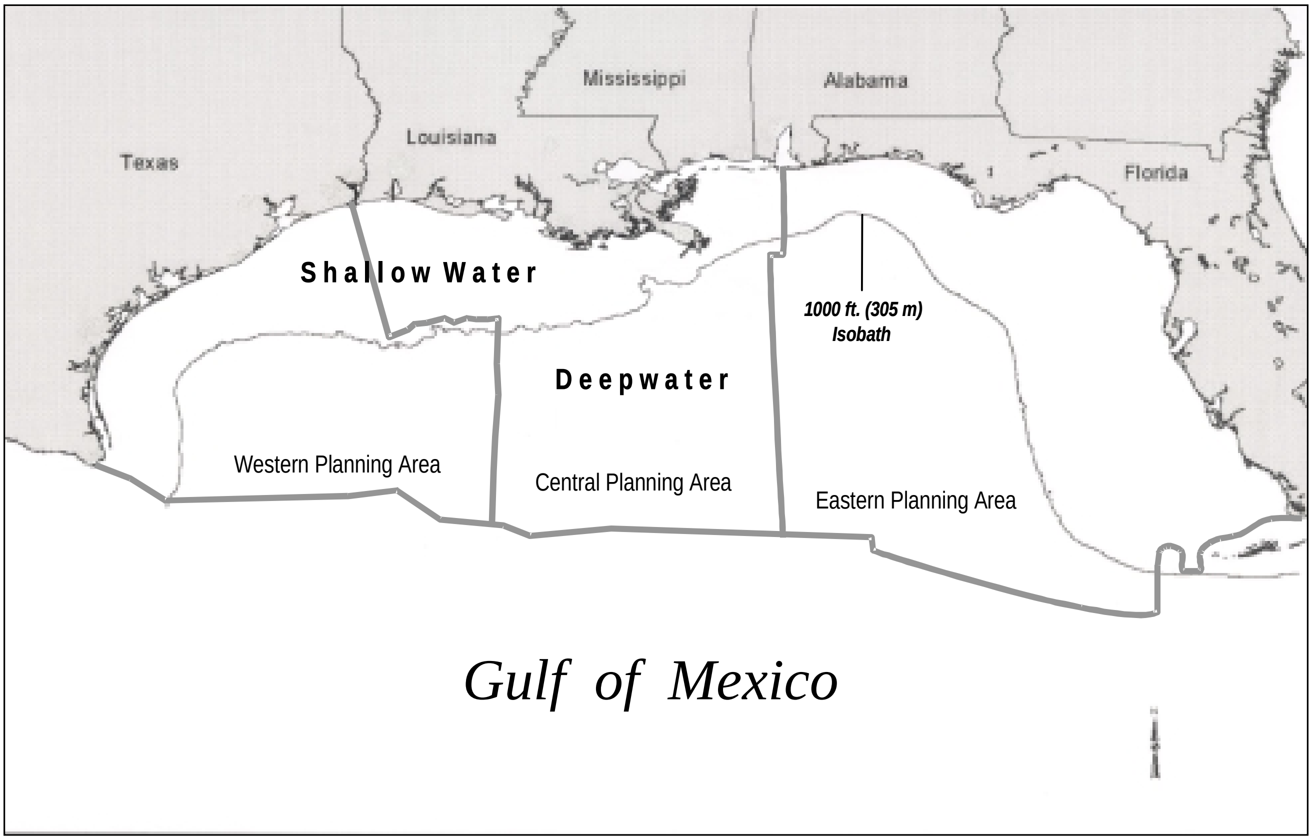
OCS Study
MMS 2001-011

Deepwater Program: Literature Review, Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil and Gas Operations

Volume I: Technical Report



U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Region

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Deepwater Program: Literature Review, Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil and Gas Operations

Volume I: Technical Report

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COVER

The cover shows the Gulf of Mexico Region, its three planning areas, and the 1,000 ft (305 m) isobath that separates shallow and deep water.

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EXECUTIVE SUMMARY

Chemicals have been used in offshore Gulf of Mexico (GOM) oil and natural gas exploration and production (E&P) since development of the offshore resources over a half a century ago. From 1947 to 1985, E&P activities focused on the shallow waters of the continental shelf. Since the mid-1980s, however, the pace of exploration and development in the deep waters of the GOM has accelerated rapidly. By the end of 1999, approximately 1,200 wells had been drilled in water depths exceeding 1,000 ft. (305 m) (Minerals Management Service, May 2000). Moreover, production from these deepwater wells have now surpassed production in shallow water, despite the fact that only 4% of all producing fields in the GOM are in deep water.

The United States Minerals Management Service (MMS) is mandated to manage the development of GOM oil and natural gas resources, while also ensuring safe operations and protection of the human and natural environment. As a part of this overall management responsibility, the MMS must consider possible impacts from chemicals used in oil and gas development to both the natural and human socio-economic environments. To accomplish this, an understanding of the types and quantities of chemical products used offshore, especially in deep water, as well as their potential impact is needed. This report identifies the types of chemicals used in the GOM via an extensive inventory. It presents their properties, toxicity, usage patterns, and storage and handling practices. Through the use of spill modeling, the potential for environmental risk for a select group of chemicals is evaluated. In addition, this report includes an overview of relevant legislation.

Chemicals perform critical functions during drilling; cementing; well completion, stimulation, and workover processes; and producing processes. Without these essential formulations, the safe, cost-effective extraction of oil and gas resources would not be feasible. In offshore operations, chemicals fall naturally into four major classes:

1. Drilling fluid chemicals
2. Cementing chemicals
3. Completion, stimulation, and workover chemicals
4. Production-treating chemicals

This document presents the inventory of chemicals typically used in ongoing oil and gas E&P activities in the GOM. The compiled data and inventories are based primarily on information received from three major energy companies operating in both the shallow and deep waters of the GOM; annual reports provided in World Oil magazine (June 1999, August 1999, and November 1999) on available chemicals; MSDS sheets from chemical suppliers; and a review of Hudgins’ (1991) report on chemical usage in the North Sea, that explains the need, use, and function of chemicals used offshore.

Twenty-one chemicals were selected for detailed characterization based on volumes used and stored offshore, toxicity, and fate in the environment. A standard chemical profile was developed to present the data collected on each chemical and their impact on the marine environment. The chemicals profiled are:

Acids Hydrochloric Acid Hydrofluoric Acid	**Chemical Stabilizer** Sodium Hydroxide Potassium Chloride	**Oxygen Scavenger** Sodium Bisulfite
Antifoam/Defoaming Agents Silicones	**Corrosion Inhibitor** Amides/Imidazolines Amines & Amine Salts	**Insoluble Solids** Barite
Biocides Glutaraldehyde Quaternary Compounds Tetrakishhydroxymethyl Phosphonium Sulfate (THPS)	**Fluid-Loss Agents** Lignite	**Thinners & Dispersants** Lignosulphonate
Reactive Salt – Solid Zinc Bromide Calcium Bromide Ammonium Chloride	**Gas Hydrate Prevention** Methanol Ethylene Glycol Triethylene Glycol	**Solvents/Carriers** Heavy Aromatic Naphtha

Models were developed for offshore E&P operations to estimate the volume of chemical transported, stored, and expected to be used at any one time in the GOM. For this report we utilized a small, but representative subset of chemical usage data from 1998 obtained from three operators and their chemical suppliers. Once unitized, these data were extrapolated to total GOM usage volume estimates for 1998 for each chemical. Given future information on the number of wells, types of wells, well depth, water depth and production data, these models can be used to extrapolate from the unitized data the total volumes of a chemical(s) used in the GOM in any year or, if needed, on a project-specific basis for any number of wells to be drilled or quantity of fluid produced.

Definite differences are apparent in chemical use in deep and shallow waters in the GOM. For individual locations, these include:

- Higher amounts of drilling fluid chemicals needed in individual wells in deep water, some of which are probably due to the nature of the formations and reservoirs being accessed
- Higher amounts of some production-treating chemicals (e.g., hydrate inhibitors) needed in deepwater production, which may be due to the deepwater environment
- Higher amounts of other production-treating chemicals (e.g., defoamers) needed in deepwater production, which may be due to the nature of the produced fluids

It is not clear how comparisons of the total volumes of chemical used in the future will change. However we do know that, with the increasing use of subsea completions in deep water, there will be an increase in the use of umbilicals to supply chemicals to them. The use of umbilicals will result in the storage of larger volumes offshore, which will be transported on the sea floor. There is nothing fundamentally different about chemical treating in deep water. The same chemicals are used to complete the same functions in both shallow and deep water. As with any area within the GOM, the nature of the geologic formation, the reservoir, and the local environment are the primary factors that will affect chemical use.

As part of this study, the types and volumes of hazardous substances used, handled, and stored in offshore E&P operations were identified. Hazardous chemicals were defined as those substances listed in the U.S. Code of Federal Regulations (CFR) – Chapter 40, Protection of the Environment, Part 116, that designates hazardous substances per the Clean Water Act. Only eight hazardous substances were found to be stored in amounts exceeding reportable quantities: sodium hydroxide, potassium hydroxide, zinc bromide, hydrofluoric acid, diethylamine, toluene, xylene and naphthalene.

Over the past decade, the number of liquid chemical spills in the Gulf of Mexico (GOM) has steadily increased. In 1998, the percentage of spill incidents across the Gulf region accounted for almost 27% of all incidents in U.S. water bodies. Of the four chemical classes, a disproportionately large ratio (i.e., eight of 17, or 47%) of spills related to completion, stimulation, and workover chemicals were reported. Completion, stimulation, and workover chemicals are likely to be directly applied from supply boats instead of being transferred to the platform or rig and then used. While the number of chemical spills in the Gulf are certainly related to the ongoing E&P activities in the region, the increase in number of spills reported since 1990 may not be directly correlated to an increase in operations. A portion of the increase in spill reports can be attributed to the improvement in reporting and management practices by offshore operators and chemical supply companies over the last decade.

Jurisdiction for regulations for the transportation, storage, and use of chemicals is divided between the federal government and individual states. Onshore and in state waters, the state has primary jurisdiction, followed by the federal government. In outer continental shelf (OCS) waters in the GOM, the U. S. Congress specifically delegated jurisdiction to the federal government. In the Continental Shelf Lands Act (43 U.S.C. 1333), the authority of enforcement for “the subsoil and seabed of the outer continental shelf” and “all devices permanently or temporarily attached to the seabed” are areas of “exclusive federal jurisdiction.” Federal agencies that issue regulations that apply to chemicals used offshore include:

- U.S. Department of Transportation (DOT, Title 49, Part 172 of the Code of Federal Regulations)
- Occupational Safety and Health Administration (OSHA, Title 29)
- U.S. Environmental Protection Agency (EPA, Title 40)

As chemicals move through the supply chain from the manufacturing to the formulation stage, packaging containers, record keeping, and handling policies are adopted to meet all potential domestic and international regulatory requirements. Frequently, chemicals are stored offshore in the containers in which they were transported. Therefore, the same safety and containment standards that were used for transportation are met or exceeded for storage.

Exploration for oil and gas is increasingly extending into the deeper waters of the Gulf of Mexico. Biological communities potentially at risk from the use of chemicals, therefore, extend past the break of the continental shelf (generally accepted as the upper limit of the deep sea). This fact puts deep-sea benthic pelagic biological communities and oceanic pelagic communities potentially at risk. Certain aspects of deepwater development may possibly pose novel threats of impact, either because of the technology, the chemical compounds, the differing environment, or the different biological communities and ecological processes (Carney 1998).

The major types of benthic communities within the continental shelf zone are those associated with soft-bottom habitats that vary in sedimentary composition. Many biogenically structured communities, such as coral reefs or “live” bottoms, occur throughout the Gulf of Mexico. Within the deep sea, the benthic communities are dominated by soft-bottom dwelling organisms, with an added importance of microhabitat structuring. Hydrocarbon seeps with their chemosynthetic, or otherwise specialized biological communities, are places where gas and oil flow naturally out of the sea floor and are quite common on the continental slope of the northern Gulf of Mexico. Much less is known of the deep sea and oceanic communities.

Our knowledge base for the effects of chemicals or habitat perturbation is the most meager for the deep sea. It is expected, however, that ecological processes in the deep sea are fundamentally similar to those of the continental shelf. Biological communities at risk from chemical spills associated with deepwater E&P are most likely those which are deeper than the continental shelf break. Biologically sensitive communities in coastal and continental shelf depths may be affected from spills during transit of materials either via ship or pipeline.

Spill modeling was performed to estimate concentrations resulting from worst-case chemical spill scenarios that were developed from the assembled inventory data. The results were used to evaluate the potential impacts of spills of selected chemicals on the marine environment. The modeling was performed using Applied Science Associates’ (ASA) chemical spill model CHEMMAP. A total of 17 spill scenarios was developed, modeled, and reviewed. Sixteen spill scenarios were modeled using shallow water data and one spill scenario was modeled in deep water. The shallow water current data were obtained from measurements made by Texas A&M University as part of the LATEX program. For each of the chemicals modeled, habitat areas exposed to peak concentrations or mass loadings within range intervals were tabulated. These peak exposure concentrations were compared against acute toxicity data to estimate the potential impact to the environment. The results of the modeling effort are discussed in conjunction with the detailed chemical profiles in Section 8.0.

Detailed chemical profiles were developed for selected chemicals used in deepwater E&P operations. Each profile is a description of the subject chemical and contains a summary, background information (i.e., fate in the environment, fate in the process system, other components, CAS number, chemical formula, and important synonyms and trade names), chemical and physical properties, health and safety properties, use and handling properties, environmental concentrations and toxicological effects, spill modeling results, aquatic toxicity levels, risk characterization, references, and spill modeling results in the form of tables and figures.

The process we have used to estimate the ecological risks associated with spills of oilfield chemicals is subject to several inherent sources of uncertainty. No toxicity data were found for the Gulf marine species actually potentially affected by the chemicals. Many of the species for which data were found are test species used in compliance testing for waste stream discharges. All comparisons of toxicity data were to average or worst-case peak modeled concentrations. Because these modeled peak concentrations would generally last only a short time, comparison to toxicity results from standard 96-hour tests probably provides an exaggerated estimate of acute impacts. Conversely, overall impacts may be underestimated because we have included no consideration of long-term or chronic exposures to spilled chemicals.

Summary

This report includes a general inventory of chemicals employed during exploration and production operations in the Gulf of Mexico, a brief history of their use, the drivers, triggers, and regulatory guidelines for their use, and a discussion of their spill history and potential for spillage. While a majority of the chemicals utilized in E&P operations are not, or do not, contain hazardous materials, as specified by U.S. Code of Federal Regulations (CFR) – Chapter 40, Protection of the Environment, Part 116, those that are, or do, have been identified. In addition, utilizing data collected from operators in the Gulf, models were developed and usage and storage estimates were made for chemicals/functional groups of chemicals. These models can be used to estimate total volume usage at any time in the future or to estimate the chemical usage for a particular project.

As part of the risk characterization, the results of the modeling effort were integrated with the toxicity data collected for the chemical profiles. The results of this analysis indicate that a potential for impact exists for both zinc bromide and ammonium chloride. The modeled impacts for zinc bromide were predicted based on a 45,000 gallon release to the environment. While a spill of ammonium chloride was not modeled, a review of the chemical's structure and properties indicate that it would behave similarly to potassium chloride. Utilizing the modeled exposure concentrations for potassium chloride as a surrogate for ammonium chloride, a comparison with marine toxicity thresholds was conducted that indicates a positive potential for environmental impact. Since the analysis was conducted by proxy, this predication must be qualified as only an indicator of potential risk and the need for a more focused study on the effects of ammonium chloride on the marine environment.

1.0 INTRODUCTION

Chemicals have been used in offshore Gulf of Mexico (GOM) oil and natural gas exploration and production (E&P) since development of the offshore resources over a half a century ago. From 1947 to 1985, E&P activities focused on the shallow waters of the continental shelf. Since the mid-1980s, however, the pace of exploration and development in the deep waters (Figure 1) of the GOM has accelerated rapidly. By the end of 1999, approximately 1,200 wells had been drilled in water depths exceeding 1,000 ft. (305 m) (Minerals Management Service, May 2000). Moreover, production from these deepwater wells have now surpassed production in shallow water, despite the fact that only 4% of all producing fields in the GOM are in deep water. Today these deepwater fields provide over half the Gulf's daily oil production, with an additional 50-60 deepwater wells projected to be developed by 2007 (U.S. Department of the Interior 2000). The variety and volume of chemicals used offshore to aid in the extraction of oil and gas continues to grow. In addition, many technological changes have enabled expansion into even deeper waters (e.g., underwater robotics, remotely operated vehicles, and navigational technologies). These advances will likely continue to impact deepwater chemical usage.

The unique deepwater physical/environmental conditions (e.g., increased pressure, low seawater temperature at depth, and higher formation temperature) and the unique biological habitats in these areas (e.g., benthic communities), combined with increased exploration of resources, have raised concerns about chemical usage and their impact in deep water as well as throughout the GOM. The United States Minerals Management Service (MMS) is mandated to manage the development of GOM oil and natural gas resources, while also ensuring safe operations and protection of the human and natural environment. As a part of this overall management responsibility, the MMS must consider possible impacts from chemicals used in oil and gas development to both the natural and human socio-economic environments.

To accomplish this, an understanding of the types and quantities of chemical products used offshore, especially in deep water, as well as their potential impact is needed. This report identifies the types of chemicals used in the GOM via an extensive inventory. It presents their properties, toxicity, usage patterns, and storage and handling practices. Through the use of spill modeling, the potential for environmental risk for a select group of chemicals is evaluated. In addition, this report includes an overview of relevant legislation. Specifically, objectives of this project included:

- Establishing a baseline inventory of the chemical products, compounds, and mixtures in current use by operators in the GOM, with emphasis on deep waters (over 1,000 ft. or 305 m)
- Estimating the amount of such chemicals expected to be used as exploration in the GOM increases, with emphasis on deep waters
- Locating and collecting technical information on chemical volumes in typical GOM operations
- Developing conceptual models using a range of chemical spill scenarios and predicted impacts as a result of these spills
- Developing an inventory of types and amounts of hazardous substances stored, handled, transferred to, and used on offshore oil and gas facilities in all water depths

(Not to Scale)

Figure 1. The Gulf of Mexico Region, its Three Planning Areas, and the 1,000 ft. (305 m) Isobath that Separates Shallow and Deep Water.

2.0 CHEMICALS USED IN GULF OF MEXICO OIL AND GAS OPERATIONS

2.1 Introduction

This section summarizes current information on chemical usage in the GOM in both deep and shallow water areas. It includes information on the types, variety, and volume of chemicals used in the GOM and the factors that determine their use.

2.1.1 The Need for Chemicals

Chemicals perform critical functions during drilling; cementing; well completion, stimulation, and workover processes; and producing processes. For drilling chemicals, these functions include such applications as lifting cuttings, applying back-pressure to the formation, and stabilizing the wellbore. For production-treating chemicals, the functions include such tasks as aiding phase separations, controlling corrosion, and controlling water-formed scale deposition. Without these essential formulations, the safe, cost-effective extraction of oil and gas resources would not be feasible. Technical problems encountered during the exploration and development of new reserves in deepwater areas of the GOM, such as higher bottom hole pressures and temperatures, subsea completions, and heat loss in production risers, have impacted chemical usage.

In offshore operations, chemicals fall naturally into four major classes:

1. Drilling fluid chemicals
2. Cementing chemicals
3. Completion, stimulation, and workover chemicals
4. Production-treating chemicals

Drilling, cementing, completion, stimulation, and workover chemicals are applied directly to the wells, whereas production-treating chemicals are applied to the produced streams. It is convenient to subdivide chemicals into these four classes since each group is manufactured, distributed, and supplied by a distinct group of companies and therefore information on these chemicals is typically provided in this natural grouping. In addition, different departments within operating oil companies typically manage the use of each chemical class; and, historically, this chemical division has been mirrored by the suppliers that offered each class of chemical independently.

Chemicals in each class are predominantly used during different stages of an oil or gas well's life span and serve a unique technical or economic function. The development and use of chemicals is influenced by several factors:

- Solving or addressing operating problems (such as lifting cuttings during drilling, stabilizing wellbores, increasing permeability of formations, and breaking emulsions, among many others)

- Reducing overall costs
- Improving worker safety
- Complying with environmental regulations

To help understand chemical use in offshore E&P operations, it is useful to consider the life cycle of a typical oil or gas field. Such a field will progress through the following five distinct stages; exploration, development, active production, re-development, and harvest. A brief description of each stage is provided below.

- Exploration – The search for oil and gas using seismic data, exploratory drilling for strata identification and confirmation of hydrocarbons.
- Development – the setting of platforms, drilling of production and injection wells, installation of gathering lines and separation equipment. The last part of this phase may overlap with the active production stage.
- Active production – The period when the recoverable reserves in the reservoir are brought to the surface, treated and sold.
- Re-development – When the original reserves are nearing depletion, the wells and equipment in place are used to recover minor reserves that may have been encountered while drilling the original wells. During this phase wells are re-completed in new zones where reserves might exist.
- Harvest mode - At some point a field or wells in it can no longer produce sufficient revenue to justify additional capital investment. In this case production continues as long as no new capital investment is not required. At the end of harvest mode properties are abandoned or sold.

Figure 2 represents the distribution of chemical usage (approximate) throughout the life cycle of a field. This data illustrates the differences in chemical usage between the chemical classes during each life cycle stage. For example, most of the drilling fluid chemicals are used in the development phase that will last roughly 10% or less of the total life of the field. During that period, large quantities of drilling fluid chemicals are used, but the time period is relatively short. Conversely, the greatest percentage of production-treating chemicals are used during the active production phase of the field. The shallow water region in the GOM contains many fields in different phases of their life cycle. The majority of shallow water operations are in the active production phase or later, while the deep-water region is largely in the exploration and development phases.

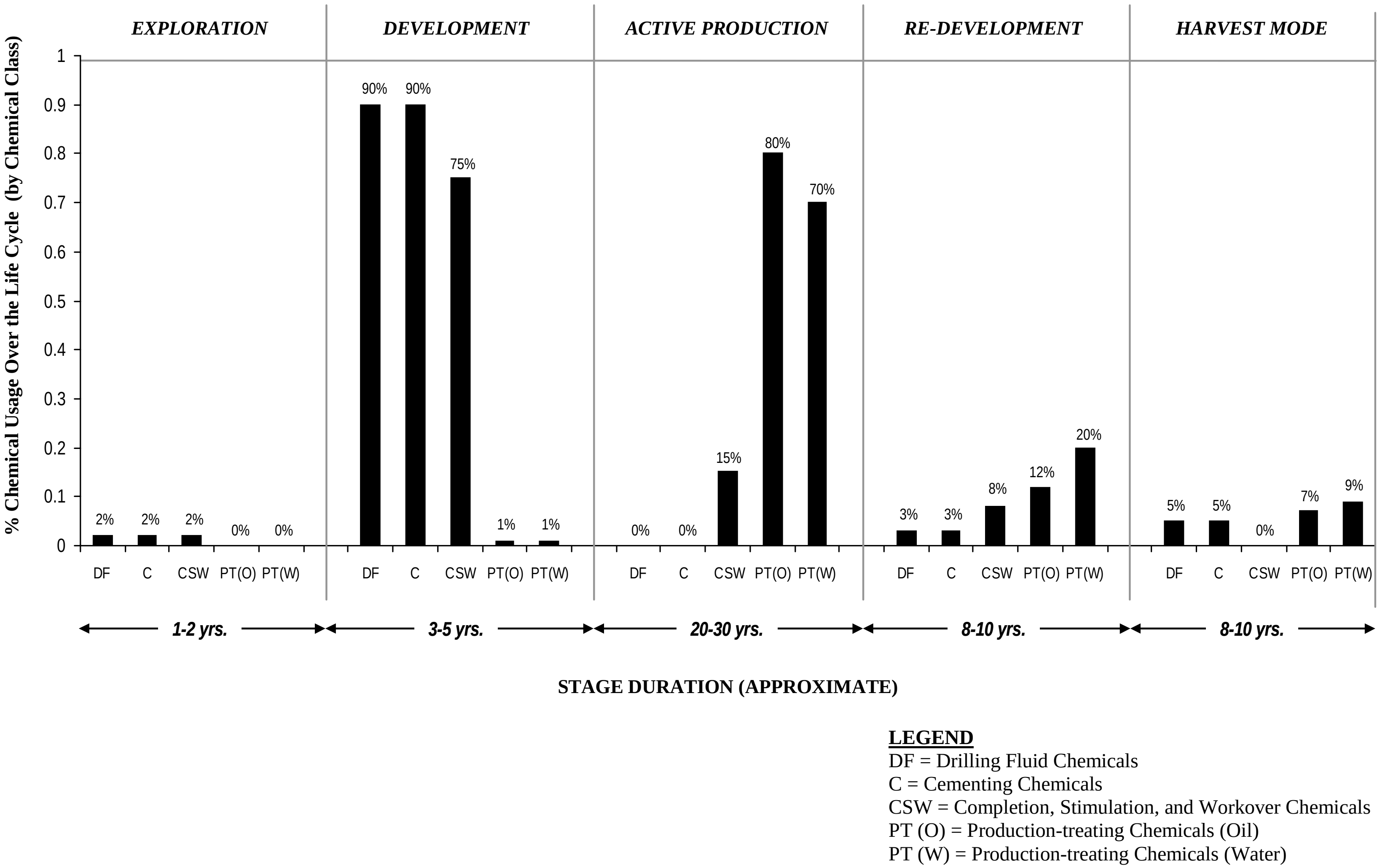


Figure 2. Chemical Use by Stage of Oil & Gas E&P (GOM).

Chemical use is an operational art as much as an engineering science. The task of selecting and managing chemicals requires the expertise of many individuals within the chain of companies/services required to take an offshore E&P project through its functional life. Therefore, when referring to the compiled GOM chemical inventory presented in this report, it is important to note that the specific types of chemicals discussed and the volumes of the chemicals are approximations and that this inventory serves as a guide to the probable chemicals and the volumes that might be used and stored for a particular offshore operation in the GOM.

2.1.2 Brief Historical Perspective

The first chemical treatment technologies were developed over 90 years ago to separate water from oil prior to refining operations. Since then, the use and application of chemicals has continued to evolve and impact every facet of the E&P process.

Since the development of rotary drilling techniques, drilling fluid chemicals have been employed to solve a wide range of well control problems and to promote efficient drilling rates. There has been a steady improvement in drilling fluid chemicals and their application, starting with early attempts to improve cuttings removal and control well flow. Drilling fluid density assists in the application of back-pressure on an oil-bearing formation and also helps to control the flow of oil. Before the use of drilling fluid chemicals, pictures of drilling rigs taken during the first half of the twentieth century regularly showed “gushers” or plumes of oil being sprayed high into the air and spreading crude oil over a wide area. At the time, environmental impacts were unknown and unregulated.

The development and use of production-treating chemicals dates back to at least 1913, when W. S. Barnickel received a chemical patent to break emulsions. In the early days of oil refining, engineers identified the need to separate water from crude oil so that the water would not cause corrosion during the refining process, leading to damaged equipment and the potential loss of life (Hilliard 1987). In 1908, F. G. Cottrell patented a dehydration apparatus using an electric field to dehydrate oil. Later Cottrell and Barnickel founded Petrolite Corporation (now part of Baker Petrolite), which became, and currently is, a major supplier of oilfield chemicals and process equipment.

During the first 20 to 30 years of E&P in the GOM, oil companies (operators) developed chemical technology within their companies to satisfy their technology needs. As illustrated in the 1958 edition of the API Green Book (NACE 1958) oil companies were supporting the development of chemical formulations through their internal research efforts.

In contrast, today most of the oilfield chemical research and development is conducted by suppliers rather than by the oil companies and is driven by market demands. In the early 1970s, in parallel with the shift in development from oil companies to suppliers, regulations on the discharge of waste by the Environmental Protection Agency (EPA) were developed. The National Pollutant Discharge Elimination System (NPDES) added environmental protection as an objective of chemical-treating technology. Oil companies demanded chemical formulations from their suppliers that would provide the same functionality as those they were using, but would not cause them to exceed NPDES limits or impact other regulations. Since many chemicals used in offshore oil and gas operations are ultimately discharged as part of a waste stream, this resulted in many new chemical formulations. Regulations and market demands continue to influence the chemical development strategies of chemical suppliers in the Gulf. (Drilling fluid chemicals, for example, will not sell on the market unless the resulting mud has a 96-hr LC50 of at least 100,000 mg/L to Mysid shrimp. Most muds on the market have 96-hr LC50s of 500,000 mg/L or more.)

Current research in chemical formulation development is now more likely to examine product improvements such as ways to improve efficiency of treatment or to decrease the impact of the product on the environment. Harless's work on biocides is an example of improving efficiency. His paper, *Mechanisms and Field Performance of 9, 10-Anthraquinone as a Biogenic Sulfide Inhibitor*, discussed using 9,10 anthraquinone in combination with glutaraldehyde to control bacterial growth more completely (Harless 2000). Salma compared several commercial biocides to a new proprietary compound in *Acrolein: A Cost Effective Solution for Iron Sulfide and Hydrogen Sulfide in Produced Waters* to determine impacts on non-target species at effective control levels (Salma 2000). One of the newer alternative biocides, Tetrakishydroxymethyl phosphonium sulfate (THPS) decreases environmental impact when discharged because it reacts with oxygen and rapidly degrades to a much less toxic form.

Examples of product development driven by environmental concerns can also be seen in the area of corrosion inhibitor development. In the early 1990s, Haslegrave et al. (1992) examined chemical structural relationships to toxicity of corrosion inhibitors and found ways of decreasing toxicity while retaining function for some inhibitors. More recently, Brenzinski and Halliburton Energy Services (1999) identified formic acid and potassium iodide as intensifiers used in acid corrosion inhibitors. These examples typify the trend in technical development and have resulted in inhibitors that are more effective, longer lasting and with lower potential to impact the environment.

2.1.3 Development of Chemical Inventory

In the following sections we provide the inventory of chemicals typically used in on-going oil and gas E&P activities in the GOM. While thousands of chemicals are sold for use in the offshore oil and gas industry, no definitive information source exists and much of the available information is considered proprietary. Therefore, the scientific literature on these chemicals is scarce and does not typically include formulations or compositions. These sections, therefore, present compiled data and inventories based primarily on data received from three major energy companies operating in both the shallow and deep waters of the GOM; annual reports provided in World Oil magazine (June 1999, August 1999, and November 1999) on available chemicals*;* MSDS sheets; and a review of Hudgins and Petrotech Consultants, Inc.'s (1991) report on chemical usage in the North Sea, which explains the need, use, and function of the chemicals used offshore.

For each of the four chemical classes: drilling; cementing; completion, stimulation, and workover; and production-treating, two tables and a searchable MS Access database that includes information on chemical products; chemical handling (i.e., storage and transportation). and physical and chemical properties for selected chemicals and/or products have been developed. The first table, presented within the body of the report, describes each of the functional categories within the class; the type of material (i.e., generic chemicals) used; and the code for each category. The second table of the inventory, presented in Appendix A, is the “product database” and lists actual products within each class; a description of these products; their functions; and suppliers. Codes for each of the functional categories link the two tables and the searchable MS Access database. The following discussions present an inventory of chemicals used in the GOM aggregated into functional categories for each class of chemical along with a description of the function and examples of the type of chemicals in each category.

2.2 Chemicals Used on Wells and Formations

2.2.1 Drilling Fluid Chemicals

2.2.1.1 Overview

Chemicals applied as part of the well drilling process are referred to as drilling fluid chemicals or *muds*. These chemicals are required to overcome technical issues in the drilling process, improve the efficiency and safety of well drilling, and protect associated equipment. To perform these tasks, a variety of chemicals may be mixed together to develop the site-specific properties required by the drilling fluid chemicals or muds. These properties may include:

- Controlled and relatively high viscosity
- Controlled and relatively high density
- Lubricity
- Low tendency to filter or lose components because of flow into the formation
- Stability to high temperature and high shear forces

To provide these qualities, nearly all drilling fluid chemicals are very stable dispersions of solids in a continuous liquid carrier or emulsions of one liquid in another. In these instances, each liquid phase will contain dispersed solids. Therefore, components are added to drilling fluid chemicals to stabilize and promote emulsions and dispersions.

Defined by the nature of the continuous phase liquid carrier, these drilling fluid chemicals can be divided into three categories; water-based, oil-based, and synthetic-based. Water-based drilling fluid chemicals are used on all wells. Even if deeper portions are drilled with oil-based or synthetic-based fluids, the upper portion of all wells is still drilled with water-based fluids.

Drilling fluid chemicals are added to muds and can generally be categorized as either necessary for the drilling of the well or necessary to protect the equipment or formation. The various properties of drilling fluid chemicals provide the functionality that allow the drilling fluid chemical to:

- Carry cuttings from the well hole bottom to the surface for disposal (viscosity)
- Control pressure on the formation (density)
- Lubricate and cool the drill bit and string (lubrication)
- Suspend drill cuttings in the fluid when circulation is interrupted (thixotrophy)
- Support the drill string weight (density)

- Transmit hydraulic horsepower to the bit
- Control loss of drilling fluid chemicals to the formation both by flow into cracks and by filtration of the liquid portion into the formation (plugging agents)
- Stabilize the hole wall and protect the formation (filter cake)
- Protect the mud components from bacteria (bactericide)
- Protect the drilling equipment from the corrosivity of the drilling fluid chemical (corrosion inhibitor)

Drilling fluid chemicals used in the GOM have been divided into the following 18 functional categories (World Oil, March 1999).

- Alkalinity, pH control additives
- Bactericides
- Calcium reducers
- Corrosion inhibitors
- Defoamers
- Emulsifiers
- Filtrate reducers
- Flocculants
- Foaming agents
- Lost circulation materials
- Lubricants
- Pipe-freeing agents
- Shale control inhibitors
- Surface-active agents
- Temperature stability agents
- Thinners, dispersants
- Viscosifiers
- Weighting materials

These functional categories are described in the drilling fluid chemical inventory (Section 2.2.1.2).

Drivers for Drilling Chemical Use

The amount of drilling chemicals used is determined by a complex combination of the number of wells drilled, depth of the wells, and the type of drilling mud used.

The true vertical depth of a well is theoretically determined by the depth of the target formation. However, the actual depth drilled is affected by well deviation and sidetracks. The type of drilling fluid chemicals used is determined by:

- Properties of the formations penetrated
- Formation pressures encountered
- Temperatures of the formations encountered
- Environmental regulations

These properties drive the use of particular drilling fluid chemicals. For example, drilling through clay formations triggers the need for drilling fluid chemical additives that will prevent clay swelling, while drilling through salt requires a drilling fluid chemical that will not dissolve it; i.e., salt-saturated, water-based muds or non water-based muds. Water-based muds become increasingly unstable at high temperatures; thus, high temperatures trigger the use of non water-based muds. Conventional oil based muds are often not used because of the possibility of an emergency disconnect of the marine riser releasing hundreds of barrels of whole mud to the water-column.

Application

Figure 3 shows the mud circulating system on a drilling rig. Mud components are added in the mixing hopper and are mixed in the mud pit. Drilling fluid chemicals are transported to and stored at the well site, and drilling fluids are prepared on site from the various functional components. The time required to drill an exploratory well is typically 70-90 days (Minerals Management Service 2000). A supply of drilling fluid chemicals sufficient to complete the well being drilled is stored on the rig.

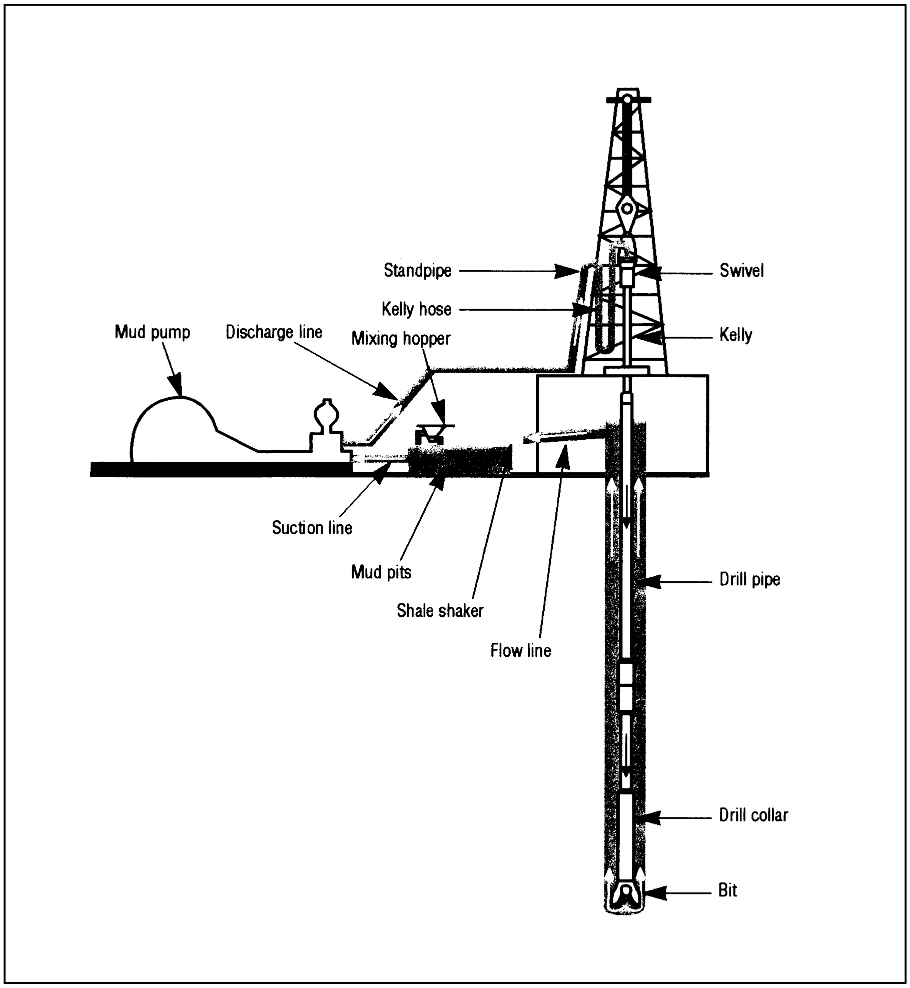


Figure 3. Mud Circulating System on a Drilling Rig. (Source: MI Drilling Fluids)

During the drilling phase, water-based drilling fluid chemicals are in continuous demand because these fluids are dynamic materials that are constantly changing in their chemical and physical characteristics as they are used. The properties of the drilling fluid in the system change as clay solids from the formation being drilled mix with drilling fluids and are thereby added to the process system. Since the clay from the formation reacts in the same manner as the clay used to make the mud, the ratio of clay to other components changes and additional chemicals are needed to restore the mud's properties. Drilling fluids are also modified as they become associated with cuttings removed from the process system. The properties of the drilling fluid in the system are monitored several times a day. Additives such as barite, caustic, lignite, and lignosulfonate are used to maintain the functionality of the fluid. Thus, the addition of chemicals to the mud system is on-going throughout the drilling process.

Characterization

Almost all water-based drilling fluid chemicals used in large amounts are fine solids. They are designed to be dispersed or dissolved in water; both processes are enhanced if the solids are in a very fine, powdered form. Chemical characteristics of the drilling fluid chemicals range from chemically inert and insoluble in water to soluble and highly reactive. Therefore, solids can be generally classified into five groups according to their solubility and chemical reactivity with seawater constituents as follows:

- Water insoluble, non-reactive (e.g., barite, bentonite clay)
- Partially water-soluble, non-reactive (e.g., lignite)
- Water-soluble, non-reactive (e.g., potassium chloride)
- Water-soluble, mildly reactive (e.g., calcium chloride)
- Water-soluble, vigorously reactive (e.g., sodium hydroxide)

SBF and OBF drilling formulations are essentially water-based drilling fluids dispersed in an organic carrier or emulsified in an organic carrier. Similar solids are used in these formulations, however some of the inert solids such as weighting agents and viscosifiers used in these are treated with amines and other organic additives to make them more oleophillic. In addition to the universal constituents found in all drilling fluids non-water-based fluids also contain emulsifiers.

Fate in the Process System

All drilling fluid chemicals eventually become drilling wastes. Drilling fluid chemicals become part of the drilling waste stream in two ways. First, they cling to drill cuttings as the cuttings are discharged. Second, they become excess material either made during drilling operations or at the end of the well.

Water-based drilling waste and associated drilling fluid chemicals are discharged where permitted. Drilling wastes, from wells drilled in Coastal Areas or in the Territorial Seas, are collected in cuttings boxes and hauled ashore for disposal in landfills. Oil-based fluids are prohibited from discharge in the Gulf of Mexico. Synthetic-based fluids are prohibited, however cuttings can be discharged in the Central and Western Planning Areas (Figure 1). In the Outer Continental Shelf (OCS), such discharges are allowed if the waste meets discharge limits. The discharge limits include a toxicity limit, a limit on cadmium and mercury in barite, and a sheen test. Water-based drilling fluid components are designed to comply with these limits.

Fate in the Marine Environment

Permitted discharges are limited by several factors, including the rate of discharge, the formulation of the mud and cuttings, and the state of the material (i.e., free dispersion of solids in a liquid). Accidental discharges (“spills”) may be sudden and consist of a single component product that might be a solid contained in paper sacks or a steel container.

Some drilling fluid chemicals are chemically inert (e.g., barite, clay, etc.) and will become part of the sediment and disperse along the bottom. Others strongly react with the environment (i.e., caustic materials such as caustic soda, caustic potash, acids, etc.) and produce reaction products (sodium chloride, potassium chloride), some of which are natural constituents of seawater. Most organic materials (e.g., lignite, lignosulfonate, polymers, etc.) will eventually be degraded in the environment by bacterial action.

2.2.1.2 Drilling Fluid Chemicals Inventory

Drilling fluids are typically formulated to meet the site’s unique requirements off-shore and then transported to the site. Additional drilling fluid components and base fluid may than be added to maintain the needed properties. Drilling fluid chemical components can be divided into 18 functional categories. Each operation will employ a unique formulation of these components that incorporates an appropriate subset of the functional categories.

Table 1 summarizes the 18 functional categories of drilling fluid chemicals used in offshore operation in the Gulf of Mexico. Each drilling fluid category is defined and examples of chemicals are included in each category.

Table 1

Drilling Fluid Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used

Code	Functional Categories	Description	Material Types Used
A	Alkalinity, pH control additives	Controls the alkalinity or acidity of a fluid. These factors are important in controlling mud properties.	Lime (CaO), caustic soda (NaOH), soda ash (Na_2CO_3), bicarbonate of soda ($NaHCO_3$), other common acids and bases
B	Bactericides	Prevents bacterial degradation of organic additives.	Aldehydes and others
CA	Calcium reducers	Used to counteract the effects of calcium from seawater, cement contamination, anhydrites, and gypsum from the formation on mud properties.	Soda ash (Na2CO3), bicarbonate of soda (NaHCO3), caustic soda (NaOH). and certain polyphosphates
CO	Corrosion inhibitors	Controls corrosion acids and acid gases.	Amine- and phosphate-based products and other specially formulated chemicals
D	Defoamers	Used to reduce foaming action that affects mud properties.	Alcohol-based materials, silicone-based materials, aluminum stearate, alkyl phosphates

Table 1
Drilling Fluid Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used (continued)

Code	Functional Categories	Description	Material Types Used
E	Emulsifiers	Used to create a heterogeneous mixture of two insoluble liquids. They may be anionic (-), non-ionic (no charge), or cationic (+).	Detergents, soaps, organic acids, and water-based surfactants are used in water-based muds
FR	Filtrate reducers	Used to decrease fluid (as opposed to whole mud) loss through the filter cake on the walls of the wellbore.	Bentonite clays, lignite, CMC (sodium carboxymethylcellulose), polyacrylate, and pregelatinized starch
FL	Flocculants	Used to increase viscosity, increase effectiveness of clay viscosifiers, or clarify or de-water low solids fluids.	Inorganic salts, hydrated lime, gypsum (calcium sulfate penta hydrate), soda ash (Na2CO3), bicarbonate of soda (NaHCO3), sodium tetraphosphate, and acrylamide-based polymers
FO	Foaming agents	Used to create foam in water to permit air or gas drilling through water-bearing formations.	See inventory for product examples (e.g., amplifoam, airfoam B)
LO	Lost circulation materials	Used to plug leaks in the wellbore and prevent the loss of whole drilling fluid to the formation.	Nut shells, natural fibrous materials, inorganic solids
LU	Lubricants	Used to reduce torque and drag on the drill string.	Oils, synthetic liquids, graphite, surfactants, glycols, and glycerin
P	Pipe-freeing agents	Spotted at a particular point in a well to prevent the drill pipe from sticking to the formation.	Detergents, soaps, oils, surfactants, and other chemicals
SH	Shale control inhibitors	Used to control shale hydration and subsequent wellbore enlargement, heaving and caving of water-sensitive shales.	Soluble calcium and potassium salts, other inorganic salts, and organic compounds
SU	Surface-active agents	Used to modify the interfacial tension between contacting surfaces. They may act as emulsifiers, de-emulsifiers, wetting agents, flocculants, or deflocculants.	See inventory for product examples (e.g., avabiowet, anco rope)
TE	Temperature stability agents	Used to increase the stability of dispersions, emulsions, and rheological properties at high temperatures.	Acrylic polymers, sulfonated polymers, copolymers, lignite, lignosulfonate, and tannin-based additives

Table 1
Drilling Fluid Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used (continued)

Code	Functional Categories	Description	Material Types Used
TH	Thinners, dispersants	Used as a deflocculant to reduce the attraction (flocculation) of clay particles which causes high viscosity and gel strength. That is, they balance the effect of viscosifiers and control mud viscosity and gel strength.	Tannins, various polyphosphates, lignite, lignosulfonates
V	Viscosifiers	Used to increase viscosity in muds.	Bentonite, attapulgite clays, CMC, and other polymers
W	Weighting materials	Used to increase the density of the mud and thereby enable it to control formation pressures.	Barite (barium sulfate), lead compounds, iron oxides, calcium carbonate, and similar products

2.2.2 Cementing Chemicals

2.2.2.1 Overview

Cements ensure structural integrity in wells and are essential to the drilling and completion of wells. During the drilling process, the internal walls of the hole are maintained by drilling fluid chemicals. When more stability is needed to keep the hole from collapsing or becoming unstable, steel casing is placed in the hole. Cement is then used to bind the steel casing to the formation and to seal off unwanted flow between the wellbore and the formation.

Cement formulations are placed in wells as a liquid slurry of dry particulate solids in water. The solids chemically react with the water to form a dense, contiguous solid mass, impermeable to liquids To position the cements in the well, they are preceded by volumes of spacer fluid and followed by displacer fluids. Similar to drilling fluid chemicals in form, they have many of the same properties as drilling fluid chemicals. A cement formulation must:

- Not react until it is put in place
- Not filter out onto the formation
- Be temperature stable
- Remain dispersed until it reacts
- Have the correct density
- Bond to the steel and the formation

Cementing chemicals that are used in the GOM to achieve the properties discussed above can be divided into one of 15 functional categories (World Oil, March 1999).

