels (1973)
	Lobster larvae encounter difficulty in surviving; unable to achieve 4th moult		Wells (1972)
	Reduction in blood hematocrit in <i>Siganus rivulatus</i> (rabbitfish) with 168 hr. exposure		Eisler (1975)
	No cell division or division delayed in <i>Glenodinium foliaceum</i>		Perkins (1974)
	No cell division or division delayed in <i>Chlorella curvisetum</i>	L <sup>g</sup>	Perkins (1974)
	No effect on <i>Molocira moniliformis</i>	L <sup>g</sup> , A <sup>g</sup>	Perkins (1974)
	Lethal toxicity to <i>Diogenes pugilator</i> (crustacean)		Perkins (1974)
	Abnormal development of <i>Balanus</i> and <i>Pachyscapus</i> larvae	A <sup>g</sup>	Mironov (1970)
	4.2 days to death for <i>Gadus morhua</i> (cod) larvae		Moore et al. (1974)
	99% <i>Gadus morhua</i> (cod) killed by 100 hr. exposure		Moore et al. (1974)
	24 hr. TL50 for <i>Menidia beryllina</i> (silverside)	L <sup>s</sup>	Anderson et al. (1974)
	No avoidance response from <i>Oncorhynchus gorbuscha</i> (pink salmon) fry at 7.5° C	A <sup>s</sup>	Rice (1973)
	48 hr. TL50 for <i>Mysidopsis almyra</i> (mysid)		Anderson et al. (1974)
	48 hr. TL50 for <i>Menidia beryllina</i> (silverside)	L <sup>g</sup>	Anderson et al. (1974)
	65% reduction in photosynthesis of <i>Caldophora stimuleonii</i>	A <sup>g</sup>	Shiels (1973)
	Photosynthesis reduced in <i>Ulva fenestrata</i> , <i>Laminaria saccharina</i>	A <sup>g</sup>	Shiels (1973)
	48 hr. TL50 for <i>Menidia beryllina</i> (silverside)	L <sup>s</sup>	Anderson et al. (1974)
	48 hr. TL50 for <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)
	96 hr. TLM for <i>Oncorhynchus gorbuscha</i> (pink salmon) fry in salt water	A <sup>s</sup>	Rice et al. (1975)
	96 hr. exposure toxic to sunfish		Cairns and Scheier (1962)
	96 hr. TLM for <i>Menidia beryllina</i> (silverside)	L <sup>s</sup>	Anderson et al. (1974)
	96 hr. TLM for pink salmon eggs	A <sup>s</sup>	Thomas and Rice (1975)
	20% decrease in respiratory rate of <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)

\* 1 mg/l = 1 ppm

TABLE 6-9 (CONT.)  
TOXICITY TABLE - CRUDE OILS

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
100,000	20% mortality of <i>Clupea harengus</i>		JWPCF (1972)
	Increase in opercular rates of <i>Oncorhynchus gorbuscha</i> (pink salmon) fry with 24 hr. exposure	A <sup>B</sup>	Thomas and Rice (1975)
	50% inhibition of phytoplankton photosynthesis in June, Port Valdez	A	Shiels (1973)
	Toxic to <i>Balanus balanoides</i> (barnacle)	A <sup>B</sup>	Moore et al. (1974)
	No mortality of <i>Clupea harengus</i> at 240 hrs.		JWPCF (1972)
	50% inhibition of photosynthetic rate in Port Valdez plankton	A	Shiels (1973)
10,000	25% decrease in respiratory rate of <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)
	Avoidance response by pink salmon fry in sea water at 11.5° C	A <sup>B</sup>	Rice (1973)
	96 hr. Tim for pink salmon fry, parr, smolts	A <sup>B</sup>	Thomas and Rice (1975)
	10 day exposure suppressed growth in <i>Chlorella vulgaris</i> (phytoplankton)		Moore et al. (1974)
	<i>Cosmarium</i> Sp. (phytoplankton) growth inversely proportional to percent saturation during 12 day exposure		Moore et al. (1974)
	10 day exposure had no effect on <i>Chlorococcum</i> Sp. (phytoplankton)		Moore et al. (1974)
1,000	No cell division or delayed cell division of <i>Licmophora ehrenbergii</i> (diatom)		Perkins (1974)
	100% death of <i>Gymnodinium kovalenskii</i> (dinoflagellate)	L <sup>B</sup>	Perkins (1974)
	8-4 days to death for <i>Gadus morrhua</i> (cod) larvae exposed 1 day		Moore et al. (1974)
	63% <i>Gadus morrhua</i> (cod) killed during 100 hr. exposure		Moore et al. (1974)
100	100% mortality of flounder spawn	L	Environmental Studies Board (1972)
	Copepods show "sensitivity"	L, A	Environmental Studies Board (1972)
	Toxic to copepods <i>Acartia clausii</i> and <i>Oithona nana</i> after 4 day exposure	L <sup>B</sup>	Mironov (1968)
	93-8% fertilization of <i>Mytilus lateralis</i> eggs, 91.9% development of embryos, 84-8% survival of larvae		
	90% fertilization of <i>Crassostrea virginica</i> (American oyster) eggs, 91.5% development of embryos, 83% survival of larvae	L <sup>B</sup>	
10	30% decrease in respiratory rate of <i>Palaeomonetes pugio</i> (grass shrimp)		Anderson et al. (1974)
	No avoidance response in pink salmon at 11.5° C	A <sup>B</sup>	Rice (1973)
	Decreased growth of fry of <i>Oncorhynchus gorbuscha</i> (pink salmon); 10 day exposure	A <sup>B</sup>	Rice (1975)
	100% increase in photosynthesis of <i>Ulva fenestrata</i>	A <sup>B</sup>	Shiels (1973)
	100% death of <i>Ditylum brightwellii</i> (diatom)	A <sup>B</sup>	Perkins (1974)
	No effect on <i>Coscinodiscus granii</i> (diatom)	A <sup>B</sup> , L <sup>B</sup>	Perkins (1974)
	No effect on <i>Chaetoceros curvisetus</i> (diatom), <i>Glenodinium foliaceum</i> (dinoflagellate)	L <sup>B</sup>	Perkins (1974)
	No cell division or delayed cell division of <i>Gymnodinium foliaceum</i> (dinoflagellate)	L <sup>B</sup>	Perkins (1974)
	No cell division or delayed cell division of <i>Gymnodinium wulfii</i>	L <sup>B</sup>	Perkins (1974)
	No effect on time to death of larvae of <i>Gadus morrhua</i> (cod) after one day exposure		Moore et al. (1974)
	57% increase in mortality of <i>Gadus morrhua</i> (cod) following 100 hr. exposure		Moore et al. (1974)
	40% increase in mortality in <i>Gadus morrhua</i> (cod) following 100 hr. exposure		Moore et al. (1974)
0.1	Fertilization not affected, fertilized egg development interfered with in <i>Seromyxionotus purpuratus</i> (sea urchin)	A <sup>B</sup>	Moore et al. (1974)
	No effect on <i>Peridinium trochoideum</i> (dinoflagellate)	L <sup>B</sup>	Perkins (1974)
	No effect on <i>Gymnodinium kovalenskii</i> (dinoflagellate)	L <sup>B</sup>	Perkins (1974)
	No effect on <i>Licmophora ehrenbergii</i> (diatom)		Perkins (1974)
	No cell division or delayed cell division of <i>Prorocentrum trochoideum</i> (dinoflagellate)		Perkins (1974)
0.01	5 day exposure delayed cell division in numerous species of phytoplankton		Mironov (1970)
	killed eggs of Black Sea turbot in 2-3 days		Moore et al. (1974)
	Delayed or inhibited cell division in plankton		Mironov (1971) (WOC 1972 342)
	No effect on <i>Licmophora ehrenbergii</i> (diatom)		Perkins (1974)
	No effect on <i>Gymnodinium kovalenskii</i>	L <sup>B</sup>	Perkins (1974)
0.001	Caused death of fish eggs and larvae		Perkins (1974)

\*1 mg/l = 1 ppm

TABLE 6-9 (CONT.)

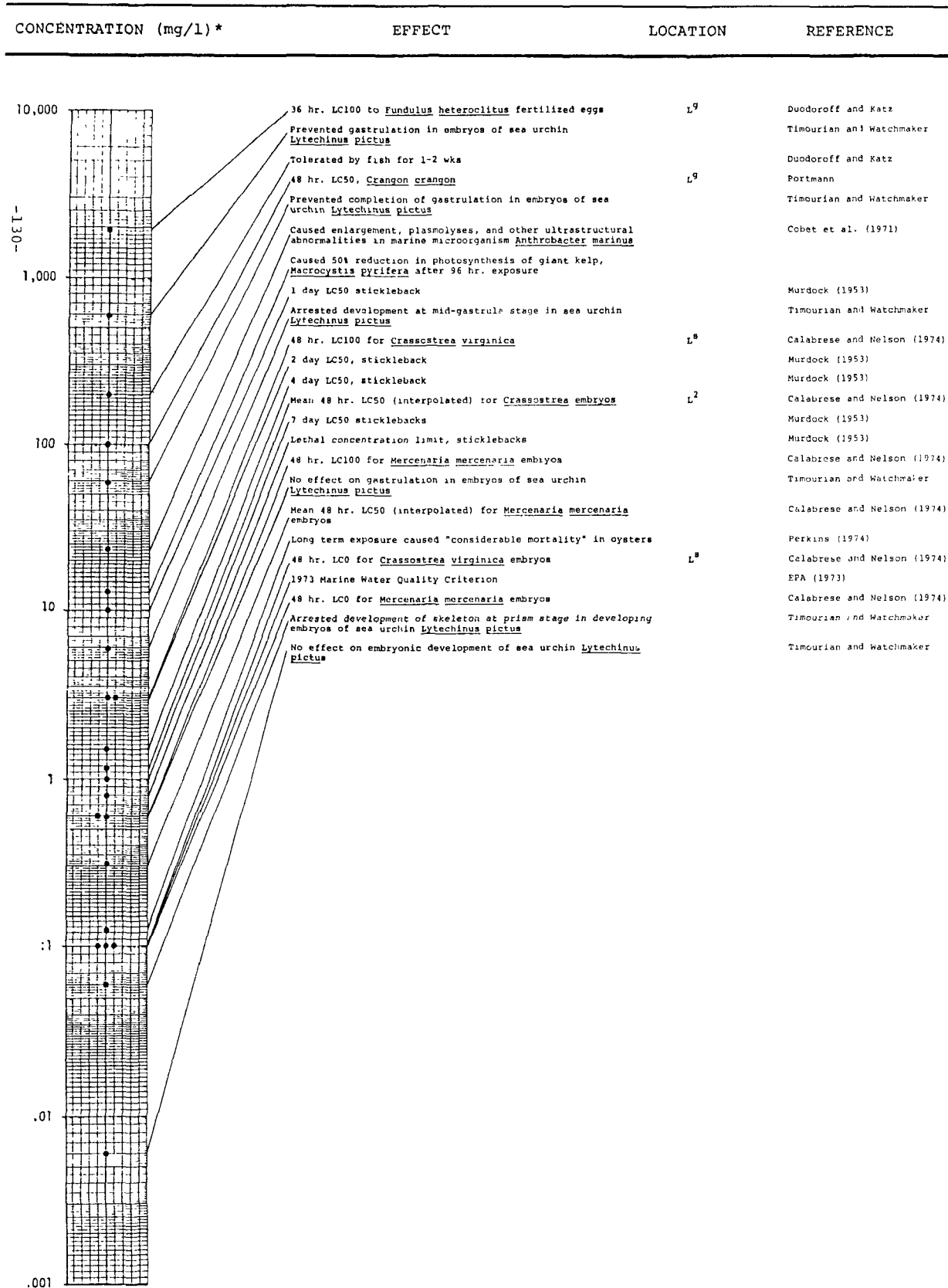
## TOXICITY TABLE - CRUDE OILS

CONCENTRATION (mg/l) *	EFFECT	LOCATION	REFERENCE
100,000	Injured embryos of <u>Rhombus maeoticus</u> (plaice); 40-100% of hatchlings degenerated and died		Mironov (1967) (WQC 1972 341)
	Abnormal development of flounder spawn		
	Taint tasted in <u>Crassostrea virginica</u> (American oyster)	L <sup>8</sup>	Menzel (1948)
	Deformed and inactivated larvae of <u>Rhombus maeoticus</u> (plaice)		Mironov (1968)
	30% increase in photosynthetic rate of <u>Costaria</u>	A <sup>9</sup>	Shiels (1973)
	100% increase in photosynthetic rate of Port Valdez plankton	A	Shiels (1973)
10,000	Inhibited attraction to food source of <u>Nassarius phaeolatus</u> (mud snail)	L <sup>9</sup>	Atema et al. (1973)
	Stimulates plankton growth		
	Inhibited feeding and mating responses of male <u>Pachygrapsus crassipes</u>		Takanashi (1973)
	Increase of carbon uptake in phytoplankton		Gordon (1973)
1,000			
100			
10			
1			
0.1			
0.01			
0.001			

\*1 mg/l = 1 ppm

TABLE 10

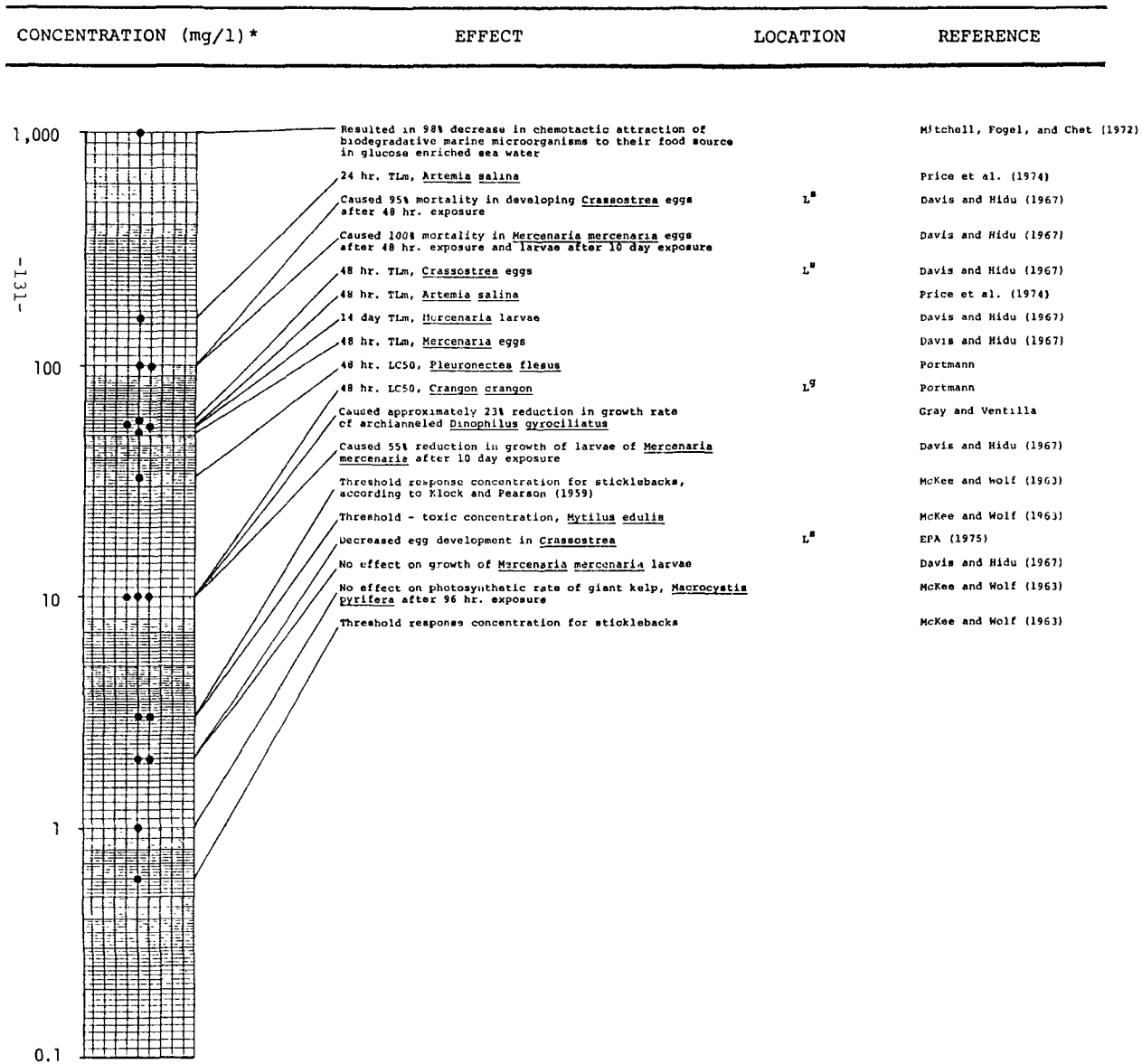
## TOXICITY TABLE - NICKEL



\*1 mg/l = 1 ppm

TABLE 6-11

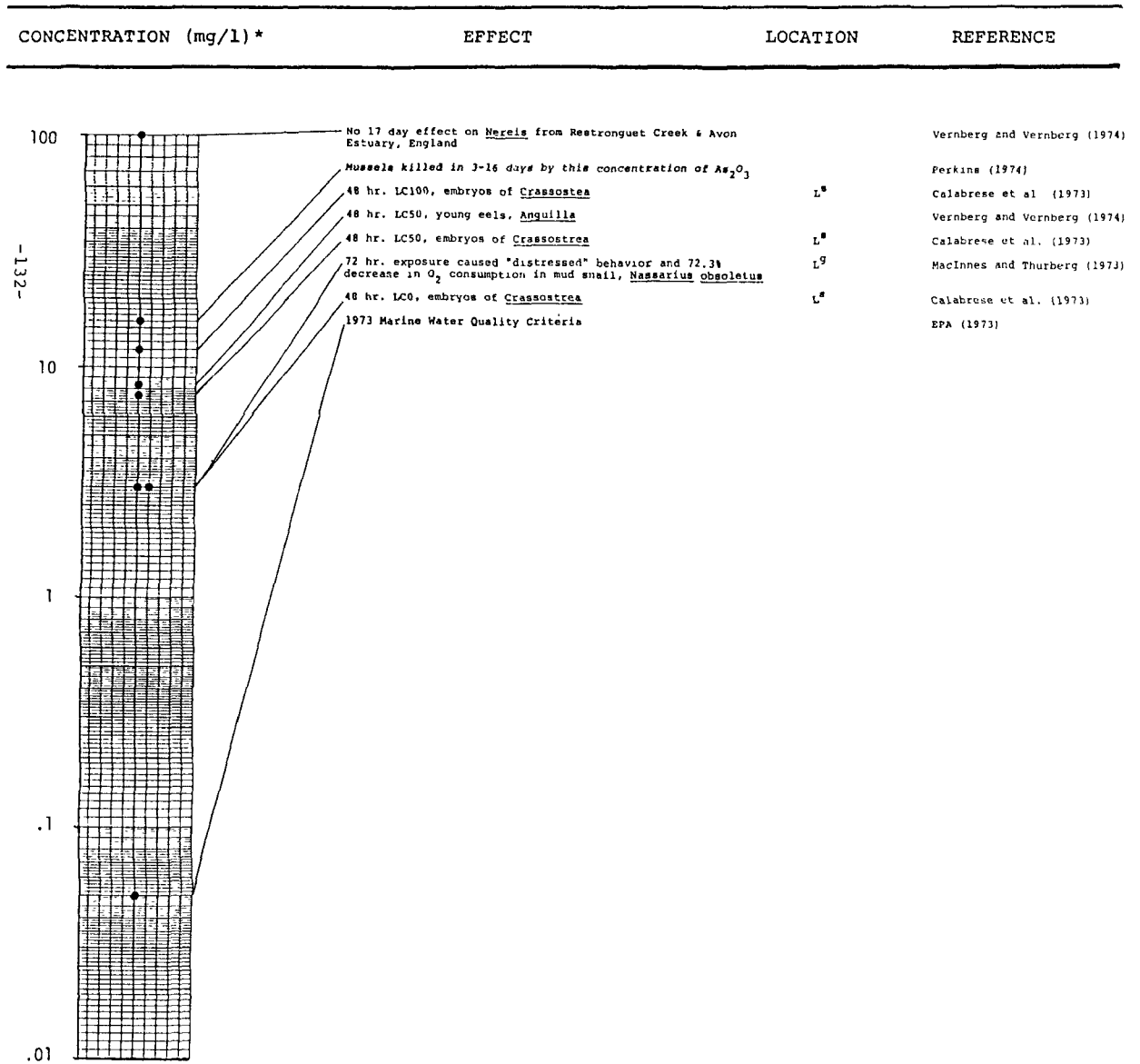
## TOXICITY TABLE - PHENOL



\*1 mg/l = 1 ppm

TABLE 6-12

## TOXICITY TABLE - ARSENIC



\*1 mg/l = 1 ppm



TABLE 6-13

EFFECTS OF CRUDE OIL FRACTIONS

CONCENTRATION (ppm)	HYDROCARBON	EFFECT	REFERENCE
0.0008	Kerosene: water-soluble fraction	No effect on attraction to scallop homogenates of <u>Nassarius obsoletus</u> (marine snail)	Jacobson and Boylan (1973)
0.001	Kerosene: water-soluble fraction	No effect on attraction to oyster extract of <u>Nassarius obsoletus</u> (marine snail)	Jacobson and Boylan (1973)
0.004	Kerosene: water-soluble fraction	Reduced attraction to scallop homogenate of <u>Nassarius obsoletus</u> (marine snail)	Jacobson and Boylan (1973)
0.06	Aromatic fraction of kerosene	Induced searching behavior in <u>Homerus americanus</u> (lobster) at distance; repulsed <u>H. americanus</u> at close range	Atema et al. (1973)
0.08	Water-soluble fraction dimethylnaphthalenes	24-hour LC50 for <u>Penaeus aztecus</u> (Brown shrimp)	Anderson et al. (1974)
0.180	#2 fuel oil	Interference with phospholipid metabolism in marine fish after 180 day exposure suggesting altered membrane structure	Sabo and Stegeman (in press) 1975
0.7	Dimethylnaphthalenes	24-hour LC50 for <u>Palaemonetes pugio</u> (Grass shrimp)	Anderson et al. (1974)
0.7	2-methylnaphthlene	24-hour LC50 for <u>Penaeus aztecus</u> (Brown shrimp)	Anderson et al. (1974)
0.75-0.8	Bunker C.	Increase in crawling and respiration rates of <u>Littorina littorea</u> (snail)	Hargrave et al. (1973)
1.00-100	Diesel fuel, emulsion	Loss of photosynthetic ability by <u>Macrocystis augustifolia</u> (seep) after 7-day exposure	Moore et al. (1974)

TABLE 6-13 (CONT.)

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CONCENTRATION (ppm)	HYDROCARBON	EFFECT	REFERENCE
1.0	Toluene, naphthalene, 3,4 benxpyrene	Not toxic to <u>Mytilus edulis</u> (mussel) after 6-day exposure	Moore et al. (1974)
2.0	2-methylnaphthlene	24-hour LC50 for <u>Cyprinodon variegatus</u> (Sheepshead minnow)	Anderson et al. (1974)
1.7	2-methylnaphthalene	24-hour LC50 for <u>Palaemonetes pugio</u> (Grass shrimp)	Anderson et al. (1974)
2.4	Naphthalene	24 hour LC50 for <u>Cyprinodon variegatus</u> (Sheepshead minnow)	Anderson et al. (1974)
2.5	Naphthalene	24 hour LC50 <u>Panaeus aztecus</u> (Brown shrimp)	Anderson et al. (1974)
2.6	Naphthalene	24 hour LC50 for <u>Palaemonetes pugio</u> (Grass shrimp)	Anderson et al. (1974)
3.4	1-methylnaphthalene	24 hour LC50 for <u>Cyprinodon variegatus</u> (Sheepshead minnow)	Anderson et al. (1974)
4.5-5.0	Phenanthrene	1 hour exposure fatal to sunfish	Moore et al. (1974)
4.0-5.0	Naphthalene	1 hour exposure fatal to sunfish	Moore et al. (1974)
4.0-15.0	Benzene	10 percent decrease in survival of <u>Engraulis</u> <u>mordax</u> (Northern anchovy) larvae with 48 hour exposure	Struhsaker et al. (1974)
4.0-25.0	Benzene	20 to 50 percent increase in abnormal <u>Engraulis</u> <u>mordax</u> (Northern anchovy) 3 day larvae as a result of 48 hour exposure	Struhsaker et al. (1974)
4.0-25.0	Benzene	Larvae of <u>Engraulis mordax</u> (Northern anchovy, larger at day 6	Struhsaker et al. (1974)
4.7	Benzene	10 percent decrease in 3 day survival of <u>Engraulis mordax</u> (Northern anchovy) larvae following 24 hour exposure	Struhsaker et al. (1974)

TABLE 6-13 (CONT.)

CONCENTRATION (ppm)	HYDROCARBON	EFFECT	REFERENCE
4.7-55.0	Benzene	20 percent increase in abnormal <u>Engraulis mordax</u> (Northern anchovy) larvae at day 6 following 24 hour exposure	Struhsaker et al. (1974)
5.0	Kerosene	Tainting of <u>Mugil cephalus</u> (mullet) tissue	Connel (1971)
5.0	Benzene	80 percent increase in oxygen consumption rate of <u>Oncorhynchus tshawytscha</u> (Chinook salmon) after 48 hours of exposure; subsequent decrease to 130 percent of normal value at 96 hours	Brocksen and Bailey (1973)
5.0	Benzene	Increased oxygen consumption in <u>Morone saxatilis</u> (Striped bass) to 24 hour peak of 130 to 145 percent of the normal value, with subsequent return to normal	Brocksen and Bailey (1973)
5.1	Dimethylnaphthalene	24 hour LC50 for <u>Cyprinodon variegatus</u> (Sheepshead minnow)	Anderson et al. (1974)
6.7	Benzene	Growth rate of <u>Clupea pallasii</u> (Herring) larvae decreased by 48 hour exposure	Struhsaker et al. (1974)
10.0	Benzene	48 hour exposure produced 120 percent increase in oxygen consumption in <u>Oncorhynchus tshawytscha</u> (Chinook salmon), with a return to normal consumption at 96 hours	Brocksen and Bailey (1973)
10.0	Benzene	Decreased oxygen consumption in <u>Morone saxatilis</u> (Striped bass) after 24 to 48 hours of exposure, with a return to normal by 96 hours	Brocksen and Bailey (1973)
10.0	Benzene	3 to 4 hour exposure produced lethal toxicity in <u>Rutilus sp.</u> (Roach)	Moore et al. (1974)
10.0	Methylcyclohexane	3 to 4 hour exposure produced lethal toxicity in <u>Rutilus sp.</u> (Roach)	Moore et al. (1974)

TABLE 6-13 (CONT.)

CONCENTRATION (ppm)	HYDROCARBON	EFFECT	REFERENCE
10.0	Benzene	Slight photosynthesis inhibition in <u>Macrocystis</u> <u>augustifolia</u> (Kelp) caused by 96 hour exposure	Moore et al. (1974)
10.0	n-hexane	No effect of <u>Macrocystis</u> <u>augustifolia</u> (Kelp) seen with 96 hour exposure	Moore et al. (1974)
10.0	Toluene	96 hour exposure resulted in visible injury, 75 percent reduction in photosynthesis of <u>Macrocystis</u> <u>augustifolia</u> (Kelp)	Moore et al. (1974)
10.0	Cyclohexane	3 to 4 hour exposure produced lethal toxicity in <u>Rutilus</u> <u>sp.</u> (Roach)	Moore et al. (1974)
12.1	Benzene	25 percent mortality of <u>Clupea</u> <u>pallasi</u> (Herring) larvae after 48 hour exposure	Struhsaker et al. (1974)
22.0-65.0	Xylene, toluene, benzene, ethylene	Lethal toxicity to sunfish	Moore et al. (1974)
25.0-50.0	O-xylene	Slight inhibition of growth of <u>Chlorella</u> <u>vulgaris</u> (Phytoplankton), 10 day exposure	Moore et al. (1974)
25.0-250.0	Toluene	Slight inhibition of growth of <u>Chlorella</u> <u>vulgaris</u> (Phytoplankton), 10 day exposure	Moore et al. (1974)
25.0-500.0	Benzene	Initial inhibition for 2 days, then growth of <u>Chlorella</u> <u>vulgaris</u> during 10 day exposure	Moore et al. (1974)
38.0	Kerosene	Depresses growth rate of <u>Asterionella</u> <u>japonica</u> (diatom)	Aubert et al. (1969)
40.0-400.0	#2 fuel oil	Lethal to <u>Thalassiosira</u> <u>pseudonana</u> (diatom)	Pulich et al. (1974)
40.0-55.0	Benzene	Larvae of <u>Engraulis</u> <u>mordax</u> (Northern anchovy) smaller at days 3 and 6 after 24 hour exposure	Struhsaker et al. (1974)

TABLE 6-13 (CONT.)

CONCENTRATION (ppm)	HYDROCARBON	EFFECT	REFERENCE
45.0	Benzene	20 percent increase in abnormalities, 10 percent decrease in survival in <u>Clupea pallasii</u> (Herring) eggs as a result of 24 hour exposure	Struhsaker et al. (1974)
45.0	Benzene	50 percent mortality of <u>Clupea pallasii</u> (Herring) eggs	Struhsaker et al. (1974)
57.0	Kerosene	Toxic to <u>Asterionella japonica</u> (diatom)	Aubert et al. (1969)
100.0	Tetralin	Exposure up to 6 days toxic to <u>Mytilus edulis</u> (Mussel)	Moore et al. (1974)
500.0	Toluene	Lethal toxicity to <u>Chlorella vulgaris</u> (Phytoplankton) with 10 day exposure	Moore et al. (1974)
500-1,744	Benzene	Lethal toxicity to <u>Chlorella vulgaris</u> (Phytoplankton) with 10 day exposure	Moore et al. (1974)

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### 6.3.2 Sublethal Effects

Tables 6-2 through 6-13 deal with a number of different toxic effects, primarily lethality, but including a number of important sublethal effects. Although sublethal effects might not result in direct mortality, they can nevertheless have severe ecological consequences if they decrease the rate at which organisms can find food, escape predation, or produce offspring. Although the majority of past work has dealt with parameters of lethality, the direction of current research is towards further exploration of important sublethal interactions. Among the important sublethal effects of brine pollutants are:

1. "Economic effects," i.e., effects which reduce the marketability of economically important marine organisms. An example is the "greening" of oysters in solutions containing moderate concentrations of copper, due to the bioaccumulation of copper by the organism.
2. Histo- and cytopathology -- Exposure to sublethal concentrations of trace metals and hydrocarbons has been shown to produce extensive tissue damage, at the light or electron microscope levels, in gill, kidney, and liver tissue. Such damage can reduce life expectancy and productivity, and, if it occurs in lateral line or taste bud tissues, can reduce the extent to which a fish can find food or avoid predation.
3. Biochemical alterations -- Some studies are reported in the tables of the effect of trace metals on the assay levels of certain key enzymes in fish, and other studies have tried to determine by electrophoresis the effect of sublethal exposures on the concentrations of various serum proteins. The use of acetylcholinesterase levels as an indicator of exposure to certain organophosphorus pesticides has received particular attention. Although such biochemical parameters are hard to interpret in terms of effects on ecosystems, they seem to indicate pathological conditions which have the potential of reducing the survival rates, fertility, or adaptability of a species.
4. Physiological parameters -- Included in this category are effects on blood ion concentration, EKG rates, blood cholesterol levels, or hematocrit

levels of affected fish populations. A small number of studies have been conducted on the effects of pollutants on these parameters, particularly on freshwater fish; an excellent review is provided by Sprague.<sup>4</sup> Again, data such as these are hard to interpret directly, but they can be used as "early warning signs" of potentially dangerous toxic conditions.

5. Effects on growth and productivity.
6. Effects on viability, as indicated by rates of O<sub>2</sub> consumption, particularly in gill tissue.
7. A toxic substance, even if it creates no noticeable toxic effects by itself, can significantly reduce the resistance of an organism to other environmental stressors, including DO stress, salinity stress, and thermal stress.
8. Behavioral effects -- Included in this category are effects on mating or swimming behavior which might affect survival and growth rates of the organism and species. Another important sublethal behavioral response to pollutants is the avoidance response; that is, the avoidance by fish of waters which contain particular levels of a trace metal. Such an effect is important because it can prevent spawning migrations of fish. Sprague et al.<sup>5</sup> note that "in the laboratory, avoidance responses can be obtained at less than one-tenth of the incipient lethal level (i.e., threshold) concentrations." Such behavioral effects are most important if they affect behavioral patterns important for survival. Stephenson and Taylor, for example, have noted a decrease in burrowing activity of clams associated with sublethal copper toxicosis<sup>6</sup> and in an elegant experimental system involving the use of a radioactive mercury tracer,

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<sup>4</sup>Sprague, "Measurement of Pollutant Toxicity of Fish," p. 257.

<sup>5</sup>J.B. Sprague et al., "Sublethal Copper-Zinc Pollution in a Salmon River: A Field and Laboratory Study," International Journal of Air and Water Pollution 9 (1965): 531-545.

<sup>6</sup>Stephenson and Taylor, "Influence of ETDA on Mortality and Burrowing Activity of Clams."

Kania and O'Hara demonstrated that sublethal exposures to mercury(II) reduced the efficiency of the mosquitofish Gambusia in escaping predation by the bass Micropterus.<sup>7</sup>

9. Reproductive effects -- Data in the tables include some effects of trace metals on development. Such effects can range from lethality of eggs and embryos to minor developmental defect initiation (teratogenesis) which could reduce the survival rate of the hatched young. Generally, such effects occur at levels far below the lethal concentrations for the organisms.
10. Aggregate effects on production in communities -- A few experiments have been done on the effects of pollutants on harvestable crops, productivity, and diversity in natural freshwater ecosystems; presumably, in the near future similar studies will be initiated in marine or estuarine systems.
11. Effects on performance (e.g., swimming ability).
12. Effects on disease resistance.

Each of the effects discussed above is important in that it can produce gross alternations in the populations, productivity, and diversity of a community without producing any significant mortality effect in a laboratory bioassay system. For this reason, it is important that available data on sublethal effects can be taken into account in setting standards, and that such standards not be designed to simply prevent significant direct mortality as a result of exposure to a pollutant.

### 6.3.3 Restrictions of the Data Base

Ideally, toxicological data would provide us with precise qualitative and quantitative descriptions of the effects which can be expected in particular organisms in the presence of specific levels of pollutants. In practice, this is made impossible by the highly complex nature of the pollutant toxicity problem. Consider, for example, the problems associated with the assessment of oil toxicity.

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<sup>7</sup>Kania and O'Hara, "Behavioral Alterations in a Simple Predator-Prey System Due to Sublethal Exposure to Mercury," Transactions of the American Fisheries Society (1) (1974): 134-136.

First, oil itself is not a chemically well-defined substance, but a complex mixture of literally hundreds of organic and inorganic compounds, each with its own specific toxicological properties. Since oils from various parts of the world differ widely in their content of specific substances, "oil" per se can have no well-defined toxicity. Furthermore, even though extensive data are available on the toxicity of some of the individual components of crude oils, their effects when mixed together can be complicated by a variety of synergistic or antagonistic interactions. An additional problem arises from the fact that none of the components of oil are stable through time, either with respect to their physical form, their chemical composition, or their distribution over sediments and the dissolved and suspended fractions of the region being considered (as is discussed in Appendix C).

The reaction of an organism to toxic pollutants will be modified by a number of environmental factors; so that the wide diversity of possible environments, combined with the even greater difference between any natural marine environment and a laboratory bioassay system, make it practically impossible to extrapolate toxicity data obtained in one experimental system under a highly specific set of conditions to any other system or any other set of conditions. According to Evans and Rice:<sup>8</sup>

Within these environments are several...physical conditions such as temperature, salinity, oxygen, and nutrient concentration, as well as biological differences such as species composition, diversity and density, and community metabolic rate. The prediction or assessment of pollution effects on the basis of observations extrapolated from one environment to another is seldom supported by adequate data. Unfortunately, however, few data on pollution effects exist for most areas and species, which has led to the use of information from areas that may be dissimilar in critical ways.

Another problem involved in the application of published laboratory or field data to the assessment of pollutant effects was recently discussed by Smith:<sup>9</sup>

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<sup>8</sup>D.R. Evans and S.D. Rice, "Effects of Oil on Marine Ecosystems: A Review for Administrators and Policy Makers," Fishery Bulletin 72 (1974): 625.

<sup>9</sup>A.W. Smith, Oil Pollution and Marine Ecology (London: Plenum Press, 1973), p. 99.



Data about the effects of oil pollution on marine plants and animals have been obtained from experiments in the field or laboratory and from observations of actual incidents or chronically polluted habitats... Toxicity tests in the laboratory are usually designed to result in death in a few days, so they cannot be expected to reveal long-term effects. They are often made on organisms which are convenient for experimentation rather than important in a threatened environment; different results are obtained according to the way in which the pollutant is applied, the life-stage of the organism used or the season in which it is collected and tested, so that tests made in different laboratories may be far from comparable. Often the importance of these factors was not realized when the tests were made, so that many of the circumstances surrounding them were not recorded. In the field, factors other than the pollutant may also be at work and are rarely under the control of the observer, if they are even known to him; adequate measurement of those contributory factors which are recognized cannot usually be made, so that reports are often incomplete and anecdotal.

Because of these factors, toxicity data reported even for a single compound and a single organism may exhibit wide variation; it has been reported, for example, that LC50 data collected at different laboratories for a single substance may show a standard deviation of close to one-quarter of the mean.<sup>10</sup> These factors must be kept in mind in applying the data given on the toxicity tables.

Available data permit neither valid quantitative extrapolation of data from one environment to another, nor the accurate prediction of the effect of such factors as weathering and emulsification on the toxicity of crude oil to individual organisms and its overall effect on ecosystems. Nevertheless, any consideration of the analysis performed in this report should be done with at least a qualitative understanding of the important factors modifying toxicity in the marine environment. This discussion is intended to emphasize these factors.

Of course, one of the principal factors affecting the long-term toxicity of pollutants is the existence of environmental processes which can degrade or transform them, or result in their transfer between different compartments of

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<sup>10</sup>W.R. Hunter, "The Poisoning of Marinogammarus marinus by Cupric Sulphate and Mercuric Chloride," Journal of Experimental Biology 26(2) (1949): 113-124.

the marine environment (water, bottom sediments, suspended particulates, etc.). These processes are discussed in Appendix C, and they can have a significant effect on the toxicity of the compound involved. Microbial or photo-chemical degradation processes, for example, will ultimately eliminate hydrocarbon toxicants from the marine environment and therefore reduce the toxicity problem created by them. Nevertheless, some of the intermediates in the degradation process can be even more toxic than their precursors.

The toxicity of trace metals in particular will be affected by sedimentation, but the data on the relative toxicities of the dissolved and precipitated forms of various metals are sparse and occasionally contradictory. Generally, dissolved metals can be expected to be more accessible to living organisms than suspended ones, except for filter feeders or benthic burrowing organisms (e.g., *Nereis* sp.). These observations should be considered in the light of the general rule, enunciated by Bryan, that "in the absence of much evidence to the contrary, it seems reasonable to suppose that most of the factors affecting toxicity owe their influence to changing the rates at which metals are absorbed" or the extent to which they are available for biological absorption.<sup>11</sup>

Other transformations to which hydrocarbons and trace metals are subject in the marine environment, such as adsorption, complexation, oxidation and reduction, and biological transformation can also affect their toxicity. Some examples are:

1. Chelation -- Experiments with oysters<sup>12</sup> have shown that toxic effects of high levels of copper are reduced or eliminated in the presence of chelating agents such as EDTA. Presumably, the organometal complex is less readily absorbed by the organism than is the metal ion itself. Similar effects may be observed in the marine environment with natural complexing agents. Some experiments have been performed with cyanide and ammonium complexes of copper, with the result that complexation generally lowers the toxicity of a particular metal.

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<sup>11</sup>G.W. Bryan, "The Effect of Heavy Metals (Other than Mercury) on Marine and Estuarine Organisms," Proceedings of the Royal Society of London 177 (1971): 389.

<sup>12</sup>Stephenson and Taylor, "Influence of EDTA on Mortality and Burrowing Activity of Clams."

2. Biological transformations -- In situ biological transformations may drastically affect the availability or toxicity of a trace metal. One example of this which has received particularly intensive study is the microbial transformation of  $Hg^+$  ions into highly toxic methylmercury compounds. A number of recent reviews have dealt with the rate of this process and its implications for the environmental toxicology of mercury.<sup>13</sup>
3. Oxidation -- Cuprous antifouling compounds have been found to undergo slow but spontaneous oxidation to the cupric form in seawater, and similar oxidations may occur for other transition elements in seawater, for example, mercury ( $Hg^+$  to  $Hg^{++}$ ) and chromium ( $Cr^{+++}$  to  $Cr^{+6}$ ). In many cases, the toxicity of the oxidized species can differ greatly from that of the reduced form. For example, trivalent chromium compounds are known to be much less toxic than the corresponding hexavalent forms.

Such effects are often not simulated in laboratory bioassay systems, but are nonetheless important in modifying the toxicity of a trace metal to a test organism. Furthermore, the bioassay procedure itself may produce a variety of artifacts not representative of interactions in the marine environment. For example, Collier et al.<sup>14</sup> note that in static bioassay systems, scavenging of pollutants from solution by some of these processes may exceed the rates at which such scavenging occurs in a natural environment: "There are certain disadvantages inherent in tests performed in static water. Among these are possible loss of toxicant

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<sup>13</sup>See S. Jensen and A. Jernelev, "Biological Methylation of Mercury in Aquatic Organisms," Nature 223 (1969): 753; and S. Skerfving, "Mercury in Fish -- Some Toxicological Considerations," Food and Cosmetic Toxicology 10 (1972): 545-556.

<sup>14</sup>R.S. Collier et al., "Physiological Response of the Mud Crab, Euypanopeus depressus, to Cadmium," Bulletin of Environmental Contamination and Toxicology 10(6) (1973): 380.

via aeration, adsorption of the toxicant by the container, and uptake of the toxicant by the test animal."<sup>15</sup>

Other factors, including the existence of other environmental stresses (such as thermal or dissolved oxygen stress), and the conditions or life-cycle stage of the affected organism, can also influence the toxicity of pollutants in the marine environment. Table 6-14 summarizes some of the important factors influencing trace metal toxicity in the marine environment. Factors influencing hydrocarbon toxicity are summarized in Table 6-15.

#### 6.3.4 Interpretation of Data

Data on lethality, which is still the most abundant form of toxicological data for marine organisms, are reported in three key ways:

1. Measures of average percent mortality at a given level of exposure to a toxic substance (other factors held constant) for various lengths of time. The measure used here is known as the LT (lethal time)  $\times$  n, where n is the percent mortality observed in a population. This statistic is only meaningful if a particular concentration or dose of a toxic substance is specified. A 50 ppm LT50, then, refers to the mean exposure time necessary to cause 50 percent mortality in a population exposed to 50 ppm of a toxic substance. Needless to say, this statistic, like the ones below, is both substance- and organism-specific.
2. Measures of average percent mortality at a given time of exposure to a toxic substance (other factors held constant) for various levels of exposure. The measure is known as LC (lethal

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<sup>15</sup>In other words, the metal may be absorbed on the cuticle of the animal or on other body surfaces where it would have essentially no physiological effect. This process would result in a decrease in the effective metal concentration to which the organism is exposed, and could only be prevented in some sort of flow-through (non-static) bioassay system. This absorption of metal ions on external body surfaces is also important to keep in mind in interpreting bioaccumulation data: if accumulation in the whole organism is measured, substantial artifacts are created by the high, but physiologically irrelevant amounts of metal on the external cuticle.

TABLE 6-14

FACTORS INFLUENCING THE TOXICITY OF  
HEAVY METALS TO AQUATIC ORGANISMS

FACTORS			REFERENCES <sup>a</sup>	METALS	ORGANISMS
FORM OF METAL IN WATER	Soluble	ion	Clarke (1947)	Cu	Crustaceans
		complex	Doudoroff (1956)	Cu, Zn, Cd, Ni	Fish
		chelate	Grande (1967)	Cu, Zn	Fish
		compound	Corner & Sparrow (1957); Clarke (1947)	Hg, Cu	Crustaceans
	Particulate	precipitate	Herbert & Wakeford (1964)	Zn	Fish
		adsorbed			
PRESENCE OF OTHER METALS OR POISONS	Antagonistic Effects		Lloyd & Herbert (1962)	Ca on Zn, Cu, Pb	Fish
	Additive Effects		Brown (1968)	Zn, Cu, Phenol, Cyanide, Ammonia	Fish
	Synergistic Effects		Corner & Sparrow (1956)	Cu, Hg	Crustaceans
FACTORS INFLUENCING PHYSIOLOGY OF ORGANISM AND POSSIBLY FORM OF METAL IN WATER	Salinity		Herbert & Wakeford (1964)	Zn	Fish
	Temperature		Lloyd & Herbert (1962)	Zn	Fish
	Dissolved Oxygen		Lloyd (1961)	Zn, Cu, Pb	Fish
	pH		Sprague (1964a)	Zn	Fish
	Light?		Gutnecht (1963)	Zn	Seaweed
CONDITION OF THE ORGANISM	Stage in Life-history		Pyefinch & Mott (1948)	Cu	Crustaceans
	Changes in Life-cycle (e.g. Moulting)		----	----	----
	Size of Organism		Skidmore (1967)	Zn	Fish
	Activity of Organism		Herbert & Shurben (1963)	Zn	Fish
	Acclimatization to Metals		Edwards & Brown (1967)	Zn	Fish

<sup>a</sup>Complete references for this table may be found on the following two pages.

Source: G.W. Bryan, "The Effects of Heavy Metals (Other Than Mercury) on Marine and Estuarine Organisms," Proceedings of the Royal Society of London 177 (1971): 389-410.

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TABLE 6-15

FACTORS AFFECTING PETROLEUM TOXICITY

FACTOR	EXAMPLE	REFERENCE
Oil Type	Oils high in aromatic hydrocarbon content tend to have high toxicity.	Ottway (1970)
Turbidity	Suspended particulates adsorb hydrocarbons and accelerate oil sedimentation. The transfer of hydrocarbons to the sediment is generally advantageous to tidal life and detrimental to benthic life.	Blumer et al. (1971)
Season	Sensitivity to toxicants can vary on a seasonal basis or between different lifecycle stages. Juvenile forms may be particularly sensitive.	Mironov (1969)
Nature of Substrate	Oil will tend to percolate into coarse, sandy sediments, allowing closer contact with infauna. Nature of sediment affects rate and degree of hydrocarbon adsorption. Adsorption affects availability to biota and rate of microbial degradation.	NAS (1975)
Synergisms	Environmental stressors such as salinity and DO extremes may increase oil toxicity.	NAS (1975) p. 86

References are on following page.



REFERENCES FOR TABLE 6-15

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National Academy of Sciences (Ocean Affairs Board, Commission on Natural Resources), Petroleum in the Marine Environment: Workshop on Inputs, Fates, and Effects of Petroleum in the Marine Environment, 1975, p. 85.

concentration)  $n$ , where  $n$  is the percent mortality observed in the population. For this statistic to be meaningful, a particular exposure time must be specified. For example a 96 hr LC50 is the concentration of a particular toxic substance which, after 96 hours of exposure, will cause 50 percent mortality in a population of a particular organism. 96 hr LC50 is a fairly common parameter of pollutant toxicity. It is also frequently referred to as the TL50 (toxic level 50), or TLM (mean toxic level).

3. Threshold measures -- The concept behind a threshold measure is that populations of an organism will display essentially zero mortality (no matter how large the population) below a particular level of exposure. Such a level is known as a threshold level, or, sometimes, an incipient lethal level. Current policy towards regulating water pollutants for the protection of aquatic and marine life, in which maximum permissible levels of pollutant concentrations (standards and criteria) are set, draws upon this threshold concept, and indeed there is much evidence for the existence of thresholds for particular organisms and particular pollutants. Sprague, for example, in an article on the toxicity of copper and zinc to young Atlantic salmon<sup>16</sup> notes that "the relationship between concentration of metal and survival time could be fitted by a straight line when logarithms were used. A sharp break in this relation marked the incipient lethal level, where survival becomes indefinitely long. Incipient lethal levels were 48  $\mu\text{g/l}$  (ppb) of copper and 600  $\mu\text{g/l}$  of zinc." (see Figure 6-3). In terms of the two parameters described above, the threshold level could be expressed as the LC0 for a particular time of exposure, or else as the concentration at which the LT0 becomes infinite (the latter was the definition used by Sprague in the reference cited above).

Of course, either of these measurements could be extended to effects other than lethality. In this case, the parameters are expressed as the (e.g.) EC50 or ET50, for effective concentration 50 and effective time 50, respectively.

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<sup>16</sup>J.B. Sprague, "Lethal Concentration of Copper and Zinc for Young Atlantic Salmon," Journal of the Fisheries Research Board of Canada 21(1) (1964): 17-26.

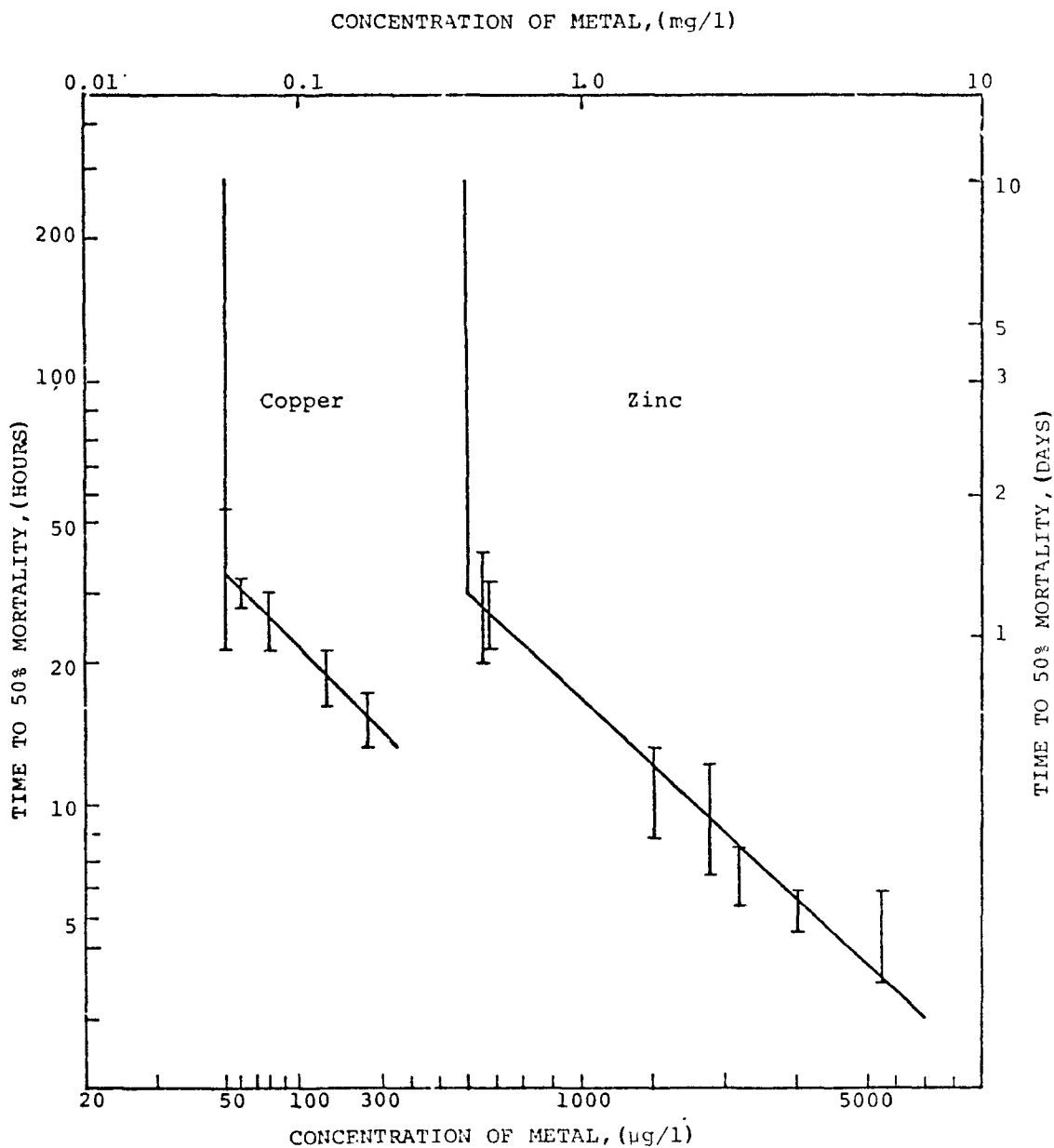


Figure 6-3. Median mortality-times of young Atlantic salmon exposed to solutions of copper and zinc. Vertical bars indicate 95 per cent confidence limits. The straight lines fitted to the points break and run parallel to the time-axis at the *incipient lethal levels*. The experimental water had a total hardness of 20 mg/l as  $\text{CaCO}_2$  temperature of 15° C and pH 7.1 to 7.5 except for two zinc tests indicated by black squares. These were at 17° and somewhat different pH values.

If threshold levels can be shown to exist for marine organisms (and a wide number of the studies reviewed for this report suggest that they do for particular pollutants and organisms), then they can be used as a basis for setting "safe levels" for the release of trace metal pollutants into seawater. It is therefore important to develop procedures for estimating threshold levels on the basis of available data.

Sprague<sup>17</sup> notes:

"Safe" level is used here in an admittedly loose way, to mean the concentration of pollutant which does not have an adverse sublethal or chronic effect on fish. It is not an entirely satisfactory term since it often implies more safety than actually exists, but other descriptive terms do not seem to have gained any wide acceptance. As used here, a safe level is a statistic, whose value is empirically determined as a result of an experiment. Its value is not assigned on the basis of judgment. If a probable safe level is inferred on the basis of incomplete information, it should be clearly labelled as probable or tentative. A safe level may be specified as referring to one particular life process such as reproduction, or to the absence of any and all observable effects. [One way of approximating the safe level would be to measure in a bioassay system] the median effective concentration (EC50), i.e., the concentration which just causes the selected response in 50 percent of the individuals...Following such practice, concentrations affecting a negligibly small percentage of individuals, such as the EC5 or EC1, could be estimated with a known degree of accuracy by conventional log probit analysis.<sup>18</sup> This has seldom been done in

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<sup>17</sup>See the data reviewed in J.B. Sprague, "Measurement of Pollutant Toxicity to Fish," p. 257.

<sup>18</sup>A probit distribution is the dose response relation expected in a population which exhibits normally distributed toxicity thresholds to a particular substance. For a particular level  $x$  of a toxic substance in water, the number of organisms affected will be all those with thresholds less than or equal to  $x$ , which is estimated, using the probit model, as the integral of the normal distribution for all concentrations below  $x$ . This model defines a relationship between level of exposure and percent mortality involving two undetermined parameters, whose value can be estimated by fitting experimental LC<sub>n</sub> data. Given values of these parameters, a dose/response curve is completely defined, so that estimates can be made of the dosage levels which would cause insignificant levels of mortality, e.g., the LC1 or LC5.

research on sublethal effects even when it might be advantageous; most investigators have attempted to estimate (directly)... the safe level. Sometimes such a "no-effect" concentration cannot be measured precisely. The parallel idea in lethal tests, of estimating the "minimum lethal concentration" has been abandoned in favor of the median lethal concentration.

Sprague here refers to two different methods for determining safe exposure levels: direct experimental determination of levels at which no effects are observed at statistically significant levels of incidence (a generally unreliable procedure), and the extrapolation of available EC<sub>n</sub> data (using probit or other models) to estimate EC<sub>1</sub>s or EC<sub>5</sub>s.

More conventionally, threshold levels are estimated using numbers called application factors. Sprague's review cites the work of Hart, who attempted to develop "an arithmetic method of extrapolating along the toxicity curve to the incipient LC<sub>50</sub>, with the ratios of different LC<sub>50</sub>s (e.g., the 96, 48, and 24 hr LC<sub>50</sub>s) simulating the slope of the curve... A basic feature of (their paper) is that they estimate the 'presumably harmless concentration' as essentially 0.3 of the incipient LC<sub>50</sub>. Indeed, Hart and colleagues recommend exactly that simple calculation when the incipient LC<sub>50</sub> is known." This factor of 0.3 is known as an application factor, and its purpose is to estimate safe or threshold levels when only median or other toxicological measures are known. Although application factors can be grounded in and confirmed by experimental results, or derived from models using probit or other assumptions, they are most generally derived from general considerations and the experience of professional toxicologists. The estimation of application factors for toxic substances for aquatic organisms has mostly been done for freshwater species, and the values used have ranged from 0.1 to 0.4 (to prevent lethality), or from 0.01 to 0.05 (to prevent chronic, sublethal and cumulative toxicity). The 1973 EPA Water Quality Criteria for marine life recommended for most metals an application factor of 0.01 of the 96 hr LC<sub>50</sub> for the most sensitive resident species, and this is the factor which should probably be used in evaluating the data presented in the tables. This application factor, applied to the median lethal level, was considered by the EPA to provide a margin of safety in preventing all significant toxic effects.

### 6.3.5 Adaptation Responses

It is reasonable to suppose that under conditions of environmental stress due to high levels of a toxic metal, a process of natural selection would favor a metal-resistant subpopulation of a particular species. Thus, relatively metal resistant organisms, having a relatively high LC50 or threshold level for the metal, would be found in chronically polluted waters, diminishing the toxic response to further pollution. This can be a significant factor in evaluating toxicity data, and in fact, it has been verified experimentally for the copper response of the estuarine polychaete Nereis. Bryan and Hummerstone<sup>19</sup> have noted that Nereis removed from an estuary with extremely high copper levels due to persistent industrial pollution exhibited a much higher LT50 at a particular copper concentration than did Nereis extracted from a relatively clean estuary.

### 6.3.6 Synergisms and Antagonisms

The interactions between two toxic substances can either be additive (i.e., the effect of exposing an organism to a concentration of one metal and another concentration of a second metal is the sum of the effects noted if the organisms are exposed to the same levels of each metal separately), synergistic (i.e., supra-additive), or antagonistic sub-additive). The literature on whether synergisms exist between toxicants is confusing and often contradictory; at a minimum, it would seem that the presence of synergisms is dependent upon the substances and species involved, and upon the levels of exposure. The degree of synergism is sometimes quantified by use of the toxic units concept. A toxic unit is defined as the concentration of a metal necessary to produce a well-defined effect (generally, the LC50 concentration for a particular exposure time is used); all concentrations of the metal can then be expressed as some fraction or multiple of this LC50. Now suppose an organism is exposed to 0.5 toxic units of copper and x toxic units of zinc, where x is variable. The interaction between the two metals is additive if 50 percent mortality is observed at the point when  $x = 0.5$  toxic units (i.e., the sum of the concentrations

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<sup>19</sup>Bryan and Hummerstone, "Adaptation of the Polychaete Nereis diversicolor to Estuarine Sediments Containing High Concentrations of Heavy Metals," Journal of the Marine Biological Association of the United Kingdom 51 (1971): 845-863.

of Zn and Cu is 1.0 toxic units), synergistic if 50 percent mortality is observed for x less than 0.5 toxic units, and antagonistic if 50 percent mortality is observed only when x becomes greater than 0.5 toxic units.

Some of the results of recent studies which bear on the synergistic or additive effects of trace metals on marine organisms are summarized below:

1. According to Sprague,<sup>20</sup> "In solutions containing both copper and zinc, fish died twice as fast as would occur if the two metals were simply additive in their lethal action" (see Figure 6-4).
2. Sprague and Ramsay<sup>21</sup> found an additive relationship between the toxicants copper and zinc in the vicinity of one toxic unit, but supra-additive relationships in the range two to five toxic units. Test organism: juvenile Atlantic salmon.
3. Barnes and Stanbury<sup>22</sup> found a synergistic interaction between the metals copper and mercury for the marine copepod Nitocra; for example 0.026 mg/l of copper produced zero percent mortality; the combination, however, produced 9.1 percent mortality (complete data are given in Table 6-16).

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<sup>20</sup>Sprague, "Lethal Concentrations of Copper and Zinc for Young Atlantic Salmon."

<sup>21</sup>Sprague and Ramsay, "Lethal Levels of Mixed Copper-Zinc Solutions for Juvenile Salmon."

<sup>22</sup>C. Barnes and Stanbury, "The Toxic Action of Copper and Mercury Salts Both Separately and When Mixed on the Harpacticoid copepod Nitocra," Journal of Experimental Biology 25(3) (1948): 270-275.

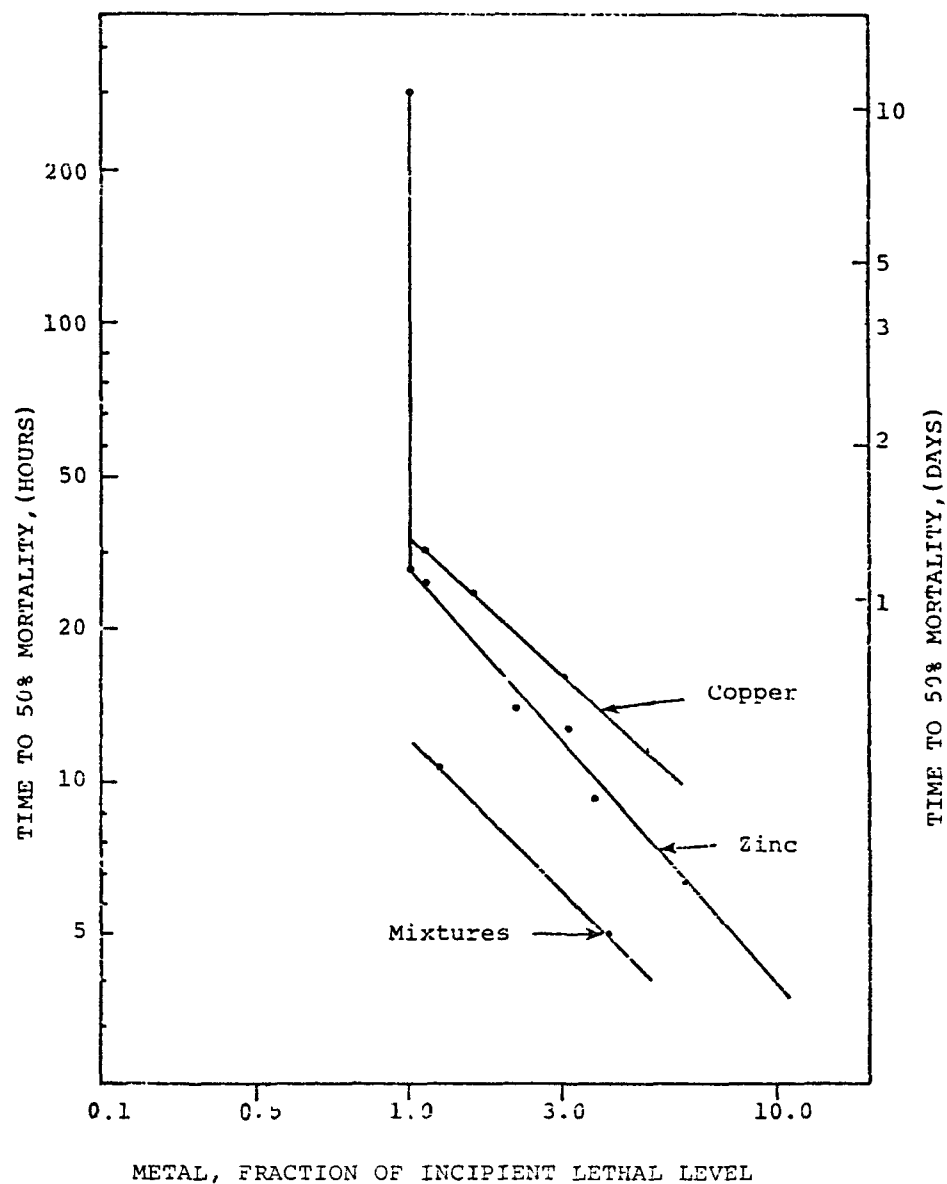


Figure 6-4. Comparison of median mortality-times of young Atlantic salmon exposed to solutions of copper, zinc, and mixtures. Concentrations are expressed as fractions of the incipient lethal levels, those for copper and zinc being added together for the 2 experiments with mixtures.



TABLE 6-16

EFFECT OF MERCURY AND COPPER ON THE  
MARINE COPEPOD NITOCRA (PERCENT MORTALITY)

Cu CONC Mg/1	Hg CONC Mg/1									
	0	0.07	0.15	0.31	0.40	0.60	0.70	1.5	3.0	4.4
0	0	0	1.4	10.0	16.7	50	72	78	84	100
0.026	1.3	9.1	14.5	12.7	50.0	61.8	76.4	87.3	100	100
0.26	11.3	11.9	20	45.6	43.7	100	100	100	100	100
2.6	21.2	-- <sup>a</sup>	78	82	98	100	100	100	100	100
26	42.5	--	--	--	--	--	--	--	--	--

<sup>a</sup>-- means not available.

4. Eisler and Gardner<sup>23</sup> found a synergistic interaction between zinc, copper and cadmium for the estuarine mummichog (Fundulus heteroclitus). Sample data: 60 ppm of zinc alone produced 27 percent mortality in 96 hours and 10 ppm of cadmium alone produced about 4 percent mortality in 96 hours; the combination of the two, however, produced 60 percent mortality in the same time period.
5. Corner and Sparrow<sup>24</sup> found evidence of synergistic interaction between copper and mercury (see Figure 6-5).

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<sup>23</sup>Eisler and Gardner, "Acute Toxicology to an Estuarine Teleost of Mixtures of Heavy Metals," Journal of Fishery Biology 5 (1972): 131-142.

<sup>24</sup>Corner and Sparrow, "The Modes of Action of Toxic Agents, I. Observations on the Poisoning of Certain Crustaceans by Copper and Mercury," Journal of the Marine Biological Association of the United Kingdom 35 (1956): 531-548.

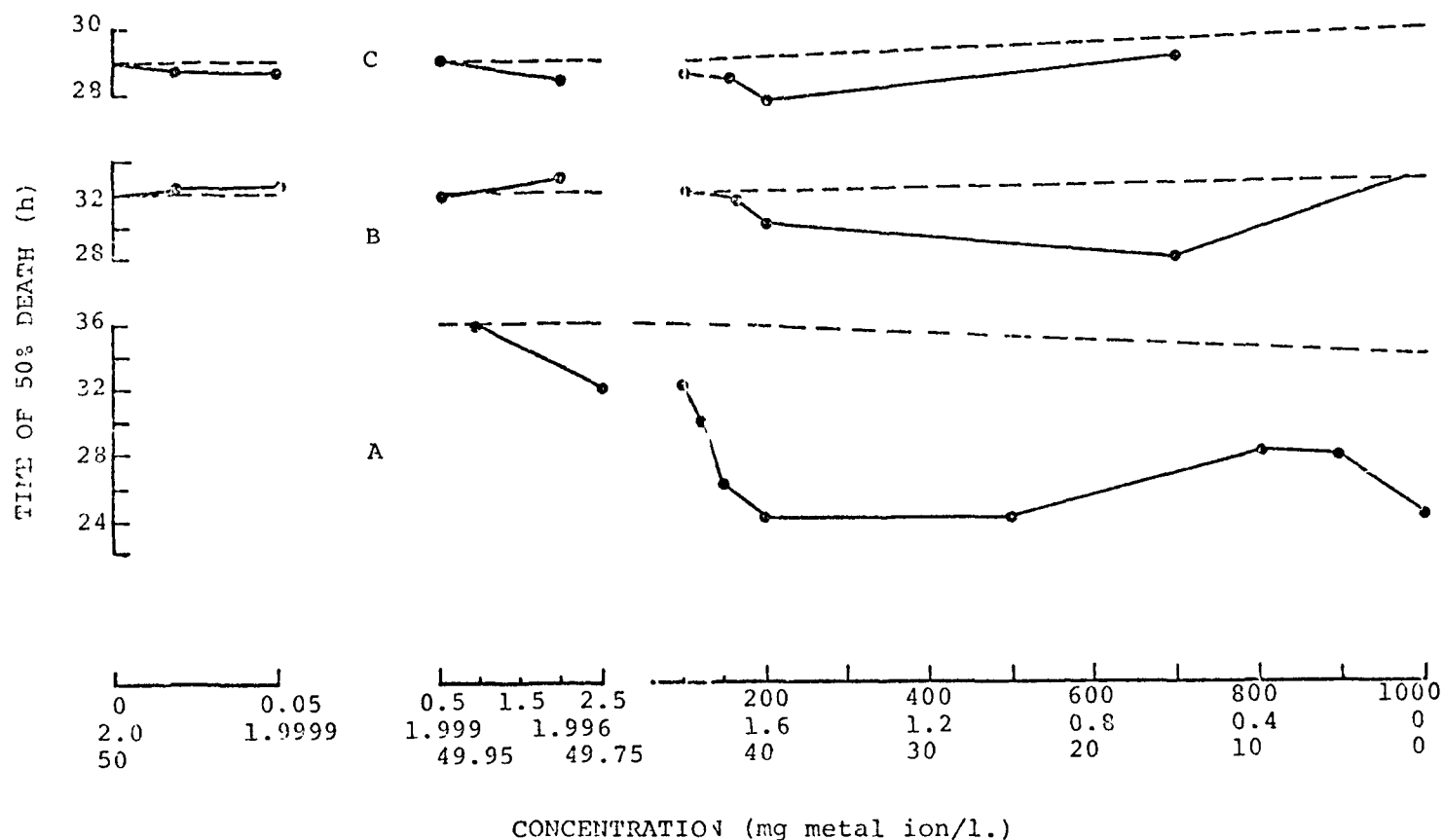


Figure 6-5. Effects of bipartite mixtures of equitoxic concentrations of copper sodium citrate and mercuric chloride (A), mercuric iodide (B), and ethylmercuric (C) on the survival of *Artemia* larvae in seawater (LT50), curves obtained experimentally; ----, theoretical curves expected if toxic effects of the mixed poisons were exactly additive). Concentrations of the metal ion measured as follows:  $\text{Cu}^{++}$  as citrate (upper row, 0...1,000),  $\text{Hg}^{++}$  as  $\text{HgCl}_2$  (lower row, 50...0).

6. Ventilla<sup>25</sup> found evidence for a synergistic effect on the growth rate of the marine protozoon Cristigera of the trace metals mercury, lead and zinc. The data are given below.

TABLE 6-17

EFFECTS OF MERCURY, LEAD AND ZINC ON THE  
GROWTH RATE OF CRISTIGERA

CONCENTRATION (ppm)	SUBSTANCE	REDUCTION IN GROWTH RATE (Percent)
0.005	HgCl <sub>2</sub>	12
0.3	Pb(NO <sub>3</sub> ) <sub>2</sub>	12
0.25	ZnSO <sub>4</sub>	13
(All three above, combined at the same concentrations)		67

Much more data are available, but the above references adequately demonstrate that synergistic interactions between trace metals can be significant in some systems.

Livingston<sup>26</sup> includes an interesting discussion on the mechanistic rationales for additive, supra-additive, and antagonistic effects.

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<sup>25</sup>Ventilla and J.S. Gray, "Growth Rates of a Sediment-Living Marine Protozoan as a Toxicity Indicator for Heavy Metals," Ambio 2(4) (1973): 118-121.

<sup>26</sup>American Petroleum Institute, U.S. Environmental Protection Agency, and Marine Technology Society, "Marine Bioassays: Workshop Proceedings" (Washington, D.C.: Marine Technology Society, 1974) pp. 245-253.

#### 6.3.7 Interactions Between Metals and Other Stressors

The presence of other environmental stressors, e.g., abnormal salt concentrations, abnormal temperatures as a result of thermal discharges, or abnormally low dissolved oxygen can increase the toxicity of brine pollutants. According to Vernberg and Vernberg:<sup>27</sup>

At optimum conditions of salinity and temperature (30 ppt, 25° C) fiddler crabs live almost indefinitely in seawater containing sublethal concentrations of mercury (0.18 ppm). They can also survive prolonged periods of time in low salinity water and high temperature (5 ppt, 35° C), but under the latter conditions the addition of sublethal concentrations of mercury resulted in an LD50 of 26 days for females and 17 days for males.

Although relatively little data are available in this area, it is an important field for further research.

#### 6.3.8 Note on Cyanide Toxicity

Sufficient data on the toxicity of cyanide to marine organisms was not available to enable a meaningful "safe" level for this toxicant to be set. Thus, the approach adopted in the 1975 Water Quality Criteria was used, in which it was stated:

The effects of cyanide on marine life have not been investigated adequately to determine separate water quality criteria, but based on the physiological mechanisms of cyanide, toxicity to marine life probably is similar to that of freshwater life. Since marine waters generally are alkaline, the toxicity of cyanide should be less than in freshwaters where pH fluctuations occur more readily and frequently. Thus, an additional safety factor exists to provide a margin of safety and compensation for a lack of specific data on which to base the criterion for marine aquatic life.

Therefore, as a tentative safe level the EPA criterion of 0.005 mg/l is adopted.

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<sup>27</sup>F.J. Vernberg and W. Vernberg, Environmental Physiology of Marine Animals (New York: Springer-Verlag, 1972), p. 331.

#### 6.4 Effects of Salinity

The natural salinity of seawater averages about 30 to 35 ‰ (parts per thousand). In the open sea this salinity is remarkably constant, although it may decrease by as much as a factor of ten in estuarine areas following heavy rainfalls, and increase by a factor of three or more in areas such as lagoons and tide pools where evaporation is important. The salinity of oilfield brines is comparatively very high; Mackin, for example, reports that Louisiana brines have salinities as high as 128 and 131 ‰.<sup>28</sup> It is reasonable to suppose that exposure of resident organisms to these abnormally high salinities would represent a severe environmental stress which could either produce direct lethal or sublethal effects or else decrease the resistance of the organisms to other environmental stressors such as temperature and trace metal pollution. Unfortunately, the overwhelming proportion of the literature on salinity stress (as reviewed by Vernberg and Vernberg<sup>29</sup> and others) deals with pathological effects of low salinities on marine or estuarine organisms (this is because salinity fluctuations downward from 30 ‰ are common in estuaries, where factors such as wind and temperature gradients can cause wide variations in the magnitude and spatial extent of seawater dilution due to the incoming river water. Low salinities have generally been considered, therefore, to be of greater environmental interest than high salinity situations). A number of papers have presented data from field studies on the effects of highly saline oilfield brines on local ecosystems, but these are of little use in estimating toxic effects of salinity alone because of the complicating presence of hydrocarbon and trace metal pollution in the brines.

The salinity of the brines would represent an extremely unsuitable environment for the internal operation of most marine organisms; so if they are to survive in the vicinity of these high salinities, they must be equipped with special osmoregulatory (e.g., active transport) systems to regulate their internal ion balance in the face of a tremendous

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<sup>28</sup>J.G. Mackin, A Review of Significant Papers on Effects of Oil Spills and Oilfield Brine Discharges on Marine Biotic Communities (College Station, Texas: Texas A&M Research Foundation, Project No. 737, February 1973), pp. 4-8.

<sup>29</sup>Vernberg and Vernberg, Environmental Physiology of Marine Animals, pp. 167-175.

salinity difference between their external environment and internal body fluids. Organisms which can maintain a constant internal environment independent of external salinity stress are known as osmoregulators, as opposed to osmoconformers, whose internal ion composition resembles that of their external medium. Another distinction commonly made is between euryhalinic species, which are capable of surviving in a wide range of salinities, and stenohalinic ones, which can only tolerate a rather narrow range of salinities. The two sets of terms are not equivalent; organisms can be partially osmoconforming and yet euryhalinic. Extreme osmotic stress may seriously weaken an organism and decrease its resistance to other environmental factors; or it may even saturate the organisms' osmoregulatory capabilities and eventually kill it.

Some quantitative data on the effect of high saline stress on organisms are summarized below.

1. Davis notes that "Colonies of the polyp Cordylohora caspia, grown from planulae, developed gonophores only in salinities between 5 and 16.7 ppt, but when normal colonies were amputated and allowed to regenerate, gonophores were formed at a wide range of salinities though not in fresh water nor in salinities higher than 30 ppt." Davis also states that the development of the eggs of the pupfish Cyprinodon macularius is inhibited at both the high and low extremes of salinity (up to about 85 ppt).
2. Figures 6-6 and 6-7, respectively, show the effect of salinity on the survival of adult fiddler crabs and the survival of Sesarma cinereum zoeae under thermal stress.
3. Vernberg and Vernberg note:<sup>30</sup> "Some animals can even survive extremely hypersaline conditions in tidal pools cut off from ocean waters. For example, fiddler crabs, Uca rapax, are commonly found living on the salt flats of Puerto Rico in salinities as high as 90 ‰. The strong ability to hyporegulate is evident in two species of crabs, Pacygrapsus crassipes and Hemigrapsus oregonensis, which are known to thrive in a hypersaline lagoon (66 ‰) cut off from the sea.

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<sup>30</sup> Vernberg and Vernberg, Environmental Physiology of Marine Animals, p. 70.

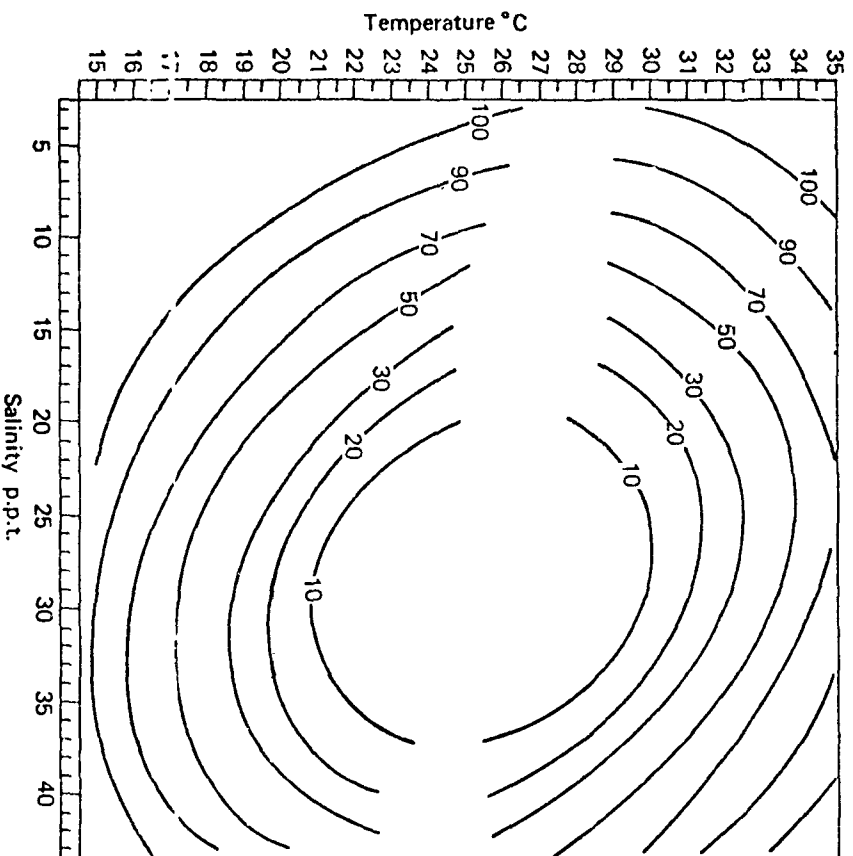


Figure 6-6. Estimate of percent mortality of first stage zoeae of Sesarma cinerium based on fitted response surface to observed mortality determined at 12 temperature salinity combinations. (In W. Verberg and F.J. Verberg, Environmental Physiology of Marine Animals (New York: Springer-Verlag, 1972), p. 167, from Costlow et al., 1960.)

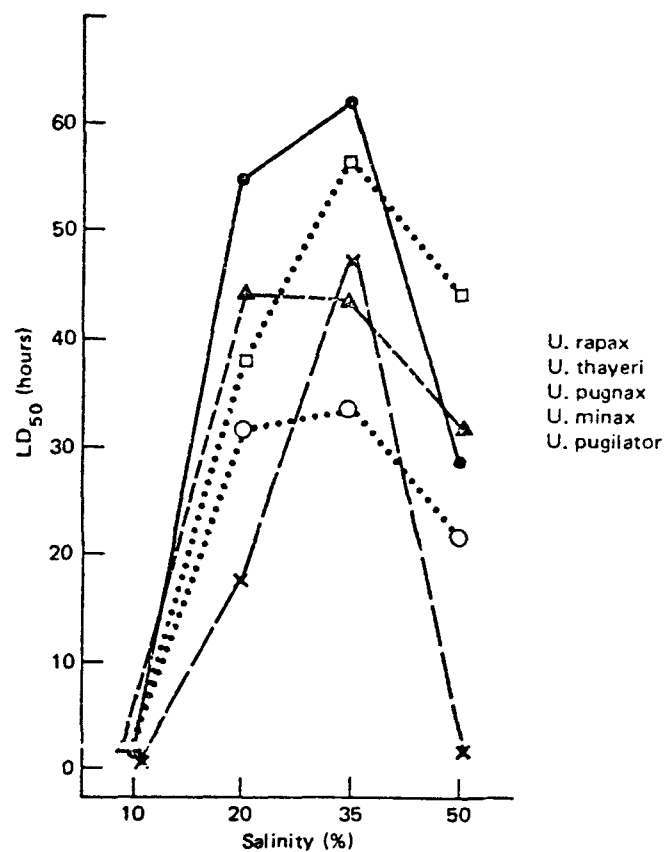


Figure 6-7. Survival of larval tropical and temperate zone fiddler crabs exposed to different salinities at 38° C. LD<sub>50</sub> indicates time required for 50 percent mortality. (Vernberg and Vernberg, Environmental Physiology of Marine Animals, p. 166.)



Some species of intertidal zone fish that inhabit protective rocky shores show remarkable tolerance to high salinities. Along the Texas coast where salinities in tide pools may reach very high levels, fish have been found living in salinities as high as 142.4 ‰.

Unfortunately, there do not seem to be enough quantitative data to support the type of analysis which is being performed for metals and oils. Salinity related effects will generally be ignored in this analysis, therefore. This may seem rather arbitrary, but that the assumption is not too severe is suggested by some of the data of Mackin,<sup>31</sup> and by our dispersion model outputs which show relatively rapid dilution of salinity within very small distances from offshore drilling rigs in Louisiana.

#### 6.5 Studies of Brine Toxicity and of the Effects of Brine Discharges at Offshore Production Sites

A key deficiency in the use of laboratory bioassay data in the prediction of on-site toxicity of oilfield brine components is that laboratory experiments are performed, almost by definition, under a single, highly controlled set of conditions. Although bioassay experiments always attempt to duplicate, to the extent possible, the conditions prevailing in the natural environment, it is impossible to capture in a laboratory system the multitude of highly variable physical, chemical and biological parameters which characterize actual oilfield sites. The issue was concisely stated by Mackin:<sup>32</sup> "The dream of developing a short-term laboratory study which would enable us to predict effects on natural communities of various pollutants is just that: a dream." For these reasons, field studies form an important complement to laboratory bioassay data.

Several studies have been performed on the ecology of oilfield production areas. Unfortunately, little, if any information is given in these studies regarding the rate of

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<sup>31</sup> Mackin, Review of Effects of Oil Spills on Marine Biotic Communities.

<sup>32</sup> Mackin, Review of Effects of Oil Spills on Marine Biotic Communities.

brine discharge at the study site so that it is difficult to evaluate the findings. The Gulf Universities Research Consortium (GURC) study on the ecology of oilfield areas is not germane to the objectives of the report since the production platforms studied were either not dischargers of brine or discharged brine only intermittently and in small quantities. Mackin has suggested a number of generalizations which can be drawn from field study data.

1. The key factor controlling the effects of oilfield brines on resident communities seems to be concentration. Dilution of the brines is extremely rapid, and reduction of the brines to apparently harmless levels seems to take place due to dilution before other environmental processes (e.g., degradation) have a chance to operate to any significant degree. According to Mackin, "The dilution in large waterbodies and comparatively deep water is almost instantaneous, and dilutions of 1,000 parts of seawater to one part of brine can be effected in even comparatively shallow water in distances of from 8 to 50 feet."
2. The area in the vicinity of an oilfield brine discharge can be divided into concentric "zones of effect," with successively less severe effects being observed in zones farther and farther from the discharge point. Mackin identified three zones: an inner zone in which all benthic organisms, except perhaps bacteria, are destroyed; a transition zone in which depression of both benthic species numbers and numbers of individuals is observed; and an outer "stimulation zone" in which productivity is actually increased over that distance from the discharge. The explanation for this stimulatory effect seems to be in the use of petroleum hydrocarbons as a nutrient source by bacteria, yeasts, fungi, and other phytoplanktonic organisms. The resulting rise in the phytoplankton populations stimulates those populations which feed on the phytoplankton. The role of petroleum as a toxicant in zones one and two but as a nutrient in zone three emphasizes again the importance of concentration and dilution in determining toxic effects of brine discharges.
3. Mobile organisms (e.g., fish) do not remain in zones one and two long enough to be effected, so the primary effect is confined to the largely sessile benthic organisms. Of course, indirect

ecological effects may result in nonbenthic populations as a result of the modification of the benthic communities.

Mackin cites a number of studies in his review to support this general model of oilfield brine toxicity. He discusses the studies of Lunz and others<sup>33</sup> on the toxicity of oilfield brines in bioassay systems to show that beyond a certain level of dilution no toxic effect is observed (note that by using the brine in a bioassay system, rather than its individual components, synergistic and antagonistic interactions are automatically taken into account). In one study of the toxicity of brines to Palaeomonetes pugio, the most toxic of the brines studied produced a 48 hr LC<sub>50</sub> of about 200,000 ppm to the most sensitive of the organisms studied. The least toxic brine had an LC 50 of about 1,000,000 ppm; i.e., a 100 percent brine solution would only kill 50 percent of the P. pugio individuals within 48 hours. The use of an application factor of .01 together with the "worst case" LC<sub>50</sub> gives an estimated "safe" concentration of about 2,000 ppm (corresponding to a dilution of one part of brine to 500 parts of normal seawater). In another study Lunz<sup>34</sup> showed that Louisiana brines (salinity 128 ppt) had no effect on the pumping rates of oysters at bioassay concentrations of from 10,000 to 50,000 ppm (1 to 5 percent). A threshold of about 3 percent was observed for any effect on the ability of oysters to clear a turbid medium.<sup>35</sup>

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<sup>33</sup>Mackin, Review of Effects of Oil Spills on Marine Biotic Communities.

<sup>34</sup>G.R. Lunz, The Effect of Bleedwater and of Water Extracts of Crude Oil on the Pumping Rate of Oysters, (College Station, Texas: Texas A&M Research Foundation, Project No. 9, 1950).

<sup>35</sup>E.J. Lund, "Effect of Bleedwater, Soluble Fraction, and Crude Oil on the Oyster," Publications of the Institute of Marine Science 4(2) (1957): 321-341.

Data collected by Menzel and Hopkins<sup>36</sup> seemed to confirm the existence of "zones of influence." These investigations were conducted in the Lake Barre Field (Texaco) in Louisiana, and showed heavy oyster mortality within about 25 feet of the drill platform, a zone of lesser mortality extending out to 75 feet from the platform, a zone of stunted growth extending out to about 150 feet from the platform, and no effect, except possibly some stimulation, beyond 150 feet. The stimulation effect was described as "weakly significant." The data for this field is shown in Figure 6-8. Note that toxic effects seemed to disappear beyond about 200 feet from the platform, so that the effects were rather local.

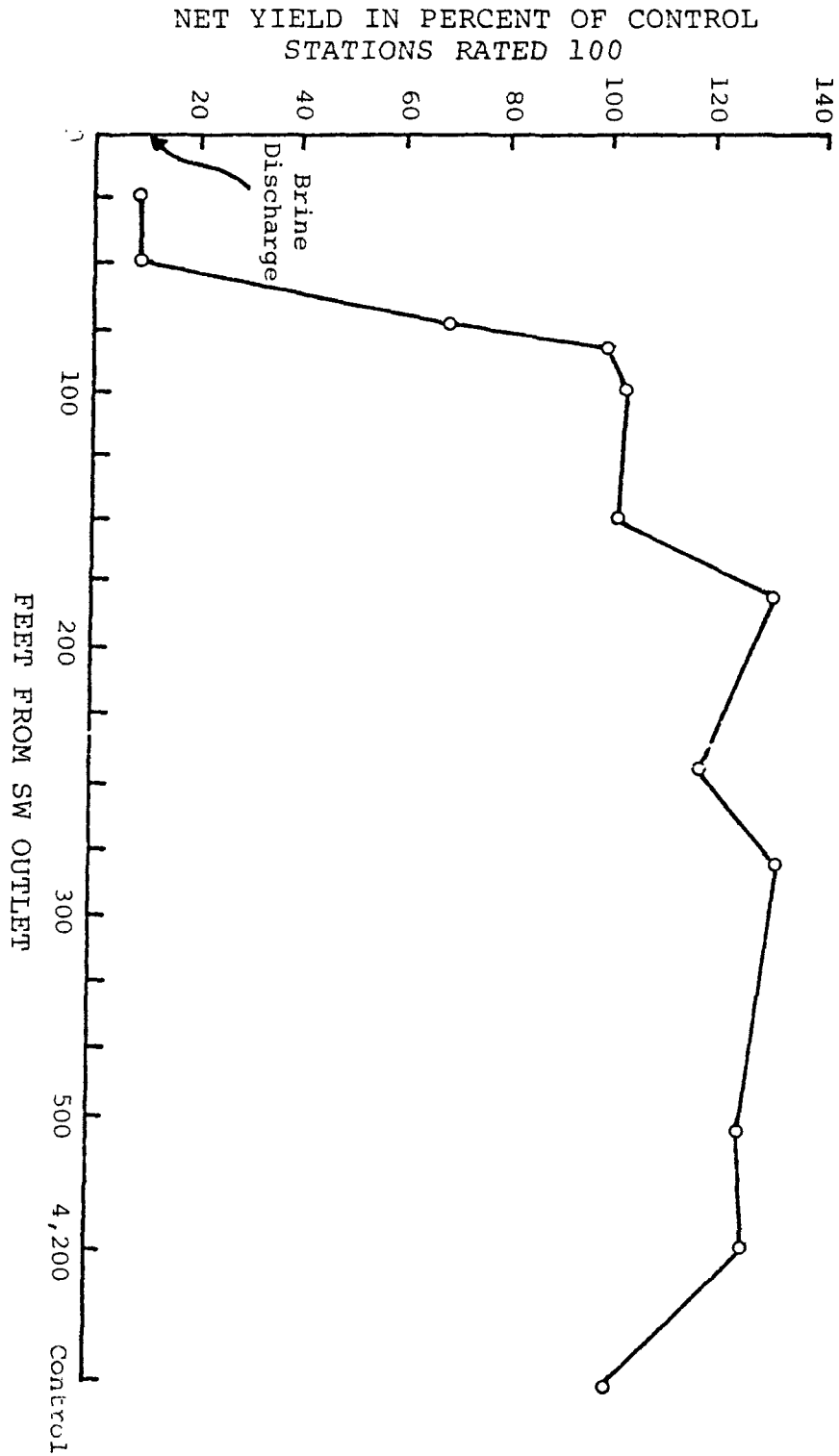
A similar study conducted by Mackin in 1971<sup>37</sup> also showed zones of effect. Zone one (as defined above) extended out to about 50 feet from the rig; zone two extended from about 150 to 200 feet; and zone three reached from 400 out to several thousand feet from the rig. This study involved an intensive program of biological characterization of the areas around six oil fields in Texas. The principal conclusions were that no effect was observed outside of a purely local one, and that the local effect was concentrated primarily on benthic organisms, with the more motile populations being totally unaffected. The indices of effect studies included number of species/station, number of individuals/sample, taxon diversity, species diversity, and reproductive capacity. Among the conclusions of this study were:

1. Exposed organisms exhibited a wide range of tolerances to the toxic effects of brines. The least sensitive were the polychaetes (this is consistent with a recent study of the adaptation

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<sup>36</sup>R.W. Menzel, Report on Oyster Studies in Caillou Island Oil Field, Terrebonne Parish, Louisiana (Texas: Texas A&M Research Foundation, Project No. 9, 1950); R.W. Menzel and S.H. Hopkins, Report on Experiments to Test the Effect of Oil Well Brine or Bleedwater on Oysters at Lake Barre Oilfield (Texas: Texas A&M Research Foundation, Project No. 9, 1951); and R.W. Menzel and S.H. Hopkins, Report on Oyster Experiments at Bay St. Elaine Oilfield (Texas: Texas A&M Research Foundation, Project No. 9, 1953).

<sup>37</sup>J.G. Mackin, A Study of the Effect of Oilfield Brine Effluents on Biotic Communities in Texas Estuaries (Texas: Texas A&M Research Foundation, Project No. 735, November 1971).



of the polychaete Nereis to high copper concentrations in an English estuary<sup>38</sup>), followed by the molluscs, followed by the Crustacea, which seemed to be the Mysicacea, the Tanaids, the grass shrimp, the amphipods, and the isopods.

2. The picture of an effect confined to a local inner zone of effect seems to be confirmed. Figure 6-9 shows typical data from the Trinity Bay field stations. Here, station 1 was located at about 50 to 75 feet from the rig; station 2 at 250 to 300 feet from the rig; station 3 at 500 to 550 feet from the rig; station 4 at 1,100 feet from the rig; and stations 5 through 12 equally spaced out to a final distance of about 2.5 miles.
3. "...All bottom invertebrates are sensitive to brine effluent if the concentration is sufficient and none are susceptible provided sufficient dilution and chemical and biological degradation occurs. In the Trinity Bay field there can hardly be any doubt...that there is a healthy, vigorous reproductive community in existence over the major area of the field."
4. "...In summary, the brine discharge showed an effect on bottom fauna in Trinity Bay field at Stations 1 and 2. The effect ended somewhere between Station 2 (300 feet from the brine discharge) and Station 3 (500 feet from the brine discharge)...and the area affected is approximately 0.015 percent of the total bay."

A somewhat less cheerful picture is presented by a number of studies conducted by the Texas Parks and Wildlife Department<sup>39</sup> on oil drilling operations in Chiltipin Creek in Louisiana. The report produced a variety of evidence to show that Chiltipin Creek was "nearly devoid of marine life"

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<sup>38</sup>Bryan and Hummerstone, "Adaptation of the Polychaete Nereis diversicolor."

<sup>39</sup>R.W. Spears, An Evaluation of the Effects of Oil, Oilfield Brine and Oil Removing Compounds, Environmental Quality Conference for the Extractive Industries of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., June 1971.

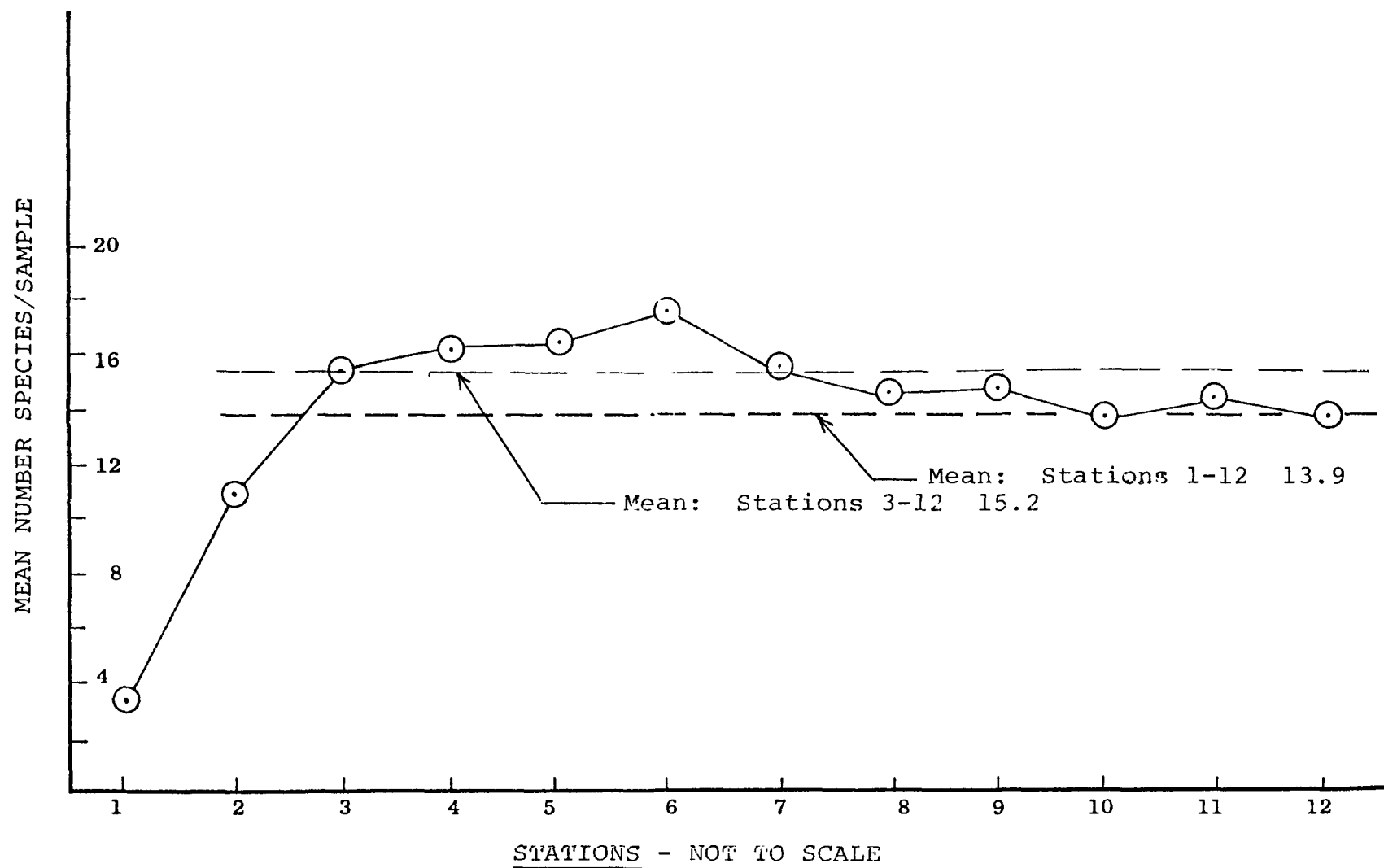


Figure 6-9. Trinity Field, Trinity Bay - Number of species in relation to the brine discharge at F<sub>1</sub> platform bottom samples. Each point is the mean of 12 monthly samples.

compared with nearby streams, unaffected by oil drilling operations, which had relatively rich populations of various organisms. Here relatively large amounts of brine were being produced and discharged into a relatively small receiving waterbody, producing highly toxic environments for marine life. (This contrasts with the situation observed in the areas studied by Mackin in which the receiving waterbody was a large bay.) Studies of the Chiltipin Creek area revealed that the production of two commercially important species (the white shrimp, Penaeus setiferus and the blue crab, Callinectes sapidus) were drastically reduced in Chiltipin Creek compared to neighboring tributaries. The effect seemed to be correlated with periods of low rainfall, and chemical investigation showed high concentrations of oil (above those specified by the Texas Water Quality Standards) in the Creek. This provided power evidence for a brine-related effect on the communities of the Creek.

A study conducted by Heffernan<sup>40</sup> under the auspices of the Chiltipin Creek project provided valuable data on the toxicity of brine. These data are summarized in Table 6-18. The bioassay test period in these figures was 48 hours.

Another important study of the effects of oilfield brines was conducted by Mackin and Hopkins in 1961 on Louisiana oilfields. The study was an attempt to trace the effects of brine discharges on the ecological communities of the study area, and involved consideration of a variety of historical, toxicological and environmental monitoring data. Four important conclusions of the study were as follows:<sup>41</sup>

1. The history of the oyster industry shows that Louisiana oysters have always been subject to high rates of mortality, and that periods of disastrously high mortality have been frequent as far back as the records go.

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<sup>40</sup>T.L. Heffernan, J. Monier, and S. Page, Effects of Oilfield Brine on Marine Organisms. An Ecological Evaluation of the Aransas Bay Area, Job No. 1, Texas Parks and Wildlife Department (1972).

<sup>41</sup>J.G. Mackin and S.H. Hopkins, "Studies on Oyster Mortality in Relation to Natural Environments and to Oil Fields in Louisiana," Publications of the Institute of Marine Science 7 (1962): 1-131.



TABLE 6-18

BIOASSAY DATA ON OILFIELD BRINES  
FROM CHILTIPIN CREEK AREA (TEXAS)

TEST ORGANISM	FACILITY	TLm (48 HOUR) (Percent)
Brown shrimp	Haas Ditch	24.5 - 26.5
White shrimp	Haas Ditch	28.0
Brown Shrimp	Southwestern Oil	18.0 - 21.5
White Shrimp	Southwestern Oil	13.5
Blue Crab	Southwestern Oil	21.0

2. The study of Louisiana oyster production statistics and oyster history showed that disastrously high mortality of oysters had occurred at times both before and after oil production began in the oyster-growing area, and that since oil production started there had been oyster mortalities in places far distant from oil operations as well as in and near oilfields.
3. Field studies of Texas A&M Research Foundation biologists, beginning in 1947, confirmed reports that mortality rates were high on many Louisiana oyster beds, and that there was a seasonal cycle

in mortality correlated with temperature. Except during abnormally warm periods there was little mortality in winter, but oysters began to die in spring and continued to die steadily all summer and into autumn until stopped by cool weather. The regular and predictable nature of this mortality indicated that it was not abnormal. The general picture was, rather, that a high rate of mortality associated with summer temperatures was normal in much of the Louisiana oyster-growing territory.

4. Field studies of Foundation biologists also showed that within the region where damage from oil operations was claimed (in general, Plaquemines, Jefferson, Lafourche, and Terrebonne Parishes) there were areas where oyster mortality was consistently low as well as areas of high mortality. No correlation was found between rates of mortality of oysters and their proximity to oilfields. Indeed, in the Barataria Bay area where most damage to oyster production was claimed, the highest mortalities were found at the stations farthest from centers of oil and bleedwater production. On the other hand, high mortality was found to be correlated with high salinity of the water.

This suggests that wide natural variations in mortality can frequently swamp any effects due to oilfield brines. One further important conclusion of the study was that "crude oil and fractions of crude oil are rapidly oxidized and destroyed by bacteria which live in Louisiana bay muds."

#### 6.6 Human Health Risks Associated with Oilfield Brines

Previous sections in this chapter have concentrated on the risk to fish, plankton, and benthic populations produced by oilfield brines. This section will consider the human health risks created by the concentration of potentially carcinogenic or otherwise toxic brine components in marine organisms which may be subsequently consumed by human beings. Two factors must be taken into account here: first, the rate at which these toxic substances are accumulated in individual organisms (bioaccumulation) and through the food chain (biomagnification); and secondly, the potential effects of these substances on human beings. Two cases in particular have attracted much attention in the technical literature: the problem of biological methylation of mercury in the

marine environment followed by bioaccumulation of the methyl mercury thus formed by shellfish destined for human consumption; and the problem of contamination of fish and shellfish with potential petroleum carcinogens such as benz[a]pyrene. First, background data on the bioaccumulation of trace metals and hydrocarbons will be reviewed, and then these two potential human health problems will be discussed.

#### 6.6.1 Bioaccumulation of Trace Metals

##### Cadmium

The normal concentration of cadmium in seawater is 0.11 parts per billion (ppb). Fleischer<sup>42</sup> has reported concentration factors for a variety of organisms. Concentration factors for zooplankton and jellyfish are 13,000 and 11,000 respectively. Most invertebrates show factors of from 1,000 to 10,000. Concentration factors in fish are generally less than 100. Accumulation is often greater in gills and visceral organs, as demonstrated by experiments on Chasmomyctus gulosus and Venerupis philippinarum.<sup>43</sup>

##### Chromium

Chromium is found in seawater at 0.05 ppb. Many marine organisms are capable of concentrating chromium by a factor of several thousand. Concentration factors on the order of 10,000 have been observed in Crassostrea Virginica (American oyster), Mya arenaria (softshell clam), and Mercenaria

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<sup>42</sup>M. Fleischer, A.F. Sarofim, D.W. Fassett et al., "Environmental Impact of Cadmium: A Review by the Panel on Hazardous Trace Substances," in Environmental Health Perspectives, May 1974, pp. 253-323.

<sup>43</sup>U.S. Environmental Protection Agency, Environmental Studies Board, Water Quality Criteria 1972, Washington, D.C. 1972.

mercenaria (quahaug).<sup>44</sup> Merlini<sup>45</sup> reports chromium levels 400,000 times those in the ambient environment in the testes of the sea urchin Tripneustis esculenta. High concentrations have also been found in the gills and gonads of the mummichog.<sup>46</sup>

### Copper

The concentration of copper in seawater is 3 ppb. Raymond<sup>47</sup> found copper accumulations in the gut and body wall of the worm Neresi virens. Copper uptake is temperature dependent, the rate roughly doubles with a 10° C increase in temperature. Uptake is proportional to animal size, and decreases with time following a peak after 20 hours of exposure. Seasonal changes influence the uptake of copper by Busycon canaliculatum, the channeled whelk. Uptake increases in the early summer with the beginning of the feeding period, and decreases during the fall and winter hibernation period. Copper is accumulated through the gills, where concentration increases to an equilibrium concentration after about one hour of exposure, when transport away from the gills equals the rate of intake. Copper is transported from the gills to the digestive gland. Experiments with Nereis diversicolor, another worm, show copper concentration to be roughly proportional to concentration in the sediments.<sup>48</sup> Worms from sediments of high

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<sup>44</sup>B. Pringle, D.E. Hissong, E.L. Katz, and S.T. Mulawka, "Trace Metal Accumulation by Estuarine Mollusks," Journal of Sanitary Engineering Division (June 1968): 455-475.

<sup>45</sup>Margaret Merlini, "Heavy Metal Contamination," in Impingement of Man on the Oceans, ed. by Donald W. Hood (New York: Wiley-Intersciences, 1971).

<sup>46</sup>U.S. Environmental Protection Agency, Water Quality Criteria 1972.

<sup>47</sup>J.E.G. Raymond and J. Shields, "Toxicity of Copper and Chromium in the Marine Environment," in Advances in Water Pollution Research, Vol. 3, ed. by E.A. Pearson, Proceedings of the International Conference, London, September 1962 (London: Pergamon Press, 1964).

<sup>48</sup>G.W. Bryan, "Adaptation of an Estuarine Polychaete to Sediments Containing High Concentrations of Heavy Metals," in F.J. Vernberg and W.B. Vernberg, Pollution and Physiology of Marine Organisms (New York: Academic Press, 1974).

copper content apparently have an increased tolerance to copper. The tolerant worms absorb copper more readily, and are not affected by copper concentrations toxic to unadapted polychaetes.

### Mercury

Mercury's seawater concentration is 0.03 ppb. Concentration factors up to 80,000 have been observed in Crassostrea virginica (American oyster), with maximum accumulation in the gills.<sup>49</sup> The highest concentration of mercury in cod exposed to mercuric nitrate was found in the gills also, where the concentration factor was 3,760.<sup>50</sup>

### Nickel

Concentration of nickel in seawater is reported to be 2 to 5.4 ppb. Concentration factors in marine organisms range from 7,000 to 74,000. Concentration factors for mussels, scallops and oysters are 14,000, 12,000 and 4,000 respectively.<sup>51</sup>

### Lead

Lead is found in seawater at a concentration of 0.03 ppb. According to Pringle,<sup>52</sup> lead concentrations in the gills, gonads, and liver of Crassostrea virginica are on the order of 1,000 times the seawater concentration. Concentration factors in the other tissues are somewhat lower. Whole organism concentration factors for Crassostrea, Mya arenaria, and Mercenaria mercenaria are 1,300, 2,300 and 1,700 respectively.

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<sup>49</sup>Frederic C. Kopfler, "The Accumulation of Organic and Inorganic Mercury Compounds by the Eastern Oyster (Crassostrea virginica)," Bulletin of Environmental Contamination and Toxicology 2 (1974): 275-280.

<sup>50</sup>U.S. Environmental Protection Agency, Water Quality Criteria 1972.

<sup>51</sup>Merlini, "Heavy Metal Contamination."

<sup>52</sup>Pringle et al., "Trace Metal Accumulation."

## Zinc

Seawater concentration of zinc is 10 ppb. Zinc is concentrated in the gills and digestive gland of Crassostrea, and in the gills and kidneys of Cyprinus carpio.<sup>53</sup> Laminaria digitata, a marine plant, accumulates zinc to concentrations up to 1,800 times the ambient concentration. Experiments with the polychaete Nereis diversicolor show that concentration factors in the worms vary by a factor of three with a factor of 30 variation in sediment concentration.<sup>54</sup> This observation implies that the worms have a substantial degree of regulatory control over zinc accumulation. Worms adapted to high concentrations are about 30 percent less permeable to zinc than nonadapted worms, and are probably better able to excrete it. Therefore, the adapted worms can maintain a relatively normal zinc concentration and can avoid toxic effects.

It is readily apparent from the above discussion that accumulation is a complicated process, affected by a number of different parameters. Present literature is insufficient to establish a totally clear understanding of the process. Much more research, and more importantly, standardized research, will be needed before a definitive understanding of accumulation can be developed. Such an understanding would be useful not only for this study, but also for numerous other analyses of effects of pollutant discharges on marine ecosystems.

### 6.6.2 Hydrocarbon Bioaccumulation

Many marine organisms have the capacity to take up and accumulate hydrocarbons from their environments. This ability has been demonstrated in mussels, clams, oysters, crabs, shrimp, sponge, and fish, among other organisms. Both field and laboratory studies have dealt with the accumulation process. Although the results of these studies are varied and often inconsistent, they do serve to demonstrate that the ability to accumulate hydrocarbons is widespread among marine organisms.

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<sup>53</sup>U.S. Environmental Protection Agency, Water Quality Criteria 1972.

<sup>54</sup>Bryan, "Adaptation of an Estuarine Polychaete."

The mechanism and available data on bioaccumulation of hydrocarbons by marine organisms are summarized in Appendix F and will not be discussed in any detail here. For the purposes of this assessment, our only interest is in the rate of bioaccumulation of one particular hydrocarbon, benz[a]pyrene. Unfortunately, long-term bioaccumulation data are not available, but one excellent short-term (24-hour) study is available for the clam Rangia cuneata. Twenty-four hour exposure of this clam to 0.0305 ppm of benz[a]pyrene resulted in tissue concentrations of 5.2 and 7.2 ppm benz[a]pyrene.<sup>55</sup> Accumulation occurred mainly in the viscera -- digestive system, gonads, and heart. Thirty days depuration left 0.07 ppm of contaminants; after 58 days less than 0.01 ppm remained.

#### 6.6.3 Hazards of Methylmercury Contamination of Marine Organisms

An important potential human health hazard is created by the presence of mercury in oilfield brines. Mercury in the marine environment can easily find its way into bottom muds and sediments, where it can be biologically methylated by anaerobic bacteria (this process is known to occur in the bottom muds of lakes, and can presumably occur in the marine environment as well). The products of this methylation are the methylmercury(I) ion,  $\text{CH}_3\text{Hg}^+$ , and dimethylmercury,  $(\text{CH}_3)_2\text{Hg}$ , which is spontaneously converted to  $\text{CH}_3\text{Hg}^+$  in low pH environments.<sup>56</sup> Although dimethylmercury is fairly volatile, the methylmercury ion is water soluble and is bioaccumulated to a significant extent (bioaccumulation factors on the order of a few thousand have been reported for a freshwater fish, the pike). The toxicology of methylmercury has been well studied, both in animals and in human beings as a result of events such as occurred in the Japanese city of Minimata, where significant fractions of the population were exposed to shellfish contaminated with methylmercury from an industrial effluent. The compound is easily absorbed through the gastrointestinal tract, passes easily through placental and blood/brain barriers, can cause extensive nervous damage, and is a powerful mutagen.

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<sup>55</sup> Jerry M. Neff and Jack W. Anderson, "Accumulation Release, and Distribution of Benzo[a]pyrene-C in the Clam Rangia cuneata," in Conference on Prevention and Control of Oil Pollution, U.S. Environmental Protection Agency, American Petroleum Institute, U.S. Geological Survey, 1975.

<sup>56</sup> Spears, An Evaluation of the Effects of Oil, Oilfield Brine and Oil Removing Compounds.

A number of legal standards have been set up for maximum permissible levels of mercury compounds in fish destined for human consumption. These standards are based on considerations of available animal and human exposure data, and are considered to represent prudent safety factors which will protect exposed human populations from all significant neurotoxic, teratogenic, and other effects of methylmercury poisoning. (For a discussion of the rationale for these standards, see Skerfving's review of mercury in fish.)<sup>57</sup> The prevailing limit in the U.S. and Canada, promulgated in 1970, is 0.5 ppm of mercury in fish. Assuming a high concentration factor of about 5,000, this translates into a level of no more than 0.1 ppb in seawater. This, of course, would only apply to sessile organisms continuously exposed to this concentration of mercury.

#### 6.6.4 Human Health Impacts of Benz[a]pyrene

Among the organic compounds known to be present in crude oil is the polynuclear aromatic hydrocarbon benz[a]pyrene, a compound which is known to be strongly carcinogenic in animals. The molecule is hydrophobic, and will partition preferentially into lipids of marine organisms, where it can be subject to both bioaccumulation and biomagnification effects. Although no data are available on benz[a]pyrene levels in oilfield brines, its presence in parent crude oil, together with the fact that oilfield brines are known to be enriched in the aromatic fractions of crude oil, makes it highly plausible that it is present in these brines. Unlike mercury, enough data do not exist for this compound to predict any reasonable safe level for its concentration in food. Therefore, an unacceptable level of benz[a]pyrene was defined as one which, after bioaccumulation, would not produce a level of BaP in shellfish which would exceed the minimum background levels of BaP in other food sources.<sup>58</sup> For this purpose a final concentration in food of 1 ppb was defined as unacceptable. It should be emphasized that this is not to be interpreted as a "safe" level, only

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<sup>57</sup>S. Skerfving, "Mercury in Fish -- Some Toxicological Considerations," Food and Cosmetics Toxicology 10 (1972): 545-556.

<sup>58</sup>For data on levels of BaP in food sources, see National Academy of Sciences, Committee on Biologic Effects of Atmospheric Pollutants, Particulate Polycyclic Organic Matter, Chapter 14 (Washington, D.C., 1972), pp. 160-165.



as an unacceptable level which should not be exceeded. BaP is a potent carcinogen, and no information is available to estimate a threshold level or even to suggest that such a level exists.

## CHAPTER SEVEN

### IMPACT ASSESSMENT

#### 7.1 Introduction

In this chapter the data, model outputs, and assessment methods described earlier in this report will be combined to estimate the magnitude of brine-related impacts occurring at the four study sites in Cook Inlet, Hackberry Bay, near offshore Gulf of Mexico (Grand Isle), and far offshore Gulf of Mexico. The assessment methods used in this chapter were discussed in detail in Chapter Six, and are presented in summary in Figure 7-1.

Briefly, the assessment begins with the definition of a level for each brine constituent which is safe with respect to toxic impacts on marine and estuarine organisms. For two particular brine constituents, mercury and benz[a]pyrene (BaP), a further set of safe levels, designed to prevent the bio-accumulation of these substances to undesirable levels in shellfish or other organisms which might be used for human consumption, is defined. Each of these safe levels implies a "necessary dilution factor," that is, a brine dilution required to bring the particular constituent down to its safe level. The outputs of the dispersion model, described in Chapter Five, can then be used to estimate the area in which any of the constituents is at a concentration greater than or equal to its safe level. This area is taken as an estimate of the area of a zone of impact.

An alternative definition of a "safe" degree of brine dilution was also used to take into account possible interactions between the toxicities of two or more brine constituents. This alternative definition takes into account the fact that a combination of pollutants each of which is at or below its individually estimated safe level may itself be unsafe. Although inadequate data are available to estimate quantitatively the interactive toxic effects produced by a complex mixture of pollutants such as oilfield brine, a necessary dilution factor can be approximated by use of the following approach.

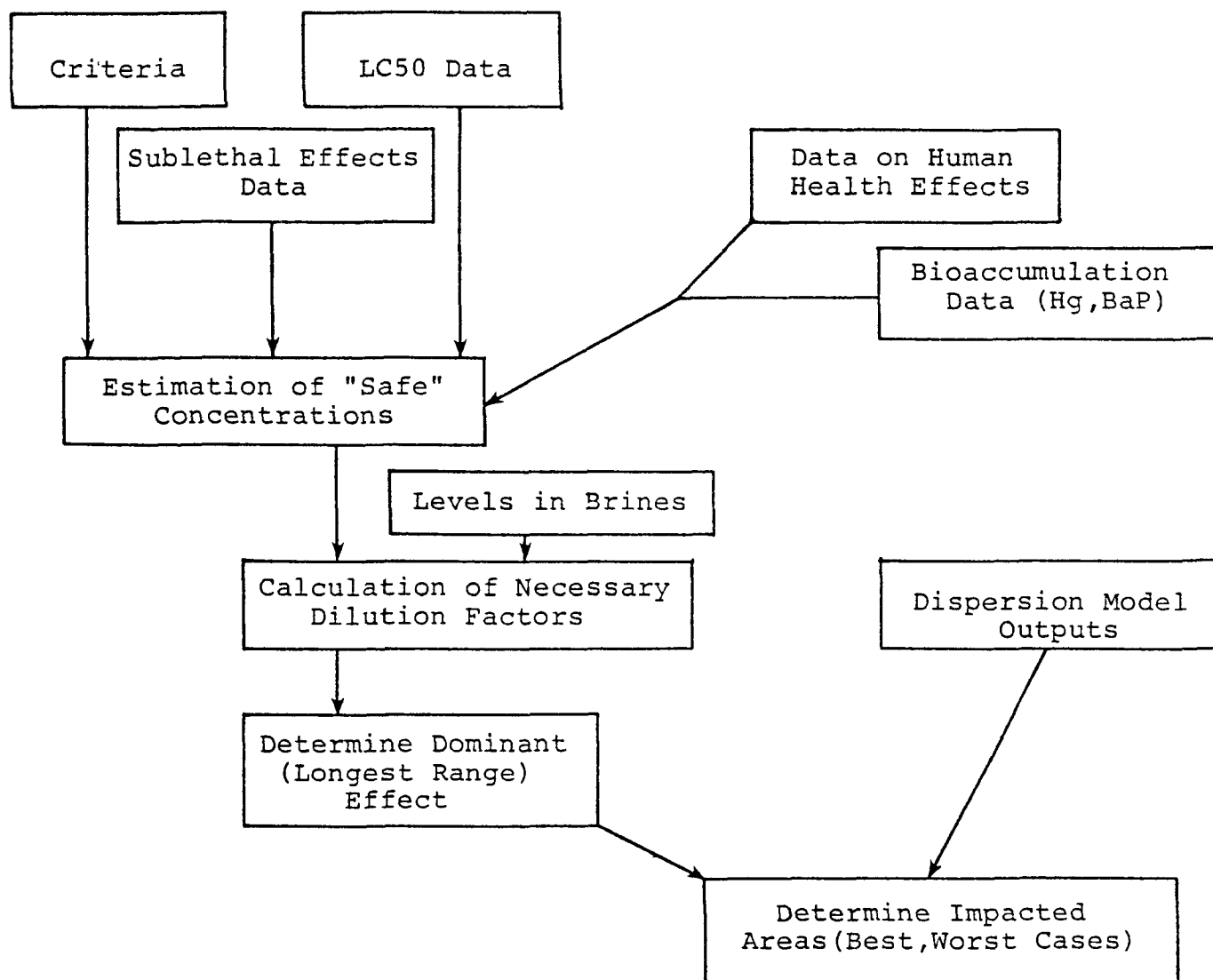


Figure 7-1. Outline of the analysis.

Assume that the toxicity of a combination of different pollutants is the sum of their respective individual toxicities; i.e., ignore the possibility of antagonistic or synergistic interactions. Then, if  $C_i$  and  $S_i$  are respectively the produced water concentration and safe level of the  $i^{\text{th}}$  pollutant, the necessary dilution factor for the mixture,  $(\text{NDF})_{\text{tot}}$ , is given by the equation<sup>1</sup>

$$\sum_{i=1}^n \frac{C_i / (\text{NDF})_{\text{tot}}}{S_i} = \frac{1}{(\text{NDF})_{\text{tot}}} \sum_{i=1}^n \frac{C_i}{S_i} = 1$$

or

$$(\text{NDF})_{\text{tot}} = \sum_{i=1}^n \frac{C_i}{S_i}$$

Since  $C_i/S_i$  is simply the necessary dilution factor for the  $i^{\text{th}}$  pollutant,  $(\text{NDF})_i$ , it follows that

$$(\text{NDF})_{\text{tot}} = \sum_{i=1}^n (\text{NDF})_i ;$$

i.e., the total NDF is the sum of the individual NDF's. This combined effects calculation probably produces a very conservative estimate of the safe concentration of the mixture. The numerical calculations of individual and combined safe levels for brine constituents are shown later in this chapter.