- Basic cements
- Accelerators and salts
- Extenders and density-reducing additives
- Free-water control and solids suspending agents
- Dispersants
- Bond improving and expanding additives
- Fluid loss control additives
- Silica to reduce or prevent high temperature strength retrogression
- Retarders
- Anti-gas migration agents
- Anti-foam and defoaming agents
- Density-increasing or weighting agents
- Additives and mixtures to reduce or prevent lost circulation
- Spacers and chemical washes or pre-flushes
- Specialty cement blends

These functional categories are described in Section 2.2.2.2.

Drivers for Cement Chemical Use

The use of cement chemicals depends on the same factors as those affecting drilling fluid chemical use, therefore, the total volume of cement used is determined by the number of wells completed, the depth of the wells, and the type of cement used.

However, the type of cement used and the additives chosen to formulate it may not be affected in the same way by formation pressure, temperature, and geology. Pressures and temperatures affect setting rate of the cement, triggering the need for chemicals to adjust setting rates. For very deep wells, the weight of the cement can fracture the formation, which triggers the need for chemicals to lighten the weight of the cement.

Application

The components of cementing chemical formulations are transported to the drilling rig and are mixed and applied on site under the supervision of the cement supplier. The cement formulations are designed by the supplier to meet the needs of the particular job. As wells are drilled, a section of open hole without casing is created (see Figure 4). There is a limit to the length of hole that can be supported without casing. When that limit is reached, drilling stops and new casing is installed. The new casing is bonded to the bottom of the previous casing and to the formation below it with cement. A deep well may require several strings of successively smaller diameter casing and each string will result in a new cementing job.

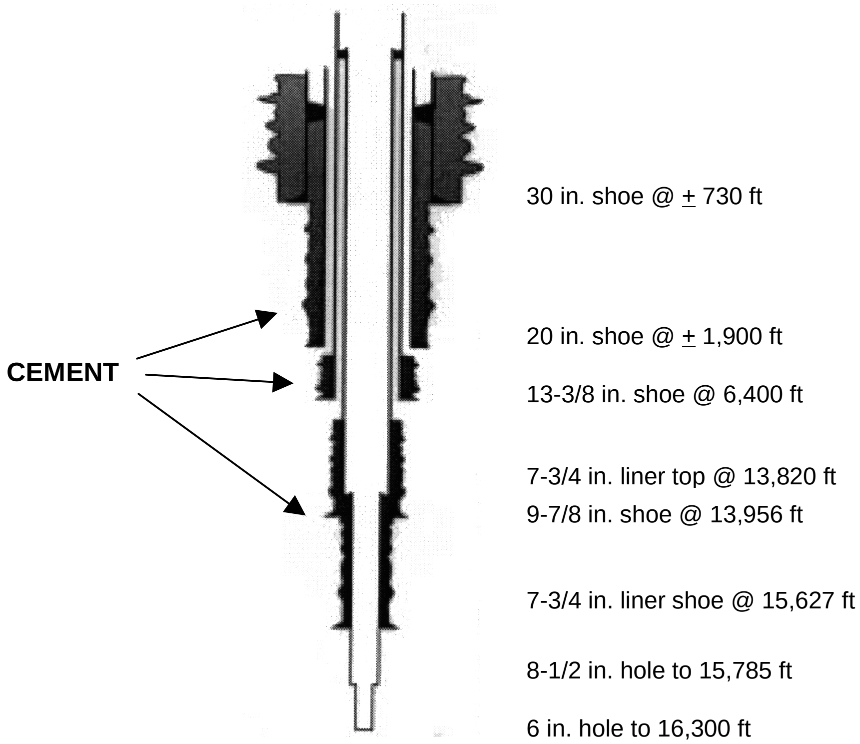


Figure 4. Well Profile Showing Cementing Intervals for a Typical Deepwater Well (Source: MI Drilling Fluids).

Characterization

Like drilling fluid chemicals, cementing chemicals are almost all solids, supplied in powdered or fine particle form. Many cementing chemicals are identical in both form and composition to drilling fluid chemicals and can similarly be classified according to solubility and reactivity in water.

Fate in the Process System

The majority of cementing chemical formulations become integrated as a part of the well, forming a solid barrier between the outside of the well casing and the inside of the formation face. It is difficult to calculate the exact amount of cement needed because the geometry of the hole not known precisely. Extra cement is therefore applied to the well to ensure that voids are completely filled. When setting the surface casing, this extra cement may be pushed up around the casing and out into the marine environment. For deeper casing, the excess is removed and becomes part of the drilling waste. Discharges of cements are included in NPDES permits as a miscellaneous discharge.

Fate in the Marine Environment

When cement itself is discharged, it will react with water just as it does in use and form solids that become part of the sediment. These solids will exist in seawater as small particulates due to dilution by seawater before the reaction is complete. If excess cement is left in the well until it cures and then drilled out, the cement is incorporated in and disposed of with the cuttings.

2.2.2.2 Cementing Chemicals Inventory

The properties of the type of cement needed are based on the characteristics of the well being cased and the geologic formation. Once these properties are determined, cement components are transported to the offshore site and a slurry is formulated to meet the unique requirements of that site. Cement chemicals used in the GOM have been divided into 15 functional categories. For any given operation, the cementing components stored on site will include a subset of these functional categories.

Some of the functional components contribute to the properties of the cement slurry itself; that is, they give it the properties it needs to function properly. Other categories act to:

- Protect the cement slurry (e.g., fluid loss control additives, anti-foam and defoaming agents, additives to prevent lost circulation)
- Place the slurry in the proper place (e.g., spacers and chemical washes or pre-flushes)
- Control slurry stability (e.g., dispersants, anti-gas migrating agents)

Table 2 lists, defines, and provides examples of each of the cement chemical categories currently used in offshore Gulf operations.

Table 2

Cementing Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used

Code	Functional Categories	Description	Materials Types Used
BC	Basic cements	Basic materials	Portland cements, blast furnace slag, calcium aluminate
AS	Accelerators and salts	Increases rate of setting	Sodium chloride, calcium chloride, sodium silicate, calcium sulfate hemihydrate
ED	Extenders and density-reducing additives	Increases volume of mix and reduces density	Bentonite, attapulgite, flyash, natural pozzolan, diatomaceous earth, perlite, fumed silica, glass microspheres
FWS	Free-water control and solids suspending agents	Improves uniformity of the mix	Polymers, sodium silicates, biopolymers, bentonite, attapulgite, fumed silica
DIS	Dispersants	Disperses fine solids and prevents settling	Polynaphthalene sulfonate, citric acid and citrate salts, proprietary additives
BIE	Bond improving and expanding additives	Improves bond to formation and casing	Styrene/butadiene copolymer, fumed silica, fumed silica/flyash blend, calcium sulfate hemihydrate, metal oxide, aluminum powder, proprietary materials

Table 2

Cementing Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used (continued)

Code	Functional Categories	Description	Materials Types Used
FCA	Fluid loss control additives	Reduces loss of liquids from mix to formation	Proprietary materials, styrene/butadiene copolymer, acrylic latex
SHT	Silica to reduce or prevent high temperature strength retrogression	Improves strength in high temperature environments	Sand, silica flour, microfine silica
RET	Retarders	Slows rate of setting	Lignosulfonate, modified lignosulfonate, organic acid, carboxymethyl hydroxyethyl cellulose, borax/borate salt, non-borax/borate salt, proprietary synthesized polymer or copolymer, citric acid or citrate salt
AGM	Anti-gas migration agents	Controls gas flow through mix	Polymeric blends (non-latex), styrene/butadiene copolymer, acrylic, fumed silica, fumed silica/polymer blends, calcium sulfate hemihydrate, proprietary polymeric blends, aluminum powder
ADA	Anti-foam and defoaming agents	Reduces foaming in the cement mix	High molecular weight alcohols, polyalcohols, silicones
DIW	Density increasing or weighting agents	Increases density of the mix	Sand, silica flour, microfine silica, ilmenite, hematite, barite, manganese oxides, calcium carbonate
LCA	Additives and mixtures to reduce or prevent lost circulation	Reduces loss of cement to the formation	Cements, foamed cement, non-aqueous slurries, sodium silicate solutions, sand, mica, cellophane flake, gilsonite, ground coal, walnut plugs, perlite, polymer fibers, wood chips, polyester, ground thermoplastic or rubber, proprietary materials
SCW	Spacers and chemical washes or pre-flushes	Helps in the placement of cement mix	Liquid materials either emulsified or with additives
SCB	Specialty cement blends	Special purpose products	Blends of cement with flyash, clay, pozzolan, silica

2.2.3 Completion, Stimulation, and Workover Chemicals

2.2.3.1 Overview

Completion chemicals are used to clean wells after drilling, to control them while they are being perforated, and to make them operational when essential equipment such as packers and tubing are added. After the last casing is set at the end of the drilling phase, perforations must be placed in the casing so that the producing formation is open to the wellbore. While creating the perforations, it is important to hold back-pressure on the formation and to avoid destabilizing or contaminating the formation.

To accomplish these objectives, clean brines, free of solids, are used. To maintain back-pressure, high-density salts may be used to prepare the brines. Once the perforations are created, the same brine may be left in the well while the tubing is set and the packers are placed. The packers isolate the annulus between the casing and tubing from the interior of the tubing. The brine is left in the annulus so that, if a packer fails, the brine will be available to help control flow from the well. The same types of brines used as completion fluids may also be used as spacers and displacement fluids in other completion, stimulation, and workover procedures.

Stimulation procedures include fracturing or acidizing to achieve a desired production rate. These procedures act to increase permeability that allows increased flow from the well. To achieve these objectives, stimulation fluids must dissolve part of the formation or contaminants in it or they must provide hydraulic pressure that can fracture the formation. Acid solutions and gel brines are used to accomplish these objectives. These procedures are performed on both old and new wells as the need arises.

Formations that are unconsolidated need to be gravel-packed to prevent the formation from flowing into the wellbore. Formations with low permeability perform better if fractures are created in them around the wellbore. Occasionally, residual drilling fluids may remain in the formation around a new well and decrease flow from the well. These fluids can be dissolved with acid. In older wells, water-formed scales can form around a wellbore and block the formation. These materials can also be dissolved by acid. Acidizing and gravel-packing are often performed together.

There are 27 functional categories of completion and acidizing fluids used in the GOM.

- Water-based completion fluid
- Water-based polymers
- Friction reducers
- Fluid loss
- Diverting agents
- Polymer plugs
- Acid inhibitors
- Acid retarders
- Emulsifiers
- Anti-sludge agent
- Foamers
- Scale inhibitors
- Iron (Fe) control
- Oxygen scavenger
- Mutual solvents
- Corrosion inhibitors
- Paraffin control
- Miscellaneous products

- Clay stabilizers
- Surfactants
- Non-emulsifiers
- Fines suspender
- Acid systems
- Retarded acid plus
- Mud acid plus surfactants
- Mud acid plus alcohol
- Regarded HF

For fracturing chemicals, there are 24 functional categories of additives and two categories of proppants (granular particles) used in the GOM.

- Water-based polymers
- Friction reducers
- Fluid loss additives (FLAs)
- Breakers
- Emulsifiers
- Clay stabilizers
- Surfactants
- Non-emulsifiers
- pH control additives
- Crosslinkers
- Foamers
- Gel stabilizers
- Defoamers
- Oil gelling additives
- Biocides
- Acid-based gel systems
- Water-based systems
- Crosslinked gel systems
- Alcohol/water systems
- Oil-based systems
- Polymer plugs
- Continuous mix gel concentrates
- Resin-coated proppants
- Intermediate-to-high strength ceramic proppants

Drivers for Completion, Stimulation, and Workover Chemicals

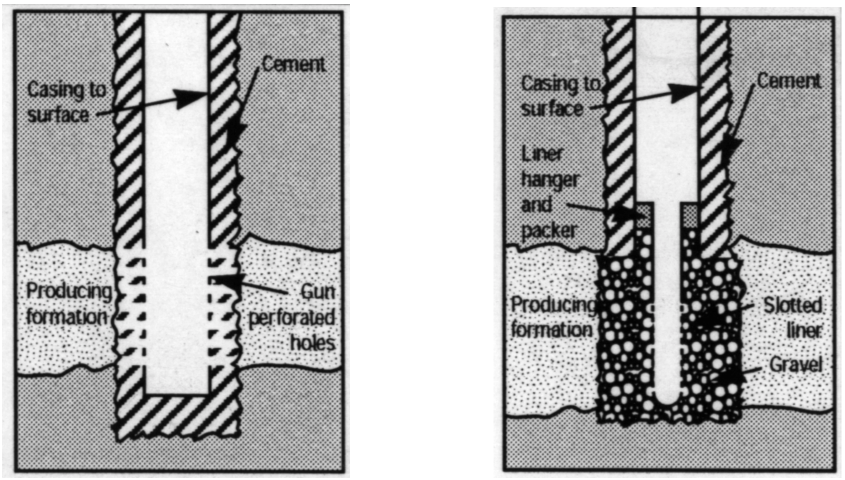
Completions, stimulations, and workovers are not limited to new wells. While new wells do require completion and stimulation, old wells are also recompleted to produce from new zones. Old wells may undergo workover and stimulation to increase production rates. The amount of these chemicals used is driven by:

- The number of wells needing treatment
- The depth and length of the interval being treated
- The type of procedure used

New wells need stimulation to remove mud residue blocking the formation or to increase porosity near the wellbore. Active, producing wells are stimulated to remove water-formed scales or clay fines that have migrated to the wellbore and blocked the formation around the perforations. Workovers are done to install new equipment or to remove obstructions such as sand in the wellbore. The need for these procedures depends on reservoir or formation-specific problems.

Application

Completions and stimulations are normal procedures used to equip a new well and put it into service. Stimulation and workover procedures are also conducted on formation intervals in existing wells to enhance production. Figure 5 shows a set of perforations in a casing and a gravel-packed formation. Completion fluids are used in the well when the perforations are made. Slurries of gravel in water are used to place gravel-packs and some types of gravel-packs include acid stimulations. Completion, stimulation, and workover chemicals are all applied as water solutions and are mixed (if needed) and pumped by the supplier's personnel. The final chemical formulation required for each procedure may be brought to the site as either a pre-mixed formulation or as component parts to be mixed on site. Typically, completion, stimulation, and workover chemicals are not stored on site for extended periods, but rather are transported to the site in the required amounts prior to the job.



(a) (b)

Figure 5. Completed Producing Zones; (a) Perforations, (b) Gravel-Pack.

Fracturing is used to create and maintain conductive tracks in the formation. Once formed, these cracks are kept open with granular particles (proppants) and provide a relatively porous structure that holds back the formation and allows flow though the crack. Cracks are created with hydraulic pressure, and fracturing (frac) fluids/chemicals are designed to transmit such pressure efficiently. The process includes several stages, including:

- Prepad – designed to penetrate the formation, help initiate fractures, and cool the formation
- Pad – viscous fracturing fluid without proppants to generate the fractures
- Proppant stages – carries proppant into the fractures
- Flush – used to displace the working solutions through the tubing and place it where it is needed

Acidizing is used to remove formation damage near the wellbore, to increase formation permeability, to remove scale and other debris, and to change the formation wetability characteristics. Formation damage may result from:

- Clay and fines (i.e., from residual drilling fluids or loose formation material)
- Perforation plugging (i.e., from compaction perforating waste)
- Emulsions (i.e., caused by chemicals added during other procedures that stabilize oil water emulsions)
- Relative permeability (i.e., caused by chemicals used in other processes which change the wetability of the formation)
- Asphaltenes and paraffin (i.e., organic materials that may precipitate from crude oil)

Characterization

Completion, stimulation, and workover chemicals include water-soluble materials and insoluble materials such as proppants. The formulations used are water solutions of acids, salts, or both. Acids are delivered to the site by the supplier in bulk tanks as ready-made solutions while proppants and salts are delivered as solids (sacks stacked on pallets) and are mixed on site.

Acidizing chemical categories can be divided into several subcategories:

- Basic functional components (i.e., acid and process control chemicals; e.g., acid systems, diverting agents, acid retarders)
- Process aids (i.e., chemicals that solve problems resulting from the acid reaction products; e.g., friction reducers, fines suspenders, iron control, mutual solvents)
- Protectors (i.e., chemicals used to protect the fluid, formation, or equipment; e.g., acid inhibitors, oxygen scavengers, corrosion inhibitors)

These materials are divided among a large number of classes according to their solubility and chemical reactivity in seawater. These include:

- Inorganic acids, highly reactive with seawater constituents (hydrochloric, hydrofluoric acids)
- Water-soluble inorganic salts, unreactive and reactive (sodium chloride, potassium chloride, calcium chloride, zinc bromide)
- Water-soluble organic polymers (xanthan gum, guar gum)
- Soluble inorganic solids (rock salt)
- Organic acids (acetic acid, benzoic acid)
- Low molecular weight organic polymers (polyacrylamides, alkyl ammonium compounds)
- Surfactants

Fate in the Process System

Completion, stimulation, and workover chemicals end up in one of three places:

- Discharged or disposed of as waste
- Remaining in the well as packer fluid or part of the well
- Injected into the formation

Clear completion fluids are used during perforations of the casing, placement of tubing, and setting of packers. Fluid remaining in the tubing after completion of the job is either disposed or recycled. In nearshore areas, the fluid must be hauled to shore, while in the OCS it can be discharged in accordance with NPDES permit limits.

Fracturing, acidizing, and gravel-packing processes also involve the use of completion, stimulation, and workover chemicals. These processes are used to improve the ability of the well to give up produced fluids by increasing permeability and/or porosity. After the fluids have performed their desired function, they are produced back and disposed of in the same manner as completion fluids. In existing fields, the returns may be combined with the produced water, processed through the treating system, and discharged. In the coastal region, they are injected underground.

Fate in the Marine Environment

Many components of completion, stimulation, and workover chemicals are either acids or salt solutions. The acids rapidly react with the seawater environment and become part of the natural constituents of seawater. Some salts, such as those containing calcium, zinc, and other reactive ions, also react with the constituents of seawater and become solids. These solids will initially be suspended in the water column and eventually become part of the sediment. Some components of this class of chemical are solid materials used as proppants or as gravel-pack. These materials are inert solids and will end up in the sediment.

Inorganic acids discharged to the marine environment will react with the carbonate equilibrium system. The reaction produces salts such as sodium chloride and sodium fluoride and carbon dioxide. The salts are natural constituents of seawater; the carbon dioxide goes into the atmosphere. The organic completion, stimulation, and workover chemicals will initially spread through the water column as dissolved material and will eventually biologically degrade.

2.2.3.2 Completion, Stimulation, and Workover Chemicals Inventory

Once the need for completion, stimulation, and workover chemicals is specified, the fluid components are either pre-formulated and transported to the offshore site or transported as components and prepared on-site. World Oil published separate articles on acidizing and fracturing in 1999. This report has adopted the division of fracturing chemicals into 22 functional categories, proppants in two categories, and acidizing chemicals into 28 functional categories.

Table 3 summarizes the functional inventory of completion, stimulation, and workover chemicals likely to be found in the GOM. It also lists and defines each of the completion, stimulation, and workover chemical categories and shows examples of chemicals included in each category.

Table 3
Completion, Stimulation, and Workover Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used

Code	Functional Categories	Description	Material Types Used
A-WBC	Water-based completion fluid	Brine solutions and surfactants for cleaning wells	See inventory for example products (e.g., MudClean OB, Wellwash-1000)
A-WBP	Water-based polymers	Used for adjusting viscosity	Xanthate, modified natural polymers
A-FR	Friction reducers	Used for decreasing resistance to flow	Anionic polyacrylamides, cationic polyacrylamides
A-FL	Fluid loss	Used for reducing loss of fluid to the formation	Graded silica flour, oil soluble resins, benzoic acid
A-DA	Diverting agents	Used to divert acid from high permeable formations to lower permeability formations	Graded rock salt, flake benzoic acid, graded oil soluble resin, oil soluble graded naphthalene
A-PP	Polymer plugs	Used similarly to diverting agents	Guar or hydroxypropylguar, hydorxyethylcellulose, crosslinked hydroxypropylguar
A-AI	Acid inhibitors	Used to keep acid from corroding steel	Propargyl alcohol, ethyl octynol, acetaldehyde, crotonaldehyde, quaternary ammonium salts
A-AR	Acid retarders	Used to slow the reaction of acid with the material being removed. Needed to spread the action of the acid deeper into the formation.	Oil wetting surfactants
A-E	Emulsifiers	Used to create emulsified acid mixtures	See inventory for example products (e.g., Nowferr 5, Claymaster 5C)
A-CS	Clay stabilizers	Used to protect integrity of formation clays	Alkyl quaternary ammonium compounds, ammonium chloride, potassium chloride
A-S	Surfactants	Used to clean surfaces being acidized	See inventory for example products (e.g., SuperFlow III, FC-100)
A-NE	Non-emulsifiers	Wetting agents that do not promote emulsification	See inventory for example products (e.g., AquaFlow, LoSurt 259)
A-FS	Fines suspender	Used to disperse fine solids in acidizing fluids	See inventory for example products (e.g., ST 100, SSO-21M)
A-ESA	Anti-sludge agent	Used to prevent the formation of emulsions	Dodecylbenzene sulfonic acid
A-F	Foamers	Used to develop light weight mixtures	See inventory for example products (e.g., FAW-18W, F100)
A-SI	Scale inhibitors	Used to prevent the formation of inorganic scales	See inventory for example products (e.g., L35, Corexit-7647)
A-IC	Iron (Fe) control	Used to complex iron three and prevent re-precipitation in the formation	Organic acids, EDTA

Table 3
Completion, Stimulation, and Workover Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used (continued)

Code	Functional Categories	Description	Material Types Used
A-OS	Oxygen scavenger	Used to remove oxygen from acidizing fluids and control oxygen corrosion	Bisulfites
A-MS	Mutual solvents	Used to control the formation of water in oil emulsions	Ethylene glycol monobutyl ether (EGMBE)
A-CI	Corrosion inhibitors	Used to control corrosion due to oxygen, carbon dioxide and hydrogen sulfide	Ammonium bisulfite, aldehydes
A-PC	Paraffin control	Used to control solid paraffin deposition	See inventory for example products (e.g., P800, Paratrol 30)
A-MP	Miscellaneous products	Special products from all areas not otherwise categorized	See inventory for example products (e.g., Ammonium Biofluoride, HCl)
A-AS	Acid systems	Basic acid types used	Hydrochloric acid, hydrofluoric acid, organic acids with various additives
A-RAS	Retarded acid plus	Mixtures of mineral acids and organic acids and other specialty acid mixes with slower reaction rates	Mixtures of inorganic and organic acids or inorganic acids and gelling agents
A-MAP	Mud acid plus surfactants	Special acid formulations for removing residual drilling fluids and clay	See inventory for example products (e.g., Available, Special Custom Blend)
A-MAA	Mud acid plus alcohol	Gas well acidizing, low surface tension, fluid clean up	See inventory for example products (e.g., Gas Well Mud Acid, Custom Formulated)
A-RHF	Retarded HF	Generates mud acid (HF) in the formation	See inventory for example products (e.g., Fluorbonic Acid, Clay Acid)
F-WBP	Water-based polymers	Natural and manufactured polymers for increasing viscosity in fracturing fluids	Guar gum, hydroxypropyl guar, hydroxyethyl cellulose
F-FR	Friction reducers	Used to reduce resistance to flow	Anionic polyacrylamides, cationic polyacrylamides
F-FLA	Fluid loss additives (FLAs)	Insoluble solids used to stop loss of fluids to the formation	Graded silica flour, oil soluble resins, benzoic acid
F-B	Breakers	Used to reduce viscosity in polymer solutions	See inventory for example products (e.g., Enzyme G, AP breaker)
F-E	Emulsifiers	Used to stabilize emulsions of multiphase fluids	See inventory for example products (e.g., PS-3, SEM-5)
F-CS	Clay stabilizers	Used to reduce clay swelling and resulting damage to formations	Alkyl quaternary ammonium compounds, ammonium chloride, potassium chloride
F-S	Surfactants	Used as wetting agents and cleaners	See inventory for example products (e.g., WS-70, InFlo 150)

Table 3
Completion, Stimulation, and Workover Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used (continued)

Code	Functional Categories	Description	Material Types Used
F-NE	Non-emulsifiers	Wetting agents that do not promote emulsification	See inventory for example products (e.g., AquaFlow, LOSURF 300)
F-PCA	pH control additives	Used to adjust the pH of fluids	Caustic soda, sodium carbonate, ammonium hydroxide, organic acids, sodium acetate, sulfamic acid
F-C	Crosslinkers	Metal compounds used to enhance polymer performance by crosslinking of polymers.	See inventory for example products (e.g., Delay, Sodium Borate)
F-F	Foamers	Used to create low density foam fluids	See inventory for example products (e.g., S-400, WF-1)
F-GS	Gel stabilizers	Used to give stability to polymers in high temperatures	Methanol. See inventory for other example products
F-D	Defoamers	Used to control foam in fluids	See inventory for example products (e.g., Defoamer, AFA-3)
F-OGA	Oil gelling additives	Gelling agents for oil-based fluids	See inventory for example products (e.g., OG-14 Gellant, J601)
F-BC	Biocides	Used to control bacterial degradation of polymers	Aldehydes
F-ABG	Acid-based gel systems	Specialty gel system used in fracturing operations. Preformulated mixture	See inventory for example products (e.g., XLA-3)
F-WBG	Water-based systems	Specialty gel system used in fracturing operations. Preformulated mixture	See inventory for example products (e.g., AquaFrac, Gelled Water)
F-CGS	Crosslinked gel systems	Specialty gel system used in fracturing operations. Preformulated mixture	See inventory for example products (e.g., Saturn I, Vicking D)
F-AWS	Alcohol/water systems	Specialty gel system used in fracturing operations. Preformulated mixture	See inventory for example products (e.g., Binary Foam, Crosslinked)
F-OBS	Oil-based systems	Specialty gel system used in fracturing operations. Preformulated mixture	See inventory for example products (e.g., Sandoil, Super Rheo Gel)
F-PP	Polymer plugs	Used to stop loss of fluid to formation fractures	Guar, hydroxypropylguar, hydoxyethylcellulose
F-CMG	Continuous mix gel concentrates	Specialty gel system used in fracturing operations. Preformulated mixture	See inventory for example products (e.g., LGC-1, XLFC-3)
F-RCP	Resin-coated proppants	Proppants for holding formation cracks open	See inventory for example products (e.g., SUPER-WEL-Frac)
F-IHC	Intermediate-to-high-strength ceramic proppants	Proppants for holding formation cracks open	See inventory for example products (e.g., MIGHTY-PAC, Z-PROP)

2.3 Chemicals Applied to Production Processing Systems

2.3.1 Overview

While drilling fluid chemicals, cementing chemicals and completion, stimulation, and workover chemicals are applied to wells, production-treating chemicals are applied to production processing systems. Chemicals applied to wells are used in large amounts over a short period of time (e.g., tons of drilling chemical are used for each well and a well is drilled in 70 to 90 days). Production-treating chemicals are used in moderate amounts over most of the life of a field (e.g., one to 10 gal. is used daily for years at a time). For drilling fluid, cementing, completion, stimulation, and workover chemicals, a single formulation is used on each well and that formulation is made on site from components transported to the offshore site. Production-treating formulations, on the other hand, are prepared at supplier facilities and transported as formulated products to the offshore site.

Wells drilled into hydrocarbon-bearing reservoirs produce a mixture of gas, liquid hydrocarbons, water, and dispersed solids. The exact composition of the produced stream depends on such factors as:

- Type of production (i.e., oil, gas, or both)
- Properties of the oil produced (e.g., paraffinic crude, asphaltic crude, condensate)
- Age of the field (i.e., the life cycle stage of the reservoir)
- Source of energy driving the reservoir (e.g., water-driven, gas-driven)
- Lifting method (e.g., free flowing, gas lift, submersible pump)

As the material is removed from the formation, it may be necessary to use chemicals to perform or facilitate the performance of one or more of the following production operations:

- Protecting downhole and surface equipment from corrosion
- Protecting downhole and surface equipment from mineral scale deposits
- Protecting gathering lines and process equipment from gas hydrates
- Separating the phases
  - Cleaning and stabilizing the gas and oil for sales
  - Cleaning produced water for disposal
- Processing water for waterflooding
- Protecting against foaming in gas liquid separations
- Removing oxygen
- Preventing or removing paraffin (solid hydrocarbon) deposits

Chemicals are an essential part of several of these operations. Published studies in the 1980s culminate with a definitive explanation of the use of chemical production and exploration operations (Hudgins and Petrotech Consultants, Inc. 1991). There are 14 functional categories of production-treating chemicals in use in the GOM. In each of these functional categories, generally several generic classes of chemicals possess the required properties.

- Biocides
- Corrosion inhibitors
- Scale inhibitors
- Emulsion breakers
- Reverse breakers
- Antifoam
- Coagulants, flocculants
- Surfactants
- Paraffin treating chemicals
- Solvents and additives
- Oxygen scavenger
- Hydration inhibition chemicals
- Dehydration chemicals
- Sweetening chemicals

Drivers for Production-treating Chemical Use

Activities that must be performed during production operations that trigger the use of chemicals can be subdivided into:

- Separating of phases (to clean oil or gas for sale, to clean water for disposal, to prevent foaming in oil/gas separation)
- Preventing of corrosion
- Preventing of solid deposition (water-formed scales, paraffin or asphaltenes, gas hydrates)
- Controlling of bacterial growth

The scope of these activities depends on several factors, including:

- Type of production (oil or gas)
- Type of oil produced (paraffinic or asphaltic)
- Viscosity and gravity of the oil produced
- Composition and salinity of the water being produced
- Presence and level of hydrogen sulfide and carbon dioxide in the gas produced
- Relative rates of oil and water production

For example, asphaltic oils require more emulsion breaker for separation and, for all oils, the higher the density the more emulsion breaker required. The higher the carbon dioxide and hydrogen sulfide content of the produced fluids, the more corrosion inhibitor required.

The stage in the field’s life cycle has an effect on the level of chemical treatment. For example, exploration and development stages use little production-treating chemicals. As the field enters the long period of active production (e.g., five years), chemical treating becomes increasingly important. Early in the life of a field, little water is produced and emulsion problems are minimal, especially if the produced oil is hot. In these early stages, even when produced water is corrosive, corrosion inhibitor is typically not required as the produced stream is likely to oil external. As the field ages, water production will increase and oil production will decrease. If the reservoir is waterflooded, the produced stream will begin to cool. All these changes directly increase the need for emulsion breakers, water clarifiers, and corrosion inhibitors. Waterflooding can also increase the need for scale inhibitors.

One large supplier interviewed for this study summarized his company's experience in the GOM with the following general comments concerning production chemical use.

a) Defoamers are used almost exclusively in new deepwater production.
b) Asphaltene inhibitor usage is limited to new deepwater production.
c) About 95% to 100% of platforms that discharge water use water clarifiers.
d) Demulsifiers are used on 70% to 80% of oil platforms.
e) Subsea wells have not proven to be corrosive and most are not treated with corrosion inhibitors.
f) H_2S scavengers are used predominantly in the Mobile Bay and Texas Gulf areas.
g) From 80% to 85% of paraffin inhibition is used for preventing deposition in pipelines or subsea flowlines. Surface flowlines present minimal problems.
h) From 70% to 90% of corrosion inhibitor is for flowlines and pipelines rather than downhole tubulars.

Application

Applications of production-treating chemicals are made in one of three ways (Hudgins and Petrotech Consultants, Inc. 1991):

- Continuous injection at low rates at appropriate points in the process piping or downhole in producing wells
- Batch applications of high concentrations to wells or process equipment
- Squeeze treatments

Squeeze treatments use discrete volumes of high concentrations injected into the formation surrounding a wellbore so that the chemical can adsorb or precipitate in the formation and re-dissolve over a period of time. This procedure allows the placement of a volume of chemical that can provide a relatively continuous treatment concentration as it desorbs and enters the produced stream. This type of application procedure is necessary when continuous treatment of produced streams is needed at the bottom of a well where continuous injection is impractical. Figure 6 shows a generic treating system. Chemicals are injected upstream of the vessels where their function is needed. For example, emulsion breaker is added upstream of separators; water-treating chemical is added upstream of water-treating processes.

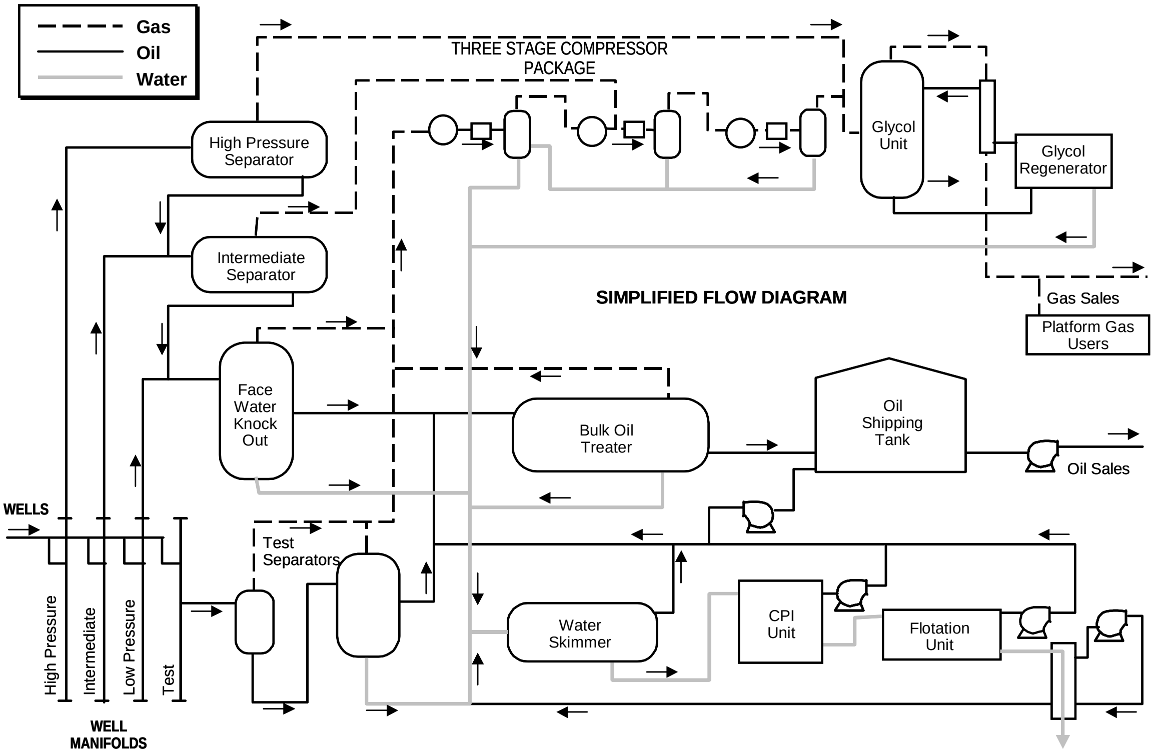


Figure 6. Simplified Typical Oilfield Process Diagram for an Offshore Platform. (Source: Hudgins and Petrotech Consultants, Inc. 1991)

Production-treating chemicals are shipped offshore on a regular basis to the platform. Continuous applications are administered using small pumps that inject chemicals at low rates into a flowline at an appropriate point. Chemicals are pumped directly from the tank they were shipped in or from a permanent bulk tank. Application rates are determined by on-site testing and usually conducted by a supplier's representative. The supplier representative is also frequently responsible for monitoring the chemical's performance. Platform operators provide daily checks on the functioning of the injection system and the status of the chemical reservoirs. Batch treatment and squeeze treatments are usually performed by a supplier's specialist who typically visits the platform to supervise and administer the chemicals required.

Characterization

Production-treating chemicals are normally supplied as liquid solutions and are either pure chemical (e.g. methanol, glycols) or complex mixtures. In general, complex mixtures consist of:

- A solvent carrier
- One or more active ingredients
- Secondary ingredients, or "helpers"

The solvent may be water-soluble or oil-soluble, depending on the phase it is meant to treat. The solvent aids in rapid dispersion of the active ingredient(s) into the production stream.

Active ingredients provide the primary function(s). Sometimes there may be only one active ingredient (e.g. sodium bisulfite). In other formulations, two or more active ingredients may be combined to produce the desired effect (e.g. quaternary ammonium compound and amides/imidazolines are both active in some water-based corrosion inhibitors). The secondary ingredients or helpers are used to solve stability or applications problems. For example, mutual solvents may be added to a product stream so that the active ingredient will stay in solution at lower temperatures. Another example of a secondary ingredient function is the use of wetting agents and surfactants in corrosion inhibitors, which enable the active ingredient to reach the surface of the steel it is meant to protect. Ethoxylated nonylphenol, a corrosion inhibitor component performs this function and is further addressed in Sections 7.0 and 8.0.

Production-treating chemicals are frequently proprietary products. To be most effective formulations are tailored to the needs of a particular site. Therefore, the same basic formulation may actually be supplied in several variations and sold under different product names. Gulf of Mexico chemical suppliers agreed to provide, on condition of anonymity, detailed information on three products used in the spill model scenarios. Compositions for these chemicals are shown in Section 7.0 as Product A, a water-soluble/dispersible corrosion inhibitor, Product B, an oil-soluble corrosion inhibitor, and Product C, an oil-soluble emulsion breaker.

Fate in the Process System

A production-treating chemical's fate depends on which phase it was designed to treat and its physical state and properties. Possible fates include:

- Leaving the production-treating system as waste in produced water (water clarifiers or flocculants)
- Being lost to the formation (biocides in waterflood water)
- Leaving the production-treating system as part of vessel bottom waste (emulsion breaker in oil adsorbed to solids)
- Being consumed in chemical reactions within the system (oxygen scavenger)
- Leaving the production-treating system as part of the sales oil and gas (organic solvents and emulsion breakers)

Fate in the Marine Environment

In the marine environment, the fate of production-treating chemical components include:

- Biological degradation of organic materials
- Chemical reaction
- Dilution to background concentrations

Organic components range from simple molecules, like methanol, to very complex ones, like amides/imidazolines. Simple chemicals, such as methanol and ethylene glycol, are used in the highest volumes. These chemicals typically partition between the gas, hydrocarbon liquid, and water phases. While more than half of these chemicals partition into the water phase and are disposed of with the water, making them one of the highest volume discharges of production-treating chemicals, these chemicals can also be recovered from the gas stream and recycled. The more complex organic molecules are usually highly surface active and are used in very low concentrations. The water-insoluble molecules tend to adsorb on solids or disperse as droplets. These phases tend to increase surface-to-volume ratios and, therefore, also increase potential biological degradation rates.

Inorganic components such as oxygen scavengers and water-treating agents used to create flocs are subject to chemical reaction. Residual sodium bisulfite, an oxygen scavenger, reacts with oxygen in the sea to form sodium ions and sulfate ions. Both these ions are natural constituents of seawater. Aluminum ions in water clarifiers will complex with seawater constituents to form solids and are eventually removed to the sediment.

2.3.2 Production-treating Chemicals

Production-treating chemicals can be classified into 14 functional categories. Table 4 lists these categories, describes the function of each, and shows some of the generic types of chemical used in each. An inventory of products identified for this project is provided in Appendix A.

Table 4

Production-treating Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used

Code	Functional Category	Description	Material Types Used
P-B	Biocides	Chemicals used to control the growth of bacteria that can generate hydrogen sulfide and cause corrosion and bacteria that produce slime and biomass.	Quaternary amine salt and amine acetate, aldehydes, THPS, sodium hypochlorite, other
P-CI	Corrosion inhibitors	Used to prevent or minimize internal corrosion in offshore production systems.	Amides/Imidazolines, amines and amines salts, quaternary ammonium salts, nitrogen heterocyclics
P-SI	Scale inhibitors	Used to prevent water-formed scales (calcium carbonate, barium sulfate, and strontium sulfate).	Phosphate esters, phosphonates, and polymers
P-EB	Emulsion breakers	Used to de-stabilize water in oil emulsions to make oil saleable.	Oxyalkylated resins, polyglycol esters, alkyl aryl sulfonates
P-RB	Reverse breakers	Used to de-stabilize oil in water dispersions and facilitate gravity separation. Used to reduce the interface tension, allowing the oil droplets to coalesce into large drops.	Polyamines, polyamine quaternary compounds
P-A	Antifoam	Used to de-stabilize foam in the separation of gas and liquids in separators. Used to reduce foaming of water during de-oxygenation for waterfloods.	Silicones, polyglycol esters

Table 4
Production-treating Chemicals: Codes, Functional Categories, Descriptions, and Material Types Used (continued)

Code	Functional Category	Description	Material Types Used
P-CF	Coagulants, flocculants	Used to make small solids agglomerate so that they can be separated by filtration or flotation. Applied to the removal of solids from injection water and to improve oil removal for overboard discharge.	Aluminum sulfate, other metal compounds, polymeric amides
P-S	Surfactants	Used to remove small amounts of oil or grease from the platform and/or equipment.	Alkyl aryl sulfonates, ethoxylated alkyl phenols
P-TC	Paraffin treating chemicals	Used to prevent solid organic deposits from depositing on the walls of the piping and equipment. Also includes solvents for removing such deposits.	Hydrocarbon polymers, solvents
P-SA	Solvents and additives	Used as carriers in the various chemical formulations. Hydrocarbon solvents are used for those chemicals meant to reach the oil phase. Alcohols and glycols are used as mutual solvents in both water-soluble and oil-soluble formulations.	Naphtha, light aromatic naphtha, heavy aromatic naphtha, kerosene, ethylene glycol, other low molecular weight glycols, methanol, isopropanol
P-OS	Oxygen scavenger	Used to remove oxygen from waterflood water.	Sodium bisulfite, ammonium bisulfite
P-HIC	Hydrate inhibition chemicals	Used to control the formation of gas hydrates in gathering piping systems.	Methanol, ethylene glycol
P-DC	Dehydration chemicals	Used to remove water vapor from natural gas.	Triethylene glycol
P-SC	Sweetening chemicals	Used to remove carbon dioxide and hydrogen sulfide from natural gas.	Proprietary products; the most common systems are monoethanolamine (MEA) or diethanolamine (DEA)

3.0 CHEMICAL USAGE

3.1 Introduction

Models were developed for offshore E&P operations to estimate the volume of chemical transported, stored, and expected to be used at any one time in the Gulf of Mexico (GOM). Since MMS anticipates more extensive and frequent use of these chemicals to enhance throughput of the oil and gas in deep water, these models are likely to contribute to a realistic evaluation of potential environmental impacts.

These models were developed as follows:

1. Data was provided by three major operators in the GOM and their chemical suppliers (total of eight).

2. The data was unitized to yield average volumes or concentrations for each operational unit (well or production amount).

3. The unitized data were multiplied by the corresponding number of wells or fluid production data to extrapolate total volume estimates for the entire GOM.

For this report we used a small, but representative subset of chemical usage data from 1998 obtained from three operators and their chemical suppliers. Once unitized, these data were extrapolated to total GOM usage volume estimates for 1998 for each chemical class and functional category. Given future information on the number of wells, types of wells, well depth, water depth and production data these models can be used to extrapolate (i.e., from the unitized data) the total volumes of a chemical(s) used in the GOM in any year or, if needed, on a project-specific basis for any number of wells to be drilled or quantity of fluid produced. Economic factors are incorporated into the projected number of wells and operations and thus into the model.

Separate models were developed for drilling fluid chemicals, cementing chemicals, completion stimulation and workover chemicals, and production-treating chemicals to account for the variability in the factors that affect chemical use in each of these categories. For example, the volume of cementing chemicals used is primarily a function of the number of wells drilled and the depth of the well, whereas the volume of production-treating chemicals is a function of the produced stream type, the operation that needs to be performed (e.g. emulsion breaking), and the length of time for the operation.

Specifics regarding the underlying data, model assumptions, and limitations, along with estimated volumes, are described in each of the following subsections.

3.2 Model Results

3.2.1 Drilling Fluid Chemicals Volume Estimates

The amount of drilling fluid chemicals applied to a well is primarily a function of well depth, though this relationship is neither simple nor linear. Factors such as the uniformity of the well diameter, a fluctuating application rate, and the occasional necessity of sidetracks and other drilling-related problems all factor into the final usage volume.

Drilling Fluid Chemicals: Subcategories

To generate drilling fluid volumes using the model, fluid use per unit well is needed. Since this is a function of the changing geometry of the bore hole and the depth of the well, information collected on drilling fluid chemicals was divided into five categories of well depth intervals. These intervals were determined from an analysis of drilling operation data received from an operator and discussions with chemical suppliers and other operators.

Location	Well Depth	Water Depth
Shelf (shallow water)	< 5,000 ft.	< 1,000 ft.
Shelf (shallow water)	5,000 – 10,000 ft.	< 1,000 ft.
Shelf (shallow water)	> 10,000 ft.	< 1,000 ft.
Deep water	> 10,000 ft.	< 4,000 ft. *
Deep water	> 10,000 ft.	> 4,000 ft. *

* This is a differentiation in water depth, not well depth. Nearly all wells in deep water are drilled to depths of 10,000 ft. or greater, but differences in drilling technology used in waters greater than 4,000 ft. require separate categories.

Drilling Fluid Chemicals: Data Sources

The base data for the model are derived from chemical usage data for 58 wells drilled in the GOM during 1998. A chart depicting the distribution of these wells across the selected intervals is shown in Figure 7. The types and amount of drilling fluid chemicals for these wells were supplied by three chemical suppliers who provided (i.e., by functional group) the quantity of drilling fluid chemicals used for each operation.

Using these data, the per operation (average) quantities of chemical for each category were calculated. These per operation volumes are shown in Table 5. The list of chemicals in Table 5 is not a mud formulation; rather, it is a list of all drilling fluid components and additives applied to the wells listed above for all types of drilling mud formulations.

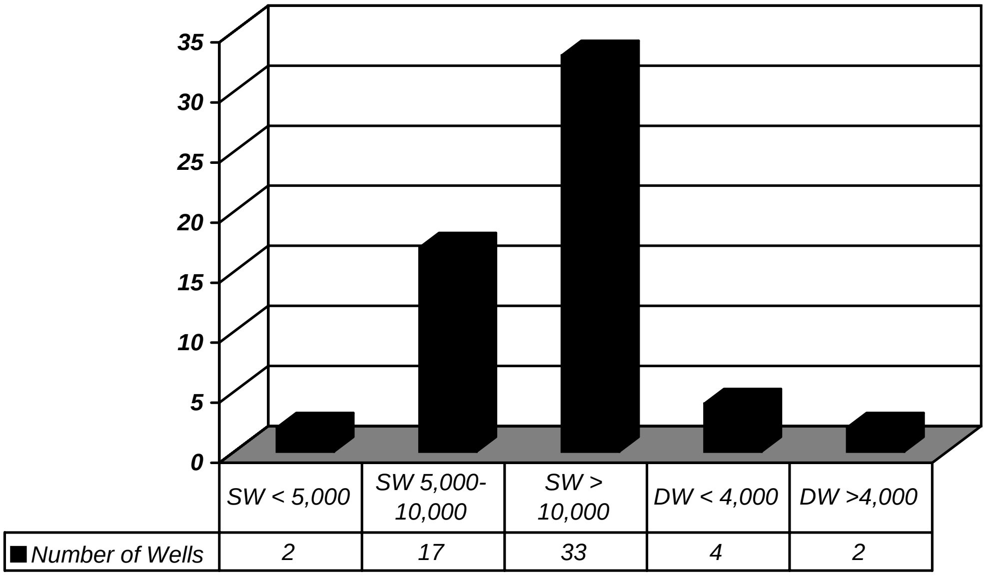


Figure 7. Number of Wells Drilled by One Operator in 1998. (Source: Operator Data)

Drilling Fluid Chemical: Volume Estimates

To estimate or extrapolate the total volume of drilling fluid chemicals used in the GOM we multiplied the total volumes of drilling fluid chemicals in 1998, using information obtained from MMS's Fast Fact database by the number of wells drilled in the GOM for each depth interval. These data include all wells spudded in 1998, regardless of whether or not they were completed in 1998. The distribution of these wells by depth interval is in Figure 8. Given production data for future years or projects, an individual could extrapolate the total volume of chemical usage for any year or proposed activity. Volume and storage estimates of drilling fluid chemicals are found in Tables 5 and 6, respectively.

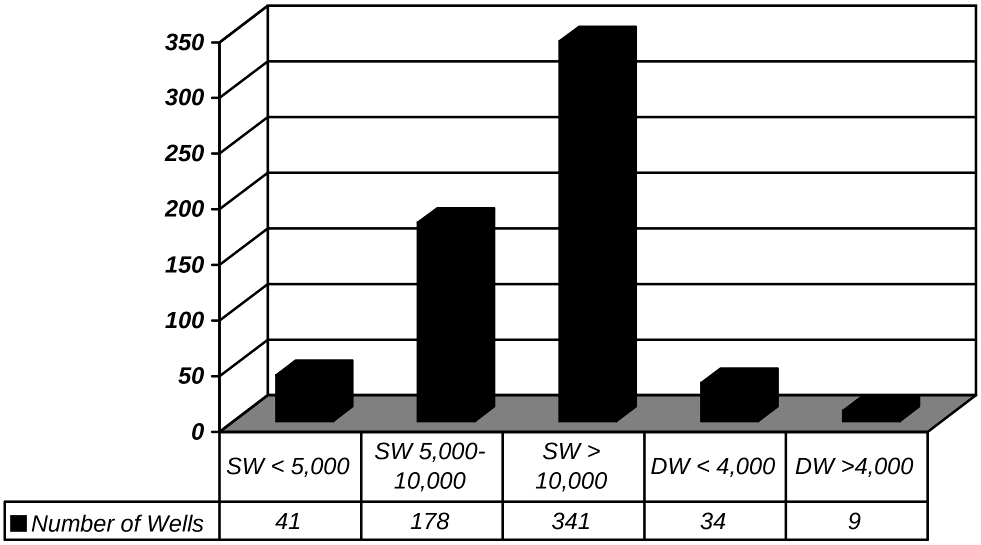


Figure 8. Total Number of Wells Drilled in the Gulf of Mexico in 1998. (Source: MMS Fast Facts Database 1998)

Table 5
Volume Estimates for Drilling Fluid Chemicals Used in the Gulf of Mexico

	Shallow Water Wells by Well Depth							Deep-water Wells by Water Depth				
Functional Categories	Wells 0-5,000 ft.		Wells 5,000 - 10,000 ft.		Wells > 10,000 ft.		Shallow Water Wells Total(s)	Water Depth < 4,000 ft.		Water Depth > 4,000 ft.		Deep-water Wells Total(s)
Wells by Depth	Total wells =	**41**	Total wells =	**178**	Total wells =	**340**	**559**	Total wells =	**34**	Total wells =	**9**	**43**
	Average Used (1)	Total	Average Used (1)	Total	Average Used (1)	Total	Total(s)	Average Used (1)	Total	Average Used (1)	Total	Total(s)
Weighting materials, lbs. Barite, iron oxides, calcium carbonates, etc	**61,200**	2,510,000	**282,000**	50,200,000	**803,000**	273,000,000	**326,000,000**	**10,100,000**	344,000,000	**3,100,000**	27,900,000	**372,000,000**
Viscosifiers - Clays, lbs.	**12,800**	525,000	**64,700**	11,500,000	**100,000**	34,00,000	**46,000,000**	**301,000**	10,200,000	**304,000**	2,740,000	**13,000,000**
Viscosifiers - Polymers, lbs.	**338**	13,800	**1,630**	291,000	**696**	237,000	**541,000**	**2,500**	85,000	**12,600**	113,000	**198,000**
Thinners, dispersants, and Temperature stability agents(2), lbs. Tannins & modified tannins (DESCO), lignosulfonate, lignite, polyphosphates	**3,270**	134,000	**12,800**	2,290,000	**18,900**	6,430,000	**8,850,000**	**145,000**	4,920,000	**5,000**	45,000	**4,960,000**
Filtrate reducers (solid), lbs. Clays, lignite, polymers, etc	**4,830**	198,000	**5,990**	1,070,000	**18,900**	6,430,000	**7,700,000**	**148,000**	5,040,000	**55,600**	500,000	**5,540,000**
Filtrate reducers (liquid), gal. Clays, lignite, polymers, etc	**-**	-	-	-	-	-	**-**	**-**	-	**345**	3,100	**3,100**
Alkalinity, pH control additives, & Calcium reducers(2), lbs. Lime, carbonate salts and certain polyphosphates	**4,500**	184,000	**9,900**	1,760,000	**33,100**	11,200,000	**13,200,000**	**124,000**	4,222,000	**43,700**	393,000	**4,620,000**
Lost circulation materials, lbs. Insoluble particulate matter	**5,740**	235,000	**22,300**	3,970,000	**21,900**	7,460,000	**11,700,000**	**93,200**	3,170,000	**246,000**	2,210,000	**5,380,000**
Lubricants, gal. Oils, synthetic liquids, graphite surfactants, glycols & glycerin	**-**	-	**625**	111,000	**212**	71,900	**183,000**	**-**	-	**-**	-	**-**

Table 5

Volume Estimates for Drilling Fluid Chemicals Used in the Gulf of Mexico (continued)

	Shallow Water Wells by Well Depth							Deep-water Wells by Water Depth				
Functional Categories	**Wells 0-5,000 ft.**		**Wells 5,000 - 10,000 ft.**		**Wells > 10,000 ft.**		**Shallow Water Wells Total(s)**	**Water Depth < 4,000 ft.**		**Water Depth > 4,000 ft.**		**Deep-water Wells Total(s)**
Wells by Depth	Total wells =	**41**	Total wells =	**178**	Total wells =	**340**	**559**	Total wells =	**34**	Total wells =	**9**	**43**
	Average Used [(1)]	**Total**	**Average Used [(1)]**	**Total**	**Average Used [(1)]**	**Total**	**Total(s)**	**Average Used [(1)]**	**Total**	**Average Used [(1)]**	**Total**	**Total(s)**
Shale control inhibitors (liq), gal.	**-**	-	**3,700**	658,000	**1,630**	554,000	**1,210,000**	**22,400**	763,000	**-**	-	**763,000**
Shale control inhibitors (solid), lbs. Inorganic salts & organics	**-**	-	**8,520**	1,520,000	**15,100**	5,140,000	**6,660,000**	**281,000**	9,550,000	**494,000**	4,450,000	**14,000,000**
Emulsifiers & Surface active agents[2], gal.	**-**	**-**	**16**	2,880	**433**	147,000	**150,000**	**50**	1,700	**-**	-	**1,700**
Minor Additives:												
Bactericides, gal.	**-**	-	**-**	-	**3**	850	**850**	**-**	-	**-**	-	**-**
Defoamers, gal.	**10**	410	**24**	4,190	**37**	12,400	**17,000**	**3,480**	118,000	**448**	4,030	**123,000**
Scale Inhibitors, gal.	**-**	-	**-**	-	**2**	584	**584**	**-**	-	**-**	-	**-**
						Total Solids (lbs.)	**420,000,000**				**Total Solids (lbs.)**	**419,000,000**
						Total Liquids (gal.)	**1,560,000**				**Total Liquids (gal.)**	**890,000**

Notes:

(1) These quantities were calculated using MMS data on number of wells drilled, and data on chemicals used by one company and its suppliers to drill their wells. Wells were subdivided into categories for projection purposes and data from each category was used to project data for wells of that category.

(2) These classes of materials are combined because they use similar or identical types of chemicals.

Table 6

Storage Volumes of Drilling Fluid Chemicals Used in the Gulf of Mexico

	Volumes Stored Offshore		
Functional Categories	**Average**	**Maximum**	**Median (1)**
Weighting materials, lbs Barite, iron oxides, calcium carbonates, etc.	1,340,000	15,600,000 (2)	296,000
Viscosifiers			
Clays, lbs	103,000	403,000	50,000
Polymers, lbs	1,490	15,000	288
Thinners, dispersants, and Temperature stability agents, lbs. Tannins & modified tannins (DESCO), lignosulfonate, lignite, polyphosphates	24,500	196,000	6,880
Flitrate reducers (solid), lbs	24,100	166,000	5,350
Flitrate reducers (liquid), gals	12	690	0
Clays, lignite, polymers, etc.			
Alkalinity, pH control additives, & Calcium reducers, lbs Lime, carbonate salts and certain polyphosphates	31,500	286,000	11,900
Lost circulation materials, lbs Insoluble particulate matter	33,900	412,000	13,900
Lubricants, gal Oils, synthetic liquids, graphite surfactants, glycols & glycerin	305	3,850	0
Shale control inhibitors (liq), gal	3,880	49,500	0
Shale control inhibitors (solid), lbs	47,200	510,000	0
Inorganic salts & organics			
Emulsifiers & Surface active agents, gal	247	7,260	0
Minor Additives:			
Bactericides, gal	1	80	0
Defoamers, gal	283	11,000	0
Scale Inhibitors, gal	1	55	0

Notes:

(1) Median is the number in the middle of the set of numbers. The number zero in the median column indicates that chemicals were not used for a majority of the wells in the study as provided by the GOM operator.

(2) This value represents the total volume needed to drill the well and was assumed to be the amount stored on-site and a conservative estimate eof the spill volume. However, the known storage capacity for barite and cement is 30,000 cubic ft. or 8.4 million lbs. on the Diamond Offshore rig Ocean Confidence.

3.2.2 Cementing Chemicals Volume Estimates

Similar to drilling fluids, the amount of cementing chemicals applied per well is primarily a function of well depth. Unlike drilling fluid chemicals, cements are used in discrete units each time a section of casing is added. Such factors as sidetracks do not add to the volume used as they do for drilling fluid chemicals.

Cementing Chemicals: Subcategories

Based on an analysis of the cementing operation data received from the operator and discussions with chemical suppliers and operators, cementing chemical usage can also be further sub-divided by well and water depth. The four categories that correspond to the depth intervals defined for drilling fluid chemicals. The water-depth related drilling issues that necessitated the two additional deepwater categories do not affect cementing chemicals.

Location	Well Depth	Water Depth
Shelf	< 5,000 ft.	< 1,000 ft.
Shelf	5,000 – 10,000 ft.	< 1,000 ft.
Shelf	> 10,000 ft.	< 1,000 ft.
Deep water	> 10,000 ft.	> 1,000 ft.

Cementing Chemicals: Data Sources

Data on the volume of cementing chemicals were provided by one operator. These data were not extensive enough to be representative of the entire GOM; therefore, the information was augmented with data from two of the operator’s chemical suppliers. Based on historical use patterns for these chemicals, the suppliers provided the average quantities of each functional chemical class used to complete a cementing job in each of the well depth intervals. Along with these data, cementing chemical formulations were provided, and these formulations were recommended as representative of all wells cemented in each well depth interval. These data provided the volumes of chemical per well for each of the depth categories.

Cementing Chemicals: Volume Estimates

The number of wells cemented in 1998 in the GOM was assumed to be the same as the number of wells drilled. Multiplying the average cementing compositions for each category by the number of wells drilled in each category yields an estimate of the total cementing chemicals used in the GOM for 1998. By replacing the number of wells with future projections, new volumes can be generated. The 1998 volume estimates are shown in Table 7.

Typical volumes used and stored at a specific site can also be found in Table 7. In this case, the single well formulations represent typical amounts stored. Using this table it can be determined that the maximum quantity likely to be found offshore at any one site is 430,000 lbs. **(**basic cements**)** for a well drilled to a depth > 10,000 ft.

Table 7
Volume Estimates for Cementing Chemicals Used in the Gulf of Mexico

Wells Drilled in 1998[2]	Shallow Wells							Deepwater Wells		Total Wells = 602
	0-5,000 ft. Total Wells = **41**		5,000-10,000 ft. Total Wells = **178**		>10,000 ft. Total Wells = **340**			All Water depths Total Wells = **43**		
Functional Categories/Components [3]	**Average Used[1] (lbs)**	**Total Weight, lbs**	**Average Used[1] (lbs)**	**Total Weight, lbs**	**Average Used[1] (lbs)**	**Total Weight, lbs**	**Shallow Wells Total (lbs)**	**Average Used[1] (lbs)**	**Deep Wells Total (lbs)**	**Grand Total (lbs)**
Basic Cements	181,700	7,450,000	278,000	49,500,000	430,000	146,000,000	203,000,000	430,000	18,500,000	222,000,000
Accelerators & salts[4]	985	40,400	985	175,000	1,410	479,000	695,000	1,410	60,600	756,000
Extenders & density- reducing additives	4,575	188,000	4,580	814,000	8,500	2,890,000	3,890,000	8,500	365,000	4,260,000
Free water control and solids suspending agents	0	0	160	28,500	230	78,200	107,000	230	9,890	117,000
Dispersants	114	4,660	569	101,000	963	327,000	433,000	963	41,400	475,000
Bond improving and expanding additives	643	26,400	643	115,000	643	219,000	360,000	643	27,700	387,000
Fluid-loss control additives	610	25,000	913	162,000	1,050	356,000	544,000	1,050	45,000	589,000
Silica to reduce or prevent high temperature strength retrogression	0	0	0	0	41,400	14,100,000	14,100,000	41,400	1,780,000	15,800,000
Retarder	0	0	255	45,400	588	200,000	245,000	588	25,300	270,000
Anti-gas migration agents	275	11,300	275	49,000	275	93,600	154,000	275	11,800	166,000
Anti-foam and defoaming agents	270	11,100	385	68,500	633	215,000	295,000	633	27,200	322,000
Density increasing or weighting agents	0	0	0	0	12,500	4,250,000	4,250,000	12,500	538,000	4,790,000
Additives and mixtures to reduce or prevent lost circulation	29	1,200	29	5,190	29	9,910	16,300	29	1,250	17,500
Spacers and chemical washes/pre-flushes	110	4,510	160	28,500	200	68,000	101,000	200	8,600	110,000

(1) Amounts are averages used on typical wells. Every well does not contain all products. Amounts are calculated from nominal cementing designs from two suppliers and checked against market share data and typical jobs performed by an operator.
(2) Data on number of wells drilled from MMS Fast Facts downloaded on September 19, 1999 (1998 data).
(3) Terminology from World Oil 1999 Cementing Supplement.
(4) Weights for liquid products calculated assuming density of 10 lbs./gal.

3.2.3 Completion, Stimulation, and Workover Chemicals Volumes Estimates

The type and volume of completion, stimulation, and workover chemicals which are likely to be used and stored at an offshore location depends on the operation needed, the length of the treatment interval, and the type of formation being treated. For example, solid formations may require fracturing which uses acids and proppants, while unconsolidated formations may require gravel-packing.

Completion, Stimulation, and Workover Chemicals: Subcategories

The number of jobs performed in each treatment class is equal to the number of new wells drilled and a small percentage of existing older wells which were recompleted, stimulated, or worked over. Using data from chemical suppliers on the number of jobs performed and their market share, the number of completion, stimulation, and workover jobs completed in 1998 was estimated. This number was compared to an operator's estimate of the fraction of their wells recompleted, stimulated, or worked over in 1998 as a check of these estimates. This process yielded the following estimates:

Treatment	Number of Jobs in Shallow Water	Number of Jobs in Deep Water
Completions	920	43
Fracturing	321	15
Acid Gravel-Packs	599	28
Acidizing	150	0

Completion, Stimulation, and Workover Chemical: Data Sources

The data provided by the operator on completion, stimulation, and workover chemical use were not extensive enough to be representative of the entire GOM. Therefore, data on each of the subclasses were augmented by information obtained from a chemical supplier. The lack of actual completion, stimulation and workover applications data on specific wells means that some fine detail is lost. The available data on specific fracturing and acid jobs were consistent with the information gathered from the chemical supplier.

For completion fluids, the supplier calculated the average well volume they treated in the GOM, the total volume of fluids they sold, and their market share. These data were used to determine average quantities of completion, stimulation, and workover chemicals used on all wells in the GOM in 1998. For the other subclasses, the supplier furnished the number of jobs, the average quantities of each functional category used, and the market share for each subclass.

Completion, Stimulation, and Workover Chemicals: Volume Estimates

Multiplying the number of jobs by the per operation or average volume of chemical used for each class of job yields an estimate for the quantities of all functional categories of completion, stimulation, and workover chemicals used throughout the GOM for 1998. These volume estimates are shown in Table 8. The per operation/average volumes represent typical volumes stored at offshore sites.

Table 8
Volume Estimates for Completion, Stimulation, and Workover Chemicals Used in the Gulf of Mexico

		Shallow Water	**Deepwater**	**Total OCS**
Functional Categories/ Components:	**Single Well Amount**	**Total Amount for 1998**	**Total Amount for 1998**	**Total Amount for 1998**
Wells	Total =	920	43	
Completion Fluid Chemicals & Packer Fluid Chemical Jobs				
Water-based Completion Fluid				
Sodium Chloride, bbls	121	111,000	5,190	116,000
Sodium Bromide, bbls	0.53	490	23	513
Calcium Chloride, bbls	236	217,000	10,100	227,000
Calcium Bromide, bbls	26	23,700	1,110	24,800
Zinc Bromide, bbls	18	16,200	755	16,900
Potassium Chloride, bbls	21	19,300	900	20,200
Water-based Completion Fluid Additives:				
Water-based Polymers				
HEC, lbs	90	82,900	3,870	86,700
Xanthum Gum, lbs	13	11,800	553	12,400
Starches, lbs	36	33,000	1,540	34,500
Corrosion Inhibitors, gal	28	25,800	1,210	27,000
Oxygen Scavengers, gal	2	1,840	86	1,930
Biocides, gal	0	358	17	374
Fluid Loss Additives				
Calcium Carbonate, lbs	167	153,000	7,160	160,000
Sodium Chloride, lbs	101	92,600	4,330	97,000
Mineral Fiber, lbs	5	4,920	230	5,150
Defoamers, gal	3	2,530	118	2,640
Surfactants				
Terpenes, gal	3	3,040	142	3,190
Surfactants, gal	17	16,100	751	16,800
Degreasers, gal	3	2,530	118	2,650
Floculants, gal	7	6,460	302	6,770
Frac Gravel Pacs	Total Wells =	321	Total Wells = 15	
Proppant, lbs	80,000	2,570,000	1,200,000	26,900,000
Water-based Completion Fluids	**25,000**	**8,030,000**	**375,000**	**8,400,000**
Water-based Polymers, lbs	625	201,000	9,380	210,000
Surfactant, gal	50	16,000	750	16,800
Clay stabilizes (KCl), lbs	7,296	2,340,000	109,000	24,500,000
Crosslinkesr, gal	100	32,100	1,500	33,600
Breakers, gal	250	80,300	3,750	84,000
Breakers (Catalyst), gal	50	16,000	750	16,800

Table 8
Volume Estimates for Completion, Stimulation and Workover Chemicals Used in the Gulf of Mexico (continued)

Functional Categories/ Components:	Single Well Amount	Shallow Water	Deepwater	Total OCS
		Total Amount for 1998	Total Amount for 1998	Total Amount for 1998
Wells	Total =	920	43	
Acid Gravel Pacs	Total Wells =	599	Total Wells =	28
Sand, lbs	9,000	5,390,000	252,000	5,640,000
Acid Systems				
MCA, gal (Total vol)	**1,120**	**670,000**	**31,300**	**701,000**
HCL, lbs	977	585,000	27,400	613,000
HCl:HF, gal (Total vol)	**2,240**	**1,340,000**	**62,800**	**1,410,000**
HCl, lbs	2,710	1,620,000	75,900	1,700,000
HF, lbs	301	180,000	8,430	189,000
Surfactants, gal	17	9,980	467	10,400
Acid inhibitors, gal	10	6,040	282	6,320
Iron (Fe) control, gal	168	101,000	4,710	105,000
MSA (acetic acid), gal	34	20,100	941	21,100
5% NH4Cl Overflush, gal	**3,120**	**1,870,000**	**87,400**	**1,960,000**
Ammonium Chloride, lbs	1,320	791,000	37,000	828,000
Mutual solvent, , gal	111	66,600	3,110	69,700
Anti-sludge agent, gal	10	5,990	280	6,270
Acidizing Producing Wells	Total Wells =	150	Total Wells =	0
MCA, gal (Total vol)	**1,120**	**168,000**	**0**	**168,000**
HCL, lbs	977	147,000	0	147,000
HCl:HF, gal (Total vol)	**2,240**	**336,000**	**0**	**336,000**
HCl, lbs	2,710	407,000	0	407,000
HF, lbs	301	45,200	0	45,200
Surfactants, gal	17	2,500	0	2,500
Acid inhibitors, gal	10	1,510	0	1,510
Iron (Fe) control, gal	168	25,200	0	25,200
MSA (acetic acid), gal	34	5,040	0	5,040
Anti-sludge agent, gal	10	1,500	**0**	1,500
5% NH4Cl Overflush, gal	**3,120**	**468,000**	0	**468,000**
Ammonium Chloride, lbs	1,320	198,000	0	198,000
Mutual solvent, , gal	111	167,000	0	167,000

3.2.4 Production-treating Chemicals Volume Estimates

The quantity of production-treating chemicals needed at a particular site depends primarily on the volume rate of the produced streams. The variety and representative quantities used at any particular location can depend on many variables, such as:

- Type of production (i.e., oil or gas)
- Type of oil produced (i.e., paraffinic or asphaltic)
- Viscosity and gravity of the oil produced
- Composition and salinity of the water being produced
- Presence and level of hydrogen sulfide and carbon dioxide in the gas produced
- Relative rates of oil and water production

Production-treating Chemicals: Subcategories

Based on an analysis of the on-going operations in the GOM, data received from the operator and discussions with chemical suppliers and operators, no single set of chemical use concentrations could represent the entire GOM. Operations in the GOM were categorized based on water depth, type of production, type of gathering system, and the presence of hydrogen sulfide in gas production. Under this approach, seven nominal models were defined for the different types of production. However, data were only collected for six, since data for deepwater gas production from wellheads above the surface was not available.

- Shallow water oil production
- Shallow water gas production
- Shallow water gas production with H_2S
- Deepwater oil with wellheads above the surface
- Deepwater oil with subsea wellheads
- Deepwater gas with wellheads above the surface
- Deepwater gas with subsea wellheads

Production-treating Chemicals: Data Sources

One of the larger operators in the GOM provided a 1998 dataset for each of the categories listed above which included the following information:

- Functional categories of production-treating chemicals used
- Specific chemical products used
- Treatment rates in gallons per day
- Monthly use volumes
- Production rates for gas, oil, and water on all their production in each of these types

With these data, it was possible to determine average concentrations used for each functional category of production-treating chemical in each of the production types. Although each chemical may not be used at all locations, it was assumed that the production chemicals were used at all locations in each subcategory.

Production-treating Chemicals: Volume Estimates

The production rates for gas, oil, and water for the GOM were taken from the MMS Fast Facts database. For both total GOM and for deep water, production data for the following were acquired:

- crude oil
- liquids from gas production (condensate liquids)
- gas production from gas wells
- gas resulting from oil production,
- water production

Using production ratios reported by the operator, these values were allocated to each of the operational subcategories. Multiplying these production rates by the unitized values for each functional category yields total volume estimates of production-treating chemical throughout the GOM. Table 9 shows these total volume estimates for 1998 as an example of model application. Comparing the total volume estimates shown in Table 9, the variability in production-treating chemical by production category is evident. For example, corrosion inhibitor use is much higher in gas production with hydrogen sulfide than for other types.

In Table 10 the maximum and average volumes for production-treating chemicals used in offshore fields are shown. These volumes are typical of the volumes of production-treating chemicals that might be stored offshore. In addition to these values, five umbilicals were identified and their holding capacity and number of storage sites are also presented.

Table 9
Volume Estimates for Production-treating Chemicals Used in the Gulf of Mexico

Annual Production Rates(2)	**Shelf Oil**		**Shelf Gas**		**Shelf Gas with H_2S**		**Deepwater DVA Oil**		**Deepwater Gas(1)**		**Deepwater Subsea Oil**		**Total(s)**
Gas, mcf	1,740,000,000		2,720,000,000		2,100,000		239,000,000		223,000,000		98,200,000		5,020,000,000
Oil, bbls	243,000,000		41,100,000		142,000		102,000,000		2,980,000		54,100,000		443,000,000
Water, bbls	471,000,000		70,100,000		29,300,000		19,100,000		457,000		110,000		591,000,000
Functional Category(3)	**Conc. (ppmv)**	**Annual Total (gal)**	**Conc. (ppmv)**	**Annual Total (gal)**	**Conc. (ppmv)**	**Annual Total (gal)**	**Conc. (ppmv)**	**Annual Total (gal)**	**Conc. (ppmv)**	**Annual Total (gal)**	**Conc. (ppmv)**	**Annual Total (gal)**	**Annual Grand Total (gal)**
Emulsion Breakers	16.5	495,000	12.7	59,200	105.5	130,000	0	0	161.7	23,400	0	0	708,000
Reverse Breakers	26.1	518,000	40.5	119,000	79.4	97,500	19.6	15,700	0	0	0	0	750,000
Scale Inhibitor	15.7	312,000	16.5	48,600	595.2	732,000	0	0	0	0	0	0	1,090,000
Corrosion Inhibitor	7.4	146,000	54.9	162,000	1763.7	2,170,000	0	0	1231.5	23,600	0	0	2,500,000
Biocide	1.6	32,300	11.5	34,000	0	0	7.8	6,300	0	0	0	0	72,600
Paraffin Treating Chemicals	15.7	160,000	7.9	13,600	0	0	18.7	80,100	0	0	0	0	254,000
Antifoam	4.3	44,200	0	0	0	0	40.7	175,000	0	0	44.5	101,000	320,000
Oxygen Scavenger	0.15	2,930	5.82	17,100	105.8	130,000	0	0	0	0	0	0	150,000
Acid	0	0	0.97	2,860	37.0	45,500	0	0	0	0	0	0	48,400
Hydration Inhibition Chemicals-Glycols(4)	0	0	3.489E-04	949,000	3.489E-04	734	1.38E-03	330,000	8.275E-04	185,000	0	0	1,460,000
Hydration Inhibition Chemicals-Methanol	0	0	2.443E-04	665,000	2.443E-04	514	2.625E-04	62,700	2.096E-02	4,680,000	1.765E-04	17,300	5,420,000
Totals	-	1,710,000	-	2,070,000	-	3,300,000	-	669,000	-	4,910,000	-	119,000	
					Total Shelf	7,080,000					**Total Deepwater**	5,700,000	**12,800,000**

Notes:

(1) Both DVA gas and subsea gas are included since there was no separate data on DVA gas.

(2) Production data (1998) was taken from the MMS Fast Facts Database and allocated to fit the pattern of industry data submitted to Arthur D. Little, Inc.

(3) Concentrations are averages of industry data submitted for each category of production-treating chemicals.

(4) All sites used glycol except one, which used TEG. One used ethylene glycol and regenerated it.

Table 10
Storage Volumes of Production-treating Chemicals Used in the Gulf of Mexico

		Volumes Stored Offshore					
		Shallow Water Production			**Deepwater Production**		
Functional Category		**Number of Sites**	**Maximum (gal)**	**Average (gal)**	**Number of Sites**	**Maximum (gal)**	**Average (gal)**
Emullsion Breakers		30	670	313	1	700	700
Reverse Breakers		34	780	288	1	280	280
Scale Inhibitor		14	500	312	-	-	-
Corrosion Inhibitor		20	2,940	528	2	500	442
Biocide		20	500	184	2	110	110
Paraffin Treating Chemicals		3	550	378	1	5,500	5,500
Antifoam		3	550	268	7	2,000	1,080
Oxygen Scavenger		3	500	252	-	-	-
Acid		2	200	200	-	-	-
Hydration Inhibition Chemicals-Glycols[1]	Storage[2]	1	63,000	63,000	3	550	550
	Umbilicals	1	106,000	106,000	1	132	132
Hydration Inhibition Chemicals-Methanol	Storage[3]	4	96,600	49,700	3	7,440	3,360
	Umbilicals	4	7,270	3,210	0	0	0

Notes:

(1) All sites using glycol except one, which used TEG. One used ethylene glycol and regenerated it.

(2) No shelf sites used glycol, however one deepwater site used a shelf platform to store ethylene glycol, which was supplied to the deepwater site by umbilical.

(3) All sites reported are for deepwater use. Shelf sites all stored small quantities. Storage at shelf sites were all for deepwater and the methanol was supplied to them by an umbilical.

3.3 Comparison of Chemical Use in Shallow and Deep Water

Comparing shallow and deep water, 559 wells in shallow water used 420,000,000 lbs. of solid chemicals and 1,560,000 gal. of liquid chemicals in 1998, compared to 419,000,000 lbs. of solid chemicals and 890,000 gal. of liquid chemicals for 43 wells in deep water. This means that the average deepwater well uses approximately 14 times more solid drilling fluid chemicals than the average shallow water well. Most of this is weighting agent (barite). While wells in deep water use more drilling fluid chemicals in most functional categories, the largest increases are in filtrate reducers, shale control inhibitors, and defoamers. Table 6 shows the maximum, average, and median volumes for drilling fluid chemicals used in all 56 wells in the database supplied by the operator. It includes data from wells in both shallow and deep water. Generally, less chemical is stored on a rig than is needed to drill the entire well. Quantities of drilling fluid chemical used per well in deep water are greater than quantities for similar depth wells in shallow water. The differences may reflect drilling problems caused by the water depth or differences in the formations being drilled. Note that median values of zero show that less than half the wells used that chemical and stored it on the rig.

Based on the data and model estimates, 559 wells used 228,000,000 lbs. of cementing chemicals in shallow water and 43 wells used 21,400,000 lbs. of cementing chemicals in deep water. On an average well basis, deepwater wells used 22% more chemicals per well than shallow water wells. As is expected, this reflects the fact that all wells in deep water are drilled to great depths, while a range of depths are drilled in shallow water.

Environmental conditions, formation/reservoir factors, deepwater production characteristics all account for differences between shallow water and deepwater use of production-treating chemicals. The data indicate that deepwater gas production requires more hydrate inhibitors per unit of production than shelf gas production. However, it cannot be determined if these differences will continue as the field ages and water production increases at these deepwater locations. Additionally, although the data indicates that defoamer is used almost exclusively in deep water, this may be due to the nature of the produced fluids and the environment through which they are produced, rather than the increase in water depth.

In summary, while the nature of the geologic formation, the reservoir, and the local environment will not alter the basic chemical treating principles governing chemical use, they will affect the type and amount of chemical employed. Definite differences are apparent in chemical use in deep and shallow waters in the GOM. For individual locations, these include:

- Higher amounts of drilling fluid chemicals needed in individual wells in deep water, some of which are probably due to the nature of the formations and reservoirs being accessed
- Higher amounts of some production-treating chemicals (e.g., hydrate inhibitors) needed in deepwater production, which may be due to the deepwater environment
- Higher amounts of other production-treating chemicals (e.g., defoamers) needed in deepwater production, which may be due to the nature of the produced fluids

It is not clear how comparisons of the total volumes of chemical used in the future will change. The life cycle of a field will likely affect the quantity of chemical used in that field over time. For example, while we know that deepwater wells use more drilling fluid chemical, we do not know the expected ratio of new shallow wells to new deep wells. Similarly, while we know that production-treating chemical use will increase as the deepwater wells age, we are unsure of the magnitude of this increase.

With the increasing use of subsea completions in deep water, there will be an increase in the use of umbilicals to supply chemicals to them. This will impact the use and storage of production-treating chemicals. Some of these subsea wells are very remote from platforms or other storage and supply points. Five umbilicals were identified in the data that form the basis for the production-treating chemical projections in this report; one of them was 62 miles long. Several of the umbilicals were supplied from platforms in shallow water. It is apparent that the use of umbilicals will result in the storage of larger volumes offshore, and these will be transported on the sea floor. Umbilicals will also impact storage on platforms that may not be in deep water.

4.0 HAZARDOUS SUBSTANCES

4.1 Introduction

As part of this study, the types and volumes of hazardous substances found in chemicals used, handled, and stored in offshore E&P operations were identified. The results may be used to both assess potential impacts of the chemicals identified, and understand future usage trends in deep waters as compared to shallow waters.

For the purposes of this report, hazardous chemicals are defined as those substances listed in the U.S. Code of Federal Regulations (CFR) – Chapter 40, Protection of the Environment, Part 116, that designates hazardous substances per the Clean Water Act. Reportable quantities for these substances are listed in Part 117 of this act.

4.2 Approach to Estimating Quantities of Hazardous Chemicals Used and Stored Offshore

The data set of chemical usage assembled (described in Section 3.0) to develop the inventories, and build the estimation models were also used to identify and predict the volume of hazardous substances used and stored in the Gulf of Mexico (GOM). Material safety data sheets (MSDSs) were collected for all products appearing in the base data set. These sheets list hazardous components and information about component concentrations. The data listed on MSDSs were used to preliminarily identify the presence of hazardous substances and to modify the prediction models to estimate volumes of hazardous chemicals used. The hazardous substances identified from the MSDSs were compared to the designations of hazardous substances found in 40 CFR, Part 116, to ensure that those chemicals listed as hazardous on the MSDSs were also identified as hazardous in the regulation.

To generate the volume of hazardous substances used in offshore operations, the volumes of each chemical in the base data set, and the percentage of hazardous substance reported on the MSDSs, were multiplied to calculate volumes of hazardous substances in each chemical. Hazardous substance concentrations reported in the MSDSs are given as ranges, such as 1% to 5% or 30% to 60%. In the calculation of hazardous substance volumes in each chemical and/or product, the concentration was assumed to be the upper limit of reported ranges. These calculated volumes of hazardous substances were substituted for the volumes of the chemicals in the models to create an estimation model for hazardous substances. The resulting models were used to estimate the total amount of hazardous substances used in 1998 from the base data sample. Estimations for any number of wells or amount of production can be obtained by entering the proper well numbers or production data as described in detail in Section 3.0.

These estimates are limited by the following assumptions:

- Only data that were actually used in the base data submitted by the participating operating companies would be included in determining typical quantities.
- If the MSDSs showed a range of concentration for a hazardous substance, the upper limit would be used in predictions so the resulting amount would be conservatively high.

4.3 Hazardous Substances in E&P Chemicals Applied to Wells

Hazardous substance volume estimates for 1998 and typical volumes stored are shown below for each class of chemicals used offshore.

Calculated amounts stored at selected sites can be compared to reportable quantities in the tables. No hazardous materials listed in 40 CFR, Part 116, were identified in the literature review of cementing chemicals; therefore, no data is presented here for this chemical class.

4.3.1 Drilling Fluid Chemicals

Table 11 shows five drilling chemical products contained three of the 296 hazardous substances listed in 40 CFR, Part 116. Table 12 shows the maximum, average, and median quantities of these substances stored offshore. These quantities were calculated from data provided by the participating operating company that supplied drilling fluid chemical usage data for 58 wells drilled in the Gulf of Mexico in 1998. The hazardous substances identified are:

- Sodium hydroxide (functional categories: alkalinity, pH control additives, filtrate reducers, emulsifiers and surface active agents)
- Potassium hydroxide (functional categories: alkalinity, pH control additives, defoamers)
- Acetic acid (functional category: alkalinity, pH control additives)

Table 11
Total Estimated Quantities of Hazardous Substances Found in Drilling Fluid Chemicals in the GOM in 1998

Hazardous Substances in Product	Functional Category (code)	Product	CAS No.	Shallow Water		Deepwater	
				Number of wells [(1)]	Total Quantity (lbs)	Number of wells [(2)]	Total Quantity (lbs)
Sodium Hydroxide	Flitrate reducers (FR)	ChemTrol-X	1310732	559	2,250	43	9,580
Potassium Hydroxide, Sodium Hydroxide	Alkalinity, pH additives (A)	Caustic Soda, Caustic Potash	1310583 1310732	559	6,800,000	43	2,280,000
Acetic Acid	Alkalinity, pH additives (A)	Acetic Acid	64197	559	25,800	43	0
Sodium Hydroxide	Emulsifiers & Surface Active Agents (E)	Mil-Clean	1310732	559	0	43	10
Potassium Hydroxide	Defoamers (D)	W.O. Deafom	1310583	559	35	43	1,100

Notes:

(1) Total number of shallow water wells from Table 5 in Section 3.0

(2) Total number of deepwater wells from Table 5 in Section 3.0

Table 12
Total Estimated Storage Volumes of Hazardous Substances Found in Drilling Fluid Chemicals in the GOM in 1998

Hazardous Substances in Product	Functional Category (code)	CAS No.	Hazardous Substance Concentration in Product (%)	Reportable Quantity lbs (kg)	Storage Volume Summary (lbs)		
					Maximum	Average	Median
Sodium Hydroxide	Filtrate reducers (FR)	1310732	1%	1000 (454)	12,800	538	0
Potassium Hydroxide, Sodium Hydroxide	Alkalinity, pH additives (A)	1310583 1310732	100%	1000 (454)	116,000	17,000	6,200
Acetic Acid	Alkalinity, pH additives (A)	64197	56%	5000 (2270)	2,400	80	0
Sodium Hydroxide	Emulsifiers & Surface Active Agents (E)	1310732	4%	1000 (454)	2	0	0
Potassium Hydroxide	Defoamers (D)	1310583	1%	1000 (454)	107	2	0

Since the alkalinity functional category is used in every drilling fluid formulation, all drilling fluid formulations contain some hazardous substances. Only two hazardous substances, sodium hydroxide (filtrate reducers and alkalinity and pH additives) and potassium hydroxide (alkalinity and pH additives), were stored in amounts greater than reportable quantities (see Table 12).

4.3.2 Completion, Stimulation and Workover Chemicals

Table 13 shows nine completion, stimulation, and workover chemical products containing hazardous substances. The products are used in six functional categories. These nine products contain 10 of the 296 hazardous substances listed in 40 CFR, Part 116. Table 14 shows the average quantities stored offshore for each of these chemicals.

Hazardous substances identified in completion, stimulation, and workover chemicals include:

- Acetaldehyde
- Acetic acid
- Ammonium bisulfite
- Ammonium chloride
- Crotonaldehyde
- Dodecylbenzene sulfonic acid
- Hydrochloric acid
- Hydrofluoric acid
- Potassium hydroxide
- Zinc bromide

The average amount of each functional category of completion, stimulation, and workover chemicals used per job is assumed to be the average amount stored offshore at any single site.

Table 13
Total Estimated Quantities of Hazardous Substances found in Completion, Stimulation, and Workover Chemicals in the GOM in 1998

CSW Class	Hazardous Substances in Product	Functional Category (code)	Product	CAS No.	Shallow Water		Deep Water	
					Number of Wells (1)	Total Quantity (lbs.)	Number of Wells(2)	Total Quantity (lbs.)
Completion Fluids & Packer Fluids Jobs	Zinc Bromide	Water-base Completion Fluid (A-WBC)	Zinc Bromide	7699458	920	7,280,000	43	340,000
	Ammonium Bisulfite	Oxygen Scavenger (A-OS)	Anhib II Inhibitor	10192300	920	5,340	43	250
Fracing /Gravel-Packs	Potassium Hydroxide	Crosslinker (F-C)	CL-31 Crosslinker	1310583	920	603,000	43	28,200
Acid Gravel-Packs	Hydrochloric Acid	Acid Systems (A-AS)	MCA Acid	7647010	599	585,000	28	27,400
	Hydrochloric Acid	Acid Systems (A-AS)	HCl:HF Acid	7647010	599	1,620,000	28	75,900
	Hydrofluoric Acid	Acid Systems (A-AS)	HCl:HF Acid	7464393	599	180,000	28	8,430
	Crotonaldehyde	Acid Inhibitor (A-AI)	SCA-130	4170303	599	2,620	28	123
	Acetaldehyde	Acid Inhibitor (A-AI)	SCA-130	75070	599	2,620	28	123
	Acetic Acid	Acid Systems (A-AS)	MSA Acid	64197	599	20,400	28	952
	Dodecylbenzene Sulfonic Acid	Anti-Sludge Agent (A-ESA)	AS 5	27176870	599	41,200	28	1,930
	Ammonium Chloride	Water-base Completion Fluid (A-WBC)	Clayfix	12125029	599	791,000	28	37,000

Table 13
Total Estimated Quantities of Hazardous Substances found in Completion, Stimulation, and Workover Chemicals in the GOM in 1998 (continued)

CSW Class	Hazardous Substances in Product	Functional Category (code)	Product	CAS No.	Shallow Water		Deepwater	
					Number of Wells (1)	**Total Quantity (lbs.)**	**Number of Wells (2)**	**Total Quantity (lbs.)**
Acidizing Producing Wells	Hydrochloric Acid	Acid Systems (A-AS)	MCA Acid	7647010	150	147,000	0	0
	Hydrochloric Acid	Acid Systems (A-AS)	HCl:HF Acid	7647010	150	407,000	0	0
	Hydrofluoric Acid	Acid Systems (A-AS)	HCl:HF Acid	7464393	150	45,100	0	0
	Crotonaldehyde	Acid Inhibitor (A-AI)	SCA-130	4170303	150	657	0	0
	Acetaldehyde	Acid Inhibitor (A-AI)	SCA-130	75070	150	657	0	0
	Acetic Acid	Acid Systems (A-AS)	MSA Acid	64197	150	5,100	0	0
	Dodecylbenzene Sulfonic Acid	Anti-Sludge Agent (A-ESA)	AS 5	27176870	150	10,300	0	0
	Ammonium Chloride	Water-based Completion Fluid (F-WBC)	Clayfix	12125029	150	198,000	0	0

Notes:
(1) Total number of shallow water wells from Table 8 in Section 3.0
(2) Total number of deepwater wells from Table 8 in Section 3.0

Table 14

Total Estimated Storage Volumes of Hazardous Substances Found in Completion, Stimulation, and Workover Chemicals in the GOM in 1998

CSW Class	Hazardous Substances in Product	Functional Category (code)	Product	CAS No.	Hazardous Substance Concentration in Product (%)	Reportable Quantity lbs. (kg)	Average Quantity Stored per Site (lbs.)
Completion Fluids & Packer Fluids Jobs	Zinc Bromide	Water-based Completion Fluid (A-WBC)	Zinc Bromide	7699458	54%	1,000 (454)	7,910
	Ammonium Bisulfite	Oxygen Scavengers (A-OS)	Anhib II Inhibitor	10192300	30%	5,000 (2,270)	6
Fracing /Gravel-Packs	Potassium Hydroxide	Crosslinker (F-C)	CL-31 Crosslinker	1310583	60%	1,000 (454)	656
Acid Gravel-Packs	Hydrochloric Acid	Acid Systems (A-OS)	MCA Acid	7647010	30%	5,000 (2,270)	977
	Hydrochloric Acid	Acid Systems (A-OS)	HCl:HF Acid	7647010	18%	5,000 (2,270)	2,710
	Hydrofluoric Acid	Acid Systems (A-OS)	HCl:HF Acid	7464393	6%	100 (45.4)	301
	Crotonaldehyde	Acid Inhibitor (A-AI)	SCA-130	4170303	5%	100 (45.4)	4
	Acetaldehyde	Acid Inhibitor (A-AI)	SCA-130	75070	5%	1,000 (454)	4
	Acetic Acid	Acid Systems (A-AS)	MSA Acid	64197	10%	5,000 (2,270)	34
	Dodecylbenzene Sulfonic Acid	Anti-Sludge Agent (A-ESA)	AS 5	27176870	80%	1,000 (454)	69
	Ammonium Chloride	Water-based Completion Fluid (A-WBC)	Clayfix	12125029	100%	5,000 (2,270)	1,320
Acidizing Producing Wells	Hydrochloric Acid	Acid Systems (A-OS)	MCA Acid	7647010	30%	5,000 (2,270)	977
	Hydrochloric Acid	Acid Systems (A-OS)	HCl:HF Acid	7647010	18%	5,000 (2,270)	2,710
	Hydrofluoric Acid	Acid Systems (A-OS)	HCl:HF Acid	7464393	6%	100 (45.4)	301
	Crotonaldehyde	Acid Inhibitor (A-AI)	SCA-130	4170303	5%	100 (45.4)	4
	Acetaldehyde	Acid Inhibitor (A-AI)	SCA-130	75070	5%	5,000 (2,270)	4
	Acetic Acid	Acid Systems (A-OS)	MSA Acid	64197	10%	5,000 (2,270)	34
	Dodecylbenzene Sulfonic Acid	Anti-Sludge Agent (A-ESA)	AS 5	27176870	80%	1000 (454)	69
	Ammonium Chloride	Water-based Completion Fluid (A-WBC)	Clayfix	12125029	100%	5,000 (2,270)	1,320

Only two hazardous substances, zinc bromide (water-based completion fluid) and hydrofluoric acid (acid systems), were stored in amounts greater than reportable quantities and these quantities are shown in Table 14.

4.3.3 Production-treating Chemicals Processing Systems

Table 15 shows six functional categories of production-treating chemicals contained 14 of the 296 hazardous substances listed in 40 CFR, Part 116. Table 16 shows quantities stored at a number of offshore sites. An operating company provided data for production-treating chemicals used at 59 production-treating facilities, 49 in shallow water and 10 in deepwater. These data were used to make estimates of the quantities used in 1998. Hazardous substances identified include:

- Acetic acid
- Aluminum sulfate
- Ammonium bisulfite
- Ammonium chloride
- Diethylamine
- Ethylbenzene
- Hydrochloric acid
- Naphthalene
- Phosphoric acid
- Potassium hydroxide
- Sodium bisulfite
- Sulfuric acid
- Toluene
- Xylene

Only four hazardous substances, diethylamine (corrosion inhibitors), toluene (paraffin inhibitors), xylene (demulsifiers and corrosion inhibitors), and naphthalene (demulsifiers and corrosion inhibitors) were stored in amounts greater than reportable quantities (see Table 16). Of these four hazardous substances, three are aromatic solvents (i.e., toluene, xylene, naphthalene).