Two other factors are taken into account in determining magnitude of impact at each site. The first, which only applies to enclosed areas such as Hackberry Bay, is the percentage of the area of the bay which is covered by an "unsafe" zone. The second, which can only be taken into account qualitatively, is the ecology of the area being impacted. Detailed ecological characterizations of the study sites are provided in Appendix A, and will be referred to here as a way of describing the value of the area being

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<sup>1</sup>National Academy of Sciences and National Academy of Engineering, Water Quality Criteria 1972, 1972: p. 123.

impacted. Thus, a particular level of brine impacts in a highly fertile, productive region which supports large populations of ecologically and economically important organisms would probably be more significant than an equivalent level of impacts in an area which is naturally infertile and nonproductive. Unfortunately, it was not possible within the scope of this project to quantitatively assess the ecological impacts of the different types of ecosystems which might be affected by brine discharge.

It should be emphasized that this assessment procedure only takes direct effects into account, and does not attempt to analyze subsequent ecological interactions and longer-range indirect effects resulting from brine toxicity. For example, although a particular ensemble of brine constituent concentrations in an area might cause 25 percent mortality in a population of embryonic oysters, the reproductive potential of the oyster population may be large enough to maintain the population at its pre-impact levels. Thus, although a significant direct effect would be produced (and would be predicted by this assessment) in the long run the effect may be relatively insignificant. Conversely, an ecological system may be poised in a relatively delicate equilibrium, so that toxic stresses resulting from brine discharges may produce long-range effects much greater than any direct toxic impacts which would be estimated by the analysis described in this report.

Another factor ameliorating brine impacts which cannot be taken into account in this analysis is the selection, over the course of several generations, for subpopulations which are relatively insensitive to the effects of particular brine constituents. This effect has been observed, for example, in Nereis spp. living in a copper-polluted estuary (see Section 6.2.5). Later in this chapter we will comment on the agreement between predicted impacts and field data, and on the extent to which the resiliency (or, conversely, the instability) of the ecosystem seems to modify the predicted level of toxic impacts.

The assessment methods implemented in this chapter predict significantly different impacts on the four study sites considered in this report. This fact illustrates the importance of such site specific factors as depth and current velocities in determining the level of brine impacts.

## 7.2 Results of the Hackberry Bay Assessment

The impacts analysis described in the previous chapter will first be applied in detail to Hackberry Bay to illustrate the form of the analysis and the methods used. The methods are practically identical for the other three study sites, so for these only the results will be discussed.

### 7.2.1 Area/Concentration Relationships

As described in Chapter Five, the brine dispersion model was used to generate a set of contours of equal brine dilution (isopleths) for each of the sites being studied. A typical set of predicted isopleths for the Hackberry Bay site is shown in Figure 7-2. A number of computer runs were made for each site, in order to assess the sensitivity of the results to assumptions relating to current velocities, diffusion coefficients, and other model input parameters. For each run, the areas enclosed by each isopleth were measured by planimetry, and the data were plotted on a concentration versus included area graph, which shows, for a particular concentration value, the area of a site over which concentration is greater than or equal to that value. Each site therefore generated a set of these area/ concentration curves, one for each set of numerical assumptions tested. The upper envelope of this sheaf of curves defines a worst (maximum impacted area) case, and the lower envelope defines a best case. A base case was also defined using most probable estimates for the values of each input parameter. The calculated best, worst, and base case curves for the Hackberry Bay site are repeated in Figure 7-3.

Since Hackberry Bay is an enclosed area, it is appropriate to apply to it the tidal flushing calculation described in Chapter Four, Section 4.2. The relationships derived in that section imply a minimum "background" brine concentration of about 0.18 percent for Hackberry Bay. Thus, the area/ concentration curves were only extended down as far as 0.1 percent dilution, and 0.18 percent was defined as the effective minimum brine concentration over the whole bay. Areas included by higher concentrations can be estimated from Figure 7-3.

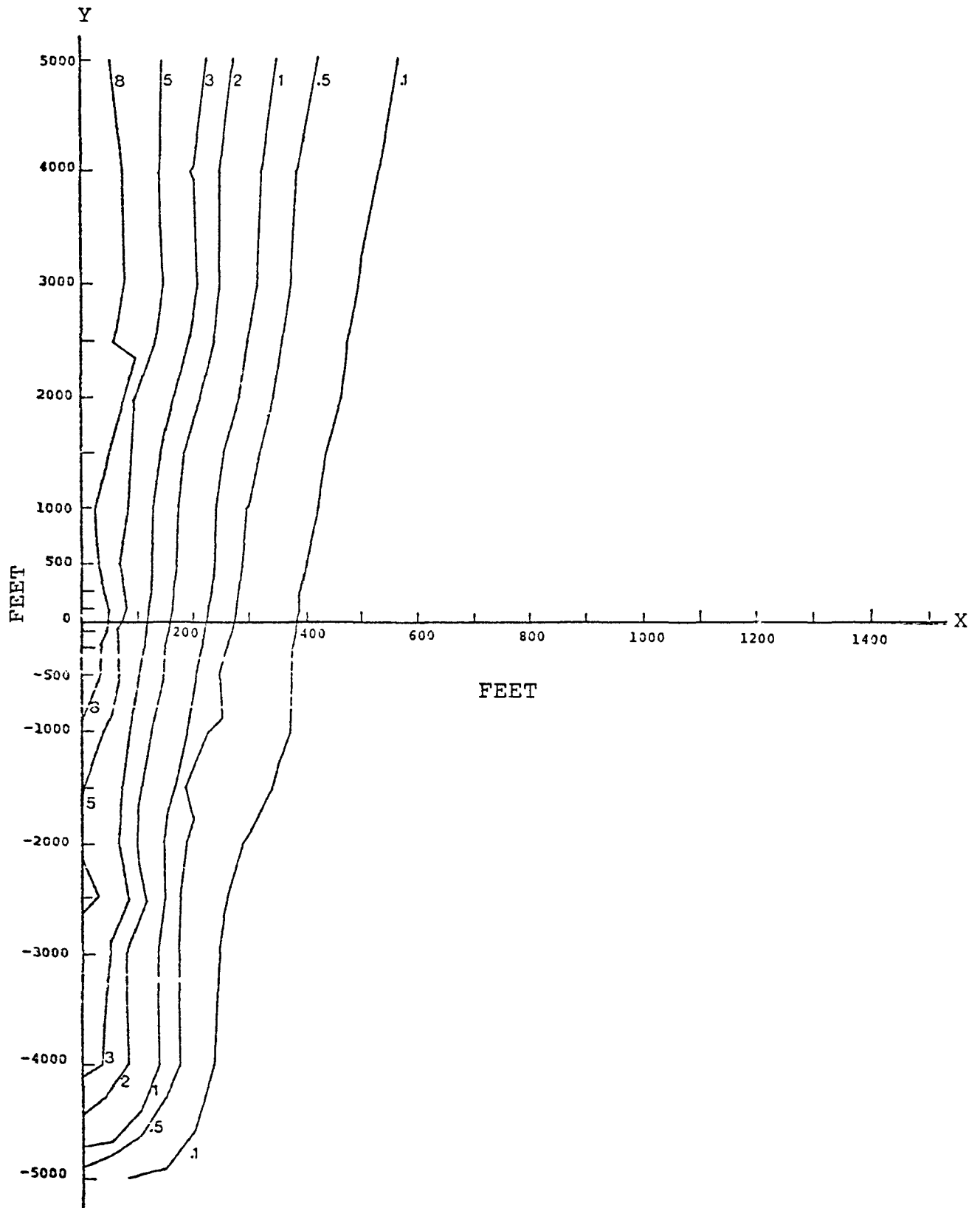


Figure 7-2. Typical set of isopleths for Hackberry Bay site (Base Case).

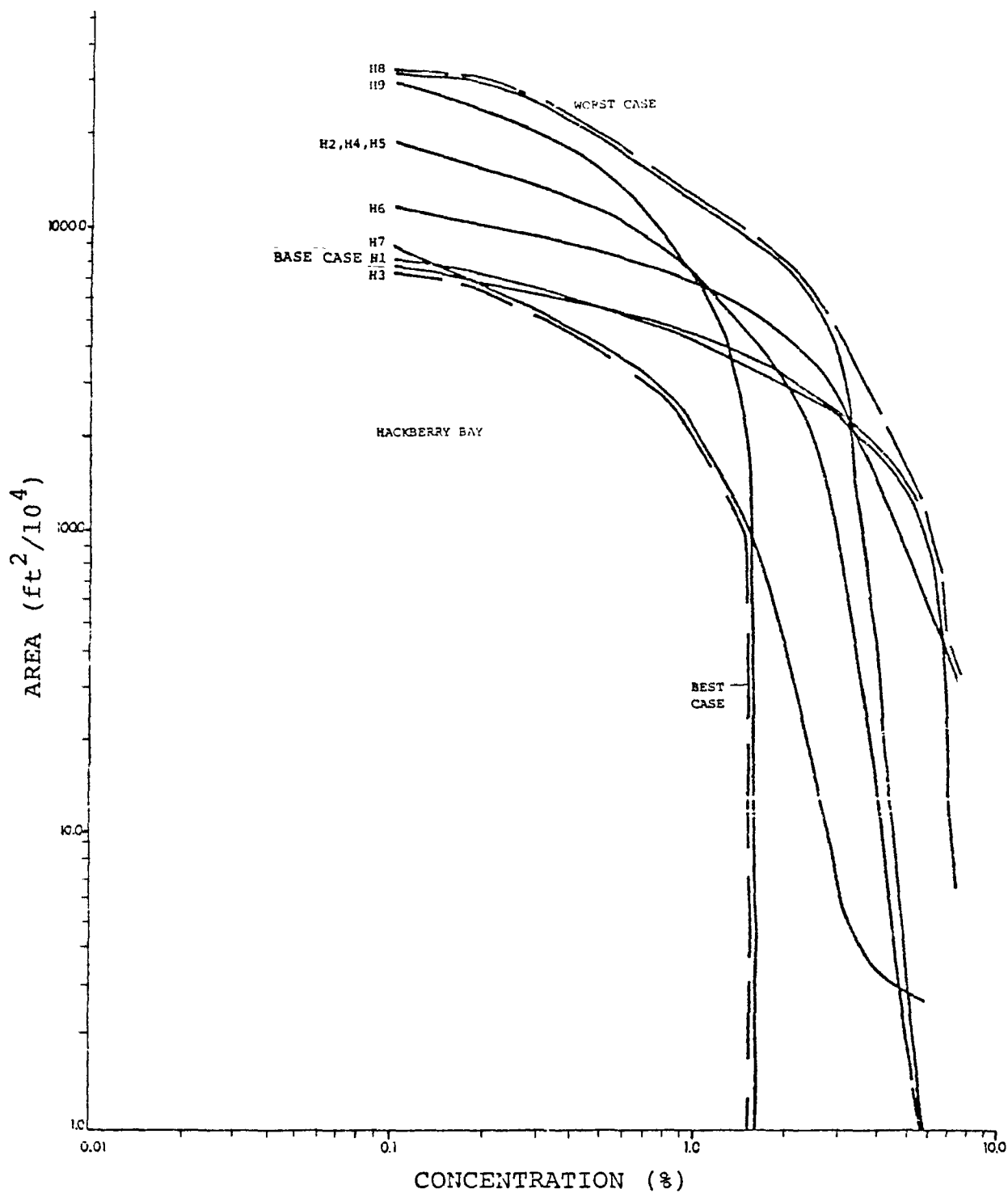


Figure 7-3. Plots of area/concentration curves for sensitivity analyses performed for Hackberry Bay site. Base Case assumes most probable values of input parameters; for other cases, input parameters are individually varied over their range of plausible values.



### 7.2.2 Numerical Data Used in Impacts Analysis

Table 7-1 summarizes the assumed values of the numerical parameters (toxic concentrations, etc.) required for this impact assessment. In each case the value is stated along with the source of the data or the rationale for the particular estimate made.

Since only incomplete data are available on the chemical composition of Louisiana brines, concentrations of trace metals in the brines were generally estimated as the mean of maximum values which had been observed at sites in California, Alaska and Texas.

Toxicological data are generally derived from the tables and text of Chapter Six. Since 0.01 application factors used are meant to be applied to 96 hr LC50 data, a technique was necessary to extrapolate to the 96 hr values from the 48 or 24 hr values which were frequently reported instead. The data from Eisler<sup>2</sup> on cadmium toxicity were used to make this estimate. Ninety-six hr LC50 data for cadmium for a number of marine species were plotted against 48 hr LC50 data for the same species, and a ray through the origin was best-fitted to the eight available data points. The points gave a reasonably good fit (correlation coefficient = 0.86) to the relationship  $(96 \text{ hr LC50}) = 0.17(48 \text{ hr LC50})$ , which was subsequently used to estimate the 96 hr figures. A similar procedure was used to obtain the relationship  $(96 \text{ hr LC50}) = 0.096(24 \text{ hr LC50})$ . Insufficient data were available to determine whether this relationship also held for toxicants other than cadmium.

Mercury safe levels in seafood were based upon the legal standard currently prevailing in the United States and Canada. Available toxicological data were totally inadequate to estimate any sort of a safe level for benz[a]pyrene. Therefore, an unacceptable level of BaP was defined as one which, after bioaccumulation, would not produce a level of BaP in shellfish exceeding the minimum background levels of

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<sup>2</sup>R. Eisler, "Cadmium Poisoning in *Fundulus heteroclitus* (Pisces: Cyprinodontidae) and Other Marine Organisms," Journal of the Fisheries Research Board of Canada 28 (9) (1971): 1225-1234.

TABLE 7-1

VALUES OF IMPORTANT NUMERICAL PARAMETERS

PARAMETER	VALUE	RATIONALE
Concentrations of brine constituents in brines:		
Ag	0.05 ppm	See Chapter Three and comments in Section 7.2.2.
As	0.37 ppm	
Cd	0.28 ppm	
CN	0.007 ppm	
Cr	0.12 ppm	
Cu	0.19 ppm	
Hg	0.036 ppm	
Ni	0.39 ppm	
Pb	0.30 ppm	
Zn	1.25 ppm	
Phenol	3.5 ppm	
Concentration of oil hydrocarbons in brines	50 ppm	Table 3-8 ; maximum post-treatment levels for "oil and grease" in brine.
Concentration of BaP in crude oil	0.4-1.6 ppm	Data cited in Neff and Anderson (1975).
Enrichment factor for aromatics in crude oil water soluble fraction (WSF)	14.29	Anderson et al. (1974). This value means that the ratio (aromatics/ other HC's) is 14.29 times as great in crude oil WSF as in the original crude oil.
Concentration of BaP in brines	0.3-1.1 ppb	Product of the above three values. (BaP is an aromatic hydrocarbon.

TABLE 7-1 (CONT.)

PARAMETER	VALUE	RATIONALE
Bioaccumulation factor:		
Hg	10 <sup>4</sup> -10 <sup>5</sup>	Laboratory bioaccumulation experiments with <u>Crassostrea</u> ; up to 80 day exposure (Kopler, 1974)
BaP	236	BaP accumulated in clam <u>Rangia cuneata</u> in 24 hr period. (Neff and Anderson, 1975)
Maximum permissible level of Hg in seafood	0.5 ppm	Skerfving (1972)
EPA Water Quality Criteria:		
Ag	0.001 ppm	Taken from 1973 and 1975 EPA Water Quality Criteria Documents.
As	0.05 ppm	
Cd	0.005 ppm	
CN	0.005 ppm	
Cr	0.01 ppm	
Cu	0.01 ppm	
Hg	0.0001 ppm	
Ni	0.1 ppm	
Pb	0.01 ppm	
Zn	0.07 ppm	
Phenol	(n.a.)	
Concentrations below which no effects were reported on marine or estuarine organisms in the literature:		
Oilfield brine	1%	Tables and text, Chapter Six.
Crude Oil	0.001 ppm	
Ag	0.0005 ppm	
As	3.0 ppm	
Cd	0.08 ppm	
CN	(n.a.)	
Cr	1.0 ppm	
Cu	0.002 ppm	
Hg	0.002 ppm	

TABLE 7-1 (CONT.)

PARAMETER	VALUE	RATIONALE
Ni	0.06 ppm	
Pb	0.1 ppm	
Zn	0.006 ppm	
Phenol	0.6 ppm	
Minimum reported 96 hr LC50's (actual or extrapolated from 48 and 24 hr values), for adult organisms:		
Crude oil	5 ppm	Tables and text, Chapter Six. See Section 7.2.3.
Crude oil WSF <sup>a</sup>	6%	
Oilfield brine	22%	
Ag	0.04 ppm	
As	8 ppm	
Cd	0.2 ppm	
CN	(n.a.)	
Cr	17 ppm	
Cu	0.2 ppm	
Hg	(n.a.)	
Ni	17 ppm	
Pb	200 ppm	
Zn	1 ppm	
Phenol	1.7 ppm	

<sup>a</sup> Extrapolated from data given by Anderson. The figure represents the dilution of the complete soluble fraction, not the concentration of hydrocarbons in the final dilution.

REFERENCES FOR TABLE 7-1

- Neff, J. and Anderson, J. "Accumulation, Release and Distribution of Benzo[a]pyrene-C<sup>14</sup> in the Clam Rangia cuneata," in American Petroleum Institute et al. 1975 Conference on Prevention and Control of Oil Pollution - Proceedings. American Petroleum Institute. Washington, D.C., 1975.
- Anderson, J., et al. "Characteristics of Dispersions and Water-Soluble Extracts of Crude and Refined Oils and Their Toxicity to Estuarine Crustaceans and Fish." Marine Biology 27 (1974): 75-88.
- Kopfler, F.C. "The Accumulation of Organic and Inorganic Mercury Compounds by the Eastern Oyster (Crassostrea virginica). " Bulletin of Environmental Contamination and Toxicology 11 (1974): 275-280.
- Skerfving, S. "Mercury in Fish -- Some Toxicological Considerations." Food and Cosmetics Toxicology 10 (1972): 545-556.

BaP in other food sources.<sup>3</sup> For this purpose a final concentration in food of 1 ppb was defined as unacceptable. It should be emphasized that this is not to be interpreted as a safe level, only as an unacceptable level which should not be exceeded. BaP is a potent carcinogen, and no information is available to estimate a threshold level or even to suggest that one exists.

### 7.2.3 Difficulties Involved in Use of Application Factors

The question arises of whether an application factor of 0.01 applied indiscriminantly to the 96 hr LC50 of the most sensitive organism studies is an appropriate criterion for use in estimating safe levels. The problems which can result when this approach is applied to the extremely low LC50s observed for juvenile and embryonic forms is illustrated by the case of silver. A 48 hr LC50 of 0.005 ppm has been reported for silver for *Crassostrea* embryos. Using the relationship between 96 hr and 48 hr LC50's discussed in Section 7.2.2, this is shown to imply a 96 hr LC50 of 0.000835 ppm, or an application factor threshold of  $(0.01)(0.000835) = 8.35 \times 10^{-6}$  ppm. This is, however, far below the concentration of silver in natural, unpolluted sea water, which is 0.3 ppb or  $3 \times 10^{-4}$  ppm. Clearly, the application factor approach is not realistic in this case, since it leaves us with the conclusion that unpolluted sea water is an unacceptable environment for marine organisms.

The application of the 0.01 factor has therefore been restricted in this study to toxicity data for adult forms. It is extremely important to emphasize, however, that the problem of choosing an application factor to derive "safe" levels of pollutants from acute toxicity data is by no means a simple one, nor is there any evidence that it can be solved in a thoroughly convincing way. Indeed, it is unreasonable to expect a simple relation to exist between the relatively high level of a pollutant capable of inducing mortality in a short period of time, and the low levels which, under conditions of chronic exposure, may affect one or more of the multitude of different biological processes or behavior patterns exhibited by various organisms at all stages of their

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<sup>3</sup>For information on levels of BaP in food sources, see National Academy of Sciences, Committee on Biologic Effects of Atmospheric Pollutants, Particulate Polycyclic Organic Matter, Chapter 14 (Washington, D.C., 1972), pp. 160-165.

life cycles. Further discussion of the complexities of the subject is given in a review paper by Bernhard and Zattera.<sup>4</sup>

#### 7.2.4 Numerical Calculations for Hackberry Bay

The calculations performed for unsafe zone areas for individual brine constituents and for combined effects in Hackberry Bay are shown in Table 7-2. Because of the significant compositional differences between crude oil and the crude oil water-soluble fraction, it was decided to use only the data on the water-soluble fraction for estimating the toxicity of the hydrocarbon fraction of brines.

A further advantage of this is that the dispersion of crude oil WSF around the discharge point can be modeled much more accurately than can the dispersion of total oil hydrocarbons. This is because the predominantly aromatic WSF hydrocarbons are degraded much more slowly by hydrocarbonoclastic (hydrocarbon degrading) microorganisms in the marine environment than are non-WSF hydrocarbons. Therefore, their concentration distributions can be predicted much more accurately by the brine dispersion model used in this report, which only takes physical dilution forces into account.

The individual effects analysis (Table 7-2) suggests a toxicity threshold of about 0.06 percent brine dilution. The combined effects analysis obtained by summing the NDF's in Table 7-2 (see Section 7.1) reduces this to about 0.04 percent. Both estimates may tend to be conservative since some of the contaminants will probably be subject to effective concentration reductions greater than those predicted by the dispersion model as a result of adsorption, sedimentation, and (in the case of trace metals) physiological inactivation by chelation. On the other hand, the individual effects analysis, as mentioned above, does not take into account the effects of emulsified oil hydrocarbons in the brines. Moreover, the facts that the limited amount of available data regarding the detailed composition of oil-field brines exhibits a wide range in the concentrations of brine constituents (see Table 3-2), and that the state of knowledge of the potential impacts of trace metals and oil

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<sup>4</sup>M. Bernhard and A. Zattera, "Major Pollutants in the Marine Environment," in E.A. Pearson, ed., Marine Pollution and Marine Waste Disposal (New York: Pergamon Press, 1975).

TABLE 7-2

## CALCULATIONS FOR HACKBERRY BAY

CONTAMINANT	ESTIMATED "SAFE" CONCENTRATION (ppm)	CONCENTRATION IN BRINE (ppm)	NDF <sup>a</sup> (ppm)	PERCENT DILUTION AT NDF (= 100/NDF)
Ag	0.0004	0.05	117	0.86
As	0.05	0.37	7	13.64
Cd	0.002	0.28	141	0.71
Cr	0.01	0.12	12	8.11
Cu	0.002	0.194	97	1.03
Hg	0.0001	0.036	356	0.28
Hg (as a food contaminant)	c	0.036	1,187 <sup>b</sup>	0.08
Ni	0.06	0.39	6	15.5
Pb	0.01	0.30	30	3.37
Zn	0.01	1.25	125	0.8
Crude Oil WSF	0.06%	100%	1,600 <sup>b</sup>	0.06
BaP (as a food contaminant)	$4 \times 10^{-6}$	0.001	250	0.4
Phenol	0.6	3.5	6	17.14
CN	0.005	0.007	1.4	71.4
Total NDF for Combined Effects Analysis <sup>d</sup>			2,500	

<sup>a</sup>NDF = necessary dilution factor, i.e. dilution necessary to reduce each constituent to its safe level.

<sup>b</sup>Largest NDF's.

<sup>c</sup>Safe level is essentially at or below natural level in seawater ( $\approx 0.03$  ppb =  $3 \times 10^{-5}$  ppm).

<sup>d</sup>See Section 7.1. The NDF's for BaP and Hg as food contaminants are not included in the total NDF.



hydrocarbons is rapidly expanding, suggest prudence in estimating the potential impacts of brine disposal in marine and estuarine waters. Accordingly, a "best guess" of a 0.05 percent (2,000:1) dilution was made as an estimate of a safe level of brine dilution.

Since the "safe" level is below the 0.18 percent background brine levels predicted by tidal flushing calculations, essentially the whole of Hackberry Bay is included in a zone of impact.

#### 7.2.5 Ecological Considerations

The Barataria Bay region, in which Hackberry Bay is located, is a highly productive coastal wetlands area and one of significant commercial importance. Therefore, any brine related impacts produced in that area are likely to be ecologically and economically significant (see Appendix A).

The salt waterbodies associated with the coastal salt marshes of the Barataria Bay region (Hackberry Bay is one such waterbody) support high levels of primary production by diatoms, coccoid blue green algae, green algae, and nanoplankton. This primary production supports a large number of herbivores, including Acartia tonsa (the dominant copepod of the region), menhaden, and mullet. Detritivores are numerous in the region including commercially important species of penaeid shrimp, blue crabs, and oysters. Important carnivores include ctenophores (which feed on zooplankton), fishing birds, diving ducks, spotted sea trout, sea catfish, silversides, anchovy, and the bottlenosed dolphin.

Many commercially important species, although they are not full-time residents of the Barataria Bay area, spend at least part of their life cycle there. The blue crab, which supports a large fishery, spawns in lower estuarine and Gulf waters, although the larval stages (zoae and megalops) are spent in open Gulf waters. Near the end of the megalops stage the blue crabs may enter tidal inlets, and the first nine months of the juvenile stage are spent in the upper and lower estuary. The second year as a juvenile is spent in the upper estuary where the crab grows to full maturity and mates. It is at this time that crabs are usually fished -- usually from ages 12 to 18 months. The penaeid shrimp (including the white, pink, and brown shrimp), also commercially important, follow a similar life cycle pattern.

Fish species which spawn in the Gulf and use the Barataria Bay as a nursery ground include the large-scale menhaden, the Atlantic croaker, the spotted and sand sea trout, the silver percy, the striped mullet, the spot, and the bay whiff.

More detailed information on the ecology of this highly productive region is given in Appendix A.

#### 7.2.6 Delineation of Alternative Impact Zones

The approach adopted in this report was to summarize impacts at each site by estimating the area of an impact zone in which some significant level of toxic impacts on marine hydrocarbons would be felt. It would be desirable, as discussed in Chapter Six, to be able to determine the nature and magnitude of impacts which would occur in each of a set of concentric regions inside of this impact zone. Unfortunately, such an analysis is made almost impossible by the complex sets of interactions which would almost certainly be observed between the toxic impacts of the dozen or so contaminants found in brines. Particular sublethal effects may be observed as the result of individual exposure to several different pollutants, and there is no method available for estimating the way these pollutants will interact in a mixture to produce these particular effects.

Some qualitative feeling for how the type and severity of effects vary with concentration can be gained from Table 7-3, in which the effects found for successive levels of dilution of silver from its initial maximum reported concentration in the brine are listed. Note that the effects become less severe towards the edge of the unsafe zone, and that at its borders only embryonic forms are affected. Unfortunately, it would be impossible to predict how the types of effects produced by silver in an inner dilution zone would interact with the effects produced by other pollutants in the same physical zone.

#### 7.3 Analysis of Impacts at Other Sites: General Comments

As was discussed in Chapter Two, this analysis incorporates a number of site specific features, including the resident species, the dispersion characteristics of the site, and the contaminant concentrations and discharge rate of the brine. An examination of the quantitative data suggests that the most important of these features in determining the magnitude of impact at a site are the discharge rate

TABLE 7-3

TYPES OF EFFECTS REPORTED IN THE LITERATURE FOR SILVER AT  
VARIOUS RANGES OF CONCENTRATIONS FOUND INSIDE THE "UNSAFE" ZONE

DILUTION RANGE	CONCENTRATION RANGE	EFFECTS NOTED
1-10	0.10-0.01	Abnormal movement in mud snail <u>Nassarius</u> induced by 72 hr exposure. 96 hr LC50 for <u>Fundulus</u> ; 96 hr exposure caused severe reduction of levels of 3 liver enzymes in <u>Fundulus</u> .
10-100	0.01 ppm-1.0 ppb	Mortality of <u>Crassostrea</u> embryos; toxicity threshold for adult sticklebacks.
100-1000	1.0 ppb-0.10 ppb	Induction of developmental abnormalities in embryos of various sea urchin species.
DILUTION	TYPES OF EFFECTS	
1-10	Lethality of adult organisms, significant sublethal effects.	
10-100	Mortality of embryonic forms.	
100-1000	Teratogenesis, induction of developmental abnormalities.	

and dispersion characteristics, the latter being determined by depth, tidal currents and drift or freshwater current velocity. Since information on toxic effects was not available for all important species at each site, it seemed reasonable to base all the impacts assessments on the total group of marine species for which data were available. Furthermore, because of the wide variability of composition of produced water at different sites within a geographical region (a variability which was in most cases larger than the differences observed between different regions), the assumption was made that the brine compositions for all sites could be adequately represented by the concentrations which were used for Louisiana brines, the derivation of which was explained earlier. Therefore, the chief focus in comparison of the sites was comparison of the dispersion model outputs. For all sites, an impacts threshold of approximately 0.05 percent brine dilution was assumed.

#### 7.4 Analysis of Impacts at Cook Inlet

##### 7.4.1 Area/Concentration Relationships

Area/concentration curves for Cook Inlet are shown in Figure 7-4. The curves were computed down to 0.05 percent dilution, the toxicity threshold being assumed in this analysis. Because of the enormous tidal flushing volumes, the calculated background concentration is far below this level and can be ignored. Notice that the base case curve is also a best case over part of its range.

The estimated area of the impact zone for this site is between 700,000 ft<sup>2</sup> (0.025 mi<sup>2</sup>) and 50,000,000 ft<sup>2</sup> (1.79 mi<sup>2</sup>). The base case estimate is 5,000,000 ft<sup>2</sup> (0.18 mi<sup>2</sup>).

##### 7.4.2 Ecological Considerations

Cook Inlet can be divided into three ecologically semi-distinct parts (see Figure 7-5). The upper Inlet lies east of a line extending northward from Point Possession; the middle Inlet, where most of the current brine discharge occurs, includes waters from the upper Inlet southwestward to the latitude of Tuxedni Bay (60° 25' N); and the remaining portion of Cook Inlet, south of Tuxedni Bay and Clam Gulch, is commonly called the lower Inlet. This last region has the clearest waters, and is the most productive, supporting all major species of fish, shellfish, and marine mammals found in Cook Inlet. It is this lower Inlet region which is of most interest to biologists and agencies concerned with

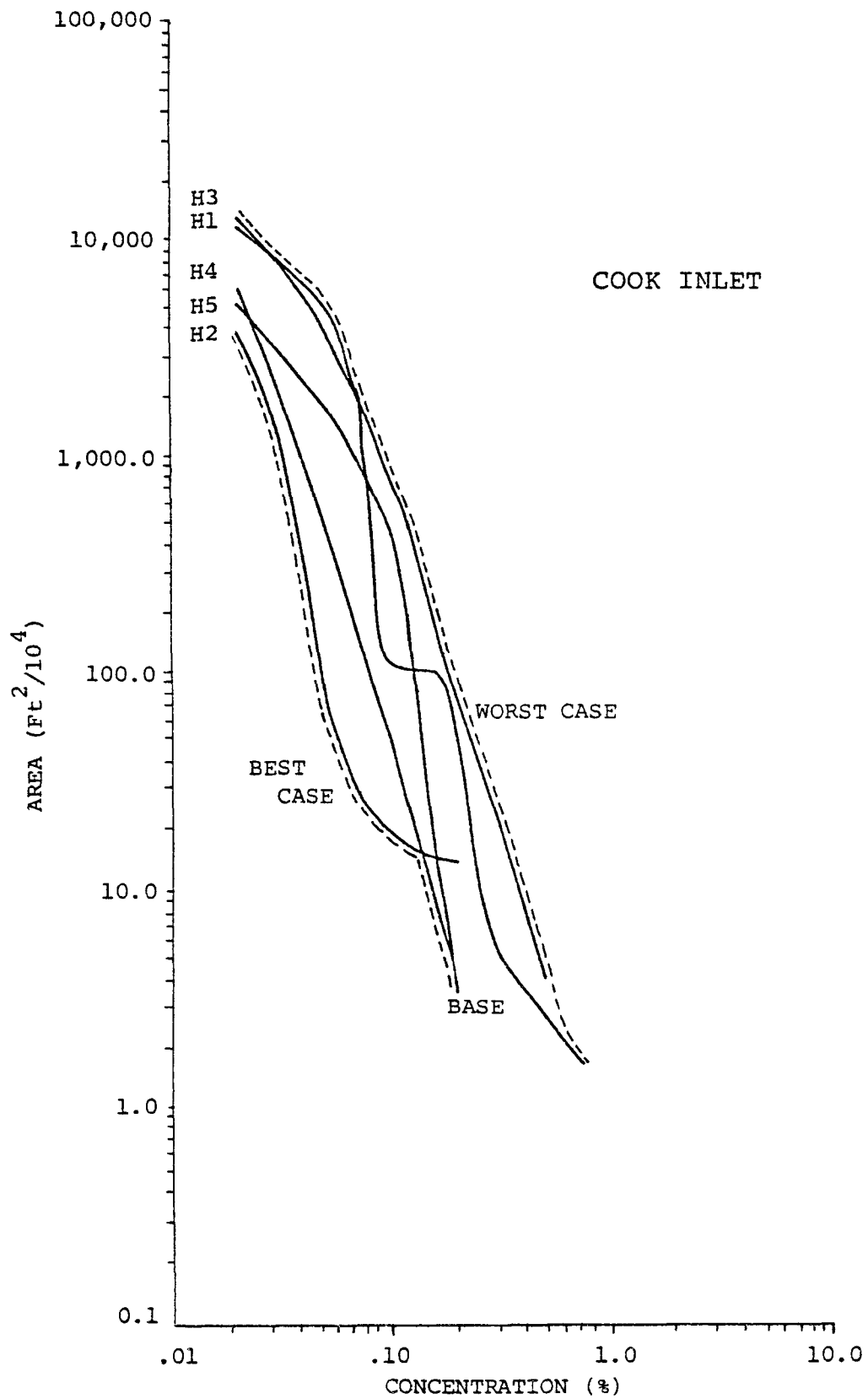


Figure 7-4. Area/concentration curves for Cook Inlet.

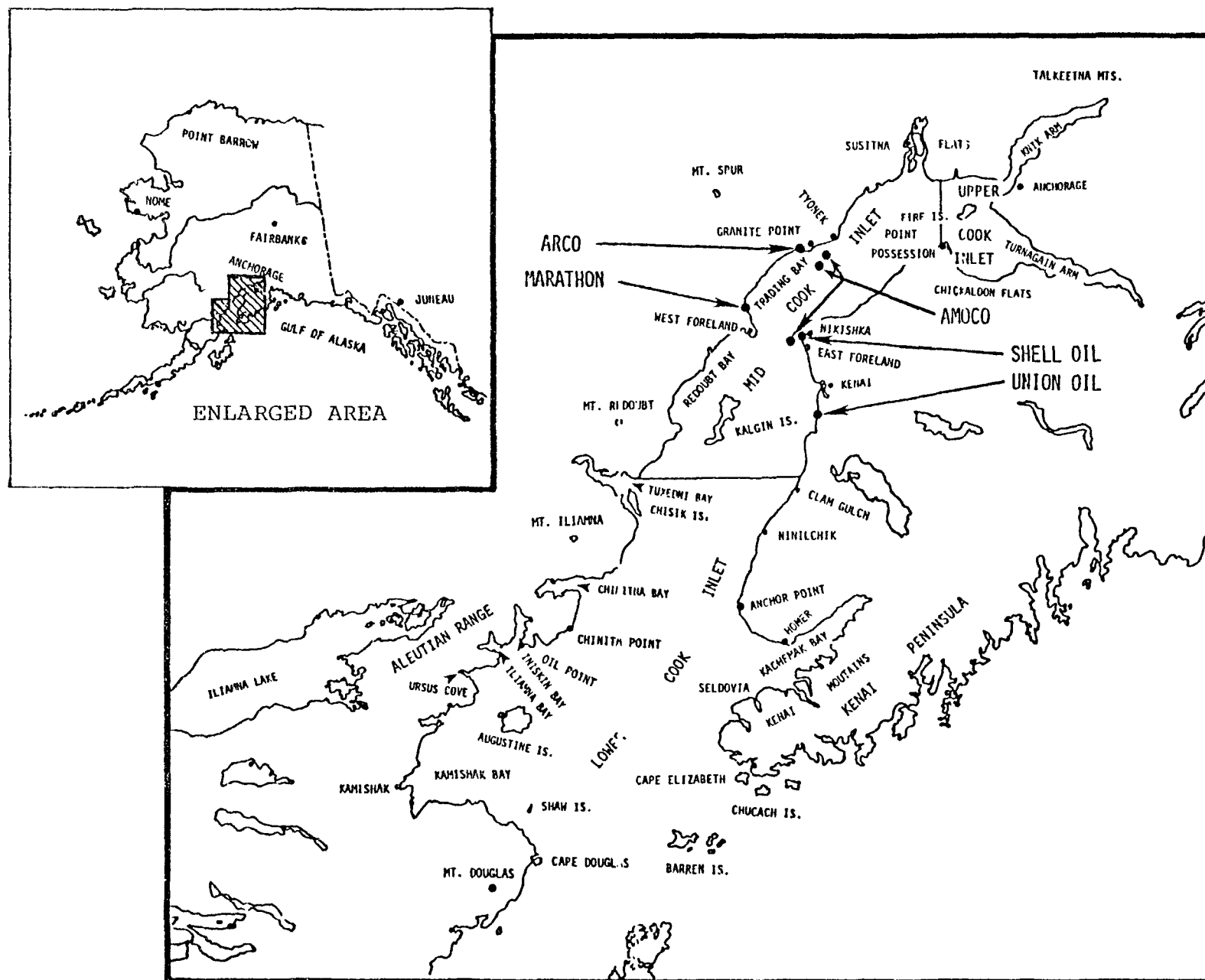


Figure 7-5. Map of Cook Inlet.

wildlife and fisheries management. Therefore, relatively little work has been done in the mid Inlet, which is the area of interest to this analysis, since it contains the major oil production areas of the Inlet. What data are available suggest that the mid Inlet is relatively non-productive.

It appears that very few species exist in the silt laden waters of the western and upper half of the Inlet (including the mid-Inlet region). The high tidal amplitude and the strong tidal currents which scour the bottom make survival difficult for most benthic organisms. The great loads of suspended sediment in these regions limit penetration of light, confining photosynthesis to a very shallow photic zone. Productivity increases as one moves oceanward, to cleaner, more saline waters. The lower Inlet waters provide habitat for a variety of sport and commercially important fish and shellfish, and numerous other non-fished species.

In short, the impacts produced by oil platforms in the mid-Cook Inlet provide us with a case which contrasts strongly with that of Hackberry Bay. Not only are the zones of impact smaller in Cook Inlet (as a result of site specific dispersion patterns), but the area impacted seems much less important, both ecologically and economically.

## 7.5 Analysis of Impacts at Grand Isle

### 7.5.1 Area/Concentration Relationships

Area/concentration curves for the near offshore site at Grand Isle are shown in Figure 7-6. Since this site is in the open ocean, outside the Gulf of Mexico barrier islands, the tidal flushing calculations were inappropriate, and no minimum background level was assumed. Two different base cases were used, one assuming a discharge site located fairly close to the shore of Grand Isle, and one assuming a site further away from shore. (These two base cases are cases N1A and N2A, using the nomenclature of Chapter Five. The discharge-to-shore distances and other input parameters assumed for these cases are discussed in detail in that chapter.)

The estimated area of the impact zone for this site is between about 900,000 ft<sup>2</sup> (0.032 mi<sup>2</sup>) and about 9,000,000 ft<sup>2</sup> (0.32 mi<sup>2</sup>).

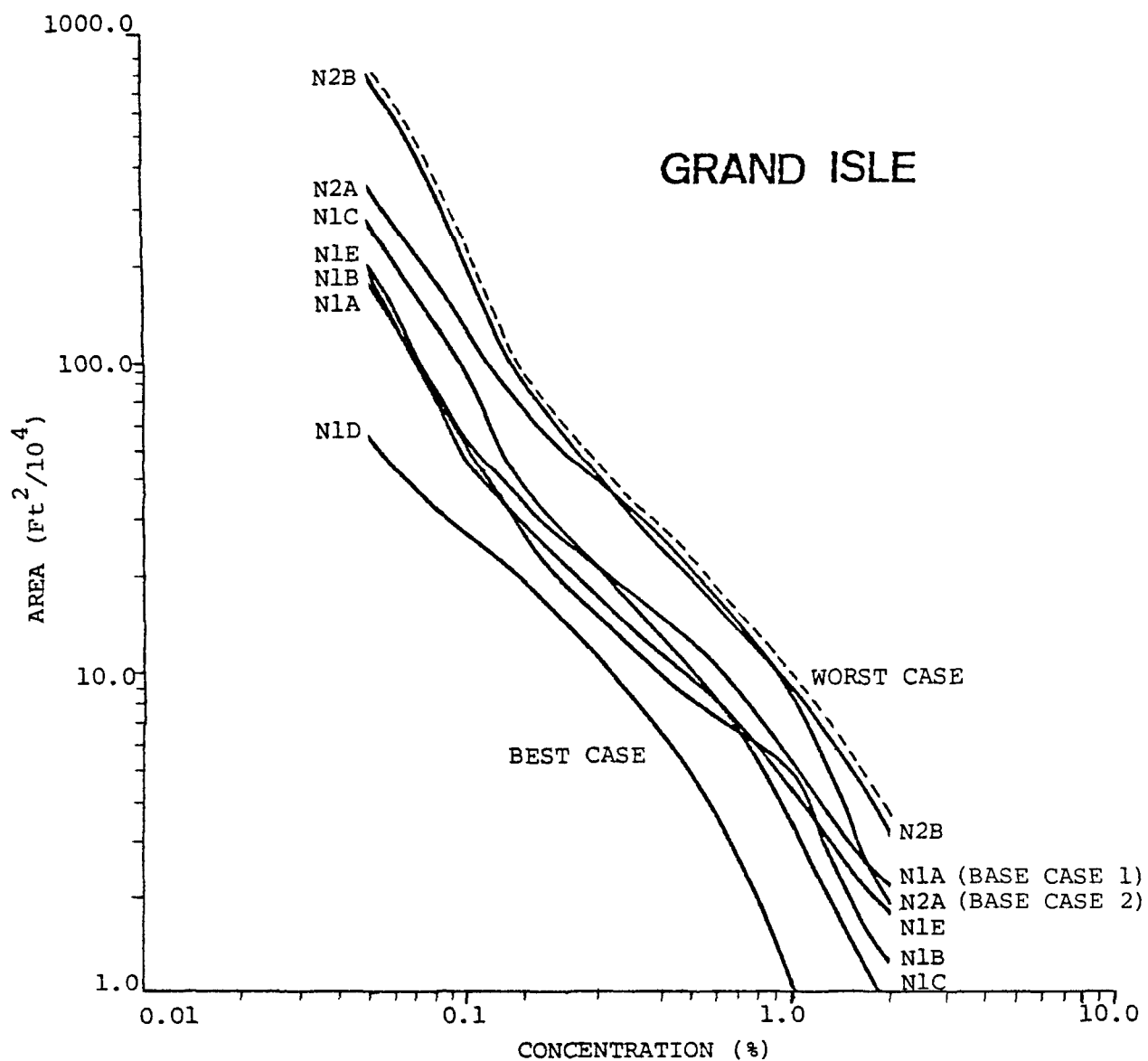


Figure 7-6. Area/concentration curve for Grand Isle site in near offshore Gulf of Mexico.



### 7.5.2 Ecological Considerations

The near offshore Gulf of Mexico is a highly productive region (see Appendix A), which yields extremely high catches of commercially important fish and shellfish. The variety and productivity of this region is suggested by Table 7-4, which lists some of the significant consumer species found there.

## 7.6 Analysis of Impacts at the Far Offshore Gulf of Mexico Site

### 7.6.1 Area/Concentration Relationships

Area/concentration curves for the far offshore site in the Gulf of Mexico are shown in Figure 7-7. Since this site is in the open ocean, tidal flushing calculations are inappropriate, and no minimum background level is assumed.

The estimated area of the impact zone for this site is between about 3,000,000 ft<sup>2</sup> (0.1 mi<sup>2</sup>) and about 10,000,000 ft<sup>2</sup> (0.33 mi<sup>2</sup>).

### 7.6.2 Ecological Considerations

The far offshore Gulf of Mexico is a highly productive region, which yields extremely high catches of commercially important fish and shellfish, as does the near offshore Gulf. The species shown in Table 7-4 can also be found in the far offshore waters of the Gulf.

## 7.7 Summary of Impacts Analysis

The magnitude of impacts observed at each of the study sites is summarized in Table 7-5.

## 7.8 Comments on Agreement of Results with Field Studies

The extension and, more importantly, the validation of this model will require the implementation of field studies specifically concerned with the analysis of brines, water column samples, and ecological communities in the vicinity of production platforms. Previous studies in general have not generated sufficient data on the relationship between concentrations of metals and hydrocarbons in the water column and in the discharged brine to confirm the predictions

TABLE 7-4

KEY CONSUMERS - NEAR AND FAR OFFSHORE GULF WATERS  
(ADJACENT TO BARATARIA BAY, LOUISIANA)

	INVERTEBRATE	FISH	BIRD	MAMMALS
COMMERCIAL SPECIES	★ <u>Penaeus aztecus</u> (Brown Shrimp)  ★ <u>Penaeus setiferus</u> (White Shrimp)  ★ <u>Penaeus duorarum</u> (Pink Shrimp)  ★ ★ <u>Callinectes sapidus</u> (Blue Crab)	★ ★ <u>Anchoa mitchilli</u> (Bay Anchovy)  ★ <u>Cynoscion arenarius</u> (Sand Sea Trout)  ★ <u>Peprilus burti</u> (Gulf Butterfish)  ★ <u>Etropus crassostus</u> (Fringed Flounder)		
SPORT SPECIES		★ <u>Centropistes philadelphia</u> (Rock Sea Bass)  ★ <u>Trichiurus lepturus</u> (Cutlass Fish)  ★ <u>Leiostomus xanthurus</u> (Spot)  ★ ★ <u>Arius felis</u> (Sea Catfish)  ★ ★ <u>Microogon undulatus</u> (Atlantic Croaker)  ★ <u>Chloroscombrus chrysurus</u> (Atlantic Bumper)		
TROPHICALLY IMPORTANT SPECIES	• <u>Gammarus sp.</u> (Amphipod)  • ★ <u>Acartia tonsa</u> (Copepod)  • ★ <u>Paracalanus sp.</u> (Copepod)  ★ <u>Xiphopenaeus sp.</u> (Sea Bob)  ★ <u>Squilla sp.</u> (Mantis Shrimp)  • ★ <u>Mulina sp.</u> (Pelecypod)  ★ ★ <u>Cibanarius vittatus</u> (Hermit Crab)  <u>Loliguncula brevis</u> (Squid)	<u>Prionotus roseus</u> (Blue Spotted Sea Robin)	★ <u>Sterna sp.</u> (Tern)  ★ <u>Avtha affinis</u> (Lesser Scaup)  ★ <u>Larus atricillia</u> (Laughing Gull)  ★ <u>Fregata magnificens</u> (Frigate Bird)  ★ <u>Larus philadelphia</u> (Bonaparte's gull)	★ <u>Tursiops truncatus</u> (Bottlenose Dolphin)
ENDANGERED SPECIES			★ <u>Pelecanus occidentalis</u> (Brown Pelican)	

- ★ Detritivore
- ★ Carnivore
- Herbivore

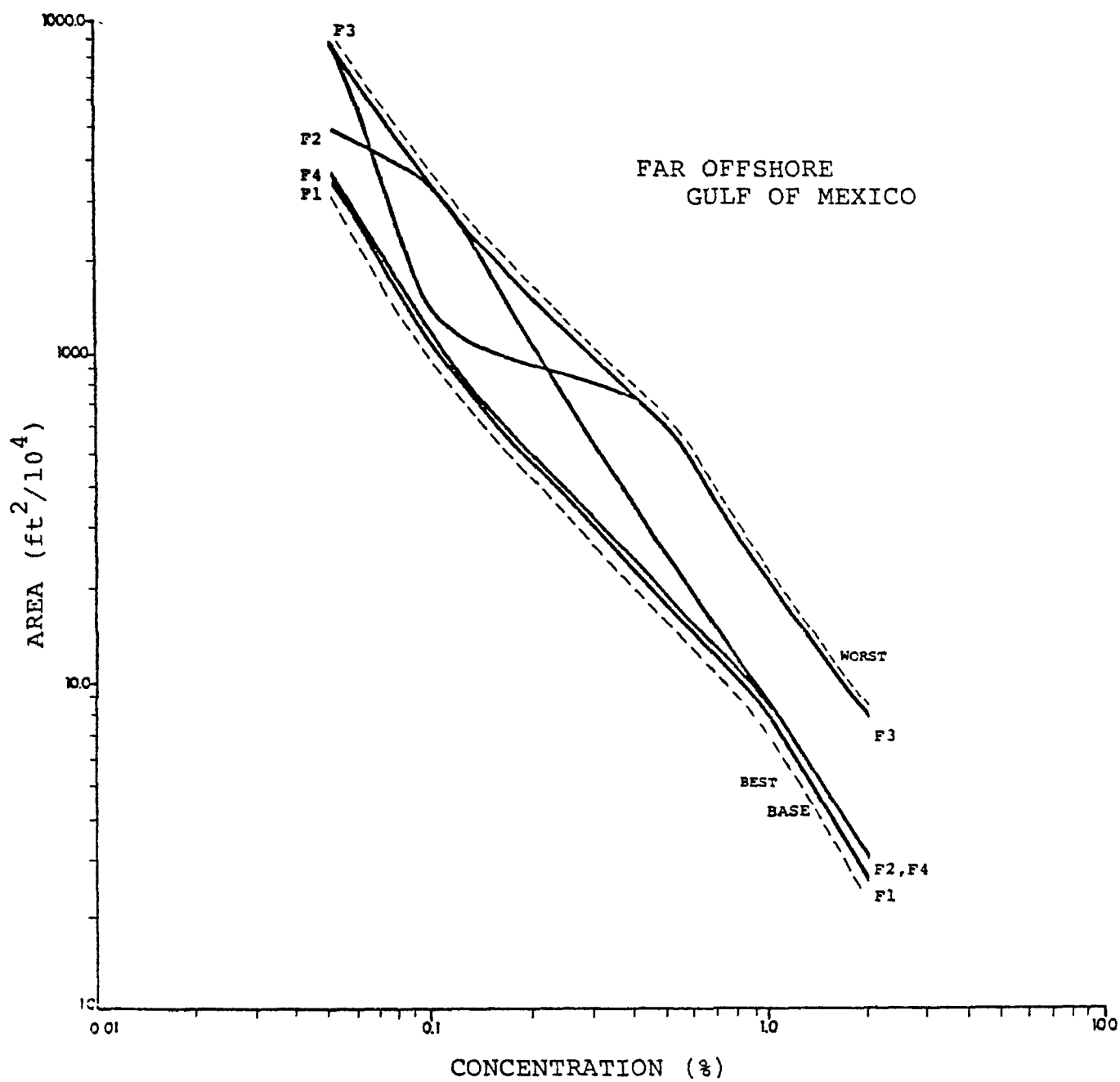


Figure 7-7. Area/concentration curves for far offshore Gulf of Mexico site.

TABLE 7-5  
SUMMARY OF IMPACTS

SITE	LOCATION	PROBABLE AREA OF IMPACT ZONE	ECOLOGY
Hackberry Bay	Onshore	entire bay (ca. 192,000,000 ft <sup>2</sup> or 6.9 mi <sup>2</sup> )	highly productive, supports blue crab, panaeid shrimp, and other commercially important spp.
Cook Inlet	Onshore	ca. 5,000,000 ft <sup>2</sup> (0.18 mi <sup>2</sup> )	relatively infertile due to continuous bottom scouring by tidal currents and to high turbidity
Grand Isle	Near Offshore	700,000 - 9,000,000 ft <sup>2</sup> (0.025 - 0.32 mi <sup>2</sup> )	highly productive; supports several commercially important or sport species
Gulf of Mexico Site	Far Offshore	3,000,000 - 10,000,000 ft <sup>2</sup> (0.11 - 0.36 mi <sup>2</sup> )	highly productive; supports several commercial or sport species

of this dispersion model used in this report, nor have they provided detailed information on brine discharge rates at study sites. Furthermore, studies of the condition of ecological communities near production platforms frequently suffer from an important methodological deficiency in that they often analyze the condition of the ecosystem by comparison with reference points distant from the production platform, and therefore presumably unimpacted. The existence of chronic, long-term pollution problems in some areas, however, may mean that these reference points are themselves strongly impacted. For this reason, the actual magnitude of impacts is probably best determined through comparison with a temporal, rather than a spatial, reference point. The Bureau of Land

Management is currently in the process of organizing such a "pre-impact" baseline study at the site of future offshore drilling operations at Georges Bank, Maine, and at other sites off California, Virginia, and South Carolina.

Furthermore, field studies on the health of ecosystems do not provide any data on what may well be the most important impact of offshore oil operations, which is the bioaccumulation of toxic brine constituents by organisms which are eventually destined for human consumption. Potential toxic impacts of the bioaccumulation of mercury and benz[a]pyrene by marine organisms have already been discussed, and similar problems may be expected as a result of the bioaccumulation of other metal or hydrocarbon brine contaminants. The data in Table 7-2 suggest that this class of impact would be serious down to about three orders of magnitude of brine dilution. This is an especially serious problem in areas such as Hackberry Bay, which are important fishery regions.

For these reasons it is difficult to confirm the predictions of the model on the basis of field data. Nevertheless, the following general comments can be made:

1. The literature of brine impacts shows that the magnitude of the impact is highly site specific, and seems to be correlated most strongly with the dilution characteristic of the receiving waterbody. Thus, Mackin found little ecological damage in the relatively open waterbodies he studied in the Gulf of Mexico, while the Chiltipin Creek studies demonstrated an extremely strong and significant impact in an area with insufficient current and tidal flow to rapidly dilute discharged brines (see discussion in Chapter Five). Furthermore, Chiltipin Creek impacts were found to be considerably ameliorated during periods of high rainfall, which suggests the importance of dilution effects.
2. The tendency for resiliency in established ecosystems and the possibility of selection for pollution-resistant subpopulations over the course of several generations may considerably ameliorate the effects predicted in this analysis. Furthermore, the oxidation of oil hydrocarbons by marine microorganisms may lessen the magnitude of oil-related impacts (although metals would probably be scavenged much more slowly than hydrocarbons from the water column). Extensive examination of this possibility through the implementation of field studies in the Hackberry Bay and Cook Inlet areas is indicated.

3. Mackin and Hopkins<sup>5</sup> reported that oyster mortality along the Louisiana coast (including the Barataria Bay area) was not correlated with proximity to oil fields. Levels of trace metals in oysters and the existence of a number of sublethal effects were not examined in this study. The report also demonstrated that there is a significant natural variation in oyster mortality, due to current, tide, and salinity variations which is much greater than the estimated magnitude of brine-related mortality, and which was observed before offshore operations began in the Louisiana area. According to Mackin and Hopkins: "Field studies of Texas A&M Research Foundation biologists, beginning in 1947, confirmed reports that mortality rates were high on many Louisiana oyster beds and that there was a seasonal cycle in mortality correlated with temperature. ... The regular and predictable nature of this mortality indicated that it was not abnormal."
4. Mackin (see Chapter Five) and, more recently, Neff, observed a zone of ecological stimulation lying outside of the zone of impact which they observed in their field studies. They attribute this to the biodegradation of petroleum hydrocarbons by communities of marine microorganisms, which enable the hydrocarbons to be used as a nutrient source by the marine communities. This may be a significant feature of the impact of petroleum on marine ecosystems, and deserves further attention. It is suggested that further field and laboratory studies be carried out in this area.

In short, the currently available field data are inadequate for quantitative validation of the model, although some of the qualitative data are consistent with the analysis (existence of concentric zones of impact, importance of site specific dilution rates, etc.). Ecological field studies are hampered at many sites by the existence of wide natural variations in mortality parameters (both seasonal and random) which swamp variation due to brine-related impacts.

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<sup>5</sup>J.G. Mackin and S.H. Hopkins, "Studies on Oysters in Relation to the Oil Industry," Publications of the Institute of Marine Science (7) (1961): 1-131.

## CHAPTER EIGHT

### CONCLUSIONS

The data and analyses discussed in this report support the following conclusions:

- Presence of Toxic Substances in Oilfield Brines

Produced brines contain a variety of substances known to have lethal and sublethal toxic effects on marine and estuarine organisms. These toxic constituents include oil hydrocarbons, trace metals (including arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc), phenol, and cyanide. Some of these toxicants have been measured in produced waters at concentrations up to several orders of magnitude higher than the corresponding EPA water quality criteria. In addition to their effect on marine organisms, many of the brine components (particularly mercury and the polynuclear aromatic hydrocarbon benz[a]pyrene) are known to be bioaccumulated in shellfish which may be used for human consumption and so present a potential human health threat.

- Treatment Methods

Current methods used for separating oil hydrocarbons from produced water have little if any effect on levels of dissolved contaminants. These include the dissolved aromatic hydrocarbons which are among the most toxic hydrocarbon components of brines, and the trace metals.

- "Safe" Levels

The impact exerted by contaminants present in the discharged produced water depends on the concentration levels of the contaminants to which biota in the receiving waters are exposed. The concentrations will be a maximum in the immediate vicinity of the point of discharge, and will in general decrease with increasing distance from the discharge point. Toxicological data on the effects of brine toxicants on marine and estuarine organisms, in conjunction with data on produced water contaminant concentrations, suggest (as discussed in Chapter Seven) that a 0.05 percent level

of dilution of oilfield brines (i.e., 1 part brine to 2,000 parts receiving water) is "safe"; i.e., it will produce no significant level of lethal or sublethal effects on resident organisms and will prevent the bioaccumulation of brine constituents to dangerous levels in human food organisms. Accordingly, a convenient measure of the impact associated with a given brine discharge is the area around the discharge point that can be expected to be subjected to produced waters at concentrations greater than or equal to 0.05 percent. It should be noted, however, that the 1:2,000 safe level is based on the maximum produced water contaminant concentrations which have been measured. Since data on contaminant levels in produced waters are sketchy, and since contaminant concentrations are highly variable, both between different geographic regions and different sites in the same region, "safe" levels at all sites will not necessarily occur at the 1:2,000 dilution level used in this analysis. It is also extremely important to bear in mind the fact that the state of knowledge regarding toxic effects of trace metals and oil hydrocarbons is expanding rapidly at present. Hence, the estimate of a safe level used here should be regarded as provisional only, subject to revision on the basis of increased knowledge of toxic effects.

- Evaluation of Impacts

The area of the 0.05 percent dilution zone depends on a number of highly site specific factors. Such factors include the rate at which produced water is discharged, the depth of the receiving water, currents (tidal, freshwater, drift), and diffusion coefficients. Other site specific processes also affect contaminant dispersion but cannot be readily quantified. Processes in this category include adsorption of contaminants on suspended particles, sedimentation and transport of sediments, chemical transformation, and biodegradation. Severity of impact depends not only on the numerical size of the affected area but also on its ecology. Ecological characteristics are important in that they determine the value of the area being impacted in terms of the primary production the area supports, the commercially important species which live there, and the importance of the region to particular lifecycle stages of other economically or ecologically important organisms. Finally, impacts may also be evaluated in terms of the size of the impacted area relative to the size of the receiving waterbody. The same area may represent a much severer impact in a relatively small bay than in a larger, less enclosed waterbody.



● Modeling of Brine Dispersion

The site specific factors of discharge rate, depth of receiving water, currents, and diffusion coefficients have been incorporated into a computerized dispersion model which can be used for estimating the areas of the unsafe (concentration greater than or equal to 0.05 percent) zones at each site. For each of four specific sites (Hackberry Bay, Louisiana; Grand Isle, Louisiana; Cook Inlet, Alaska; and the Ship Shoal oil field in the far offshore Gulf of Mexico), the computer model was used to give estimates of areas expected to be subjected to concentration levels down to 0.05 percent. Several sensitivity analyses were performed for each site in order to allow for uncertainties in available data on input parameter values and simplifying assumptions incorporated in the model. The results of the computations for the four sites are summarized in Table 8-1.