Table 15
Total Estimated Quantities of for Hazardous Substances Found in Production-treating Chemicals in the GOM in 1998

Hazardous Substances in Product	Functional Category	CAS No.	Total Estimated Quantities of Hazardous Substances (lbs)		
			Shallow Water	Deep Water	Grand Total
Acetic Acid	Emulsion Breakers (P-EB)	64197	322,000	0	322,000
Acetic Acid	Reverse Breakers (P-RB)	64197	400	0	400
Aluminum Sulfate	Reverse Breakers (P-RB)	10043013	9,900	0	9,900
Ammonium Bisulfite	Corrosion Inhibitors (P-CI)	10192300	5,400	0	5,400
Ammonium Bisulfite	Oxygen Scavenger (P-OS)	10192300	132,000	0	132,000
Ammonium Chloride	Scale Inhibitors (P-SI)	12125029	500	0	500
Ammonium Chloride	Reverse Breakers (P-RB)	12125029	500	0	500
Diethylamine	Corrosion Inhibitor (P-CI)	124403	600	0	600
Ethylbenzene	Corrosion Inhibitor (P-CI)	100414	12,300	0	12,300
Ethylbenzene	Emulsion Breakers (P-EB)	100414	101,000	0	101,000
Hydrochloric Acid	Reverse Breakers (P-RB)	7647010	600	0	600
Hydrochloric Acid	Emulsion Breakers (P-EB)	7647010	5,600	0	5,600
Hydrochloric Acid	Scale Inhibitors (P-SI)	7647010	19,300	0	19,300
Naphthalene	Corrosion Inhibitors (P-CI)	91203	18,300	0	18,300
Naphthalene	Emulsion Breakers (P-EB)	91203	231,000	11,700	243,000
Naphthalene	Reverse Breakers (P-RB)	91203	3,400	0	3,400
Phosphoric Acid	Reverse Breakers (P-RB)	7664382	1,400	0	1,400
Potassium Hydroxide	Emulsion Breakers (P-EB)	1310583	3,100	0	3,100
Potassium Hydroxide	Reverse Breakers (P-RB)	1310583	12,700	0	12,700
Sodium Bisulfite	Oxygen Scavenger (P-OS)	7631905	9,000	0	9,000
Sulfuric Acid	Reverse Breakers (P-RB)	7664939	800	0	800
Toluene	Paraffin Treating Chemicals (P-TC)	108883	420,000	0	420,000
Xylene	Corrosion Inhibitors (P-CI)	1330207	3,100	0	3,100
Xylene	Emulsion Breakers (P-EB)	1330207	143,000	0	143,000
		Totals	1,460,000	11,700	1,470,000

Table 16
Total Estimated Storage Volumes of Hazardous Substances Found in Production-treating Chemicals in the GOM in 1998

Hazardous Substances in Product	Functional Category (code)	CAS No.	Hazardous Substance Concentration in Product (% - Range)	Reportable Quantity lbs (kg)	Avg./Max. Quantity Stored per Site (lbs)
Acetic Acid	Emulsion Breakers (P-EB)	64197	47%	5,000 (2270)	1,440/2,060
Acetic Acid	Reverse Breakers (P-RB)	64197	5%	5,000 (2270)	24/24
Aluminum Sulfate	Reverse Breakers (P-RB)	10043013	10%	5,000 (2270)	1,270/1,760
Ammonium Bisulfite	Corrosion Inhibitors (P-CI)	10192300	40%	5,000 (2270)	1,350/1,350
Ammonium Bisulfite	Oxygen Scavenger (P-OS)	10192300	60%	5,000 (2270)	2,030/2,030
Ammonium Chloride	Scale Inhibitors (P-SI)	12125029	4%	5,000 (2270)	94/94
Ammonium Chloride	Reverse Breakers (P-RB)	12125029	5%	5,000 (2270)	35/35
Diethylamine	Corrosion Inhibitors (P-CI)	109897	10%	100 (45.4)	173/227
Ethylbenzene	Corrosion Inhibitors (P-CI)	100414	20%	1,000 (454)	557/557
Ethylbenzene	Emulsion Breakers (P-EB)	100414	5%-10%	1,000 (454)	264/485
Hydrochloric Acid	Emulsion Breakers (P-EB)	7647010	5%	5,000 (2270)	98/98
Hydrochloric Acid	Reverse Breakers (P-RB)	7647010	20%	5,000 (2270)	394/394
Hydrochloric Acid	Scale Inhibitors (P-SI)	7647010	20%	5,000 (2270)	108/108
Naphthalene	Emulsion Breakers (P-EB)	91203	3%-10%	100 (45.4)	207/386
Naphthalene	Reverse Breakers (P-RB)	91203	5%	100 (45.4)	250/250
Naphthalene	Corrosion Inhibitors (P-CI)	91203	5%-10%	100 (45.4)	287/451
Phosphoric Acid	Reverse Breakers (P-RB)	7664382	70%	5,000 (2270)	1,970/1,970
Potassium Hydroxide	Emulsion Breakers (P-EB)	1310583	5%	1,000 (454)	47/47
Potassium Hydroxide	Reverse Breakers (P-RB)	1310583	5%-7%	1,000 (454)	270/468
Sodium Bisulfite	Oxygen Scavenger (P-OS)	7631905	37%	5,000 (2270)	1,270/1,270
Sulfuric Acid	Reverse Breakers (P-RB)	7664939	1%	1,000 (454)	18/18
Toluene	Paraffin Treating Chemicals (P-TC)	108883	30%-100%	1,000 (454)	1,600/2,760
Xylene	Corrosion Inhibitors (P-CI)	1330207	5%	100 (45.4)	138/138
Xylene	Emulsion Breakers (P-EB)	1330207	3%-10%	100 (45.4)	168/309

5.0 OFFSHORE CHEMICAL STORAGE AND HANDLING REGULATIONS AND PRACTICES, AND CHEMICAL SPILL HISTORY EVALUATION

5.1 Introduction

In general, factors that determine the overall risk from chemicals spilled into the marine environment include the toxicity of the chemical spilled, the volume of the spill, and the number of spills that will occur. Ultimately, the magnitude of these factors will be determined by the quality of the external environment (i.e., presence of a sensitive marine habitat, metocean conditions, and general weather conditions).

This section discusses regulations impacting chemical transportation and storage, offshore chemical storage and handling practices, possible failure modes (e.g., transfers, collisions, mechanical failures), and state of the art practices related to chemical spill response in the Gulf of Mexico (GOM).

Over the past decade, the reported number of liquid chemical spills in the GOM has steadily increased. In 1998, the percentage of spill incidents across the Gulf region accounted for almost 27% of all incidents in U.S. water bodies (Table 17). The information provided in this section presents the offshore chemical storage and handling data and summarizes chemical spill information publicly available for the GOM. Based on this data, a qualitative analysis of spill potential is presented for both shallow and deep water. Since none of the data obtained distinguishes between activities and/or events that caused these chemical spills it is not possible to determine which were a result of E&P related activities.

Agencies such as the U.S. Department of Transportation (DOT), the Occupational Safety and Health Administration (OSHA), and the Environmental Protection Agency (EPA) have jurisdiction over various aspects of chemical transportation, storage, and use offshore. Regulations promulgated by these agencies impact container types and transport methods, transportation safety, control of the types of chemicals allowed offshore, and other issues. These regulations provide safety controls that limit the potential of a chemical spill offshore. For example, vessel wall thickness for shipping containers is controlled so that the containers can withstand rough handling without rupturing. Chemical use, storage, and transport offshore are regulated and the combination of the various regulations exerts considerable control over protection of workers, the public, and the environment.

Storage and handling practices include factors such as different types of storage containers used, shipping practices, how transfers are made, and how the chemicals are used with regard to particular E&P activities. Other factors include offshore transport/support vessel traffic density, and current/future application practices (e.g., the use of umbilicals) in chemical delivery to drill rigs, production-treatment systems (including producing wells), and other treatment points.

The National Response Center (NRC), a division of the United States Coast Guard (USCG), is the sole federal point of contact for reporting oil and chemical spills above reportable quantities as per the CERCLA listed chemicals table (40 CFR Part 302.4: Designation of Hazardous Substances). The primary function of the NRC is to serve as the sole national point of contact for reporting all oil, chemical, radiological, biological, and etiological discharges into the environment anywhere in the United States and its territories. In addition to gathering and distributing spill data for Federal On-Scene Coordinators and serving as the communications and operations center for the National Response Team (NRT), the NRC maintains agreements with a variety of federal entities to make additional notifications regarding incidents meeting established trigger criteria. The NRC is staffed by USCG personnel who maintain a 24 hour per day, 365 day per year telephone watch. NRC watch standers enter telephonic reports of pollution incidents into the EPA's Incident Reporting Information System (IRIS) and immediately relay each report to the predesignated Federal On-Scene Coordinator (FOSC). The NRC also provides emergency response support to the FOSCs. This includes extensive reference materials, state of the art telecommunications and operation of automated chemical identification and chemical dispersion information systems.

In addition to the NRC, offshore operators are also required to report spills (i.e., chemical and oil) to the state EPA's (i.e., Alabama, Florida, Louisiana, Mississippi, or Texas) within whose boundary the spill occurs. The MMS, has access to both databases (i.e., the NRC's and IRIS's) and thus is able to retrieve information regarding chemical spills reported within the GOM.

The USCG is currently developing regulations that address the implications of hazardous substance releases in the marine and freshwater environments. These regulations are required under the 1990 Oil Pollution Act (OPA-90) and are currently undergoing a public review process. The proposed regulations define the response plans that need to be prepared for all marine transportation-related facilities and tank vessels carrying hazardous substances. These response plans are to include an impact analysis for a worst case discharge and will pre-identify the areas where impact to human health and the environment could occur. The plans will also identify worst case planning volumes, endpoints, and distances to endpoints. The proposed regulations state that dispersion modeling will be necessary to assess the potential risks and develop response strategies. The proposed rules state that dispersion modeling capabilities will need to be available within 2 hours of a spill, along with air and water sampling resources, and readiness of various response equipment. This regulation would be the first of its kind (Applied Science Associates 2000).

Information on regulatory guidelines for the transportation and storage of chemicals, and storage and handling information, was obtained from three operating companies which agreed to provide data for this study, five of their eight chemical suppliers, and other industry sources. Historical spill data was obtained from publicly available reports published by the USCG since 1990 (USCG 1990-1999). Where available, specific chemical spill volumes are cited in Tables 17 and 18. Importantly, the information on chemical spills does not provide specific locations within the GOM nor is the particular activity and/or cause identified. This fact makes it very difficult to quantitatively or qualitatively determine the number of chemical spills with the GOM either in shallow or deep waters that resulted from E&P activities.

5.2 Chemical Transportation and Storage Regulations Related to Offshore E&P Operations

Jurisdiction for regulations for the transportation, storage, and use of chemicals is divided between the federal government and individual states. Onshore and in state waters, the state has primary jurisdiction, followed by the federal government. In outer continental shelf (OCS) waters in the GOM, the U. S. Congress specifically delegated jurisdiction to the federal government. In the Continental Shelf Lands Act (43 U.S.C. 1333 Public Lands: Interior), the authority of enforcement for "the subsoil and seabed of the outer continental shelf" and "all devices permanently or temporarily attached to the seabed" are areas of "exclusive federal jurisdiction." By this act, the U.S. Congress has indicated that it expects the USCG to be the principal federal agency on matters of worker health and safety, as well as continuing the present role it exercises for safety of vessels, diving, artificial islands, fixed drill rigs, and similar structures (Memorandum of Understanding Between the Occupational Safety and Health Administration and the USCG, 1982).

Regulations on offshore chemical transportation, worker safety, hazardous substances, and waste handling and disposal impact the storage and handling of chemicals offshore. These regulations often intertwine with one another, affecting the implementation of both. For example, OSHA regulates the methods and containers in which chemicals are stored, and DOT regulates the containers used for transport of chemicals offshore. Since the containers used in transport are often also used for storage, containers are designed to comply with both DOT and OSHA requirements. While a detailed explanation of these regulations is beyond the scope of this study, a brief outline of the primary regulations and requirements is provided to demonstrate the effects of regulations on offshore chemical storage and handling.

Federal agencies that issue regulations that apply to chemicals used offshore include:

- U.S. Department of Transportation (49 CFR, Part 172: Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements)
- Occupational Safety and Health Administration (OSHA) (29 CFR, Chapter 17: Occupational Safety and Health Standards)
- U.S. Environmental Protection Agency (EPA) (40 CFR: Protection of the Environment)

The DOT regulations (49 CFR) control transportation. Part 172 addresses hazardous materials for all overland and marine transportation of chemicals from source to shore base. These codes cover packaging standards, labels and markings on containers, labeling exceptions, and emergency response. Each type of packaging has its own standards for materials of construction, wall thickness, labeling, and other elements.

Once transported offshore, chemicals stored and used are subject to Federal OSHA regulations. These laws may be enforced by State OSHA or the USCG on behalf of Federal OSHA, depending on the boundary for state waters. OSHA also mandates that chemical suppliers provide Material Safety Data Sheets (MSDSs) for their products. MSDSs summarize several regulatory requirements and are frequently used by industrial consumers as guides for their employees in complying with regulations, even when the chemicals are not hazardous and they are not required to do so. The larger chemical suppliers of offshore oilfield chemicals are engaged in international business/trade and ship products into and out of the United States. For this reason, many have adopted the international (United Nations) MSDS format to comply with international laws. MSDSs for chemicals/products selected for detailed analysis (Section 8.0) are presented in Appendix B.

Chemicals may fall under several EPA regulations that implement legislative acts passed by the U.S. Congress, including:

- Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), which not only encompasses all media but includes those materials formally regulated by the Federal Water Pollution Act (FWPA)
- Resource Conservation and Recovery Act (RCRA)
- Toxic Substances Control Act (TSCA)

The USCG applies regulations to transportation of chemical products on boats from a shore base to offshore rigs and/or platforms. These regulations address much of the same details as mandated by OSHA (29 CFR, Chapter 17) and DOT (49 CFR, Part 172) regulations, but have there own specific rules and reporting requirements. In addition, they also require information on hazards and health impacts.

As chemicals move through the supply chain from the manufacturing to the formulation stage, packaging containers, record keeping, and handling policies are adopted to meet all potential domestic and international regulatory requirements. Frequently, chemicals are stored offshore in the containers in which they were transported. Therefore, the same safety and containment standards that were used for transportation are met or exceeded for storage.

Chemical supply companies and operating companies typically provide specific training to their employees regarding chemical transportation, storage, handling and use. The complexity of regulations affecting these issues and the number of agencies involved, often make it difficult for most workers, chemical suppliers, and consumers to maintain a complete understanding of offshore chemical storage and handling. Chemical supply companies therefore, address this by maintaining specialists who develop policies and procedures that ensure all regulatory requirements are met.

5.3 Chemical Storage and Handling by Chemical Class

5.3.1 Chemicals Applied to Wells

A supply of chemical components is normally kept on site (offshore) to provide the necessary chemicals for drilling, cementing, and completion, stimulation, and workover. For exploratory wells, a quantity of each drilling fluid component sufficient to drill the well may be brought to the drilling rig. For development drilling, in which the drill rig remains in one place and drills a number of wells from the same surface site, supply boats regularly deliver drilling components to the site to maintain the supply at a level sufficient to drill the well underway.

5.3.1.1 Drilling Fluid Chemicals

Drilling fluid chemicals are used during the exploration and development stages. Normally, these stages comprise approximately 10% or less of the life of an oil or natural gas field. The majority of these chemicals are inorganic materials that are unreactive in the marine environment, such as barite and clays.

Once on site, chemical storage becomes the responsibility of the operating company. Waste resulting from the use of the chemical is treated and disposed of by the operating company. A chemical supplier may agree, as part of their service, to take back empty containers and excess chemicals and dispose of them, but responsibility remains with the customer.

Solid drilling fluid components are customarily shipped in sacks, which are stacked on pallets. On a drilling rig, they are stored on pallets, in the sacks, and within a storage area provided specifically for drilling chemicals. A typical sack of weighting agents and viscosifiers weighs approximately 100 lbs. For all other solids, a sack typically weighs 50 lbs. The number of sacks per pallet depends on the sack size and bulk density of the material. Some low-density materials are shipped in larger sacks and a pallet may contain as few as 30 sacks. Some conventional sacks of lower density material such as lignite may be shipped on pallets containing 70 sacks. High-density materials such as barite may be shipped on pallets of 40-60 sacks.

On some types of drill rigs, bulk tanks are used to store high volume materials such as barite and clay. These bulk tanks are refilled from cargo tanks on supply boats. The transfer from supply boat to bulk tank is made using an air blower that suspends the fine solids of barite or clay in air and carries them into the bulk tank. Almost all water-based drilling fluid components are solids. Those that are not solids are usually minor components and are shipped in buckets or drums.

Single well amounts shown in Table 5, Section 3.0, illustrate those typical for each category of well.

5.3.1.2 Cementing Chemicals

Cementing chemicals are used primarily during the exploration and development stages. Normally, these stages comprise 10% or less of the life of an oil or natural gas field. The majority of these chemicals are basic cements that react with seawater to form natural constituents found in marine sediments.

Cementing chemicals are transported to drill rigs by the chemical supplier as needed for each cementing job. Solid cement components are customarily shipped in sacks and stacked on pallets. Since the casing in each well is installed in several separate stages, the amount of cement chemicals stored and used for each job is less than the total for the entire well. On drilling rigs, solid cementing chemical components are typically stored in sacks and placed on pallets. Individual sacks of cements typically weigh 94 lbs.

The number of sites storing and using cementing chemicals at any one time is a subset of the number of drilling rigs operating. Only a few rigs are engaged in cementing at any one time; therefore, the number of sites storing cement is much fewer than the number of rigs operating at the time.

Single well amounts shown in Table 7, Section 3.0, illustrate those typical for each category of well.

5.3.1.3 Completion, Stimulation, and Workover Chemicals

Completion, stimulation, and workover chemicals are used primarily during the development and active production stages. Normally, these stages comprise 50% to 60% or more of the life of an oil or natural gas field. The majority of these chemicals are acid formulations, brine solutions, and solid proppants.

Completion, stimulation, and workover chemicals are delivered to well sites on an as-needed basis. Acid solutions are supplied in bulk tanks as ready mixed products. Additives are typically supplied in 5 gal. buckets or 55 gal. drums. Salt solutions may be prepared on site by adding solid salts and additives to water.

Storage offshore is temporary, since these chemicals are shipped for each job and stored until the job is completed. Chemicals are mixed and used under the supervision of the chemical supplier. The empty containers are frequently reusable vessels and are returned to the supplier. Sacks and smaller containers are disposed of as waste.

The number of sites storing completion, stimulation, and workover chemicals at any one time is related to the number of wells being completed, stimulated, or repaired. The number of wells being completed in any one year will be related to the number of drilling rigs working in that year although the actual completions may be done using workover rigs rather than drilling rigs. Therefore, the total number of sites storing completion, stimulation, and workover chemicals is less than the number of working drilling rigs.

Single well amounts of completion, stimulation, and workover chemicals are shown in Table 8, Section 3.0, and illustrate typical amounts for each category of well.

5.3.2 Chemicals Applied to Production Processing Systems

Production-treating chemicals are primarily applied during the development, active production, and re-development stages. Normally, these stages comprise 60% to 70% or more of the life of an oil or natural gas field. The majority of these chemicals are not concentrated in any one functional category.

Production-treating chemicals used offshore are delivered by the chemical supplier to the customer's shore base. They are shipped on the customer's boat to the offshore platform. An amount sufficient to meet chemical requirements for an interval longer than the re-supply time is usually maintained on the platform. Re-supply times are determined by factors such as boat schedules and may potentially be impacted by weather delays. Data on typical volumes for each category of production-treating chemicals stored on platforms was gathered from the operating companies participating in this study. There are thousands of sites, in both shallow and deep waters in the GOM that store and use production-treating chemicals.

Production-treating chemicals are stored in one of two ways on platforms:

- In the shipping containers
- In bulk tanks that serve as the reservoir feeding the injection pumps

If bulk tanks are used, chemicals are transferred from the shipping containers to the bulk containers once they reach the platform. If chemicals are stored in the shipping containers, they are pumped directly from the container or transferred to pump reservoirs as needed.

Typical shipping container sizes were gathered from two major GOM production-treating chemical suppliers and include containers with volumes of 500 gal., 385 gal., 200 gal., 55 gal., and 5 gal.

One supplier provided data on the percentage of the product shipped in specific containers for 35 of its major chemical products. An evaluation of the information indicates that 55 gal., 200 gal., and 385 gal. containers were the most common container sizes used, with the 200 gal. container being used for at least a portion of most products. For all but three of the 35 products, the shipping container was the final storage container. For these three, a permanent on-site storage tank was used.

The second chemical supplier reported that several central facilities that it supplies use 550 gal. stainless steel transporters as permanent storage. In addition, a second tank is also kept in reserve. Smaller structures use 275 gal. stainless steel transporters or 220 gal. polypropylene (poly) tanks as permanent storage. Poly tanks may be dictated by the ability of the platform crane to pick them up. Usually, chemicals are shipped in similar tanks, but can also be supplied in smaller transporters as reported above. For deepwater structures, the supplier reported that 500 to 1,000 gal. permanent storage tanks are designed into some facilities and piping is provided to connect transport tanks to the built in storage tanks. Most offshore platforms normally receive a weekly boat run for chemical re-supply.

Alternative Chemical Delivery Systems

In conventional shallow water systems, production-treating chemicals are delivered to a platform and are added to the system on the platform. In deep water, there is an increasing use of subsea completions, and the use of umbilicals. Umbilicals are used to carry the produced stream to the platform as well as to deliver production-treating chemicals to production wells. This technology is becoming more prevalent as a result of its efficiency in treating very deep subsea flowlines. These wells might be several miles (i.e., over 60 miles) from the platform or structure receiving the production.

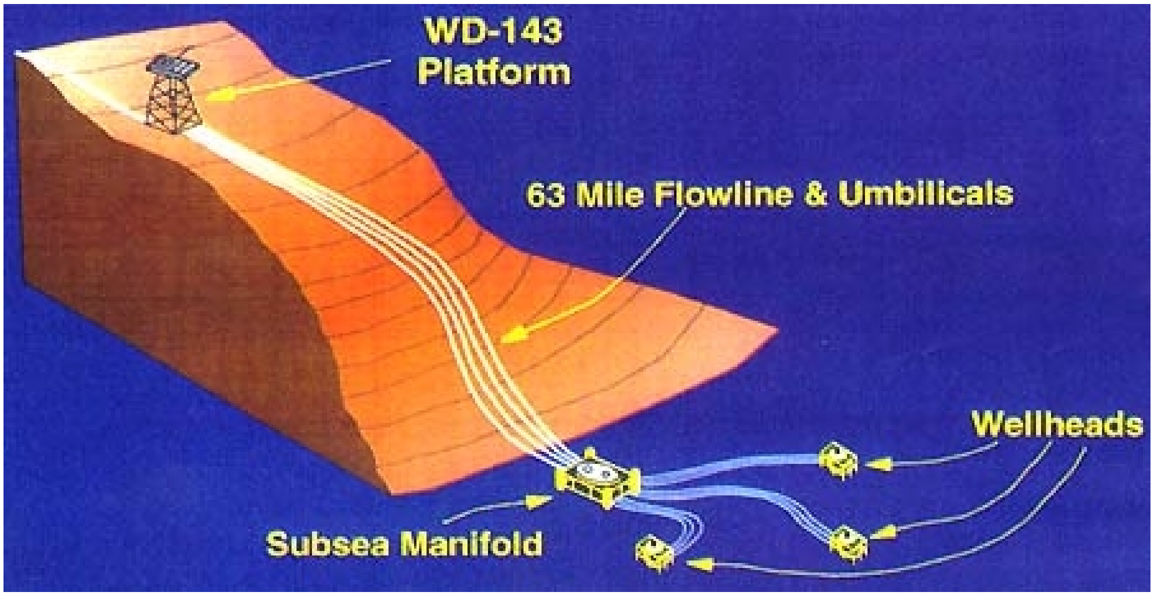
Methanol and various types of glycols (e.g., ethylene glycol) are the primary types of production-treating chemicals transported in umbilicals to support deepwater operations. Their primary functions are to inhibit hydrate formation that results from the interaction of gas and water as a result of the physical conditions of the deepwater environment. Very deep water always has low temperature, and considerable heat loss will occur in long flowlines. If the temperature goes below the hydration point, solids can form and block the flowline.

The volume estimation models described in Section 3.0 were developed using 1998 data to provide estimates of the quantity of chemicals stored and used offshore. The models contain information on chemical storage that aids in estimating the size of individual shipments that are a factor in determining the risk of accidental discharges.

5.3.3 Factors Affecting Chemical Spills

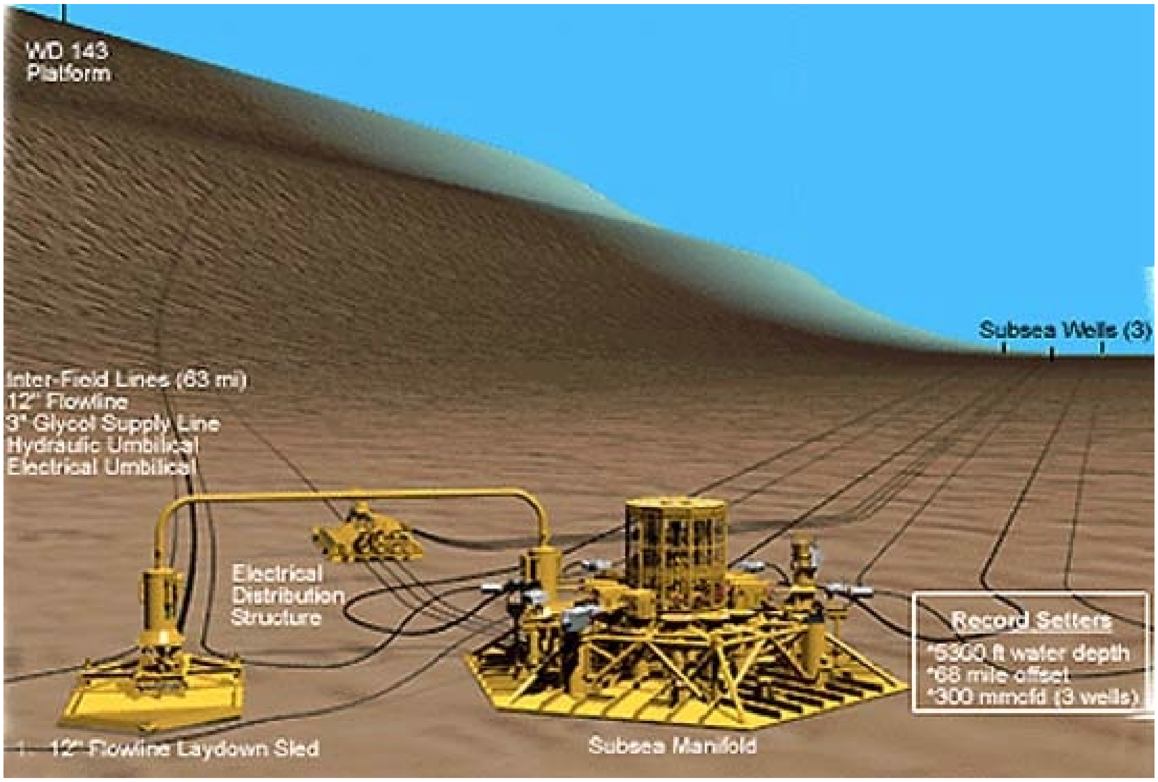
The shallow water region of the GOM has a long history of development. There are many small fields with multiple platforms that require a significant amount of support as part of normal operations. However, most shallow water trips by transport/support vessels are relatively short and metocean conditions are typically milder than the deepwater region. Conversely, the deepwater region of the GOM has a relatively short history of development (i.e., since the mid- to late-1980s). Deepwater fields are and will continue to be located much further from shore, and trips by transport/support vessels are and will be of longer duration. In addition, metocean conditions may be more extreme than in shallow water. These factors will require careful monitoring since little is known about spill potential and risk in deep water.

New technological advancements, specifically for deepwater applications, such as the use of umbilicals to supply production-treating chemicals to subsea producing wells, are an example of a new tool that increases the probability and adds a new potential source for accidental chemical spills. These umbilical lines are typically long and have a relatively high volume compared to topside storage vessels. Importantly, umbilicals have been in use for a relatively short period of time (i.e., 3-5 years), limiting any measurable performance and/or safety data. Most of the umbilicals used for chemical transport purposes are flexible and may be constructed of carbon steel with zinc coating. They usually range between three- to less than one-inch in diameter. For example, a production well system operating in the Mississippi Canyon region of the Gulf ties back to a platform at West Delta 143, which is over 63 miles away. To supply that system with needed production-treating chemicals, the operator has laid a three-inch umbilical line. Figures 9 and 10 show examples of umbilicals used in deepwater operations.



Source: www.offshore-technology.com/projects/mensa/mensa5.html

Figure 9. Schematic of Flowline and Umbilical Subsea Architecture in the Gulf of Mexico.



Source: www.offshore-technology.com/projects/mensa/mensa4.html

Figure 10. Detailed Schematic of Subsea Manifold and Template Base.

5.4 Gulf of Mexico Chemical Spill Data and Recorded Spills

5.4.1 Background

With the passage of the Federal Water Pollution Control Act (FWPC) (i.e., the Clean Water Act) in 1972, the USCG was provided with statutory authority to regulate oil pollution prevention and response activities in the United States waterways. The FWPC requires that any discharge of an oil and or hazardous substance in a harmful quantity be reported to the appropriate agency of the United States. Most importantly, it provided for the development of a National Contingency Plan (NCP) which would "provide for efficient, coordinated and effective action to minimize damage from oil and hazardous substances discharges, including containment, dispersal, and removal of oil and hazardous substances." The President of the United States delegated the authority and responsibility of establishing this plan to the Council on Environmental Quality.

In August of 1973, the President, in executive order No. 11735, delegated the authority and responsibility of establishing this plan to the Council on Environmental Quality. As a result, the National Oil and Hazardous Substances Pollution Contingency Plan was developed and implemented later that year. This plan established the NRC, which became operational in August of 1974 at USCG Headquarters in Washington, D.C. for the reporting of, and coordination of response to, pollution by oil and hazardous substances.

Since 1973, the USCG has been maintaining the Marine Safety Management System (MSMS) at USCG Head Quarters in Washington, DC. The MSMS data represents discharges reported to the USCG by responsible parties, other government agencies (e.g., MMS), or as discovered and reported by USCG personnel. The current MSMS database is a combination of three databases:

1. The Pollution Incident Reporting System (PIRS) with data from 1973 to 1985
2. The Marine Safety Information System (MSIS) with data from 1985 to 1991
3. The Modified MSIS System (MIN-MOD) with data from 1991 to present

In the event of a chemical spill offshore, proper protocol is to contact the NRC at 1-800-424-8802. Spill information, including material involved, mode of transportation, injuries, damage, fatalities, and other incident details is collected and the information entered directly into the U.S. EPA's Incident Reporting Information System (IRIS).

As discussed, CERCLA requires that all releases of hazardous substances (including radionuclides) exceeding reportable quantities be reported by the responsible party to the NRC. 40 CFR, Part 302 Designation, reportable quantities, and notification, promulgates reportable quantities and reporting criteria. SARA Title III requires that all extremely hazardous chemicals that exceed reportable quantities be reported to the NRC as well as to State Emergency Response Commissions (SERC) and Local Emergency Planning Committees (LEPC). See Table 19 which lists those organizations/agencies to be contacted following a chemical spill. Links to internet resources are also provided as are sites of general interest related to this subject.

5.4.2 Historical Chemical Spill Data

Currently, there is limited information on chemical spill events in the Gulf of Mexico and more specifically, there is little to no information available on chemical spills that resulted from E&P activities in the GOM. What chemical spill information found is presented in this section and when possible, a distinction is made regarding the activity and/or cause of the documented spill.

Statistical information on chemical spills in the GOM was obtained from the USCG and the MMS. While data on historical spills were requested from operators and suppliers, no information could be obtained from these sources. Since 1990, the USCG has maintained records of reported chemical spills that are collated and presented as national summaries within an annual report. These summaries are available on the USCG's website, see Table 19.

The data sets for chemical spills are subsets of pollution incidents in and around U.S. waters and have been available since 1990. Chemical spill data are divided by the following types of categories and presented in individual tables by:

- Chemical spill sizes (from 1 to 100 gal. to > 1,000,000 gal.)
- Water body (the Gulf of Mexico is one of nine listed)
- Location
- Major source overview

Waterbody category data for the GOM was combined from the available annual chemical spill summaries (i.e., 1990-1998). Table 17 shows the total quantity of liquid (i.e., in gallons) chemicals spilled, and Table 18 shows the total quantity of solid (i.e., in pounds) chemicals spilled. The data does not distinguish between the activity that caused the chemical spills or whether the spill was from fixed structures and/or transport vessels.

Table 17

Gulf of Mexico Chemical (Liquids) Spill Data (1990-1998)

Year	Number of Spills	% of Spill Incidents (U.S. Waters)	Spill Volume (gal)	% of Spill Volume (U.S. Waters)	Average Spill Size (gal)	Median Spill Size (gal)	Maximum Spill Size (gal)
1990	4	2.90%	1,217	1.20%	304	108	1,000
1991	11	6.90%	5,189	1.70%	472	8	5,000
1992	8	5.30%	162	0.00%	20	5	70
1993	11	8.30%	597	0.30%	54	2	550
1994	8	5.80%	6,055	0.10%	757	1	5,922
1995	7	4.70%	1,133	0.40%	162	1	1,000
1996	13	10.70%	3,501	5.60%	269	1	3,276
1997	27	22.90%	390,842	77.60%	14,476	1	381,565
1998	32	26.70%	65,577	18.40%	2,049	1	63,000(1)

(1) This information was obtained from the National Response Center Database. The data provided by the USCG for 1998 was supplemented with this information.

Table 17 indicates that the number of liquid chemical spills (i.e., excluding oil) has steadily increased in the GOM from 1990-1998. The percentage of spill incidents for the Gulf region has also increased and accounted for almost 27% of all incidents in U.S. water bodies by 1998.

Analyzing the chemical spill data provided, it is important to recognize that a few large single events accounted for the majority of the volume of chemicals spilled. For example, in 1997 and 1998, the average size of the average liquid chemical spills appeared to increase from previous years in the GOM. However, this was a result of high volume single-event spills that accounted for the majority of the liquid chemicals discharged into U.S. waters. For example, one liquid chemical spill in the GOM in 1997 accounted for 381,565 gal. (not an E&P related spill) of the total 390,842 gal., leaving a total of 9,277 gal. from the remaining 26 spill incidents. Likewise, one liquid chemical spill (zinc bromide) in 1998 accounted for 63,000 gal. of the total 65,677 gal., leaving a total of 2,577 gal. from the remaining 31 spill incidents.

The 1997 liquid chemical spill of ethylene dichloride (not used in E&P operations) was a result of a collision between two vessels near the sea buoy entrance to the lower Mississippi River. The 1998 chemical spill of zinc bromide was a result of a valve being left in the wrong position on an offshore platform. The zinc bromide chemical spill was the largest E&P spill found in the survey, and a 45,000 gal. spill of zinc bromide was selected for spill modeling and detailed chemical profiling (Profile 7) in Section 8.0.

Table 18

Gulf of Mexico Chemical (Solids) Spill Data (1990-1998)

Year	Number of Spills	% of Spill Incidents (U.S. Waters)	Spill Size (lbs)	% of Spill Volume (U.S. Waters)	Average Spill Size (lbs)	Median Spill Size (lbs)	Maximum Spill Size (lbs)
1990	6	14.60%	604,082	69.80%	100,680	33,684	446,000
1991	4	8.00%	9,787	1.80%	2,447	27	9,730
1992	1	3.00%	3,000	0.50%	3,000	3,000	3,000
1993	7	35.00%	13,729	52.10%	1,961	1,800	4,178
1994	1	2.70%	27,000	1.50%	27,000	27,000	27,000
1995	0	0.00%	0	0.00%	0	0	0
1996	3	12.50%	29,802	22.20%	9,934	14,742	14,960
1997	0	0.00%	0	0.00%	0	0	0
1998	1	3.10%	10,822	1.30%	10,822	10,822	10,822

Table 18 data do not indicate any clear patterns regarding spills of solid chemicals in the GOM. When spilled, the average quantity is usually large, and this is most likely due to how these solid chemicals are transported (i.e., sacks, containers on pallets). There is no information available regarding sources and or causes for any of these chemical spills.

As part of this study, the MMS provided chemical spill data from February 1997 to February 2000, for a total of 17 recorded spills in federal waters of the GOM. An evaluation of the data set indicates that of the four chemical classes, a disproportionately large ratio (i.e., eight of 17, or 47%) of spills related to completion, stimulation, and workover chemicals were reported. Within this chemical class, zinc bromide was the primary chemical spilled (i.e., total of six spills), with spill volumes ranging from 168 gal. to 7,140 gal. Geographically, five of 17 spills occurred in the Garden Banks region and three spills occurred in the Mississippi Canyon area of the Gulf. The 12 other spills were spread throughout the Gulf with no more than two spills within one area or block.

Completion, stimulation, and workover chemicals are likely to be directly applied from supply boats instead of being transferred to the platform or rig and then used. Such a handling system may afford more opportunity for spills to occur, and as a result some chemical suppliers have developed containment systems and “slop tanks” that address some of the problems associated with such operations. Completion, stimulation, and workover chemicals are probably stored at over 300-400 offshore sites in the GOM at any one time. Another eight spills were reported for production-treating chemicals that are stored at over 2,000 sites in the GOM (i.e., not drilling sites).

5.5 Chemical Spill Response

Currently, there are no federal or state regulations and/or protocols for responding to chemical spills related to E&P activities in the Gulf of Mexico and/or other U.S. waters. As discussed, the USCG is in the process of developing regulations that will address the implications of hazardous substance releases in the marine and freshwater environments.

Today, the responsible party transporting/storing/using chemical(s) at the time a spill incident occurs (i.e., during transport, release from an offshore drill and/or production rig) follow individual protocols that normally result in one or all of the following organizations being contacted immediately; the National Response Center (NRC), the U.S. Coast Guard (USCG), and the state’s environmental regulatory agency. Chemical spill response may be divided into three distinct stages.

First Responder Level

The responsible party will normally secure the area or terminate the action that caused the chemical spill while ensuring safety to workers on the particular offshore structure. The responsible party will then communicate with the USCG to ensure human safety has been addressed and they will team together to determine if any additional measures are required. At this level, awareness is at the lowest level and trained individuals should only recognize that there is a problem, provide some assessment if it can be done safely, and ensure that the proper authorities are notified.

Second Responder Level

The team of the USCG and responsible party now work to get more information regarding the chemical spill with emphasis on the safety of personnel and the general public. Immediate actions to reduce the risk (i.e., source control) to those immediately at threat are taken. Next, the USCG's team will often call on specialists pre-identified to provide technical support, such as the National Oceanic Atmospheric Administration (NOAA) Scientific Support Coordinators (SSCs) and the EPA's Emergency Response Team (ERT). The SSCs are divided into nine districts and serve on the Federal On-Scene Coordinators (FOSC) staff as the lead of a scientific team and provide expertise in environmental chemistry, oil slick tracking, pollutant transport modeling, natural resources at risk, environmental trade-offs of countermeasures and cleanup, information management, contingency planning and liaison to the scientific community and the natural resources trustees. The ERT group is a specialty group of trained scientists and engineers who's capabilities include multimedia sampling and analysis, hazard assessment, cleanup techniques, and technical support.

The USCG's team will then obtain the following technical information specific to the chemical substance; density of the substance spilled in seawater (i.e., to determine if the substance will float or sink) and packaging/container details (if any), solubility in seawater (i.e., slight, high, insoluble), fate and transport characteristics of the chemical substance (i.e., persistence in the marine environment), chemical toxicity, geological conditions of the receiving environment (i.e., sandy, silty, rocky). During this phase, the USCG's team (i.e., USCG, the responsible party, SSCs or ERT) will consult with various experts from the chemical manufacturers company, the USCG, and might also contact CHEMTREC whose extensive database of 24-hr. contacts contains experts including chemical manufacturers, shippers, carriers, emergency response contractors and other organizations that have information and resources.

As information is gathered, the USCG's team will evaluate the need for a hazardous materials response often coordinating this strategy with various spill response organizations. Since there are no protocols and/or regulations such as the Oil Pollution Act of 1990 (OPA-90) that require all those who transport petroleum and petroleum products in U.S. coastal waters to ensure by contract the resources necessary to respond to "worst case discharge" to the "maximum extent practicable," all chemical spills are treated on a case-by-case basis and evaluated using the criteria as described here.

Within shallow water, the determination whether there is a response action is often based on whether or not the chemical substance can be recovered and whether the recovery effort is economical based both on the value of the chemical substance and the cost of the recovery mission. In addition, much more is known about the shallow water environment (i.e., biological communities, geology, etc.) as compared to the deep waters of the GOM.

Third Responder Level

By the third stage, significantly more resources are available and a Unified or Joint approach is taken to respond to the spill incident. The USCG's team, with the consultation of chemical experts and spill response specialists, have determined an action plan that includes an environmental assessment, mitigation, and cleanup plan determination and implementation. At this point, the company responding to the chemical spill, which may include the USCG, government organizations (i.e., the Marine Preservation Association (MPA) which funds the

Marine Spill Response Corporation (MSRC)), and/or commercial spill response companies, will initiate the spill response with the assistance and guidance from the USCG as well as the responsible party. The technical specialist (i.e., SSCs or ERT) will provide input either on-scene or through various communication means to the Unified Command (i.e., lead person responding for the responsible party, federal government, and effected states).

Often, in developing the chemical spill cleanup strategy, the USCG and responsible parties will refer to the CAMEO database. CAMEO ® is a system of software applications used widely to plan for and respond to chemical emergencies. It is one of the tools developed by EPA's Chemical Emergency Preparedness and Prevention Office (CEPPO) and NOAA's Office of Response and Restoration to assist front-line chemical emergency planners and responders. CAMEO can be used to access, store, and evaluate information critical for developing emergency plans. In addition, CAMEO supports regulatory compliance by helping users meet the chemical inventory reporting requirements of the Emergency Planning and Community Right-to-Know Act (EPCRA, also known as SARA Title III). The CAMEO system integrates a chemical database and a method to manage the data, an air dispersion model, and a mapping capability. All modules work interactively to share and display critical information in a timely fashion. CAMEO initially was developed because NOAA recognized the need to assist first responders with easily accessible and accurate response information. Since 1988, EPA and NOAA have collaborated to augment CAMEO to assist both emergency responders and planners. CAMEO has been enhanced to provide emergency planners with a tool to enter local information and develop incident scenarios to better prepare for chemical emergencies. The Bureau of Census and the USCG have worked with EPA and NOAA to continue to enhance the system.

To support information presented in this section, multiple government and private organizations specializing in hazardous materials response were contacted to determine state of-the-art response to chemical spills, particularly in the GOM regions. Each of the spill response companies specialize in responding to oil spills, and have little or no experience in responding to chemical spills. Most companies and/or organizations indicated that they were waiting for the USCG to issue regulations with respect to chemical substances before developing protocols related specifically to chemical spill response. As discussed, the USCG has been in the process of evaluating the need for and developing regulations for responding to chemical spills and has initiated the development of regulations.

Table 19 contains a compilation of chemical spill response contact information for the Gulf of Mexico.

Table 19

Emergency Response Contact Information for Chemical Spills in the Gulf of Mexico

Organization/Agency	Contact Information	
	Internet URL Reference	Phone Number
National/Federal Contacts		
National Response Center (NRC)	http://www.nrc.uscg.mil/index.htm	1-800-424-8802 (24 Hours)
United States Coast Guard (USCG)	http://www.uscg.mil/	1-800 424-8802 (24 Hours) – same as the NRC
USCG Department of Marine Safety and Environmental Protection	http://www.uscg.mil/hq/g-m/gmhome.htm	---
U.S. EPA's Incident Reporting Information System (IRIS)	http://www.epa.gov/ngispgm3/iris/	1-513-569-7254 or e-mail: RIH.IRIS@epamail.epa.gov
National Oceanic and Atmospheric Administration (NOAA) – Office of Response and Restoration / Scientific Support Coordinators (SSCs)	http://response.restoration.noaa.gov/	1-504-589-4414; NOAA's District 8 office located in New Orleans, Louisiana. This district office covers the coastal and offshore zones of Texas, Louisiana, Mississippi, Alabama, and part of Florida
State/Local Contacts		
State Emergency Response Commissions (SERC)	http://www.epa.gov/tri/sercs.htm	---
Local Emergency Planning Committees (LEPC)	http://www.epa.gov/tri/lepcs.htm	---
Alabama Waters (Alabama Department of Environmental Management)	http://www.adem.state.al.us/	---
Florida Waters (The Florida Department of Environmental Protection)	http://www.dep.state.fl.us/	---
Florida State Emergency Response Commission	---	1-800-320-0519 (24 Hours)
Florida Marine Patrol (FMP)	---	1-800-342-5367 (24 Hours, In State)
Louisiana Waters (Louisiana Department of Environmental Quality)	http://www.deq.state.la.us/	1-225-342-1234 (24 Hours)
Mississippi Waters (Mississippi Department of Environmental Quality)	http://www.deq.state.ms.us/newweb/homepages.nsf	---
Mississippi Emergency Management Agency (MEMA)	---	1-800-222-MEMA (6362) or 1-601-352-9100
Texas Waters - (The Texas Natural Resource Conservation Commission – TNRCC)	http://www.tnrcc.state.tx.us/	1-800-832-8224 (24 Hours)
Texas General Land Office (TGLO)	http://www.glo.state.tx.us/	1-512-475-1575

Table 19

Emergency Response Contact Information for Chemical Spills in the Gulf of Mexico (continued)

Organization/Agency	Contact Information	
	Internet URL Reference	Phone Number
Industry/Other Contacts		
CHEMTREC	http://www.chemtrec.org/	1-800-262-8200
GOM spill summaries (oil and chemicals) from the USCG	http://www.uscg.mil/hq/g-m/nmc/response/stats/ac.htm	---

5.6 Summary

The information provided in this section summarizes the majority of chemical spill information available for the GOM. The type and extent (i.e., 1990-1998) of these data allow for purely qualitative judgments on the sources and/or causes of chemical spills. In addition, given the quality of the data collected and evaluated there is no definitive way to determine whether these chemical spills occurred in shallow or deep water (i.e., since geographic locations within the Gulf and/or water depths are not included in the data set) or to determine the activities and/or events that caused these chemical spills.

While the number of chemical spills in the Gulf may be related to the ongoing and increasing E&P activities in the region, the increase in number of spills reported since 1990 may not be directly correlated to an increase in E&P operations. A percentage of the overall increase in reported spills can likely be attributed to the improvement in reporting and management practices by offshore operators and chemical supply companies over the last decade.

Of the four chemical classes, the application of completion, stimulation, and workover chemicals from supply boats poses the greatest potential for accidental spills to the marine environment. This risk is largely the result of the method in which these chemicals are handled and transferred. In order to address this potential risk, some supply companies have developed containment systems and “slop tanks” that address some of the problems associated with such operations.

6.0 BIOLOGICAL COMMUNITIES POTENTIALLY AFFECTED FROM SPILLS OF CHEMICALS USED IN DEEPWATER E&P

6.1 Introduction

This section of the report is an overview of the biological communities potentially affected by spills of chemicals used in deepwater E&P. An emphasis is afforded the deep sea because the focus of chemicals selected for this study are those new or specific to deepwater oil and gas activities.

Exploration for oil and gas is increasingly extending into the deeper waters of the Gulf of Mexico. Biological communities potentially at risk from the use of chemicals, therefore, extend past the break of the continental shelf (generally accepted as the upper limit of the deep sea). The Law of the Sea sets this break at 1,000 ft. (305 m); however, for the Gulf of Mexico, the depth of 656 ft., or 200 m, more closely coincides with the shelf break and is used in the Deepwater Oil and Gas Royalty Relief Act and for resources estimation. This fact puts deep-sea benthic pelagic biological communities and oceanic pelagic communities potentially at risk. Certain aspects of deepwater development may possibly pose novel threats of impact, either because of the technology, the chemical compounds, the differing environment, or the different biological communities and ecological processes (Carney 1998).

Many wastes and/or accidental discharges from drilling activities will migrate towards the bottom. Due to multiple wells and horizontal drilling, there is an expected greater volume of cuttings to be discharged from deepwater operations than from shallow water operations. However, there is a predicted lower density of structures for deepwater operations. Production activities are likely to be similar with a shift in the location of subsea hardware. Processing and separation will likely be similar. The shore infrastructure already exists.

While E&P occurs in deepwater, the infrastructure that supports these activities resides mainly in the coastal zone; transportation and transport facilities (e.g., pipelines) span the distance from the activities in deep water to the coastal facilities. Transportation of fluids will probably tie in to existing shallow pipeline systems, so that the environmental risks will be similar. Differences emerge in the types of chemicals carried and the deepwater extension of pipelines. Thus, a broad range of biological communities can potentially be exposed to spilled chemicals used in deepwater activities.

The major types of benthic communities within the continental shelf zone are those associated with soft-bottom habitats that vary in sedimentary composition. Many biogenically structured communities, such as coral reefs or “live” bottoms, occur throughout the Gulf of Mexico. These ecosystems are usually more taxonomically diverse than the surrounding soft-bottom communities and are likely to differ in their sensitivities and responses to environmental perturbations. Within the deep sea, the benthic communities are dominated by soft-bottom dwelling organisms, with an added importance of microhabitat structuring. Hydrocarbon seeps with their chemosynthetic, or otherwise specialized biological communities, are places where gas and oil flow naturally out of the sea floor and are quite common on the continental slope of the northern Gulf of Mexico. Much less is known of the deep-sea and oceanic communities.

Several habitats within the coastal and oceanic portion of the Gulf of Mexico have been afforded special status as National Marine Sanctuaries and National Estuarine Research Reserves.

6.2 Deep-sea Benthos and Demersal Fauna

The deep sea is the largest habitat on Earth. It is predominantly dark and cold; the food supply is low; and colossal pressures are exerted on its inhabitants by the great depth of the overlying waters. It is mostly inaccessible to human exploration and experimentation. It is not surprising that knowledge of deep-sea life is limited, especially more so for dynamics of populations and biological processes.

Oil and gas development in deepwater environments pose different technical and environmental considerations than in shallow waters. Production sites are generally farther from shore, reducing the potential of oil spills from blowouts reaching shore, although a notable exception is the *Ixtoc* spill of 1979-1980. Dispersion of contaminants released from the rig or platform are likely to be greater due to the larger volumes of receiving water. However, geohazards related to seabed slumping may be more likely, and accidental spills may be more difficult to control. In addition, any effects on the benthic environment may be longer lasting because of the expected slower recovery rates of deeper benthos (Boesch and Rosenberg 1981, Rabalais and Boesch 1987).

6.3 Physical Environmental Setting

Carney (in draft) provides a good summary of the importance of pressure, density, light, oxygen, and currents in the deepwater environment for oil and gas activity impacts.

- Pressure increases uniformly with depth at 1 atmosphere (atm) per 10 m. This affects the solution chemistry of discharges and spills, as well as the ecological differences in calcium carbonate dissolution (important to meiofaunal organisms such as foraminiferans) above and below the calcite compensation depth (CCD), at which depth the dissolution of sinking tests equals the rate at which the material accumulates (i.e., shallow water models for fates and effects of carbonate containing discharges must be re-evaluated). Clathrates in the upper part of the stability envelope (approx. 500 m) may constitute a special habitat.
- Density (temperature and salinity) changes nonuniformly to 1,000 m where it becomes uniform and high in cold, deep bottom-water. Limited stratification in deep water will allow discharge plumes to easily propagate.
- Light decreases exponentially with depth, is present in low intensity below 200 m, and is generally thought to be absent deeper than 1,000 m. Bioluminescence is important for deepwater animals. Animals adapted to low light might be especially impacted by increased turbidity from deep plumes of low transmission water. Below sensible sunlight, turbidity may impact biological light interactions.
- Oxygen minimum (3 mg/l) lies between 200 m and 750 m in the Gulf of Mexico, mostly at 400 m. Below 750 m, oxygen is again high and relatively constant. Spills of compounds with labile carbon may alter the local balance of oxygen consumption and replacement, especially in the OMZ, and result in local deep anoxia.

- The benthic boundary layer (BBL) varies in thickness from 5 to 100 m and is a steady-state feature of fluxed and resuspended particles important to deep pelagic fauna (i.e., aspects of deep activities should not just focus on the seabed, but include the overlying water in the BBL). BBL conditions redistribute the detritus pulse into a complex patchwork on the bottom, suggesting a mechanism for environmental heterogeneity.

Currents

The deep bottom is characterized as a habitat with low energy, low tidal, geostrophic, and thermohaline currents with episodes of high current velocity. (Nowlin 1998) indicated that Loop Current speeds may exceed 150 cm/s at the surface with velocities as high as 5 cm/s still persistent at 1,000 m. These speeds are restricted to the southeastern and northeastern Gulf of Mexico and may intrude to the continental edge of the Florida panhandle. Cyclonic and anticyclonic eddies (40-150 km) are ubiquitous on the northern slope region (LATEX-C and GULFCET programs).

Eddie Juggernaut, in the northwestern Gulf, currently has speeds up to 150 cm/s at the surface (N. Walker, personal communication). Eddies in the western Gulf showed velocity spikes to 30-40 cm/s at 500 m (Nowlin 1998). Loop Current rings off south Texas influence currents in the 200-700 m depth range, with the 200-m currents exceeding 30 cm/s during 40% of the record and 50 cm/s during 19% of the record. Hurricane Andrew effects in the surface waters exceeded 150 cm/s (also at 20 m off Terrebonne Bay, N. Rabalais personal observation), but speeds decreased rapidly with depth so that at 100 m currents did not exceed 50 cm/s, and at 490 m about 5 cm/s was reached. Hurricane Allen (south Texas, mooring 9) produced currents of 90 cm/s at 200 m, 15 cm/s at 700 m, and 15 cm/s just above the bottom at the 730 m water depth.

Geology

Geologically the northern-to-western Gulf of Mexico continental slope is perhaps the most complex continental slope environment in the ocean. It is technically difficult for deepwater E&P, and results in a myriad of habitats for biological communities, including hard substrate, chemosynthetic communities associated with a spectrum of hydrocarbon venting and seepage areas, and variable sediment, slope and stability types.

Zonation

The continental shelf occupies 5.8% of the earth's surface. The continental slope (200-3,000 m) and rise, (3,000-4,000 m) occupy 10.7%, and the deep-sea basin and trenches make up the remainder with 54.3% (earth surface above sea level 29.2%). The continental slope occupies an especially important place at the boundary between the continental blocks and the deep-sea. Terrestrial sediments predominate to its landward side, and the pelagic oceanic sediments lie offshore. The gradient can be greater than 1 in 40, as opposed to the less than 1 in 1,000 found on the shelf and abyss, and the relief can be (especially locally where submarine canyons intrude) as much as 2,000 m (not the Gulf of Mexico). The gradients, topographically and hydrographically (in terms of the meeting of shelf and oceanic water masses) are strong ones, and the area is one of dynamic tensions with advantageous implications in terms of niche space for resident fauna. The only other part of the ocean that is as rich in topographic features is the boundary between the tectonic plates (the great mid-ocean ridges).

6.4 Biological Processes

Our knowledge base for the effects of chemicals or habitat perturbation is the most meager for the deep sea. It is expected, however, that ecological processes in the deep sea are fundamentally similar to those of the continental shelf, slope, or rise. The dichotomy between deepwater and shelf environments is mostly artificial since the people working on the various areas do not overlap in their studies. There are, however, additional environmental and physical parameters at work in the deep sea that make populations and communities there unique. What is not known are the sensitivities of individuals and communities to contaminants; the rates and mechanisms for population control, biological interactions, recruitment and rates; or potential for recovery from impact.

Carney (in draft) states that management perspectives for deep water need to address the same issues as for shallow water.

Maximum protection should be allocated to the most important and sensitive components. For non-fisheries, management is habitat rather than species directed, because it is easier to delineate habitats than to assess ecological importance. Resource values in shallow water are often driven by a fishery or aesthetic component; for deepwater, fisheries are less important, but still fuel an aspect of the economy (see below). With regard to aesthetics, the deep sea is not readily accessible, but there remains a public perception of high diversity; new species remaining to be discovered, exotic morphologies, etc. In shallow water, uniqueness of habitat has basically been defined and region- or habitat-specific management strategies can be developed. The information base for the deep sea, however, is inadequate to do this. For the vast majority of deep-sea species, even the most abundant, we do not know the basic information of feeding type, reproduction, life span, predators, and population biology.

MMS needs to know if the deep benthos - with its dependence upon detrital influx, its poorly understood diversity, and its vertical zonation - is especially more sensitive to impact than the shelf benthos. Management, in absence of adequate information, must turn to published generalities about deep-sea adaptation to make the “first cut” on relevance (Carney in draft). These generalities may be based on actual evidence, prevailing paradigms, and fashions of science. Today’s knowledge of the deep sea has replaced some of the prevailing paradigms, so generalities must be approached cautiously.

The deep-sea benthos is mostly a soft-bottom benthic fauna with additional physiological constraints imposed by no light, cold temperatures, and high pressure. Alteration of the soft bottom will affect two generalities of deep species animal sediment adaptations:

1. The predominance of soft-bottom dwelling organisms and the importance of habitat structuring.
2. Domination of deposit feeders (Carney in draft). The shallow-water strategy of recognizing special habitats on the basis of gross substrate (hard versus soft) will be insufficient in the deep environment where important habitat variation may occur within the vast soft bottom.

Other generalities are not necessarily accepted:

1. More restrictive reproductive patterns; rather, deep fauna show as much adaptive variation as encountered in shallow water
2. Larger fauna are more the unusual and a size shift to smaller appears to be an adaptation to low food levels (avoid disruption of food supply)
3. Dark adaptation is not supported by the presence of well-developed eyes in some animals or forms of bioluminescence (avoid increasing turbidity)

Bathymetric Zonation – There is a progressive change of fauna with depth, with the causal mechanisms remaining largely speculative (reviewed by Carney et al. 1983). The deep sea cannot be treated as a uniform environment. The faunal zones most identifiable in the deep sea are upper slope (200 to 1,000 m), an abyssal plain fauna (> 3,000 m), and a lower slope fauna (1,000 to 3,000 m) that overlaps the others. Unfortunately, research directions in the deep sea are not in zonation, an aspect that needs better understanding to develop management strategies across vast areas. Current DNA techniques (Etter and Rex 1990) show that the prevailing idea of widening vertical ranges with increasing depth is correct. Co-variance of factors with depth complicates separating causality from correlation. Physiologically relevant factors, such as increasing pressure with depth (Seibenaller and Somero 1989), are important. Biological factors, such as detrital influx rate gradient (Rowe and Pariente 1992) and their effects on feeding mode (Rex 1981) and biotic interactions, subsequently contribute to differences in community structure. Therefore, management decisions should not presuppose any particular mechanism.

Biomass Pattern – The unit per area (weight, carbon, nitrogen, counts) decreases exponentially with depth (variability with surface productivity, width of the continental shelf, and latitude). With regard to potential impacts, the community subject to the impact may decrease in size with depth. Conflicts with biomass exploiting activities, such as fishing, should decrease, and any impact studies will be plagued by small sample sizes. Dramatic biomass differences between the shelf break at 200 m and the slope bottom at 3,000 m suggest that these environments are different and require depth-specific management strategies. In areas where food biomass is rare, the disruption of natural patterns of detritus input may be the primary agent of environmental impact.

Diversity Pattern – The deep sea is species rich and, for some areas, there is a well-defined species maximum on the lower continental slope (approx. 2,000 to 3,000 m). With regard to impacts, they may be rightly or unjustly compared with more “charismatic” high diversity habitats such as coral reefs and tropical forests. Since the explanation of high diversity remains elusive, one possible interpretation is that we do not know how deep-sea ecosystems function and are unable to predict impacts. Some of the diversity explanations suggest a high dependence on subtle environmental variables (more than in shallow water) with an implication for greater sensitivity to perturbation. While it is always hoped that some index of diversity might be a precise indicator of ecosystem health, this simply has never been established (Carney, in draft).

The time-stability hypothesis (Sanders 1979) states that species somehow accommodate to each other and partition resources rather than compete in environments that are vast, old, and stable. Such accommodation implies a fine and easily upset balance among species for a narrow range of resources.

Cropper control is direct cropping by animals on species lower on the food chain that were about to exclude competitively weaker species (Dayton and Hessler 1972). This idea emphasizes the importance of predator-prey relationships, the importance of keystone species, and the potential disruption of larger communities if a keystone species were subject to impact.

Grain matching explanation (Jumars and Ekman 1983) states that the deep-sea bottom is finely divided into many habitats, many of which are biogenic, and that these fine-scale differences (centimeters and smaller) indicate that the system is not as homogeneous as most methods and scales of human observation would suggest. Biogenic structures should be more persistent in the deep sea and are likely to be a very important agent of habitat heterogeneity. Impacts that physically alter this finely structured sediment-water interface may have major impacts.

Contemporaneous disequilibrium proposed by Grassle and Maciolek (1992) produces a very dynamic picture of deep-sea diversity with a broad sea floor populated by species emigrating from many small and temporally varying centers of high competitive success so that large areas never come to a low diversity equilibrium. Thus, some areas of the sea floor (source areas) may be more important than others in diversity maintenance. In order to protect these areas, management must be able to identify them, a feat not yet accomplishable.

Current deep-sea ecology does not identify conclusively those processes maintaining diversity. Of two views, a homogeneous environment with complex competition or a heterogenous environment with normal competition, the second is more tractable. If the deep benthos is a habitat-rich system on a very small scale, then processes causing this variety need to be known and protected; these include biogenic structure, flow interactions at the sediment water interface, and redistribution of detritus.

The process of influx of organic detritus and the biogenic structuring of the benthos are processes of considerable management relevance because both processes are far more important in the deep sea than on the continental shelf. The influence of detritus influx is most readily seen in biomass or population density data. Biogenic structuring is much less understood. Potential impacts of deep-sea nodule mining that introduced a layer of older sediment, thus diluting the labile carbon supply, was seen as the main mechanism for impact with those operations (Jumars 1981). Burial under layers of mined sediments was expected to cause asphyxiation of the fauna, but the experimental design to test differences between 1 and 4 cm burial was not adequate to detect differences (Smith et al. 1988). Similar impacts might be expected with drilling activities in the deep Gulf of Mexico.

For the purposes of defining management scenarios, the deep-sea benthos should be divided into depth categories at 1,000 m, based on physical and chemical parameters, and set at the statistical lower limit of the permanent thermocline (Carney in draft). The 200 to 1,000 m range, or upper continental slope, is where sunlight effectively vanishes, where temperature and salinity become stable, and where oxygen drops to a minimum value. The interaction of physical processes and potentially impacting activities must be different in this physical transition zone than deeper, where uniformity of physical characteristics begin.

Until recently it was agreed that deep-sea animals exhibited natural histories (primarily reproductive strategies) that would make them especially sensitive to environmental impact. This generality is under attack. A generality that remains valid for relevant management purposes is that most deep-sea animals are deposit feeders. This fact, coupled with low levels of detritus influx, suggests that the spill of any chemical spill that caused the alteration of food availability would be potentially significant.

The high species diversity in a seemingly monotonous environment challenges core ideas about diversification. Ideas that the deep-sea floor is vastly more complex have the greatest management utility. Biogenic structures and small variations in sediment fabric may be more important sources of heterogeneity than in the shallow environment. If true, then human activities might be designed so as to minimize disruption.

6.5 Chemosynthetic Communities

Chemosynthetic seep communities occur along the northern Gulf slope between 95° and 88° W, between approximately 300 and 2,200 m, and coincide with the oil and gas rich areas of the Gulf (biased by the geography of sampling) (CS in Figures 11-13). The presence of perennial oil slicks, which form over many seeps and can be detected by satellite remote sensing, indicate that seeps are present across the entire continental slope of the northwestern Gulf. Seep communities are known to occur in some areas of acoustic wipeout, of authegenic carbonates and of observable seepage.

One deepwater seep site in Alaminos Canyon (2,200 m) has a thriving chemosynthetic community (Brooks et al. 1990). To the east, the Mississippi Fan and Mississippi Canyon areas appear to have more limited seepage and a hiatus of chemosynthetic seep communities. The easternmost occurrence of hydrocarbon fauna is in the Viosca Knoll area (88° W) (Figures 11 and 13). The existence of chemosynthetic fauna at the far eastern edge of the Gulf (Hecker 1985), unrelated to hydrocarbons, raises the possibility that such systems are even more widespread than presently known (no sampling south of 26° N). The Florida Escarpment limits the eastward occurrence of known seep communities; however, there are tube worms and mytilids at the base of the Florida Escarpment at 3,600 m in areas of connate fluid seepage from the highly porous Florida carbonate platform (Paull et al. 1984). It is reasonable to assume that there are other exotic communities (e.g., specialized for brine seeps) which may be present.

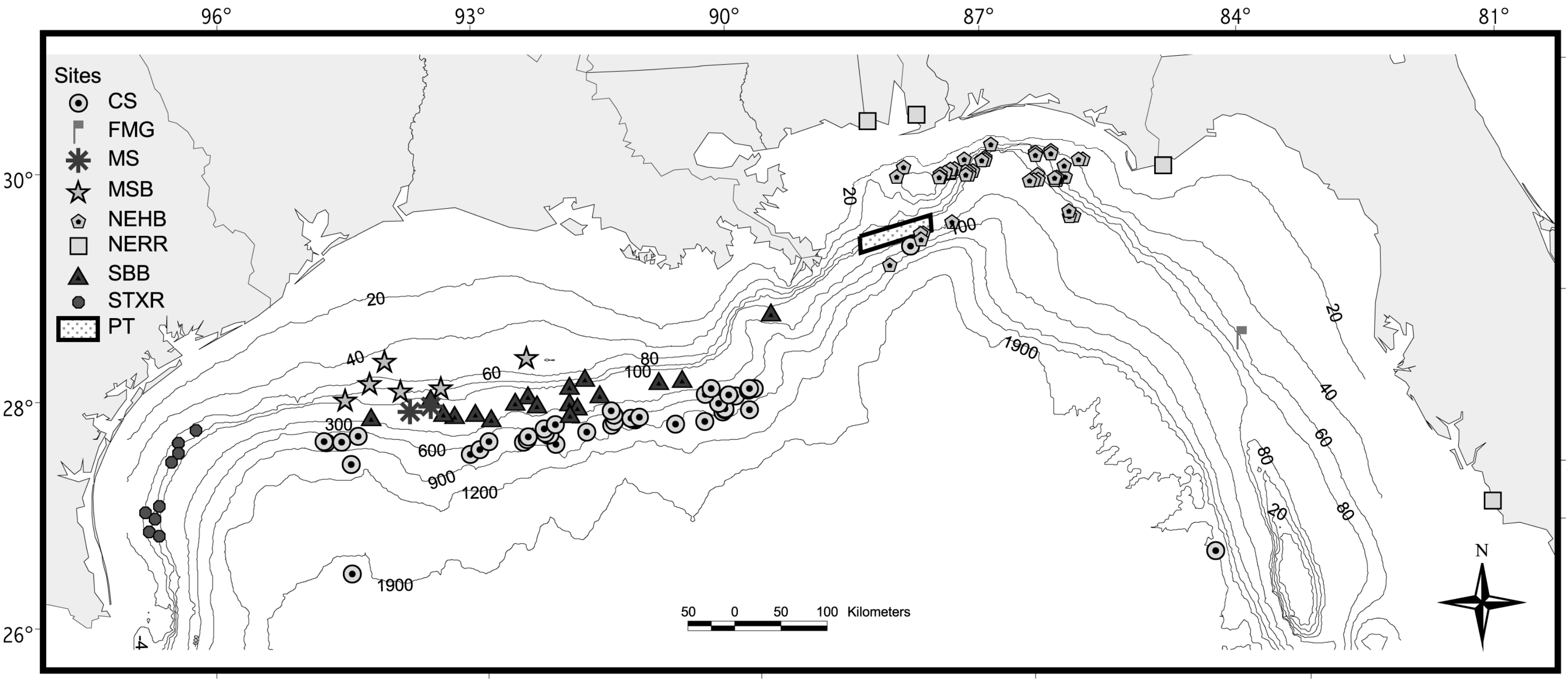


Figure 11. Location of live-bottom, chemosynthetic and biogenically-structured communities of the northern Gulf of Mexico. Symbols indicate CS-chemosynthetic community, FMG-Florida Middle Grounds, MS-marine sanctuary, MSB-mid-shelf bank, NEHB-northeastern Gulf hard-bottom, NERR-National Estuarine Research Reserve, SBB-shelf break bank, STXR-south Texas reef, PT-pinnacle trend. Bathymetric contours are in meters.

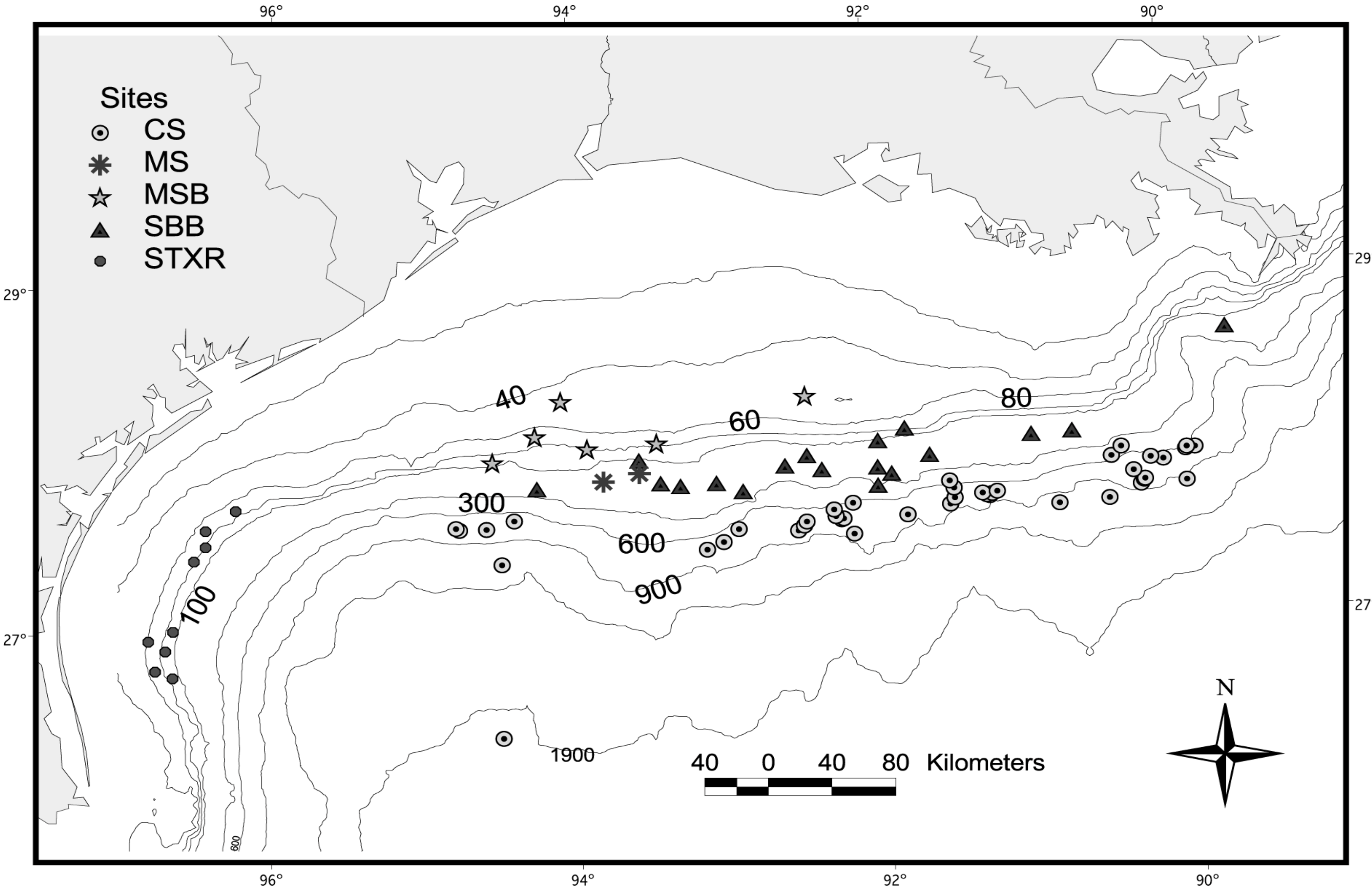


Figure 12. Location of live-bottom and chemosynthetic communities of the northwestern Gulf of Mexico. Symbols indicate CS-chemosynthetic community, MS-marine sanctuary, MSB-mid-shelf bank, SBB-shelf break bank, STXR-south Texas reef. Bathymetric contours are in meters.

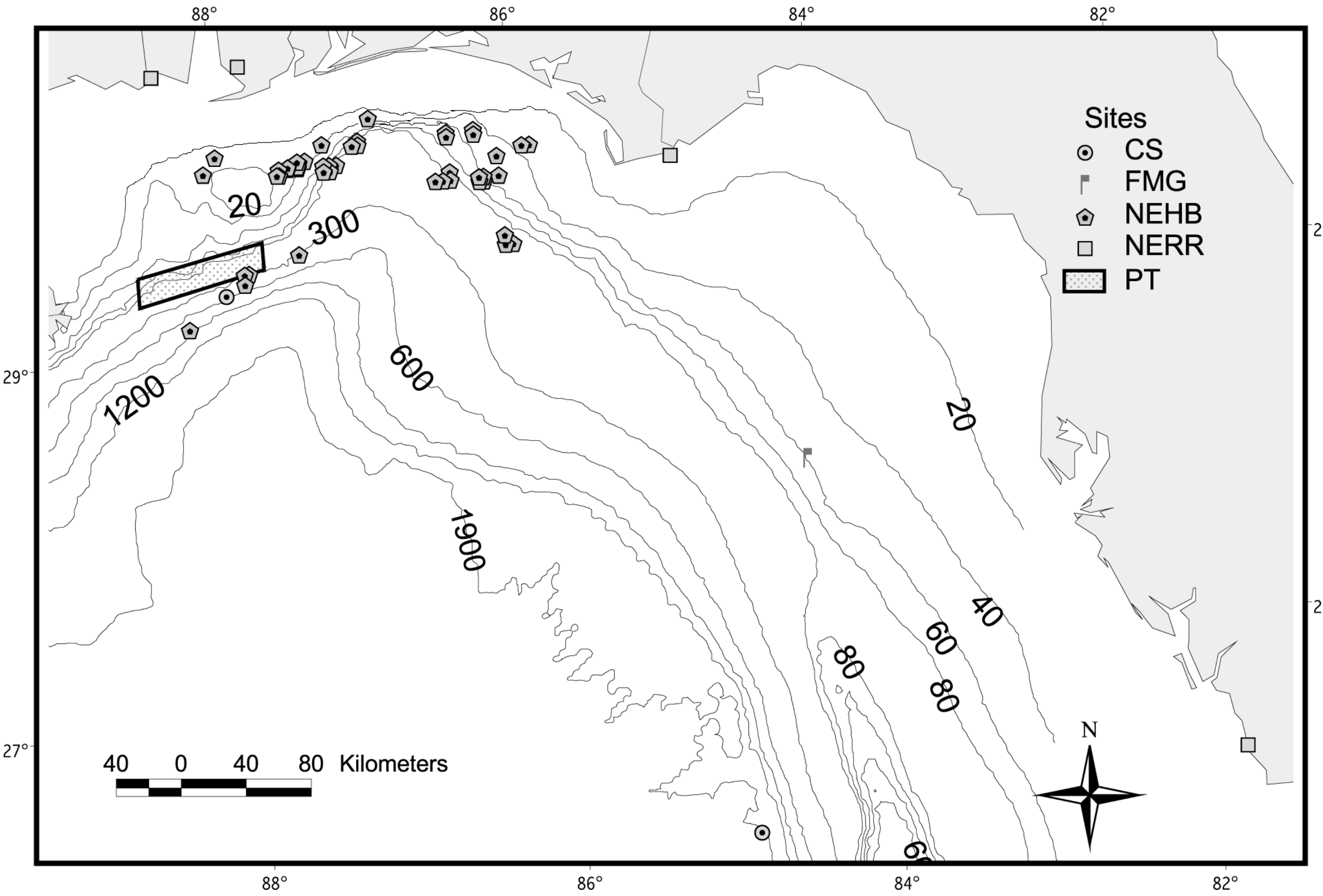


Figure 13. Location of live-bottom, chemosynthetic and biogenically-structured communities of the northeastern Gulf of Mexico. Symbols indicate CS-chemosynthetic community, FMG-Florida Middle Grounds, NEHB-northeastern Gulf hard-bottom, NERR-National Estuarine Research Reserve, PT-pinnacle trend. Bathymetric contours are in meters.

There is general agreement that the seep communities are an invaluable resource and may have a broad ecological role. Notice to Leasees NTL-98-11 protects them from development. Hydrocarbon seeps are places where gas and oil flow naturally out of the sea floor, and are quite common on the continental slope of the northern Gulf of Mexico (MacDonald and Joye 1997).

The autotrophic component of the seep community is chemoautotrophic bacteria that use the chemical energy contained in compounds like methane and hydrogen sulfide that are produced by the seepage. Other organisms, such as vestimentiferan tube worms and mussels (seep mytilids), epibenthic vesicomyid clams, and infaunal lucinid and thyasirid clams form a symbiotic partnership with bacteria. These faunal groups display distinctive characteristics in terms of how they aggregate, the size of aggregations, the geologic and chemical properties of the habitats in which they occur, and, to some degree, the heterotrophic fauna that occur with them. A variety of other animals, including fishes, crustaceans, and mollusks, are attracted to the resulting food supply. The result is diverse assemblages comprised of chemosynthetic fauna, specialized for the seep environment, and predators and browsers that commonly occur across the continental slope, but attain unusually high abundances at seeps.

Gas hydrates are ice-like minerals that form at the low temperatures and high pressures in the deep sea (Sassen 1997). Hydrates contain gases, such as hydrocarbons, that are trapped inside symmetrical cages of water molecules to form hydrate crystals. In the Gulf of Mexico gas hydrates outcrop on the sea floor as mounds in water depths as shallow as 425 m to depths greater than 2,000 m. Oil is usually plentiful in the sediments surrounding hydrates. The hydrate mounds on the sea floor are covered with white and orange bacterial mats as well as various filter-feeding bivalves and other specialized organisms. Mounds are sometimes surrounded by rings of chemosynthetic organisms such as tube worms and mussels. The dense hesionid polychaete populations found on the surface of an exposed hydrate at a depth of 550 m in 1997 indicates undiscovered microhabitats remain.

MacDonald et al. (1996) in their Executive Summary stated "…the seep communities are a unique and important component of the slope ecosystem of the Gulf of Mexico. Although susceptible to mechanical damage by offshore drilling or production activities, the ecosystems are prevalent enough that localized disturbances should not effect [sic] the viability of these communities." MacDonald further stated that hydrocarbon and brine seepage has persisted in spatially discrete areas for thousands of years. Commonality, however, is not suitable for relaxing criteria for acceptable impact, without knowledge of the ability of undamaged or damaged fauna to ultimately repopulate any impacted areas. The potential to repopulate can be inferred from faunal and genetic similarity studies. The underlying supposition is that site-specific seepage may be intermittent and that existing communities reflect numerous repopulation events. Preliminary results indicate communities sampled above 1,000 m are quite monotonous, but that the fauna of deeper communities are quite distinct. The genetic closeness of the < 1,000 m sites will be determined by molecular studies in a project currently underway.

Cold seep vestimentiferan worms can be extremely old invertebrates, with some individuals exceeding 250 years (Bergquist et al. 2000). They must have a hard substrate upon which to attach. The hard substrate results from a succession of geochemical and sedimentary changes facilitated by the *Beggiatoa* bacterial mats. This is in stark contrast to hot vents where related species grow at exceptionally fast rates. Fisher (2000) notes that physically damaged communities would likely never recover.

Seep mussels grow at site-specific rates that approximate those of shallow water heterotrophic species (if methane levels are high). Large individuals may be as old as 50 years (where methane conditions are suboptimal). Fisher states that mytilids might even increase with an increase of hard substrate from oil activities. These results could be interpreted in two ways with regards to potential impacts: (1) a population of old animals exists because the population has survived natural environmental perturbation and is robust, or (2) the community has not experienced perturbation and would be fragile in the face of disturbance. Good estimates of recruitment and mortality are needed to better define the stability and resilience of the community. On the other hand, seep communities appear to be persistent through time, and regionally may be resilient, with communities being obliterated and reestablished on a 500 year-and-less time frame. Rigorously determined recruitment and mortality rates for major species are needed. Presently formed conjectures about resilience and stability must be tested by well designed experiments.

An abundant heterotrophic fauna exploits both the food source and habitat of the upper slope seeps. This fauna is numerically dominated by gastropods, but there are also galatheid crabs, decapod crabs and shrimp, giant isopods, sea-stars, sea urchins, and several fish (listed by species in MacDonald et al. 1996 Ex Summ). It is expected that some are truly endemic to chemosynthetic communities, some are colonizers from surrounding benthos, and others are temporary vagrants. Foodweb tracing indicates that mobile megafauna from the surrounding mud bottoms do exploit the seeps as a food source. There is low endemism in the Gulf seep sites, especially the upper slope, and a high degree of colonization by fauna from the surrounding sea floor, in marked difference from the hydrothermal vent systems.

Faunal composition of chemosynthetic and heterotrophic fauna at sites above 1,000 m is remarkably uniform. Faunal similarity above 1,000 m would indicate similarity in response to impacts. Poorly studied deeper sites are known to be different. The differences in fauna with increasing depth suggest that rules of “no impact” should persist until more is known of them.

6.6 Biogenically-Structured and Live-Bottom Habitats

“Live-bottom” habitats are “…those areas which contain biological assemblages consisting of such sessile invertebrates as sea fans, sea whips, hydroids, anemones, ascidians, sponges, bryozoans, or corals living upon or attached to naturally occurring hard or rocky formations with rough, broken, or smooth topography; or areas whose lithotope favors the accumulation of turtles, fishes, and other fauna” (Yourk 1999). The definition used by MMS also includes seagrass communities. Although no seagrass beds exist in the deeper offshore waters covered by this section of the report, they do occur in the coastal zone where onshore logistic facilities and transport activities occur.

The organisms on or associated with hard-bottom outcrops in the northern Gulf of Mexico are controlled by: (1) proximity to the Mississippi River discharge, (2) size, relief, and texture or rugosity of the outcrop, (3) temperature, and (4) depth and/or light availability (Gittings et al. 1992). Colonial invertebrates, such as scleractinians and gorgonians that form the live-bottom habitats grow slowly, require relatively stable environmental conditions, and are very sensitive to temperature, water quality, and sedimentation. Live-bottom community development progressively improves towards the east away from the Mississippi River plume. Complexity of live-bottom communities (abundance and diversity) increase with vertical relief and surface area. Community development is less extensive on isolated low-relief features compared to similar sized areas that are part of a larger complex of such features. Live-bottom habitats are dominated by suspension feeders, and sedimentation rates definitively influence community structure. Only the coralline algae are depth limited (within depths less than 78 m) and are limited by light transmission within their depth range. The discharge of the Mississippi River influences the east-west and depth location of coralline algae in the northeastern Gulf.

The faunal composition of the live-bottom communities near the head of the DeSoto Canyon are more complex than those farther to the west, but represent essentially the same faunal assemblage (Shipp and Hopkins 1978). The live-bottom faunal assemblage east of the DeSoto Canyon are more similar to those found on the southwest Florida shelf hard-bottoms. The near-shore live-bottom communities in the northern Gulf are subjected to relatively high seasonal temperature variations and resemble the warm, temperate Carolinian Province communities (Schroeder et al. 1989). The offshore live-bottom communities in the northern Gulf have clear tropical affinities, but are less diverse than similar communities in the southern Gulf and in the Caribbean.

Given the importance of sedimentation or physical damage to the community structure and the viability of organisms forming the live-bottom communities, any deepwater exploration or production activities that would approximate these environmental forcing factors should be avoided. Lease stipulations of MMS that regulate drilling activities near live-bottom features and the EPA NPDES permitting process should afford protection to these areas. These mechanisms generally work, although the effects of drilling operations were observed by Shinn et al. (1993) near a pinnacle site. Given below are general locations and descriptions of live-bottom habitats that are in areas where deepwater activities may occur.

6.7 Hard-Bottom Northwestern Gulf of Mexico

A variety of hard substrate south Texas shelf reefs (STXR in Figures 11 and 12) are dead coral-coralline algal reefs between 60 and 90 m isobaths. The reefs vary in relief from 1 to 22 m. They are not associated with salt diapirs, but rather were reefs growing on a carbonate shelf during the Late Pleistocene and Early Holocene. A nepheloid layer prevents the continuous encrustation of live-bottom organisms except from the surface of the banks. Cover organisms consist of tubicolous polychaetes, algae, sponges, soft corals, and ascidians.

The north Texas and Louisiana reefs and banks located on the continental shelf and slope are associated with salt diapirs or structures caused by salt tectonics (Rezak et al. 1985, Rezak 1988). On the outer continental shelf of Louisiana (Shelf Break Banks, SBB in Figures 11 and 12) are a series of rock outcroppings on which live-bottom communities flourish. The geologic formations resulted from the movement of Pleistocene rocks to the seabed surface from salt dome forcing and related faulting. During low sea level stand-in Pleistocene glacial periods, the rocks were eroded by wind and water so that the central salt dome collapsed, the less resistant rock beds eroded away, and the hard rock pinnacles remained. The pinnacles vary in size and depth. Consolidated silts, clays and sands cover the rock pinnacles to depths of less than 0.3 m. MMS views the banks as areas of greater biological importance, diversity, and interest than the surrounding sea floor areas (Dempre and Bull 1999). There are 28 named topographic features that rise from the surrounding mud/clay bottom; all are protected by MMS lease stipulations.

The mid-shelf banks (MSB in Figures 11 and 12) rise from depths of 80 m or less and have a relief of 4 to 50 m (Rezak et al. 1985). These are outcrops of relatively bare, bedded Tertiary limestones, sandstones, claystones, and siltstones. Stetson, Claypile, Coffee Lump, Sonnier, Fishnet, and 32 Fathom Banks are typical of this category. Sonnier Bank in Vermilion Block 305 is in 70 m water depth, rises to within 23 m of the water surface, and is composed of eight pinnacles. Cover on Sonier Bank is highly variable but averages 70% and is dominated by sponges, fire coral, brown algae, and tube-forming polychaetes. The lack of live corals indicates that the water temperature falls below 20° C during winter. There is a high density and diversity of fish.

The shelf-edge carbonate banks and reefs are located on complex diapiric structures. They are carbonate caps that have grown over outcrops of a variety of Tertiary and Cretaceous bedrock and salt dome caprock. The relief varies from 35 to 150 m. The East and West Flower Garden Banks are thriving coral reefs. The two Flower Garden banks harbor the most diverse and thoroughly developed offshore hard-bottom epibenthic communities of the region.

East and West Flower Garden Banks, National Marine Sanctuaries

The East and West Flower Garden Banks are located 175 km SSE of Galveston, Texas and are designated as a National Marine Sanctuary by NOAA (MS in Figures 11 and 12). Coral cover averages 47.3% for both banks and has probably not changed significantly in over 25 years (Gittings 1998, 1999). No significant temporal trends in accretionary growth are evident, and the recent data suggest that corals have been growing at or above mean rates for the last decade or two. Neither coral community characteristics nor growth data hint at a significant upward or downward trend in environmental quality at the Flower Gardens. On the whole, the reef communities have so far remained largely unaltered by human activities, despite numerous isolated insults of anchoring, towing and fishing activities. Recovery from coral bleaching incidents and mortality of long-spined sea urchins in 1983-84 indicate that the Flower Garden Banks are resilient to short-term temporal change.

6.8 Northeast Gulf of Mexico Hard-Bottom Habitats

Within five OCS areas between Cape San Blas, Florida and the Chandeleur Islands, Louisiana, there is an approximately 5% incidence of hard-bottom on the areas mapped (Continental Shelf Associates 1992). These are indicated in Figures 11 and 13 by the NEHB symbols and the rectangle outlining the area of the Pinnacle Trend (PT).

To the east of DeSoto Canyon, which separates the Florida carbonate platform from the mud and clay sediment regimes off Mississippi and Alabama, are live-bottom communities associated with rock outcrops and areas of extensive, but very low-relief hard-bottom that are periodically covered by sand. To the west of DeSoto Canyon, the outer edges of the continental shelf and, on the upper slope, there are a number of trends of reef-like and pinnacle hard-bottom areas. The organisms that live on these hard substrates represent new colonization rather than a continuation of original reef communities.

A region of topographic relief, known as the “pinnacle trend,” is located at the outer edge of the Mississippi-Alabama shelf between the Mississippi River and DeSoto Canyon (Continental Shelf Associates 1992) (PT in Figures 11 and 13). The pinnacles are a series of topographic irregularities with variable biotal cover that provide structural habitat for a variety of pelagic fish. The pinnacle trend region contains a variety of features from low-relief rocky areas to major pinnacles, as well as ridges, scarps, and relict patch reefs. Additional hard-bottom features are located nearby on the continental shelf outside the actual pinnacle trend area.

Inshore, or slightly behind the shelf break at the head of the DeSoto Canyon, areas of rock outcrop composed of a granulated sandstone are seen. These outcrops lie in bands or trends that roughly parallel existing bathymetric contours. They were formed by consolidation of riverine deposits transported to the shelf edge during a period of lower sea level (Benson et al. 1997).

Less well-defined hard-bottom outcrops occur on areas of the inner Mississippi/Alabama continental shelf where sandstones and mudstones protrude through the surficial sediments (Schroeder et al. 1989). These areas are rare and poorly developed on the Mississippi-Alabama shelf due to the high rates of sedimentation. Hard-bottom habitat in these inner shelf areas include reef-like outcrops with vertical relief of $\leq$ 2 m, moderately sloping ridges of rock rubble and shell hash, and surficial rock and shell rubble with little or no vertical relief (Thompson et al. 1999).

6.9 Pelagic, Oceanic Communities

As with the infauna, the population densities and biodiversity of deepwater fish and macroinvertebrates is poorly understood, and the potential oil industry impact is unknown. Elsewhere in the world, as in the U.S., as traditional near-shore fisheries collapse or become more regulated, fishers switch to different target species, including the exploitation of lower trophic-level fishes in the upper ocean and deep demersal populations. If such a switch occurs in the Gulf of Mexico, there is a potential for conflicts of fisheries with deepwater activities (Carney 1998).

Multimillion-dollar fishing efforts currently in deep water include (1) upper-ocean trolling for billfish, (2) mixed-depth long-lining for yellowfin tuna and shark, and (3) deep-bottom trawling for royal red shrimp. There is a potential for equipment incompatibilities with deepwater infrastructure, potentially environmentally hazardous exposures, and possibly a human safety hazard. It was speculated that platforms that act as fish-attracting devices (FADs) could impact management of highly migratory fish such as yellowfin and bluefin tunas and broadbill swordfish that are thought to use the slope edge for spawning and feeding grounds, if in fact FADs do attract these animals or they disrupt spawning and feeding.

Carney (in draft) states that biomass harvesting (i.e., fishing) is unlikely to be a serious conflicting use of the deep-sea floor. To be commercially attractive species, they must be abundant, widespread, often schooling, generally large-sized, and capable of relatively rapid growth. Merrett and Haedrich (1997) made a strong case against large scale deep-sea fisheries based on the patterns of biomass decline and trophic structure of the deep sea. Fish show the same biomass decline, with high biomass species being rare and of considerable age. Fish in the deep sea are the top predators and the populations are not adapted to being prey. Harvesting deep-sea fish biomass would remove animals that have spent many years growing to reproductive size, resulting in decades for populations to recover from even minimal fishing pressure.

A. S. Bull (in Carney 1998) cites the potential for deepwater oil spills to affect larval and juvenile stages of species that might aggregate in deepwater areas; examples include gag grouper, yellowedge grouper, yellowfin and bluefin tunas, oceanic sharks, broadbill swordfish, and marlin. While there exists no direct evidence that an oil spill has affected a stock as a result of mortality of eggs and larvae (Spies 1987), there is concern that a large spill occurring during a critical recruitment period could seriously diminish recruitment to the stock for the year (Boesch et al. 1987). Still, effects on the stock, other than catastrophic effects, would be difficult to detect and attribute to toxicity because of the great and largely unexplained year-to-year variability in recruitment.

In near-shore environments, contaminants resulting from petroleum activities are more likely to reach the seabed and be incorporated into bottom sediments or bioaccumulate in platform-fouling communities. Juveniles of many economically important species live in inshore environments and events there may affect those species, even though offshore adult populations are not directly or immediately affected. Uncertainties similar to those discussed above for larval mortality on adult stocks pertain to near-shore areas as well. Most studies of demersal or pelagic organisms associated with offshore drilling and production platforms fail to demonstrate an effect of chemical contaminants. The failure to detect evidence of exposure or sublethal impacts on fishes and most larger invertebrates is a joint consequence of their mobility over the relevant scales of environmental change and their negligible exposure to hydrocarbons and other contaminants (Peterson et al. 1996).