TABLE 8-1  
SUMMARY OF IMPACTS

SITE	LOCATION	PROBABLE AREA OF IMPACT ZONE	ECOLOGY
Hackberry Bay	Onshore	entire bay (ca. 192,000,000 ft <sup>2</sup> or 6.9 mi <sup>2</sup> )	highly productive, supports blue crab, panaeid shrimp, and other commercially important spp.
Cook Inlet	Onshore	ca. 5,000,000 ft <sup>2</sup> (0.18 mi <sup>2</sup> )	relatively infertile due to continuous bottom scouring by tidal currents and to high turbidity
Grand Isle	Near Offshore	700,000 - 9,000,000 ft <sup>2</sup> (0.025 - 0.32 mi <sup>2</sup> )	highly productive; supports several commercially important or sport species
Gulf of Mexico Site	Far Offshore	3,000,000 - 10,000,000 ft <sup>2</sup> (0.11 - 0.36 mi <sup>2</sup> )	highly productive; supports several commercial or sport species

- Onshore Benefits

No similarity was observed between estimated impacts at the two onshore study sites. In Hackberry Bay the impacts are estimated to be rather severe (see Table 8-1). Hackberry Bay is also a productive fishery area. In the mid Cook Inlet area tidal mixing results in a rapid dilution of the discharge away from the discharge point. The impacted area is proportionally small compared with the area of the mid Cook Inlet, and, in addition, is naturally unproductive due to tidal bottom scouring and high natural turbidity levels. Therefore, impacts are judged to be relatively small in the mid Cook Inlet.

The benefits which would be achieved if the proposed near offshore BATEA regulations are extended to apply to onshore discharges are thus highly site specific. Small, enclosed, shallow, and biologically productive bays with large brine discharges will probably stand to benefit considerably. The benefits to be achieved by prohibiting small discharges of produced water into larger and deeper coastal embayments with adequate tidal and freshwater mixing are likely to be correspondingly small. A first order estimate of the magnitude of the benefits to be achieved by a "no discharge" regulation can be obtained through the use of the tidal flushing calculations described in Chapter Four, together with some considerations of the ecology and economic importance of the region being impacted.

- Near Offshore Benefits

In the near offshore Gulf of Mexico waters, the analysis performed for a single site is insufficient to serve as a complete basis for estimating regional impacts. In order to extrapolate from impacts at a single platform to regional impacts, data on platform locations and discharge rates throughout the region are needed.

The benefits to be achieved by prohibiting the discharge of produced waters into near offshore waters will therefore depend critically on the density of production platforms and rates of discharge in a particular region. In areas where platforms are highly concentrated, aggregate discharge levels are likely to be large, and impact zones may overlap. In such areas significant benefits could probably be achieved. In areas with low platform densities and only small rates of brine discharge the benefits are likely to be less pronounced. The analysis performed in this study should, therefore, be supplemented by the assembly

of a data base providing information on the location and discharge rates of production platforms in near offshore Gulf of Mexico waters (projected development might also be incorporated in this supplementary study). Since the rate at which water is produced in a given field tends to increase with the age of the field, assessment of the benefits to be achieved by prohibiting the discharge of produced water should take into account not only the present rate at which water is produced in a field, but also the increased rate at which water can be expected to be produced in the future.

- Far Offshore Benefits

In far offshore Gulf of Mexico waters, the major conclusion to be drawn from this study is that there would probably be little reduction in impacts resulting from the imposition of BATEA regulations over and above those already achieved by the BPCTCA restrictions. The more stringent treatment requirements imposed on far offshore platforms by the BATEA requirements will do little to remove the dissolved hydrocarbons and trace metals which are responsible for much of the toxic impact of oilfield brines. The impacts resulting from the produced water discharge of a given field can be expected to increase with the age of the field, since the rate of water production generally increases with the age of the field.

- Field Data

It is recommended that programs of field data collection be initiated to provide further information on the composition and composition variability of produced waters, and on dispersion characteristics and ecological features of brine discharge sites.

## APPENDIX A

### ECOLOGICAL CHARACTERIZATION OF PRODUCTION SITES

#### A.1 Introduction

The ecological characterization of Cook Inlet, Alaska and Barataria Bay, Louisiana, presented in the following sections, provides an introduction to the key physical, chemical, and geological features of these areas. These sections attempt to present the study areas as ecological systems, involving dynamic interactions between biota and environmental variables, and to describe the dynamics of the principal factors which determine the fates of contaminants contained in discharged produced water.

Physical parameters play an important role in determining pathways of discharged brine in the environment and in determining the nature and severity of effects which the hydrocarbons, trace metals and high salinities have on marine organisms. Currents, winds, tides and depth of water are known to be the key factors influencing effluent dispersion in the water column, while turbidity, suspended sediments, and sedimentation rates will influence the residence time of effluent components in the water column and in the bottom sediments, through absorption, sedimentation and flocculation. Bottom sediments of varying mineral composition, and grain size have different capacities to adsorb, desorb, and retain effluent components. In assessment of impacts, factors such as temperature, salinity, and dissolved oxygen levels, which often increase or decrease the toxicity of trace elements to aquatic organisms by changing metabolic rates or enzyme activity, are of great importance. These parameters also influence rates of microbial degradation of oil.

In some instances physical data can be used to draw quantitative assumptions about effluent fates, as in the case of dispersion models. Often, however, the state of scientific knowledge is such that the interactions between physical parameters and effluent components (e.g., temperature and trace metals), and the effects of these interactions on living systems, are only understood qualitatively, and must be discussed as potential events. It is felt that description of these parameters (and discussion of their interactions in a later section) will provide some insight into the variable nature of effluent impacts on these systems.

Information on the biota of Cook Inlet and Barataria Bay has been collected to facilitate identification of potential impacts from brine discharge. For the species of commercial, sport and trophic importance, a description is given of their preferred habitat at various stages in the life cycle, and their place in the food chain.

The susceptibility of an organism to the toxic effects of contaminants may vary with an organism's life cycle stages. Habitat preferences may also vary throughout a life cycle. For this reason, both factors must be considered together. This will help to identify the pathways by which oil in the water column or sediments can make contact with the biota. Knowledge of feeding mechanisms such as deposit feeding, filter feeding or membrane diffusion, will assist identification of pathways in a similar manner.

Contaminant-induced effects, which change population numbers of species in one trophic level, will in turn affect predator and prey populations on other trophic levels. Predicting impacts of this nature requires knowledge of important trophic interactions (food webs).

The characterizations of the study sites have been organized by ecological units rather than by the "near offshore," and "far offshore" distinctions made in the EPA Development Document. For Louisiana, the ecological characterization has been divided into two sections, one consisting of the marshes and the waterbodies of Barataria Bay (which are actually near offshore waters). The other section describes the near offshore and far offshore waters in the Gulf of Mexico. The Cook Inlet characterization presents combined information for near offshore and far offshore water of Cook Inlet, because little data are available with which to make a distinction. The Cook Inlet intertidal region is treated as a separate ecological unit.

## A.2 Cook Inlet Characterization

### A.2.1 Introduction

Cook Inlet is a large tidal estuary in south central Alaska, which flows into the Gulf of Alaska just east of the base of the Alaskan Peninsula. It is 150 nautical miles wide at its widest point and Knik and Turnagain Arms at the

head of the Inlet are 45 and 43 nautical miles long, respectively.<sup>1</sup>

Figure A-1 depicts the major bays, points, capes and islands of Cook Inlet. For ease of discussion, we have divided Cook Inlet into three semi-distinct ecological parts. The Upper Inlet lies east of a line extending northward from Point Possession. The waters of the Upper Inlet receive great loads of suspended glacial sediment from the Susitna River, Little Susitna River and the rivers emptying into Knik and Turnagain Arms, and are extremely turbid.

The Middle Inlet, where brine discharge occurs, includes waters from the Upper Inlet southwestward to the latitude of Tuxedni Bay (60°25' N). There are four onshore separation platforms and three offshore facilities discharging brine into the Inlet: the Union Oil facility located just south of Kenai discharges the wastewater into a ravine along which it flows to Cook Inlet waters. The Shell Oil facility near Nikiska and the Marathon plant near West Foreland in Trading Bay both discharge wastes into the Inlet by pipe.

Atlantic Richfield Company has a separation facility at Granite Point which discharges wastes into a trough which leads into Cook Inlet. Three offshore platforms owned by Amoco have separation facilities and dump wastes directly into Inlet waters. Figure A-1 depicts the location of onshore and offshore separation facilities.

The remaining portion of Cook Inlet, south of Tuxedni Bay and Clam Gulch, is commonly called the Lower Inlet. This region has the clearest waters, and is the most productive, supporting all major species of fish, shellfish, and marine mammals found in Cook Inlet.

Cook Inlet is bordered by a combination of tidal marsh, mudflats, mountains and lowlands. Over 100 square miles of tidal marsh are found in the Susitna Flats, upper Knik Arm, Chickaloon Flats (in Turnagain Arms), in Trading Bay and in Redoubt Bay. The Aleutian Range and Alaska Mountains lie to the Northeast and the Chugach and Kenai Mountains lie to the southeast. A rim of lowlands separates the mountains from most of the Inlet though this rim is narrow or absent in the Lower Inlet, where the mountains meet the sea. In the Upper

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<sup>1</sup>C.D. Evans, E. Buck, R. Buffler, et al., The Cook Inlet Environment, A Background Study of Available Knowledge (Anchorage: University of Alaska, Resources and Science Center, Alaska Sea Grant Program, August 1972).

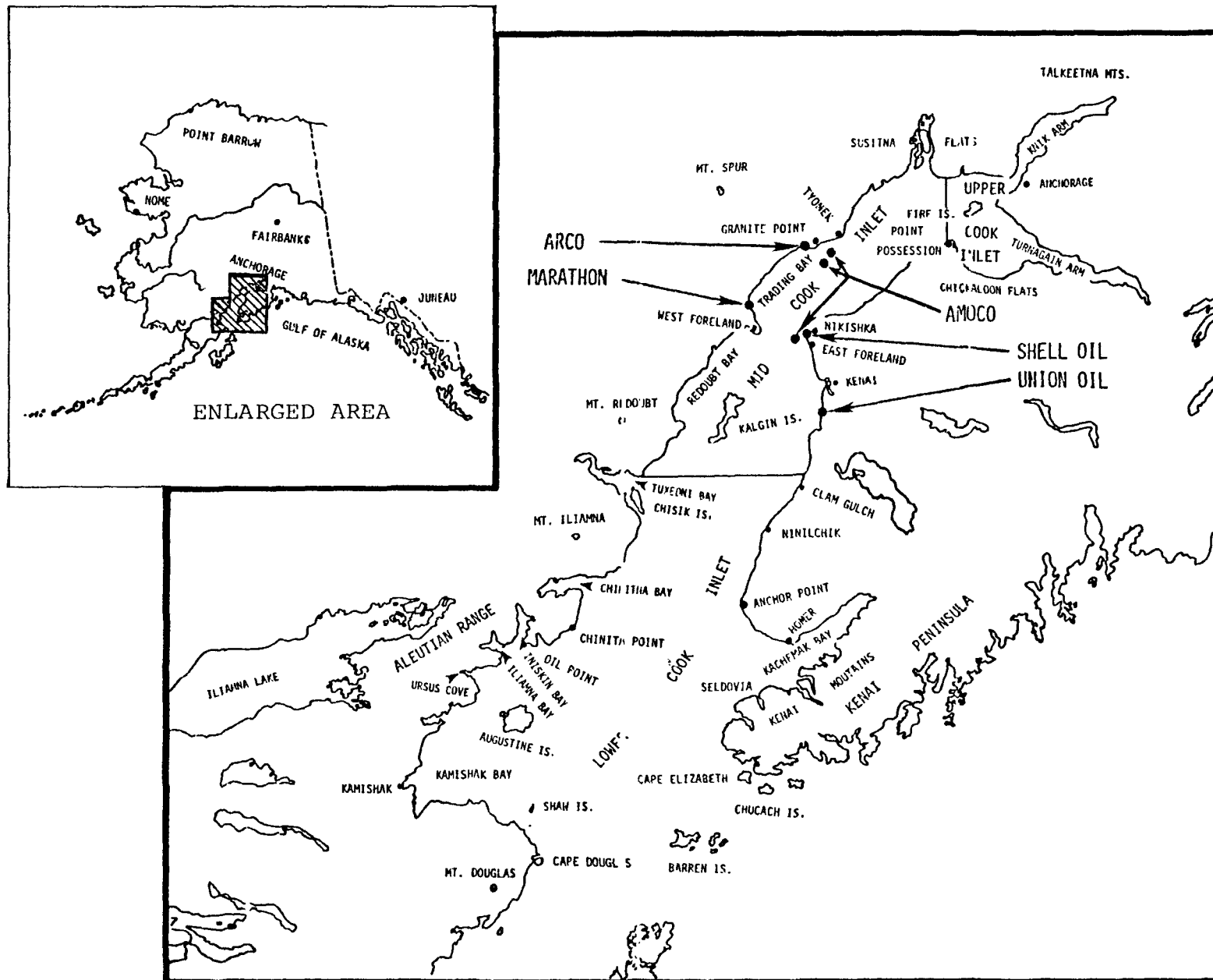


Figure A-1. Cook Inlet.

and Mid Inlet these lowlands are wide, often forming mudflats, and support fairly high densities of waterfowl.

Oceanographic and biological information is not readily available on Cook Inlet waters. Interest in this type of data has only developed recently, within the past 10 years, and the logistics of data collection have presented problems. The Lower Inlet is the area of most interest to biologists and agencies concerned with wildlife and fisheries management. Most Cook Inlet investigations seem to have produced data for this region in particular. The Upper Inlet also has been of interest to planners and managers due to the density of human population found along Knik and Turnagain Arms. A number of studies relating to waste disposal and civil engineering have generated information about the Upper Inlet. The major items of interest in the Mid Inlet are the offshore oil platforms and the onshore separation facilities, refineries and chemical plants. Aside from one major study performed by the University of Alaska for the Collier Carbon and Chemical Corporation,<sup>2</sup> there are very little data available about the Mid Inlet open ocean or coastal environments. The characterization presented here has pieced together published and unpublished information into a coherent description of the ecology of Cook Inlet.

#### A.2.2 Temperature

Water temperatures in Cook Inlet range from near freezing ( $-1.2^{\circ}\text{C}$ ) in February to a high of  $15.2^{\circ}\text{C}$  in August. The Inlet is generally well mixed vertically and temperatures are fairly uniform from top to bottom. Some thermal stratification is observed on the western side of the Mid and Upper Inlet in the region of freshwater outflow.<sup>3</sup> Figure A-2 depicts surface temperature distribution in May.

#### A.2.3 Depth

The Upper Inlet is a shallow, silt laden basin with depths less than 20 fathoms. Turnagain and Knik Arms are

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<sup>2</sup>F.W. Hood, K.W. Natajan, D.H. Rosenberg, and D.D. Wallen, Summary Report on Collier Carbon and Chemical Corporation Studies in Cook Inlet, Alaska (College, Alaska: Institute of Marine Science, University of Alaska, December 1968).

<sup>3</sup>Hood, Natajan, Rosenberg, and Wallen, Summary Report on Collier Carbon and Chemical Corporation.



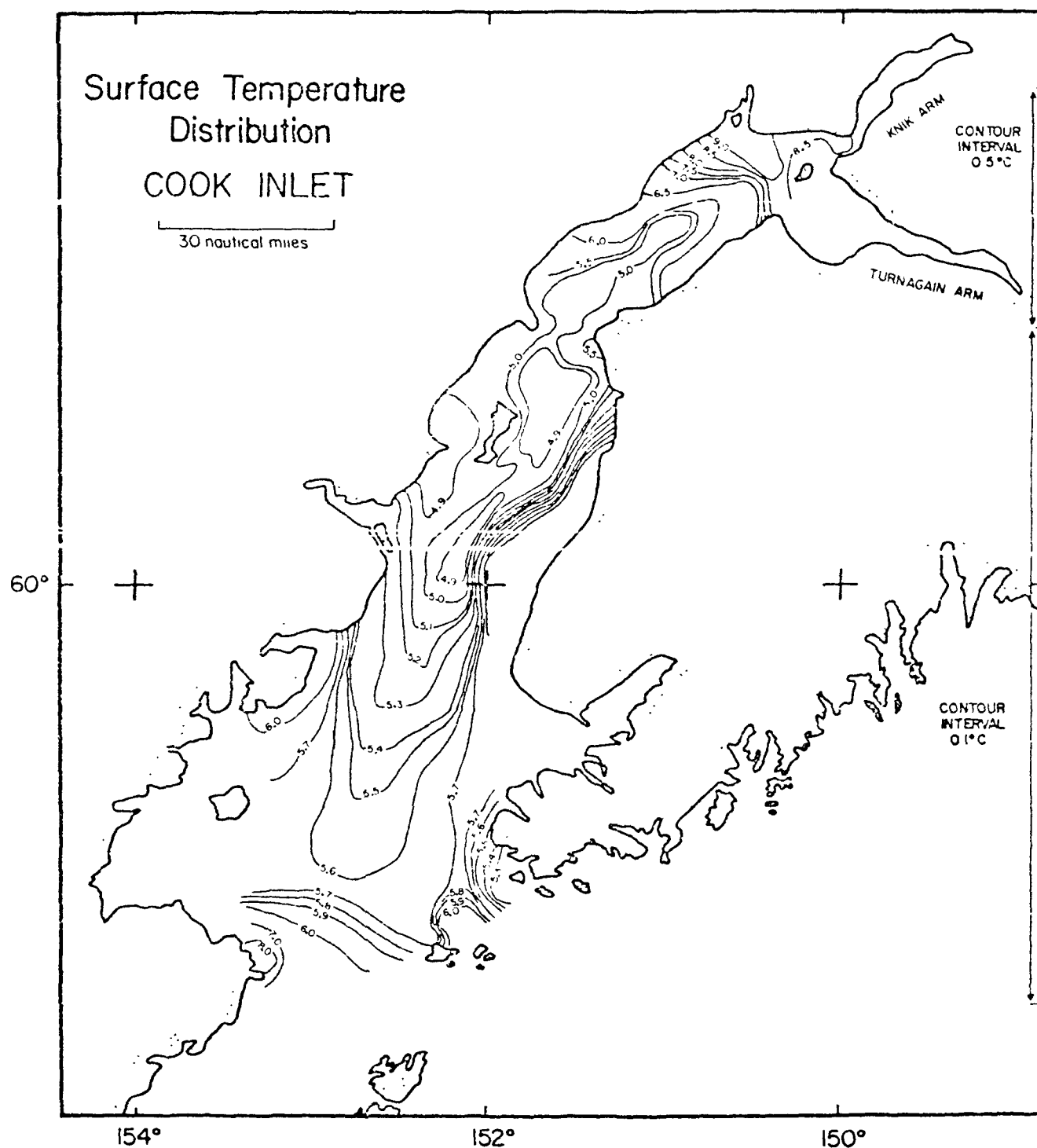


Figure A-2. Surface temperature distribution - Cook Inlet. (P.J. Kinney, J. Groves, and D.K. Button, Cook Inlet Environmental Data, R/V Cruise 065 - May 21-28, 1968 (College, Alaska: Institute of Marine Science, University of Alaska, Report No. R-70-2, 1970), p. 14.)

the shallowest areas with much of the bottom exposed as tidal flat during low tide. There are two channels which extend southward in the Mid Inlet and past Trading Bay, Redoubt Bay and Upper Kenai, joining in an area west of Cape Ninilchik. In the Lower Inlet south of Cape Ninilchik, the channel deepens to 80 fathoms and widens to extend across the mouth of the Inlet. Below the Forelands, the bottom slopes downward, reaching depths over 100 fathoms south of the Inlet entrance.<sup>4</sup>

The Mid Inlet bottom has a fairly gentle slope on the eastern side, the waters reach a depth of 10 fathoms 2 miles (near East Foreland) to 12 miles (in Upper Mid Inlet) off-shore. On the western side of the Mid Inlet 10 fathom depths occur from several hundred yards to 5 miles offshore. Figure A-3 depicts changes in depth along a transect running from the Marathon facility at West Foreland across the Inlet to the Shell Oil plant in Nikiska. Shallow regions, less than 10 fathoms, are found surrounding Middle Ground Shoal, an island adjacent to Trading Bay, and Kalgin Island off of Redoubt Bay.

Cook Inlet has several deep holes, most of which result from scouring of the sea floor. Between East and West Foreland in the Mid Inlet the bottom reaches a depth of 75 fathoms and an 85-fathom hole occurs at the entrance to Kachemak Bay in the Lower Inlet. In contrast, Kamishak Bay, on the western side of the Lower Inlet, is relatively shallow, sloping toward the Inlet center at a grade of 5 to 10 feet per mile.

#### A.2.4 Ice

Ice begins forming in the Upper Inlet in October and extends into Lower Cook Inlet as determined by wind and temperature. Intertidal areas become coated with ice during repeated exposures. Along the tidal flats, ice and sand accumulate and are stranded with each successive tide, forming large clumps called *stamuki* which may reach a

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<sup>4</sup>D.M. Anderson, L.W. Gatto, H.L. McKim, and A. Petrone, "Sediment Distribution and Coastal Processes in Cook Inlet, Alaska," in Symposium on Significant Results Obtained from the Earth Resources Technology Satellite-1, Vol. 1, Section B, S.C. Freden, E.P. Mercanti, and M.A. Becker (eds.), (Washington, D.C.: National Aeronautics and Space Administration, 1973); and Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

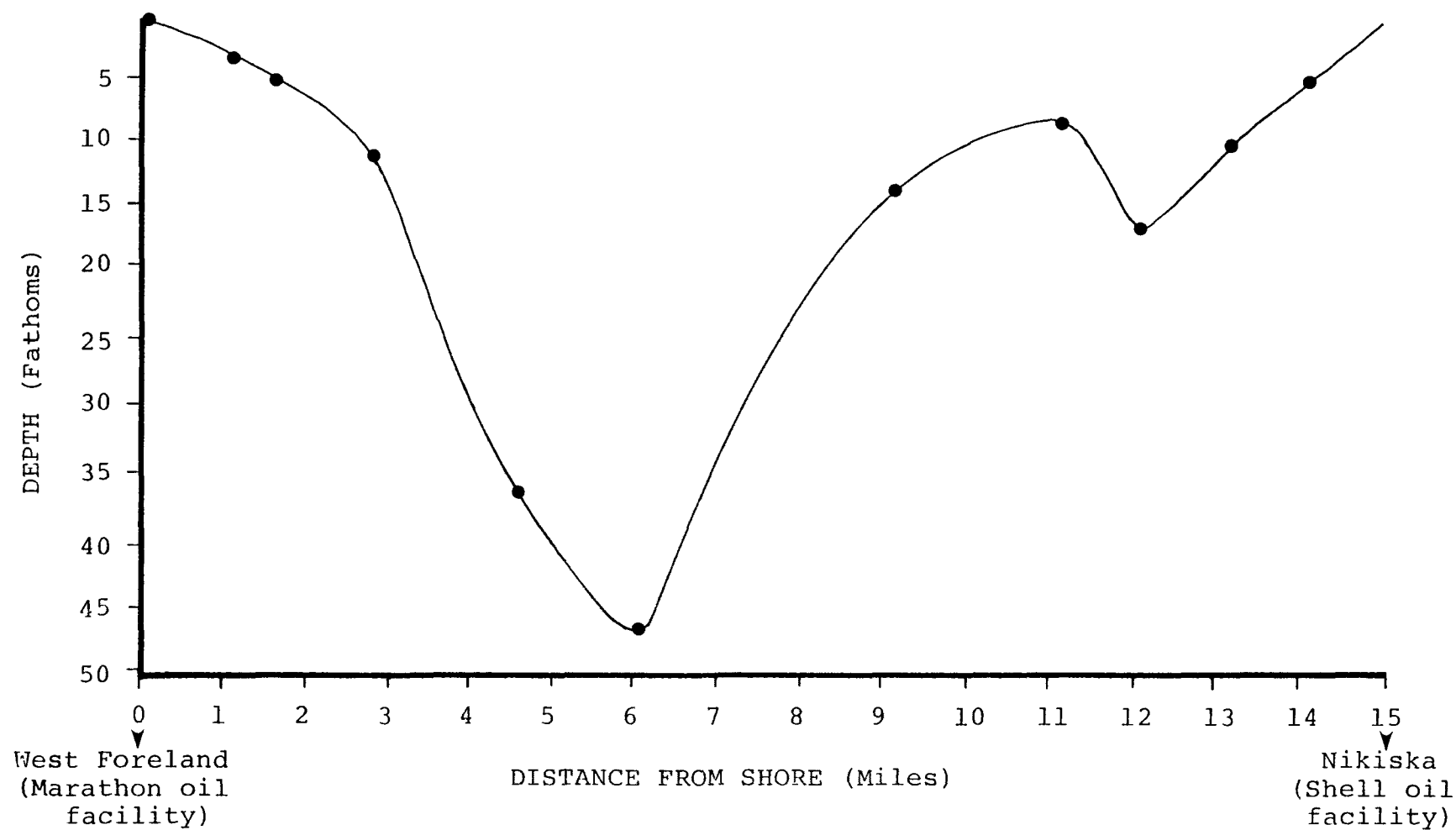


Figure A-3. Bathymetry profile along a Mid Inlet transect, West Foreland to Nikiska.

thickness of 40 feet. Much of the ice found in the Inlet is floe ice, which increases in thickness up to 1 inch per day. Ice puts additional stresses on marine organisms in the winter, particularly those in the intertidal region which must freeze and thaw with each tidal cycle.<sup>5</sup>

#### A.2.5 Tides and Currents

The tides of Cook Inlet are semi-diurnal with a notable inequality between successive low waters. Mean diurnal range of the tides varies from 13.7 feet at the entrance to the Inlet to 29.6 feet at Anchorage. There is a 4.5 hour time lag between high water at the mouth of the Inlet and high water at Anchorage. The mean diurnal tidal range on the east side of the Inlet is greater (19.1 feet in East Lower Inlet) than it is on the west side (16.6 feet in West Lower Inlet). Tidal bores sometimes occur in Turnagain Arm, reaching heights of 10 feet.<sup>6</sup> Table A-1 gives the mean range (the difference in height between mean high water and mean low water), the diurnal range (the difference in height between mean higher high water and mean lower low water), and the mean tide level (a plane midway between mean low water and mean high water measured from the mean lower low water level) for locations in Cook Inlet.

Three features strongly influence the tides in Cook Inlet: topography, friction, and the Coriolis force. The topography of the Inlet may increase tidal amplitude at certain locations. In the absence of friction, tidal height would remain constant between the mouth of the Inlet and the Forelands, and then would steadily increase. The amplitude at Anchorage would be twice that at the entrance. However, as a result of friction, energy is lost. There is a net inward transport of energy through the entrance to replace this loss. Therefore, the form of the wave is progressive, with maximum currents occurring less than 3 lunar hours before local highwater. The stronger the currents are, the greater the tidal amplitude on the east side of the Inlet than on the west.<sup>7</sup>

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<sup>5</sup>Alaska Department of Fish and Game, Habitat Protection Section, "Lower Cook Inlet Currents, Tides, Winds, Bathymetry and Ice" (map), Anchorage, Alaska, 1976 (unpublished).

<sup>6</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>7</sup>J.C.H. Mungall, Cook Inlet Tidal Stream Atlas, Institute of Marine Science, University of Alaska, Fairbanks, Alaska, 1973.

TABLE A-1

RANGE OF TIDES AND MEAN TIDE LEVEL IN COOK INLET

LOCATION	MEAN	RANGES (ft)	
		DIURNAL	MEAN TIDE LEVEL
Ushagat Island, Barren Islands	11.4	13.7	7.2
Port Chatham	12.0	14.3	7.5
Port Graham	14.4	16.5	8.6
SELDOVIA, Kachemak Bay	15.4	17.8	9.3
Homer, Kachemak Bay	15.7	18.1	9.5
Cape Ninilchik	16.5	19.1	10.1
Ninilchik	16.7	19.1	10.0
Kenai River entrance	17.7	20.7	11.0
Kenai City Pier	17.5	19.8	10.4
Nikiski	17.9	20.7	11.1
East Foreland	18.0	21.0	11.2
Fire Island	24.4	27.0	14.2
Sunrise, Turnagain Arm <sup>a</sup>	30.3	33.3	17.1
ANCHORAGE, Knik Arm	26.1	29.0	15.3
Eklutna, Knik Arm <sup>b</sup>	b	b	b
North Foreland	18.3	21.0	11.3
Drift River Terminal	15.4	18.1	9.7
Texedni Channel	14.0	16.6	8.9
Snug Harbor	13.2	15.7	8.3
Illamna Bay	13.2	14.5	7.5
Nordyke Island, Kamishak Bay	12.9	15.2	8.0

<sup>a</sup>A bore frequently occurs in Turnagain Arm just after low water. Under favorable conditions it is said to reach a height of 6 feet.

<sup>b</sup>Because of the shoal condition of the upper part of Knik Arm, the channel off Eklutna becomes practically a nontidal stream during the period when the height of the tide at Anchorage is less than 15 feet above mean lower low water.

Source: National Ocean Survey of the National Oceanic and Atmospheric Administration, Tide Tables 1976, West Coast of North and South America, Washington, D.C., 1975, p. 178.

The currents of Cook Inlet have been described as being of moderate velocity. In the Forelands region, where the brine discharge points are located, currents are strongest, reaching a mean maximum velocity of 3.8 knots, with peak maximum velocities exceeding 6.5 knots at monthly tidal extremes.<sup>8</sup> In the Lower Inlet, maximum inward currents occur 1.5 hours before local high water; in the Upper Inlet they occur 1.5 to 3 hours before local high water.<sup>9</sup> Table A-2 gives the direction of the flood current, the average velocity of the flood current, the ebb current direction, and the average velocity of the ebb current, all at strength of current. Flood and ebb current directions are the directions toward which the current flows measured in degrees, clockwise, from 000° at north.

Circulation patterns and tidal currents are important factors in the distribution of nutrients (hence productivity) in the Inlet, in determining the impact of localized contaminants in the water, and in their effects on unconsolidated bottom sediment. Depth of water, coastline morphology and freshwater drainage combine with tidal effects to divide the Inlet into the three parts which were mentioned earlier.

The Upper Inlet waters are well mixed laterally, longitudinally and vertically with each tidal cycle. In summer, there is a net outward movement of Upper Inlet waters with each tidal cycle, due to the large inflow of glacial meltwater from tributary streams. In winter with the freezing of these streams, there is no net outflow from the Upper Inlet and water sloshes back and forth with each tide.<sup>10</sup>

The Middle Inlet, where brine discharge sites occur, is characterized by the net inward movement of saline oceanic waters up the eastern shore and a net outward movement of freshwater runoff along the western shore. There is extensive vertical mixing due to turbulence from swift current and high Coriolis force; however, lateral separation of highly saline incoming water and less saline waters is maintained throughout the Middle Inlet.<sup>11</sup>

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<sup>8</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>9</sup>Mungall, Cook Inlet Tidal Stream Atlas.

<sup>10</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>11</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

TABLE A-2

MAXIMUM CURRENTS IN COOK INLET

LOCATION	MAXIMUM CURRENTS			
	FLOOD		EBB	
	DIRECTION (TRUE)	AVERAGE VELOCITY	DIRECTION (TRUE)	AVERAGE VELOCITY
	DEGREES	KNOTS	DEGREES	KNOTS
Chugach Passage	355	3.1	170	1.8
Iniskin Bay	000	0.9	180	1.2
Anchor Point, 3 miles southwest of	000	2.4	195	1.9
Chinitna Bay	260	1.0	080	1.1
Cape Ninilchik, 1 mile west of	020	2.2	205	1.4
Tuxedni Channel	330	1.1	160	1.9
Cape Kasilof, 3 miles west of	020	3.0	205	2.3
Kenai, 6 miles southwest of	020	2.4	195	2.6
Kenai Packers Cannery Warf	115	0.7	285	1.4
Nikiski	000	3.8	180	2.6
Nikiski, 0.8 mile west of	354	3.8	175	3.6
West Foreland, midchannel	025	3.8	205	3.8
Moose Point, 3 miles northwest of	065	2.9	245	2.6
Anchorage, 0.2 mile offshore	030	1.5	205	2.5
Anchorage, 1 mile off of	050	2.9	220	2.9
Knik Arm, south of Goose Creek	015	3.6	180	3.9

Source: National Ocean Survey of the National Oceanic and Atmospheric Administration, Tidal Current Tables 1976, Pacific Coast of North America and Asia, Washington, D.C., 1975, p. 223..

In the Lower Inlet, the water masses of differing salinity maintain separation. On the west side a vertical stratification occurs with colder saline ocean water underlying warmer, less saline inlet waters. Near Tuxedni Bay, the rising basin floor creates an upwelling of deeper, oceanic water -- bringing important nutrients up to the photic zone.<sup>12</sup>

#### A.2.6 Salinity

Salinity in Cook Inlet ranges from 32 ppt at the mouth of the Inlet to 8 ppt at the mouth of the Susitna River in May.<sup>13</sup> Figure A-4 presents surface salinity distribution in May.

Salinities in the Mid Inlet region, where brine discharge occurs, range from 30 ppt in February to 21 ppt in August. Saltwater enters the Inlet on the eastern side and freshwater exits on the western side, a combined result of the Coriolis force and geographic location of the rivers.<sup>14</sup>

The waters are well mixed from top to bottom on the eastern side of the Mid and Upper Inlet. In the Lower Inlet stratification is observed with the entering cold saline ocean water underlying warmer Inlet waters.

In areas where large quantities of freshwater are contributed, such as Susitna River, there is a pronounced halocline and thermocline. However, freshwater inflow from the Kenai River enters the Inlet in an area of maximum currents and creates no salinity stratification. Waters

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<sup>12</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>13</sup>P.J. Kinney, J. Groves, and D.K. Button, Cook Inlet Environmental Data, R/V Cruise 065 - May 21-28, 1968, (College, Alaska: Institute of Marine Science, University of Alaska, 1970).

<sup>14</sup>Kinney, Groves, and Button, Cook Inlet Environmental Data.



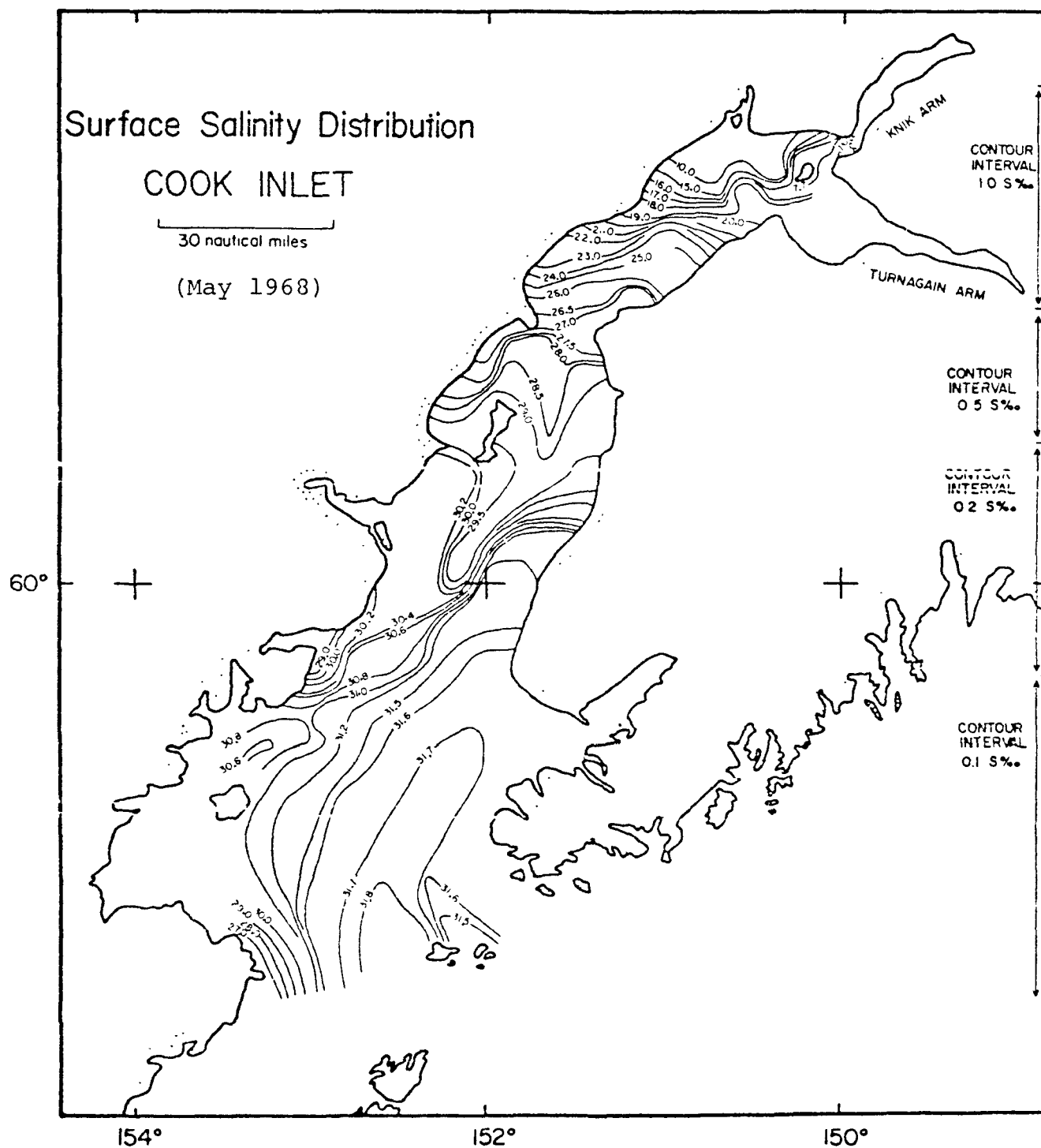


Figure A-4. Surface salinity distribution - Cook Inlet. (P.J. Kinney, J. Groves, and D.K. Button, Cook Inlet Environmental Data, R/V Cruise 065 - May 21-28, 1968 (College, Alaska: Institute of Marine Science, University of Alaska, Report No. R-70-2, 1970), p. 13).

along the western shore have more salinity stratification due to lesser currents and freshwater input. Less stratification is observed during flood tides than during ebb tides.<sup>15</sup>

For any estuary a key factor determining the rate at which pollutants are removed from the estuary is the freshwater flow into the estuary. Table A-3 gives available data on the sources of freshwater influx for Upper and Mid Cook Inlet.

#### A.2.7 Wind

Wind speed and direction in Cook Inlet show a notable seasonal variation. In January and February, winds are from the north at 7 to 40 knots. By April, winds are to the northwest and have decreased to a maximum of 21 knots. May, June, and July are very calm, less than 1 knot. Summer winds have a southerly component and pick up speed in August and September. In November and December, high velocity (30 knots) winds blow from the north. Open waters in Cook Inlet tend to have higher wind speeds than nearshore waters.<sup>16</sup>

Storms of gale force, with 50 to 75 knot winds, are experienced in the Cook Inlet each winter. Waves may reach heights of 15 feet and 6-second periods have been recorded. Under extreme conditions winds may reach 75 to 100 knots.<sup>17</sup>

#### A.2.8 Turbidity and Suspended Sediment

Suspended sediment varies from 0 at the mouth of the Inlet to 1,540 mg/l at Anchorage (Figure A-5). These sediments, often of glacial origin, are derived primarily from headwaters of the Matanuska River system. Suspended sediments seem to be uniformly distributed with depth in areas not immediately in the river plume. Highest values of suspended sediment occur in well-mixed regions of strong tidal currents -- on the east side of the Inlet. Suspended sediment is nearly absent at the central and western portions

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<sup>15</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>16</sup>Alaska Department of Fish and Game, "Lower Cook Inlet Currents, Tides, Winds, Bathymetry and Ice."

<sup>17</sup>Alaska Department of Fish and Game, "Lower Cook Inlet Currents, Tides, Winds, Bathymetry and Ice."

TABLE A-3

STREAMFLOW DATA, MID AND UPPER COOK INLET

NAME OF STREAM	DRAINAGE AREA (sq. mi.)	MEAN DAILY DISCHARGE (ft <sup>3</sup> /s)	MAXIMUM DAILY DISCHARGE (ft <sup>3</sup> /s)	MINIMUM DAILY DISCHARGE (ft <sup>3</sup> /s)
Susitna R.	19,400	--	--	--
near Denali	950	2,665	--	--
near Cantwell	4,140	6,824	55,000	460
near Gold Creek	6,160	10,250	77,700	950
Tributaries of Susitna				
Maclaren R.	280	1,092	8,200	55
Tyone R.	1,400	--	--	--
Skwentna R. near Skwentna	2,250	6,937	47,500	600
Talkeetna R. near Talkeetna	2,006	5,299	63,000	400
Chulitna R. near Talkeeta	2,570	8,406	45,000	900
Matanuska R. at Palmer	2,070	4,196	40,700	360
Knik R.	1,200	5,800	--	--
Ship Creek near Anchorage	90.5	149	1,420	0
McArthur R.	350	--	--	--
Chakachatna R. near Tyonek	1,120	4,658	90,000	460
Beluga R.	930	--	--	--
Kenai R. At Soldotna	2,010	5,958	23,900	1,100

Source: L.L. Selkregg, Alaska Regional Profiles; South Central Region (Anchorage: University of Alaska, Arctic Environmental Information and Data Center, 1974), pp. 87,90.

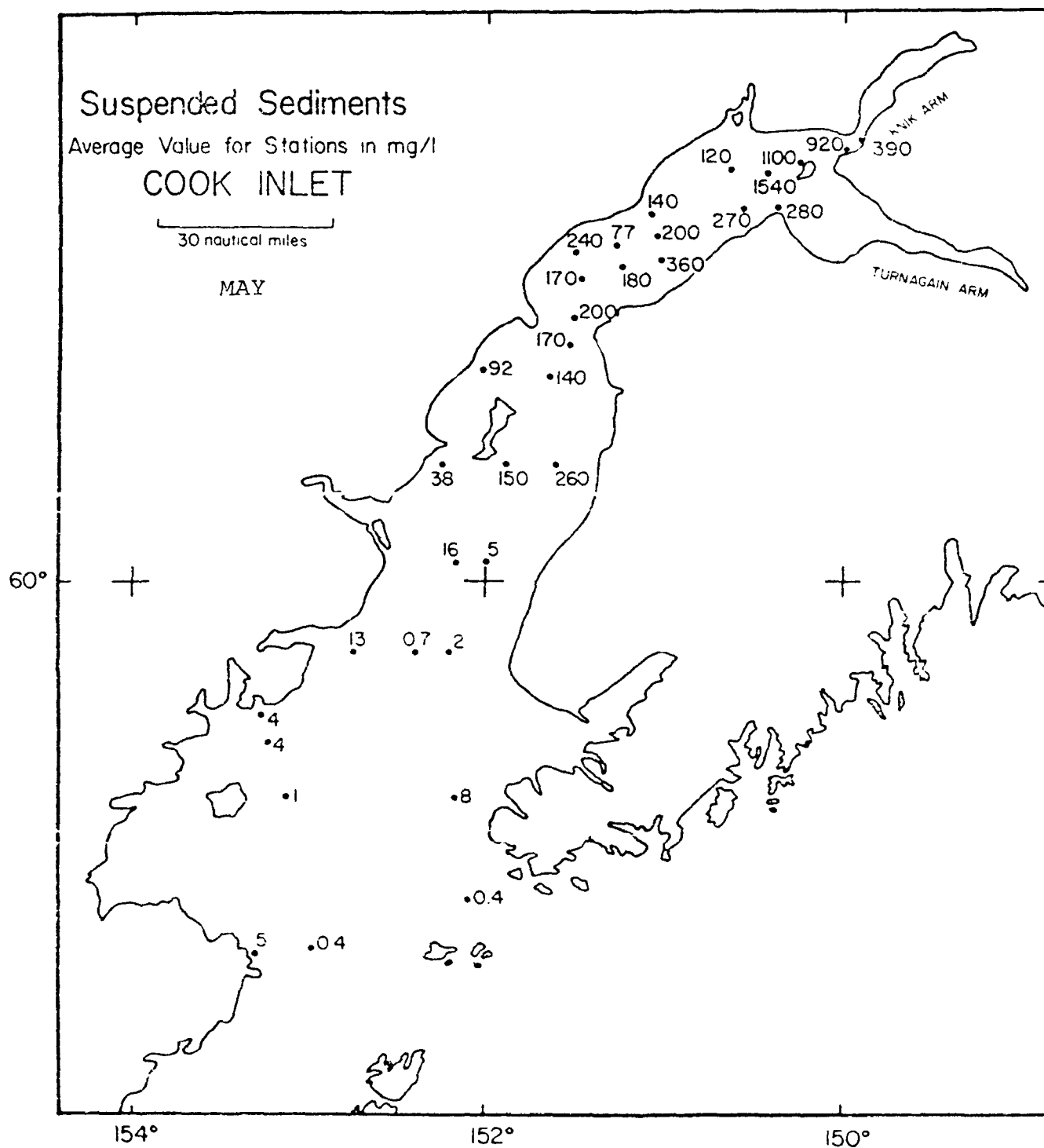


Figure A-5. Suspended sediments - Cook Inlet. Average value for stations in mg/l. (P.J. Kinney, J. Groves, and D.K. Button, Cook Inlet Environmental Data, R/V Cruise 065 - May 21-28, 1968 (College, Alaska: Institute of Marine Science, University of Alaska, Report No. R-70-2, 1970), p. 23.

of the Inlet mouth. Organic carbon and silicate concentrations follow the same patterns as do suspended sediment.<sup>18</sup>

#### A.2.9 Bottom Sediments

Lower Cook Inlet bottom sediments consist of silty sand and gravelly sand; Mid Inlet sediments are primarily gravel; and Upper Inlet sediments contain well-sorted sand (Figure A-6). Little deposition of sediments takes place in the Upper Inlet though much of the flocculation may be deposited on the extensive mudflats north of the Forelands.<sup>19</sup>

#### A.2.10 Biology -- Cook Inlet Open Waters

The distribution of plants and animals in the Cook Inlet waters reflects the complex interactions of tidal mixing of fresh and salt waters, the large tidal amplitude resulting in extensive tidal flats, the large loads of suspended glacial sediments, the scouring action of tidal currents, and the presence of ice during winter months.

Little is known about the distribution and abundance of benthic species in Cook Inlet. It appears that very few species exist in the silt laden waters of the western and upper half of the Inlet. The high tidal amplitude and strong tidal currents which scour the bottom make survival difficult for most benthic organisms. The great loads of suspended sediment in these regions limit penetration of light, confining photosynthesis to a very shallow photic zone. Productivity seems to increase as one moves oceanward in the Inlet to clearer, more saline waters. The Lower Inlet waters provide habitat for a variety of sport and commercially important fish and shellfish, and numerous other non-fished species.

#### A.2.11 Primary Productivity

Most primary production in the open waters of Cook Inlet occurs in the form of phytoplankton. The high silicate content of incoming sediments and of Inlet waters seems to favor the growth of diatoms, which appear to be the dominant

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<sup>18</sup>Kinney, Groves, and Button, Cook Inlet Environmental Data.

<sup>19</sup>Anderson, Gatto, McKim, and Petrone, "Sediment Distribution and Coastal Processes in Cook Inlet"; and Kinney, Groves, and Button, Cook Inlet Environmental Data.

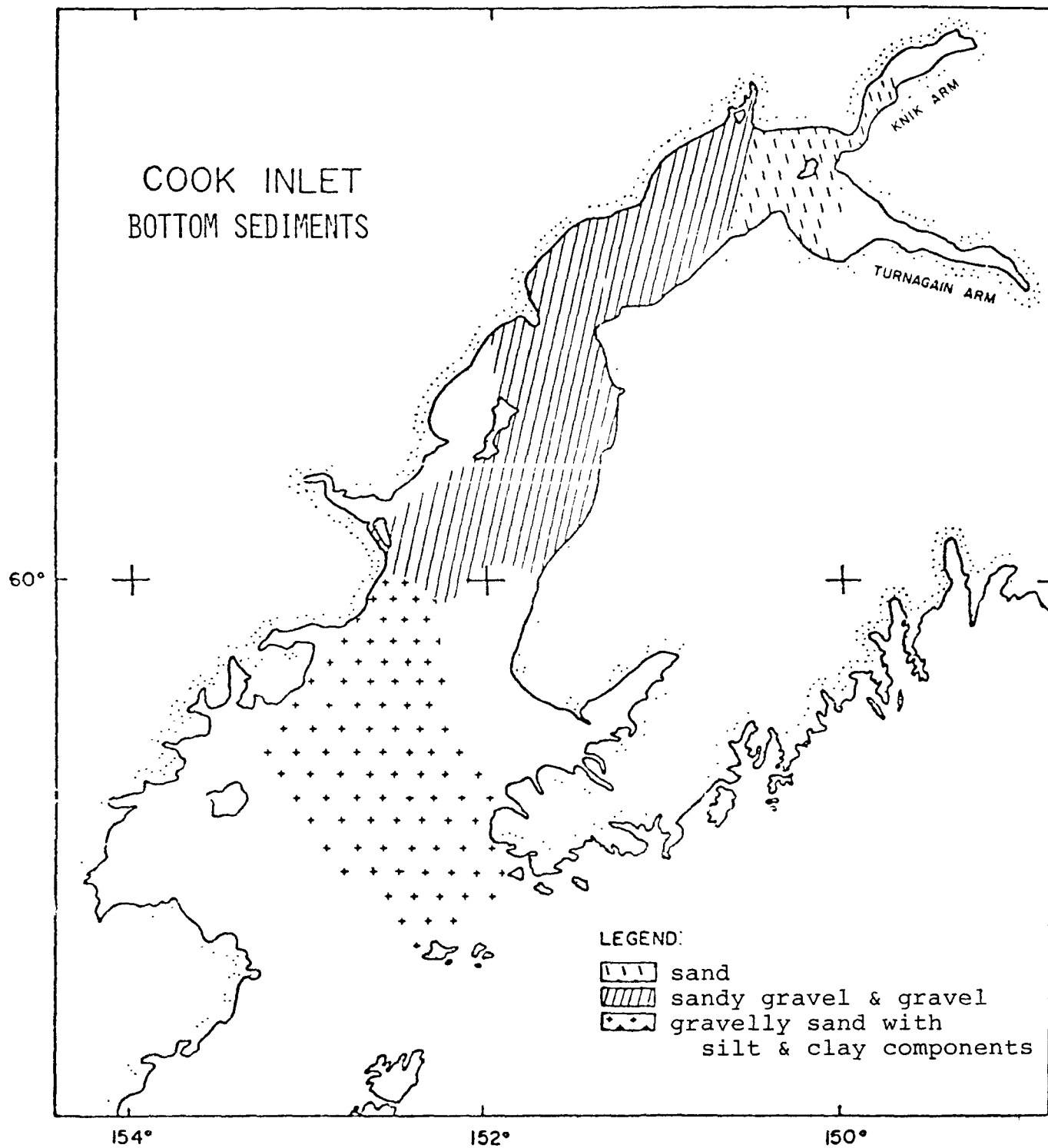


Figure A-6. Bottom sediments - Cook Inlet. (P.J. Kinney, J. Groves, and D.K. Button, Cook Inlet Environmental Data, R/V Cruise 065 - May 21-28, 1968 (College, Alaska: Institute of Marine Science, University of Alaska, Report No. R-70-2, 1970), p. 24.

phytoplankton. The presence of silicoflagellates, dino-flagellates and tintinnids have also been reported.<sup>20</sup> It is quite possible that the majority of the phytoplankton consists of nanno and ultra plankton, which are too small to accurately collect and identify generically. Table A-4 presents the major identifiable primary producers in the open waters of Cook Inlet.

The rapid exchange of water with the Gulf of Alaska and strong vertical mixing on the lower east side of the Inlet support the growth of numerous diatoms and macrophytes. There are more species of primary producers found in this region than in the Mid and Upper Inlet, where higher turbidity, brackish water and less nutrient turnover limit photosynthesis. Diatom blooms, which occur periodically, are limited by light intensity and by nitrogen and silica concentrations in the water. In the Lower Inlet, macrophytic algae (kelp) (see Table A-4) found in subtidal and intertidal waters provide food, shelter and living substrate for epifaunal organisms. They also serve as nursery grounds for fish and as wave dampeners and tethers for floating mammals and birds.<sup>21</sup>

Productivity in the Mid Inlet, while greater than that in Upper Inlet waters, is considerably less than in the lower portion of Cook Inlet. Phytoplankton is the only primary producer and the combination of strong currents, severe ice conditions in winter and high suspended sediment loads in summer, limits rates of photosynthesis. This in turn affects the number and types of heterotrophic species which can be supported in the Mid Inlet.

#### A.2.12 Consumers

Zooplankton of Cook Inlet have not been studied in great detail, but representatives of the phyla Protozoa, Coelenterata, Ectoprocta, Nematoda, Annelida, Mollusca, Rotifera, Chordata, and Arthropoda have been found in Inlet

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<sup>20</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>21</sup>U.S. Fish and Wildlife Service, Office of Ecological Services, Resources Assessment Lower Cook Inlet (unpublished), Anchorage, Alaska.

TABLE A-4  
PRIMARY PRODUCERS - COOK INLET

INTERTIDAL (MUDFLAT AND GRAVEL)		NEAR OFFSHORE WATERS		FAR OFFSHORE WATERS	
MACROPHYTIC ALGAE		DIATOMS	MACROPHYTIC ALGAE	DIATOMS	
<u>*Ulothrix laetevirens</u>		<u>*Melosira sulcata</u>	<u>Laminaria sp.</u>	<u>*Melosira sulcata</u>	
<u>*Enteromorpha intestinalis</u>		<u>*Cocconeis scutellum</u>	<u>Fucus sp.</u>	<u>*Biddulphia aurita</u>	
<u>*Enteromorpha compressa</u>		<u>*Biddulphia aurita</u>	<u>Alaria sp.</u>	<u>*Coscinodiscus sp.</u>	
<u>*Ulva lactuca</u>		<u>*Asterionella kariana</u>	<u>Nereocystus sp.</u>	<u>*Coscinodiscus lineatus</u>	
		<u>*Fragilaria sp.</u>		<u>*Coscinodiscus oculus-iridis</u>	
				<u>*Coscinodiscus stellaris</u>	
				<u>*Actinopterychus sp.</u>	
				<u>*Actinopterychus undulatus</u>	
				<u>*Fragilaria sp.</u>	
				<u>*Cocconeis sp.</u>	
				<u>*Cocconeis scutellum</u>	
				<u>*Ditylum brightwellii</u>	
				<u>*Cyclotella sp.</u>	
				<u>*Asterionella sp.</u>	
				<u>*Asterionella kariana</u>	

NOTE: \*indicates species found in Mid Inlet.



waters.<sup>22</sup> These species graze on the phytoplankton species listed in Table A-4.

The Cook Inlet (primarily the lower portion) provides a suitable habitat for all the commercially harvestable species in Alaska and for most of the sport species.<sup>23</sup> Table A-5 presents some of the key consumers in Cook Inlet. The important shellfish harvested include three species of crabs, five shrimp species, razor clams and scallops. The crab and shrimp species are primarily detritivores, feeding on newly dead animal material and occasionally on live amphipods or polychaetes. The clams and scallops feed by filtering planktonic material and organic particulate matter out of the water column.

The principal fish caught in Cook Inlet are salmon, steelhead, Dolly Varden, halibut, herring, and smelt.<sup>24</sup> Five species of Pacific salmon (Oncorhynchus) are found in Cook Inlet and associated rivers and lakes. The pink salmon are most abundant; sockeye, chum and coho salmon are of intermediate abundance; and chinook salmon are least numerous.<sup>25</sup> Other finfish species caught in deep waters include butterfish, sole, yellowfin and pollock.

There are several migratory patterns which can be observed among fish and shellfish of Cook Inlet. Many of the important commercial and sport species are anadromous. They spend most of their life in Cook Inlet and return to freshwater coastal streams and rivers to spawn. In most anadromous species the adult dies after spawning. The fry develop in streams and after hatching may either migrate directly to the ocean (as do pink salmon) or may migrate to a lake entering the ocean later as a juvenile (as do sockeye salmon). Salmon, Dolly Varden, steelhead, grayling and

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<sup>22</sup>Evans, Buck, Buffler, et al., Cook Inlet Environment, Study of Available Knowledge.

<sup>23</sup>Alaska Department of Fish and Game, Habitat Protection Section, "Lower Cook Inlet Fisheries" (map), Anchorage, Alaska, 1976 (unpublished).

<sup>24</sup>U.S. Fish and Wildlife Service, Resources Assessment Lower Cook Inlet.

<sup>25</sup>Frank Stefanich, Resources Inventory, South Central Region: Fisheries Resources, Resources Planning Team, Joint Federal-State Land Use Planning Commission, Alaska, 1974.

TABLE A-5

KEY CONSUMERS - COOK INLET  
NEAR AND FAR OFFSHORE WATERS

	INVERTEBRATES	FISH	BIRDS	MAMMALS
COMMERCIAL SPECIES	★ ☆ <u>Paralithodes camtschatica</u> (King Crab)  ★ ☆ <u>Chionecetes bairas</u> (Tanner Crab)  ★ ☆ <u>Cancer magister</u> (Dugeness Crab)  ● ★ <u>Patinopecten caurinus</u> (Scallops)  ★ ☆ <u>Pandalus borealis</u> (Pink Shrimp)  ★ ☆ <u>Pandalus hypsinotus</u> (Coonstripe Shrimp)  ★ ☆ <u>Pandalus goniurus</u> (Humpy Shrimp)  ★ ☆ <u>Pandalus dispar</u> (Sidestripe Shrimp)	☆ <u>Oncorhynchus gorbusha</u> * (Pink Salmon)  ☆ <u>Oncorhynchus shawytscha</u> * (Chinook Salmon)  ☆ <u>Oncorhynchus keta</u> (Chum Salmon)  ☆ <u>Oncorhynchus kisutch</u> * (Coho Salmon)  ☆ <u>Oncorhynchus nerka</u> * (Sockeye Salmon)  ☆ <u>Clupea pallasii</u> * (Herring)		
SPORT SPECIES	★ ☆ <u>Pandalus platyceros</u> (Spot Shrimp)	☆ <u>Salmo gairdneri</u> * (Steelhead)  ☆ <u>Salvelinus malma</u> * (Dolly Varden)  ☆ <u>Hippoglossus stenolipis</u> * (Halibut)  ☆ <u>Thaleichthys pacificus</u> * (Smelt)  ☆ <u>Salmo gairdneri</u> (Steelhead trout)  ☆ <u>Atheresthes stomias</u> (Flounder)  ★ ☆ <u>Gadus macrocephalus</u> (Cod)		☆ <u>Enhydra lutria</u> (Sea Otter)  ☆ <u>Phoca vitulina</u> (Harbor Seals)

★ Detritivore

☆ Carnivore

● Herbivore

NOTE: An asterisk (\*) indicates species found in Mid Inlet.

TABLE A-5 (CONT.)

	INVERTEBRATES	FISH	BIRDS	MAMMALS
TROPHICALLY IMPORTANT SPECIES	<u>Thuriaria sp.*</u> (Hydrozoan) ★ <u>Autolytus sp.</u> (Larvae) (Polychaete) ● <u>Acartia sp.*</u> (Copepod) ● <u>Eurytemora sp.*</u> (Copepod) ● <u>Nauplius</u> (Larvae)* (Copepod) ● <u>Pseudocalanus sp.*</u> (Copepod) ● ★ <u>Balanus sp.</u> (Larvae)* (Barnacle) ☆ <u>Lamprops sp.*</u> (Cumacae) ☆ <u>Crago sp.*</u> (Decapod) ☆ <u>Pagurus sp.*</u> (Decapod) <u>Sagitta elegans*</u> (Chaetognath) ☆ <u>Eumysis sp.*</u> (Mysid) ● <u>Discorbes sp.*</u> (Foraminifera) ● <u>Strongylocentrotus droba-</u> <u>chiensis</u> (Sea Urchin) ☆ <u>Thais lamellosa</u> (Dog Welk)		☆ <u>Melanitta perspicillata</u> (Surf Scooter) ☆ <u>Larus hyperboreus</u> (Glaucous-winged Gull) ☆ <u>Larus sp.</u> (New Gull) ☆ <u>Rissa sp.</u> (Black Legged Kittiwake) ☆ <u>Sterna paradisaea</u> (Arctic Turn)	
ENDANGERED SPECIES				● ★ ☆ <u>Delphinapterus leucas</u> (Beluga Whales)

★ Detritivore

☆ Carnivore

● Herbivore

NOTE: An asterisk (\*) indicates species found in Mid Inlet.

smelt are all anadromous fish which are caught at the mouths of rivers and streams where they congregate before migrating into freshwater.<sup>26</sup>

Other species spend their entire existence in the saline waters of Cook Inlet, migrating toward shore and into deeper waters at different stages in their life cycle. Pandaeid shrimp, king crabs, snow crabs, weathervane scallops and halibut hatch in deep waters, spend several weeks or months as planktonic larvae, move inshore (to depths less than 50 fathoms) to take up a semi-benthic existence as juveniles, and migrate back to deeper waters as adults. In an opposite pattern, herring spawn in nearshore subtidal and intertidal waters, laying their eggs on living plants. The larvae mature in shallow waters and as juveniles they group in small schools and move out to sea. The dungeness crab also spends its larval life in shallow waters, often in intertidal stands of eel grass, and moves offshore as an adult.