6.10 Protected Species

Certain species or environments are deemed worthy of protection by our society, not primarily because they furnish economic benefits, but because of their aesthetic, cultural, or social values. Included are species that may be rare or near extinction, as well as air-breathing, higher vertebrates such as birds, mammals, and turtles.

Any animal exposed to spilled oil or chemicals might suffer deleterious effects as a result of physical fouling. Such an impact, if confined to a few animals within a population, would have few long-term consequences, but could have a significant effect on a discrete, concentrated stock of animals. Birds and marine mammals that surface in an oil or contaminant spill could inhale vapors, possibly enough to cause residual damage to the respiratory system and to serve as a route of entry for systemic accumulation of contaminants. Oil may impair feeding in young turtles or baleen whales. The probability that such effects could affect birds, mammals, and turtles was rated medium (in a scale of low to high) by (Boesch et al. 1987). Similar probabilities would likely extend to chemicals associated with deepwater activity, given similar levels of toxicity.

The rich and abundant marine fauna of the Gulf of Mexico includes several species that are “quite sensitive and rare” (Darnell and Schmidly 1988). Whales may never have been common in the Gulf of Mexico (except see below on sperm whales), but massive over-exploitation in the early twentieth century all but extirpated many from the world’s oceans, and Gulf populations may very well have been affected. Marine turtles were once fairly common along the coastlines of the Gulf of Mexico but are now rare, although conservation efforts are resulting in increased numbers.

Endangered mammals include the blue whale, fin whale, sei whale, right whale, great sperm whale, and West Indian manatee. All five sea turtles are threatened or endangered: Kemp’s ridley (E), loggerhead (T), leatherback (E), hawksbill (E), and green (T). Of the sea turtles, the leatherback is the more oceanic member of the group in the Gulf as opposed to the others that prefer shallower waters for feeding and migratory routes. A. S. Bull (in Carney 1998) states that the slope edge is a critical nursery ground for juvenile marine turtles, with the potential for interaction or threats for this endangered group of animals during their early life stages with deepwater activities.

More recent work on surveys of marine mammals and turtles indicate that there are viable populations in the Gulf of Mexico and that deepwater operations have the potential to affect them. The GulfCet programs sponsored by MMS, the National Marine Fisheries Service, and the U.S. Fish & Wildlife Service documented the seasonal and geographic distribution of cetaceans and sea turtles in the deeper areas of the Gulf (100 m to 2,000 m, north of 26° N) and characterized their habitat in areas potentially affected by oil and gas activities (Evans and Davis 1998). Six years of data collection in the northern and western Gulf were completed in 1997. GulfCet continues with the "Northeast Gulf of Mexico (NEGOM): Chemical Oceanography and Hydrography" program.

Based on visual surveys, the overall minimum number of cetaceans in the GulfCet I study area was 19,128. A total of 487 acoustic contacts were recorded and of that number, 124 contacts were of 12 identified species. Sperm whales were the most commonly recorded species, accounting for 56% identified contacts. At least 17 cetacean species were identified during eight GulfCet I aerial surveys (each of these species also was sighted during ship surveys).

The GulfCet II field program censused the region's 18 common species of dolphins and whales in continental margin areas of present oil and gas development and in areas further offshore to depths of 2,000 m, where oil and gas exploration will likely intensify in the near future. The sperm whale, an endangered species, was a special focus of the GulfCet II field program (Biggs and Wormuth 1998).

A combination of hydrographic measurements, determinations of chlorophyll biomass and zooplankton abundance, acoustic determination of Deep Scattering Layers (masses of fish, squid, and shrimp), and sea-surface altimetry data from satellites identified cyclones as the preferred habitat of the sperm whales. The cyclones, sea-surface lows about 100 to 150 km wide that spin counterclockwise, are areas of upwelling of cool, nutrient-rich water with higher than average stocks of phytoplankton and zooplankton. The cyclones spin off the anticyclones (eddies from the Loop Current) that spin clockwise, and are areas of downwelling and not highly productive. The cyclones and anticyclones usually occur in pairs, with the sperm whales preferring the periphery of the cyclones.

During an October 1996 NEGOM cruise, there were 41 sperm whales and 10 whale groups (acoustic survey) off the Mississippi Delta and inside or at the perimeter of a cyclone. The whales were uncommon in the deepwater canyon to the east of the cyclone and even rarer in the anticyclone. The presence of young calves supports the hypothesis that the sperms whales reproduce successfully in the Gulf. The pattern was repeated in May, June and August of 1997, with sperm whales being most abundant in the cyclone or in the water flowing counterclockwise around it (Figure 14).

Because the continental margin of the northeast Gulf of Mexico is characterized by the temporal persistence of cyclonic eddies, the region is of considerable biological interest with regard to marine mammals (Ortega-Ortiz 1999). During the five NEGOM cruises, a total of 334 hours of visual survey were completed for 5,418 kilometers of transect on the ship's track across the northeastern Gulf. During this effort, 289 marine mammal sightings were registered and the following species were identified: Atlantic spotted dolphin, Bryde's whale, bottlenose dolphin, dwarf sperm whale, false killer whale, humpback whale, killer whale, melon headed whale, pantropical spotted dolphin, pygmy sperm whale, Risso's dolphin, sperm whale, spinner dolphin, and striped dolphin.

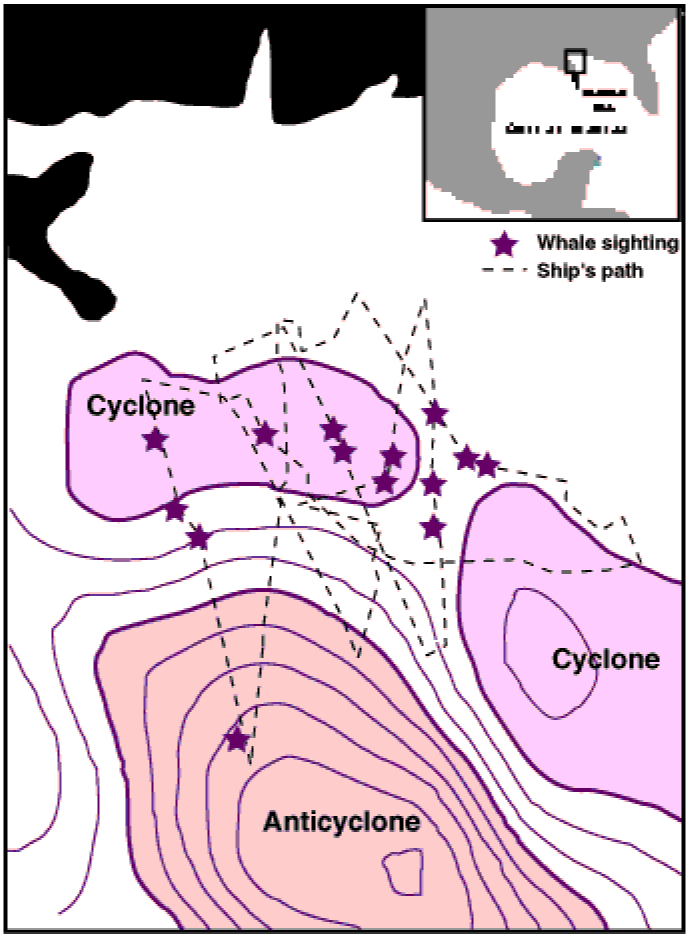


Figure 14. Cyclones are the most common place to find sperm whales, as indicated by the stars placed on this diagram of the Gulf's eddies, made from an August 21, 1997, regional altimetry map. (Data courtesy of Robert Leben, Colorado Center for Astrodynamics Research, in Biggs and Wormuth 1998).

6.11 Continental Shelf

An overview of continental shelf benthic communities of the Gulf of Mexico was provided by Rabalais et al. (1999a). Typical soft-bottom benthic communities are composed primarily of polychaetes, with fewer bivalves, gastropods, pericaridean crustaceans, sipunculans, echinoderms, and miscellaneous other fauna. Sedimentary characteristics range from terrigenous sediments delivered by major rivers, variable mixtures of sand/silt/clay, outcroppings of Beaumont clay or its equivalents, quartz sand sheets, and carbonate sediments. There is variability in the benthic community structure in relation to depth and depth-related factors and sedimentary characteristics. Localized differences in fauna may result from proximity to natural hard-bottom habitats, artificial habitats, and oil and gas production facilities. Broad-scale differences in the benthic fauna result from the extensive and severe zone of bottom-water hypoxia that forms along the inner to middle Louisiana continental shelf and extends periodically onto the upper Texas coast (Rabalais et al. 1995, 1999b). A dominant feature of the Texas-Louisiana shelf is the nepheloid layer created by the resuspension of muddy sediments and subsequent flow across the bottom to the outer shelf and shelf edge where episodic deposition may occur. The nepheloid layer is reduced in summer months.

Most studies of the discharges onto the continental shelf from oil and gas activities outline localized impacts, with a range of negative impacts to enhanced populations, and a range of temporal effects, some of which may be short-lived while others are persistent.

Drilling fluid chemicals dilute rapidly in the water column and, in all but very deep or high-energy environments, much of the drilling fluid and cuttings solids settle rapidly to the bottom near the rig site (Neff 1987). Concentrations of barium, as a tracer for drilling effluents, may be 10 to 20 times above background in surficial sediments near the discharge and decrease to background within 2,000 m down current. Produced water dilutes rapidly following discharge but significant elevations of hydrocarbons or metals can be observed up to 250 m from the discharge (Rabalais et al. 1992). Most of the ingredients of drilling fluid chemicals have a low toxicity to marine organisms (Neff 1987), but the fluids and cuttings that settle on the seabed can significantly alter the benthic sedimentary regime. That, along with the sloughing of organic material from the fouling community on submerged parts of the platform structure and the increased bottom microrelief, may attract motile animals to the vicinity and alter the character of the infaunal community. Contaminants from produced waters, on the other hand, may reduce the abundance and diversity of infaunal organisms (Rabalais et al. 1992). Peterson et al. (1996) concluded that long lasting effects of drilling activity exist in the sedimentary environment around gas production platforms. The dual effects of toxicity and organic enrichment probably drive readily detectable responses in benthic meiofauna and macroinfauna to 100-200 m.

The GOOMEX studies (Kennicutt et al. 1996) were intended to test and evaluate a range of biological, biochemical and chemical methodologies to detect and assess chronic sublethal biological impacts in the vicinity of long-duration activities associated with oil and gas E&P. Location of the study was in a gas field in the western Gulf on the continental shelf and as removed as possible from confounding effects of Mississippi River discharge. Sediments close to platforms (< 500 m) were enhanced in coarse-grain materials primarily derived from discharged muds and cuttings. Hydrocarbon and trace metal (Ag, Ba, Cd, Hg, Pb, and Zn) contaminants were associated with these coarse-grain sediments. Contaminants were asymmetrically distributed around each platform in response to the prevailing currents. The positive relationship between sand content and contaminant levels is contrary to the view of contaminants being associated with finer-grain sediments. Contaminant concentrations at most locations were below levels thought to induce biological responses. At a few locations close to one platform, trace metal (i.e., Cd, Hg) concentrations exceeded levels thought to induce biological effects. In deeper water (> 80 m), sediment trace metal contaminant patterns were stable over time frames of years. A few metals (Pb, Cd) exhibited evidence of continued accumulation in sediments over the history of the platform at the deeper water sites (> 80 m) immediately after cessation of drilling cf 5-10 years after the last discharge (i.e., there was persistence of contaminants in the lower energy environments).

The meiofauna and macrofauna effects (Montagna and Harper 1996) were localized, extending to 100 m from the platforms (less distance than in the North Sea). The pattern of community change were increases in deposit-feeding polychaetes and nematodes that indicated organic enrichment, while density declines of harpacticoid copepods and amphipods indicated toxicity. Harpacticoid abundance, community diversity, genetic diversity, reproductive success, and survivability declined nearer the platforms with an increasing contaminant gradient at all study sites. Changes in meiofaunal responses were most noticeable within 50 m of platforms. It was stated that in the GOOMEX study, it was apparent that the chemical contaminants originated from the drilling mud discharge and not from production.

Sediment chemical analyses and porewater toxicity tests with sea urchin fertilization and embryological development assays from the GOOMEX study (Carr et al. 1996) indicated toxicity near four of the five platforms, the majority collected within 150 m of a platform and those with the highest concentrations of contaminants. Samples from the deepest site (> 80 m near the Flower Gardens), which contained the highest contaminant concentrations, were the most toxic samples of the sites. Repeatability of toxicity between seasons demonstrated the persistence of the toxicity.

Peterson et al. (1996) drew general conclusions from the GOOMEX studies and provided a good review of environmental fate and effects studies using benthos. For the GOOMEX platforms, the consequences were the result of environmental forcing, organic enrichment, and metals toxicity. The hydrocarbons occurred in concentrations that seemed too low to be important contributors to the observed toxicological effects. PAHs were generally less than 100 ng/g which was an order of magnitude lower than what Spies (1987) suggested was needed to induce biological response. They concluded that sediment grain pattern was unlikely to be the primary driver of the observed biological responses. The increase in annelids closer to the platforms occurred despite the steep gradient in sand content: total annelids would be expected to be more abundant in finer sediments, not coarser. In contrast with annelids and oligochaetes, amphipod abundances were depressed around all platforms, with effects confined to 50 to 100 m. This was also consistent with literature on modest pollution and is suggestive of a toxic response. Sea stars were reduced near the platform, but that pattern did not hold for ophiuroids. Harpacticoid copepod abundance was depressed near the platforms, while total nematodes were enhanced. Patterns were absent at the shallowest site (29 m) where the relatively high-energy physical environment has led to more extensive dispersion of materials discharged. The other sites were in 80 m and 125 m.

The disparity in results with North Sea studies (effects to 2 to 6 km) is that oil-based drilling fluids are used in the North Sea vs. water-based in the Gulf of Mexico. They concluded that patterns of response to sedimentary contamination were detectable at higher taxonomic levels and that these responses were driven by intrinsic physiological and ecological characteristics of higher taxa. Crustaceans (especially amphipods and harpacticoid copepods) and echinoderms are sensitive to toxics whereas polychaetes, oligochaetes, and nematodes (especially non-selective deposit feeders) are enhanced by organic enrichment (either from hydrocarbons or biologically-produced materials falling from the platform structure). They concluded that metals drove the toxicity effects, and that the dual effects of toxicity and organic enrichment resulted in readily detectable responses in benthic meiofauna and macrofauna to 100-200 m. In contrast to the emphasis on trace metals, the effects of volatile hydrocarbons from a produced water discharge were apparent for at least one high energy, inner continental shelf station off Louisiana (Rabalais et al. 1991, 1992).

6.12 Coastal Habitats

Transport of product from deep water or transport of chemicals used in drilling and production may be the aspect of deepwater development with the greatest environmental risks, but these will vary widely in means and geographic extent for different offshore areas (Boesch et al. 1987). Virtually all of the oil and gas produced in the Gulf of Mexico flows through pipelines because the extensive development and existence of onshore facilities makes this feasible. The effects of oil spills which might occur as a result of pipeline ruptures and transshipment accidents are dependent on the environmental characteristics of the habitats affected.

Long-term effects result from acute damage due to an oil spill on biogenically structured habitats such as coral reefs, mangrove swamps, salt marshes, oyster reefs and seagrass beds. Here the concern is that even though oil may not persist following an oil spill, the time required for recovery of damaged populations of organisms that provide the physical structure of the habitat will be many years. In some cases, where the structure-forming species actually stabilizes the habitat, it is conceivable that permanent modification of that habitat could result from an acute incident. The discharge of produced waters on salt marsh habitats will kill the vegetation, but discharges into receiving waters do not affect the peripheral marsh habitat (Boesch and Rabalais 1989). The effects of chemicals used in deepwater oil production on biogenically structured habitats is not known.

6.13 Summary

Biological communities at risk from chemical spills associated with deepwater E&P are most likely those which are deeper than the continental shelf break. Biologically sensitive communities in coastal and continental shelf depths may be affected from spills during transit of materials either via ship or pipeline.

Certain features of the deep sea and the fauna that inhabit it make them potentially more susceptible to certain types of chemical spills. Increased turbidity from a spilled chemical such as a drilling mud could impact animals adapted to low light (including, possibly, those with bioluminescent capabilities) by increased turbidity from deep plumes of low transmission water and indirectly through biological light interactions. Spills of chemicals with labile carbon may alter the local balance of oxygen consumption and result in hypoxia or anoxia, especially in the oxygen minimum zones. Microhabitat diversity is a key to deep-sea diversity, and any chemical spill that alters deep habitats will likely have an impact. Chemical spills that disrupt the accessibility of fluxed detrital material for the dominant deposit feeding-mode organisms will affect feeding and subsequently the health of the organism(s). Chemicals that affect mortality, population levels, biological interactions, recruitment, growth rates, through either acute or chronic, sublethal toxicity or habitat alteration or both are likely to affect soft-bottom benthos in the deep sea similarly to continental shelf organisms. However, basic information for most deep-sea organisms (e.g., feeding type, reproduction, life span, growth rates, predators, and community ecology) is fundamentally nonexistent.

Chemosynthetic seep communities are considered prevalent between 300 and 1,000 m water depth on the northern Gulf slope. Commonality, however, is not suitable for relaxing criteria for acceptable impact without knowledge of the ability of undamaged or damaged fauna to ultimately repopulate any impacted areas. Some organisms that inhabit the cold seep communities may be extremely old, and damaged communities would be slow or unlikely to recover. Hard-bottom communities with highly diverse biogenically-structured communities are afforded protection from drilling operations, and any chemical spills that approximate these types of effects would be expected to produce similar harm to live-bottom communities.

7.0 SPILL SCENARIOS AND MODELING PARAMETERS

7.1 Introduction

Spill modeling was performed to estimate concentrations resulting from worst-case chemical spill scenarios that were developed based on the inventory data presented earlier in Section 3.0. The results of the modeling were used to evaluate the potential impacts of spills of selected chemicals on the marine environment, in both shallow and deep water (Section 8.0). The modeling was performed using Applied Science Associates' (ASA) chemical spill model CHEMMAP (Section 7.3).

A total of 17 spill scenarios was developed, modeled, and reviewed. Sixteen spill scenarios were modeled using shallow water data and one spill scenario was modeled in deep water. The shallow water current data were obtained from measurements made by Texas A&M University as part of the LATEX program (a major study of Gulf of Mexico environmental variables). The deepwater current data were from a current meter mooring in the central-western Gulf of Mexico in 3,000 m deep water. Most spill scenarios are for surface spills. Assuming that surface current and wind patterns are similar in deeper water, the 16 scenarios at the shelf site are applicable to deepwater spills at the water surface. However, while loop current eddies are common in deep water, they are not prevalent on the shelf. Thus, the shallow water results would not be applicable in deep water when there are eddies present at the spill site. A subsurface spill of ethylene glycol on the shelf is hypothesized from a broken umbilical in 113 m of water, a depth that was selected as representative of this technology.

7.2 Selection of Chemicals for Profiling

While a detailed assessment for each of the thousands of offshore chemicals or products used was outside the scope of this project, a subset of representative chemicals used in the deep water and shallow water were selected based on the following criteria:

- Chemicals used offshore in high volumes
- Potential impact on the environment, including:
  - Toxicity
  - Oxygen depletion
  - Habitat modification
- Factors determining fate in the environment, including:
  - Physical state - solid or liquid
  - Organic or inorganic
  - Chemical reactions in seawater
  - Solubility
  - Biological degradation
  - Location of final destination (sediment, water column, or atmosphere)

The chemicals selected are representative of the type/range of chemicals used in offshore Gulf of Mexico. By using this approach, an analyst in need of data on any chemical used in the GOM can derive some information on the chemical's behavior in the marine environment by using one of the representative chemical or product profiles.

Twenty-one chemicals were selected for detailed characterization. A standard chemical profile was developed to present the data collected on each chemical and their impact on the marine environment. These profiles are presented in Section 8.0.

Table 20
List of Twenty-one Chemicals Selected for Detailed Chemical Profiles

Selected Chemical/Product (Spill Scenario Number)	Chemical Class	Chemical Profile Number
Acids		
Hydrochloric acid (1)	CSW	1
Hydrofluoric acid (no spill model)	CSW	2
Antifoam/Defoaming Agents		
Silicones (no spill model)	DF,PT	3
Biocides		
Glutaraldehyde (11 and 12)	PT,DF	4
Quaternary Compounds (14a)	PT	5
Tetrakishhydroxymethyl phosphonium sulfate (THPS) (13)	PT	6
Reactive Salt – Solid		
Zinc Bromide (4)	CSW	7
Calcium Bromide (no spill model)	CSW	8
Ammonium Chloride (no spill model)	CSW	9
Chemical Stabilizer		
Sodium hydroxide (2)	DF	10
Potassium chloride (3)	DF,CSW	11
Corrosion Inhibitor		
Amides/Imidazolines (15t)	PT	12
Amines & Amine salts (15t)	PT	13
Fluid Loss Agents		
Lignite (8)	DF	14
Gas Hydrate Prevention		
Methanol (9)	PT	15
Ethylene glycol (10)	PT	16
Triethylene glycol (no spill model)	PT	17
Oxygen Scavenger		
Sodium bisulfite (5)	PT	18

Table 20

List of Twenty-one Chemicals Selected for Detailed Chemical Profiles (continued)

Selected Chemical/Product (Spill Scenario Number)	Chemical Class	Chemical Profile Number
Insoluble Solids		
Barite (6, 17)	DF	19
Thinners & Dispersants		
Lignosulphonate (7)	DF,C	20
Solvents/Carriers		
Heavy aromatic naphtha (15,16)	PT	21

Notes: Chemical Class Definitions: DF (Drilling Fluids), C (Cementing Chemicals), CSW (Completion, Stimulation, and Workover Chemicals), PT (Production-treating Chemicals)

The chemicals selected for spill evaluation and the selection criteria are discussed in Section 2.0. These chemicals include:

- Hydrochloric Acid
- Sodium Hydroxide
- Potassium Chloride
- Zinc Bromide
- Sodium Bisulfite
- Barite
- Lignosulfonate
- Lignite
- Methanol
- Ethylene Glycol
- Glutaraldehyde
- Tetrakishydroxymethyl phosphonium sulfate (THPS)
- Quaternary Ammonium Compounds (component of product a)
- Amides/Imidazolines (component of Product B)
- Aromatic Naphtha (component of Product C)

See Section 7.8 for spill model assumptions.

These chemicals include both single- and multi-component products. For the multi-component products, separate fates and concentrations were determined for each component.

In Section 8.0, the results of the spill modeling are combined with chemical/physical properties, toxicity data, and typical storage and handling information to evaluate potential impacts of the selected chemicals and/or selected constituents. Storage and handling data provided by operators and chemical suppliers yielded typical and worst-case spill volumes. Worst-case spill volumes were used in the modeling analysis described below.

Mean-expected and worst-case consequences of spills were estimated using Applied Science Associates' (ASA) CHEMMAP in stochastic mode. The stochastic model was used to determine the range of distances and directions contamination from spills would be likely to travel from a particular site, given the historical current and wind speed direction data for the area. A large number of model simulations were run for a given spill site, randomly varying the spill date and time, and thus the wind and current conditions, for each run. The time histories of multiple simulation runs were then used to generate probabilities that water surface, water column, sediment, and shoreline areas would be exposed above thresholds of concern, as well as areas/volumes exposed. Each simulation was evaluated to determine the maximum exposure concentration for each location around the spill site at any time after the spill. The worst-case (i.e., caused by worst-case environmental conditions), and the mean (expected) of all the simulations, and the peak exposure concentrations were calculated for each location around the spill site. These concentrations may be compared to concentrations that have been shown to have toxic effects to determine the potential for impacts. Calculations were made to estimate volume and total habitat area exposed above potential thresholds of concern.

Contour maps of model outputs were prepared to show the distances chemical concentrations would extend from the spill site. The maps may be considered relative to the spill location's origin and representative of other potential spill sites of similar environmental (wind and current) conditions. In this study, two spill sites were assumed: one on the continental shelf and one in deep water (> 1,000 m). The shelf spill results are generally applicable for the Louisiana-Texas shelf region. The deep-water results are applicable to the western Gulf of Mexico offshore area near the site of the current data used. The mean-expected and worst-case exposure concentrations for each location around the potential spill site may be compared to bioassay data indicating concentrations with toxic effects and to maps of resources of concern.

7.3 CHEMMAP Model Description

The chemical spill model developed by ASA, CHEMMAP, predicts the trajectory and fate of a spectrum of chemical products, including floating, sinking, soluble and insoluble chemicals, and product mixtures. CHEMMAP incorporates a number of processes including:

- Simulation of the initial release and plume dynamics of a product lighter or denser than water
- Slick spreading and transport of floating materials
- Transport of dissolved and particulate materials in three dimensions (through the entire water column)
- Evaporation and volatilization
- Dissolution and adsorption
- Sedimentation and re-suspension
- Degradation of the chemical of concern to presumably inert product(s) (biological and chemical degradation, modeled as a constant rate)

The model uses physical-chemical properties to predict the fate of a chemical spill. These include density, vapor pressure, water solubility, environmental degradation rates, adsorbed/dissolved partitioning coefficient (K_{OC}), viscosity, and surface tension.

CHEMMAP was developed from the fates and biological effects' submodels in the Natural Resource Damage Assessment Model for Coastal and Marine Environments (NRDAM/CME). The NRDAM/CME (Version 2.4, April 1996) was published as part of the United States Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Type A Natural Resource Damage Assessment (NRDA) Final Rule (U.S. Federal Register, May 7, 1996, Vol. 61, No. 89, p. 20559-20614). The model is also incorporated in the U.S. Oil Pollution Act of 1990 NRDA regulations. The technical documentation for this model is in French et al. (1996a, b, 1999).

The fates model estimates the distribution of spilled substance (as mass and concentrations) on the water surface, on shorelines, in the water column, and in the sediments. Algorithms based on state-of-the-art published research include spreading, evaporation, transport, dispersion, emulsification, entrainment, dissolution, volatilization, partitioning, sedimentation, and degradation. The model is three-dimensional, using a latitude-longitude grid for environmental data.

CHEMMAP includes the physical fates and biological effects models in the NRDAM/CME, with several changes and additions. The biological model was not used in this study. Most of the additions to the fates model were made to increase model resolution; allow modification and site-specificity of input data; allow incorporation of temporally varying, three-dimensional current data; and facilitate analysis of results. The stochastic modeling approach was also added so that CHEMMAP could be run in either deterministic (single scenario) or stochastic mode.

7.3.1 CHEMMAP Chemical Database

The CHEMMAP chemical database contains the physical-chemical properties required by the model to simulate the transport and fate of the spilled material. The database includes a variety of text and numeric descriptors to identify and characterize the spilled chemical or mixture. The model is capable of simulating spills of pure chemicals, chemicals in aqueous or hydrophobic solutions, or chemicals in emulsions (i.e., mixtures of particulate material suspended in an aqueous base). Thus, the database also includes characteristics that define these mixtures and solutions.

The model uses physical-chemical properties with which the user may characterize the spilled chemical or mixture. A discussion of these properties is given in French et al. (1996a).

Table 21 lists the physical-chemical properties included in the data base. Initial data base values were taken from French et al. (1996a). These values were updated with new information developed as part of this study.

Several properties vary with temperature. Thus, the data base values are for a standardized temperature of 25^{o} C. The model corrects these parameters to the ambient temperature for the spill incident. The algorithms for changing viscosity and vapor pressure to ambient temperature are taken from French et al. (1996a). For pure chemical processes (i.e., solubility), the increase per 10 degrees Celsius is assumed to be two. For biological processes (degradation rates), the increase in rate per increase of 10 degrees Celsius is assumed to be three.

Table 21

Chemical Database: Physical – Chemical Properties

Chemical type code (integer) (inorganic or organic category, from French et al., 1996a)
Molecular weight (g/mole)
Particle size as diameter, assumed spherical (m) (if solid; or suspended in bulk liquid emulsion; or droplet size for liquid, gas, or hydrophobic solution subsurface releases; or initial plume thickness at release for dissolved chemicals)
Density (g/cm^3) at standard temperature (25^o C)
Freshwater Solubility (mg/kg = mg/l = ppm) at standard temperature (25^o C)
Seawater Solubility (mg/kg = mg/l = ppm) at standard temperature (25^o C)
Vapor pressure (atm.) at standard temperature (25^o C)
Dissolution rate (per day) at standard temperature (25^o C)
Viscosity (cp = centipoise) at standard temperature (25^o C)
Surface tension at standard temperature (25^o C) (dyne/cm)
Minimum thickness of a floating chemical slick, at standard temperature (25^o C) (m)
Degradation rate (per day) when exposed to the atmosphere (on water surface and shorelines) at standard temperature (25^o C)
Degradation rate (per day) in the water column, at standard temperature (25^o C)
Degradation rate (per day) in sediments, at standard temperature (25^o C)
Octanol water partition coefficient as log10 (Kow) (dimensionless)
Sorption partition coefficient for organic carbon, as log10 (K_{OC}); K_{OC} = adsorbed/dissolved partition coefficient (g/kg adsorbed per g/l dissolved)
Melting point temperature (deg. C)
Boiling point temperature (deg. C)
Density of the bulk liquid at standard temperature (25^o C)
Concentration of particles in the bulk liquid (i.e., for an emulsion where liquid is aqueous) (by weight, mg/kg)
Concentration dissolved in hydrophobic solvent (13) or in suspended particles (14,15) (by weight, mg/kg)
Concentration dissolved in water (11) or aqueous phase (14,15) (by weight, mg/kg)

7.3.2 Chemical Fates Model

The chemical fates model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column, and in the sediments. The model is three-dimensional. It separately tracks surface slicks, entrained droplets or particles of pure chemical, chemical adsorbed to suspended particulates, and dissolved chemical. Processes that are simulated include spreading, transport, dispersion, evaporation-volatilization, entrainment, dissolution, partitioning, sedimentation, and degradation.

The model initializes the spilled mass at the location and depth of the release in a state dependant upon the physical-chemical properties of the material. The state code and solubility are the primary determining factors for the initialization algorithm.

If the chemical is already dissolved in water, the chemical mass is initialized in the water column in the dissolved state. Chemical in the water column is treated as partially adsorbed to suspended sediment particles and partially dissolved. Partitioning between these states is assumed to be in constant proportions (based on linear equilibrium theory), using K_{OC} from the chemical database (Table 21).

If the chemical is an insoluble liquid or a gas, the following initialization is used. If the density is less than or equal to that of water, and the release is at or above the water surface, the model initializes the material in surface slicks. Otherwise, the spilled mass is initialized in the water column at the release depth in a plume volume defined for the dissolved chemicals. Once dissolution has occurred, chemical in the water column is treated as partially adsorbed to suspended sediment particles and partially dissolved. Partitioning between these states is assumed to be in constant proportions (based on linear equilibrium theory, using K_{OC} from the chemical database).

Soluble solids, which are spilled in a particulate form, dissolve and then are partitioned in the water column between dissolved and particulate-using equilibrium partitioning. Insoluble solids remain in particulate form and are transported.

If the chemical is particulate in an aqueous emulsion or dissolved in a hydrophobic solvent, the spilled mass is initialized as particles (droplets) in the water column at the release depth. The particle size is based on product specification data. The initial plume volume is that of the bulk liquid volume spilled. Where the chemical of interest is both adsorbed to particles and dissolved in the water phase of the bulk liquid, dissolved mass is also initialized in the initial plume volume. The mass of chemical spilled is corrected from the bulk spill volume using the appropriate density and concentration data.

Chemical mass is transported in three-dimensional space and time by surface wind drift, other currents, vertical movement (in accordance with buoyancy), and random dispersion.
The model simulates adsorption onto suspended sediment, resulting in sedimentation of material. Stokes Law is used to compute the vertical velocity of pure chemical particles or suspended sediment with adsorbed chemical. If rise or settling velocity overcomes turbulent mixing, the particles will float or settle to the bottom. Settled particles may later resuspend. However, if the chemical is specified in the database as sticky in water, resuspension will not occur.

Wind-wave driven current (surface drift) is calculated within the fates model based on hourly wind speed and direction data. Surface wind drift of oil has been observed in the field to be 1-6% of wind speed in a direction 0-30 degrees to the right (in the Northern Hemisphere) of the down-wind direction (Youssef and Spaulding 1993). It is assumed that other floating insoluble chemicals behave similarly.

The horizontal diffusion (randomized mixing) coefficient normally ranges from 1-10 m^2/sec in coastal and marine waters. The vertical diffusion (randomized mixing) coefficient is typically 0.0001-0.001 m^2/sec. These are reasonable values based on (Okubo 1971) and modeling experience. The vertical diffusion coefficient of 0.0001 m^2/sec keeps a shallow water column well mixed.

For surface slicks, the model estimates surface spreading, slick transport, entrainment into the water column, and evaporation to determine trajectory and fate at the surface. Spreading is simulated using the algorithm of Fay (1971). Entrainment is modeled as for oil, using data in Delvigne and Sweeney (1988). Surface slicks interact with shorelines, depositing and releasing material according to whether the material is sticky and to shoreline type. The algorithms used are those developed for oil spills, as described in French et al. (1999).

Volatilization from the water column is calculated from the chemical’s vapor pressure using Henry’s Law, and is a strong function of temperature. Degradation is estimated assuming a constant rate of "decay" specific to the environment where the mass exists (i.e., atmosphere, water column or sediment).

The fates model computes, in space and time, the following:

- Water surface:
  - area covered by surface slicks
  - radius and thickness of surface slicks
- Water column:
  - total concentration
  - pure chemical droplet or particulate concentration
  - dissolved concentration
  - concentration adsorbed to suspended sediments
  - concentration in hydrophobic droplets (state codes 13-15)
- Sediments:
  - total concentration
  - pure chemical droplet or particulate mass per unit area
  - dissolved concentration
  - concentration adsorbed to sediments
- Shorelines:
  - area and length contaminated
  - mass per unit area

These model output data are mapped by the user interface in an animated display. For the stochastic model, mean-expected and worst-case exposure concentrations are plotted.

7.4 Environmental Data

The following data are used by the model. Sources of the data for this study are described.

7.4.1 Geographical Data

Data for water depth, shoreline type, sediment type, and habitat type throughout the domain were taken from several geographical databases. The model uses gridded maps to determine location of the shoreline, habitat (or shore) type, and water depth. The geographical data around the spill site are gridded using the shoreline location to define land and water cells. Arc View (ESRI) Geographical Information System (GIS) software was used to create the maps. Stochastic output is saved on this grid, allowing quantification of habitat area exposed. A depth data grid of the same dimensions and area coverage as the habitat grid contains bathymetry from the NOS soundings database (National Ocean Service, Hydrographic Survey Data, Version 3.2).

In anticipation that hypothetical spills might contaminate shoreline habitats, shoreline habitat type was mapped using Arc Info (ESRI) GIS data sets available from the states of Texas and Louisiana. Environmental Sensitivity Index (ESI) and coastline data for Texas were obtained from the Texas General Land Office (TGLO) web site. The TGLO shoreline features were extracted from National Wetland Inventory data and other hydrography data sets and assigned ESI values by the University of Texas Bureau of Economic Geology. Oyster reefs in the Galveston Bay system (except for part of Trinity Bay) were mapped by Dr. Eric Powell, formerly of Texas A&M University, and downloaded from the TGLO web site (http://www.glo.state.tx.us/oilspill/osdata.html).

Coastline and wetland data for Louisiana were obtained from the Louisiana Department of Wildlife and Fisheries, Fur and Refuge Division, and the U.S. Geological Survey, Biological Resources Division's National Wetlands Research Center. The data were published on June 1, 1997 as the 1997 Louisiana Coastal Marsh Vegetative Type Map. The data consist of polygons coded as one of six vegetation types. Those shoreline habitats not mapped as wetland were assumed sandy beach (by far the dominant shoreline type in areas that are not wetlands).

Figures 15 and 16 show the habitat types as gridded for input to the model. Figures 17 to 19 show the bathymetry in gridded format (as seen by the model). Figures 17 and 18 are for the area of the shelf spill, while Figures 19 and 20 are for the area near the deepwater spill site. In the deep water, depth data was missing for some points, which were avoided in selecting the representative spill site.

7.4.2 Wind Data

The model uses, as input, an hourly wind time series of speed and direction. These data are important for insoluble floating chemicals, but have little influence on dissolved contaminants. Surface wind drift (current) for the upper 5 m of the water column is calculated from the wind data.

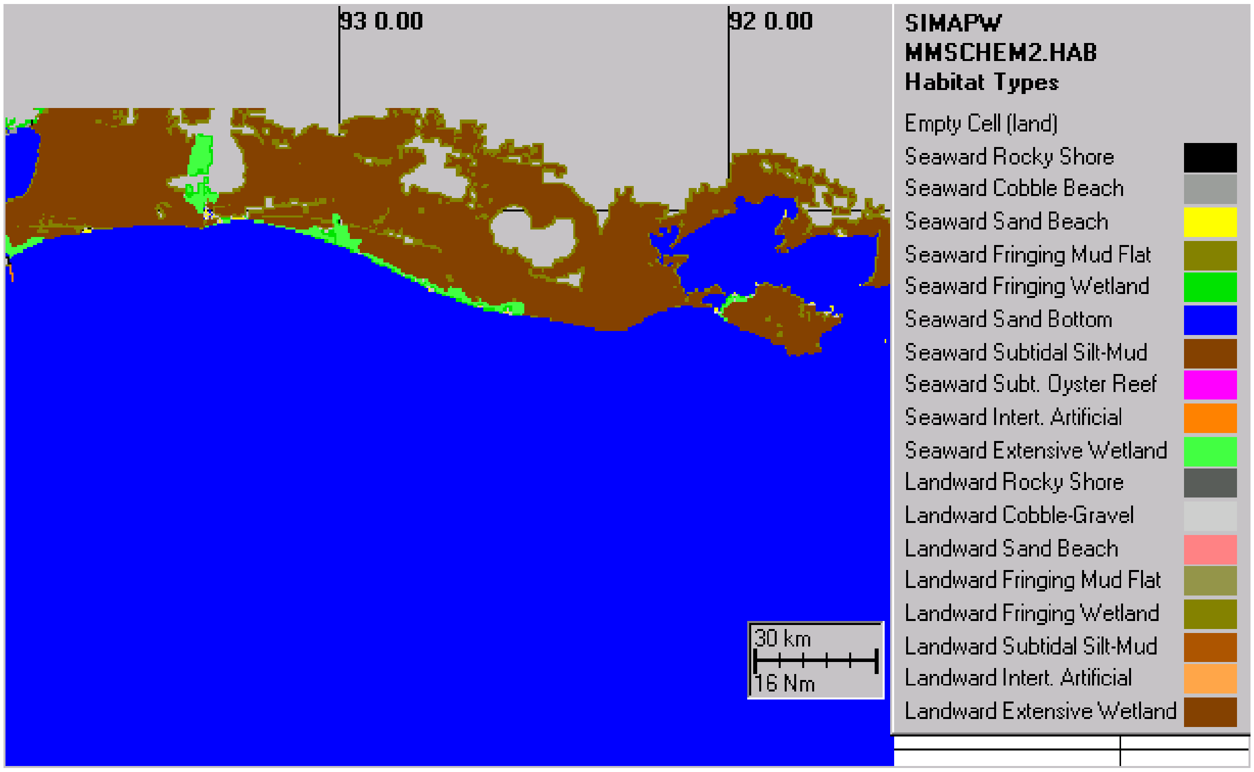


Figure 15. Gridded map of habitats in eastern portion of the study area.

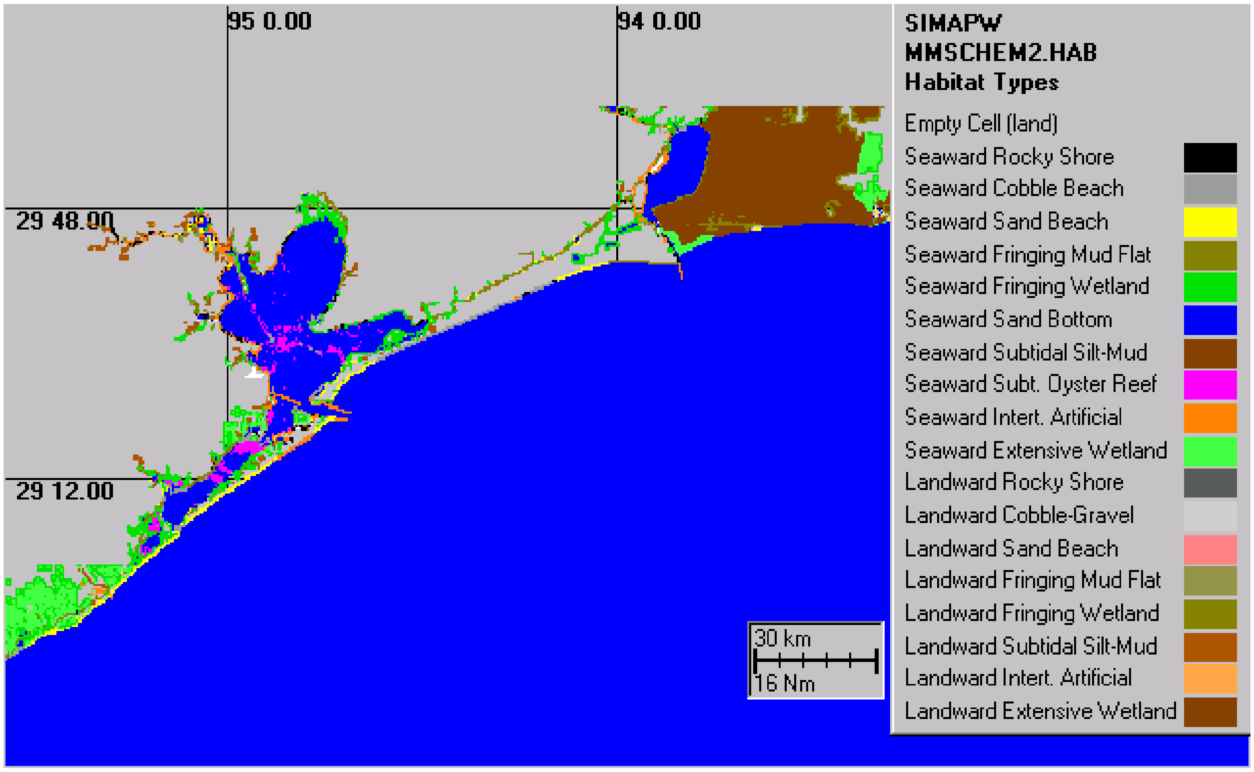
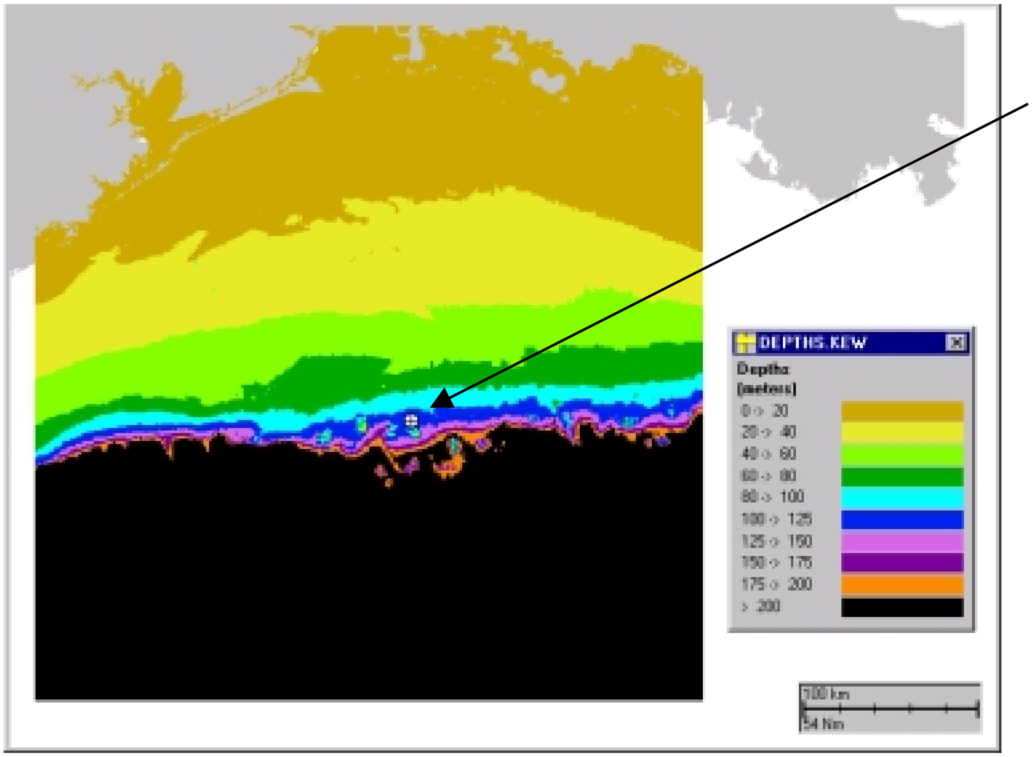
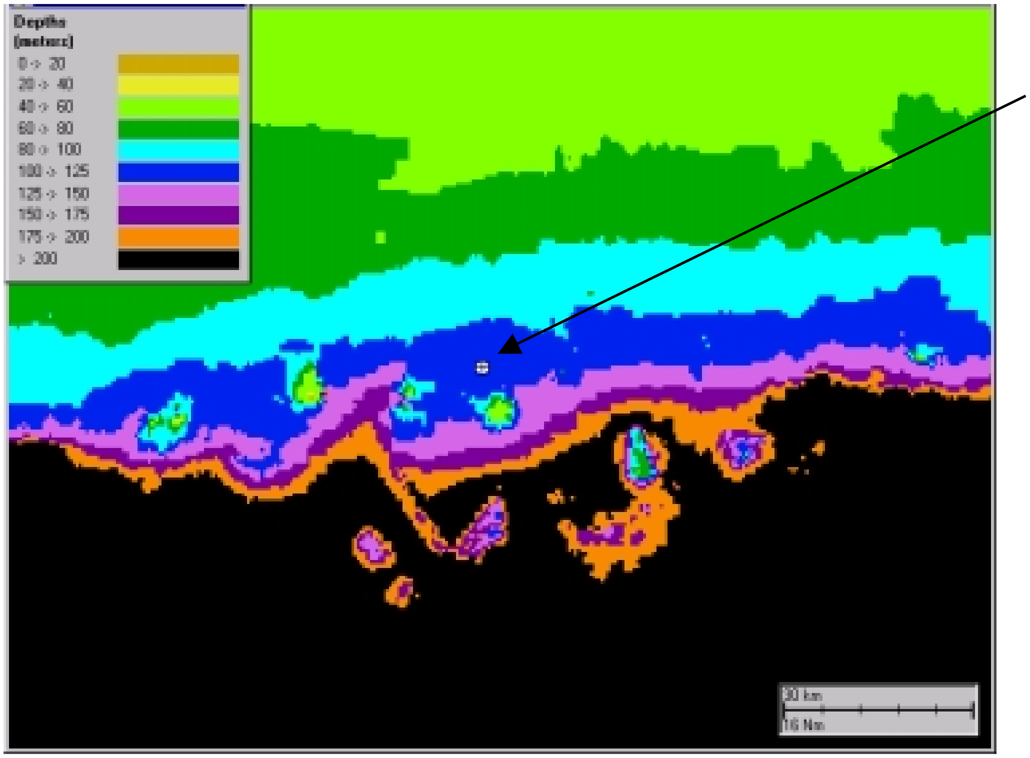


Figure 16. Gridded map of habitats in western portion of the study area.



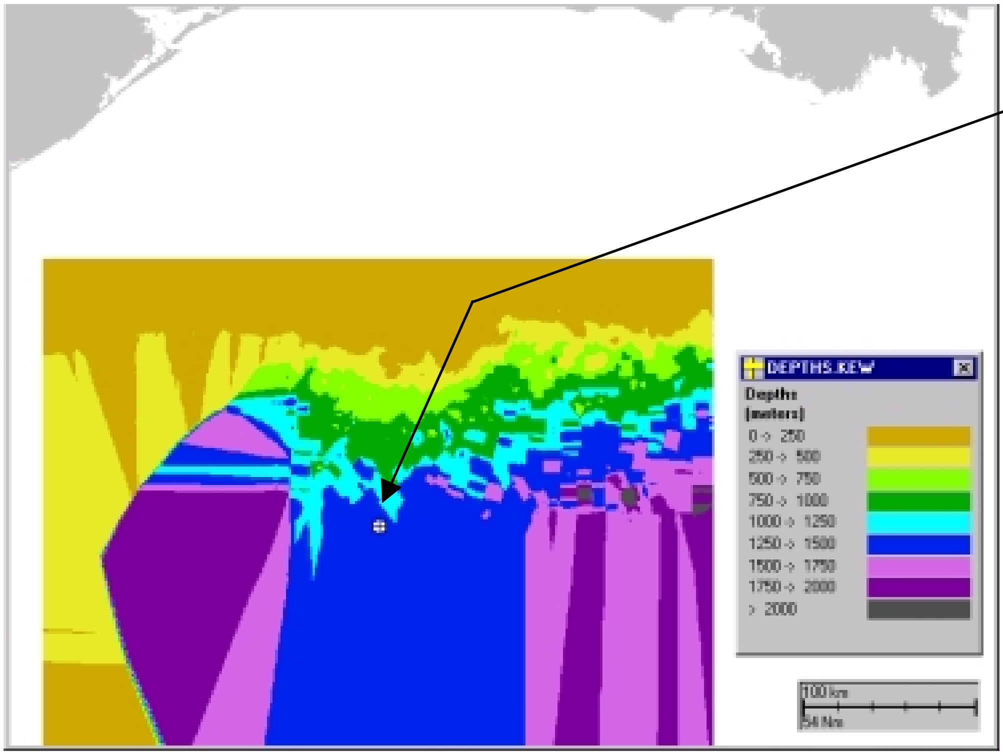
Shelf Spill Site Location
Lat. 27° 56' 52.9" N
Long. 93° 15' 1.6" W

Figure 17. Gridded map of bathymetry used in the modeling for the shelf spill site.



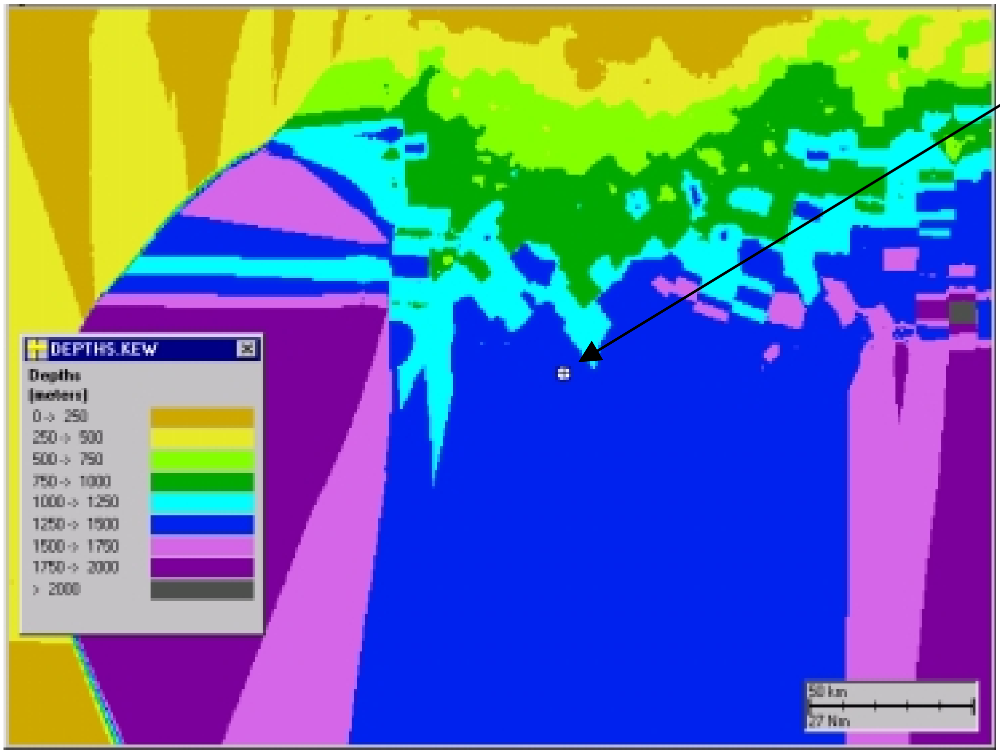
Shelf Spill Site Location
Lat. 27° 56' 52.9" N
Long. 93° 15' 1.6" W

Figure 18. Gridded map of bathymetry in the area of the shelf spill site.



Shelf Spill Site Location
Lat. 27° 56’ 52.9” N
Long. 93° 15’ 1.6” W

Figure 19. Gridded map of bathymetry used in the modeling for the shelf spill site.



Shelf Spill Site Location
Lat. 26° 48’ 17.8” N
Long. 93° 32’ 6.1” W

Figure 20. Gridded map of bathymetry in the area of the deepwater spill site.

Data are available from NOAA buoys and land-based weather stations. Historical time-series data from all NOAA buoys and stations are quality controlled by the National Data Buoy Center. The data were formatted for model use at ASA.

For the deepwater spill site, winds were for the period 24 May 1990 through 23 December 1998, with a gap between 29 April and 28 October 1997. For the shelf spills, the wind time series was chosen to be for the same time as the available current data (15 April 1992 to 4 December 1994; see below). Comparison of winds from this time to the decade long record from the same source showed that the period from 1992-1994 was representative.

Data were predominantly from NOAA buoy 42019, located 60 nautical miles off Freeport at 27.92^{o} N, 95.35 ^{o} W. Gaps in the buoy 42019 data were filled with data from nearby buoys. The first choice substitute was buoy 42035 (6/27/94-7/28/94) and secondarily C-Man Station SRST2 (4/29/92-6/3/92, 10/16/92-11/20/92). Buoy 42035 is located at 29.25^{o} N, 94.41^{o} W (22 nautical miles east of Galveston). C-Man Station SRST2 is located at 29.67^{o} N, 94.05^{o} W (Sabine).

7.4.3 Currents

The chemical transport model is designed so that it may accept current (hydrodynamic) data from a variety of sources. For the best spatial and temporal coverage, these data are in the form of gridded time series data, or gridded tidal constituent data, which allow the transport model to automatically generate current vectors for the time period of the spill. A hydrodynamic model may be used to compute tidal, density driven, or wind-driven motion of water. The model may be either two- or three-dimensional, with currents varying spatially in both horizontal and vertical directions. Alternatively, constant background currents and cyclic tidal current vectors may be manually entered into a database. The model may also use data from current meter studies. In this study, current meter data was used.

7.4.3.1 Shelf Currents

Current meter data from the LATEX program of Texas A&M University is used for spills in the continental shelf region (DiMarco et al. 1997). The objective in this study was to provide the model with current velocities, which vary vertically but are spatially representative in the horizontal. In this way, the model results may be applied to other spill sites with a similar vertical profile of current velocities. The results are most applicable to shelf sites with similar water depth (i.e., along the bathymetric contour running through the current meter site).

As the present analysis is of chemical spills associated with deepwater oil and gas activities, current data for the shelf break region at about 200 m was used. The LATEX study included a series of current meters along the 200 m isobath from near the Mississippi Delta to south Texas reaching about 27^{o} N (Figure 19). The meters were deployed from April 1992 to December 1994. Mooring 10 (27° 56’ 9.6” N, 92° 44’ 42” W), which is located on the 200 m isobath and is in an active oil and gas production area, was selected as representative for the shelf break region. Examination of the data from this and adjacent moorings along the 200 m isobath (DiMarco et al. 1997) showed that the currents indicate similar net transport from mooring 48 to 7. The net transport at mooring 12 and 13 is more frequently to the northeast because loop current eddies intersected the slope and shelf.

At mooring 10, as for all of the moorings, there are periods in which data records are missing. In order to fill in the missing periods, data from four nearby moorings (8, 9, 11 and 48) were inserted into the current data file. These moorings are all on the 200 m isobath. Whenever mooring 10 lacked observations, records of the closest mooring available with the same depth levels (surface, mid-depth, and bottom) were substituted. The resultant current record, other than these substitutions, is identical to original records provided by National Oceanographic Data Center, CD-ROM Data Sets.

The current data from the three depths measured were linearly interpolated to provide a continuous current profile in the vertical. Current was assumed zero at the sea floor, with (linear) interpolation to the next current meter above the bottom.

7.4.3.2 Deepwater Currents

For the deepwater spill site, current meter data from mooring GG, deployed in 1987-1988 by SAIC, were used (Hamilton 1990, 1992). These data are presently maintained by Texas A&M University, the source of the data files used in this analysis.

This mooring is in the central-western Gulf of Mexico (25° 39' 12" N, 92° 1' 54" W), where the depth is 3,000 m. Loop current eddies are often in this area, slowing down and dying in the western basin. Thus, current data from other offshore regions to the east, which may be more extensive, may not be applicable to the central-western Gulf of Mexico. The one-year of data at mooring GG is limited, but is the best available at this time as representative of the region. Hamilton (1990) describes the data record for mooring GG and the fact that several warm- and cold-core eddies passed through the region during that year of data collection.

Meters were deployed at 5 depths: 100 m, 300 m, 725 m, 1,650 m, and 2,500 m. Data were collected from all five depths at 30-min intervals from 9 November 1987 to 30 October 1988. (Only the data from 300 m, 1,650 m and 2,500 m are described in Hamilton 1990).

In model runs, these data were assumed to apply to all years, for the corresponding month, day and hour. For the missing period noon 30 October to noon 9 November, available data from 1,650 m were used for other depths after multiplying by the average ratio in November of current speed of the depth of interest to speed at 1,650 m. The ratios used were:

- 100 m : 1,650 m – 13.83
- 200 m : 1,650 m – 3.99
- 725 m : 1,650 m – 3.71
- 2,500 m : 1,650 m – 1.368

The current data from the five depths measured were linearly interpolated to provide a continuous current profile in the vertical. Current was assumed zero at the sea floor, with (linear) interpolation to the next current meter above the bottom.

7.5 Scenario Specification

The data that are required to run the CHEMMAP fates model and the assumed values used in the model scenarios are listed in Table 22. Table 23 describes the habitat grid dimensions used in the modeling and to tabulate results. The results are saved as average concentrations over the area of each grid cell. Thus, the size of the habitat grid cell determines the resolution of the model results. The habitat grid was defined such that (1) the spill site was near the center, (2) the shoreline was included (shelf spill), and (3) the maximum possible resolution was used, given the memory limits of the computer used to make the model runs. In addition, the chemical must be included in the chemical database with appropriate physical-chemical properties (to be discussed below).

Table 22

Scenario Specification Data Required by the Model

Name	Description	Units	Value(s)	Source of Information
Spill Site for shelf spills	Location of the spill site	-	27^o56’52. 9” N 93^o15’1. 6” W	Representative shelf location
Spill Site for deepwater spills	Location of the spill site	-	26^o48’17. 8”N 93^o32’6. 1”W	Representative deep-water location in western G. of Mexico
Depth of release	Depth below the water surface of the release	M	1 (for at water surface) or > 0 (for sub-surface)	(See Table 25)
Start time and date	Date and time the release began	Date, hour, minute	-	-
Duration of release	Time over which the release occurred	Hours	0 (instantaneous)	-
Total spill volume or mass	Total volume (or weight) released (for bulk mixture)	Bbl, gal., MT, kg, L, m^3	(See Table 25)	(See Table 25)
Substance released: name, #	Chemical of concern released (name and identification #s)	-	Name (CAS #)	(See Table 25)
Salinity	Surface water salinity	ppt	32ppt	(French et al. 1996a)
Water Temperature	Surface water temperature	Deg. C	18-29^oC	(French et al. 1996a)
Wind data	Hourly wind speed and direction	Kts or m/sec, deg.	Hourly wind speed and direction for 4/15/92-12/4/94 (shelf spills) or 5/24/90-12/23/98 (deepwater spills)	NOAA buoy 42019, with data gaps filled with data from neighboring NOAA buoy 42035 and CMAN station SRST2
Current data for shelf spills	Current speed and direction as function of time and space	cm/sec by x,y,z,t	LATEX current meter data for 4/15/92-12/4/94	Current mooring 10

Table 22
Scenario Specification Data Required by the Model (continued)

Name	Description	Units	Value(s)	Source of Information
Current data for deepwater spills	Current speed and direction as function of time and space	cm/sec by x,y,z,t	Current meter data for 11/9/87-10/30/88	Current mooring GG (Hamilton 1990)
Coastline data	Data set of shoreline locations	Latitude, longitude	-	(GIS data)
Shoreline type	Shoreline classification	-	(See Note 1)	ESI and other mapping; GIS data
Habitat type	Habitat mapping (shoreline and subtidal)	-	(See Note 2)	Shore type and habitat GIS data
Wind drift speed	Speed water surface moves downwind relative to wind	% of wind speed	1-6% (3.5% average)	(Youssef and Spaulding 1993)
Wind drift angle	Angle to right of downwind (in northern hemisphere)	Deg. To right of downwind	0-40	(Youssef and Spaulding 1993)
Horizontal dispersion coefficient	Randomized turbulent dispersion parameter in x & y	m^2/sec	3.0 (typical value)	(French et al. 1999)
Vertical dispersion coefficient	Randomized turbulent dispersion parameter in z	m^2/sec	0.0001 (typical value)	(French et al. 1999)
Suspended sediment	Average concentration	mg/l	10 mg/l	(French et al. 1996a)
Time step	Calculation interval	Hours	1	-
Number of particles	# Lagrangian elements simulating spill	#	1,000	-

Notes:

1. Shore types include: rocky, gravel, sand beach mud flat, wetland (salt marsh, mangrove), mollusk reef, coral reef, algal bed, sea grass bed, artificial, ice edge. Environmental Sensitivity Index (ESI) data are mapped to these categories.
2. Habitat types include the shore types listed above, plus subtidal habitats: rock bottom, gravel bottom, sand bottom, silt-mud bottom, algal bed, sea grass bed, coral reef, mollusk reef, and subtidal areas within wetlands.

Table 23
Model Habitat Grid Dimensions

Attribute	Shelf Spill Grid	Deepwater Spill Grid
Grid W edge	95°34'15.3"W	95°33'14.7" W
Grid S edge	26°27'54.5" N	25°19'9.4" N
Cell size (° longitude)	0.00542	0.00542
Cell size (° latitude)	0.00542	0.00542
Cell size (m) west-east	533.1	533.1
Cell size (m) west-east	601.4	601.4
# cells: west-east	737	742
# cells: south-north	658	537
Water cell area (m^2)	320,573	320,573
Shore cell length (m)	566	566
Shore cell width – rocky, artificial (m)	1	1
Shore cell width – beach (m)	5	5
Shore cell width – wetlands (m)	50	50

7.6 Stochastic Modeling of Trajectory and Fates

In order to determine risks to resources, multiple scenarios and conditions need to be evaluated to develop an expectation of risk of a pollutant reaching each site of concern. There may be specific sites of concern, or the goal may be to identify what sites are at risk.

Mean-expected and worst-case consequences of spills were estimated using CHEMMAP applied in stochastic mode. The stochastic model was used to determine the range of distances and directions contamination from spills are likely to travel from a particular site, given the historical current and wind speed direction data for the area. A large number of model simulations were run for a given spill site, randomly varying the spill date and time, and thus the wind and current conditions, for each run. The time histories of multiple simulation runs may be used to generate probabilities that water surface, water column, sediment and shoreline areas would be exposed above thresholds of concern, as well as areas/volumes exposed. Each simulation was evaluated to determine the maximum (= peak) exposure concentration (over time after the spill) for each location around the spill site at any time after the spill. The worst case (i.e., caused by worst case environmental conditions), and the average (i.e., mean of all environmental conditions) over all simulations, of the peak exposure concentrations were calculated for each location (grid cell) affected. The grid cells are 320,573 m^2 in area (for all locations) and 113 m deep at the spill site. The peak concentrations are for one hour or more of exposure, which is the time step used in the model runs. Of course, concentrations at the spill site at time zero are at the maximum, i.e., at the concentration in the spill volume. The peak concentrations calculated by the model are those at one hour after the spill, averaged over one grid cell of volume (36 million m^3) around the spill site. Concentrations continue to decrease from these levels over time.

Contamination in the water column after a spill changes rapidly in space and time. Toxicity to aquatic organisms increases with time of exposure, such that organisms may be unaffected by brief exposures to the same concentration that is lethal at long times of exposure. For a brief exposure, a dosage measure of concentration times exposure time is a more appropriate index of toxicity than the peak concentration. For example, if a 96-hour LC50 is 1.0 mg/L, the dosage is 96 mg L^{-1} hrs. Assuming a linear time-response model, the LC50 for a 1 hour exposure would be about 96 mg/L, and for a 10-hour exposure would be about 9.6 mg/L. Total dosages calculated by the model are:

- **Water surface**: Slick thickness multiplied by time present (mass per area - time) for each dosage level (g-m^{-2}-hrs)
- **Concentrations in water**: Water volume and habitat area exposed at each dosage level (concentration-time, i.e., (mg-m^{-3}-hrs or ppb-hrs)
- **Mass loading to sediments and shorelines**: Mass per unit area multiplied by time present (mass per area - time) for each dosage level (g-m^{-2}-hrs)

Contour maps of model outputs were prepared to show the distances chemical concentrations would extend from the spill site. The maps may be considered relative to the spill site and representative of other potential spill sites of similar environmental (wind and current) conditions. The shelf spill results are generally applicable for the Louisiana-Texas shelf region, especially along the 200 m isobath. The deepwater spill results are applicable to the slope and offshore region of the western Gulf of Mexico to the extent that the one year of data at mooring GG are representative. (See discussion of current data above.) The mean-expected and worst-case exposure concentrations for each location around the potential spill site may be compared to maps of resources of concern.

The three-dimensional stochastic model in CHEMMAP quantifies, in space and over time, for each individual model run, the following components:

- Mass or thickness (mass or volume per unit area) on water surface
- Mass or thickness (mass or volume per unit area) on shorelines
- Subsurface (water) particulate (solid or liquid droplets) concentration
- Subsurface (water) dissolved concentration
- Subsurface (water) adsorbed (to suspended sediment) concentration
- Sediment concentration

The range of possible scenarios includes various wind and current conditions, volume spilled and other parameters. To sample this universe of possibilities, long-term wind and current records are developed (as described above). The list of input assumptions that may be randomized is below.

- Release date (and so wind and current patterns):
  - All months of the year (quantifies risks for spills at any time of year, used in this study)
  - Selected month(s) or season (quantifies risks for spills at that time of year)

- Spill volume:
    - randomized up to a maximum possible (quantifies typical, mean risk)
    - constant at maximum possible (quantifies risks for worst-case volume, used in this study)

A stochastic model case is a quantification of probabilities (statistics) based on multiple model runs, for selected:

- Chemical or chemical mixture (with associated physical and chemical characteristics)
- Spill volume
- Location
- Thresholds of concern for:
    - Surface (water or shoreline) mass or thickness
    - Subsurface particulate concentration
    - Dissolved chemical concentration
    - Sediment concentration

For each of the components of the spill, an effects endpoint is selected which provides a threshold above which probabilities are to be reported. These thresholds may be for mortality, sub-lethal or chronic effects, tainting, human health impacts, or for impacts on recreational or other human uses.

The results of multiple model runs for a stochastic case are evaluated to develop the following statistics for each of the components listed above:

- Probability of exposure greater than a threshold (thickness or concentration)
- Time to first exceedance of the threshold
- Maximum thickness, volume or concentration at any time after the spill, at a given location (peak exposure at each location)
    - Worst-case maximum amount for all possible releases (i.e., maximum peak exposure for all the model runs). This is calculated in two steps: (1) For each individual run (for each spill date run), the maximum amount over all time after the spill is saved for each location in the model grid. (2) The runs are evaluated to determine the highest amount possible at each location. Note that these *worst-case maximum* amounts are not additive over all locations. These represent maximum possible amounts that could ever reach each site, considered individually. The spill date and time for the worst-case run is also saved.
    - Mean-expected maximum amount for all possible releases (i.e., mean-peak exposure of all model runs). This is calculated in two steps: (1) For each individual run (for each spill date run), the maximum amount over all time after the spill is saved for each location in the model grid. (2) The runs are evaluated to determine the mean-expected peak exposure (mean amount for all runs) at each location. Note that these *mean-expected maximum* amounts are not additive over all locations. These represent the mean of many different runs, affecting different sites to maximum extent at different times after the spill.

The CHEMMAP graphical user interface produces maps of these statistics. For each stochastic model case, maps are produced of probability of exceeding the chosen threshold, time of first exceedance, and of peak exposure. The exposure maps are average expected and worst possible exposure by location. These exposure maps contain contours of thickness or concentration. Mapped geographical data of sensitive resources may be compared and/or overlaid with model results. This will show where resources would be most at risk, and giving indications of where protection would be most beneficial.

Table 24 lists the stochastic model inputs used in this study. Because specific toxic endpoints are uncertain for the chemicals evaluated in this study, very low thresholds were input to the model. This allowed the entire spill mass to be plotted, even when concentrations would not be expected to be toxic. Thus, the probability feature was not used in evaluating the results. The results are expressed as exposure concentrations.

Table 24
Stochastic Model Inputs

Number of stochastic runs	100
Spill dates	Randomize months 1-12
Spill volume	Constant at maximum spill size
Threshold: Surface slick	Mass $\geq$ 0.00001 g/m^2
Threshold: Shoreline	Mass $\geq$ 0.00001 g/m^2
Threshold: Dissolved	Average over the water cell $\geq$ 0.01 mg/m^3
Threshold: Particulate	Average over the water cell $\geq$ 0.01 mg/m^3
Threshold: Adsorbed to suspended sediment	Average over the water cell $\geq$ 0.01 mg/m^3
Threshold: Total in Sediment	Average over the water cell $\geq$ 0.00001 g/m^2 (which is 0.1 mg/m^3 averaged over the top 10cm)

7.7 Chemical Spill Scenarios

Spill modeling was done for 16 shallow water scenarios, plus one deepwater scenario. All but three of the 16 spill model scenarios were performed on single component chemicals or mixtures of a single active ingredient in a solvent. The properties of such materials are usually readily available and their concentrations easily determined. Production-treating chemicals, however, presented a different issue. Many production-treating chemicals are complex mixtures containing proprietary materials, in which both the composition and the concentration of ingredients are not available. As a result of trade secret privileges, complete characterization of these materials is challenging. Production-treating chemicals such as corrosion inhibitors, emulsion breakers, and some defoamers are members of these types of materials. To overcome this obstacle chemical suppliers agreed to provide detailed, representative compositions, for several products so that fate and effects modeling could be completed on chemicals from each class. For protection against potential competitors, the selected chemical products are not identified by product name or supplier. Moreover, the actual composition is not reported in this document, but was supplied to the MMS under separate cover. In Scenarios 14 and 16 described below, these chemical formulations are referred to as Product A, Product B, and Product C.

For each spill scenario, assumptions were made on how the chemical could be spilled and how it would enter the environment. Using information from the chemical inventory (Section 2.0) and analysis (Section 3.0), materials and volumes selected are the worst cases taken from the range of actual use/storage volumes found in this study. The worst-case spill volumes for Scenarios 11-16 are quite small. Preliminary test runs showed that the model need not be run for two weeks, as for the larger spills of Scenarios 1-10. For very small spill volumes, fewer stochastic simulations were made as well, as these scenarios produced very low concentrations. In modeling these scenarios, it was assumed that releases were immediate. That is, if the product is in a container that is lost or packaged in sacks when lost, the container is assumed to immediately rupture and the material is immediately released to the environment. If the discharge is a bottom discharge, it is assumed that the container reaches the bottom and then immediately ruptures, releasing the material. In the Scenario 10 case, it is assumed that the umbilical breaks at the high point of the line (i.e., a location that is closer to shore and where the water is shallow). If an umbilical were to break at the low point, once the line is secure, the surrounding seawater, having a greater density, will act as a plug, trapping the ethylene glycol inside the line.

Scenarios 1-16 were at the shelf spill site. The same representative spill site (27^{o}56°52.9” N, 93^{o}19’ 1.6” W) was used for all shelf spill scenarios (for consistency). This site was chosen because the water depth was 114 m (370 ft.), the depth of the high umbilical release of ethylene glycol (Scenario 10). It is also near the LATEX current meters used to generate the current data input to the model.

Scenarios 1-13 and 17 are spills of single chemicals (pure or in aqueous solution). Thus, a single model run was made for each. DESCO and lignosulfonate (Scenario 7) are modeled as a class, as these products have similar properties. Multiple runs were made for Scenarios 14-16.

Table 25 lists the chemical scenarios run in the stochastic model of CHEMMAP. Section 7.8 describes the 16 (plus the deepwater barite spill) selected spill scenarios in more detail. In Table 25, the scenarios that are spills of chemical mixtures are broken down into individual chemical model runs, as the model evaluates results for one chemical at a time.

Spill Scenario 1 – Hydrochloric and Hydrofluoric Acids

Acids are used in stimulation and workover operations. The acid formulation selected is a common mix used offshore. These acids are water-soluble materials and react rapidly with seawater and enter into the buffered equilibrium system in seawater. The hydrogen ion component becomes indistinguishable from the hydrogen ion occurring naturally in seawater. Both chloride and fluoride ions are constituents of seawater and chloride ion is a major constituent. Excess fluoride will precipitate as calcium fluoride or other insoluble material, some of which may settle to the sediments.

Spill Scenario 2 – Sodium Hydroxide

This scenario models strong inorganic bases. These are water-soluble materials and react rapidly with seawater and enter into the buffered equilibrium system in seawater. Sodium hydroxide was selected to represent these materials because it is commonly used in drilling fluids in large amounts. In the sea, the hydroxide ion component becomes indistinguishable from the hydroxide ion occurring naturally in seawater. Sodium ion is a major constituent of seawater. If spilled, these materials or their reaction products will remain in the water column.

Spill Scenario 3 – Potassium Chloride

This scenario models non-reactive, water-soluble salts. Water-soluble salts are used extensively in drilling, completion, stimulation and work-over operations, as well as in cementing operations. Although potassium chloride is no longer used often it was selected because it has a potentially toxic impact at some concentrations. These materials will remain in the water column. Both potassium and chloride ions appear naturally in seawater and eventually potassium chloride will dilute to become indistinguishable from background seawater concentrations.

Spill Scenario 4 – Zinc Bromide

The fourth scenario models water-soluble reactive salts. Zinc bromide will immediately dissociate in seawater to the two component ions. Zinc and bromide ions react with other constituents of seawater, forming insoluble precipitant. Most of the positive ion constituent (Zn) will eventually end up in the sediment.

A commonly used zinc bromide/calcium bromide mixture was selected to represent this type. Such mixtures are used as completion or packer fluids. It was chosen because there was a relatively large volume spill of zinc bromide in the Gulf of Mexico in 1999.

Spill Scenario 5 – Sodium Bisulfite

This scenario involves a variation of water-soluble reactive salt for which the reaction in the environment is an oxidation/reduction reaction and not a precipitation, as for previous types discussed. This type of material is soluble in seawater, but reacts on contact with the oxygen in seawater. Sodium bisulfite is used in production operations as an oxygen scavenger to remove unwanted oxygen from waterflood water and produced water. On contacting seawater containing oxygen, the bisulfite ion will react to form sulfate ion, a common constituent of seawater. Spills of this material could cause localized oxygen depletion. This material and its reaction products will remain in the water column.

Spill Scenario 6 – Barite

This scenario models water insoluble solids. Barite was selected to represent this chemical type because large amounts of it are used in drilling fluids, and relatively large volumes of it are occasionally stored offshore. The concern is that a large accidental discharge might cause a habitat modification in the sea floor sediments. Barite is a natural constituent of sediments at low concentration, but has the potential for short-term impacts related to habitat modification.

Spill Scenario 7 – Lignosulfonate

This scenario models water-soluble organic solids or their metal salts. These materials would be spilled as solids that will dissolve in seawater. They are known to be toxic. Two common types of such materials are lignosulfonates and DESCO (a proprietary product made from modified lignin). Both materials are commonly used in drilling fluids and are frequently stored offshore during drilling operations. They are surface active, and will partition between the water (dissolved) and sediments (suspended and on the bottom) as adsorbed material. Lignosulfonate was used in the spill modeling because there is more data available.

Spill Scenario 8 – Lignite

This scenario models water-insoluble organic solids. The material selected for modeling, lignite, is not soluble in fresh water, but is highly dispersible and will go into the water column as suspended solids. Lignite is slightly water soluble in seawater at higher pHs. Because seawater (i.e., in the Gulf of Mexico) has a pH of about 8, it will slowly dissolve as its concentration decreases. Ultimately, it will be degraded by bacterial action and will place an oxygen demand on the environment. Lignite was selected because large quantities are used in drilling fluids and it is commonly stored offshore on drilling rigs.

Spill Scenario 9 – Methanol

This scenario models pure organic liquids soluble in water. This type of chemical is used in very large volumes and is a chemical type where there is a significant difference in shallow water and deepwater usage. Methanol was selected for this profile. Being highly water soluble, it will remain in the water column and ultimately will biologically degrade in the environment. The spill scenario for this chemical type is a spill at the surface. Potential impacts include both oxygen demand and toxicity.

Spill Scenario 10 – Ethylene Glycol

This scenario also models pure organic liquids soluble in water. Ethylene glycol was selected for profiling because it is sometimes recovered and reused. Both it and methanol are delivered to deepwater subsea wells by umbilicals. The spill scenario for this type is a spill from a broken umbilical. The spill from the umbilical is assumed to be at the shallow water end of the umbilical since that would result in the highest immediate release. These materials, being highly water-soluble will remain in the water column and will ultimately biologically degrade in the environment. Potential impacts include both oxygen demand and toxicity.

Spill Scenarios 11 and 12 – Glutaraldehyde

This scenario models water-miscible organic mixtures consisting of a water-soluble active ingredient and a solvent system containing an alcohol and possibly a glycol. This type of chemical includes biocides, reverse breakers, and scale inhibitors. These materials will remain in the water column and most of them will degrade biologically. The most common biocide used in produced water, glutaraldehyde was selected for modeling. Scenario 11 represents surface spills and Scenario 12 represents bottom discharges.

Spill Scenario 13 – Tetrakis (hydroxymethyl) Phosphonium Sulfate (THPS)

This scenario models water-miscible organic mixtures consisting of a water-soluble active ingredient that degrades chemically in the environment. The solvent is water. The active ingredient is an organic phosphonium compound. Tetrakis (hydroxymethyl) phosphonium sulfate (THPS) was selected to represent this class because it also represents recent chemical developments that attempt to improve environmental compatibility. Although it may not offer significant advances in environmental protection over older conventional chemicals, it illustrates one direction of change in the technology of oilfield chemical treating. THPS degrades in the presence of oxygen to tetrakis (hydroxymethyl phosphonium oxide (THPO), which has a much lower toxicity. The rate of degradation is dependent on several factors. The half life of the conversion of THPS to THPO is reported to be six hours and the total degradation THPS to final products has been estimated by the supplier to be 25 days (Albright and Wilson 1997). The ultimate degradation products are sulfate ion, phosphate ion and carbon dioxide, all of which are natural constituents of seawater.

Spill Scenario 14 – Quaternary Ammonium Compounds

This scenario models organic materials that may be either water-soluble or oil soluble and are applied in water solutions. Quaternary ammonium compounds represent this type of chemical. These chemicals are used in corrosion inhibitors and biocides. The chemical formulation used in Scenario 14 is referred to as Product A, is a water-soluble corrosion inhibitor, containing the following components:

• Water	22%
• Methanol	42%
• Acetic acid	3%
• Ethoxylated nonylphenol	3%
• Amides/Imidazolines	15%
• Quaternary ammonium chloride	15%

When spilled, the solution will dilute into the water column and the active ingredient will disperse as dissolved material or as a fine dispersion of liquid droplets. Model runs were made for the methanol, acetic acid, nonylphenol (representing the ethoxylated nonylphenol mixture), and amides/imidazolines plus quaternary ammonium chloride. Data on the properties of amide/imidazoline and quaternary ammonium chloride are limited. However, these active ingredients are as (particulate) emulsions in the aqueous solvent, and have similar properties, and so would have a similar fate. The total spill volume for these two compounds is 165 gal. (30%). Their fate is modeled as if the particulate is insoluble and does not degrade.

It should be noted that, after the model runs were made, the corrosion inhibitor mixture was corrected slightly to include 4.2% isopropanol (isopropyl alcohol) and 11.2% quaternary ammonium chloride instead of 15% quaternary ammonium chloride. Thus, the model runs were made with slightly more chemical mass spilled than the corrected composition would indicate. This means that the model results are slightly conservative (slightly high) in concentrations predicted.

Spill Scenarios 15 and 16

Scenarios 15 and 16 model water-insoluble organic solvents that are used in many production-treating chemical formulations. These solvents contain aromatic constituents that may be the component of highest concern in a production-treating chemical formulation. These solvents are constituents of production-treating chemicals B and C.

Scenarios 15 and 16 involve hydrophobic active ingredients (amides/imidazolines, amines, amine salts, and alkylbenzene sulfonic acids) in a naphtha solvent (653 aromatic solvent). The active ingredients, at least initially, will move in the environment along with and similarly to the naphtha solvent. However, naphtha is volatile (and also degrades), while the active ingredients are not volatile. Thus, the active ingredients will be left behind in the water as the naphtha volatilizes or degrades. Scenarios were run for the two products, Product B as Scenario 15 and Product C as Scenario 16.

1. The scenarios (15t and 16t) are modeled as spills of naphtha mixture. Naphtha is a mixture of low molecular weight aromatics and other hydrocarbons (Whiticar et al. 1992) with physical properties similar to naphthalene (Mackay et al. 1992). Thus, the properties of naphthalene are used in the model simulations for naphtha plus hydrophobic active ingredient(s). To calculate the concentration of one component of the mixture, the results may be multiplied by the fractional composition. Naphtha solvents will initially spread on surface water or be dispersed as fine droplets. They will evaporate from the water surface to the atmosphere, adsorb to suspended solids, or disperse into the water column as fine droplets.
2. For scenarios (15a and 16a), the active ingredient disperses as fine liquid droplets free of the solvent, modeled as an insoluble particulate that does not volatilize or degrade. This is the worst-case scenario for the active ingredient being left after the naphtha volatilizes or degrades.

Spill Scenario 15 – Product B: Aromatic Naphtha Mixture

Product B, an oil soluble corrosion inhibitor, has the following components:

- Heavy aromatic naphtha
- Isopropanol
- Amides/Imidazolines
- Polyglycols
- Fatty acid dimers
- Ethoxylated amine

Scenario 15 is 400 gal. of the following mixture:

- 84% naphtha
- 3.5% isopropyl alcohol
- 12.5% amides/imidazolines and other active ingredients (fatty acid dimers, polyglycol, ethoxylated amines, amine salts)

In addition to the naphtha solvent and the active ingredients, isopropyl alcohol is an ingredient. An additional run of isopropyl alcohol is made (Scenario 15I).

Spill Scenario 15a – Amides/Imidazolines, Amines and Amine Salts

This scenario models oil-soluble organic materials that are applied in aromatic solvents. Amides/Imidazolines, amines and amine salts were selected as representative of this type. They are components of Product B. These materials are used in corrosion inhibitors. They were selected because they represent potentially toxic materials. These chemicals are stored offshore in relatively small amounts, 50 gal. or less, therefore spills of these chemicals are likely to be small with respect to volume.

When spilled, the solution will spread on the water surface and evaporate or disperse into the water column as fine droplets. The active ingredient will disperse as a fine dispersion of liquid droplets once free of the solvent.

Spill Scenario 16 – Product C: Aromatic Naphtha Mixture

Scenario 16 is 700 gal. of Product C, an oil-soluble emulsion breaker, having the following components:

- Heavy aromatic naphtha 40%
- Alkyl benzenesulfonic acids 60%

Spill Scenario 16a – Alkyl Benzenesulfonic Acids

This scenario models oil-soluble organic materials that are applied in aromatic solvents. They are components of Product C. They were selected because they represent potentially toxic materials. These chemicals are stored offshore in relatively small amounts, 300 gal. or less; therefore spills of these chemicals are likely to be small with respect to volume.

When spilled, the solution will spread on the water surface and evaporate or disperse into the water column as fine droplets. The active ingredient will disperse as a fine dispersion of liquid droplets once free of the solvent.

Scenario 17

For scenario 17, a spill of barite in deep water (> 1,000 m), both single scenario and stochastic modeling were performed. The spill site selected was in the middle of the habitat-depth grid and also in water > 1,000 m. Barite is an insoluble particulate, about 10 microns in diameter and with a very high density. The high density of barite causes it to sink, but the small particle size causes it to sink slowly. More neutrally buoyant particulates and dissolved substances would not sink, but would disperse at about the same rate as the barite plume. Because of the small particulate size, the particulate sinks only very slowly and disperses widely. Scenario 17 may be considered a typical dispersion pattern for any non-reactive chemical.

7.8 Spill Modeling Assumptions

Table 26 lists the chemical properties assumed in the modeling. Much of the data are from French et al. (1996a). Solids were assumed released as powder of 5-25 micron diameter, as indicated in Table 26. Liquids were assumed released as 5 mm droplets, a typical particle size for oil releases under low turbulence (Delvigne and Sweeney 1988).

Those chemicals indicated as dissolved in Table 26 were released in that state. Thus, dissolution rates and solubility were not used for these chemicals. For undissolved chemicals, the dissolution rate was set based on the solubility, as data for dissolution rates are not available. For chemicals with solubility > 10%, dissolution was assumed very rapid, such that 99% would dissolve in just over an hour (rate = 100/day). For other chemicals, dissolution rate was assumed proportionately slower.

Vapor pressure of methanol, ethylene glycol, and glutaraldehyde are from Section 8.0. For other chemicals, vapor pressures are from French et al. (1996a). The chemical type code is used to select parameters for the temperature correction to vapor pressure (see French et al. 1996a). Thus, its value is immaterial if the vapor pressure is zero.

THPS degradation to sulfate ion, phosphate ion and carbon dioxide was assumed slow, with a half-life of 25 days, based on information from the supplier (collected at pH = 8, with no oxygen supplied to the system). However, the half-life for degradation to the reportedly less toxic product THPO is about 6 hours (Amides/Imidazolines, quaternary ammonium chloride, and alkylbenzene sulfonic acids were assumed to degrade extremely slowly (rate = 0.001/day). Other degradation rates are from French et al. (1996a). (The degradation rates for acids and bases are for neutralization, rather than true degradation.) Values of sorption/partition coefficient (log K_{OC}) are from French et al. (1996a) or assumed as for similar chemical

Table 25
Spill Model Assumptions

Spill Model #	Scenario Name	Chemical Name	State	Release Depth (m)	Amount Spilled	Model Duration (days)
1	MAcid1	Hydrochloric acid solution GOM	14% aqueous solution	1	3,361 gal.	14
2	MNaOH1	Sodium hydroxide	Powder	1	43,545 kg	14
3	MKCl1	Potassium chloride	Powder	1	4,717 kg	14
4	MZnBR1	Zinc bromide solution GOM	54% aqueous solution	1	45,000 gal.	14
5	MNaSO31	Sodium bisulfite solution GOM	40% aqueous solution	1	500 gal.	14
6	MBarite1	Barite	Powder	1	7,257.55 MT	14
7	MDesco1	DESCO/ Lignosulfonate	Powder	1	95,797 kg	14

Table 25
Spill Model Assumptions (continued)

Spill Model #	Scenario Name	Chemical Name	State	Release Depth (m)	Amount Spilled	Model Duration (days)
8	MLignite	Lignite	Powder	113	52,786 kg	14
9	Mmeth1	Methanol	Pure liquid	1	96,000 gal.	14
10	Methgly1	Ethylene glycol	Pure liquid	113	106,447 gal.	14
11	MglutS1	Glutaraldehyde solution GOM	25% aqueous solution	1	500 gal.	4
12	MglutB1	Glutaraldehyde solution GOM	25% aqueous solution	113	500 gal.	4
13	MTHPS1	THPS solution GOM	20% aqueous solution	1	500 gal.	4
14 m	M14 m-1	Methanol	Liquid	1	231 gal.	1 (20 runs)
14aa	M14aa-1	Acetic acid	Liquid	1	16.5 gal.	1 (20 runs)
14np	M14np-1	Nonylphenol	Liquid	1	16.5 gal.	7
14a	M14a-1	Amides/Imidazolines and quaternary ammonium chloride (miscible organic mixture)	Insoluble particulate	1	165 gal.	4
15a	M15a-1	Amides/Imidazolines	Insoluble particulate	1	50 gal.	4 (not run, see 14a)
15n	M15n-1	653 Aromatic solvent (naphtha) – run as naphthalene	Liquid	1	336 gal.	4 (not run, see 15t)
15t	M15t-1	Amides/Imidazolines in 653 Aromatic solvent (naphtha) – run total mixture as naphthalene	Liquid	1	386 gal.	4
15I	M15i-1	Isopropyl alcohol	Liquid	1	14 gal.	1 (20 runs)
16a	M16a-1	Alkylbenzene sulfonic acids	Insoluble particulate	106	280 gal.	4
16n	M16n-1	653 Aromatic solvent (naphtha) – run as naphthalene	Liquid	106	420 gal.	4 (not run, see 16t)
16t	M16t-1	Alkylbenzene sulfonic acids in 653 Aromatic solvent (naphtha) – run total mixture as naphthalene	Liquid	106	700 gal.	4
17	BarDeep1	Barite	Powder	1	7,257.55 MT	14

Table 26
Chemical Properties Assumed For Model Runs

Model Scenario #	Chemical Modeled	Particle Size	Density (g/cm^3)	Seawater Solubility (mg/l)	Dissolution Rate (day^{-1})	Vapor Pressure (atm)	Chemical Type Code	Sorption/partition coefficient (Log K_{OC})	Degradation Rate (per day) (water column) = Degradation Rate (per day) (sediment)
1	Hydrochloric acid	(dissolved)	1.16	100%	100	0	101	0.31	0.01899
2	Sodium hydroxide	10 um	2.13	42%	100	0	102	0.49	0.01899
3	Potassium chloride	25 um	2.04	34.4%	100	0	103	0.31	0.01899
4	Zinc bromide	(dissolved)	4.22	5 ppm	-	0	133	0.31	0
5	Sodium sulfite	(dissolved)	1.51	33%	-	0	103	0.59	0
6, 17	Barite	10 um	4.3	0	0	0	190	0.1	0
7	DESCO/ Ligno-sulfonate	5 um	1.3	> 10%	100	0	242	0.1	0
8	Lignite	5 um	1.7	0.2 ppm	1.0	0	242	0.1	0
9, 14 m	Methanol	5 mm	0.791	> 10%	100	0.168	201	0.92	0.1131
10	Ethylene glycol	5 mm	1.14	100%	100	0.0001	201	0.59	0.02132
11, 12	Glutaraldehyde	(dissolved)	1.08	> 10%	-	0.022	202	0.31	0.02132
13	THPS	(dissolved)	1.1637	> 10%	-	0	252	0.31	0.0277
14aa	Acetic acid	5 mm	1.05	57%	100	0.015	203	1.21	0.1131
14np	Nonylphenol	5 mm	0.95	1.0 ppm	0.01	0	224	6.18	0.1131

Table 26
Chemical Properties Assumed For Model Runs (continued)

Model Scenario #	Chemical Modeled	Particle Size	Density (g/cm^3)	Seawater Solubility (mg/l)	Dissolution Rate (day^{-1})	Vapor Pressure (atm)	Chemical Type Code	Sorption/partition coefficient (Log K_{OC})	Degradation Rate (per day) (water column) = Degradation Rate (per day) (sediment)
14a	Amides/ imidazolines and quaternary ammonium chloride	10 um	1.01	0	0	0	206	3.0	0.001
15a	Amides/ imidazolines	10 um	1.01	0	0	0	206	3.0	0.001
15n, 15t, 16n, 16t	Naphthalene	5 mm	1.162	22 ppm	0.1	0.0001	230	3.14	0.02132
15I	Isopropyl alcohol	5 mm	0.785	25%	100	0.0567	201	1.38	0.1131
16a	Alkylbenzene sulfonic acids	10 um	1.01	0	0	0	206	3.0	0.001

7.9 Summary

The model run results are one of the important factors in determining which chemicals would be of concern in causing impacts if they were spilled. The objective was to evaluate the potential areas and volumes surrounding a spill site that could be contaminated at any concentration above ~0.01 ppb. The resolution of the grid used was necessarily 533 m X 601 m (= 320,573 m^2 for each cell) in order to cover the potential distances chemicals might be transported. Thus, details at a finer scale were not saved on the grid.

The model outputs represent a simplified summary for the purpose of screening which chemicals pose an ecological risk. This summary is necessary because the model calculates concentration in three dimensions and over time (in fine scale and at hourly increments), which generates an inordinate amount of data for each of the 100 runs for each scenario (and chemical within a scenario).

Additional model runs could evaluate the fine-scale exposure above specified thresholds of actual concern for impacts. The spill modeling results, combined with the results of the research on toxicity, which will be presented Section 8.0, may be used to define smaller scale grids with which to project results.