Many Cook Inlet species have annual inshore-offshore migration patterns which may be associated with life history stages, but are often induced by seasonal changes in water temperature and ice cover.

Though many of the species mentioned above are found predominantly in the Lower Inlet, king, sockeye, coho and pink salmon, Dolly Varden and steelhead trout all spawn in rivers and streams of the Mid Inlet. The Kenai River is an extremely productive spawning ground for these species.

A variety of marine mammals inhabit the entire coastal region of Cook Inlet, but they breed on the islands of the Lower Inlet. Sea otters and harbor seals are found on the west side of the Inlet and in Kachemak Bay. Sea lions concentrate on the barrier islands south of Cook Inlet, and Beluga whales swim up the Inlet as far as the Susitna River. Killer whales and Dali porpoises are also commonly observed in the Lower Inlet.<sup>27</sup>

A simplified food web for Cook Inlet waters, involving many of the species discussed here is displayed in Figure A-7.

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<sup>26</sup> Stefanich, Resources Inventory, South Central Region: Fisheries Resources.

<sup>27</sup> M.P. Wennekens, L.B. Flagg, L. Tratsky, et al., Kachemak Bay, A Status Report (Anchorage: Alaska Department of Fish and Game, Habitat Protection Section, December 1975).

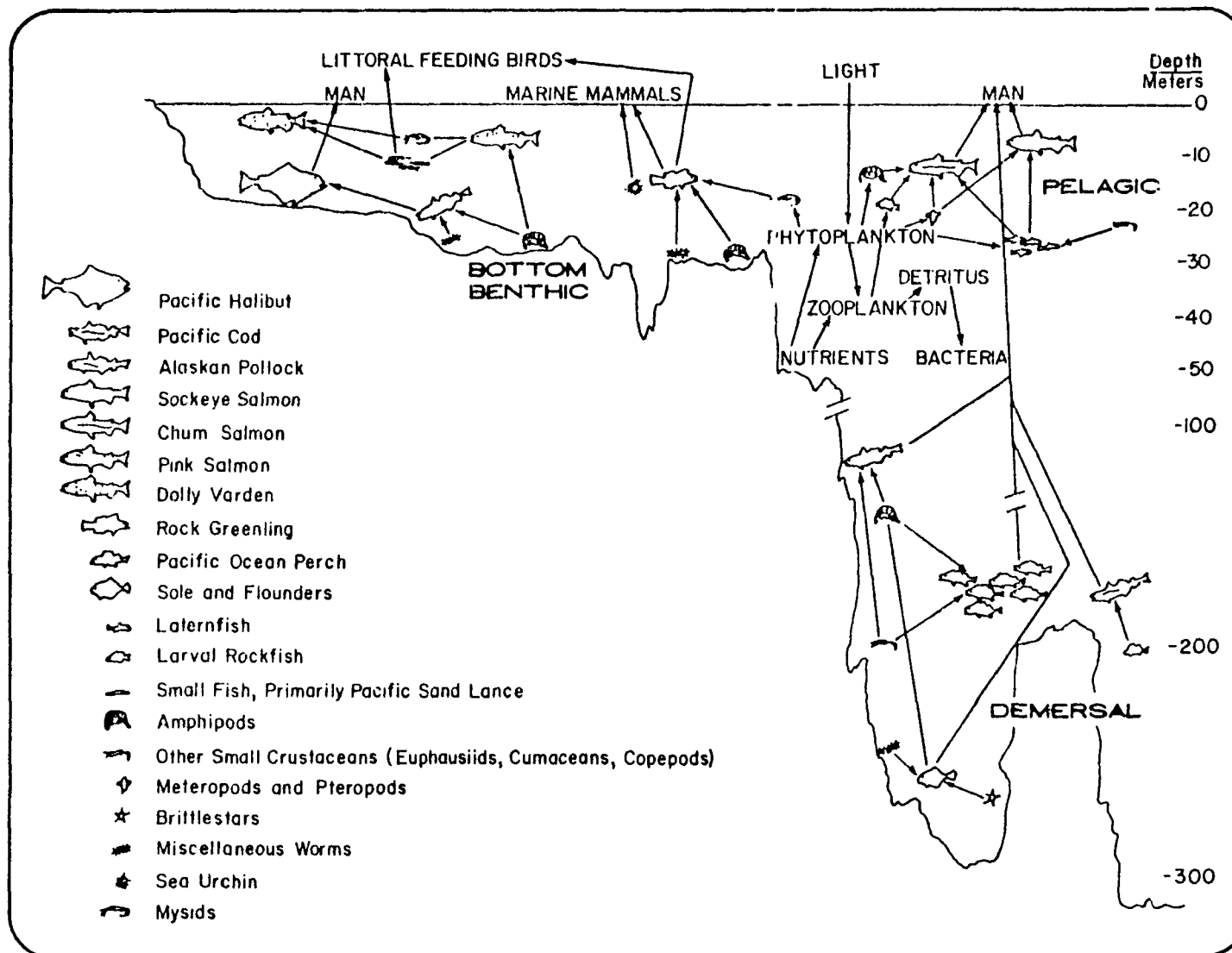


Figure A-7. Cook Inlet food chain. (L.L. Selkregg, Alaska Regional Profiles; South Central Region (Anchorage: University of Alaska, Arctic Environmental Information and Data Center, 1974), p. 153.)

#### A.2.13 Biology - Cook Inlet Intertidal Region

Cook Inlet is bordered by a variety of community types. Tidal marshes, mudflats, and rocky shores dominate the Mid and Upper Inlet; rocky coastline, fjords and cliffs dominate the Lower Inlet. One hundred square miles of tidal marshes are found in the Susitna Flats, Chickaloon Flats, Trading Bay and Redoubt Bay in the Upper and West Mid Inlet. These areas support high densities of waterfowl.

The onshore separation facilities at Nikiska and just below Kenai on the east side of the Mid Inlet, are located along coasts characterized by upland spruce-hardwood forests. These forests extend almost directly down to the shoreline, and are separated from the water by a small drop (50 feet) and some gravel and rocks. The diversity of species occupying the intertidal region in these areas is considerably less than in the Lower Inlet. A study performed by the University of Alaska for the Collier Carbon and Chemical Corporation, in May 1968, reported only five species of green algae on the Nikiska shoreline. Most of the faunal organisms found were relatively sessile, attached to rocks or burrowing in gravelly sand. These included hydrozoans, flatworms, coelenterates, brachiopods, amphipids, isopods, clams, snails, barnacles, limpets, polychaetes and pycnogonids (sea spiders). A total of 46 taxa were reported in this study.<sup>28</sup> Table A-6 presents the most important of these.

The two onshore separation facilities on the West Mid Inlet are located at Granite Point and near West Foreland in tidal marsh and swamp communities. Marsh grasses and waterfowl are the dominant species. These areas are also part of an important bald eagle migration route.<sup>29</sup>

The Collier Carbon Study referred to here is one of the only studies which has sampled organisms from Mid Inlet intertidal zones. There are few roads and most observations of biota seem to have been made by air. As mentioned in the introduction to this section, the lack of data makes a complete onshore characterization of the discharge sites (particularly the western sites) impossible.

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<sup>28</sup>Hood, Natajan, Rosenberg, and Wallen, Summary Report on Collier Carbon and Chemical Corporation.

<sup>29</sup>L.L. Selkregg, Alaska Regional Profiles; South Central Region (Anchorage: University of Alaska, Arctic Environmental Information and Data Center, 1974).

TABLE A-6

KEY CONSUMERS - COOK INLET  
INTERTIDAL (MUDFLAT - ROCKY)

	INVERTEBRATES	BIRDS	MAMMALS
COMMERCIAL SPECIES	★ <u>Siliqua patula</u> * (Razor Clam)		
SPORT SPECIES	★ <u>Siliqua patula</u> * (Razor Clam)		● <u>Alces alces</u> (Moose)  ● <u>Rangifer tarandus granti</u> (Caribou)  ★ <u>Lutra canadensis</u> (Otter)
TROPHICALLY IMPORTANT SPECIES	● <u>Anisogammarus sp.*</u> (Amphipod)  ● <u>Gammarus wilkitzkii*</u> (Amphipod)  ● ★ <u>Macoma sp.*</u> (Clam)  ● ★ <u>Balanus crenatus*</u> (Barnacle)  ● <u>Idotea entomon*</u> (Isopod)  ● <u>Littorina sp.*</u> (Snail)  ● <u>Acmea sp.*</u> (Limpet)  ★ <u>Buccinum sp.*</u> (Dog Whelk)  ★ ★ <u>Cancer magister*</u> (Crab)  ★ <u>Evasterias trochellii</u> (Sea Star)  ★ <u>Thais lamellosa</u> (Snail)  ★ ★ <u>Teleosteus cheiragonus</u> (Horse Crab)  ★ <u>Pycnopodia sp.</u> (Sea Star)	★ <u>Fraterula sp.</u> (Puffin)  ★ <u>Rissa sp.</u> (Kittiwake)  ★ <u>Uria sp.</u> (Murre)  ★ <u>Phalacrocorax sp.</u> (Cormorant)  ★ <u>Larus sp.</u> (Gull)	
ENDANGERED SPECIES		★ <u>Haliaeetus leucocephalus</u> (Bald Eagle)	

★ Detritivore

☆ Carnivore

● Herbivore

NOTE: An asterisk (\*) indicates species found in Mid Inlet.

### A.3 Gulf of Mexico Characterization

#### A.3.1 Introduction

The study site in the Gulf of Mexico encompasses the marshes and nearshore waters of Barataria Bay, Timbalier Bay, and Terrebonne Bay in Louisiana, and the offshore waters adjacent to these Bays. These bays are part of a larger drainage basin system which divides Louisiana into distinct hydrologic units. The study area is depicted in Figure A-8.

The Barataria drainage basin encompasses 1,900 square miles (1,216,000 acres) of land and water<sup>30</sup> and is bordered by the Mississippi River on the east and Bayou Lafourche on the west. The drainage basin encompassing Terrebonne and Timbalier Bays, bordered by Bayou Lafourche on the east and the Houma Navigation Canal on the west, contains 597,900 acres of land and water.<sup>31</sup>

The two drainage basins are morphologically, physically, chemically and biologically similar. Both regions are composed of a large estuarine waterbody separated from the Gulf of Mexico waters by a string of barrier islands, Grand Island, and Grand Terre Islands in Barataria Bay, East Timbalier Island, Timbalier Island, Wine Island and Dernieres in Timbalier and Terrebonne Bays. Both these estuarine regions are bordered by an intricate system of salt marshes and bays, extending northward into brackish and freshwater marshes, lakes and bayous. These two estuarine systems are similarly influenced by Gulf currents, by the Mississippi outflow and by freshwater and tidal inundation.

The offshore Gulf waters adjacent to Barataria Bay are also very much like those waters adjacent to Timbalier and Terrebonne Bays. They receive similar hydrologic and organic input from the nearshore and marsh areas, and from the Mississippi River. They experience the same meteorologic conditions and have a similar physical and biological regime.

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<sup>30</sup>Barney Barrett, Water Measurements of Coastal Louisiana (New Orleans: Louisiana Wildlife and Fisheries Commission, Oyster, Water Bottoms and Seafood Division, 1970).

<sup>31</sup>Barrett, Water Measurements of Coastal Louisiana.



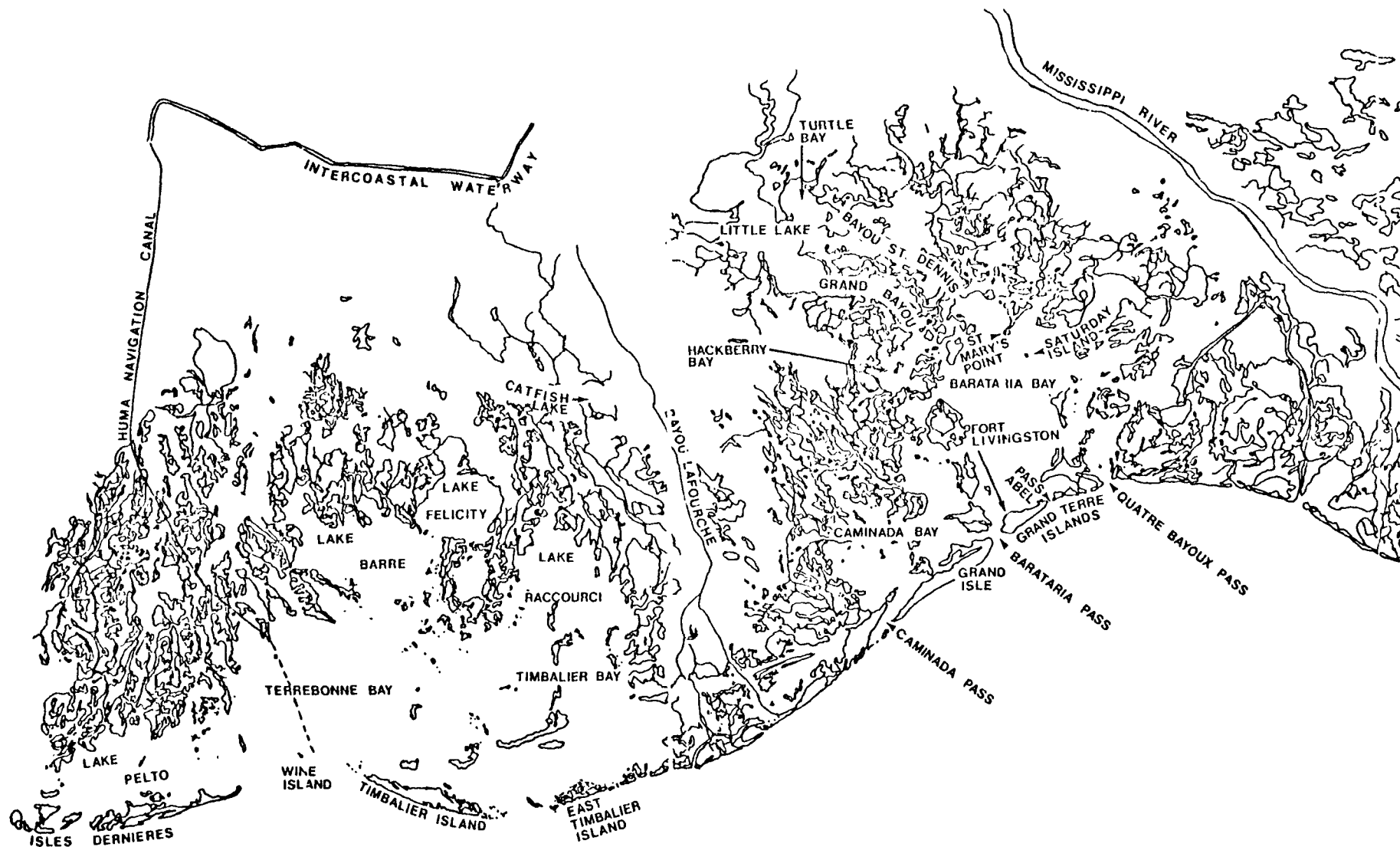


Figure A-8. Barataria - Timbalier - Terrebonne Bay area.

Both the Barataria and the Timbalier-Terrebonne nearshore-offshore systems are of interest in this study, but because the hydrologic, chemical and geologic features, and resulting vegetation and associated fauna are alike in these two systems, only one of these, the Barataria Bay and adjacent Gulf system, will be discussed in depth in this characterization. The first section will describe Barataria Bay, its marshes and associated waterbodies. The second section discusses the near offshore and far offshore waters in the Gulf of Mexico adjacent to Barataria Basin.

### A.3.2 Barataria Bay

The areas dealt with in this section of the characterization are the brackish and salt marshes and their associated waterbodies. This includes a number of lakes, Barataria Bay and Caminada Bay. Approximately 1,150,000 acres of the Barataria Basin are wetland and 66,000 acres are water. Sixty-six percent of the wetlands are freshwater marsh and swamp (salinity 0 to 5 ppt), 20 percent are brackish marsh (salinity 5 to 13 ppt), and 14 percent are salt marsh (salinity 13 to 30 ppt).<sup>32</sup> Figure A-9 displays the distribution of these wetland communities in Barataria Basin.

#### A.3.2.1 Temperature<sup>33</sup>

Average surface water temperature in Barataria Bay is approximately 22° C, with monthly averages ranging from a high in August of 29.5° C to a low in February or March of 13° C. During a 12-year period (1958-1969) the temperature extremes, measured by a continuous recorder at Ft. Livingston (near Barataria Pass), have ranged from 0° C to 36° C. Warming of Barataria waters begins in February or March and continues through August; cooling trends begin around September, though this may vary in unusually warm or cool years.

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<sup>32</sup>L.M. Bahr and J.J. Hebrard, Barataria Basin: Biological Characterization (Louisiana State University, Center for Wetland Resources, 1976), unpublished.

<sup>33</sup>Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study, Phase II Hydrology, New Orleans, 1971

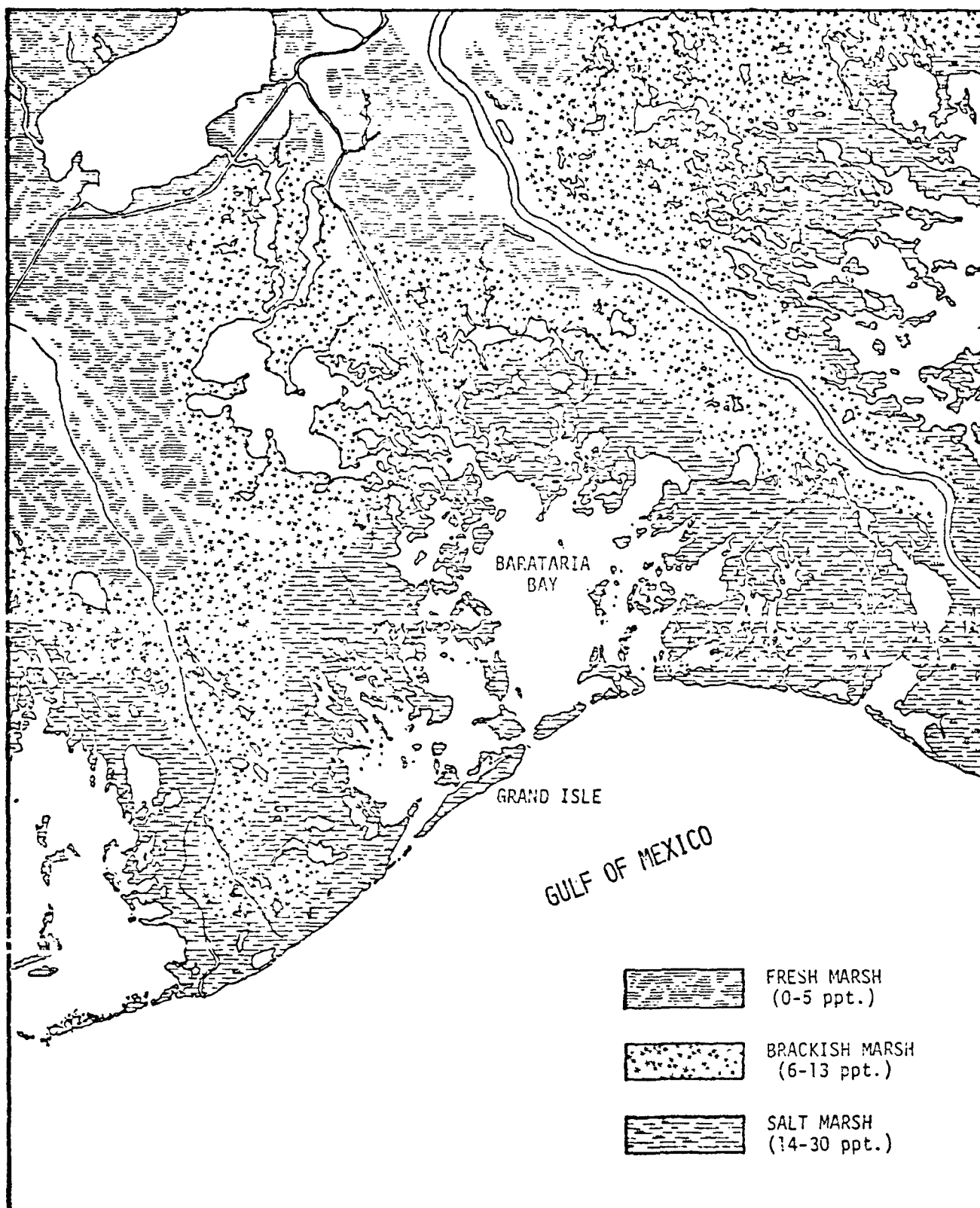


Figure A-9. Barataria Bay marsh types. (S.H. Gagliano et al., "Environmental Atlas and Multiuse Management Plan for South Central Louisiana," Hydrologic and Geologic Studies of Coastal Louisiana, Report 18, Vol. 2, plate 8 (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1973).

The southern waters of Barataria Bay are warmer in winter months than northern bay waters; however, in the spring water temperatures are a few degrees higher in the north bay. Top and bottom temperatures rarely differ more than one degree in Barataria Bay, due to the shallow depths and mixing action of waves and currents. In the winter surface water temperatures are slightly lower than bottom water temperatures, while the reverse is true in summer. Figure A-10 depicts a summer isotherm profile across the middle of the bay.

#### A.3.2.2 Depth<sup>34</sup>

The Barataria-Caminada Bay water system (which will be referred to as one unit), occupies 57,709 acres and a volume of 275,002 acre-ft. This estuary is extremely shallow, most of it is less than 4 feet in depth. The following list describes the depth patterns of the Barataria-Caminada system.

DEPTH (ft)	BARATARIA BAY (acres)	CAMINADA BAY (acres)	TOTAL (acres)
0- 1.5	10,771	13,413	24,184
1.5 - 4.5	28,982	541	29,523
4.5 - 7.5	2,553	204	2,757
7.5 -10.5	685	--	685
10.5 -50	560	--	560

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<sup>34</sup>Barrett, Water Measurements of Coastal Louisiana

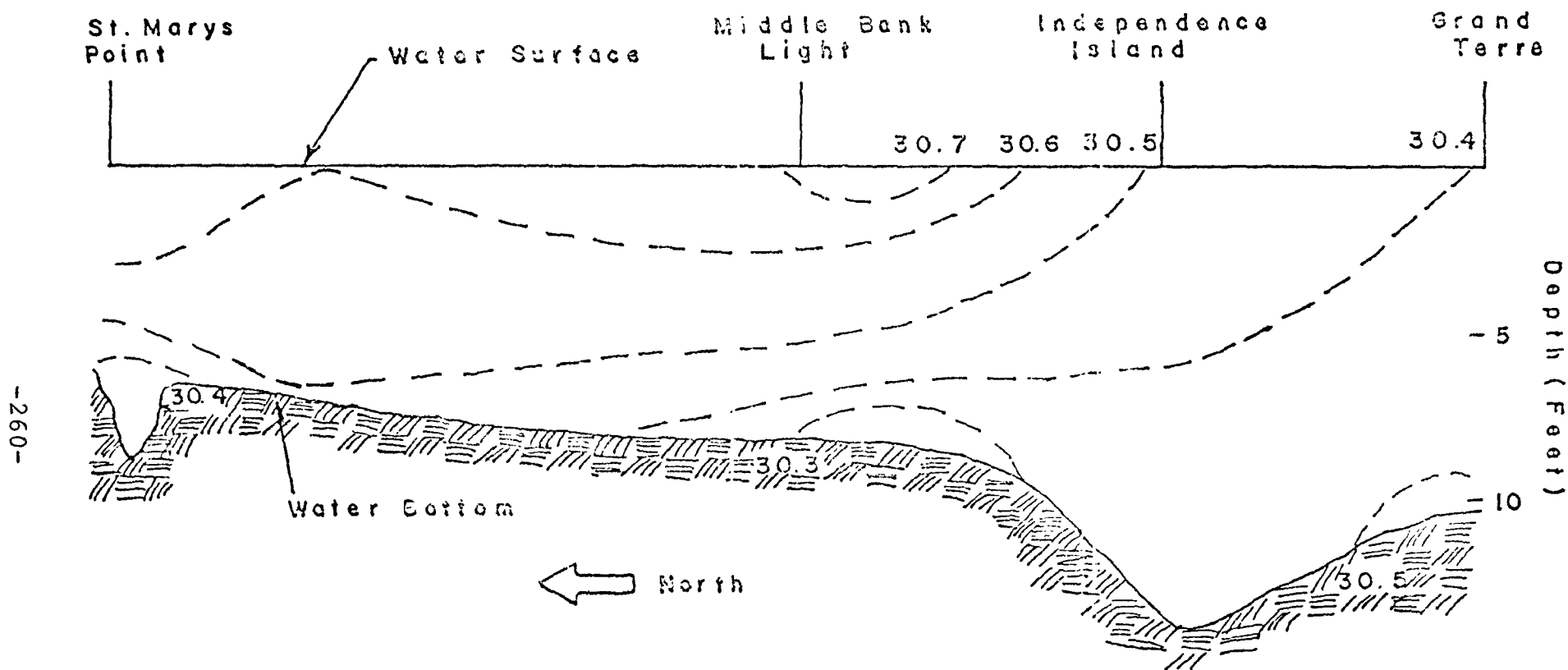


Figure A-10. Isotherm profile in degrees centigrade along a north-south line in Barataria Bay on August 8, 1967. Distance between Grand Terre and St. Marys Point is 10 miles. (Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study, Louisiana, Phase II Hydrology, 1971, p. 46).

#### A.3.2.3 Tides and Currents<sup>35</sup>

The normal tide along the Louisiana coast is diurnal though these are subject to the effects of changing meteorologic conditions, such as strong winds or barometric pressure. North winds lower water levels, lengthen the duration of ebbing tides and reduce the range of flooding tides, while southerly winds have the reverse effect.

The average annual tidal range near the mouth of Barataria Bay is 13.3 inches. Most of the Louisiana coastline experiences an average tidal range near 1 foot. Neap tides range from 3 to 4 inches, while spring tidal ranges average almost 2 feet. One of the highest tides recorded was 91.0 inches during hurricane Betsy (September 9, 1965) and the lowest was -25.7 inches, recorded during a strong north-northwest wind (December 21, 1960). Table A-7 gives the diurnal range (the difference in height between mean higher high water and mean lower low water), and the mean tide level (the plane midway between mean low water and mean high water measured from the mean low water level) at selected locations along the Louisiana coast.

Gulf waters enter Barataria Bay through Barataria Pass, Pass Abel, Quatre Bayoux Pass and Caminada Pass. Flooding waters are normally reflected to the western side, by the earth's rotation.

Water circulation in Barataria Bay is primarily tidal. Tidal currents are strongest at the moon's maximum declination, with a velocity between 2 and 3 knots. The velocity is greatest just below low and high tides, with slack tidal currents occurring just after low and high water. The current in Barataria Pass continues to ebb for a short time after low water (while the tidal height is rising) and continues to flood just after high water (while the tide is falling). Table A-8 gives the direction of the flood current, the average velocity of the flood current, the ebb current direction, and the average velocity of the ebb

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<sup>35</sup>J.G. Gosellink, R.R. Miller, M. Hood, and L.M. Bahr, Jr., Louisiana Offshore Oil Port: Environmental Baseline Study, Vol. II (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1975); and Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study.

TABLE A-7

RANGE OF TIDES, AND MEAN TIDE LEVEL  
ALONG LOUISIANA COAST

LOCATION	<u>RANGE (ft)</u>	
	DIURNAL	MEAN TIDE LEVEL
Bastian Island <sup>a</sup>	1.2	0.6
Quatre Bayoux Pass <sup>a</sup>	1.3	0.6
Barataria Pass <sup>a</sup>	1.2	0.6
Barataria Bay		
Bayou Island, Grand Islet <sup>a</sup>	1.0	0.5
Independence Island <sup>a</sup>	0.9	0.4
Manilla <sup>a</sup>	1.0	0.5
Caminada Pass (bridge) <sup>a</sup>	0.9	0.4
Timbalier Island, Timbalier Bay <sup>a</sup>	1.2	0.6
Pelican Islands, Timbalier Bay <sup>a</sup>	1.2	0.6
Wine Island, Terrebonne Bay <sup>a</sup>	1.3	0.6
Caillou Boca <sup>a</sup>	1.4	0.7
Raccoon Point, Caillou Bay <sup>a</sup>	1.7	0.8
Ship Shoal Light <sup>a</sup>	1.6	0.8

<sup>a</sup>Tide is chiefly diurnal.

Source: National Ocean Survey of the National Oceanic and Atmospheric Administration, Tide Tables 1976, East Coast of North and South America, Washington, D.C., 1975, p. 236.

TABLE A-8

MAXIMUM CURRENTS ALONG LOUISIANA COAST

LOCATION	MAXIMUM CURRENTS			
	<u>FLOOD</u>		<u>EBB</u>	
	DIRECTION (TRUE)	DIURNAL VELOCITY	DIRECTION (TRUE)	DIURNAL VELOCITY
	DEGREES	KNOTS	DEGREES	KNOTS
Quatre Bayoux Pass, Barataria Bay	290	1.2	105	1.3
Pass Abel, Barataria Bay	315	0.9	145	1.6
Barataria Pass, Barataria Bay	315	1.5	120	1.3
Barataria Bay, 1.1 miles NE of Manilla	355	0.4	160	0.5
Caminada Pass, Barataria Bay	295	1.5	120	1.5
Seabrook Bridge, New Orleans	350	1.2	170	0.9
Cat Island Pass, Terrebonne Bay	015	1.1	195	1.5
Wine Island Pass	325	1.7	160	1.9
Caillou Boca, Caillou Bay	095	1.3	265	0.7
Calcasieu Pass	020	1.7	205	2.3
Calcasieu Pass, 35 miles south of	WEAK AND VARIABLE CURRENT			
Calcasieu Pass, 67 miles south of				

Source: National Ocean Survey of the National Oceanic and Atmospheric Administration, Tidal Current Tables 1976, Atlantic Coast of North America, Washington, D.C., 1975, p. 165.



current, all at strength of current, for the Barataria-Caminada Bay passes and other selected locations along the Louisiana coast.

The volume and velocity of ebbing waters through the barrier island passes is usually greater than that of the flood tide due to freshwater drainage from the north (Table A-9). As a result, the western sides of the passes are much deeper than the eastern sides. Barataria Pass is 160 to 190 feet deep on the west and 10 to 20 feet deep on the east side.

#### A.3.2.4 Salinity<sup>36</sup>

The salinity regime of Barataria Bay changes seasonally and annually as a function of freshwater flow into the bay, rainfall, saltwater intrusion via tides and storm surges.

The bay itself is a broad freshwater-saltwater mixing zone, characterized by low salinity gradients. Freshwater, originating as overflow from the Mississippi River and its tributaries, and by precipitation surpluses, is stored in the marsh-swamp environment, and numerous lakes of the upper estuary, and is gradually released seaward. Much of the freshwater drains from the northwest, mainly through Bayou St. Denis and Grand Bayou, and moves down the west side of the bay. Thus, salinities are higher in the east and northeast sectors of Barataria Bay.

Saltwater influx is dictated by tidal range, seasonal wind patterns, shape and size of the estuarine tidal prism, and size and number of tidal passes between barrier islands. The salinity of water entering Barataria Bay through passes which open into the Gulf of Mexico, changes as a function of Mississippi River discharge and offshore circulation.

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<sup>36</sup>Gosselink, Miller, Hood, and Bahr, Louisiana Offshore Oil Port; C.L. Ho and B.B. Barrett, Distribution of Nutrients in Louisiana Coastal Waters Influenced by the Mississippi River, Technical Bulletin No. 17 (New Orleans: Louisiana Wildlife and Fisheries Commission, Oyster, Water Bottom and Seafood Division, 1975); and Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Inventory and Study.

TABLE A-9

FLOOD AND EBB FLOW THROUGH THE  
FOUR MAJOR PASSES OF BARATARIA AND CAMINADA BAYS  
(Mft<sup>3</sup>)

PASS	FLOOD FLOW	EBB FLOW	EBB EXCESS
Barataria	3,229	3,438	209
Quatre Bayoux	874	1,005	131
Caminada	627	653	26
Abel	129	212	83
TOTAL	4,859	5,308	449

Source: Louisiana Wildlife and Fisheries Commission,  
Cooperative Gulf of Mexico Estuarine Inventory and Study,  
Louisiana, Phase II Hydrology, 1971, p. 57.

Surface salinities in Barataria Bay vary from a low of 5 ppt in the upper reaches of the estuary (North of Saturday Island) to 25 ppt or more as one nears the Gulf of Mexico. Figure A-11 depicts average surface isohalines for Barataria Bay. During ebbing and rising tides the waters in Barataria Bay become less saline and more saline, respectively, thus diurnal variation in salinity is observed.

Fluctuations in normal salinity patterns are observed during periods of high river discharge. Freshwater from the mouth of the Mississippi follows the Louisiana coastline from east to west, diluting coastal salinities. These waters enter Barataria Bay and may extend northward up to 10 miles, causing a decrease in salinity conditions from normal levels. Dilutions also occur as a result of increased freshwater flow of bayous and rivers directly entering Barataria Bay.

Salinity stratification and salt wedges are kept at a minimum in Barataria Bay by shallow depth, tidal action, winds and heavy boat traffic. However, in several areas, near Independence Island and just north of Middle Bank Light, there are steep surface salinity gradients. During periods of very high river discharge the differences between top and bottom waters may vary up to 5 ppt. Figure A-12 displays a salinity profile of Barataria Bay along a transect from Grand Terre to St. Marys Point.

#### A.3.2.5 Winds<sup>37</sup>

Strong northerly winds occur in Barataria Bay from fall to early spring, striking with speeds up to 30 to 40 miles per hour. The velocity decreases to 15 to 20 miles per hour after passage of the front and the winds may persist for three or four days. These winds, called Northers, are accompanied by rainfall when there is a rapid drop in temperature. High barometric pressure combined with these north winds results in extremely low water levels. The water piles up along the northern shores of Grand Isle and Grand Terre as the passes are unable to transport windblown water out into the Gulf as rapidly as it accumulates. This lasts only briefly, then the waters of the bay and Gulf begin to flow in the same direction, lowering the water levels of the bay.

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<sup>37</sup>Gosselink, Miller, Hood, Bahr, Louisiana Offshore Oil Port; and Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study.

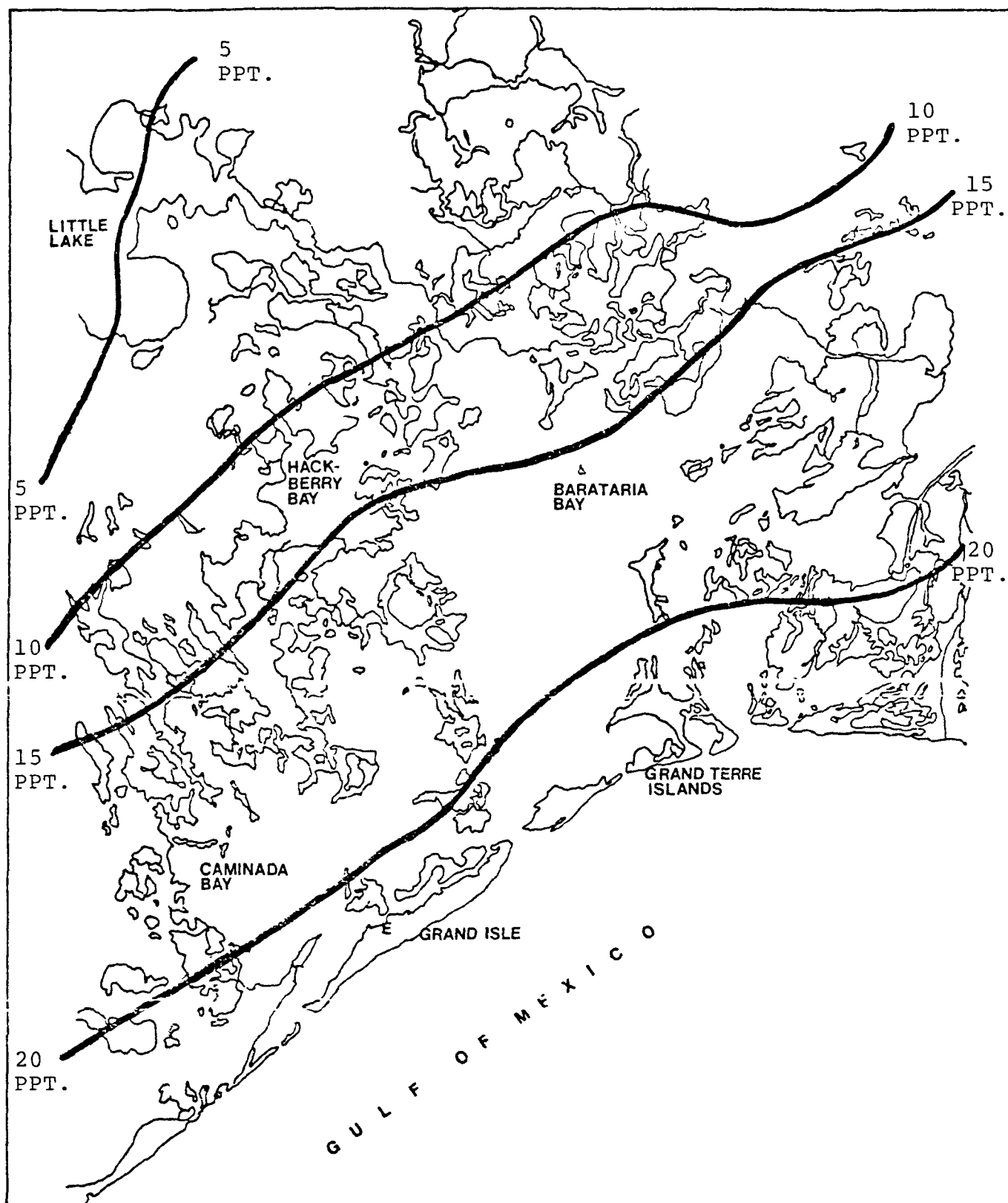


Figure A-11. Isohaline map of Barataria Bay. (Fred Dunham, Study of Important Estuarine Dependent Fishes, Technical Bulletin No. 4 (New Orleans: Louisiana Wildlife and Fisheries Commission, Oyster, Water Bottoms and Seafood Division, 1972), p. 7.)

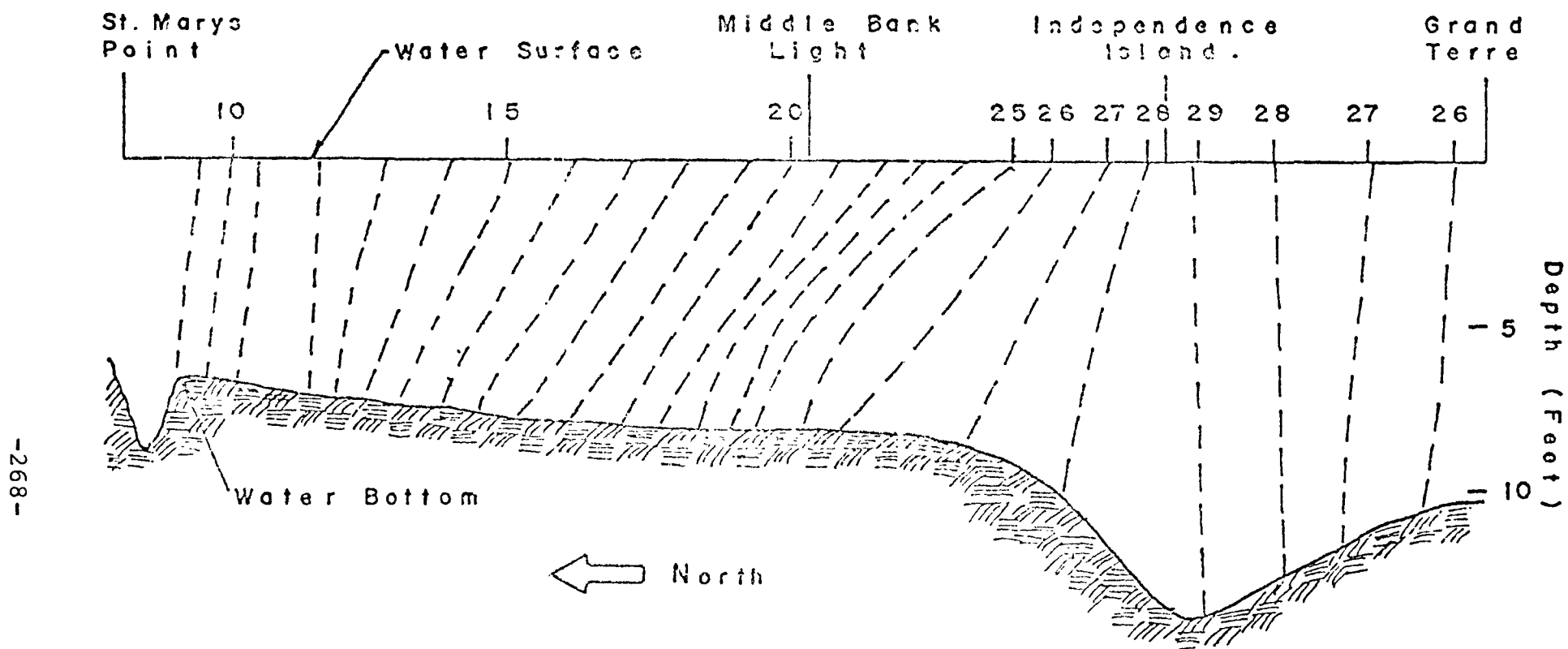


Figure A-12. Salinity profile of Barataria Bay. Numbers are in parts per thousand. Data taken on August 8, 1967. Distance between Grand Terre and St. Marys Point is 10 miles. (Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study, Phase II Hydrology, 1971, p. 51.)

Winds also have an important effect on salinity. Strong southwest to west winds reduce the westward drift of river water entering the bay, increasing salinities in the lower estuary and near offshore areas, while east to south winds bring river water into the area resulting in lowered salinities in the lower estuary.

From September to February the prevailing winds are north to northeast, from April to August they are from southeast to southwest. The most infrequently occurring winds are from the southwest to northwest.

#### A.3.2.6 Turbidity<sup>38</sup>

Barataria Bay waters are quite turbid due to freshwater drainage, tidal mixing action and the influence of the Mississippi River. The average visibility for a 1968-1969 study was 1.9 feet with extremes ranging from 3.7 to 0.9 feet. Turbidities were higher in the upper estuary and decreased towards the Gulf. Turbidity does not vary consistently with salinity, but seems to fluctuate directly with total phosphorus concentrations.

#### A.3.2.7 Sediment Chemistry<sup>39</sup>

Sediments in Barataria Bay are contributed mainly by the Gulf of Mexico, the Mississippi River, erosion of the wetlands, and drainage waters from north of the Bay. Clayey silt is the dominant sediment type, found along the boundaries of the bay. The sediment becomes more silty towards the marshes, and more sandy towards the Gulf side of the bay.

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<sup>38</sup>Gosselink, Miller, Hood, Bahr, Louisiana Offshore Oil Port; and Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study.

<sup>39</sup>C.L. Ho and J. Lane, "Interstitial Water Composition in Barataria Bay (Louisiana) Sediments," Estuarine and Coastal Marine Science 1 (1973): 125-135; Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study; and J.F. Mayer, Jr., Modification of Solvent Extraction Methods and Determination of Trace Metals in Selected Aquatic Ecosystems in Louisiana (Master's Thesis, Louisiana State University, 1975).

The center of Barataria Bay is primarily sandy silt. Figure A-13 depicts sediment type distribution in the Barataria region. The predominant grain size in Barataria Bay is coarse and percentage of sand content is high relative to clay content.

#### A.3.2.8 Soil Chemistry<sup>40</sup>

The wetlands of Barataria Bay have a higher clay content (16 to 30 percent) than do the bay and nearshore sediments, with clay content decreasing from freshwater, to brackish, to salt marsh. Soil salinity increases along this succession of marshes. The organic content of soil is higher in the brackish marsh at 26.7 percent organic carbon and 1.6 percent organic nitrogen, than it is in fresh or saltwater wetlands. In the salt marsh soils, organic carbon content ranges from 6 to 9 percent. A high level of sulfide exists in the brackish marsh and strongly anaerobic conditions are found beneath the surface layer of soil. Heavy metals which readily absorb to clay minerals are found at higher levels in the brackish soils (which have a higher percentage of clay content) than in the salt marsh soils. Table A-10 and Figure A-14 present data collected along Bayou Lafourche, which demonstrates these trends.

The soils of the salt marsh are gradually being eroded by marine waters, thus the salt marsh is in a senescent state. The boundary between brackish and salt marsh is gradually migrating inland as the entire coastal zone subsides.

#### A.3.2.9 Water Chemistry<sup>41</sup>

The nutrient content of Barataria Bay waters varies spatially and temporally as a function of salinity, rainfall, river discharge and related nutrients. Table A-11 presents 1968-1969 nutrient levels for dissolved oxygen, nitrate (NO<sub>3</sub>) nitrite (NO<sub>2</sub>), inorganic phosphorus and total phosphorus.

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<sup>40</sup>Bahr and Hebrard, Barataria Bay: Biological Characterization; and Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study.

<sup>41</sup>Ho and Barrett, Distribution of Nutrients in Louisiana Coastal Waters; and Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study.

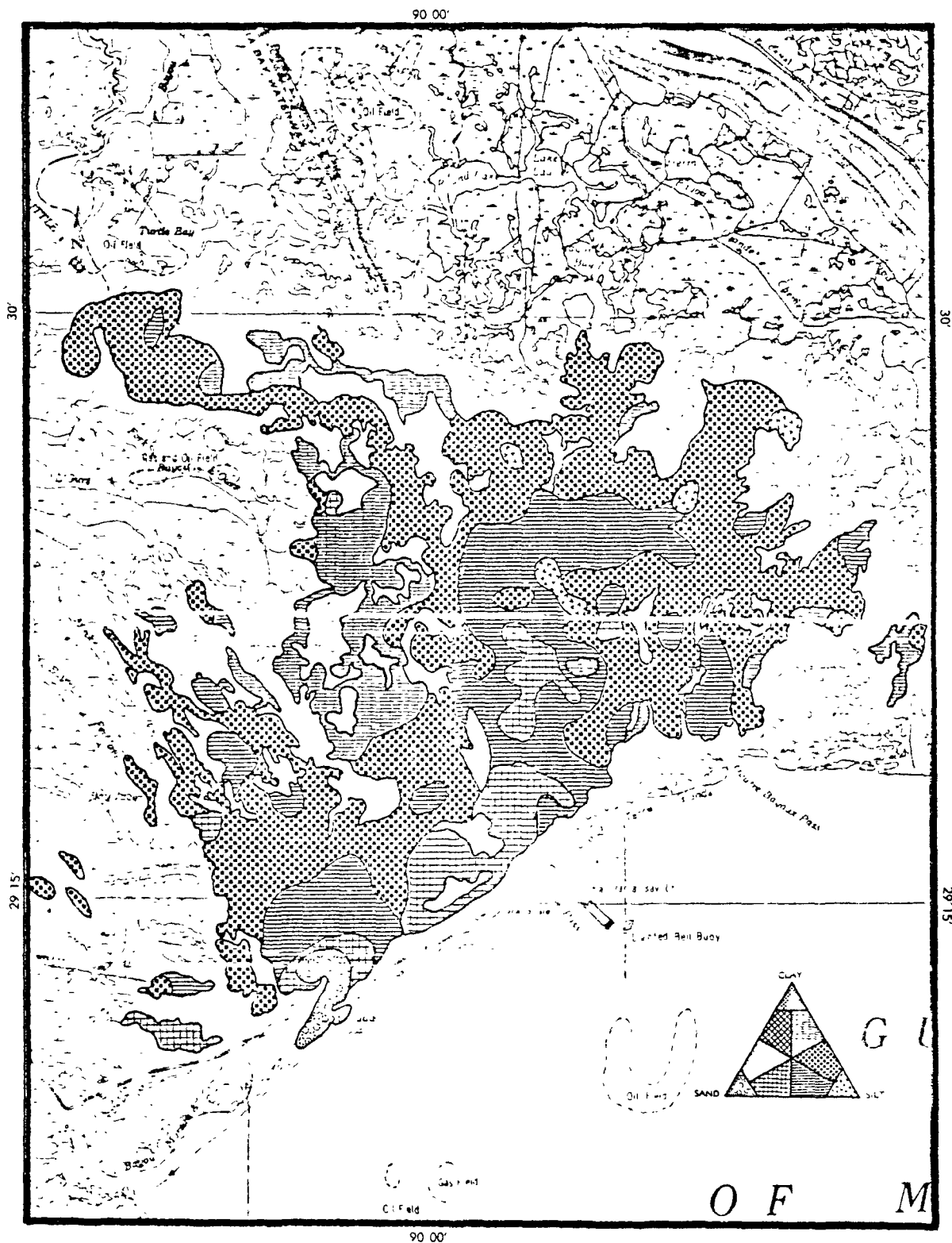


Figure A-13. Sediment type distribution in the Barataria-Caminada Bay Area. Base map: U.S. Army Corps of Engineers, scale 1:250,000. (Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study, Phase III Sedimentology, 1971, p. 155.)



TABLE A-10

SEDIMENT CONTENT - BARATARIA DRAINAGE BASIN

SAMPLING STATION	SALINITY (ppt)	SEDIMENT ORGANIC CARBON (%)	SEDIMENT CLAY (%)	Fe (ppm)	Mn (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
1. Salt marsh	19.7	7.5	19.7	494.8	50.0	1.02	1.64	0.83	4.06
2. Salt marsh	21.8	9.0	24.7	598.9	27.1	2.00	1.61	0.67	3.64
3. Brackish marsh	8.4	6.5	30.2	625.0	62.5	2.21	1.52	0.96	4.48
4. Brackish marsh	6.1	26.6	16.8	562.5	48.8	3.63	1.50	0.90	5.88
5. Fresh marsh	0.62	15.0	33.6	286.4	30.2	5.00	1.17	1.31	3.96
6. Fresh marsh	0.29	7.5	24.5	729.1	44.8	2.35	1.42	1.71	52.03
7. Fresh marsh	0.10	7.1	38.1	833.1	60.4	4.54	1.79	1.14	5.62

Source: J.F. Mayer, Jr., Modification of Solvent Extraction Methods and Determination of Trace Metals in Selected Aquatic Ecosystems in Louisiana (Master's Thesis, Louisiana State University, 1975).

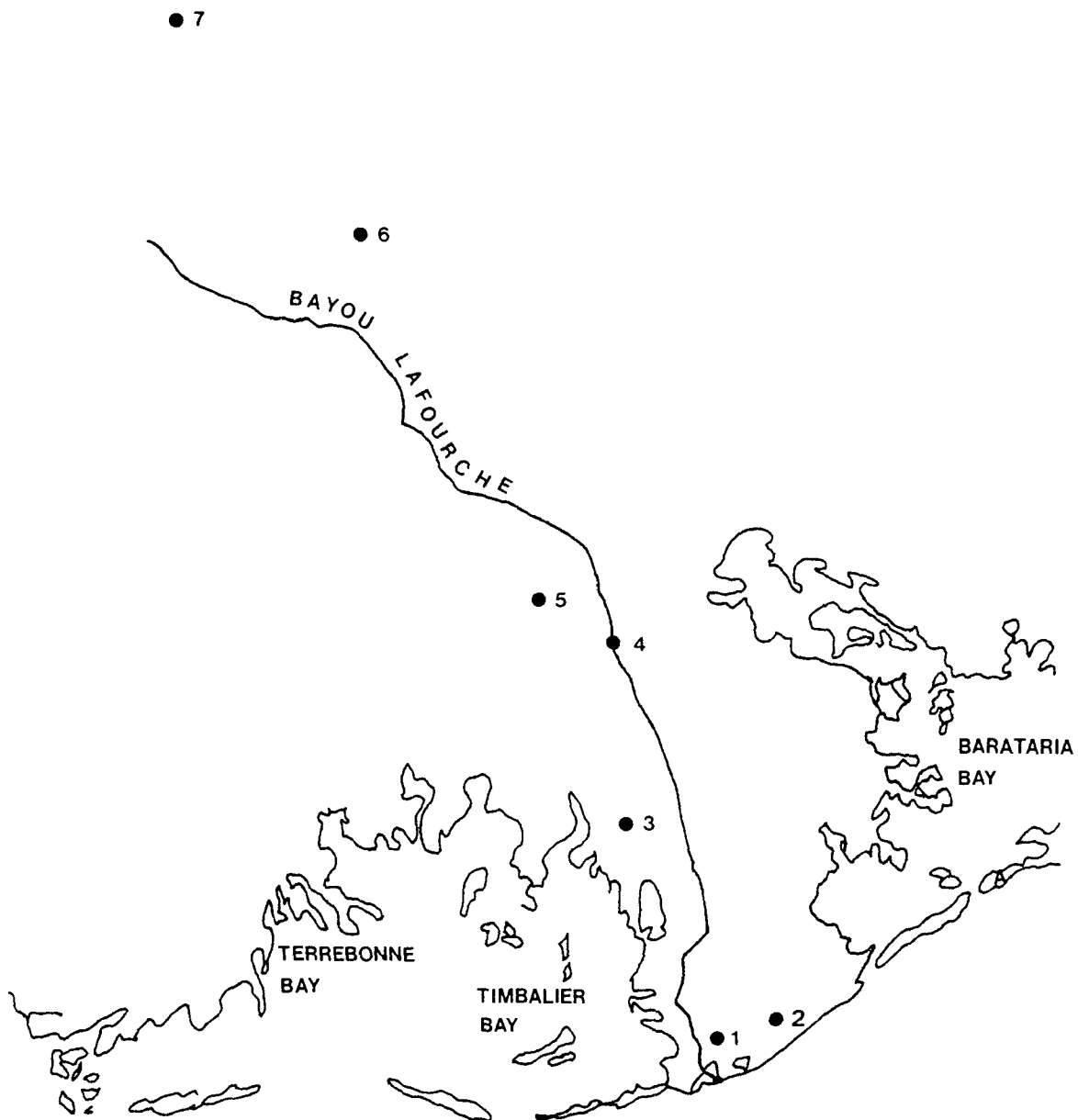


Figure A-14. Sampling stations for sediment study (Table 5-10). (Mayer, Modification of Solvent Extraction Methods and Determination of Trace Metals in Selected Aquatic Ecosystems in Louisiana (Master's Thesis, Louisiana State University, 1975).

TABLE A-11

NUTRIENT LEVELS -- BARATARIA BAY WATER COLUMN (1968-1969)

	YEARLY AVERAGE	LOW MONTHLY AVERAGE	HIGH MONTHLY AVERAGE	ABSOLUTE RANGE
Dissolved O <sub>2</sub> (ppm)	8.0	6.6 (Aug.)	9.5 (March)	6.0-10.5
Nitrite (mg-at/l)	0.45	0.16 (June)	0.87 (April)	0.05-1.98
Nitrate (mg-at/l)	4.50	0.08 (Oct.)	18.90 (March)	0.00-56.63
Inorganic Phosphate (mg-at/l)	0.78	0.42 (Nov.)	1.31 (Sept.)	0.25-2.06
Total Phosphorus (mg-at/l)	2.93	1.65 (Jan.)	3.91 (April)	0.59-6.68

Source: Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study, Louisiana, Phase II Hydrology, 1971.

Dissolved oxygen levels are directly related to water temperatures. In summer months, dissolved oxygen reaches a low, and increases as temperature sinks and wave action (due to winds and current) increases. In general, dissolved oxygen levels are higher where salinities are lower, in the upper and western portions of the Bay. Average dissolved oxygen levels in Barataria Bay are close to 8 ppm.

Nitrate levels are highest in periods of high rainfall and in regions of low salinity. This suggests that input of large volumes of water draining from the north -- which carry with it nutrients and detritus from fresh and brackish marshes, will increase nitrate levels in Barataria Bay. The average nitrate level found in Barataria Bay is 4.5 micro-moles per liter ( $\mu\text{g-at/l}$ ).

Nitrite levels correspond closely to nitrate levels. Highest nitrite levels occur shortly after high nitrate values are observed indicating that high nitrite concentrations may result from nitrate reduction.

Inorganic phosphate, which averages 0.78  $\mu\text{g-at/l}$ , is highest in the upper reaches of Barataria Bay and like nitrite and nitrate, may be related to freshwater drainage from wetlands to the north. Similarly, total phosphorus is higher during periods of peak river discharge and corresponding low salinities, and is higher in the upper estuary than it is near the Gulf of Mexico. An average value for total phosphorus is 2.9  $\mu\text{g-at/l}$  of which approximately 26 or 27 percent is organic.

#### A.3.2.10 Wetlands Biology<sup>42</sup>

The wetlands of the Barataria drainage basin have been divided into three subunits: freshwater swamps and marshes, brackish marshes, and salt marshes. Each of these subunits has a characteristic salinity range, vegetative assemblage, and productivity. Approximately 66 percent of the Barataria wetlands is a freshwater environment (0 to 5 ppt); 20 percent is brackish marsh (6 to 13 ppt) and 14 percent is salt marsh (14 to 30 ppt). Figure A-9 depicts the distribution of wetlands near Barataria Bay. For the purposes of this study, we will deal only with the brackish and salt marshes, two systems which have interdependent hydrology, nutrient cycles, and energy flow.

#### A.3.2.11 Brackish Marsh

The brackish marsh represents an intermediate zone between the freshwater and marine ends of the Barataria Drainage Basin. This area forms a band stretching across the drainage basin from below the Intracoastal Waterway to the salt marsh, lakes, and estuaries fringing Barataria Bay.

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<sup>42</sup>Bahr and Hebrard, Barataria Basin: Biological Characterization; Barrett, Barney, Gillespie, and Cannon, Primary Factors Which Influence Commercial Shrimp Production in Coastal Louisiana, Technical Bulletin No. 9 (New Orleans: Louisiana Wildlife and Fisheries Commission, Oysters, Water Bottoms and Seafood Division, 1973); J.W. Day, Jr., W.G. Smith, P.R. Wagner, W.C. Stowe, Community Structure and Carbon Budget of a Salt Marsh and Shallow Bay Estuarine System in Louisiana (Baton Rouge: Louisiana State University, Center for Wetland Resources, May 1973); Galdry, J. Wilson, and C.J. White, Investigations of Commercially Important Penaeid Shrimp in Louisiana Estuaries, Technical Bulletin No. 8 (New Orleans: Louisiana Wildlife and Fisheries Commission, Oysters, Water Bottoms and Seafood Division, March 1973); Eugene Jaworski, The Blue Crab Fishery, Barataria Estuary, Louisiana (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1972); Louisiana Wildlife and Fisheries Commission, Cooperative Gulf of Mexico Estuarine Inventory and Study; and J. Thomas, P. Wagner, and H. Loesch, "Studies on the Fishes of Barataria Bay, an Estuarine Community," Coastal Studies Bulletin No. 6 (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1971).

At the basin's center the band of brackish marsh is 15 miles wide, tapering as it approaches the Mississippi River and Bayou Lafourche on either side. The major waterbodies of the brackish marsh are Little Lake, Turtle Bay and Bayou Perot.

The dominant plant species in the brackish marsh are Spartina patens (wire grass) which comprises 45.8 percent of the marsh vegetation, and Distichlis spicata (salt grass) which contributes 29 percent. Spartina alterniflora (oyster grass, Juncus roemerianus (black rush) and Scirpus olneyi (three-cornered grass) are also important primary producers. Table A-12 lists key species of primary producers found in brackish and salt marsh environments. Total annual net primary production in the brackish marsh is estimated at 1 kg/m<sup>2</sup>, though this is somewhat speculative.<sup>43</sup> The brackish marsh does have the greatest live biomass of any marsh type, attributed to the dense stands of wire grass and salt grass which make up 75 percent of the vegetative cover.

All the marsh trophic systems are detritus-based, meaning that energy trapped in primary production is utilized as dead plant material by community heterotrophs. Herbivores play a relatively minor role in utilization of primary productivity. Insects and marsh snails graze approximately 7 percent of live plant material and muskrats account for another 2 percent. The low level of grazing is responsible for the net buildup of detritus (as peat) which occurs in the brackish marsh. The detritus is consumed by a variety of detritivores including numerous amphipods, nematodes, and microbes. These are, in turn, consumed by higher invertebrates, oysters, shrimp and crabs, which are preyed on by a variety of marsh birds and mammals.

The trophic systems of the waterbodies associated with the brackish marsh are similarly detritus-based. Rapid chemical changes are characteristic of these areas and organisms which reside in these estuaries tolerate changes in salinity and water chemistry through various physiological mechanisms. Aquatic macrophytes such as widgeon grass, and dwarf spikerush, phytoplankton, and shallow water benthic diatoms, are the primary producers in these waterbodies. Ducks and other waterfowl graze on some of the macrophytes but the dominant energy flow pathway is through detritivorous polychaetes, nematodes, amphipids, ostracods, blue

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<sup>43</sup> Bahr and Hebrard, Barataria Basin: Biological Characterization.

TABLE A-12

PRIMARY PRODUCERS - BARATARIA BAY  
BRACKISH AND SALT MARSHES AND ASSOCIATED WATERBODIES

MACROPHYTES	EPIPHYTES		BENTHIC	PHYTOPLANKTON
	FILAMENTOUS	DIATOMS		
<u>Spartina</u>	<u>Enteromorpha</u>	<u>Denticula</u>	<u>Achnanthes</u>	<u>Coelosphaerium</u>
<u>alterniflora</u>	<u>Ectocarpus</u>	<u>Amphiprora</u>	<u>Amphiprora</u>	<u>Gomphosphaeria</u>
	<u>Cladophora</u>	<u>Amphora</u>	<u>Amphora</u>	<u>Merismopedia</u>
<u>Juncus</u>	<u>Polysiphonia</u>	<u>Nitzschia</u>	<u>Anaulua</u>	<u>Microcystis</u>
<u>romerianus</u>	<u>Rhizoclonium</u>	<u>Melosira</u>	<u>Caloneis</u>	<u>Anabaena</u>
	<u>Bostrychia</u>	<u>Rhopalodia</u>	<u>Cocconeis</u>	<u>Spirulina</u>
<u>Distichlis</u>	<u>Erythrotrichia</u>	<u>Diploneis</u>	<u>Cosmiodiscus</u>	<u>Oscillatoria</u>
<u>spicata</u>	<u>Spirulina</u>	<u>Cymbella</u>	<u>Diploneis</u>	<u>Actinoptychus</u>
	<u>Oscillatoria</u>	<u>Cylindrotheca</u>	<u>Eunotogramma</u>	<u>Biddulphia</u>
<u>Spartina</u>	<u>Lyngbya</u>	<u>Grammatophora</u>	<u>Gyrosigma</u>	<u>Chaetoceros</u>
<u>patens</u>		<u>Surirella</u>	<u>Mastogloia</u>	<u>Coscinodiscus</u>
		<u>Achnanthes</u>	<u>Melosira</u>	<u>Melosira</u>
<u>Eleocharis</u>		<u>Cocconeis</u>	<u>Navicula</u>	<u>Amphiprora</u>
<u>parvula</u>		<u>Pleurosigma</u>	<u>Nitzschia</u>	<u>Camphylodiscus</u>
		<u>Navicula</u>	<u>Plagiogramma</u>	<u>Navicula</u>
<u>Scirpus</u>		<u>Camphylodiscus</u>	<u>Pleurosigma</u>	<u>Nitzschia</u>
<u>olneyi</u>			<u>Rhaphoneis</u>	<u>Ankistrodesmus</u>
			<u>Stauroneis</u>	<u>Gymnodinium</u>
			<u>Surirella</u>	<u>Eugena gracilis</u>
			<u>Trachysphenia</u>	<u>Cocoid greens</u>

crabs, and other crustaceans. Acartia tonsa, the dominant copepod, is both herbivorous and detritivorous. Estuarine finfish, such as the spot, flounder, croaker, sea trout, black drum and red drum feed on these detritivores. Wading birds and mammals such as raccoon and otters are often the top carnivores in the brackish marsh food chains. Table A-13 lists the key consumers of the brackish marsh, salt marsh, and associated waterbodies, their importance, and trophic characteristics.

#### A.3.2.12 Salt Marsh

Salt marshes are normally more subject to modification by physical processes than other types of wetlands. The salt marshes of Barataria Bay (and the whole Louisiana coast) are closely associated with the physical regime of the Gulf of Mexico. The diurnal and seasonal variations in water level produced by tidal inundation, storm surges and freshwater floods, are important to the species which spend one part, or all of their life cycle in the marshes, and to the nutrient cycling and waste removal processes so essential to high marsh productivity.

A conservative estimate of annual salt marsh production is 1 kg/m<sup>2</sup>; however, published estimates have exceeded 3 kg/m<sup>2</sup>.<sup>44</sup> It is generally agreed that salt marshes are the most productive wetlands and have the lowest species diversity. Spartina alterniflora (oyster grass) is the dominant producer, comprising 63 percent of the vegetative cover. Distichlis spicata (salt grass) and Juncus roemerianus (black rush) comprise another 25 percent. Benthic diatoms and epiphytes on Spartina stems contribute significantly to primary productivity during winter and early spring, before Spartina becomes dense.

Several functional advantages are obtained from a Spartina-based community. The extensive root system provides erosion resistance to the surface sediments, a feature especially valuable in strong storms or hurricanes. The roots also act as a nutrient pump by extracting phosphorus from aerobic sediments and transporting it to upper portions of the plant where it can be released to surrounding waters during tidal inundation.

First order consumers of the salt marsh (herbivores and detritivores) include bacteria, fungi, copepods, amphipods,

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<sup>44</sup>Bahr and Hebrard, Barataria Basin: Biological Characterization.



TABLE A-13

KEY CONSUMERS - BARATARIA BAY  
BRACKISH AND SALT MARSHES AND ASSOCIATED WATERBODIES

	INVERTEBRATES	FISH	BIRDS	MAMMALS
COMMERICAL AND SPORT SPECIES	★ <u>Callinectes sapidus</u> (Blue Crab)	● ★ ★ <u>Brevoortia patronus</u> (Menhadden)		★ <u>Procyon lotor</u> (Raccoon)
	★ <u>Penaeus aztecus</u> (Brown Shrimp)	★ <u>Anchoa mitchilli</u> (Bay Anchovy)		★ <u>Lutra canadensis</u> (Otter)
	★ <u>Penaeus setiferus</u> (White Shrimp)	● ★ ★ <u>Micropterus undulatus</u> (Atlantic Croaker)		● <u>Ondatra zibethicus</u> (Muskrat)
	★ <u>Penaeus duorarum</u> (Pink Shrimp)	★ <u>Arius felis</u> (Sea Catfish)		
	● ★ <u>Crassostrea virginica</u> (Oyster)	★ <u>Leiostomus xanthurus</u> (Spot)		
		<u>Chloroscombrus chrysurus</u> (Bumper)		
		★ <u>Cynoscion arenarius</u> (Sand Sea Trout)		
		★ <u>Cynoscion nebulosus</u> (Spotted Sea Trout)		
		● ★ <u>Mugil cephalus</u> (Striped Mullet)		
		★ <u>Paralichthys lethostigma</u> (Southern Flounder)		
		★ <u>Pogonias cromis</u> (Black Drum)		
		★ <u>Sciaenops ocellata</u> (Red Drum)		
		★ <u>Menidia beryllina</u> (Tidewater Silverside)		
TROPICALLY IMPORTANT SPECIES	● <u>Acartia tonsa</u> (Copepod)		★ <u>Pelecanus erythrorhynchos</u> (White Pelican)	★ <u>Tursiops truncatus</u> (Bottlenose Dolphin)
	● <u>Littorina sp</u> (Marsh Snail)		★ <u>Dichroanassa rufescens</u> (Reddish Egret)	
	● ★ <u>Rangia cuneatus</u> (Clam)		★ <u>Circus cyaneus</u> (Marsh Hawk)	
			★ <u>Larus sp.</u> (Gull)	
			★ <u>Florida caerulea</u> (Little Blue Heron)	
ENDANGERED SPECIES			★ <u>Pelecanus occidentalis</u> (Brown Pelican)	

- ★ Detritivore
- ☆ Carnivore
- Herbivore

snails, fiddler crabs, polychaetes, mussels, insects, birds and mammals. Grasshoppers and similar insects are the only true grazers. Insects are thought to remove about 4 percent of net primary production. Microfauna and small macrobenthos are important consumers in salt marsh sediments, ingesting approximately half the weight that macrofaunal forms do. The total biomass of primary consumers is estimated to be 16 g/m<sup>2</sup> at the ocean edge of the estuary, 40 g/m<sup>2</sup> 10 feet inland, and declining further inland to 5 g/m<sup>2</sup>.<sup>45</sup>

Salt marsh predators include a variety of wading birds, mammals, insects and spiders.

The waterbodies associated with salt marshes are the bays which interface with the Gulf of Mexico, Barataria and Caminada Bays, and attached lakes. The salt waterbodies are about half as productive as the salt marshes themselves, but the primary production of diatoms, coccoid blue-green algae, green algae and nannoplankton, may be utilized more directly than marsh grass. These waterbodies have the greatest primary productivity relative to consumption of all waterbodies in Barataria Basin.

Major herbivores of these systems include Acartia tonsa (the dominant copepod), menhaden and mullet. Detritivores are quite numerous including commercially important species of penaeid shrimp, blue crabs, and oysters. Important carnivores include ctenophores (which feed on zooplankton), fishing birds, diving ducks, spotted sea trout, sea catfish, silversides, anchovy and the bottlenosed dolphin (see Table A-13).

Many of the faunal species of Barataria Bay mentioned above have rather complex life-history and migration patterns, spending different parts of their cycles in different habitats. There are four basic patterns or categories into which these species fall: (1) truly estuarine species, which spend their entire lives in the bay; (2) marine species which spawn in the sea and use the estuary as a nursery ground; (3) marine forms which visit the estuary as adults; and (4) freshwater fish which occasionally enter the brackish waters of Barataria Bay.

Those species which spend all or almost all of their life in the brackish and saline waters of Barataria Bay and associated lakes include the eastern oyster, the bay anchovy,

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<sup>45</sup>Day, Smith, Wagner, and Stowe, Community Structure and Carbon Budget, 1973.

the Atlantic needlefish, the tidewater silverside, the hogchoker and various killifish. Many benthic species of nematodes, polychaetes, bivalves, and amphipids also spawn, hatch, mature and die in estuarine waters.

Some of the most commercially important species fall into the second pattern, living in both open Gulf waters and enclosed bay waters. The blue crab, which supports a large fishery, spawns in lower estuarine and Gulf waters. The larval stages, zoea (31 to 49 days) and megalops (6 to 20 days) are spent in open Gulf waters. Near the end of the megalops stage the blue crabs may enter tidal inlets, and the first nine months of the juvenile stage are spent in the upper and lower estuary. The second year as a juvenile is spent in the upper estuary where the crab grows to full maturity and mates. It is at this time that crabs are fished -- usually from ages 12 to 18 months. Those crabs not caught return to open ocean waters to spawn.<sup>46</sup>

The penaeid shrimp, white, pink and brown shrimp, follow a similar pattern. They spawn in offshore Gulf waters at depths of 5 to 17 fathoms. After hatching the nauplii lead a planktonic existence for 3 to 5 weeks, then metamorphose into a postlarval stage and enter the estuary. Five or six months after hatching the shrimp are mature and migrate into the open ocean to spawn.<sup>47</sup>

Fish species which spawn in the Gulf (usually in spring) and use the Barataria Bay as nursery grounds include the large-scale menhaden, Atlantic croaker, spotted and sand sea trout, silver perch, striped mullet, spot, and bay whiff.<sup>48</sup> Most of these species remain in the estuary until late summer and return to the open ocean as subadults in the fall. However, the sand sea trout and the mullet move inshore in the fall, spending warmer months in the Gulf.

Some fish spawn and live primarily in offshore waters but seasonally visit the estuary in late summer and early

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<sup>46</sup>Jaworski, Blue Crab Fishery.

<sup>47</sup>Barrett, Barney, Gillespie, and Cannon, Primary Factors which Influence Commercial Shrimp Production; and Galdry, Wilson, and White, Investigation of Commercially Important Penaeid Shrimp.

<sup>48</sup>Thomas, Wagner, and Loesch, "Studies on Fishes of Barataria Bay."

fall. The jacks, sea catfish, moonfish, and lizard fish follow such a pattern.

Occasionally freshwater fish will move downstream and enter the brackish waters of the Barataria system. The spotted gar is one such species.

Table A-14 lists, by migratory patterns, various species of fish and invertebrates commonly found in Barataria Bay.

### A.3.3 Gulf Of Mexico Waters

#### A.3.3.1 Temperature<sup>49</sup>

Surface and bottom temperatures vary seasonally. There is little difference in temperatures of surface and bottom waters in the fall and early winter. During the cooler months, December to April, surface temperatures become lower than bottom temperatures, and in spring and summer they become warmer than bottom temperatures.

Surface temperatures average 26° C, rising to over 30° C in summer and sinking to 16° C in winter. Bottom temperatures average 22° C to 23° C, rising just slightly in summer and sinking to 19° C in winter. Surface temperature varies little with distance from shore; however, in summer near offshore bottom temperatures are one or two degrees higher than those far offshore, and the trend is reversed in winter.

#### A.3.3.2 Depth<sup>50</sup>

The near offshore region of the continental shelf slopes seaward at 15 ft/mi (2.5 m/km). The average depth

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<sup>49</sup>Barrett, Barney, Gillespie, and Cannon, Primary Factors which Influence Commercial Shrimp Production; and Gosselink, Miller, Hood, and Bahr, Louisiana Offshore Oil Port.

<sup>50</sup>P. Detking, R. Buck, R. Watson, and C. Merks, "Surface and Shallow Subsurface Sediments of the Nearshore Continental Shelf of South Central Louisiana," in Offshore Ecology Study (Galveston, Texas: Gulf Universities Research Consortium, October 1974).

TABLE A-14

MIGRATORY PATTERNS OF BARATARIA BAY SPECIES

ENTIRE LIFE SPENT IN THE ESTUARY	SPAWN IN OFFSHORE WATERS MATURE IN ESTUARY	ENTER ESTUARY SEASONALLY AS AN ADULT	FRESHWATER SPECIES OCCASIONALLY ENTERING BRACKISH WATERS
<u>Anchoa mitchilli</u> - bay anchovy <u>Strongylura marina</u> - Atlantic needlefish <u>Menidia beryllina</u> - tidewater silverside <u>Trinectes maculatus</u> - hogchoker <u>Cyprinodon variegatus</u> - sheepshead minnow <u>Crassostrea virginica</u> - eastern oyster	<u>Brevoortia patronus</u> - menhaden <u>Mugil cephalus</u> - striped mullet <u>Micropogon undulatus</u> - Atlantic croaker <u>Cynoscion nebulosus</u> - spotted sea trout <u>Cynoscion arenarius</u> - sand sea trout <u>Bairdiella chrysura</u> - silver perch <u>Leiostomus xanthurus</u> - spot <u>Githarichthys spilopterus</u> - bay whiff <u>Meticirrhus americanus</u> - southern kingfish <u>Callinectes sapidus</u> - blue crab <u>Penaeus aztecus</u> - brown shrimp <u>Penaeus setiferus</u> - white shrimp <u>Penaeus duorarum</u> - pink shrimp	<u>Caranx hippos</u> - crevalle jack <u>Caranx bartholomaei</u> - jack <u>Polydactylus actonemus</u> - threadfin <u>Synodus foetens</u> - lizardfish <u>Arius felis</u> - sea catfish <u>Vomer satapinnis</u> - moonfish	<u>Lepisosteus oculatus</u> - spotted gar

3 miles offshore is approximately 30 feet. Beyond this point, the grade lessens to a slope of 4 ft/mi to 6 ft/mi (0.7 m/km to 1 m/km).

#### A.3.3.3 Tides And Currents<sup>51</sup>

Tides in this area are dominantly diurnal, and exert their maximum influence on shelf currents in December and June when the sun reaches its maximum declination. The minimum influence is felt in March and September when the sun is over the equator. Any effects of tides on currents are superimposed on the net drift of regional currents.

Movement of the water column offshore Barataria Bay is driven primarily by local and regional winds, passage of diurnal tides, and impingement of regional Gulf of Mexico currents onto the continental shelf. Figure A-15 depicts general circulation patterns in the Gulf of Mexico. The site area for this study is located on the northeast corner of a counter clockwise circulation current in the northwest Gulf of Mexico. This circulation is modified by those factors mentioned above.

The annual net movement of waters offshore of Barataria Bay is westerly. However, net water movement is easterly in summer with surface currents averaging 0.40 knots, onshore (towards shore) offshore (away from shore) mid-depth currents averaging 0.26 knots, and onshore bottom currents averaging 0.22 knots. In winter and early spring net water movement is westerly, with surface currents averaging 0.82 knots. Mid-depth currents are offshore and bottom currents occur onshore and offshore. In general, current speed tends to decrease with depth. Figure A-16 depicts seasonal variations in current movement in the northwestern Gulf waters.

#### A.3.3.4 Salinity<sup>52</sup>

In general, salinities on the Louisiana continental shelf increase with increasing distance from shore, and with

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<sup>51</sup>Detking, Buck, Watson, and Merks, "Currents on Nearshore Continental Shelf."

<sup>52</sup>P. Detking, R. Buck, R. Watson, and C. Merks, "Hydrography on the Nearshore Continental Shelf of South Central Louisiana," in Offshore Ecology Investigation (Galveston, Texas: Gulf Universities Research Consortium, May 1974).

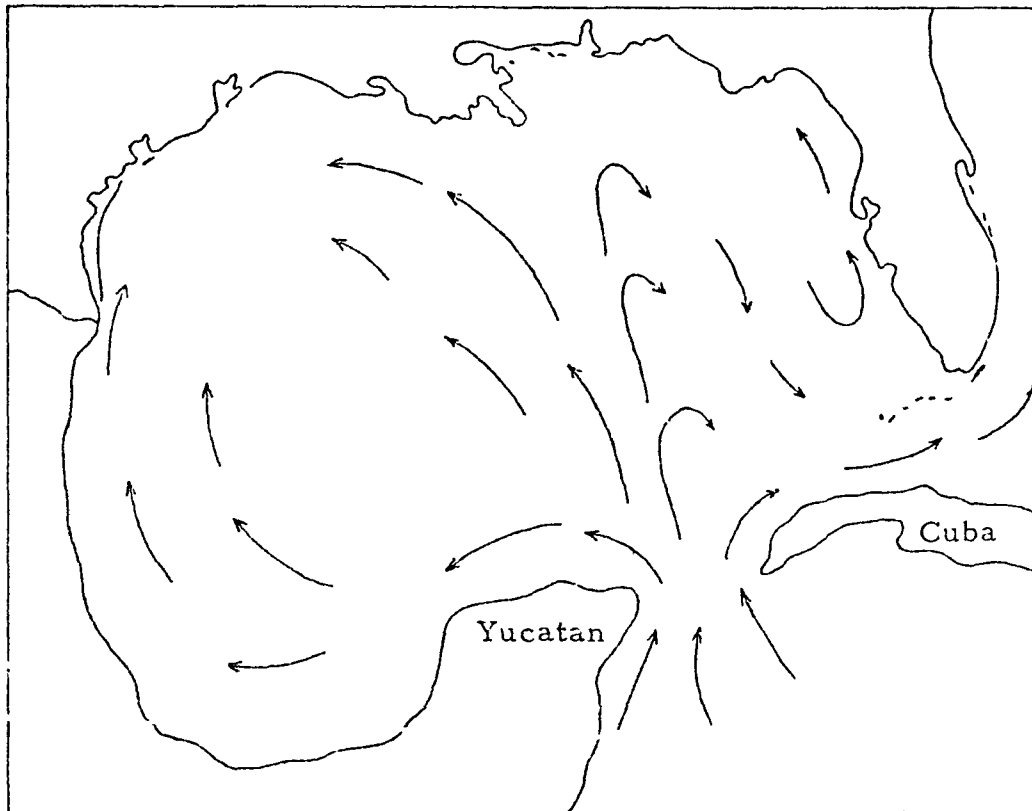


Figure A-15. General circulation patterns in the Gulf of Mexico. (U.S. Naval Oceanographic Office, Oceanographic Atlas of the North Atlantic Ocean, No. 700, Sect. 1, Tides and Currents.)

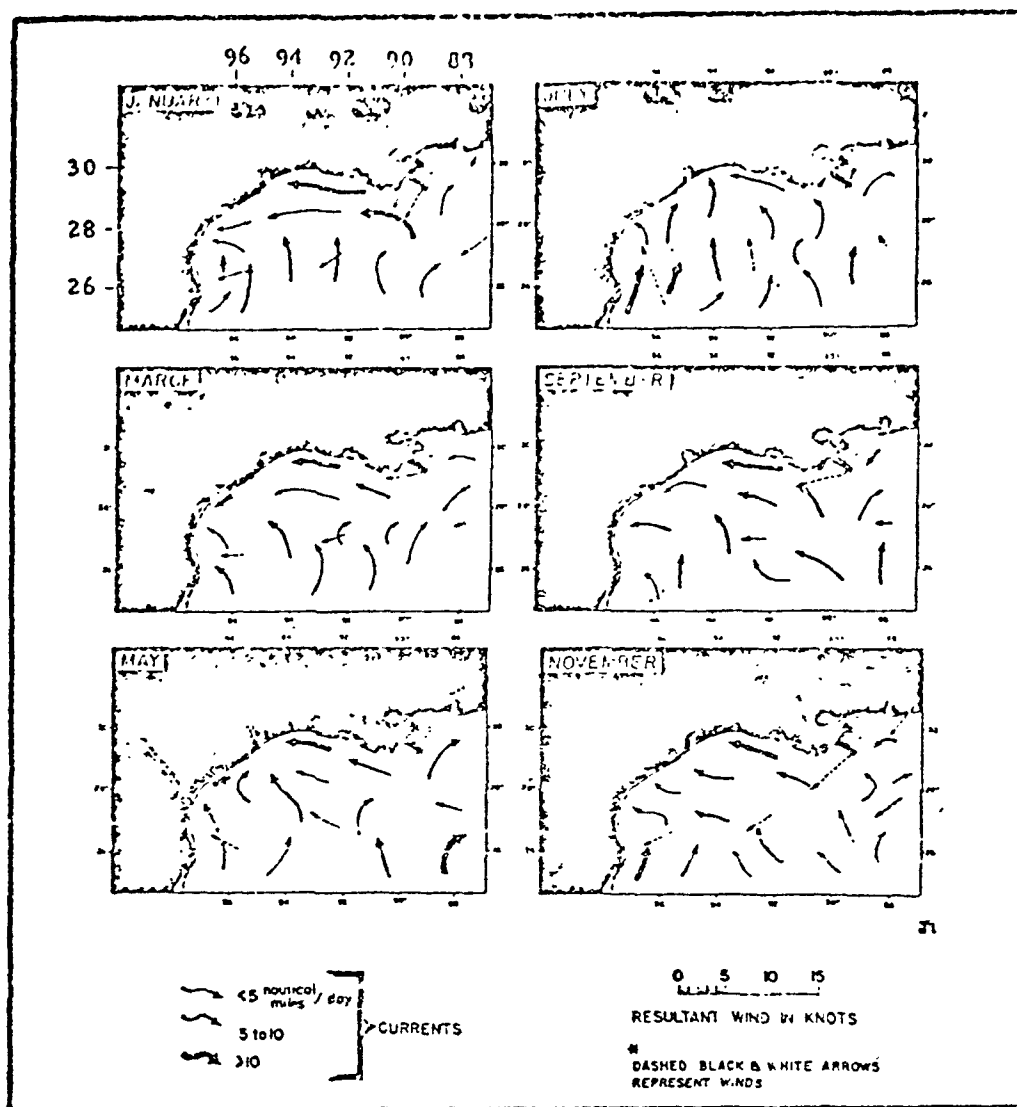


Figure A-16. Seasonal variations in current movement in the northwestern Gulf waters. (J.R. Curray "Sediments and History of Holocene Transgression, Continental Shelf, Northwest Gulf of Mexico," in Sediments, Northwest Gulf of Mexico, American Association of Petroleum Geologists.)



greater depths. Freshwater discharge from local runoff and the Mississippi River acts to lower salinity in surface waters and waters closer to shore. Mean surface salinities range from 19 to 21 ppt, while mean bottom salinities vary from 31 to 33 ppt. During the second half of the year surface salinities are only slightly lower than bottom salinities and no steep vertical salinity gradients occur. This lack of stratification is due to thorough mixing of water by winds and currents in fall and early winter. In mid-winter the lessening of freshwater runoff and the bottom currents are responsible for a rise in bottom salinities to 35 or 36 ppt, the normal salinity of open ocean. In late winter, spring, and early summer pronounced vertical salinity gradients are observed, beginning at depths of 10 feet. In spring surface salinities often fall below 15 ppt, a result of heavy input from local runoff and the flooding Mississippi River. During this period there is little exchange between surface and bottom waters.

Surface and bottom salinities usually increase in an offshore direction. Mean surface salinities in near offshore waters do not vary significantly from surface salinities far offshore; they are approximately 19 ppt. However, mean near offshore bottom salinities average 25.6 ppt, a value notably lower than far offshore bottom salinities. At certain times of the year offshore waters are highly diluted and salinity increases in a shoreward direction. This occurs when the Mississippi River is in a flood stage and near offshore surface currents flow to the west, or when strong north winds push brackish waters out of the bays.

#### A.3.3.5 Turbidity<sup>53</sup>

Turbidity of offshore Gulf waters is strongly influenced by the magnitude and turbidity of Mississippi River discharge, by local freshwater discharge, and by current patterns carrying this flow. Turbidity is greatest in shallow waters and areas closest to shore. Near offshore stations exhibit visibility ranging from 1.5 to 21 feet

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<sup>53</sup>G.M. Griffin and B.J. Ripy, "Turbidity, Suspended Sediment Concentrations, Clay Mineralogy of Suspended Sediments and the Origin of the Turbid Near-Bottom Water Layer, Louisiana Shelf South of Timbalier Bay," in Offshore Ecology Investigation (Galveston, Texas: Gulf Universities Research Consortium, May 1974).

with far offshore visibility ranging from 3.5 to 50 feet. Surface turbidity is highest in May, June, and February, and lowest in September and March.

During most of the year a very turbid layer of water is found near the shelf floor, though it varies seasonally in thickness and concentration. The sediments of this turbid bottom layer have a clay mineral composition identical to the suspended sediments of the Mississippi River. During spring flooding the suspended sediment of the entire water column bears this same composition. The turbid bottom layer is associated with low dissolved oxygen concentrations which drop further in summer.

#### A.3.3.6 Sediment Chemistry<sup>54</sup>

Offshore sediments originate from the Mississippi River, estuarine marshlands and settling siliceous and calcareous organisms living in Gulf waters. The sediments contain high levels of organic materials, associated heavy metals, and nutrients.

Nutrient concentrations in sediments seem to be five to eight times as high as the adjacent water column. They also seem to decrease further offshore. Nitrogen (nitrite plus nitrate) averages 0.5 to 0.6 ppm and total phosphorus averages 2.2 to 2.3 ppm. Hydrocarbon content in sediment ranges from 3.4 to 19.7 ppm. Biological Oxygen Demand ranges from 100 to 740 mg/kg (40 percent of total OD) and decreases with distance offshore. COD ranges from 14,700 to 21,000 mg/kg and decreases with increased water depth. Heavy metal values are summarized in Table A-15. No distinct trends are observable in metal content relative to depth, season or distance offshore.

#### A.3.3.7 Water Chemistry<sup>55</sup>

Oxygen, nutrients, and metals are key parameters in determining the chemical nature of a water body, and the

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<sup>54</sup>Gosselink, Miller, Hood, and Bahr, Louisiana Offshore Oil Port, Appendix V.

<sup>55</sup>Gosselink, Miller, Hood, and Bahr, Louisiana Offshore Oil Port, Appendix V; and Ho and Barrett, Distribution of Nutrients in Louisiana Coastal Waters.

TABLE A-15

GULF WATERS - HYDROCARBON AND METAL CONTENT

	SEDIMENTS (ppm)	WATER (ppb)
HYDROCARBONS	3.4 - 19.7	18 - 64
HEAVY METALS		
Cd	ND - 1.5	ND - 3.1 (surface) ND - 2.8 (bottom)
Cr	ND - 39.6	ND - 55.3 ND - 29.0
Cu	1.2 - 8.7	ND - 5.7 ND - 15.1
Fe	1430 - 5100	ND - 18.2 ND - 14.2
Pb	5.1 - 92.8	ND - 36.7 ND - 26.7
Mn	17.5 - 247	ND - 6.8 ND - 7.6
Hg (ppb)	0.0061 - 0.0417	0.22 - 1.36 0.22 - 1.14
Ni	2.3 - 57.9	ND - 5.2 ND - 22.1
Zn	10.1 - 39.9	ND - 17.0 ND - 32.8
V	28 - 79	

ND = not detectable.

Source: J.G. Gosselink, R.R. Miller, M. Hood, and L.M. Bahr, Jr., Louisiana Offshore Oil Port: Environmental Baseline Study, Appendix V (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1975).

type of life it can support. Often the levels of these constituents vary spatially with depth or distance from shore, or temporally with season.

Surface and bottom concentrations of dissolved oxygen reflect seasonal trends in temperature, mixing, salinity, respiration, decomposition and photosynthesis. High DO levels are found in conditions of low temperature, high wave turbulence, low salinity and high photosynthetic rates.

Surface dissolved oxygen ranges from 6 ppm in summer to 10 ppm in winter. While cold water and winter storms increase the probability that surface waters will become supersaturated with oxygen, uptake by organisms will have little effect on surface DO levels because oxygen can be easily replenished at the air/sea interface.

Bottom dissolved oxygen has greater seasonal variations, ranging from 1.1 ppm in summer to 7.5 ppm in winter, with an annual average of 2 ppm in far offshore waters. Near offshore waters have somewhat higher levels with an annual mean of 3.4 ppm. A large portion of the bottom waters both near and far offshore are anoxic (0 to 2 ppm DO) during the warmer months of the year. This is thought to be associated with a turbid bottom layer and high BOD.

Nitrogen, measured as nitrate plus nitrite, averages 0.14 ppm in offshore waters. Nitrogen content remains constant with depths but has higher values in summer months and in areas further offshore.

Total phosphorus averages 0.33 ppm with levels slightly higher in surface waters. Means of surface, mid-depth and bottom waters average 0.35, 0.31 and 0.30 ppm, respectively. Highest surface and mid-depth values are found in winter months. Phosphorus levels seem to be a function of salinity and Mississippi River discharge.

Mean organic carbon content of near offshore waters is 5 mg/l, while more open Gulf waters average 1.5 to 2.0 mg/l. High organic content of offshore waters may be contributed by the Mississippi River plume, detritus exported from the southern Louisiana salt marshes, and the oil industry.

Heavy metal concentrations are presented in Table A-15. All levels are normal for coastal water with the exception of mercury which is unusually high.

#### A.3.3.8 Gulf Biology<sup>56</sup>

The Gulf of Mexico waters adjacent to Barataria Bay yield extremely high catches of commercially important fish and shellfish. This high faunal productivity is attributable to elevated nutrient levels, resulting from export of primary production from adjacent wetlands to the Gulf via waterways draining the coastal system, and from organic matter carried in the Mississippi plume. It has also been suggested that the productiveness of these fisheries partially results from entrapment of offshore marine animals, which are prevented from eastward migration by the fresh-water Mississippi discharge and by the extension of the modern delta (which narrows the adjacent shelf area).

Primary production in offshore waters is almost entirely planktonic. Diatoms, dinoflagellates and nanno and ultra-plankton are the dominant phytoplankton forms. Macrophytes are found only on man-made structures such as oil platforms. Table A-16 lists major primary producers in offshore waters. Planktonic productivity (both phyto- and zooplankton) is greatest in near offshore waters and decreases further offshore along a gradient of decreasing organic content in the water column.

Herbivores play a more significant trophic role in offshore energy transport than they do in the wetlands. Acartia tonsa and Paracalanus sp. feed on huge amounts of phytoplankton and particulate detritus, forming a major link between primary production and higher trophic levels in the offshore ecosystem. Despite the high level of grazing, detritivores still form a key part of the offshore community. The benthic macrofauna, which are an important food source for bottom feeding nekton such as flounders, silversides, spot, and croakers, are dependent on a continual rain of detritus from the euphotic zone above. These benthic filter and deposit feeders include clams, polychaetes, sand dollars, sea cucumbers, brittle stars, bryozoans, sponges, barnacles and mussels. Mud crabs, mud snails and amphipods are motile forms which scrape detritus from the surface of the ocean

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<sup>56</sup>Fred Dunham, A Study of Important Estuarine Dependent Fishes, Technical Bulletin No. 4 (New Orleans: Louisiana Wildlife and Fisheries Commission, Oyster, Water Bottoms and Seafood Division, 1972); and Gosselink, Miller, Hood, and Bahr, Louisiana Offshore Oil Port.

TABLE A-16

PRIMARY PRODUCERS - GULF WATERS  
NEAR AND FAR OFFSHORE

DIATOMS	DINOFLAGELLATES
<u>Asterinella</u>	<u>Ceratium</u>
<u>Biddulphia</u>	<u>Exuviaella</u>
<u>Coscinodiscus</u>	<u>Gonyaulaux</u>
<u>Cyclotella</u>	<u>Gymnodinium</u>
<u>Lithodesmium</u>	<u>Peridinium</u>
<u>Navicula</u>	
<u>Pleurosigma</u>	
<u>Surirella</u>	
<u>Stauroneis</u>	
<u>Thallasiosira</u>	
<u>Fragilaria</u>	
<u>Rhizosolenia</u>	

floor. Smaller meiofauna such as nematodes, ciliate protozoa, and microbes are also important detritivores. Detritivorous finfish include menhaden, mullet, anchovy, croakers, silversides and threadfins. These fish feed indiscriminately on detritus in offshore waters as adults; however, they seem to be much more selective, searching out specific zooplankton forms, during the larval and juvenile stages of their life cycle.

Many of the offshore predators are the same predators found in the salt marsh estuaries. In fact most of these species are hatched offshore and migrate into the estuary during their greatest growth periods, to take advantage of the abundant food supply present. Offshore predators include spotted sea trout, red and black drum, red snapper, flounder, and blue marlin. Invertebrates such as shrimp, starfish and boring snails prey on benthic organisms. Predatory birds feeding offshore include the laughing gull, ring billed gull, herring gull, frigate birds and brown pelicans. The only mammal found in this offshore environment is the bottlenosed dolphin. Table A-17 presents the key consumer species in the ecosystem offshore of Barataria Bay. These species were selected for their commercial importance, abundant numbers, or endangered-species status.

TABLE A-17

KEY CONSUMERS - NEAR AND FAR OFFSHORE GULF WATERS  
(ADJACENT TO BARATARIA BAY, LOUISIANA)

	INVERTEBRATE	FISH	BIRD	MAMMALS
COMMERCIAL SPECIES	★ <u>Penaeus aztecus</u> (Brown Shrimp)  ★ <u>Penaeus setiferus</u> (White Shrimp)  ★ <u>Penaeus duorarum</u> (Pink Shrimp)  ★★ <u>Callinectes sapidis</u> (Blue Crab)	★★ <u>Anchoa mitchilli</u> (Bay Anchovy)  ☆ <u>Cynoscion arenarius</u> (Sand Sea Trout)  ☆ <u>Peprilus burti</u> (Gulf Butterfish)  ☆ <u>Etropus crassostus</u> (Fringed Flounder)		
SPORT SPECIES		☆ <u>Centropistes philadelphia</u> (Rock Sea Bass)  ☆ <u>Trichiurus lepturus</u> (Cutlass Fish)  ☆ <u>Leiostomus xanthurus</u> (Spot)  ★★ <u>Arius felis</u> (Sea Catfish)  ★★ <u>Micropogon undulatus</u> (Atlantic Croaker)  ☆ <u>Chloroscombrus chrysurus</u> (Atlantic Bumper)		
TROPHICALLY IMPORTANT SPECIES	● <u>Gammarus sp.</u> (Amphipod)  ● ★ <u>Acartia tonsa</u> (Copepod)  ● ★ <u>Paracalanus sp.</u> (Copepod)  ★ <u>Xiphopenaeus sp.</u> (Sea Bob)  ★ <u>Squilla sp.</u> (Mantis Shrimp)  ● ★ <u>Mulina sp.</u> (Pelecypod)  ★★ <u>Cibanarius vittatus</u> (Hermit Crab)  <u>Loliguncula brevis</u> (Squid)	<u>Prionotus roseus</u> (Blue Spotted Sea Robin)	☆ <u>Sterna sp.</u> (Tern)  ☆ <u>Aythya affinis</u> (Lesser Scaup)  ☆ <u>Larus atricillia</u> (Laughing Gull)  ☆ <u>Fregata magnificens</u> (Frigate Bird)  ☆ <u>Larus philadelphia</u> (Bonaparte's gull)	☆ <u>Tursiops truncatus</u> (Bottlenose Dolphin)
ENDANGERED SPECIES			☆ <u>Pelecanus occidentalis</u> (Brown Pelican)	

- ★ Detritivore
- ☆ Carnivore
- Herbivore



## APPENDIX B

### DESCRIPTION OF DISPERSION MODELS

#### B.1 Introduction

Oilfield brines, once discharged into the receiving waterbody, are subjected to the processes of dilution, transport, and diffusion which play a very important role in determining the distribution of pollutant concentrations. Since the impact exerted on the marine environment by the brine discharge depends in large part on the concentration distributions of the discharged contaminants in the receiving waters, it is of great importance to understand and predict the physical dispersion processes which determine these distribution patterns. The purpose of this appendix is to discuss the principles of dispersion modeling and the models used in this study to estimate the dispersion of the discharged brine. The simplest type of calculation, the tidal prism flushing model, is discussed in Section B.2. This model is useful for giving the average concentration of a pollutant in a small bay area but cannot give any information regarding concentration contours. Section B.3 treats the basic ideas and principles involved in modeling eddy diffusion. These principles are then applied in Section B.4 to an analysis of the problem of the dispersion of a pollutant in a steady uniform current in one direction. The final section discusses the computerized diffusion model used in this study to predict concentration contours. This model is capable of incorporating three-dimensional diffusion as well as time varying tidal currents which play a key role in estuarine dispersion.

#### B.2 Simple Tidal Flushing Calculations for Shallow, Enclosed Bays

Pollutants introduced into an estuary are flushed out over a period of time by the combined actions of seaward river flow and mixing at high tides followed by tidal outflow. The residence time of estuarine pollutants is highly dependent on the overall rate at which this flushing occurs. Therefore, one important indicator of the ability of an estuary to rid itself of pollutant discharges -- especially if they are conservative -- is the flushing time, or the length of time required for the river flow and tides to flush an amount of water equal to the low tide volume of

the estuary. For very large estuaries or those which have complicated geometries the flushing time is quite difficult to compute; however, for small estuaries or rough calculations, a relatively simple method has been developed to make reasonable estimates of the length of time, measured in units of tidal periods, needed to replace the estuary volume.

Such calculations are useful for two reasons. First, they can be used to gain a rough idea of the length of time it takes an estuary to rid itself of oilfield brine pollutants dissolved in the water column. Second, in the case of continuous discharges, they can be used to determine the steady state concentrations of those pollutants. This second reason is an important one, for the computer model described in Section B.5, used to determine concentration profiles around the discharge points, is not capable of accounting for more than one straight-line boundary of an estuary. The rougher, less sophisticated calculations described below in this section can be used to supplement the predictions of the computer model in small, enclosed bays by supplying order-of-magnitude estimates of the average background levels of discharged pollutants. These estimates are not only useful in their own right but can also serve as checks on the reasonableness of the results obtained from the computer model.

The simplest version of the method to be discussed is based on the fairly crude assumption that the total volume of water entering the estuary between low and high tides (incoming river water plus incoming seawater) becomes thoroughly mixed with the low tide volume before the ebb tide begins. On the basis of this assumption, the fraction of the low tide estuary volume ("old water") flowing seaward during the ebb tide can be computed. In particular, if  $V$  is the low tide volume of the estuary and  $P$  is the volume entering between low and high tides (called the tidal prism), then  $V + P$  is the volume of the estuary at high tide. Since the tidal prism  $P$  is carried away on the next ebb flow and since the total high tide volume is assumed to be thoroughly mixed, the fraction of the volume  $V$  of old water carried away per tidal period is  $P/(V + P)$ . The number  $T$  of tidal periods needed to flush out all of the old water is just the inverse of this fraction:

$$T = \frac{V + P}{P}$$

This number is a first estimate of the flushing time.<sup>1</sup>

As ought to be expected, this simple-minded method generally yields shorter-than-realistic flushing times for most types of estuaries.<sup>2</sup> For most real estuaries, complete mixing during high tide does not occur, and the ebb tide does not always carry waters near the head of the estuary all the way past the mouth and into the open sea.

Despite this drawback, the approach leads to an equation relating the low-tide, steady-state concentration of a given contaminant to the amount of pollutant discharged into an estuary. For simplicity we will assume that all of the discharge occurs between low tide and the following high tide. Let the concentration of the contaminant at low tide (ambient concentration) be  $C_L$  and its concentration in the discharge stream be  $C_D$  in a total volume  $V_D$  of discharge in one tidal cycle. Then the quantity of contaminant present at low tide is  $VC_L$ , and the quantity present at high tide is  $VC_L + V_DC_D$ . From the discussion above, the quantity of contaminant removed during each ebb tide is

$$Q_- = \frac{P}{V + P} (VC_L + V_DC_D)$$

Since the concentration is assumed to be at a steady state,  $Q_-$  must equal the amount of contaminant  $Q_+ = V_DC_D$  added per tidal cycle. Hence

$$\frac{P}{V + P} (VC_L + V_DC_D) = V_DC_D$$

Solving for  $C_L$ , the steady-state low tide concentration, gives

$$C_L = C_D \frac{V_D}{V} \left( \frac{V + P}{P} - 1 \right) = C_D \frac{V_D}{P} \quad (B-1)$$

Hackberry Bay, 29°14', 90°15' (see Figure B-1) in the northwest corner of Barataria Bay, Louisiana, provides a

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<sup>1</sup>F.F. Wright, Estuarine Oceanography, Council Education in the Geological Sciences Publication No. 18 (New York: McGraw-Hill Inc., 1974), pp. 28-33; and K.R. Dyer, Estuaries: A Physical Introduction (London: John Wiley and Sons, 1973), pp. 109-114.

<sup>2</sup>Dyer, Estuaries: A Physical Introduction, pp. 109-114.



Figure B-1. Location of Hackberry Bay study area.

good example of the kind of bay for which this approach can be useful. It harbors Texaco's Bay de Chene oilfield, the site of the largest brine discharge ( $V_D = 9,747 \text{ m}^3$  per tidal period) in Barataria Bay. The average tide height in Barataria Bay<sup>3</sup> is 0.3 m; if we assume this datum for Hackberry Bay our estimate of  $C_L$  is likely to be slightly low, since the smaller bay probably experiences less extreme tides than the larger one. This tide height multiplied by the surface area of Hackberry Bay of  $1.77 \times 10^7 \text{ m}^2$  gives  $P = 5.33 \times 10^6 \text{ m}^3$ ; if the tide height is 0.1 m,  $P = 1.78 \times 10^6$ . By (B-1), assuming 0.3 m tides gives

$$C_L = 1.8 \times 10^{-3} C_D ;$$

assuming 0.1 m tides gives

$$C_L = 5.5 \times 10^{-3} C_D$$

Table B-1 shows the computed dilution factors for Hackberry Bay and two other enclosed discharge sites (the Lake Washington field operated by Texaco and Exxon and Getty's Manila Village field in Mud Lake.

It is important to emphasize that these results have considerable limitations. To begin with, the methodology is based on the assumption that complete mixing occurs during the flood tide, an approximation which can be used reasonably only for relatively small, shallow bays like the three treated above. Thus no attempt is made to reproduce the concentration isopleths, in direct contrast to the computer model. The implicit assumption that the surface area of a natural body of water remains constant over a tidal cycle introduces yet another source of error. Another underlying assumption in these calculations is that the concentrations of pollutants are at a steady state. While this may be true over short time intervals or in a time-averaged sense, seasonal and even weekly variations in the tides and river inflow may cause significant discrepancies between the computed concentrations and observed values of background concentrations. The method is valid as a means of arriving at an order of magnitude approximation to the average background concentrations of contaminants in relatively small, shallow estuarine bays.

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<sup>3</sup>Barney Barrett, Cooperative Gulf of Mexico Estuarine Inventory and Study, Louisiana, Phase II Hydrology, and Phase III Sedimentology (New Orleans: Louisiana Wildlife and Fisheries Commission, 1971), p. 55.

TABLE B-1

COMPUTED FLUSHING TIMES AND STEADY STATE DILUTION FACTORS  
FOR OIL FIELD BRINE DISCHARGES IN BARATARIA BAY

NAME OF BAY	V (M <sup>3</sup> )	AREA (M <sup>2</sup> )	V <sub>D</sub> (M <sup>3</sup> )	T (TIDAL PERIODS)	DILUTION FACTOR	TIDAL HEIGHT
HACKBERRY BAY	1.30x10 <sup>7</sup>	1.78x10 <sup>7</sup>	9747	8.30	5.5x10 <sup>-3</sup>	.1M
				3.43	1.8x10 <sup>-3</sup>	.3M
LAKE WASHINGTON	2.64x10 <sup>6</sup>	5.78x10 <sup>6</sup>	508	5.57	8.8x10 <sup>-4</sup>	.1M
				2.52	2.9x10 <sup>-4</sup>	.3M
MUD LAKE	1.47x10 <sup>6</sup>	3.22x10 <sup>6</sup>	368	5.57	1.1x10 <sup>-3</sup>	.1M
				2.52	3.6x10 <sup>-4</sup>	.3M

### B.3 General Fluid-Dynamic Considerations for Open Bodies of Water

The assumption of uniform mixing employed in the tidal flushing calculations described in Section B.2 rules out the possibility of predicting concentrations contours around the discharge point since averaging pollutant concentrations over the entire receiving waterbody volume does not give any information concerning concentration gradients. For large bays and estuaries, especially, uniform mixing is not a reasonable or useful assumption, since the averaging process will effectively mask the existence of localized areas of relatively high concentrations. The impact resulting from brine discharges depends on the extent to which regions in the receiving waterbody are subjected to particular levels of pollutant concentration, and these pollutant concentration levels vary with distance from the brine discharge sites. The prediction of pollutant concentration contours requires a level of modeling more sophisticated than that of the tidal flushing model. A very useful approach to the problem of predicting pollutant concentrations in the receiving waterbody is to apply the physics of fluid dynamics to modeling the actual diffusion process responsible for the dispersion of concentrated effluents. This kind of analysis yields concentration distributions instead of averages. Thus, diffusion modeling generates a more desirable (i.e., more informative) type of output than the tidal flushing calculations, provided the former is applied in a regime where it is valid. Large bays are valid regimes because there is room enough for a variety of current scales -- a condition which, as will be explained, is essential to the estimation of a natural diffusion rate.

The problem of interest here is what happens to a parcel of brine containing pollutants when it is subjected to a field of currents in an estuary. Where does it go? How fast is it diluted? What area contains concentrations which are worthy of concern? To answer these questions, it is necessary to analyze the actual current fields themselves. Water currents can be examined at various scales, and the scale chosen determines to what extent the curvature of the streamlines, or directions of fluid flow, is significant. Since logically one chooses the scale of analysis to fit the size of the pollutant stream, which is constantly expanding, it is necessary to consider several different ways of viewing currents.

If the scale is small compared to the streamline curvature, i.e., if the pollution stream is small compared to the

distance over which the current remains relatively uniform, then the current will not disperse the pollutants very much. Rather, it will tend to carry them more or less intact along the overall direction of flow. This situation, illustrated in Figure B-2, is often described by saying that the characteristic eddy of the current is much larger than the pollutant stream, and the resulting transport is called advection.

On the other hand, if the characteristic eddy is smaller than the pollutant stream, the pollutants will be subject to several different directions of flow over any small period of time. The resulting transport pattern, illustrated in Figure B-3, tends to disperse the pollutant parcel. This situation is often described by saying that turbulent flow causes more pronounced diffusion of the pollutant stream. (The reason for the adjectives "more pronounced" is that diffusion occurs on a molecular scale, independent of any observable fluid flow. The component of diffusion attributable to turbulence is usually called "eddy diffusion.")

Modeling this process of diffusion offers a convenient framework in which to analyze the tendency of pollutant streams to spread out after they enter the receiving water. Pollutant streams are characterized by a range of concentrations strewn about a volume of water in some fashion. For a given stream, the function  $c(x,y,z)$  expressing the concentration at each point  $(x,y,z)$  in the volume defines a distribution of the pollutant; the degree to which such a distribution is spread out in any direction (say  $y$ ) is measured by the variance,

$$\sigma^2 = \int_{-\infty}^{\infty} y^2 c'(x,y,z) dy \quad (B-2)$$

For a diffusing pollutant stream, the distribution is continually spreading, so that the variance increases with time. The rate of this increase indicates the rate of diffusion, so that a very large part of the task of characterizing a diffusion process is accomplished by defining a diffusion coefficient  $E$  in terms of the time rate of change <sup>4</sup> in the variance (spatial spreading) of the pollutant stream:

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<sup>4</sup>Frank D. Masch, "Mixing and Dispersion of Wastes by Wind and Wave Action," in Advances in Water Pollution Research, ed. by E.A. Pearson (New York: Pergamon Press, 1964), p. 146.



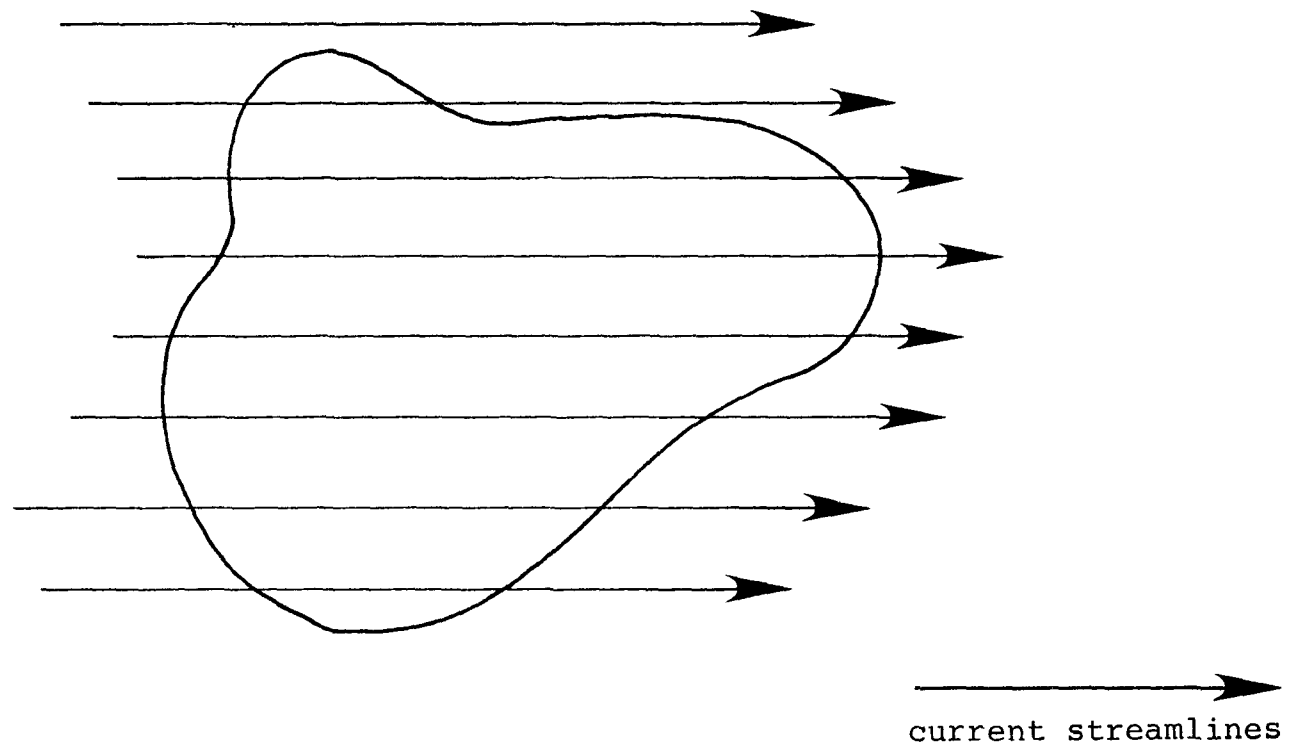


Figure B-2. Advection due to uniform, steady flow.

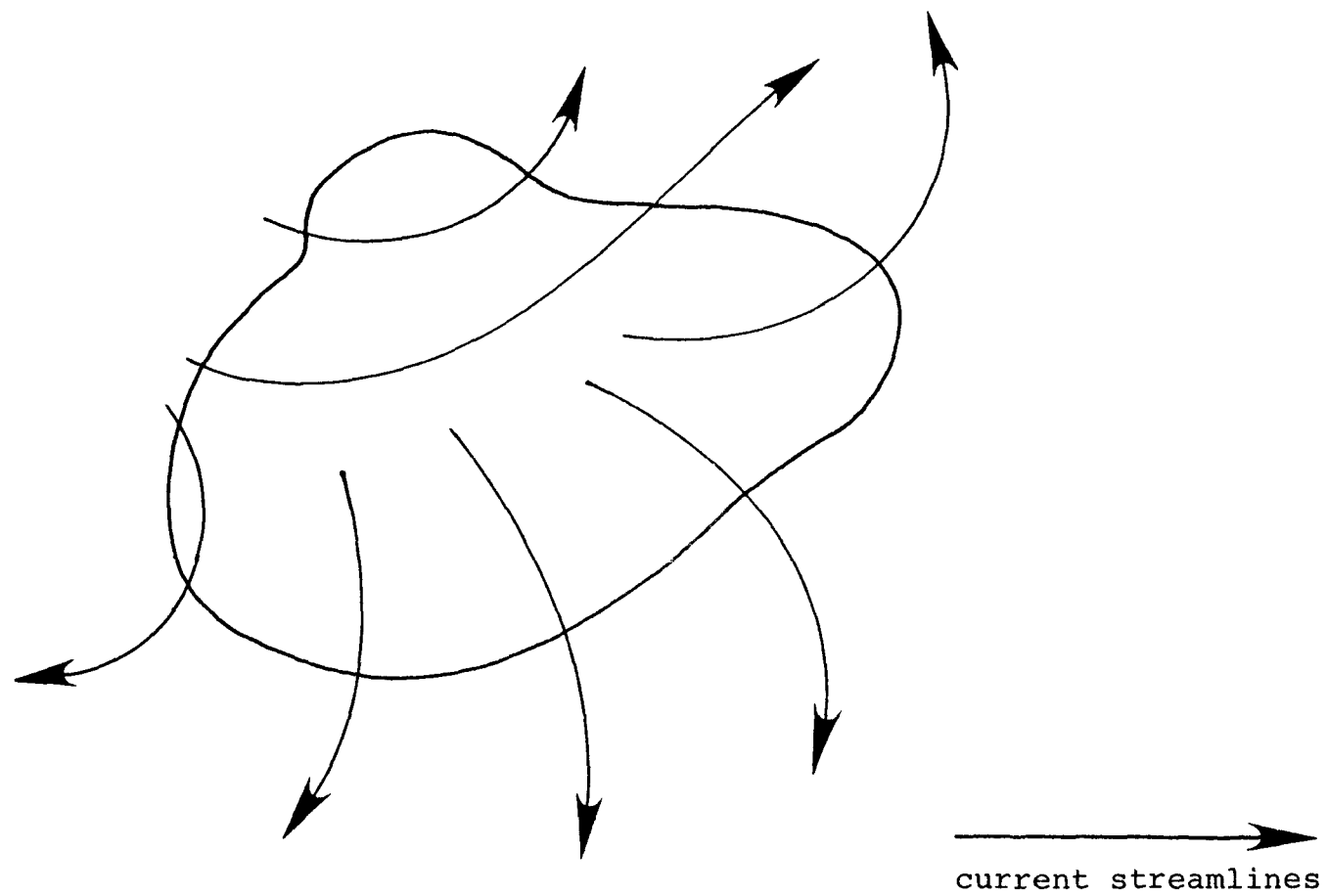


Figure B-3. Diffusion due to turbulent flow.

$$E = \frac{1}{2} \frac{d}{dt} (\sigma^2) \quad (B-3)$$

Notice that E has the dimensions of area/time. The reason for the factor 1/2 is that the variance  $\sigma^2$  measures spatial spreading in both the positive and negative directions relative to the center of mass of the pollutant stream, whereas it is customary in discussing diffusion mechanics to measure dispersion in a given direction in terms of the positive spreading only.

The analysis is complicated by the experimental fact that the spreading rate  $(d/dt)(\sigma^2)$  of pollutant streams in natural waters increases as the diffusion process progresses. In other words, as the scale of the pollutant stream increases because of diffusion, the rate at which further diffusion occurs also increases, causing more and more rapid dispersal. This observation can be explained in terms of the turbulent effects discussed above. When a pollutant stream is small in scale, only currents with comparatively small characteristic eddies can be considered turbulent with respect to the stream. Two representative particles moving in such an eddy will tend to have very similar trajectories because of their proximity to each other, so that they will not be separated quickly at this small scale. As the scale increases, the degree to which the motions of two representative pollutant particles are correlated diminishes, resulting in a more rapid overall rate of separation.<sup>5</sup> Therefore, the eddy diffusion coefficient E is a function of the scale (i.e., the largest dimension) L of the parcel formed by the pollutant stream. Empirical studies have found that a reasonably accurate expression for the dependence of E on L is given by a power law such as

$$E = \alpha L^{4/3} \quad (B-4)$$

where  $\alpha$  is an empirically determined constant.

Several observations about Equation (B-4) deserve some attention. To begin with, there remains considerable controversy over the accuracy to which eddy diffusion coefficients can be evaluated. It is likely that different flow and depth regimes are best characterized by different diffusion

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<sup>5</sup>Henry Stommel, "Horizontal Diffusion Due to Ocean Turbulence," Journal of Marine Research 8 (1949): 199-225.

laws. The  $4/3$  law in (B-4) fits data for ocean regimes summarized by Pearson<sup>6</sup> and has been used in many investigations of ocean diffusion.

The second observation is that eddy diffusion, as defined by (B-4), is nothing more than a sort of statistical construct devised to alleviate the difficulties encountered in solving differential equations for complicated velocity fields. Analysis at the microscopic scale would involve a set of equations of motion tracing the path of each minute parcel of the pollutant as it moved through a current field which varied both spatially and temporally in a complicated and irregular way. Such problems are hopelessly intractable. The saner approach normally taken for eddy diffusion is to view the background current field from a macroscopic standpoint, taking into explicit account only the major features of speed and direction of the flow. So that the important dispersing effect of the irregular details (turbulence) of the current fields is not thereby ignored, it is modeled by lumping all of the eddy-diffusive flow characteristics into a single factor representing, in a sense, their aggregate effect on the pollutant stream. This factor is the non-molecular diffusive component of the eddy diffusion law given in (B-4). The justification for the form of such a simplifying assumption must be provided by actual empirical studies verifying that the hypothetical law accurately models the measurable behavior of dispersing pollutant particles in real bodies of water.

This last point is related to<sup>7</sup> the third observation regarding Equation (B-4). Stommel and others have emphasized two approaches to eddy diffusion laws, one "inductive" (empirical) and the other "deductive" (analytical or theoretical). The inductive approach consists in observing the scale dependence of the diffusion rate and then calculating the functional form of this dependence on the basis of field measurements. The deductive approach consists in deriving the functional form from one or more diffusion theories from physics. Stommel, for example, demonstrates the derivation of a  $4/3$  law from both the Weisaecker-Heisenberg postulates

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<sup>6</sup>N.H. Pearson, An Investigation of the Efficacy of Submarine Outfall Disposal of Sewage and Sludge, No. 14, State Water Pollution Control Board Publication, Sacramento, California, 1956.

<sup>7</sup>Stommel, "Horizontal Diffusion," pp. 199-225.

and the Kolmogoroff postulates. He cautions, however, that the empirical approach possesses a more solid foundation in fact, whereas the theoretical considerations are more useful in finding an explanation of observed diffusion phenomena in terms of more fundamental physical laws. This caveat is important in light of the fact that several successful studies of eddy diffusion have deviated from the 4/3 law, reflecting the view that empirical description, rather than theoretical explanation, is the overriding concern of engineering modeling studies.

The next step in modeling ocean diffusion is to produce a mathematical expression of the physical relationships which govern the process. The basic principle behind diffusion mechanics is that the mass of the pollutant must be conserved in the absence of decay. The simplest situation in which this principle can be applied is also perhaps the most illustrative: it concerns the lateral diffusion of pollutants in a longitudinal current field which is uniform, i.e., horizontal diffusion perpendicular to the direction of current flow. Implicit in this statement of the problem is the assumption that it is in fact realistic to absorb the turbulent, non-advective velocity components of the flow into the eddy diffusion coefficient, leaving explicit only the hypothesized steady and uniform component. It should be noted also that the problem as stated ignores diffusion in the direction of flow and vertical diffusion through the water column.

The conservation of mass for this problem means that the time rate of change of the pollutant concentration around every point (x,y) must be accounted for completely by variations in the net flux of concentration into or out of the volume element containing (x,y). In mathematical language,

$$\frac{dc}{dt} = \frac{\partial}{\partial y} (E \frac{\partial c}{\partial y}) = \frac{\partial}{\partial y} \quad [\text{flux in the y direction}]$$

Expanding the total time derivative of the concentration (left side) using the chain rule gives

$$\frac{\partial c}{\partial t} + \frac{\partial x}{\partial t} \frac{\partial c}{\partial x} + \frac{\partial y}{\partial t} \frac{\partial c}{\partial y} = \frac{\partial}{\partial y} (E \frac{\partial c}{\partial y})$$

But the problem as stated indicates no explicit dependence of c on the time (although there is implicit dependence, since diffusion depends directly on distance traveled, which in turn depends on time); also, the axes have been chosen so that there is no component of the current velocity lying in

the y direction. The first of these considerations forces  $\partial c / \partial t = 0$ ; the second implies  $\partial y / \partial t = 0$ . By hypothesis, the velocity of pollutants in the x direction (i.e.,  $\partial x / \partial t$ ) is the current speed U. All of these observations reduce the equation to

$$U \frac{\partial c}{\partial x} = \frac{\partial}{\partial y} \left( E \frac{\partial c}{\partial y} \right) \quad (\text{B-5})$$

The term on the left in (B-5) represents the advective transport of the concentration gradient along the x-direction; the term on the right represents the local spatial variation of the concentration flux in the lateral (y) direction. This equation, along with its higher-dimensional analogues, serves as the basis for the plume model.

#### B.4 Plume Dispersion in a Steady Uniform Current

The model to be described in this section is an analytical method for predicting the dispersion of a pollutant plume in a steady uniform current. This model is applicable to situations in which tidal current oscillation can be neglected compared to a steady current flow in a specified direction. The model is thus suitable for simulating the dispersion of brine that is discharged into waters in the Gulf of Mexico sufficiently far offshore so that tidal currents are insignificant. For the Louisiana bay area or for Cook Inlet, where tidal currents play an important role in the dispersion of discharge, a model that can incorporate temporal variation of current is needed. Such a model will be discussed in Section B.5.

The problem analyzed in some detail below is shown in Figure B-4. The method used here is essentially that of Brooks.<sup>8</sup> A discharge orifice width (diameter) b is located at x=0 in a constant ocean current U in the x-direction. After the initial concentration  $c_0$  of the pollutants has been established just beyond the point of discharge, the pollutant stream is swept downstream with the current speed U. As it travels, dispersion in the y-direction occurs, so that the scale L of the pollutant stream increases with

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<sup>8</sup>N.H. Brooks, "Diffusion of Sewage Effluent in an Ocean-current," Proceedings of the First International Conference on Waste Disposal in the Marine Environment held at the University of California, Berkeley, July 22-25, 1959, ed. by E.A. Pearson (New York: Pergamon Press, 1959), pp. 246-267.

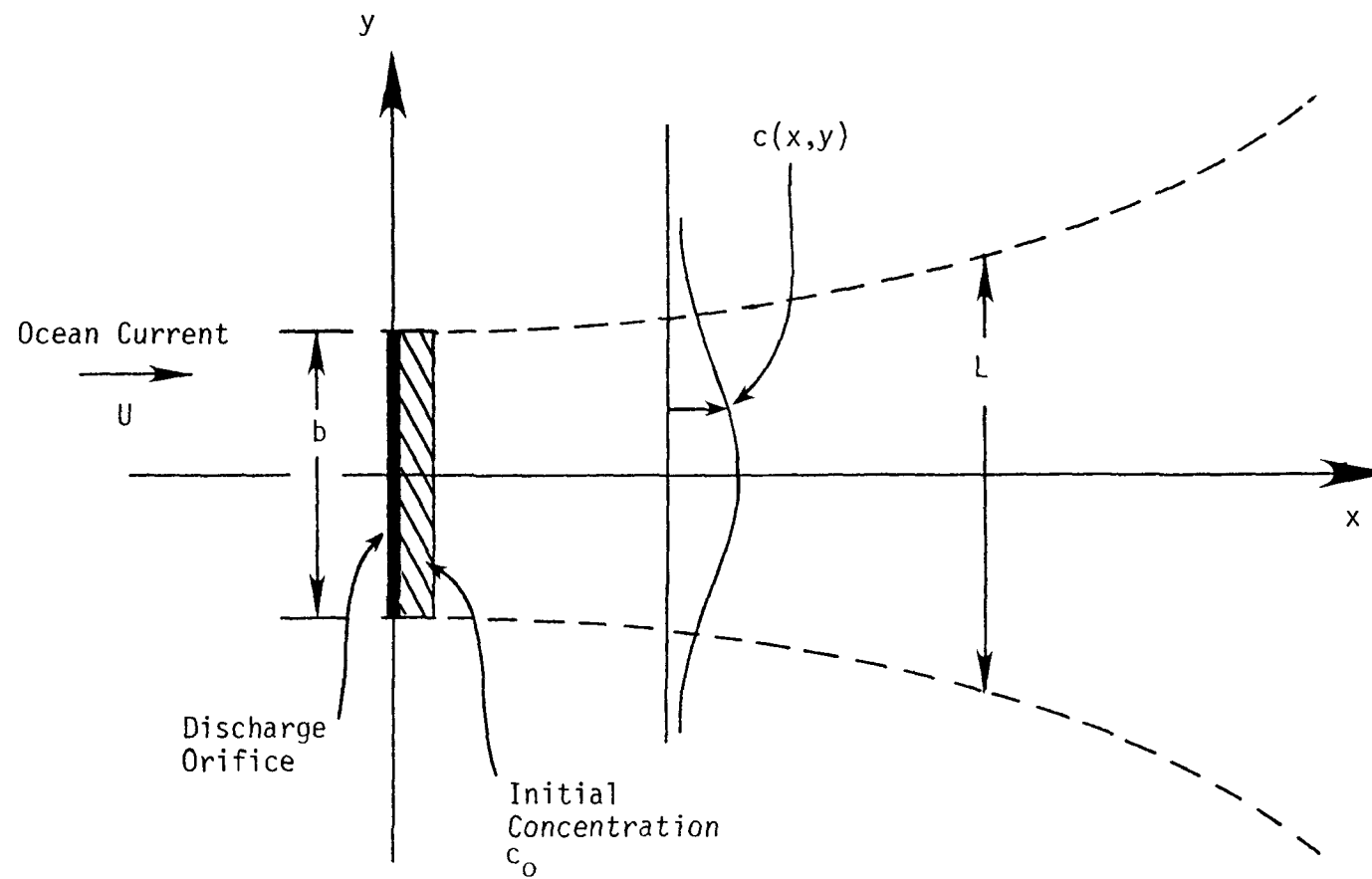


Figure B-4. Lateral diffusion from discharge in a steady, uniform current field  $U$ .

increasing  $x$ . The concentration of pollutant at any point  $(x,y)$  in the plane will be denoted by  $c(x,y)$  and, from the discussion above, will be governed by (B-5) along with the appropriate boundary conditions at the point of discharge ( $x = 0$ ):

1. If  $|y| < b/2$  then  $c(0,y) = c_0$  [the initial concentration]
2. If  $|y| \geq b/2$  then  $c(0,y) = 0$

The following assumptions are necessary to simplify the analysis:

1. There is no variation in the vertical direction. This assumption limits the applicability of the model to the cases of (1) uniform mixing throughout the water column, and (2) no vertical mixing (as a result, for example, of a pronounced density stratification not uncommon in estuaries) in which case the analysis can be applied to the dispersion of a pollutant in a particular layer of the water column.
2. Diffusion in the direction of the current (the  $x$ -direction) is negligible compared to the current-induced advection.
3.  $U$  is constant in time and uniform, so that the diffusive effects of all eddy currents are accounted for by the diffusion coefficient  $E$ . This assumption has the effect of limiting the validity of the analysis to a region within which the instantaneous spatial variations of current speed and direction are small.
4. The diffusion coefficient depends spatially only on the scale of the pollutant stream, which in turn is a function of the distance  $x$  over which the current (including turbulence) has had a chance to disperse the stream.

The fourth assumption allows an immediate simplification of equation (B-5): spatially,  $E$  is a function only of  $x$ , so

$$E(x) \frac{\partial^2 c}{\partial y^2} = U \frac{\partial c}{\partial x} \quad (B-6)$$



This is very nearly the form of a classical partial differential equation known as the heat equation, except that  $E$  is a nonconstant function of  $x$ . Since the heat equation has been solved for a multitude of problems, it is advantageous to manipulate (B-6) until it can be solved via the simpler equation.

To begin with, define  $E_0$  to be the value of  $E(x)$  when  $x = 0$ , so that

$$E(x) = E_0 f(x)$$

and therefore Equation (B-6) can be written

$$E_0 \frac{\partial^2 c}{\partial y^2} = \frac{U}{f(x)} \frac{\partial c}{\partial x} \quad (B-7)$$

From here it is a relatively easy matter to "hide" the  $x$ -dependence in the coefficient on the right hand side behind a change of variables: define a new "diffusion distance"  $\xi$  by

$$\xi = \int_0^x f(w) dw \quad (B-8)$$

Then

$$\frac{d\xi}{dx} = f(x)$$

By the chain rule, (B-7) can be written in terms of  $\xi$  as a heat equation:

$$\frac{\partial^2 c}{\partial y^2} = \frac{U}{E_0} \frac{\partial c}{\partial \xi} \quad (B-9)$$

The solution to this equation has been derived many times; Carslaw and Jaeger's volume is almost entirely concerned with it. The solution which fits boundary conditions (a) and (b) is a form of Laplace's solution for an infinite solid<sup>9</sup> (see the supplement to this appendix):

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<sup>9</sup>H.S. Carslaw and J.C. Jaeger, Conduction of Heat in Solids (London: Oxford University Press, 1959), pp. 53-56.

$$c(\xi, y) = \frac{c_0}{2} \left[ \operatorname{erf} \left( \frac{y + b/2}{2E_0\xi/U} \right) - \operatorname{erf} \left( \frac{y - b/2}{2E_0\xi/U} \right) \right] \quad (\text{B-10})$$

At this point it is useful to clear up a question regarding the scale parameter  $L$ . Since the extent of the nonzero portion of  $c$  is infinite in both the positive and negative directions for all  $x > 0$ , it is pointless to define  $L$  as the boundary of the nonzero concentration. Rather,  $L$  will have to be defined in terms of the width parameter defined for the concentration distribution by Equation (B-2). Thus  $L$  will establish the boundary defined by the distribution of a certain percentage of the pollutants clustering around the line of greatest concentration,  $y = 0$ . For convenience,  $L$  might as well be chosen so that it will equal  $b$  at  $x = 0$ . At this point, Equation (B-2) reduces to

$$\sigma^2(0) = \frac{1}{c_0 b} \int_{-\infty}^{\infty} y^2 c(0, y) dy = \frac{1}{c_0 b} \int_{-b/2}^{b/2} y^2 c_0 dy = \frac{b^2}{12}$$

Hence,

$$\sigma(0) = \frac{b}{2\sqrt{3}}$$

So the expression  $L = 2\sqrt{3}$  satisfies the stipulation  $L(0) = b$ .

The relationship between  $L$  and  $\sigma$  can be used to determine  $\xi$  as a definite function of  $x$ , which is precisely the information needed to convert (B-9) and (B-10) to a solution  $c(x, y)$ . Recalling the definition of the diffusion coefficient  $E$ , (B-3) yields

$$E = \frac{1}{2} \frac{d}{dt} (\sigma^2) = \frac{1}{2} \frac{d}{dt} \left( \frac{L^2}{12} \right)$$

An appeal to the chain rule converts the time derivative to the  $x$ -derivative:

$$E = \frac{1}{24} \frac{d}{dx} (L^2) \frac{dx}{dt} = \frac{u}{24} \frac{d}{dx} (L^2)$$

since the speed  $dx/dt$  of the pollutant stream is assumed to be the current speed  $U$ . Differentiating  $L^2$  then gives

$$E(x) = \frac{UL}{12} \frac{dL}{dx}$$

But the function  $f(x)$  defining the relationship between  $x$  and  $\xi$  is just  $E(x)/E_0$ , and from Equation (B-4)

$$\frac{E(x)}{E_0} = \left[ \frac{L(x)}{b} \right]^{4/3}$$

Hence,

$$\left( \frac{L}{b} \right)^{4/3} = \frac{UL}{12E_0} \frac{dL}{dx}$$

i.e.,

$$\frac{dL}{dx} = \left( \frac{12E_0}{Ub} \right) \left( \frac{L}{b} \right)^{1/3} \quad (B-11)$$

This equation is a version of Bernoulli's equation, and its solution (see the supplement to this appendix) is:

$$\frac{L}{b} = \left( 1 + \frac{2\beta x}{3b} \right)^{3/2}, \quad \beta = \frac{12E_0}{Ub}$$

This solution indicates that the functional relationship between  $\xi$  and  $x$  is determined by

$$f(x) = \left( \frac{L}{b} \right)^{4/3} = 1 + \frac{2\beta x}{3b}$$

Now the solution to the diffusion equation given in (B-11) may be evaluated in terms of  $x$  instead of  $\xi$ , using the relationship (B-8) to get

$$\frac{\xi}{b} = \frac{1}{2\beta} \left[ \left( 1 + \frac{2\beta x}{3b} \right)^3 - 1 \right] \quad (B-12)$$

The final solution, therefore, may be summarized as follows:

$$c(x,y) = \frac{c_0}{2} \left[ \operatorname{erf} \left( \frac{y + b/2}{\gamma} \right) - \operatorname{erf} \left( \frac{y - b/2}{\gamma} \right) \right]$$

where

$$\gamma = \sqrt{\frac{b\xi\beta}{3}}$$

$\xi$  being given by (B-12).

The value of this analysis is threefold. To begin with, the results given in (B-9) in combination with (B-12) are applicable to far-offshore discharges into an approximately steady, uniform current regime. Second, the numerical values obtained for special problems by using (B-9) and (B-12) can be used to check the computer program used to solve the more complicated three-dimensional diffusion problem encountered for nearshore discharges. Third, several qualitative conclusions may be drawn from the foregoing analysis regarding the nature of the concentration distribution. Among these are:

1. The diffusion equation for ocean dispersion can be solved as a modified form of the classical heat equation. The solution indicates, that after the initial concentration at the discharge point has been established, pollutants are distributed in the lateral direction according to an expression involving the error function. This distribution spreads as the pollutants travel downstream.
2. The scale of the pollutant stream, measured in terms of the variance of its spatial distribution, expands slightly faster than the  $3/2$  power of the distance travelled (see Figure B-5).
3. As a result of the spreading, the concentration at the center of the pollutant stream decreases as the stream travels, approaching zero asymptotically with increasing distance from the discharge point (see Figure B-6).

## B.5 Plume Dispersion in an Unsteady Uniform Current

### B.5.1 Introduction

The model to be described in this section is an analytical model for predicting the dispersion of a pollutant plume in a transient but spatially uniform current. This model is applicable to situations in which current variability is important but in which the assumption of a uniform current is acceptable, at least for the portion of the receiving water that is of primary interest. The model is essentially the Transient Plume Model described by Adams et al.<sup>10</sup>

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<sup>10</sup>E. Eric Adams, Keith D. Stolzenback, and Donald R.F. Harleman, Near and Far Field Analysis of Buoyant Surface Discharges into Large Bodies of Water, Report No. 205, Ralph M. Parsons Laboratory for Water Resources and Hydrodynamics, Department of Civil Engineering, Massachusetts Institute of Technology, August 1975.

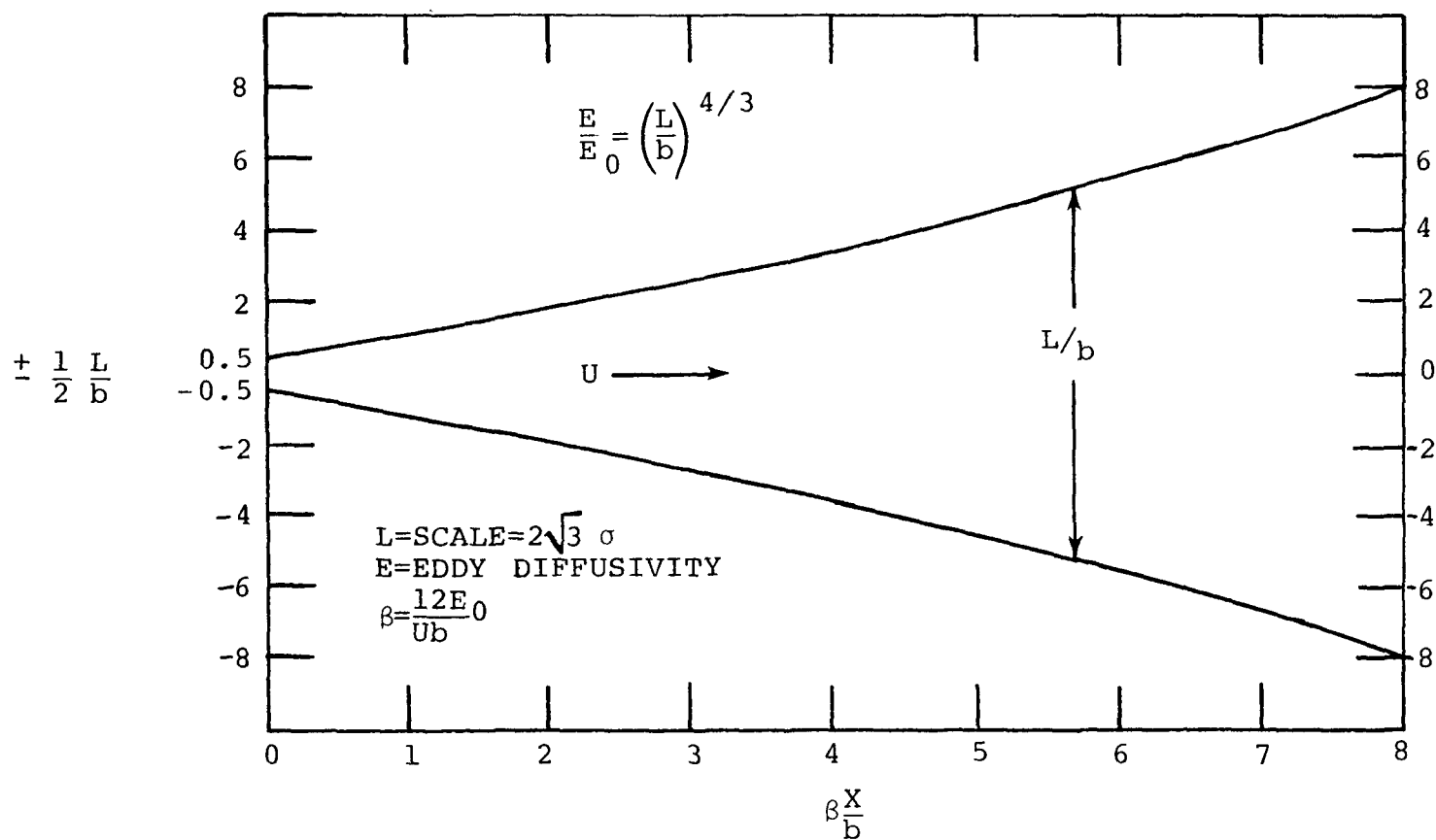


Figure B-5. Plot of pollutant stream scale as a function of distance travelled.

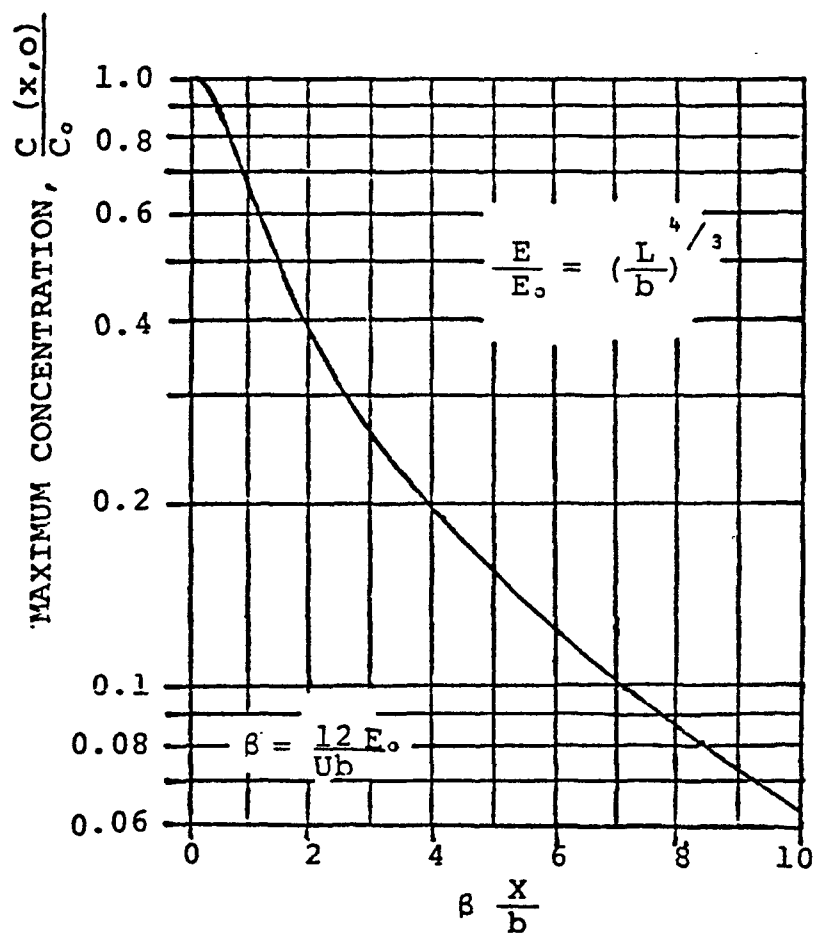


Figure B-6. Plot of centerline (maximum) concentration as a function of distance travelled.

which was developed to predict water temperatures near a proposed offshore power station. More recently the model has been used to analyze the far field temperature distribution associated with power plants sited on Lake Ontario and Cayuga Lake.<sup>11</sup>

#### B.5.2 The Governing Equation for the Far Field

The principle of mass (or heat) conservation applied to a differential control volume leads to a governing equation, the convection-diffusion equation, for the concentration of the effluent. In the coordinate system in Figure B-7, this equation and its boundary conditions may be expressed as

$$\begin{aligned} \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} + w \frac{\partial c}{\partial z} &= \frac{\partial}{\partial x} \left( E_x \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( E_y \frac{\partial c}{\partial y} \right) \\ &+ \frac{\partial}{\partial z} \left( E_z \frac{\partial c}{\partial z} \right) - K_d c \end{aligned}$$

$$E_z \frac{\partial c}{\partial z} = \begin{cases} q_s, & z = 0 \\ q_b, & z = H \end{cases} \quad (B-13)$$

$c(x,y,z,t)$  is the concentration of the effluent;  $u$ ,  $v$ , and  $w(x,y,z,t)$  are the  $x$ ,  $y$ , and  $z$  components of the velocity field;  $E_x$ ,  $E_y$ ,  $E_z(x,y,z,t)$  are turbulent "eddy-diffusion" coefficients;  $K_d(t)$  is a first order decay coefficient (via radioactivity, chemical reaction, etc.);  $q_s$  and  $q_b$  are transport rates across the surface and the bottom respectively (positive values of  $q_s$  and  $q_b$  imply transport of effluent out of the liquid volume); and  $H(x,y,t)$  is the water depth.

Instead of solving for the actual concentration  $c$  from Equation (B-13), the present model solves for excess concentration (the difference in concentration observed with and without the effluent discharge) by writing a similar equation (with boundary conditions) for the concentration of

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<sup>11</sup>Keith D. Stolzenbach et al., Analytical and Experimental Studies of Discharge Designs for the Cayuga Station at the Somerset Alternate Site, Report No. 211, Ralph M. Parsons Laboratory for Water Resources and Hydraulics, Massachusetts Institute of Technology, May 1976.

effluent in ambient water and subtracting it from Equation (B-13). The result is a third equation (with boundary conditions) of the same form as Equation (B-13) for the new variable

$$\Delta c = c - c_{\text{amb.}} \quad (\text{B-14})$$

Several simplifications are made to reduce the equation to a form yielding tractable solutions.

First the velocity field is considered to be two-dimensional ( $w = 0$ ), horizontally uniform, and vertically sheared (with arbitrary shear distribution). Thus

$$\begin{aligned} u &= \bar{u}(t) + u''(z, t) \\ v &= \bar{v}(t) + v''(z, t) \end{aligned} \quad (\text{B-15})$$

where  $\bar{u}(t)$  and  $\bar{v}(t)$  are instantaneous depth averaged velocities. Because there is no horizontal variation of velocity, the assumed velocity field may be ascertained from a time series of currents measured at one station (vertical water column).

Second, because a solution is to be obtained by superposition of instantaneous sources, horizontal diffusion is described by "relative diffusion coefficients." For horizontally homogeneous, stationary turbulence the magnitude of these coefficients depends only on depth and the size of the diffusing patch. The size is described by the horizontal standard deviations,  $\sigma_x$  and  $\sigma_y$ . Thus,

$$\begin{aligned} E_x &= E_x(z, \sigma_x) \\ E_y &= E_y(z, \sigma_y) \end{aligned} \quad (\text{B-16})$$

The vertical diffusion coefficient is assumed to be a function of  $z$  only.

Finally, the water depth,  $H$ , is assumed to be constant. Using the concept of excess concentration and the above simplifications, Equation (B-13) may be rewritten as



$$\begin{aligned}
& \frac{\partial \Delta c}{\partial t} + [\bar{u}(t) + u''(z, t)] \frac{\partial \Delta c}{\partial x} + [\bar{v}(t) + v''(z, t)] \frac{\partial \Delta c}{\partial y} \\
& = E_x(x, \sigma_x) \frac{\partial^2 \Delta c}{\partial x^2} + E_y(z, \sigma_y) \frac{\partial^2 \Delta c}{\partial y^2} + \frac{\partial}{\partial z} \left[ E_z(z) \frac{\partial \Delta c}{\partial z} \right] - K_d \Delta c \\
& E_z \frac{\partial \Delta c}{\partial z} = \begin{cases} K_s \Delta c, & z = 0 \\ -K_b \Delta c, & z = H \end{cases} \quad (B-17)
\end{aligned}$$

### B.5.3 Solution for an Instantaneous Vertical Line Source

The excess concentration at time  $T$  caused by a vertically distributed line source instantaneously released at time  $\tau$  is sought. The first step is to transform to a coordinate system moving with the mean current velocity:

$$\begin{aligned}
x_r &= x + \int_T^\tau \bar{u}(t) dt - x_0 \\
y_r &= y + \int_T^\tau \bar{v}(t) dt - y_0
\end{aligned} \quad (B-18)$$

Equation (B-17) is rewritten as

$$\begin{aligned}
\frac{\partial \Delta c}{\partial t} + u'' \frac{\partial \Delta c}{\partial x} + v'' \frac{\partial \Delta c}{\partial y} &= E_x \frac{\partial^2 \Delta c}{\partial x_r^2} + E_y \frac{\partial^2 \Delta c}{\partial y_r^2} \\
&+ \frac{\partial}{\partial z} \left( E_z \frac{\partial \Delta c}{\partial z} \right) - K_d \Delta c \\
E_z \frac{\partial \Delta c}{\partial z} &= \begin{cases} K_s \Delta c, & z = 0 \\ -K_b \Delta c, & z = H \end{cases} \quad (B-19)
\end{aligned}$$

Equation (B-19) is solved for an instantaneous release by the method of moments. Each term of the equation is multiplied by

$$x_r^i y_r^i$$

and integrated over the domain  $-\infty < x_r, y_r < \infty$ , to obtain equations for the moments  $c_{ij}(z, t, \tau)$ . For instance, for

$i = j = 0$ ;  $i = 1, 2, 3$ ,  $j = 0$ ; and  $j = 1, 2, 3$ ,  $i = 0$ , the following seven equations are derived:

$$\begin{aligned}
\frac{\partial c_{00}}{\partial t} &= \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{00}}{\partial z} \right) \\
\frac{\partial c_{01}}{\partial t} - v'' c_{00} &= \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{01}}{\partial z} \right) \\
\frac{\partial c_{10}}{\partial t} - u'' c_{00} &= \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{10}}{\partial z} \right) \\
\frac{\partial c_{20}}{\partial t} - 2u'' c_{10} &= 2E_x c_{00} + \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{20}}{\partial z} \right) \\
\frac{\partial c_{02}}{\partial t} - 2v'' c_{01} &= 2E_y c_{00} + \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{02}}{\partial z} \right) \\
\frac{\partial c_{30}}{\partial t} - 3u'' c_{20} &= 6E_x c_{10} + \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{30}}{\partial z} \right) \\
\frac{\partial c_{03}}{\partial t} - 3v'' c_{02} &= 6E_y c_{01} + \frac{\partial}{\partial z} \left( E_z \frac{\partial c_{03}}{\partial z} \right)
\end{aligned} \tag{B-20}$$

where

$$c_{ij}(z, t, \tau) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta c x_r^i y_r^j dx_r dy_r \tag{B-21}$$

The boundary condition associated with each equation in (B-20) is

$$E_z \frac{\partial c_{ij}}{\partial z} = \begin{cases} K_s c_{ij}, & z = 0 \\ -K_b c_{ij}, & z = H \end{cases} \tag{B-22}$$

Equations (B-20) are weakly coupled and can be integrated numerically in the order in which they are presented from  $t = \tau$  to  $T$ . Initial conditions (for an instantaneous release at  $t = \tau$ ) are:

$$c_{ij} = \begin{cases} M_z(z), & i = j = 0 \\ 0, & i \neq 0 \text{ or } j \neq 0 \end{cases} \tag{B-23}$$

where  $m_z(z)$  is the mass released per unit depth at depth  $z$ . In the computer program, Equations (B-20) are made non-dimensional and are solved using finite difference with a Crank-Nicholson time scheme.

Familiar statistics describing the distribution of the instantaneously released effluent patch can be derived from the moments  $c_{ij}$ . For example

$$x'' = \frac{c_{10}}{c_{00}} \quad (B-24)$$

$$y'' = \frac{c_{01}}{c_{00}}$$

$$\sigma_x^2 = \frac{c_{20}}{c_{00}} - \frac{c_{10}^2}{c_{00}^2} \quad (B-25)$$

$$\sigma_y^2 = \frac{c_{02}}{c_{00}} - \frac{c_{01}^2}{c_{00}^2}$$

$$\alpha_x = \frac{\frac{c_{03}}{c_{00}} - \frac{3c_{01}c_{02}}{c_{00}^2} + \frac{2c_{01}^3}{c_{00}^3}}{\sigma_x^3} \quad (B-26)$$

$$\alpha_y = \frac{\frac{c_{30}}{c_{00}} - \frac{3c_{10}c_{20}}{c_{00}^2} + \frac{2c_{10}^3}{c_{00}^3}}{\sigma_y^3}$$

$x''$  and  $y''$  are the  $x_r$  and  $y_r$  coordinates of the centers of mass of the patch excess concentration distribution,

$$\sigma_x^2 \text{ and } \sigma_y^2$$

are the variances (squares of the standard deviations) of the patch distribution, and  $\alpha_x$  and  $\alpha_y$  are skewness coefficients. A large number of moments are necessary to accurately describe a single patch. However, when a number of

point source solutions are superimposed to form a continuous solution, it is reasoned that the 0th, 1st, and 2nd moments for each patch are sufficient to approximate the continuous plume. That is, each skewed patch is replaced by a Gaussian patch with the same 0th, 1st, and 2nd moments. The peak concentration of this Gaussian patch is

$$c_{\max} = \frac{c_{00}^2}{2\pi\sqrt{c_{20}c_{02}}} \quad (\text{B-27})$$

and the approximate excess concentration distribution at time T after release at time  $\tau$  is

$$c_{\text{inst}}(x_r, y_r, z, T, \tau) = c_{\max}(z, T, \tau) \exp \left\{ -\frac{[x_r - x''(z, T, \tau)]^2}{2\sigma_x^2(z, T, \tau)} - \frac{[y_r - y''(z, T, \tau)]^2}{2\sigma_y^2(z, T, \tau)} \right\} \quad (\text{B-28})$$

#### B.5.4 Solution for a Continuous Release of Finite Size

The far field plume shown in Figure B-7 can be generated by a set of continuously emitting vertical line sources of effluent distributed across the cross section illustrated in the main diagram below. Concentrations can be obtained by integrating Equation (B-28) from  $\tau = 0$  to T and over the width of the source from  $y' = -B/2$  to  $y' = B/2$ . A weighting factor,  $m_y(y')$ , is used to adjust the strength of the vertical line sources to match the observed (from a near field analysis) lateral distribution of concentration.

$$c(x, y, z, T) = \int_0^T \int_{-B/2}^{B/2} c_{\text{inst}}(x_r, y_r, z, T, \tau) m_y(y') dy' d\tau \quad (\text{B-29})$$

In practice the above integrations are replaced by a finite series (summation) using NI laterally distributed instantaneous sources at each time step and NT time steps,

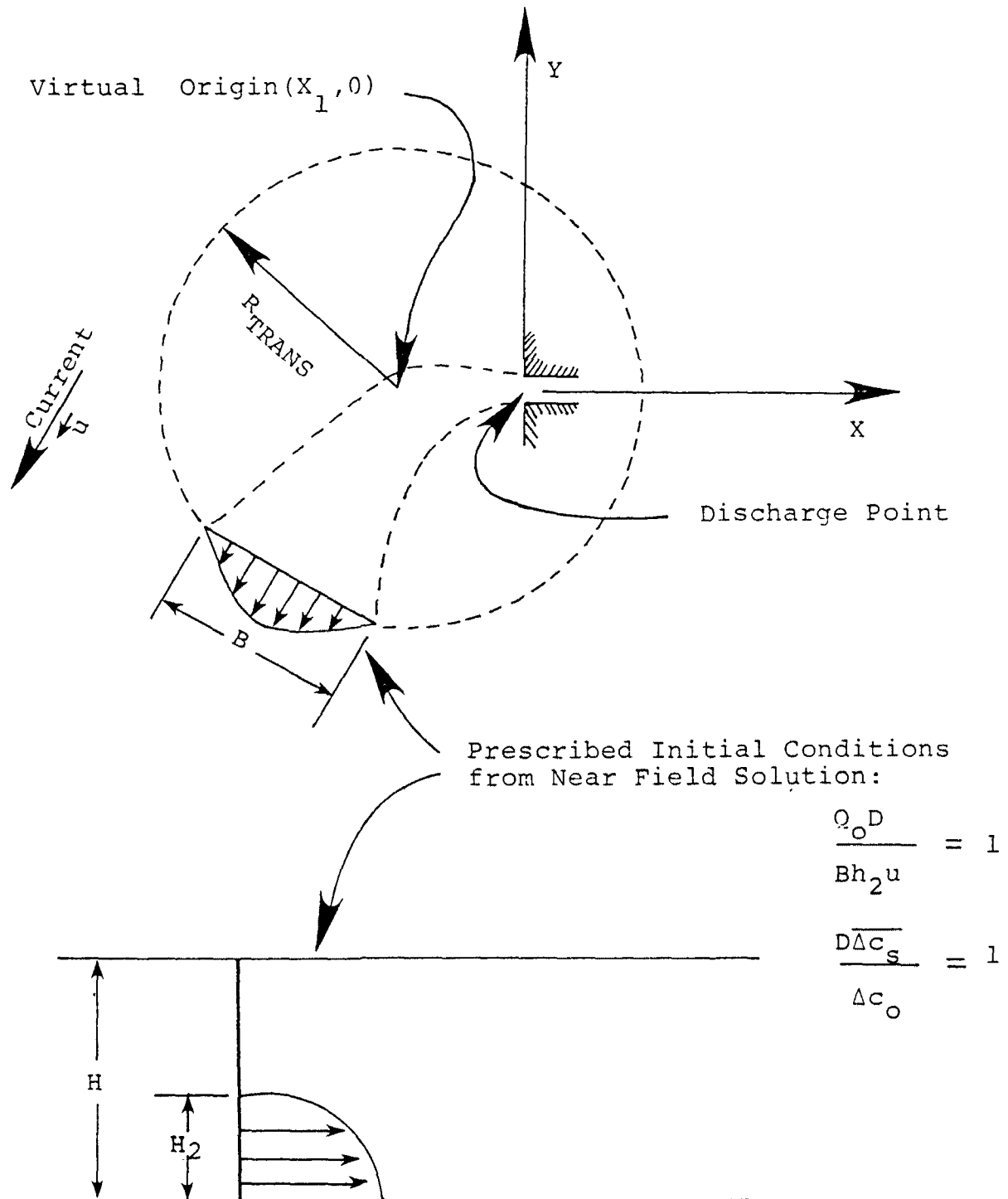


Figure B-7. Far field source conditions. (E. Eric Adams, Keith D. Stolzenback, and Donald R.F. Harleman, Near and Far Field Analysis of Buoyant Surface Discharges into Large Bodies of Water, Report No. 205, Ralph M. Parsons Laboratory for Water Resources and Hydrodynamics, Department of Civil Engineering, Massachusetts Institute of Technology, August 1975.)

$$c(x, y, z, T) = \sum_{t=1}^{NT} \sum_{n=1}^{NI(T, \tau)} \text{FACTOR } c_{\text{inst}}(x_r, y_r, z, T, \tau) m_y(y')$$

$$\text{FACTOR} = \frac{Q_0(\tau) \Delta c_0(\tau) \Delta \tau(T, \tau)}{NI(T, \tau) H} \quad (\text{B-30})$$

where  $Q_0$  is the initial (discharged) flow rate and  $\Delta c_0$  is the initial concentration or temperature rise (without recirculation). Also, the initial conditions for  $c_{20}$  and  $c_{02}$  in Equation (B-23) are altered to represent a partially developed patch; i.e., one which was "effectively released" at a previous time and position such that it has migrated to the source location and has grown to a finite size by the time  $t = \tau$ . Thus a smooth concentration distribution can be achieved near the source.

#### B.5.5 Source Conditions

The characteristics of the far field source of pollutant are determined as follows with reference to Figure B-7. First, the source is assumed to be displaced a distance  $x_1$  to account for the possible length of the steady state portion of the mixing zone. (The coordinate system is assumed to be chosen such that the discharge is in the positive  $x$  direction.) Secondly, the remaining portion of the mixing zone is assumed to have a length  $R_{\text{TRANS}}$  and to be oriented in the direction of the prevailing current direction. Next, the initial source is assumed to be distributed evenly over a portion  $H_2$  of the total depth. Finally, the discharge flow is assumed to be mixed with the receiving water in an amount given by the dilution,  $D$ , which is the ratio of the mixed flow to the initial flow.

With the above information given, the width,  $B$ , of the source is determined by the following mass continuity relationship:

$$B = \frac{DQ_0}{H_2 |V|} \quad (\text{B-31})$$

where  $Q_0$  = the initial flow

$|V|$  = magnitude of the current speed

### B.5.6 Form of Horizontal Diffusion Coefficients

Horizontal diffusion of each patch is described by relative diffusion coefficients,  $E_x$  and  $E_y$ , that are related to the size of the patch by:

$$\begin{aligned}
 E_x &= A\sigma_x^{n_x} & \sigma_x < \sigma_{xc} \\
 E_x &= A\sigma_{xc}^{n_x} & \sigma_x > \sigma_{xc} \\
 E_y &= A\sigma_y^{n_y} & \sigma_y < \sigma_{yc} \\
 E_y &= A\sigma_{yc}^{n_y} & \sigma_y > \sigma_{yc}
 \end{aligned}
 \tag{B-32}$$

The form of Equations (B-32) suggests that over a certain range of length scales ( $\sigma < \sigma_c$ ) patches undergo "accelerated diffusion" due to current shear effects, while for large length scales ( $\sigma > \sigma_c$ ) diffusion is more accurately (or conservatively in the absence of data) described by constant diffusion coefficients. From Equations (B-3) and (B-32) it follows that

$$\sigma_x(\tau, T)^{2-n_x} = \sigma_{x0}(\tau)^{2-n_x} + (2 - n_x)A(T - \tau) \quad \sigma_x < \sigma_{xc}$$

$$\sigma_y(\tau, T)^{2-n_y} = \sigma_{y0}(\tau)^{2-n_y} + (2 - n_y)A(T - \tau) \quad \sigma_y < \sigma_{yc}$$

$$\sigma_x(\tau, T)^2 = \sigma_{xc}^2 + 2A\sigma_{xc}^{n_x} \left[ T - \tau - \frac{\sigma_{xc}^{2-n_x} - \sigma_{x0}(\tau)^{2-n_x}}{(2 - n_x)A} \right]$$

$\sigma_x > \sigma_{xc}$

$$\sigma_y(\tau, T)^2 = \sigma_{yc}^2 + 2A\sigma_{yc}^{n_y} \left[ T - \tau - \frac{\sigma_{yc}^{2-n_y} - \sigma_{y0}(\tau)^{2-n_y}}{(2 - n_y)A} \right]$$

$\sigma_y > \sigma_{yc}$

### B.5.7 Shoreline Imaging

When the discharge is located near a straight shoreline, two constraints must be imposed. First, the currents must be assumed to flow parallel to the shoreline to prevent advection of the pollutant mass across the boundary. Secondly, to prevent effective diffusion across the boundary, an image source corresponding to each real source is assumed to be located on the opposite side of the shoreline.

### B.5.8 Summary of Model Parameters

The model described in the previous section requires the specifications of the following parameters:

$Q_0$  = initial discharge flow

$\Delta c_0$  = initial discharge excess concentration

$D$  = initial dilution

$x_1$  = initial fixed mixing distance

$H_2$  = initial depth of source

RTRANS = initial variable mixing distance

$H$  = total water depth

XSHORE = distance to shoreline (if applicable)

$u(t), v(t)$  = horizontal components of velocity as a function of time

$k_d, k_s, k_b$  = internal, surface, and bottom decay coefficients

$E_z$  = vertical diffusion coefficient

$A_x, A_y, n_x, n_y, \sigma_{xc}, \sigma_{yc}$  = parameters describing the horizontal diffusion coefficients



## SUPPLEMENTS TO APPENDIX B

### LAPLACE'S SOLUTION TO THE HEAT EQUATION<sup>12</sup>

This section examines in detail the solution of the heat equation (B-9) given in Appendix B, Section B.4:

$$\frac{\partial^2 c}{\partial y^2} = \frac{U}{E_0} \frac{\partial c}{\partial \xi} \quad (\text{a-1})$$

given the boundary conditions

$$c(0, y) = \begin{cases} c_0 & \text{if } y < b/2 \\ 0 & \text{if } y \geq b/2 \end{cases}$$

for a finite line source. The method of solution employed here is typical for problems involving spatially continuous sources in that it considers a continuous source to be a collection of point sources each contributing to the total solution. A refined version of this method is used in the computer model developed by Adams et al.

The solution to Equation (a-1) is most easily found by appealing to the superposition principle: since the equation is linear, the solution corresponding to a line source from  $y = -b/2$  to  $y = b/2$  is just the superposition (i.e., the sum or, for continuous sources, the integral) of the solutions for the point sources comprising the line. The equation describing a point source at  $(0, y')$  is just (B-8), with the boundary condition being given by the conservation of mass principle: if the initial discharge at  $(0, y')$  is such that the resulting average concentration on the unit area surrounding it is  $c_0$ , then for any value of  $\xi$ ,

$$c_0 = \int_{-\infty}^{\infty} c_{\delta}(\xi, y) dy \quad (\text{a-2})$$

where  $c_{\delta}$  is the point source concentration. It is easily checked that

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<sup>12</sup>G.T. Csanady, Turbulent Diffusion in the Environment (Dordrecht, Holland: D. Reidel Publishing Co., 1973), Chapter 1.

$$\begin{aligned}
c &= \frac{A}{\sqrt{\xi}} \exp \left[ \frac{-(y - y')^2}{4(E_0/U)\xi} \right] \\
&= \frac{A}{\sqrt{\xi}} \exp \left[ \frac{-(y - y')^2}{4E_0\tau} \right] \quad (\tau = \xi/U) \quad (a-3)
\end{aligned}$$

is a solution to (a-1) for all  $\xi > 0$ ; the arbitrary constant A can be evaluated by imposing (a-2):

$$\begin{aligned}
c_0 &= 2A\sqrt{E_0/U} \int_{-\infty}^{\infty} \exp \left( \frac{y_0^2}{4E_0\tau} \right) d \left( \frac{y}{2\sqrt{E_0\tau}} \right) \\
&= 2A\sqrt{\pi E_0/U}
\end{aligned}$$

Therefore,

$$\frac{A}{\sqrt{\xi}} = \frac{c_0}{2\sqrt{\pi E_0\tau}}$$

and the point-source solution is

$$c_\delta(\xi, y) = \frac{c_0}{2\sqrt{\pi E_0\tau}} \exp \left[ \frac{-(y - y')^2}{4E_0\tau} \right]$$

Integrating  $c_\delta$  over all points constituting the line segment  $-b/2 \leq y \leq b/2$  gives the solution for the line source:

$$c(\xi, y) = \frac{c_0}{2\sqrt{\pi E\tau}} \int_{-b/2}^{b/2} \exp \left[ \frac{-(y - y')^2}{4E_0\tau} \right] dy' \quad (a-4)$$

By the definition

$$\operatorname{erf}(w) = \frac{2}{\sqrt{\pi}} \int_0^w \exp(-z^2) dz$$

of the error function, (a-4) can be written as

$$c(\xi, y) = \frac{c}{2} \left[ \operatorname{erf} \left( \frac{y + b/2}{2\sqrt{E_0\xi/U}} \right) - \operatorname{erf} \left( \frac{y - b/2}{2\sqrt{E_0\xi/U}} \right) \right] \quad (B-10)$$

### SOLUTION TO BERNOULLI'S EQUATION

The equation (3-5)

$$\frac{dL}{dx} = \left( \frac{12E_0}{Ub} \right) \left( \frac{L}{b} \right)^{1/3} \quad (b-1)$$

is more readily recognized after a change of variables

$$\lambda = L/b, \quad \chi = x/b$$

and a renaming of constants

$$\beta = \frac{12E_0}{Ub} \quad (\text{dimensionless})$$

These simplifications throw (b-1) into the form of Bernoulli's equation:

$$\frac{d\lambda}{d\chi} = \beta \lambda^{1/3} \quad (b-2)$$

The standard technique for solving (b-2) proceeds as follows: divide both sides by  $\lambda^{1/3}$  to get

$$\lambda^{-1/3} \frac{d\lambda}{d\chi} = \beta$$

Then define a new variable  $U = \lambda^{2/3}$ , so that

$$\frac{du}{d\chi} = \frac{2}{3} \lambda^{-1/3} \frac{d\lambda}{d\chi}$$

Thus,

$$\frac{3}{2} \frac{du}{d\chi} = \beta$$

Integrating and substituting for  $U$  (and then  $\lambda$ ) and  $\chi$  in terms of  $L$  and  $x$  gives:

$$\left( \frac{L}{b} \right)^{2/3} = \frac{2}{3} \beta \frac{x}{b} + c$$

The initial condition requiring that  $L = b$  at  $x = 0$  is sufficient to determine that the constant  $C$  of integration is equal to unity; therefore,

$$\frac{L}{b} = \left(1 + \frac{2}{3} \beta \frac{x}{b}\right)^{3/2}$$

## APPENDIX C

### FATES OF HYDROCARBONS AND TRACE METALS IN THE MARINE ENVIRONMENT

#### C.1 Introduction

A central assumption of the analysis performed in this report is that the key process leading to the observed concentrations of oilfield brine constituents in the vicinity of a production platform is the dilution of the brine due to diffusion forces and current patterns. Thus, it is assumed that the spatial distributions of brine concentrations around a platform are adequately represented by the predictive model described in Appendix B, which takes only currents and diffusion into account. This is an excellent approximation, but it is not the complete story. The components of oilfield brines are subject to a number of physical, chemical, and biological processes other than dilution, which can all affect their physical form, chemical nature, and, therefore, their toxicity.

Fundamentally, there are three types of relevant processes:

1. Degradation processes, such as the microbial or photo-degradation of hydrocarbons in the marine environment.
2. Alteration processes, such as the biological methylation of mercury or the oxidation of  $\text{Cu}^+$  ions.
3. Transfer processes, which move the pollutant from one compartment of the marine environment to another (e.g., the transfer of metals from the water column to the bottom sediments via precipitation and sedimentation).

Generally, data are not yet available which would enable these effects to be incorporated in any reliable way in a theoretical or semi-empirical predictive model. Furthermore, actual data on the rates of these processes in situ is rare, and only one or two studies have reported actual metal or hydrocarbon monitoring data in the vicinity of production platforms. Therefore, these processes will not

be incorporated into the primary analysis of this report. Nevertheless, the more important of these processes are discussed in this appendix to indicate their approximate rates and the qualitative way in which they might affect brine toxicity.

One of the most important of these environmental modification processes, and one to which both hydrocarbons and trace metals are subject, is sedimentation. The transfer of a toxic substance from the dissolved to the suspended or settled fraction of the marine environment drastically affects its accessibility to resident organisms. On a priori grounds, for example, one might expect precipitation and sedimentation processes to decrease the toxicity of metals and hydrocarbons to most swimming fish, but to create a much more severe toxicity problem for benthic or filter feeding organisms, and to a large extent these conclusions are supported by the literature. (Sedimentation is an example of a process which alters toxic impact by affecting the accessibility of a substance. Other environmental modification processes, such as oxidation of trace metals, can affect toxicity more directly). Because of the importance of sedimentation, it will be given primary emphasis in this appendix.

## C.2 Sedimentation

In general, sedimentation in estuaries occurs as a result of the aggregation and settling of suspended particulates. Two major processes have been proposed to explain this aggregation for general particles: salt flocculation and agglomeration by organisms. Settling is due to a number of factors including net transport of suspended sediments from swift river currents to calmer bays (the last is important in estuaries and is highly dependent on the hydrological nature of the estuary in question).

The principle behind salt flocculation is that the presence of salt ions in water results in an electrolytic effect which increases the tendency of suspended particles to adhere to one another. Flocculation can be regarded as the result of two separate mechanisms: interparticle collisions and cohesion between particles which have been brought into contact with each other. Fine-grained suspended sediments tend to acquire small amounts of electrical charge as they are buffeted about in the water, and, since similar particles tend to pick up the same kind of charge, small repulsive forces develop which inhibit the cohesion phase.

The ions in electrolytic saline water act to neutralize these small friction-generated charges, increasing the probability of cohesion.<sup>1</sup>

The rate at which flocculation occurs depends on a number of interacting variables, the most important being:

1. Relative distribution of mineral components in the sediments.
2. Particle size (the electrochemical forces causing flocs are too small to have noticeable effects on clay particles much larger than about  $1\mu$ ).<sup>2</sup>
3. Salinity.
4. Suspended sediment concentration.
5. Turbulence and water depth.

Thus salt flocculation is very difficult to analyze in any quantitative manner. Although the mechanism has been studied in detail under controlled laboratory conditions, there is presently little evidence to support the widely held belief that increased aggregation due to net particle transport up the saline gradient is a substantial factor in estuarine sedimentation.<sup>3</sup>

The second major aggregation process, agglomeration by organisms, is largely the result of filter feeding activity by oysters, copepods, clams, mussels, scallops, tunicates, and barnacles. For example, oysters filter water through their gills in order to extract food. The rejected material is emitted in clumps loosely held together by mucus, and the

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<sup>1</sup>A.T. Ippen, ed., "Sedimentation in Estuaries," in Estuary and Coastline Hydrodynamics (New York: McGraw Hill, 1966), pp. 648-672.

<sup>2</sup>Ippen, "Sedimentation in Estuaries."

<sup>3</sup>R.H. Meade, "Transport and Deposition of Sediments in Estuaries," in Environmental Transport of Coastal Plain Estuaries, Geological Society of American Memoir 133, ed. by B.W. Nelson (Boulder, Colorado: Geological Society of America).

suspended matter that is eaten is agglomerated into small fecal pellets. It is estimated that oysters can deposit suspended matter at a rate seven or eight times of that ordinarily caused by gravity.<sup>4</sup> In estuaries where filter feeders are a significant component of the trophic web, organic agglomeration can be a substantial factor in sediment deposition.

The third process by which sedimentation of suspended particulates may occur is due to the general hydrological features of estuaries as compared to rivers. The currents in a river are often strong enough to support a much greater suspended sediment load than could be sustained by standing water. In estuaries characterized by wide bays and sluggish currents, the inflowing particulates may encounter less turbulence than that provided by river flow and may sink as a result. Naturally, the extent to which this process explains sedimentation in a given estuary depends on the relative turbulence of tidal and current flows in the estuary as compared to the turbulence of the incoming, sediment-carrying flow. Moreover, the extent to which this process applies to oilfield brine discharges in the estuary depends on the location of the discharge points with respect to the incoming flow, i.e., whether brine is discharged into waters experiencing significant river currents, or into waters which are already relatively calm.

#### C.2.1 Sedimentation of Oil-Associated Hydrocarbons

Most of the existing studies of oil species sedimentation focus on the fate of oil from accidental spills. Four basic processes have been identified in the sedimentation of materials from oil slicks:<sup>5</sup>

1. Evaporation and dissolution of lighter compounds.
2. Uptake of particulate matter (both organic and inorganic) by petroleum.

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<sup>4</sup>Meade, "Transport and Deposition in Sediments in Estuaries."

<sup>5</sup>C.B. Gelelele, "Sedimentation Processes Involving Hydrocarbons in the Marine Environment," in Background Papers for a Workshop on the Inputs, Fates, and Effects of Petroleum in the Marine Environment, compiled by the Ocean Affairs Board, National Academy of Sciences (Washington, D.C.: National Academy of Sciences, 1973), pp. 462-466.



3. Agglutination of dispersed globules followed by the uptake of particulates.
4. Sorption of dissolved species onto suspended particulates.

Of these processes, (1) is not particularly applicable to oilfield brines, since they seldom contain large masses of undissolved, unsuspended, and unevaporated oil species; (2) is applicable only as it pertains to (3); (3) may be applicable to brines containing significant amounts of emulsified hydrocarbons following the oil-water separator process; and (4) is likely to be an important mechanism for hydrocarbon sedimentation from brines.

The uptake of suspended particulate matter by petroleum globules is most important nearshore, where high concentrations of suspended sediments frequently result from inflowing river loads. The accumulated sediments increase the density of the hydrocarbon mass, causing fairly rapid deposition onto the ocean floor. There may be a biological contribution to this process: oil-soaked suspended particles foster some algal growth, which in turn, attracts small invertebrates. The invertebrates attach themselves to the particles, again increasing their density.<sup>6</sup>

It is likely that this process is preceded by some agglutination of dispersed oil particles in the case of oilfield brine, since the brine itself usually contains very little oil in any substantially aggregated form. Because the surface tension of a volume of water is inversely related to surface curvature, oil dispersed in water tends to accumulate into larger aggregations with boundaries of smaller curvature, thereby reducing the net potential energy of the oil-seawater interface. (This process may be inhibited in the well by higher temperatures.) The resulting increase in volume enhances the uptake of suspended particulates and hence the rate of deposition. This rate is also highly dependent on the quantity of suspended particulates present, turbulence of the receiving water, and the specific gravity of the oil particles. For example, Bunker C oils and Venezuela and California crudes with specific gravities very close to

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<sup>6</sup>Gebelein, "Sedimentation Processes Involving Hydrocarbons."

1.000 do not need to accumulate much particulate matter in order to acquire the density necessary to sink.<sup>7</sup>

Dissolved species of oil enter the sediment phase primarily via absorption or adsorption onto suspended particulates. The most effective absorbers normally present in estuarine waters are fine-grained clays of cross-section less than about 45 $\mu$ . There is some indication that clays with high organic content absorb oil species more effectively than those with less organic matter. Also, in general, sorption increases with salinity and decreases with temperature.<sup>8</sup>

Very little is known about the actual rates of deposition associated with any of these processes. Research on this problem is hampered not only by the lack of systematically conducted fieldwork but also by the fact that the quantitative understanding of sedimentation gained in controlled laboratory experiments cannot be used with any confidence in applications to field studies in actual estuaries. The mechanisms by which deposited brine organics may become resuspended also are not understood. It is thought that reworking of sediments by tidal activity and by surface and infaunal organisms may lead to resuspension.<sup>9</sup> If this is the case, then this same reworking may also lead to greater longevity of oil-associated organics in estuaries. Biogenic reworking of sediments may plow some organics down into the anaerobic subsurface layers of the estuary floor, inhibiting aerobic degradation. Despite the current lack of knowledge concerning its mechanisms, however, sedimentation of oil species is an important aspect of the long-term fate of oil-field brine pollution.

#### C.2.2 Sedimentation of Metals

Oilfield brine generally contains appreciable concentrations of heavy metal ions. It is not surprising, therefore, that some of these metals find their way into the

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<sup>7</sup> National Academy of Sciences, Petroleum in the Marine Environment (Washington, D.C.: National Academy of Sciences, 1975), pp.50-51.

<sup>8</sup> National Academy of Sciences, Petroleum in the Marine Environment.

<sup>9</sup> National Academy of Sciences, Petroleum in the Marine Environment.

sediments of estuaries where brine is discharged. For example, Montvalvo and Brady found higher levels of Zn, Cd, Pd, and Hg in Louisiana bays harboring oilwell activity than in offshore areas, with levels of Zn, Cd, and Pb substantially higher near the rigs themselves.<sup>10</sup> Of these three metals, no correlation was found between Cd concentrations and depth; however, Zn and Pb concentrations were highest in bottom samples containing more sediment. These results indicate that sedimentation should be considered an important fate of certain heavy metals in discharged oilfield brine.

Several processes have been proposed to explain the mechanisms by which metal ions are deposited on the bottom of estuaries. Perhaps the most important of these processes is adsorption onto suspended clay particles which eventually sink to the estuarine floor. Rivers carry great quantities of clays containing oxides of both manganese ( $MnO_x$ ) and iron ( $FeO_x$ ).<sup>11</sup> These oxides exhibit an affinity for metal cations, so that trace metal ions introduced into estuarine waters fed by the rivers tend to be adsorbed onto the clay particles.<sup>12</sup> This process is influenced by the relative ion concentrations as measured by pH and salinity, since increases in the relative concentrations of lighter ions may displace heavier absorbed cations, and vice versa for increases of heavy metal concentrations. However, the wide variation in composition among different oilfield brines renders the extent to which brine/seawater pH and salinity differences perturb the adsorption by clays difficult to quantify.

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<sup>10</sup>J.G. Montavalo and D.V. Brady, Toxic Metal Determinations in Offshore Water Samples, Final Report to Gulf Universities Research Consortium, Contract No. GU 853-5, Investigation No. OE-53-HJM, April 30, 1974.

<sup>11</sup>K.K. Turekian, "Rivers, Tributaries, and Estuaries," Chapter 2, in The Impingement of Man on the Oceans, ed. by Donald Hood (New York: John Wiley & Sons, 1971).

<sup>12</sup>J.J. Morgan and R.D. Pomeroy, "Chemical and Geochemical Processes Which Interact with and Influence the Distribution of Wastes Introduced into the Marine Environment, and Chemical and Geochemical Effects on the Receiving Waters," in Background Papers on Coastal Wastes Management, National Academy of Engineering, Vol. 1 (Washington, D.C.: NTIS, 1969), pp. X-1-X-44.

Chemical reactions resulting in precipitation are another possible mode of metal sedimentation from brine/sea-water mixtures. It has been suggested that many oil deposits contain bacteria which reduce sulfate ions in brine to hydrogen sulfide.<sup>13</sup> Over long periods of time, this action generates a solution which is highly reducing relative to the comparatively sulfate-rich ocean environment. When the two waters are mixed, sulfates in seawater oxidize certain cations, often resulting in precipitation. The low concentrations of sulfates in the brines produced from many Louisiana wells<sup>14</sup> corroborate this hypothesis; however, the precipitates formed are principally those of Ba, Sr, and Ca.<sup>15</sup> Oxidation by sulfates in seawater does not appear to be a significant factor in the precipitation of heavy metals from discharged brine.

A related process may explain, though, how heavy metals introduced by discharged waters are precipitated when they are not themselves present in heavy enough concentrations to precipitate from aqueous solution. This process involves the formation of a solid solution of heavy metals with the more abundant solids dissolved in seawater. Discharging oilfield brine into estuarine waters can be regarded as mixing two aqueous solutions, each in equilibrium. If no solubility changes result from this mixing, as in the case of mixing two unsaturated aqueous solutions of NaCl, then no precipitation will occur. However, it is likely that the equilibrium configuration for some aqueous solutions containing ions of both light and heavy metals consists of a solid solution of heavier metals in some lighter ones,<sup>16</sup> in equilibrium with an aqueous solution. The solid solution may have a lower solubility than its separate components, and hence some precipitation may occur before equilibrium is reached, even though none of the ions comprising the solid solution would have precipitated were they to have remained in aqueous

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<sup>13</sup>Telephone conversation with A.G. Collins, March 31, 1976.

<sup>14</sup>A.G. Collins, Geochemistry of Some Petroleum-Associated Waters from Louisiana, U.S. Bureau of Mines Report of Investigations 7326, Washington, D.C., 1970.

<sup>15</sup>Telephone conversation with A.G. Collins, March 31, 1976.

<sup>16</sup>Morgan, "Chemical and Geochemical Processes."

solution.<sup>17</sup> Examples of such solid solutions are  $\text{Ca}(\text{OH})_2$  in  $\text{Fe}(\text{OH})_2$ ,  $\text{PbO}_2$  in  $\text{MnO}_2$  and  $\text{SrCO}_3$  in  $\text{CaCO}_3$ . Since the elements in these complexes generally are not present in stoichiometric proportions, the precipitates cannot be considered strictly to have been formed via chemical reactions. Therefore this mechanism may explain the sedimentation (formation of solid phase) of trace metals for which distinct precipitate phases in seawater appear thermodynamically unlikely.<sup>18</sup>

Marine organisms also play a role in the long-term deposition of trace metals. Organic debris and skeletal fluorapatite in the deep-sea, or bathypelagic, zone are known to accumulate trace quantities of Zn, Sn, Pb, Ti, Cu, and Ag.<sup>19</sup> Brown algae and plankton are also important bio-accumulators of metals. Brown algae accumulate tetravalent and trivalent elements most effectively, then divalent transition metals, divalent Group IIA metals, and univalent Group I metals. Plankton tend to accumulate in order of decreasing affinity, Fe, Al, Ti, Cr, Si, Ga, Zn, Pb, Cu, Mn, Co, Ni, Cd.<sup>20</sup> Mollusks also concentrate trace metals very effectively.<sup>21</sup>

All of these processes are highly dependent on ambient conditions of temperature, turbidity, and flow patterns as well as the chemical composition of the brines in question. All that can be said given the present state of knowledge is that, on the basis of sampling studies, measurable amounts of trace metals discharged from oilfield operations find their way into estuarine sediments. The major mechanisms of this deposition can be identified; however, no reliable information has been gathered to quantify either their absolute rates or their relative importance.

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<sup>17</sup>Stumm, Werner, and James J. Morgan, Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters (New York: John Wiley & Sons, 1970).

<sup>18</sup>Morgan, "Chemical and Geochemical Processes."

<sup>19</sup>Morgan, "Chemical and Geochemical Processes."

<sup>20</sup>Morgan, "Chemical and Geochemical Processes."

<sup>21</sup>Energy Resources Co. Inc., A Review of Concentration Techniques for Trace Chemicals in the Environment, for the U.S. Environmental Protection Agency, EPA-560/7-75-002, November 1975, pp. 452-455.

### C.2.3 Basic Sediment Transport Patterns

The ultimate distribution of sediments in estuaries depends on their long-term sediment transport patterns. These patterns result from the processes by which sediments are introduced or resuspended into the water column, carried by currents, winds, and tides, and deposited in more or less stable configurations on the bottom. Several general observations, independent of the specifics of estuarine hydrology, can be made regarding these processes:<sup>22</sup>

1. Resuspension occurs where mechanical or biogenic reworking of sediments is appreciable or where shear currents along the bed rise above a critical value. Above this value, increasing bed shear generally leads to increased resuspension.
2. Deposition occurs where bed shear is below a critical value; below this value, decreased bed shear generally leads to increased deposition.
3. The rate of sediment deposition is limited by the rate of sediment formation, e.g., flocculation, uptake of particulates by oil, etc.
4. Deposited sediments may flow to lower lying adjacent areas.
5. Deposited sediments may be eroded under certain flow conditions such as floods or spring tides.

In addition to these general considerations, the saline wedge structure of estuaries has some very important effects on the patterns of sediment transport and deposition. Although the net flow of water in estuaries is from upriver to downriver and then out into the open ocean, the greater density of seawater and the periodic longitudinal movement of saltwater/freshwater interface caused by tides often gives rise to a net bottom flow upstream in the saline portion of the wedge. At the bottom edge of the saline intrusion this upstream flow is countered by the opposing river flow, which tends to be lifted over the wedge as it moves downstream. The saline wedge thus acts as a sort of dam or weir, since net flow at its base is nearly zero as a

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<sup>22</sup>Ippen, "Sedimentation in Estuaries."

result of opposing upstream and downstream flows. This region of very small longitudinal flow is the nodal point of bed shear.

Because sediment transport is most significant in the bottom layers of water, sediments in the saline portion of an estuary tend to travel upstream, whereas sediments suspended in the river load tend to be carried downstream. At the nodal point, some of the suspended sediments from both the fresh and saline flows are lifted up from the bottom zone and carried out toward the ocean; the remainder are deposited at the node in shoals. As can be expected, the intensity of this shoaling depends on the extent of the saline wedge effect -- that is, on the extent of estuary stratification.

Highly stratified estuaries, such as the Southwest Pass of the Mississippi River, are characterized by low tidal ranges and a large influx of freshwater. Here, the shear drag of seaward flowing freshwater on the relatively gently sloping halocline pulls intruding saltwater toward the upper layer of the wedge and seaward, drawing more saltwater landward along the bottom of the wedge. The weir effect of the nodal point is therefore enhanced, and shoaling tends to be more pronounced. The special nature of highly stratified estuaries, however, subjects this sediment transport pattern to significant periodic variations. For example, the landward flow of suspended sediments is weakest at low, falling tides, and seaward flow dominates at all depths of the water column during river flood conditions.<sup>23</sup>

In well-mixed, vertically homogenous estuaries, on the other hand, the saltwater/freshwater interface is not so well defined. Instead of vertical differentiation (a salt wedge), the transition between saline and freshwater in this type of estuary is more accurately described by a salinity gradient upward in the direction of river flow. Hence, there is not localized saltwater boundary, and the weir effect characteristic of stratified estuaries is drastically reduced. Shoaling in such cases will be dispersed, and such factors as local topographical peculiarities and the Coriolis force may play a more dominant if less predictable role in determining sediment distribution.

Of course, sediment transport patterns in any given estuary may vary according to the locally prevailing conditions of topography, major ocean currents, and sediment

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<sup>23</sup>Meade, "Transport and Deposition in Sediments in Estuaries."

characteristics. The Coriolis force also has a significant effect on the movement of suspended sediments, depending on the shape and width of the estuary. Despite these effects which may vary from location to location, the dynamics of saline intrusion play the largest role in determining transport patterns in many estuaries. This role can be summarized as follows.

1. Sediments settling on the bottom of an estuary tend to be transported upstream.
2. Sediments tend to accumulate near the end of the saltwater intrusion, forming shoals at the nodal point of the bed shear.
3. The intensity of this shoaling is greatest for stratified estuaries, least pronounced in well-mixed estuaries.

### C.3 Other Processes Affecting Marine Hydrocarbons

Oils and oil fractions will undergo a variety of chemical, physical, and biological alteration processes after their introduction into the marine environment, and these can significantly affect the toxic properties of these oils. The analysis of these effects is greatly complicated by the fact that previous studies have dealt almost exclusively with the crude oil slicks produced as a result of tanker accidents, a situation which is of little relevance to the dispersion or degradation of oilfield brines. Nevertheless, some generally applicable conclusions do emerge from the recent literature.

After their introduction into seawater, crude oil fractions will begin to disperse, in a manner and at a rate which will depend upon the physical properties of the oil (viscosity, density, etc.) and on the magnitude of local dispersion forces such as current or wind. As the oil disperses, some of its more polar components will begin to dissolve, and the lighter and more volatile hydrocarbons will volatilize. Laboratory studies have suggested a strong molecular weight dependence of the rate at which oil components volatilize from seawater.<sup>24</sup> The volatilization process

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<sup>24</sup>R.E. Kredier, "Identification of Oil Leads and Spills," in Proceedings of the Joint Conference on Prevention and Control of Oil Spills (Washington, D.C.: American Petroleum Institute, 1971), pp. 119-124.



results in the loss to the atmosphere of the hydrocarbons. According to a recent National Academy of Science (NAS) report:

These evaporated hydrocarbons enter the atmospheric pool of hydrocarbons, and very little is likely to return to the oceans as hydrocarbons. Chemical reactions in the atmosphere, such as phototcatalytic oxidations, convert an unknown amount of these hydrocarbons into less volatile nonhydrocarbon compounds that may re-enter the oceans. The fate<sup>25</sup> and effect of these types of compounds are unknown.

The sum of these two processes of solubilization and volatilization is known as weathering, and the end result is a weathered oil which is denser, more viscous, and enriched in its content of high molecular weight hydrocarbons relative to the original unweathered oil. The quantitative literature on the weathering rates of oil under different circumstances has dealt mostly with oil spill weathering, and so has little relevance to the dilute, emulsified, highly solubilized hydrocarbons which are contained in oilfield brines. Another consideration to keep in mind is the fact that these brines are generally higher in aromatic hydrocarbon content than their parent crude oils, due to the differential solubility of the various oil components in the brine water (benzene, for example, has a saturation solubility of about 1,800 ppm in distilled water, as compared with about 10 ppm for the normal alkane of equivalent molecular weight (hexane)). Since much of the toxic activity of crude oil is concentrated in its aromatic fraction, the toxicity of the brines is probably higher than would be predicted from an equivalent dilution of ordinary crude oil. Although volatilization may remove many of the more toxic components from the brine, it will also enrich the brine in a number of others, including the relatively heavy polynuclear aromatics.

One of the most important processes involved in scavenging oil-derived hydrocarbons from the water column is adsorption onto suspended particulates which are subsequently deposited in bottom sediments as was discussed in the previous section. Hydrocarbons can become entrapped in marine sediments through a number of processes. These include ingestion by zooplankton and the subsequent sedimentation of oil containing

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<sup>25</sup> National Academy of Sciences, Petroleum in the Marine Environment, pp. 45-46.

fecal material, adsorption onto suspended mineral particles which subsequently settle out, and direct adsorption onto bottom silt and clay. The chief effect of the adsorption process is probably to decrease the effect of the hydrocarbons on organisms other than benthic organisms and filter feeders. The effect on these two groups will probably be greatly increased because of the tremendous concentration factor which is associated with adsorption onto particulates. In fact, it has been noted that areas which have significant concentrations of oil in their sediments usually have "an impoverished benthic fauna,"<sup>26</sup> although the causal relationship has not been clearly demonstrated.

Although adsorption onto particles seems to facilitate biological and chemical oxidative degradation of hydrocarbons, particle-adsorbed hydrocarbons which settle into sediment seem remarkably stable, probably because of the anaerobic conditions prevailing within the sediment. Sediment-entrapped hydrocarbons also seem to be unusually resistant to photochemical degradation, except at the very top of the sediment layer. According to Blumer and Sass, "The preservation of hydrocarbons in marine sediments for geologically long time periods is one of the accepted key facts in current thought on petroleum formation."<sup>27</sup> Experimental studies of oil-contaminated sand columns have suggested that although 10 percent of the trapped oil oxidized over a period of several months, the remainder deteriorated at a much slower rate.<sup>28</sup> Solubilization of hydrocarbons from sediment, and the ingestion of sediment particles by benthic organisms, provide processes whereby the transfer of hydrocarbons from water to sediment may be reversed.

In addition to these essentially physical alterations, crude oil in seawater is subject to a number of chemical degradation processes. Chiefly, these are oxidative processes (auto-oxidative and photo-oxidative) which change the

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<sup>26</sup>U.S. Environmental Protection Agency, Water Quality Criteria, 1972.

<sup>27</sup>Blumer and Sass, "Oil Pollution: Persistence and Degradation of Spilled Oil," Science 176 (1970): 1120-1122.

<sup>28</sup>Evans and Rice, "Effects of Oil on Marine Ecosystems: A Review for Administrators and Policy Makers," Fishery Bulletin 72 (1974): 625.

relatively reduced aromatic and aliphatic hydrocarbons species found in crude oil into more oxidized acids, aldehydes, and alcohols. Light acts as an important inducer of oxidation through the formation of free radical intermediates and hydroperoxides. (Photo-chemically induced free radical intermediates can also polymerize. The end product of the polymerization reaction is dense, viscous, relatively polar "tar.") Oxidation will be accelerated by physical factors which tend to disperse or emulsify the oil, and by metallic catalysts, and many sulfur compounds are strong inhibitors of oxidation. A priori chemical arguments support some general conclusions regarding the relative rates at which different oil-derived hydrocarbons will oxidize in the marine environment.<sup>29</sup>

Another important class of processes which alter oil in seawater is biodegradation; indeed, it is probably the chief pathway by which polluting oils are removed from the marine environment. According to Atlas and Bartha:

Microbial degradation of crude oil appears to be the natural process by which the bulk of the polluting oil is eliminated and may be the reason that the oceans are not entirely covered with oil today. Under favorable conditions microorganisms are quite effective in degrading low levels of petroleum. In areas that are well aerated and where the microbial population is adapted to oil influx, the rate of oil oxidation at 20° C to 30° C may range from 0.02 g to 2.0 g of oil oxidized/m<sup>2</sup>/day.... Microorganisms will degrade a substantial portion (40 percent to 80 percent) of crude oil, but the degradation is never complete; n-alkanes are utilized preferentially and highly branched alkanes, cycloalkanes, and aromatics are utilized with difficulty; and mixed enrichments are more effective in petroleum degradation than mixed cultures.<sup>30</sup>

Although much laboratory and field data are now available on the microbiological degradation of crude oils and oil components, it remains impossible to make any reliable quantitative estimates of the rate at which this process will remove oil from oilfield brines. According to the NAS:

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<sup>29</sup>Atlas and Bartha, "Fate and Effects of Polluting Petroleum in the Marine Environment," Residue Review (1973c): 49-85.

<sup>30</sup>Atlas and Bartha, "Fate and Effects of Polluting Petroleum in the Marine Environment."

Neither a single rate nor a mathematical model for the rate of petroleum biodegradation in the marine environment can be given at present. On the basis of available information, the most that can be stated is that some microorganisms capable of oxidizing chemicals present in petroleum (under the right conditions) have been found in virtually all parts of the marine environment examined.<sup>31</sup>

Nevertheless, a number of factors can be isolated as being important in controlling the rate of oil degradation. The composition of the available substrate is critical, since microorganisms are limited in the range of hydrocarbons they can oxidize. Pure cultures rarely degrade more than one hydrocarbon fraction. Mixed cultures isolated from the marine environment possess wider degradative capacities, although preference for intermediate length n-paraffins is usually observed. It is uncertain whether this pattern is a result of the isolation procedure used; certain wild, mixed cultures developed in media containing cyclic hydrocarbons, notably naphthalenes and polynuclear aromatics, have been found to degrade such compounds more rapidly than n-paraffins.<sup>32</sup>

Hydrocarbon-oxidizing microorganisms are widely distributed in soil and water. Relatively few hydrocarbonoclastic microbes are found in soils or areas of the open ocean remote from oilfields or oil pollution; they are most numerous and diverse in places that have been subjected to chronic oil pollution either from natural seeps or by the activities of man. Hydrocarbon-degrading microorganisms are only rarely found in petroleum as it emerges from oil wells or in unpolluted ground waters. One preliminary indication based on laboratory experimentation is that the abundance and physiological types of hydrocarbon-oxidizing microbes in soil and aquatic environments seem to be influenced by the quantities and kinds of hydrocarbons which have been present.<sup>33</sup>

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<sup>31</sup>National Academy of Sciences, Petroleum in the Marine Environment, pp. 45-46.

<sup>32</sup>C.E. Zobell, "Microbial Degradation of Oil: Present Status, Problems, and Perspectives," in The Microbial Degradation of Oil Pollutants, ed. by D.G. Ahearn and S.P. Meyers (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1973), p. 5.

<sup>33</sup>Zobell, "Microbial Degradation of Oil," p. 3.

Environmental conditions can significantly affect microbial hydrocarbon degradation. Temperature and salinity changes, wave action, and sunlight can alter the physical state (emulsification) and ultimately the chemical nature (oxidation) of the hydrocarbons. Oil dispersed in aqueous systems is more susceptible to enzymatic attack; dispersion is influenced by viscosity, density, chemical composition, wind speed, current velocity, and temperature. Some microbial species produce surfactants which tend to emulsify oil in water.<sup>34</sup>

The growth and metabolism of the microorganisms themselves are intimately related to environmental parameters. Free or dissolved oxygen is essential, as is the presence of accessory growth factors such as nitrogen and phosphorous. Temperature can exert a profound influence upon growth and metabolic activity of microbial species. In general, temperature increases accelerate growth rates, while low temperatures reduce the rates of biological processes. The microbial degradation of oil has been observed at temperatures ranging from the freezing point of seawater (around -2° C) to about 70° C. Most species are most active in the mesothermic range, 20° C to 35° C.

Deleterious environmental influences upon hydrocarbonoclastic microbes are microbial predators and toxic substances. Cytophagic protozoans and other invertebrates can ingest large numbers of microbes. Toxic components of oil include the low molecular weight hydrocarbons and the metal ions frequently associated with petroleum. It is thought that low molecular weight hydrocarbons disrupt functional phospholipids of the cell envelope,<sup>35</sup> and that heavy metals decrease the efficiency of the microbial transport system.<sup>36</sup>

It is apparent from the above discussion that the number of factors influencing microbial hydrocarbon degradation is

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<sup>34</sup>Zobell, "Microbial Degradation of Oil," p. 6.

<sup>35</sup>D.K. Button, "Petroleum -- Biological Effects in the Marine Environment," in Impingement of Man on the Ocean, ed. by Donald H. Wood (New York: Wiley-Interscience, 1971), Chapter 14.

<sup>36</sup>P.J. Kinney et al., Quantitative Assessment of Oil Pollution Problems in Alaska's Cook Inlet (College, Alaska: University of Alaska, 1970), p. 9.

vast. Consideration of the various parameters must be made from one location to another as well as within the context of a given site. The limited number of reliable and comprehensive fluid measurements poses a barrier to large-scale generalizations; what information that exists for Barataria Bay and Cook Inlet is discussed briefly below.

### Barataria Bay

According to Meyers and his associates:

The vast productivity of wetland regions along the Louisiana coast, and their proximity to oil-producing sites, necessitates a more comprehensive understanding of the significance of alterations in the microbial community concurrent with oil intrusion and massive depositions of petroleum effluents.<sup>37</sup>

Unfortunately, few studies have been conducted on the effects of oil pollutants on inshore plant-dominated communities and their complex microbial ecosystems. Meyers and his associates have noted exposure of marsh areas of Barataria Bay to controlled additions of oil significantly alters the composition of the yeast community. Shifts toward an asexual hydrocarbonoclastic yeast flora have been documented. The impact of oil deposition upon major microbial components of the marshland ecosystem has only recently received attention; studies on the marine bacteria Benecka have indicated an ability to readily metabolize a wide range of organic compounds, including aromatic and aliphatic hydrocarbons.<sup>38</sup>

### Cook Inlet

Average concentrations of  $10^3$  hydrocarbon-utilizing microorganisms per liter have been reported for Cook Inlet. According to Kinney and associates, "Biodegradation is more important than physical flushing in removing hydrocarbon

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<sup>37</sup>S.P. Meyers et al., "The Impacts of Oil on Marshland Microbial Ecosystems," in The Microbial Degradation of Oil Pollutants (Baton Rouge: Louisiana State University, Center for Wetland Resources, 1973), p. 221.

<sup>38</sup>Meyers et al., "The Impact of Oil on Marshland Microbial Ecosystems," p. 225.

pollutants from Cook Inlet...the biodegradative capacity of Cook Inlet is large."<sup>39</sup>

The low temperature and high silt content of Alaskan waters have been examined as potential inhibitors of oil biodegradation. It appears that silt does not interfere significantly with the emulsification properties of hydrocarbonoclastic microbes. The extremely cold water lowers growth rates, so that nutrient concentrations are probably non-limiting. Growth rates of isolated microbes grown on kerosene as a sole carbon source were reduced by a factor of seven at 50° C, the prevailing summer temperature of Cook Inlet.<sup>40</sup> Psychrophilic (i.e., low-temperature adapted) oil-oxidizing bacteria from Cook Inlet have been reported active at 5° C; bacteria from northern Alaska have been shown to oxidize mineral oil at -1° C.<sup>41</sup> In addition to depression of metabolism, low temperatures interface with the dispersal of oil by entrapment in ice.

In both Barataria Bay and Cook Inlet, it is unknown whether the composition of produced petroleum waters has any special impact on microbial biodegradation. Heavy metal ion concentrations may be inhibitory. The effect of putative aromatic enrichment of produced waters cannot be properly assessed until water composition and aromatic-oxidizing potentials of hydrocarbonoclastic microbes are determined. Further characterization of these parameters is critical for meaningful impact assessment.

#### C.4 Other Processes Acting on Trace Metals in the Marine Environment

Three processes, in addition to precipitation, adsorption and sedimentation (discussed in Section C.2) are important in altering and modifying the toxicity of heavy metals in the marine environment. Their effect on toxicity is discussed more completely in Chapter Six, so they will only be briefly mentioned here. The first is chelation and

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<sup>39</sup>Kinney et al., Quantitative Assessment of Oil Pollution Problems in Alaska's Cook Inlet, p. 1, 9.

<sup>40</sup>Kinney et al., Quantitative Assessment of Oil Pollution Problems in Alaska's Cook Inlet, p. 1, 9.

<sup>41</sup>Zobell, "Microbial Degradation of Oil," p. 153.

other forms of chemical complexation with organic materials in water. The second is biological transformation, including, most notably, the microbiological methylation of mercury; and the third is oxidation. This last process is especially significant since the oxidized forms of many metals (e.g. Cr (VI)) can be much more toxic than the equivalent reduced species (Cr(III)). As with hydrocarbons, not enough quantitative field or laboratory data is available to enable reliable predictions of the rates at which these processes will occur in the marine environment, or the extent to which they will affect toxicity.



## APPENDIX D

### PRODUCTION PLATFORM AND DISCHARGE DATA

The Bay de Chene oil field located in Hackberry Bay, Louisiana, adjacent to Barataria Bay, is operated by Texaco. The Salt Water Disposal Well Report for calendar year 1975 filed with the Louisiana Department of Conservation, Geological Oil and Gas Division, Baton Rouge, Louisiana, gives a figure of 22,374,127 barrels produced salt water (i.e., an average rate of 61,000 barrels per day).

Table D-1 lists the sources of produced water in Cook Inlet, Alaska. The two facilities chosen for analysis in this study were the Granite Point Production Facility operated by Atlantic Richfield Company, and the Trading Bay Production Facility, operated by Marathon Company.

Block 16 of the Grand Isle Oil Field Area is operated by Exxon Co. Produced water data filed with the Houma office of the Louisiana Department of Conservation gives a 1975 figure of 3,231,300 barrels produced water (i.e., an average discharge rate of 9,000 barrels per day).

Block 108 of the Ship Shoal Oil Field Area is operated by Chevron Company. Produced water disposal data filed with the U.S. Geological Survey in Metairie, Louisiana lists two platforms disposing produced water, S-93 with an average rate of 9,000 barrels per day, and S-94 with an average rate of 12,000 barrels per day.

TABLE D-1

SALT WATER DISPOSAL - COOK INLET, ALASKA

OFFSHORE PLATFORMS <sup>a</sup>	LOCATION	DISCHARGE (bbl/d)	OPERATOR
Bruce Granite Point	60°59'56" N 151°17'52" W	493	Amoco
Anna Granite Point	60°58'37" N 151°18'45" W	41	Amoco
Dillon Middle East Ground Shoal	60°44'08" N 151°30'45" W	5,231	Amoco
ONSHORE FACILITIES	LOCATION	DISCHARGE (bbl/d)	OPERATOR
Granite Point Production Facility <sup>b</sup>	61°01'14" N 151°25'14" W	5,000	Atlantic Richfield
Trading Bay Production Facility <sup>c</sup>	60°49'05" N 151°46'59" W	12,500	Marathon
Kenai Gas Field <sup>d</sup>	60°23'53" N 151°16'36" W	262	Union
North of East Foreland Pro- duction Facility <sup>e</sup>	60°44'13" N 151°21'05" W	3,809	Shell

NOTE: Footnotes are on the following page.

FOOTNOTES TO TABLE D-1

<sup>a</sup>Data were obtained from Danforth G. Bodien, Chief, Water Permits Section, U.S. Environmental Protection Agency, Seattle, Washington. Data are for 1975.

<sup>b</sup>Atlantic Richfield Company, U.S. Army Corps of Engineers, "Application for Permit to Discharge or Work in Navigable Waters and Their Tributaries," AK-NPD-NPS-2-00019, 1971.

<sup>c</sup>Marathon Oil Company, U.S. Army Corps of Engineers, "Application for Permit to Discharge or Work in Navigable Waters and Their Tributaries," AK-NPA-NPA-2-000148, 1971.

<sup>d</sup>Union Oil Company of California, "National Pollutant Discharge Elimination System Application for Permit to Discharge," AD-002455-4, 1974.

<sup>e</sup>Shell Oil Company, U.S. Army Corps of Engineers, "Application for Permit to Discharge or Work in Navigable Waters and Their Tributaries," AK-NPD-NPA-2-000047, 1971.

## APPENDIX E

### CALCULATION OF DISPERSION MODEL INPUT PARAMETER VALUES

#### E.1 Estimate of Tidal and Freshwater Current Velocities for Hackberry Bay, Louisiana

In the absence of actual current measurements it is necessary to estimate current magnitudes. Relatively simple hydrological calculations will suffice for the purpose of supplying input parameter values for the dispersion model. To estimate the tidal velocity, the estuary is assumed to be represented by a channel as in Figure E-1. The end at  $y=0$  is assumed to be closed, the width at a distance  $y=y'$  along the channel is given by  $W(y')$ , and the area enclosed by the channel boundaries between  $y=0$  and  $y=y'$  is given by  $K(y')$ . Thus

$$K(y') = \int_0^{y'} W(y) dy.$$

The depth  $H$  is a function of both location,  $y$ , and of time,  $t$ , since it varies with the tidal influx and ebb. It is further assumed that (1) there is no vertical variation in the velocity of water in the  $y$ -direction,  $V(y,t)$ , and that (2) the tidal level rises and falls simultaneously at the same rate for all points in the estuary channel. A simple consideration of the relation of the volume of water in the estuary in the portion which lies between  $y=0$  and  $y=y'$  to the influx or ebb of water through a vertical cross section at  $y=y'$  then gives the equation:

$$K(y') \frac{\partial H(y',t)}{\partial t} = -V(y',t)W(y')H(y')$$

Solving for  $V$  gives the equation:

$$V(y',t) = - \frac{K(y')}{W(y')} \frac{\frac{\partial H(y',t)}{\partial t}}{H(y',t)}$$

The depth of water,  $H(y', t)$  can be expressed as a sum of two components: (1) a mean depth,  $H_0(y')$ , which is time independent, and (2) a sinusoidally varying component,  $(\Delta/2)\sin[(2\pi/T)t]$ , where  $\Delta$  is the tidal range (i.e., the difference between low tide and high tide) and  $T$  is the tidal period. Thus

$$H(y', t) = H_0(y') + \frac{\Delta}{2} \sin\left(\frac{2\pi}{T} t\right),$$

$$\frac{\partial H(y', t)}{\partial t} = \frac{\pi}{T} \Delta \cos\left(\frac{2\pi}{T} t\right),$$

and,

$$\frac{\frac{\partial H(y', t)}{\partial t}}{H(y', t)} = \frac{\frac{\pi}{T} \Delta \cos\left(\frac{2\pi}{T} t\right)}{H_0(y') + \frac{\Delta}{2} \sin\left(\frac{2\pi}{T} t\right)}$$

The maximum value of this ratio is

$$\frac{\pi}{T} \frac{\Delta}{H_0(y')}$$

so that the maximum current speed is given by:

$$V_{\max}(y') = \frac{K(y')}{W(y')} \frac{\pi}{T} \frac{\Delta}{H_0(y')}$$

For Hackberry Bay, considering a cross section at the lower end of the bay:

$$K = 4,386 \text{ acres} = 19,105 \times 10^4 \text{ ft}^2$$

$$W \approx 2 \text{ miles}$$

$$T = 24 \text{ hours (diurnal tides)}$$

so that,

$$\frac{K(y')}{W(y')} \frac{\pi}{T} = 0.658 \text{ ft/sec}$$

Thus,

$$V_{\max} = 0.658 \frac{\Delta}{H_o} \text{ ft/sec}$$

For  $\Delta = 1 \text{ ft}$ ,  $H_o = 2.4 + 0.5 = 2.9 \text{ ft}$

and,

$$V_{\max} = 0.658 \times \frac{1}{2.9} = 0.22 \text{ ft/sec}$$

For  $\Delta = 0.25 \text{ ft}$ ,  $H_o = 2.4 + 0.125 = 2.5 \text{ ft}$

and,

$$V_{\max} = 0.065 \text{ ft/sec}$$

Given the value of  $V_{\max}$  the tidal velocity is then given by  $V_{\max} \sin [(2\pi/T)t]$ .

To estimate the freshwater current speed, reference is made to a tabulation<sup>1</sup> of the flood and ebb flow volumes through the four major passes to Barataria and Caminada Bays. This table is reproduced in Appendix A as Table A-9. The total ebb excess through the four passes is  $449 \times 10^6 \text{ ft}^3$ . If this is taken to be a measure of the freshwater influx to the Barataria and Caminada Bay basin each day, then the freshwater influx in  $\text{ft}^3$  per second is  $5,197 \text{ ft}^3/\text{sec}$ . It may be assumed that this freshwater flow must come from the north through Hackberry Bay and adjacent bay areas. Assume further that the freshwater flow is uniformly distributed

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<sup>1</sup>B. Barrett, Cooperative Gulf of Mexico Estuarine Inventory and Study, Louisiana, Phase II: Hydrology (New Orleans: Louisiana Wildlife and Fisheries Commission, 1971), p. 57.

through a vertical cross section through Hackberry Bay and the adjacent bay areas. The width of this cross section is approximately 11.8 miles (3 inches on a 1:250,000 scale map). Hackberry Bay itself has a width of about 2 miles. Hence the freshwater flow through Hackberry Bay can be estimated to be:

$$\frac{2}{11.8} \times 5,197 \text{ ft}^3/\text{sec}.$$

Let  $V_0$  be the freshwater current speed in ft/sec. Then the product of  $V_0$  and the area of a vertical cross section through Hackberry Bay must be equal to freshwater flow through Hackberry Bay. Thus, taking the average depth of Hackberry Bay equal to 2.4 feet,

$$V_0 \times (2 \times 5,280 \times 2.4) = \frac{2}{11.8} \times 5,197$$

or,

$$V_0 = 0.035 \text{ ft/sec}$$

## E.2 Calculation of Tidally Averaged Diffusion Coefficient for Cook Inlet

The procedure used for incorporating the effects of the Cook Inlet tidal currents into the alongshore diffusion coefficient,  $E_y$ , is as follows. First the steady downstream freshwater flow,  $V_0$ , was estimated starting with the stream flow data for mid and upper Cook Inlet given in Appendix A, Table A-3. Since stream flow data is available only for some of the sources feeding into Cook Inlet, an estimate of the total freshwater influx was obtained by dividing the sum of the known mean daily discharges (62,234 ft<sup>3</sup>/sec) by the sum of the corresponding drainage areas (24,847 square miles) to give an average ratio of 2.5 ft<sup>3</sup>/sec freshwater discharge per square mile of drainage area. Multiplied by the total drainage area of 46,927 square miles, this gives an estimated mean daily freshwater runoff rate of 117,500 ft<sup>3</sup>/sec. The vertical cross section area of mid Cook Inlet in the vicinity of the oil fields was estimated by computing the area enclosed by the depth profile curve given in Appendix A, Figure A-3 to be 8,120,000 square feet. Assuming that the freshwater flow is equally distributed over this vertical cross section (a reasonable assumption in view of

the expected vigorous mixing resulting from the rapid tidal currents), the ratio of the estimated freshwater discharge rate to the cross section area gives an estimated downstream freshwater flow speed of 0.014 ft/sec.

The analytical solution for the steady-state distribution of a conservative substance discharged into a uniform estuary at  $y=0$  is:<sup>2</sup>

$$C(y) = C(0)e^{-\frac{V_o}{E_y} y}$$

where  $y$  is the distance upstream from the discharge point and  $E_y$  is the diffusion coefficient. The diffusion coefficient can be estimated if it is assumed that at a distance of one tidal excursion,  $y_T$ , (the distance that a particle can be moved upstream by the tidal currents during half a tidal cycle) the concentration will have decreased approximately to  $e^{-1}$  ( $=0.37$ ) times its value at the discharge location. Then,

$$\frac{V_o}{E_y} y_T = 1$$

and,

$$E_y = V_o y_T$$

Since the mean upstream tidal velocity is approximately 4 ft/sec in mid Cook Inlet,

$$y_T \approx 4 \times (6 \text{ hrs} \times 3,600 \frac{\text{sec}}{\text{hr}}) = 86,400 \text{ ft.}$$

Using this value for  $y_T$  and the value of 0.014 ft/sec for  $V_o$  gives an estimated value for  $E_y$  of

$$E_y = 1,250 \text{ ft}^2/\text{sec.}$$

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<sup>2</sup>Tracor, Inc., "Estuarine Modeling: An Assessment," February 1971, NTIS No. PB-206807.



This value is not far removed from the value of  $4700 \text{ ft}^2/\text{sec}$  obtained for  $E_y$  in a study<sup>3</sup> of discharges into an arm of Cook Inlet, Knik Arm.

### E.3 Computation of Diffusion Coefficients for Hackberry Bay, Louisiana

The computation of the values of the diffusion coefficients,  $E_x$  and  $E_y$ , for Hackberry Bay, Louisiana, is based on the theory of diffusion in turbulent shear flows.

The general form for the diffusion coefficient in a shear flow is:

$$E = \alpha u_* H$$

where,

$E$  = diffusion coefficient

$\alpha$  = dimensionless coefficient

$u_*$  = friction velocity

$H$  = water depth

The friction velocity,  $u_*$  is further related to the bottom shear stress by the relationship:

$$\tau_o = \rho u_*^2$$

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<sup>3</sup>R. Sage Murphy, et al., Effect of Waste Discharges into a Salt Laden Estuary. A Case Study of Cook Inlet, Alaska, Publication IWR 26 of the Institute of Water Resources, University of Alaska, Fairbanks, Alaska, November 1972.

where,

$\tau_o$  = bottom shear stress

$\rho$  = water density

The relationship between  $u_*$  (or  $\tau_o$ ) and the mean current velocity,  $U$ , is always an empirical one. The most general correlation is the following:

$$\tau_o = \frac{f}{8} \rho U^2$$

where  $f$  is a dimensionless friction factor that is a function of the roughness of the bottom. With this formulation one obtains:

$$\frac{u_*}{U} = \sqrt{\frac{f}{8}}$$

Values of  $f$  for natural channels range from 0.01 to 0.1 resulting in a range of  $u_*/U$  values of from 0.035 to 0.110.

Another often used correlation is the Mannings formula which is equivalent to the following equality:

$$\frac{u_*}{U} = 3.8 n H^{-1/6}$$

where  $n$  is a coefficient that varies from 0.020 to 0.040 for natural channels. Thus for channels from 1 to 10 feet deep, the resulting  $u_*/U$  ratio varies from 0.050 to 0.140, a slightly higher range than indicated by the values of the friction factor.

For the purposes of further discussion, the value of  $u_*/U$  will be based on a value of  $n = 0.035$  which is commonly used for natural channels. Assuming a water depth of 3 feet yields:

$$\frac{u_*}{U} \approx 0.1$$

The value of the dimensionless coefficient,  $\alpha$ , will depend on the type of mixing being parameterized by the coefficient,  $E$ . The following table summarizes results given in a review paper by Fischer:<sup>4</sup>

<u>Type of Mixing</u>	<u>Range of <math>\alpha</math></u>
Transverse diffusion	
1-D Flows (Channels)	0.1 - 0.7
2-D Flows (Bays)	1 - 2.4
Longitudinal Diffusion	
1-D Flows (Channels) }	5 - 400
2-D Flows (Bays) }	

The above results can now be applied to Hackberry Bay. The water depth is

$$H = 3 \text{ feet}$$

and mean velocity approximately,

$$U = 0.25 \text{ ft/sec}$$

Using the values of  $\alpha$  in the above table, and a value of  $u_*/U = 0.1$  the following values of  $E$  are obtained:

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<sup>4</sup>H. Fischer, "Longitudinal Dispersion and Turbulent Mixing in Open-Channel Flow," Annual Review of Fluid Mechanics Volume V, ed. by Van Dyke (Palo Alto, Calif: Annual Reviews, Inc., 1972).

<u>Type of Mixing</u>	<u>Range of E</u>	<u>Base Values Used In Analysis</u>
Transverse Diffusion		
1-D Flow	0.0075-0.053 ft <sup>2</sup> /sec	E <sub>x</sub> = 0.1
2-D Flow	0.075-0.18 ft <sup>2</sup> /sec	
Longitudinal Diffusion	0.375-30 ft <sup>2</sup> /sec	E <sub>y</sub> = 1.0

#### E.4 Calculation of Initial Dilution for Gulf of Mexico Computations

Produced water is generally more saline and hence more dense than sea water. Accordingly, the discharged effluent tends to sink through the receiving waters and to form a layer at the bottom of the water column. In the course of sinking, sea water becomes mixed with the discharged effluent. The resulting dilution can be estimated using methods developed for thermal plume prediction,<sup>5</sup> since the dilution of heated water as it rises through cooler receiving waters is completely analogous to the sinking plume situation encountered in brine discharge.

To estimate the initial dilution, it is first necessary to calculate the Froude number, F, defined as:

$$F = \frac{U_o}{\sqrt{g \frac{\Delta \rho}{\rho} d}}$$

where,

U<sub>o</sub> = effluent discharge velocity

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<sup>5</sup>M.S. Shirazi and L.R. Davis, Workbook of Thermal Plume Prediction, Volume 1: Submerged Discharge, EPA-R2-72-005a (Corvallis, Oregon: National Environmental Research Center, U.S. Environmental Protection Agency, August 1972).

$g$  = gravitational acceleration

$d$  = diameter of discharge pipe

$\rho$  = density of receiving water

$\Delta\rho$  = difference in density of effluent and receiving water

Assuming a discharge pipe diameter of one foot and a rate of effluent discharge of  $1 \text{ ft}^3/\text{sec}$ ,  $U_0 = 1.27 \text{ ft/sec}$ . The density of water as a function of salinity has been tabulated by the U.S. Navy Hydraulics Office, and salinity can be related to the chloride ion concentration by the relation:<sup>6</sup>

$$S(\text{ppt}) = 1.80655 \text{ Cl}^- (\text{ppt})$$

Using the value of 61 ppt  $\text{Cl}^-$  in Louisiana produced water and the value of 19 ppt  $\text{Cl}^-$  in sea water gives

$$S_{\text{sea water}} = 34.3 \text{ ppt}$$

$$S_{\text{produced water}} = 110.1 \text{ ppt}$$

The above-mentioned density-salinity tabulation then gives (using linear extrapolation to obtain the density corresponding to the produced water salinity):

$$P_{\text{sea water}} = 1.0228$$

$$P_{\text{produced water}} = 1.0797$$

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<sup>6</sup>A. Duxbury, The Earth and Its Oceans (Reading, Mass.: Addison-Wesley Publishing Co.), p. 116.

Hence,

$$F = \frac{1.27}{\sqrt{(32.15) \frac{1.0797 - 1.0228}{1.0228}} 1} = 0.95$$

For a conservative estimate of dilution, assume that the effluent is discharged vertically downward. Then the chart on p. 81 of the EPA Workbook (reproduced as Figure E-2) can be used together with the value of the Froude number,  $F = 1$ , and data on the total water depth to estimate the initial dilution. The normalized vertical distance  $Z/D$  plotted on the horizontal axis in Figure E-2 is, in our notation, the water depth  $H$  divided by the diameter of the discharge pipe,  $d$  (more accurately,  $Z/D$  is equivalent to  $(H - H_2)/d$  where  $H_2$  is the thickness of the layer formed by the effluent at the bottom of the water column;  $H_2 \approx H/6$ ). The vertical axis of Figure E-2 is, in our notation,  $1/D$ , where  $D$  is the initial dilution. Thus, for example, using a value of  $H = 33$  feet, and a value of  $d = 1$  foot, the normalized vertical distance is  $[33 - (33/6)]/1 = 27.5$ . Reading upwards from 27.5 on the horizontal axis of Figure E-2 until the  $F = 1$  curve is reached, and then reading across to the vertical axis gives a value of  $1/D = 0.04$  or  $D = 25$ .

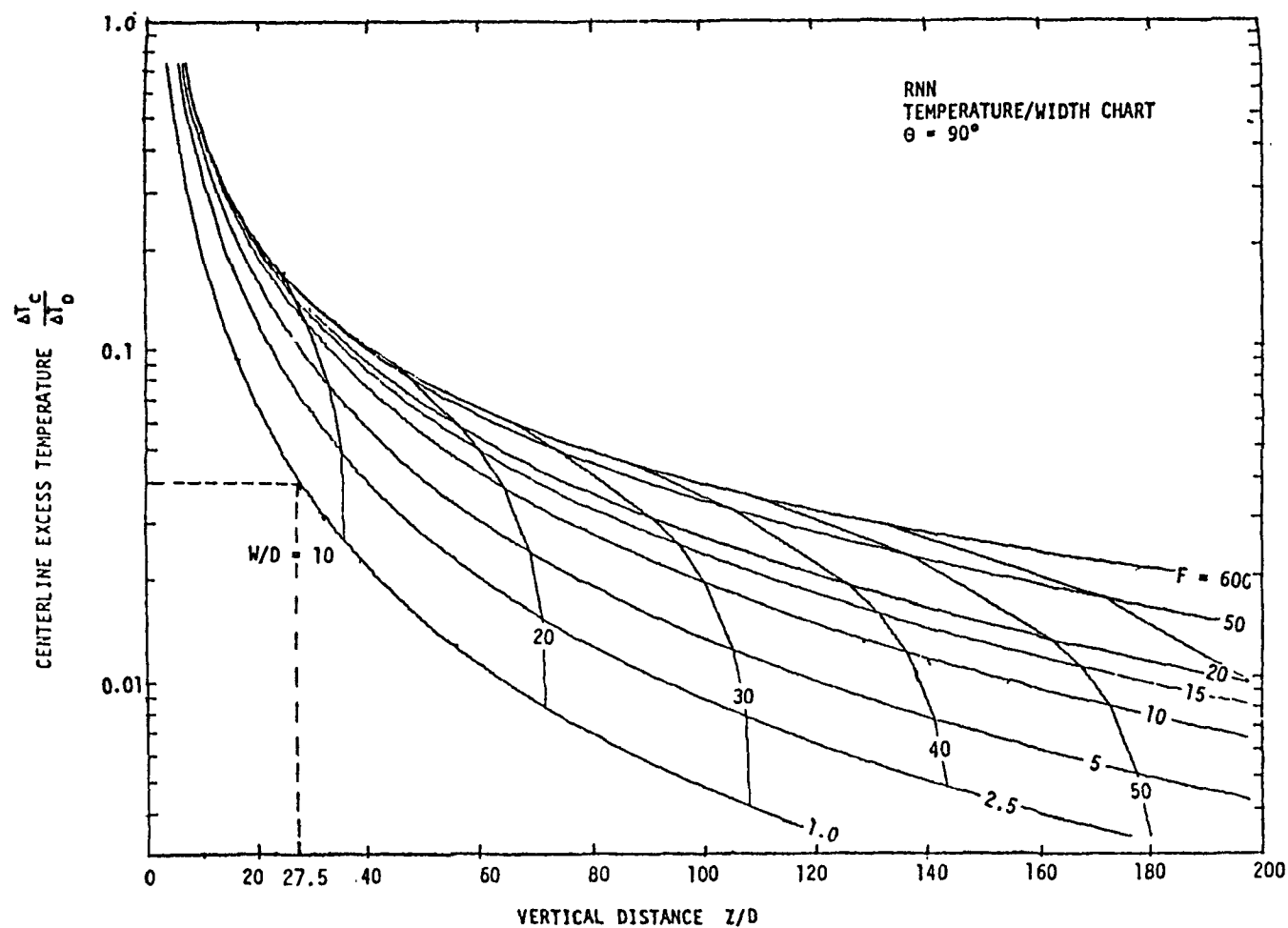


Figure E-2. Temperature-width chart for single jets discharging into a non-stratified stagnant large body of water: RNN,  $\theta=90^\circ$ . (U.S. Environmental Protection Agency, Workbook of Thermal Plume Prediction, Volume 1: Submerged Discharge, August 1972, p. 81.)

## APPENDIX F

### HYDROCARBON BIOACCUMULATION

Many marine organisms have the capacity to take up and accumulate hydrocarbons from their environments. This has been demonstrated in mussels, clams, oysters, crabs, shrimp, sponge and fish, among others. Both field and laboratory studies have dealt with the accumulation problem. Although the results of these studies are varied and often inconsistent, they do succeed in demonstrating that the ability to accumulate hydrocarbons is widespread among marine organisms. In this section the general nature of hydrocarbon uptake, metabolism, storage and discharge will be discussed, and summaries of the current understanding of accumulation capabilities of various organisms will then be presented.

Uptake of petroleum hydrocarbons from seawater can be accomplished by four means:

1. Ingestion of particles onto which hydrocarbons have been adsorbed. These particles can be either biotic (e.g., plankton) or non-biotic (e.g., sand).
2. Adsorption onto exposed body surfaces.
3. Active uptake of dissolved or dispersed petroleum, as in the gills of bivalves.
4. Intake of water into the gut of organisms that drink or gulp water.

Entry through the gill membranes of dissolved or dispersed oil occurs widely in molluscs, crustaceans, and fish. Many marine animals ingest contaminated food, sediment particles, or water. To date there has been no conclusive demonstration of food web magnification of petroleum hydrocarbons.

Once hydrocarbons have been taken up by an organism, they can be stored and accumulated, metabolized, or discharged. In general, storage takes place in the hepatopancreas of invertebrates, and in the liver of fish. There are many other sites of accumulation, however, as will be discussed below.



Marine fish and some marine invertebrates can metabolize both paraffinic and aromatic hydrocarbons.<sup>1</sup> Some copepods can metabolize paraffins, but not aromatics. Organisms such as phytoplankton, zooplankton, and many marine invertebrates appear to be unable to metabolize any hydrocarbons. Petroleum metabolism occurs in the liver of fish and in the hepatopancreas of invertebrates.

Most marine organisms which have accumulated significant internal concentrations of petroleum hydrocarbons have been found able to release much of the contamination upon transfer to clean, unpolluted water. Blumer<sup>2</sup> reported long term retention of hydrocarbons by shellfish, but his results have not been reproduced in subsequent studies. As will be shown below, tissue contamination, if not lethal, can generally be discharged when the source of pollution is removed.

Clark and Finley<sup>3</sup> studied accumulation by sea urchins and crabs exposed to Navy Special Fuel Oil following the grounding of a Navy vessel on the coast of Washington. Purple sea urchins accumulated 2.4 ppm dry weight of n-paraffins; the crabs (*Hemigrapsus nudus*) contained 1.2 ppm. These animals were exposed to a continuous low level of contamination, since oil leaked continuously from the wrecked ship for a long period of time.

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<sup>1</sup>Richard F. Lee and A.A. Benson, "Fate of Petroleum in the Sea: Biological Aspects," in Background Papers for a Workshop on Inputs, Fates, and Effects of Petroleum in the Marine Environment (Washington, D.C.: National Academy of Sciences, 1973).

<sup>2</sup>M. Blumer, S. Souza, and J. Sass, "Hydrocarbon Pollution of Edible Shellfish by an Oil Spill," Marine Biology 5 (1970): 195-202.

<sup>3</sup>Robert C. Clark, Jr. and John S. Finley, "Long-Term Chemical and Biological Effects of Persistent Oil Spill Following the Grounding of the General M.C. Meigs," in Proceedings of the 1975 Conference on Prevention and Control of Oil Pollution, American Petroleum Institute, U.S. Environmental Protection Agency, 1975.

Hydrocarbon accumulation in shrimp has been studied by a number of investigators, since shrimp are an important commercial product, and are consumed directly by humans. Grass shrimp (Palaemonetes pugio) exposed to 0.07 ppm naphthalenes in an oil-water dispersion accumulated up to 3 ppm wet weight of naphthalenes during a 12-hour exposure period.<sup>4</sup> Upon transfer to clean water the shrimp discharged the hydrocarbons readily. Tissue hydrocarbon levels were normal after 14 to 38 hours of depuration. Brown shrimp exposed to 0.3 ppm No. 2 fuel oil for 20 hours accumulated up to 800 ppm of naphthalenes in the digestive gland. After one hour of depuration the abdominal muscle tissue -- the part consumed by humans -- had returned to the normal background hydrocarbon level. Hydrocarbons were retained in the digestive gland and the gills after 250 hours depuration. This is due to the much greater accumulation in the digestive gland. The gills, a site of hydrocarbon uptake and release, can be expected to retain high concentrations for a longer period of time than other tissues.

Mussels are often used for contamination experiments for a number of reasons. They are widespread and readily available. They are a convenient size -- small enough to sample adequately but large enough to dissect for specific organ analysis. They are a major energy transfer pathway in intertidal ecosystems, utilizing plankton and debris as food sources. Finally, they have a well known capacity to accumulate pollutants. Clark and Finley<sup>5</sup> maintained mussels (Mytilus edulis) beneath an experimental No. 2 fuel oil slick for 48 hours, and observed body concentrations of 29 ppm dry weight. The n-paraffin residual pattern (the n-paraffin composition of the exposed animal minus the normal n-paraffin composition) was similar to the fuel composition, indicating non-selective uptake of hydrocarbons. Most of the accumulated paraffins were released when the mussels were transferred to clean water, although a certain residual remained.

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<sup>4</sup>Jack W. Anderson, ed., Laboratory Studies on the Effects of Oil on Marine Organisms: An Overview, American Petroleum Institute Publication #4249, 1975.

<sup>5</sup>R.C. Clark, Jr. and J.S. Finley, "Uptake and Loss of Petroleum Hydrocarbons by the Mussel, Mytilus edulis, in Laboratory Experiments," Fishery Bulletin 73 (1975): 508-515.

Lee et al.<sup>6</sup> examined distribution of hydrocarbons in different tissues of M. edulis after exposure to heptadecane and to naphthalene for 24 hours. Twenty-four hour exposure to 6.2 ppm heptadecane resulted in the following tissue concentrations: (ppt dry weight) Whole 6.0, Gill - 13.0, Mantle - 7.8, Adductor muscle - 1.4, and Gut - 20.0. Results were similar for a four hour exposure to 32 ppm naphthalene: (ppt dry weight) Whole - 7.0, Gill - 9.0, Mantle - 2.0, Adductor muscle - 6.0, and Gut - 7.0. Over 90 percent of the accumulated hydrocarbons were discharged after transfer to clean water. No evidence was found for hydrocarbon metabolism.

Fossato<sup>7</sup> transferred mussels (Mytilus galloprovincialis) from an environment polluted with diesel fuels, gasoline, and lubricating oils to an unpolluted environment and monitored depuration. In the first 10 to 15 days the concentration dropped exponentially to about 12 percent of its initial value. Thereafter the decrease was extremely slow. Within the range 7.5° C to 26.0° C the rate of depuration appeared to be temperature independent.

Mytilus californianus transferred from clean water to a polluted area of the San Francisco Bay accumulated 325 ppm dry weight hydrocarbons in three months.<sup>8</sup> Five weeks after the mussels had been transferred back to the unpolluted water they had released 90 percent of the hydrocarbons to the environment. However, M. edulis that had grown up in the polluted area experienced only minor losses of contaminants during a 10-week period in clean water. Eggs from unpolluted organisms of the same species accumulated 332 ppm dry weight of hydrocarbons during a 10-week exposure to polluted water. Seventy-six percent of the contamination was composed of aromatics. Results of this study indicate that mussels transferred from clean to polluted water and

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<sup>6</sup>Richard F. Lee, Richard Sauerheber and A.A. Benson, "Petroleum Hydrocarbons: Uptake and Discharge by the Marine Mussel Mytilus edulis," Science 177 (1972): 344-346.

<sup>7</sup>Valentino U. Fossato, "Elimination of Hydrocarbons by Mussels," Marine Pollution Bulletin 6 (1975): 7-10.

<sup>8</sup>Louis H. Disalvo, Harold E. Guard, and Leon Hunter, "Tissue Hydrocarbon Burden of Mussels as Potential Monitor of Environmental Hydrocarbon Insult," Environmental Science and Technology 9 (1975): 247-251.

back readily discharged accumulated petroleum, whereas mussels originally taken from the polluted waters retained much of their hydrocarbon body burden even in clear water. This may suggest the existence of two types of accumulation: short-term accumulation in which take-up and release are rapid, and long-term or chronic accumulation where the concentration is built up over an extended period of time and is not readily discharged.

The American oyster, Crassostrea virginica, has also been the subject of much study. J. Anderson<sup>9</sup> exposed oysters to 1 percent oil-water dispersions of four oils for four days with the following resultant tissue concentrations of hydrocarbons: No. 2 fuel oil - 96.7 ppm net weight; Bunker C oil - 47.4 ppm; South Louisiana crude - 65.8 ppm; and Kuwait crude - 107.1 ppm. These results agree with results of an identical experiment performed by R. Anderson.<sup>10</sup> In this second study aromatics were found to accumulate to a greater extent than saturated hydrocarbons. R. Anderson also collected contaminated oysters from a polluted area of Galveston Bay, Texas, and transferred them to clean water to observe depuration processes. Within 52 days tissue hydrocarbon levels were below 0.1 ppm. This result differs from the observations described above regarding M. edulis, which were not found to depurate readily having grown up in polluted waters.

Stegeman and Teal<sup>11</sup> exposed two groups of oysters (Crassostrea virginica) to 106 ppb No. 2 Fuel oil for different lengths of time and observed hydrocarbon uptake. The original lipid content of one group was, for unknown reasons, twice that of the other. Rate of petroleum uptake was proportional to lipid content. The rate of increase of the Accumulated oil/original lipid ratio was the same for

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<sup>9</sup>Anderson, Laboratory Studies of Oil on Marine Organisms.

<sup>10</sup>Roger D. Anderson, "Petroleum Hydrocarbons and Oyster Resources of Galveston Bay, Texas," in Conference on Prevention and Control of Oil Pollution, U.S. Environmental Protection Agency, U.S. Geological Survey, American Petroleum Institute, 1975.

<sup>11</sup>J.J. Stegeman and J.M. Teal, "Accumulation, Release, and Retention of Petroleum Hydrocarbons by the Oyster Crassostrea virginica," Marine Biology 22 (1973): 37-44.

the two groups. Hydrocarbon concentrations were 334 ppm after 50 days exposure, and 161 after 35 days exposure for the high lipid content group. Uptake was found to increase to a peak, and then to decrease with increasing time of exposure. Aromatics comprised a greater percentage of accumulated hydrocarbons than of the original oil. Forty-one percent of tissue contamination was aromatics versus only 15 percent of the fuel oil. This indicates either selective uptake or selective discharge. For seawater hydrocarbon concentrations up to 450 ppb the uptake rate is proportional to hydrocarbon concentration in the medium. Thereafter the rate falls. At 900 ppb, the oysters remain closed, and uptake is minimal. Oysters eliminated all but 34 ppm of the accumulated oil upon transfer to clean water.

Twenty-four hour exposure of the clam Rangia cuneata to 0.0305 ppm benzo[a]pyrene resulted in tissue concentrations of 5.2 to 7.2 ppm benzo[a]pyrene.<sup>12</sup> Accumulation occurred mainly in the viscera -- digestive system, gonads, and heart. Thirty days depuration left 0.07 ppm of contaminant; after 58 days less than 0.01 ppm remained.

Anderson<sup>13</sup> found Rangia cuneata to accumulate 3 ppm n-paraffins and 158 ppm aromatics during a 24-hour exposure to a 1,000 ppm dispersion of No. 2 fuel oil in seawater. The mechanism leading to the disproportionate concentration of aromatics is unknown.

In Mya arenaria (soft shell clam) small micelles of No. 2 fuel oil appeared to be ingested in the same manner as food, and were passed directly to the stomach.<sup>14</sup> Larger oil particles were bound by mucus secreted by the gills. This mucus-oil mixture can later be released or ingested.

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<sup>12</sup>Jerry M. Neff and Jack W. Anderson, "Accumulation, Release and Distribution of Benzo[a]pyrene-C in the Clam Rangia cuneata," in Conference on Prevention and Control of Oil Pollution, U.S. Environmental Protection Agency, American Petroleum Institute, U.S. Geological Survey, 1975.

<sup>13</sup>Anderson, Laboratory Studies of Oil on Marine Organisms.

<sup>14</sup>Dennis M. Stainken, "Preliminary Observations on the Mode of Accumulation of No. 2 Fuel Oil by the Soft Shell Clam, Mya arenaria," in Conference on Prevention and Control of Oil Pollution, U.S. Environmental Protection Agency, American Petroleum Institute, U.S. Geological Survey, 1972.

Discharge of the accumulated oil in mucus may present a hazard to bottom dwelling organisms by enhancing petroleum concentration in the sediment.

Anderson demonstrated a range of responses of the fish Fundulus similus to No. 2 fuel oil. Some fish accumulated oil to a much greater extent than others. Accumulation was found to occur in the gall bladder, heart, liver and brain. Complete depuration took 366 hours.

Cod (Gadus morhua) exposed to Kuwait crude accumulated C<sub>15</sub>-C<sub>33</sub> n-alkanes in the liver.<sup>15</sup> C<sub>24</sub>-C<sub>28</sub> n-alkanes were particularly concentrated, suggesting either selective accumulation or selective metabolism. An experiment showing that hexadecane concentrated in cod liver remains unmetabolized indicated that selective accumulation is probable. The process of selective accumulation is not known.

In summary, it is clear that many organisms do have the ability to take up and accumulate petroleum hydrocarbons from their environment. In some cases concentration to toxic levels can occur. In many cases, however, marine organisms appear to be relatively unaffected by internal hydrocarbon accumulation. Some organisms can metabolize oils; most are able to release the contaminants upon transfer to clean water. There is no evidence for biomagnification in the food chain of petroleum concentrations as a result of accumulation by individual organisms. It is not clear that bioaccumulation of hydrocarbons has any particularly significant negative effects on many organisms. More comprehensive, standardized research in this field is needed before the mechanisms and consequences of oil accumulation will be understood.

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<sup>15</sup>R. Hardy, P.R. Mackie, and K.J. Whittle, "Discrimination in the Assimilation of n-alkanes in Fish," Nature 252 (1974): 557-578.

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