The results of the 17 model scenarios may be used to infer potential impacts within specified distances of a spill site. The shelf results (Scenarios 1-16) are most transferable along the outer shelf, where the current patterns are very similar. As the currents are usually wind-driven and relatively weak (except when eddies move on to the outer shelf), spills can move in any direction.

Scenario 17 shows the dilution of a spill of a conservative substance occurring in the offshore region of the western Gulf of Mexico (slope and deep water > 1,000 m). Loop current eddies will be likely in this area, and more likely than in the outer shelf region. The one-year current data record used for this offshore area is assumed representative for the region and over time. No other measured current data are presently available, but on-going studies will show how representative the mooring GG data are to the region.

8.0 PROFILES OF SELECTED CHEMICALS AND THEIR ASSOCIATED RISK CHARACTERIZATION

8.1 Introduction

One of the objectives of this study included the development of detailed chemical profiles for selected chemicals used in deepwater exploration and production operations. The approach, as described in Section 2.0, was to select a subset of representative chemical or product types used offshore and present the information in a series of profiles, rather than researching only the "worst" or highest risk chemicals. Using this approach, information on the majority chemicals used in the Gulf of Mexico (GOM) can be estimated by referencing one of the representative chemical or product profiles.

This section provides detailed chemical profiles for 21 selected chemicals and assumptions and results of spill models in both shallow and deep water in the Gulf of Mexico. It also provides a risk characterization of the modeled chemicals based on available toxicological data and spill model results. Since there is very limited or no information on deepwater biological communities, as discussed in detail in Section 6.0, a complete risk evaluation was not possible. Table 27 contains a summary of the spill modeling and risk characterization results.

Table 27

Chemical Risk Characterization Summary

Chemical Class	Amount Spilled	Worst-Case Environmental Exposure	Toxicity Type	Toxicity Value	Receptor	Margin of Safety (1)	Potential Impact
CSW	3,400 gal.	1.0 ppm	LC50	33 ppm	Crangon crangon (brown shrimp, marine crustacean)	0.03	No
CSW	NM		NM	NM	NM	NM	NM
DF,PT	NM	-	NM	NM	NM	NM	NM
PT,DF	500 gal.	0.1 ppm	LC50	6 ppm	Crangon crangon (brown shrimp, marine crustacean)	0.02	No
PT	165 gal.	0.1 ppm	LC50	0.9 ppm	Unspecified crustacean	0.1	No
PT	500 gal.	0.1 ppm	LC50	119 ppm	Oncorhynchus mykiss (rainbow trout, freshwater fish)	0.001	No
CSW	45,000 gal.	10 ppm	LC50	0.5 ppm	Daphnia magna (freshwater crustacean)	20	Yes
CSW	NM	-	LC50	1,000 ppm	Crangon crangon (brown shrimp, marine crustacean)	-	No
CSW	NM	1.0 ppm	LC50	0.24 ppm	Salmo salar (Atlantic salmon-saltwater species)	4.17	Yes
DF	44,000 kg.	10 ppm	Threshold Limit Median	15 ppm	Daphnia magna (water flea, freshwater crustacean)	0.67	No
DF,CSW	4,700 kg.	1.0 ppm	LC50	368.5 ppm	Puntius conchonius (freshwater fish)	0.003	No
PT	50-165 gal.	0.1 ppm	LC50	2.0 ppm	Unspecified crustacean	0.05	No

Table 27

Chemical Risk Characterization Summary (continued)

Chemical Class	Amount Spilled	Worst-Case Environmental Exposure	Toxicity Type	Toxicity Value	Receptor	Margin of Safety (1)	Potential Impact
PT	400 gal.	0.1 ppm	LC50	250 ppm	Mutilus edulis (blue mussel, marine bivalve mollusk) Crassostrea gigas (Japanese oyster, marine bivalve mollusk)	0.0004	No
DF	53,000 kg.	10 ppm	LC50	163,000 ppm	Mysidopsis bahia (marine shrimp)	6.1E-05	No
PT	96,000 gal.	0.1 ppm	LC50	12,539 ppm	Nitroca spinipes (harpacticoid copepod, marine crustacean)	8.0E-06	No
PT	106,000 gal.	100 ppm	LC50	34,400 ppm	Ceriodaphnia dubia (water flea, freshwater crustacean)	0.003	No
PT	NM	100 ppm	LC50	10,000 ppm	Daphnia magna (water flea, freshwater crustacean)	0.1	No
PT	500 gal.	0.1 ppm	No toxicity data found	No toxicity data found	No toxicity data found	No toxicity data found	No toxicity data found
DF	7,300 MT	1,000 ppm	EC50	16200 ppm	Pandalus danae larvae (coon-stripe shrimp, marine species)	0.06	No
DF,C	96,000 kg.	1.0 ppm	LC50	290,000 ppm	Pandalus danae (coon-stripe shrimp, marine crustacean)	0.003	No
PT	400-700 gal.	1.0 ppm	LC50	3.0 ppm	Elasmopus pectenicrus	0.3	No

NM – Not Modeled

Notes:

(1) The worst-case margin of the safety is equal to the maximum exposure concentration divided by the toxicity value. Values in this column greater than one indicate a potential for impact. These comparisons are one-hour peak exposure concentrations versus 48-96 hour LC50 toxicity data and provide a conservative estimate of risk. Actual exposure dosage and toxicity comparisons are discussed in the text.

(2) Although a spill of ammonium chloride was not modeled it would be similar to a spill of potassium chloride, therefore we used the estimated concentrations for potassium chloride as a surrogate to estimate the risk from a spill of ammonium chloride.

(3) Although a spill of triethylene glycol was not modeled it would be similar to a spill of ethylene glycol, therefore we used the estimated concentrations for ethylene glycol as a surrogate to estimate the risk from a spill of triethylene glycol.

8.2 Profile Explanation

8.2.1 Summary

Each profile is a description of the subject chemical and contains information in the following order; summary, background information (i.e., fate in the environment, fate in the process system, other components, CAS number, chemical formula, and important synonyms and trade names), chemical and physical properties, health and safety properties, use and handling properties, environmental concentrations and toxicological effects, spill modeling results, aquatic toxicity levels, risk characterization, references, and spill modeling results in the form of tables and figures.

Each profile represents chemical or product types. These 21 profiles should contain at least one profile similar to every chemical or product type used in offshore E&P operations.

The data in these profiles were gathered from:

- Operating companies who provided information on chemicals used, concentrations used, and amounts stored
- Chemical suppliers who augmented the operating companies’ information and provided explanations on how chemicals are used and transported
- MSDSs for the chemicals used by the operating companies and provided by their chemical suppliers
- Standard reference books (e.g., CRC Handbook of Chemistry and Physics)
- Spill models prepared and run by Applied Science Associates, Inc. (ASA)
- Literature on toxicity collated by Applied Marine Sciences, Inc. (AMS)
- Industry technical and trade literature (e.g., *World Oil* or *Journal of Petroleum Technology)*

The following model profile shows the form of the information presentation and provides a detailed explanation on each individual section within a profile.

8.2.2 Model Profile

Profile Number (#)
Single Component/Product

Summary

The summary describes which of the four chemical classes the single component/product falls into (Drilling Fluids, Cementing Chemicals, Completion, Stimulation and Workover Chemicals, or Production-treating Chemicals), the component’s function, phase, and form, and the component’s potential impacts if discharged to the marine environment.

Background Information

Fate in the Environment

Fate in the environment describes the physical and chemical fate of the chemical or product when it enters the marine environment and where it may ultimately end up, due to either physical properties and/or chemical reactions.

Fate in the Process System

Fate in the process system describes how the chemical or product is used in the process system, how the chemical leaves the system, and where the chemical ultimately goes upon leaving the system.

The following information helps identify and explain the nature of the chemical or product.

Other Components

CAS Number

Chemical Formula

Important Synonyms and Trade Names

Chemical and Physical Properties

Property	Component (1)	Product
Molecular Weight	233.39	Same as Component
Boiling Point	1,600°	Same as component
Melting Point	1,580°	
Specific Gravity	4.5 @	
Solubility in Water	Insolu	
Solubility in Organics	Insolu	
Vapor Pressure	NA	
Vapor Density (Air = 1)	NA	
Physical State (Phase)	Solid Powder	Same as Component
Chemical Reactivity in the Environment	None	Same as Component

In this section, chemical and physical data for both the chemical being profiled, and the product that it is being supplied in, is presented. This data was obtained from manufacturer MSDS sheets and various standard technical reference books (as referenced).

Health and Safety Properties and Effects

Property	Component	Product (2)
Autoignition Temperature	NA	
Flash Point	NA (3)	
Upper Explosive Limit	NA (3)	
Lower Explosive Limit	NA (3)	
Air Toxicity	TLV 1 no asbe (1)	
OSHA PEL (8)	15 mg/ respirable dust (1)	

This table provides Health and Safety information for the chemicals profiled and the product that they are components of.
A qualitative discussion from information provided in MSDS sheets and standard safety tables is provided following presentation of this table.

Notes: NA = Not Available

Use and Handling Properties

Use and Handling Properties covers typical and maximum offshore storage volumes, transport containers, and handling practices offshore. This allowed for a qualitative assessment of the amount of chemical that might be spilled offshore and how storage containers could potentially impact a release into the marine environment. Information was collected and synthesized from a variety of sources, including operator data from actual sites in the Gulf, chemical supplier documents, etc. These data sources are discussed in detail in Section 3.0.

Environmental Concentrations and Toxicological Effects

This section contains modeled average peak exposure and worst-case peak exposure concentrations from the modeling scenarios described in Section 7.0. Spill models were only completed for 16 (of the 21) chemicals selected for detailed chemical profiling.

The chemical profiles were coordinated with the various spill scenarios in cooperation with ADL, MMS, Applied Science Associates, Inc. (ADL's spill modeling subcontractor), and Applied Marine Sciences, Inc. (ADL's toxicological data research subcontractor). Data from the spill scenarios were used to estimate distributions in the marine environment. For most of the chemical profiles, this information was obtained from spill scenarios for the same chemical, and for several others, concentrations and fate were estimated from spill scenario results for similar chemicals.

Spill Modeling Results

If a spill scenario was developed for the chemical being profiled, the objective was to evaluate the potential areas and volumes surrounding a spill site that could be impacted. The spill model results are presented on a series of tables and figures within each profile.

Contour maps show plots of the peak exposure concentrations at each location around the spill site. This is calculated as follows.

- For each individual run (for each spill date and time run), the maximum amount over all time after the spill is saved for each location (cell) in the model grid. This is the peak exposure concentration for each location for a single randomly selected spill date and time.
- For the worst-case maximum amount for all possible releases (i.e., maximum peak exposure for 100 randomly-selected spill dates and times), the 100 runs are evaluated to determine the highest amount possible at each location.
- For the mean expected maximum amount for all possible releases (i.e., mean-peak exposure of all randomly selected dates and times), the 100 runs are evaluated to determine the mean peak exposure (mean amount for all runs) at each location.

Note that these amounts are not additive over all locations. These represent maximum possible or mean amounts that would ever reach each site, considered individually. Different sites are affected at different times after the spill.

Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact. The chemical forms are:

- Dissolved concentration
- Particulate (solids or liquid droplets) concentration
- Concentration adsorbed to suspended sediment
- Mass loading to the bottom sediment (g/m^2)
- Surface slick (mass per unit area, g/m^2)
- Shoreline contamination (mass loading, g/m^2)

The figures vary in scale, depending on how far away from the spill site the 0.01 mg/m^3 (~0.01ppb) threshold falls. Note the distance scale in the lower right corner of each figure as well as the form of the chemical in the concentration plot.

The concentrations are calculated as total weight of the chemical, in the spilled form, divided by volume of seawater. The notation ppb for mg/m^3 is used herein for convenience. A conversion was not made to account for the weight of the seawater being slightly greater than 1 g/ml.

For each of the chemical forms above, habitat areas exposed to peak concentrations or mass loadings within range intervals were tabulated. The peak exposure concentration is averaged over the depth of the plume. Since, for the shelf scenarios, the plume quickly (within a day) mixes over the entire water column, the plume depth generally equals the water depth near the spill site (114 m). In most cases, the chemical dispersed to < 1 mg/m^3 (~1ppb) within less than 10-50 km of the spill site. Thus, the plume is local to the spill site, and volume (m^3) exposed would be about 100 times the area (m^2) exposed.

Also, total dosage measures (concentration or mass per area times exposure time) are calculated:

- *Concentrations in water*: Habitat area exposed at each dosage level (concentration-time, i.e., mg-m-3-hrs = ppb-hrs). Volume (m^3) exposed would be about 100 times the area (m^2) exposed.
- *Water surface*: Slick thickness times time present (mass per area - time) for each dosage level ($g\text{-}m^{-2}$-hrs)
- *Mass loading to sediments and shorelines*: Mass per unit area times time present (mass per area - time) for each dosage level ($g\text{-}m^{-2}$-hrs)

Dosage is calculated in the model by summing, over all time steps, the concentration (or mass per unit area) for that time step times the length of the time step in hours. Acute toxicity (LC50) is known to decrease with increasing time of exposure (see review in French et. al. 1996a). If it is assumed that LC50 decreases linearly with time of exposure, this dosage index may be used in comparison to LC50 data from bioassays performed at several days of exposure. A dosage of 100 ppb-hours is equivalent to 100 ppb for 1 hour of exposure, or 10 ppb for 10 hours of exposure, or 1 ppb for 100 hours of exposure. Thus, if a 96-hour LC50 is the toxicity endpoint of concern, a dosage level of 96 times the LC50 concentration is equivalent. The peak exposure concentration *may* only have been present for an hour, and may not be comparable to a 96-hour LC50 (depending on the time for dilution). For this reason, the dosage is a better index of exposure.

Output tables summarize the areas of habitat affected at different peak exposure and dosage levels. The statistics include the mean, standard deviation, and the maximum and minimum habitat area affected, based on the individual simulation results. The tables also include the number of runs where zero area was affected above the threshold level. Habitat areas are for exposure within intervals and for greater than a particular level. Thus, if areas affected above several toxic endpoints are desired the appropriate threshold should be considered when interpreting the data in the tables (i.e., tables are only included if there were some non-zero results).

Note that these model runs represent a first cut at determining which chemicals may cause potential impacts if they were spilled. The resolution of the grid used was necessarily 533 m X 601 m, in order to cover the potential distances chemicals might be transported. Thus, details at a finer scale are not saved on the grid (although the model simulates the chemical distribution at very fine scale each time step).

In addition, while the model calculates concentration in three dimensions and over time (in fine scale and at hourly increments), this generates a tremendous amount of data for each of the 100 runs for each scenario. The model outputs used here represent a simplified summary for the purpose of screening chemicals with potential ecological impacts.

The results may be used to infer potential impacts within specified distances of a spill site. As the plumes are generally circular in distribution the radial distance (r) to an impact threshold ("endpoint" in EPA ecological risk parlance) is approximated by $r = (A/\pi)^{-2}$, where A = the cumulative area affected above the threshold. The results of spill scenarios 1-16 are most transferable along the outer shelf, where the current patterns are very similar.

When comparing some modeling results to reported toxicity end points, it was necessary to make certain assumptions regarding distribution of the spilled chemical within the water or sediments. Some model runs assumed that the spilled chemical would form a slick on the surface of the water (e.g., for methanol) or a layer upon the sea floor (e.g., for barite). Chemical concentrations were estimated by making the following assumptions:

- Seawater has a specific gravity of 1.0
- Sediments have a specific gravity of 2.0
- Spilled chemicals diffused into the top 1.0 centimeter of water and mixed into the top 0.5 centimeter of sediment

Average and worst case peak exposure concentrations were estimated using the spill modeling. The time histories of multiple simulation runs under varying environmental conditions were used to calculate the areas/volumes exposed at different levels of contamination. Each simulation was evaluated to determine the maximum (peak) exposure concentration (over time after the spill) for each location (model grid cell) around the spill site at any time after the spill. The worst case (i.e., caused by worst case environmental conditions), and the average (i.e., mean of all environmental conditions) over all simulations, of the peak exposure concentrations are calculated for each location (grid cell) affected. The grid cells are 320,573 m^2 in area (for all locations) and 114 m deep at the spill site. The peak concentrations are for 1 hour or more of exposure, which is the time step used in the model runs. Of course, concentrations at the spill site at time zero are at the maximum, i.e., at the concentration in the spill volume. At the spill site, the peak concentrations calculated by the model are those at one hour after the spill, averaged over one grid cell of volume (36,000,000 m^3). For surrounding grid cells, the peak concentration is the maximum for any hour after the spill averaged over one grid cell of volume (36 million m^3). Concentrations continue to decrease from these levels over time.

Aquatic Toxicity Levels

A chemical spill in open water will rapidly dilute and dissipate within days, reducing the likelihood of chronic toxicity. Therefore this report focuses on acute endpoints and less on chronic effects. Available aquatic toxicity data were collected from numerous sources including databases, technical journals, and relevant studies. Specific data sources are noted within each profile and are included in References (see Section 9.0). Although an exhaustive literature search was performed to find information on the toxicity of the prescribed drilling mud components, several components had no published data, nor was it available from chemical manufacturers. An effort was also made to obtain toxicity data from previous and current studies performed in the North Sea region, however the toxicity database is proprietary and is not currently available to the public and was not available for this study. Specifically, an attempt was made to obtain toxicity data from these proprietary European sources:

- The Oslo and Paris Commission (OSPARCOM), an international agency acting on a broad range of items that collects data on offshore chemicals used and stored by five countries (Norway, the United Kingdom, The Netherlands, Denmark, and Germany)
- The Department of Trade and Industry (DTI), a United Kingdom-based organization to increase competitiveness and scientific excellence in order to generate higher levels of sustainable growth and productivity in a modern economy. Currently, DTI administers the Offshore Chemical Notification Scheme (OCNS) using scientific and environmental advice from CEFAS.
- The Center for Environment, Fisheries and Aquaculture Science (CEFAS), a United Kingdom-based research and consultancy center.

The estimation of potential toxic impacts associated with spills of chemicals used in offshore oil and gas operations required several steps. The estimation of impacts was based primarily on available published or industry results of laboratory toxicity tests. The toxicity data were then compared to average peak and worst-case chemical concentrations obtained with the spill model.

The chemicals were categorized qualitatively relative to acute toxicity endpoints obtained from the literature, because no toxicity data were found for the Gulf species potentially affected. If modeled results were more than one order of magnitude below the lowest reported toxicity endpoint, the chemical was categorized as unlikely to cause acute toxic impacts under the modeled scenarios. If modeled results were within one order of magnitude of the lowest reported toxicity endpoint, the chemical was categorized as potentially causing acute toxic impacts under the modeled scenarios.

There are several toxicological endpoints found in published literature that differ in the way they assess potential acute impacts. Moreover, endpoints may be measured over more than one time span, incorporating the effect of exposure time. Each toxicological endpoint is described as follows:

> **LC50 (Lethal Concentration 50)** represents the concentration of material being tested that is lethal for 50% of the test organisms over the time of exposure specified. Tests with the LC50 endpoint can be performed over various exposure times. Various data sources used exposure times that varied from 24 hours to 6 weeks. Obviously, achievement of 50% lethality for the same concentration in half the time indicates a more toxic compound. Nevertheless, because the rate of increasing mortality over time is not necessarily linear, there is no way to meaningfully compare the LC50 for one exposure time with another.
>
> **EC50 (Effect Concentration 50)** represents the concentration of material being tested that has a prescribed effect on 50% of the test organisms. Tests with the EC50 endpoint also can be performed over various exposure times. Reported exposure times ranged from 4 hours to 6 weeks. Effects usually involve reduction of a biological activity or process, such as feeding, growth, fecundity, or embryonic development. Toxicity tests that measure effects on biological processes are assumed to be more sensitive than those that measure mortality. Nevertheless, because a return to normal activity or process probably occurs when the test chemical is removed (except for embryonic development) a chemical that has an LC50 equal to the EC50 of another chemical is the more toxic of the two.
>
> **LOEC (Lowest Observed Effect Concentration)** is the lowest concentration at which an effect is observed. Tests with an LOEC endpoint also can be performed over various exposure times, although reported results incorporated in the study included only 7-day tests. As with EC50, these tests usually measure effects on biological processes, but also may include mortality.

NOEC (No Observed Effect Concentration) is the highest concentration at which no effect is observed. Tests with an NOEC endpoint also can be performed over various exposure times, although reported results incorporated in the study included only 7-day tests. As with EC50, these tests usually measure effects on biological processes, but also may include mortality.

TLM (Threshold Limit Median) refers to the median threshold limit. This endpoint can be applied to either mortality, in which case it is synonymous with LC50, or to effects on biological processes, in which case it is synonymous with EC50. Tests with a TLM endpoint also can be performed over various exposure times, although reported results incorporated in the study included only 96-hour tests.

Risk Characterization

This is a discussion of the potential impacts to the marine environment as a result of the modeled spill using toxicity data of the chemical or product and exposure limits. It includes a qualitative discussion of the potential for toxic impacts on the marine species such as would occur in the GOM.

Contamination in the water column following a chemical spill changes rapidly in space and time. Toxicity to marine organisms increases with time of exposure, such that organisms may be unaffected by brief exposures to the same concentration that is lethal at long times of exposure. For a brief exposure, a dosage measure of concentration times time is a more appropriate index of toxicity than the peak concentration. For example, if a 96-hour LC50 is 1.0 mg/L, the dosage is 96 mg/L-1 hrs. Assuming a linear time-response model, the LC50 for a 1 hour exposure would be about 96 mg/L, and for a 10 hour exposure would be about 9.6 mg/L. Total dosages (concentration-time, i.e., mg-m^3-hrs or ppb-hrs) are also calculated by the modeling.

The chemical spill model also partitions the chemical into particulate (i.e., solid particles or suspended liquid droplets and surface slicks, as appropriate), dissolved, and adsorbed (to suspended sediment) phases in both water column and sediments. Concentrations in each phase and mass loading to the sediments are computed in space and time. If the concentration exceeds 0.01 ppb for a model grid cell at any time after the spill, the area of that grid cell is included in the summary data tables for the appropriate concentration interval. If no location would be expected to exceed 0.01 ppb for the phase of concern, no data table is prepared for that phase (i.e., particulate, dissolved, adsorbed, or sediment loading).

The modeled concentrations may be compared to concentrations that have been shown to have toxic effects to determine the potential for impacts. Typically, toxicity tests are performed with dissolved concentrations, so the comparison should be to the results for this phase. Comparisons are made in the profiles for the peak (1 hour duration) concentrations at the spill site. Calculations are also made of total habitat area exposed above a range of threshold concentrations. Distance to these thresholds would be approximately the radius of a circle of that exposed area. It should be noted that zero area/volume affected above a concentration threshold indicates that the volume affected did not exceed one grid cell (of area 320,573 m^2 and volume 36 million m^3). Thus, the extent of the plume above this concentration threshold is less than 320 m from the spill site.

References

Sources for data presented in the profiles.

8.2.3 Uncertainties

The process we have used to estimate the ecological risks associated with spills of oilfield chemicals is subject to several inherent sources of uncertainty. These sources of uncertainty include the assumptions used in modeling the spill scenarios, the quality and quantity of existing toxicological data for these oilfield chemicals, the use of different toxicological endpoints and experimental protocols in the published literature, and the use of freshwater species for estimating risk to marine species. In evaluating the potential impact of each chemical, it is important for the reader to understand these uncertainties.

No toxicity data were found for the Gulf marine species actually potentially affected by the chemicals. Uncertainties associated with the quality of the data and the absence of quantitative descriptions of the biological communities in the region precluded a quantitative evaluation of potential impacts of these chemicals. Many of the species for which data were found are test species used in compliance testing for waste stream discharges.

All comparisons of toxicity data were to average or worst-case peak modeled concentrations. Because these modeled peak concentrations would generally last only a short time, comparison to toxicity results from standard 96-hour tests probably provides an exaggerated estimate of acute impacts. Conversely, overall impacts may be underestimated because we have included no consideration of long-term or chronic exposures to spilled chemicals.

8.3 Twenty-one Profiles that Characterize the Qualitative Potential for Risk of Chemicals Used in the Gulf of Mexico

The 21 representative chemical/product profiles are included below. These profiles cover the entire range of chemicals used offshore, from the large volumes of single component chemicals used in the drilling fluids at relatively few locations, to the small volumes of production-treating formulations used at a large number of locations. The 21 chemicals selected for detailed chemical profiles include:

Profile 1: Hydrochloric Acid (in water solution)
Profile 2: Hydrofluoric Acid (component of product) - *no spill model*
Profile 3: Polysiloxane (component of EC9034A) - *no spill model*
Profile 4: Glutaraldehyde (component of X-CIDE 0102 and EC6111A)
Profile 5: Quaternary Ammonium Compounds (component of Product A)
Profile 6: Tetrakishydroxymethyl Phosphonium Sulfate (THPS) (component of Magnicide 535)
Profile 7: Zinc Bromide (component of a Zinc Bromide/Calcium Bromide completion fluid)
Profile 8: Calcium Bromide (component of a Zinc Bromide/Calcium Bromide completion fluid)- *no spill model*
Profile 9: Ammonium Chloride (single component) - *no spill model*
Profile 10: Sodium Hydroxide (single component)

Profile 11: Potassium Chloride (single component)
Profile 12: Amides/Imidazolines (component of Product B)
Profile 13: Amines and Amine Salts (component of Product B)
Profile 14: Lignite (single component)
Profile 15: Methanol (single component)
Profile 16: Ethylene Glycol (single component)
Profile 17: Triethylene Glycol (single component) - *no spill model*
Profile 18: Sodium Bisulfite (component of OSW3055)
Profile 19: Barite (single component)
Profile 20: Lignosulfonate (single component)
Profile 21: Naphtha, Aromatic (solvent for oil soluble products)

Profile 1

HYDROCHLORIC ACID (In Water Solution)

Summary

Hydrochloric acid is a mineral acid classified as a completion, stimulation and workover chemical. It is used in stimulation procedures to remove corrosion products, water-formed scales, and other solid materials from the formation around the wellbore, in the well, and in the processing equipment. If discharged in the marine environment, it will initially change the pH of the seawater. Ultimately, a chemical reaction with the natural buffering system will adjust the seawater to its original concentration. The most important potential impact of this chemical is worker safety. Discharge of quantities used offshore will not result in significant risk to the marine environment.

Background Information

Fate in the Environment

Hydrochloric acid is used as a solution of hydrogen chloride gas in water. It is miscible in seawater in all proportions. It is used in several standard concentrations, the most common being 15% solution by weight, in water. It is frequently used in a mixture with other acids and lesser components.

When spilled in seawater, hydrochloric acid solution will mix into the water column. Such mixing releases the heat of solution that will heat and agitate the receiving water. This release of energy helps to mix the hydrochloric acid into the seawater where oceanographic and meteorological forces provide additional mixing energy to disperse it through the water column. Immediately on mixing with seawater, the acid reacts with the carbonate equilibrium system, which acts to maintain the pH of the seawater (see Aquatic Toxicity Levels discussion below). The concentrations of the various carbonate chemical species already found in the system and the hydrogen ions released into the seawater are determined by the carbon dioxide concentration in the atmosphere. Exchanges of carbon dioxide between the seawater and the atmosphere act to convert the hydrogen ion component of the acid into bicarbonate and water. Since all the reaction products of hydrochloric acid (hydrogen ions, bicarbonate, water, and chloride) are natural components of seawater, these reaction products will ultimately mix with seawater and become undetectable.

Fate in the Process System

Hydrochloric acid is applied to wells to remove acid soluble solids and clean up the tubing and the formation around the well. During the treatment process the acid reacts with the solids it is intended to remove and becomes partially neutralized. To perform this procedure the well is taken out of service, the acid is injected, and the well is allowed to flow back to a receiving tank. The returns are pretreated to allow them to be disposed of, either overboard into the sea, into the produced water treating system then discharged into the sea, or hauled ashore for appropriate disposal. Although most of the acid will return from the well over a period of a few days, the pH concentration will be much lower due to the reactions for which it was applied. Concentrations of acid in the returning fluids will yield pH values between 0 and 4.

Other Components

Water

CAS Number (Hydrochloric Acid)

7647-01-0

Chemical Formula (Hydrochloric Acid)

HCl (H^{+1} and Cl^{-1} in solution)

Important Synonyms and Trade Names

Hydrogen Chloride (in gas form); Muriatic Acid

Chemical and Physical Properties

Property	Component (1)	Product (2)
Molecular Weight	36.46	NA
Boiling Point	- 84.9° C	110° C
Melting Point	- 114.8º C	Not established
Specific Gravity	1.0045 g/l (gas)	1.16
Solubility in Water	82.3 gm/100 gm water @ 0° C	Soluble
Solubility in Organics	Soluble in alcohol and ether	NA
Vapor Pressure	NA	13 mm Hg @ 20° C
Vapor Density (Air = 1)	See specific gravity	1.3 (HCl)
Physical State (Phase)	Gas	Fuming Liquid
Chemical Reactivity in the Environment	Very reactive, corrosive in water	Very reactive with seawater

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component	Product (2)
Autoignition Temperature	Non-combustible	NA
Flash Point	NA	NA
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity	5 ppm (ACGIH TLV)	ND
OSHA PEL	5 ppm	5 ppm (2)

Notes: NA = Not Available; ND = Not Determined

There is no identified danger for fire or explosion. Liquid or concentrated vapors can cause eye irritation, skin irritation and burns, and irritation of the respiratory tract. Ingestion can cause burns of the mouth, nausea, pain, and vomiting, and depending on the amount swallowed, could be fatal. (2)

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 3,000 gal.
Maximum = Application dependent.

Transport Container(s): Supplier's plastic lined steel bulk tanks or boat tanks.

Storage Methods: Bulk tanks on platform (temporary) or supplier's boat. The acid is usually not stored on the platform; therefore, larger jobs are completed from the supplier's boat.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Modeling Results

Hydrochloric acid was modeled as Spill Scenario 1. Results are shown in Figures 21 to 22 and Tables 23 to 29 (at the end of this section). The hydrochloric acid solution consists of entirely dissolved chemical, i.e., H^+ and Cl^- or F^- ions. The entire solution was modeled as HCl, with a molecular weight of 36.5. Thus, for example, absent any buffering 1,000 mg/m^3 is about 0.27×10^{-4} hydrogen ion concentration (pH 4.6). The concentration of H^+ in seawater is approximately 0.63×10^{-8} (pH 8.2).

Aquatic Toxicity Levels

The available literature for hydrochloric acid toxicity was reviewed and the results from relevant studies are shown below.

Benthos

Crangon crangon (brown shrimp, marine crustacean) TLM = 272 ppm (3)
Crangon crangon (brown shrimp, marine crustacean) LC50 = 33-110 ppm (3)

Risk Characterization

The only toxicity data found for HCl was for benthos in sediment. The lowest toxicity concentration found was 33 ppm (33,000 ppb), 96-hr LC50. Comparing this concentration with toxicity thresholds (ppb) presented in Table 28 shows that no unit grid cell area was exposed to a concentration of 33,000 ppb or greater, either average or worst case.

The impact of an accidental release of hydrochloric acid on the marine environment is to lower the pH of seawater, at least locally and temporarily at the spill site. The modeled worst case peak exposure concentration, 1.0 ppm, would correspond to 0.27×10^{-4} hydrogen ion concentration (a pH of about 4.6), if it were not buffered. The natural concentration of hydrogen ion in seawater is approximately 3.5 orders of magnitude lower, at 0.63×10^{-8} (pH = 8.2). The lowest acute effect concentration (LC50) is 33 ppm, a concentration of hydrochloric acid that would lower the pH of the seawater to about 3 without buffering. Based on the results of the study, the test organisms could not tolerate pH values this low. However, because the modeled concentrations do not reach 33 ppm, and because of the buffering capacity of seawater, no significant acute aquatic toxicity effect would be expected from an accidental release of hydrochloric acid.

References

(1) CRC Handbook of Chemistry and Physics (1985-1986)
(2) BJ Services Environmental Group (1998)
(3) Hudgins and Petrotech Consultants, Inc. (1991)

Table 28

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 1. Dissolved concentration of hydrochloric acid and hydrofluoric acid (modeled as hydrochloric acid) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	166,038,560	1,445,103,744	7,270	21,447
10	23,024,884	307,103,840	2,707	9,887
100	1,621,471	35,672,364	718	3,370
1,000	-	1,945,766	-	787
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 29

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01-hours (0.01 ppb-hours): Scenario 1. Dissolved concentration of hydrochloric acid and hydrofluoric acid (modeled as hydrochloric acid) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	1.26E+08	1.19E+08	8.68E+08	2.01E+07	0
10H-100H	0.1-1.0	6.26E+08	4.78E+08	3.46E+09	2.16E+08	0
100H-1,000H	1.0-10.0	1.97E+09	8.17E+08	6.07E+09	9.85E+08	0
1,000H-10,000H	10.0-100.0	1.02E+09	4.84E+08	3.19E+09	4.80E+08	0
10,000H-100,000H	100.0-1,000.0	1.24E+08	4.76E+07	3.61E+08	6.00E+07	0
> 100,000H	> 1,000.0	1.20E+07	2.39E+06	1.69E+07	6.81E+06	0
> 1H	> 0.01	3.88E+09	1.43E+09	1.12E+10	2.14E+09	0
> 10H	> 0.1	3.75E+09	1.35E+09	1.04E+10	2.08E+09	0
> 100H	> 1.0	3.13E+09	1.03E+09	6.90E+09	1.79E+09	0
> 1,000H	> 10.0	1.16E+09	5.10E+08	3.41E+09	5.89E+08	0
> 10,000H	> 100.0	1.36E+08	4.74E+07	3.72E+08	7.04E+07	0
> 100,000H	> 1,000.0	1.20E+07	2.39E+06	1.69E+07	6.81E+06	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

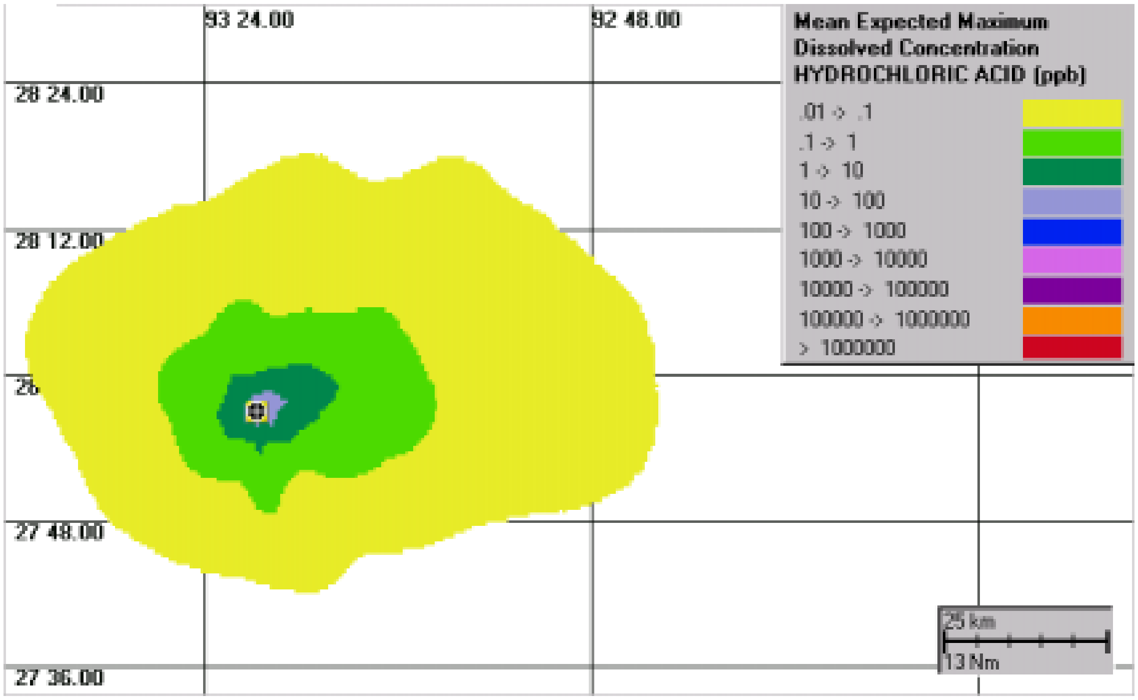


Figure 21. Peak exposure concentration (ppb) of hydrochloric acid dissolved in water at each location: averaged over all simulations (Scenario 1).

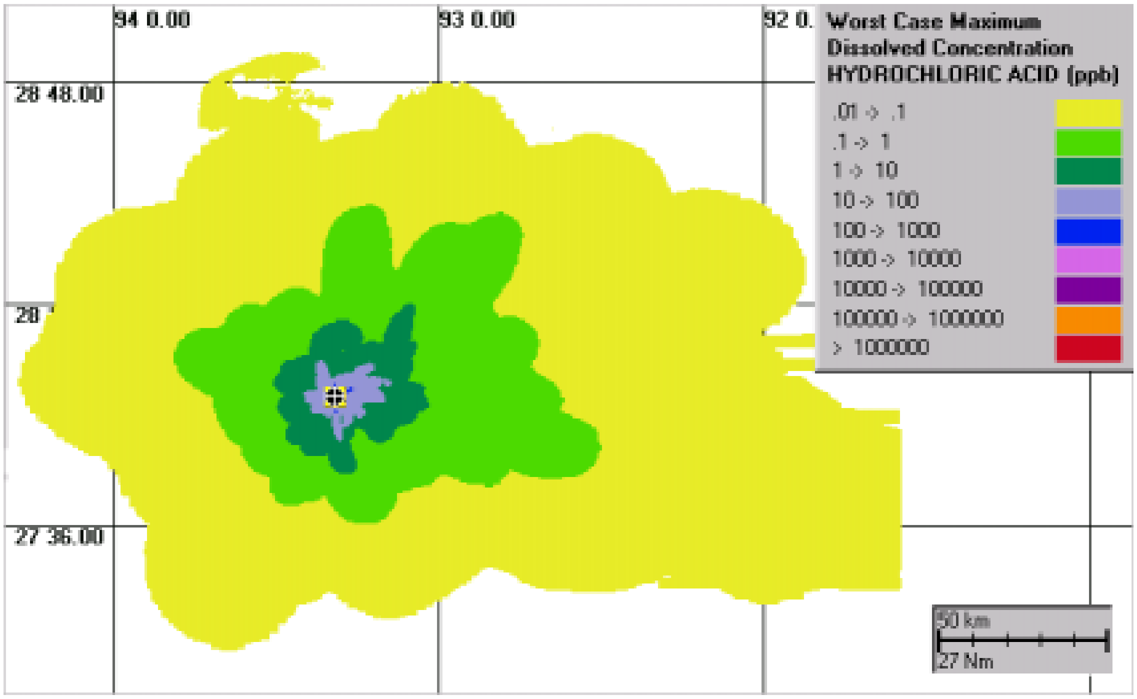


Figure 22. Peak exposure concentration (ppb) of hydrochloric acid dissolved in the water at each location: worst case of all simulations (Scenario 1).

Profile 2

HYDROFLUORIC ACID (Component of Product)

Summary

Hydrofluoric acid is a mineral acid classified as a completion, stimulation, and workover chemical. It is used in stimulation procedures to remove solid materials from the formation around the wellbore. It is almost always used in conjunction with another acid (usually hydrochloric). Its function in these mixtures is to remove clays and other materials that are not soluble in hydrochloric acid. If discharged into the marine environment, it will initially change the pH of seawater. Ultimately, it will cause a chemical reaction with the natural buffering system that will adjust the seawater to its original pH concentration. This acid differs from hydrochloric because its anion, fluoride, is present in seawater in much lower amounts. Fluoride may cause aquatic toxicity. It is normally used in much lower concentrations than hydrochloric acid. Health and safety issues may be of concern, based on data for a hydrochloric/hydrofluoric acid mixture.

Background Information

Fate in the Environment

Hydrofluoric acid is a solution of hydrogen fluoride in water. The product is miscible in seawater. It is used in mixtures of acids as a secondary component. Total acid concentrations vary, but a common total acid concentration is 15% by weight, in water. Hydrofluoric acid is commonly found in concentrations of about 10% of the total acid concentration.

When spilled in seawater, hydrofluoric acid solution will mix into the water column. Such mixing releases the heat of solution that will heat and agitate the receiving water. This release of energy helps to mix the hydrofluoric acid into the seawater where oceanographic and meteorological forces provide the mixing energy to disperse it through the water column. The hydrofluoric acid reaction products are hydrogen ion and fluoride ion. Immediately upon mixing with seawater, the hydrogen ion reacts with the carbonate equilibrium system already existing in the seawater, which acts to maintain the pH (see Aquatic Toxicity Levels discussion below). The concentrations of the various carbonate chemical species already found in the system and the hydrogen ions released into the seawater are determined by the carbon dioxide concentration in the atmosphere. Exchanges of carbon dioxide between the seawater and the atmosphere act to convert the hydrogen ion component of the acid into bicarbonate and water. The fluoride component of hydrofluoric acid becomes part of the natural concentration of fluoride in seawater.

Fate in the Process System

Hydrofluoric acid is applied to wells to remove acid soluble solids and clean up the tubing and the formation around the well. During the treatment process, the acid reacts with the solids it is intended to remove and becomes partially neutralized. To perform this procedure, the well is taken out of service, the acid is injected, and the well is then allowed to flow back to a receiving tank. The returns are pretreated to allow them to be disposed of, either directly overboard into the sea or into the produced water-treating system, followed by discharge into the sea. Alternatively, the returns are hauled ashore for appropriate disposal. Disposal choices are dictated by economics.

Other Components

Water, Hydrogen Chloride

CAS Number (Hydrofluoric Acid)

7664-39-3

Chemical Formula (Hydrofluoric Acid)

HF (H^{+1} and F^{-1} in solution)

Important Synonyms and Trade Names

Hydrogen Fluoride

Chemical and Physical Properties

Property	Component (1)	Product (2)
Molecular Weight	20.0	NA
Boiling Point	19.54° C	Depends on acid concentrations
Melting Point	- 83.1º C	Not established
Specific Gravity	NA	> 1,Varies with strength of acid
Solubility in Water	Soluble in all proportions	Soluble
Solubility in Organics	NA	NA
Vapor Pressure	NA	Approaches constant boiling mixture which boils @ 110° C
Vapor Density	0.901 g/l	See Vapor Pressure
Physical State (Phase)	Fuming liquid	Fuming Liquid
Chemical Reactivity in the Environment	H^{+1} reacts with carbonate buffering system	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component (1)	Product (2)
Autoignition Temperature	Non-Combustible	NA
Flash Point	NA	NA
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity	TWA 3 ppm	Same as Component
OSHA PEL	3 ppm	Same as Component

Notes: NA = Not Available

There is no identified danger for fire or explosion. The vapors are highly irritating to the tissue of the mucous membranes, upper respiratory tract, eyes, and skin. Liquid or concentrated vapors of HCl: HF acid can rapidly cause burns when skin contact occurs. Hydrofluoric acid, alone or in combination with hydrochloric acid, is very toxic by inhalation and by ingestion. Exposures to vapor or liquid by any route can be fatal. (3)

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 3,000 gal. (total acid solution typically containing 1.5% HF)
Maximum = Application dependent

Transport Container(s): Supplier's plastic-lined steel bulk tanks or boat cargo tanks.

Storage Methods: Bulk tanks on platform (temporary) or supplier's boat. The acid is usually not stored on the platform; therefore, larger jobs are completed from the supplier's boat.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Modeling Results

A hydrofluoric acid spill was not modeled.

Aquatic Toxicity Levels

The available literature was reviewed and no results were found specifically for hydrofluoric acid. The data shown for calcium fluoride were the only data identified.

Algae and Invertebrates

Synechococcus leopoliensis (freshwater microalgae): concentrations > 1.1 µM resulted in inhibition of growth(3) (1.1 µM of calcium fluoride is equal to 0.021 ppm fluoride ion).

Risk Characterization

Although a spill of hydrofluoric acid was not modeled, its behavior in the marine environment would be identical to that of hydrochloric acid (see Profile 1), except for the potential impact of the fluoride ion. Fluoride ions exhibit some toxicity, as the results of the calcium fluoride study described above indicate, thus the potential toxicity of fluoride must be considered.

The only toxicity data found for fluoride ion were measured on fresh water micro algae. Thus, the aquatic toxicity value reported above (1.1 µM of calcium fluoride) is questionable for application to the marine environment. A concentration of 0.021 ppm fluoride ion was found to inhibit growth. However, the average concentration of fluoride ion in seawater is 1.3 ppm. (1) The spill model for hydrochloric acid assumed a spill of 15% HCl by weight. A common use concentration of HF is 1.5% by weight. Therefore, by analogy to the HCl spill model, a worst-case peak concentration of HF (where F is 95% of HF) would be approximately 0.1 ppm, which is significantly lower than the average concentration of fluoride ion in seawater (i.e., 1.3 ppm). It appears unlikely that an impact to the marine environment would result from a discharge of hydrofluoric acid.

References

(1) CRC Handbook of Chemistry and Physics (1985-1986)
(2) BJ Services Environmental Group (1998)
(3) Nichol et al. (1987)

Profile 3

POLYSILOXANE (Component of EC9034A)

Summary

EC9034A is a solution containing a polysiloxane, an acetylenic diol, and 2-ethylhexanol in kerosene. It is a production-treating chemical used to prevent foaming of crude oil during oil/gas separations. Polysiloxane, the major active ingredient of EC9034A, is profiled here. The most important environmental concern associated with this product is the potential toxicity of the kerosene solvent (see Profile 21 for heavy aromatic naphtha).

Background Information

Fate in the Environment

EC9034A is oil soluble. The silicone component is an inorganic polymer (i.e., the polymer "backbone" is an alternating oxygen/silicon chain) with two organic radicals attached to each silicon atom. If spilled in seawater, the majority of the product will spread on the surface and a very small quantity will dissolve into the water column. Ultimately, most of the kerosene solvent component will evaporate into the atmosphere, and the alcohol will dissolve into the water column. The silicone will become particulate matter and oceanographic and meteorological forces will mix it into the water column. The magnitude of these forces will determine how rapidly these processes take place.

No information was found concerning the ultimate fate of silicone in the environment.

Fate in the Process System

EC9034A is applied to the system after water is separated. It goes into the oil phase and leaves the treatment facility in the oil export line.

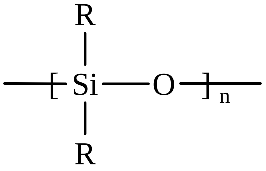
Other Components

Acetylenic diol: 2-ethylhexanol; kerosene

CAS Number (Silicone)

63148-62-9(1) (For dimethyl siloxanes, the most common industrial polysiloxane: the exact identification of the organic radical in this product is a trade secret.)

Chemical Formula (2) (Silicone)



$$-\!\left[\,\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{\mathrm{Si}}}}}-\mathrm{O}\,\right]_n\!-$$

Where R = CH_3-, C_2H_5-, etc and n = number of repeating units

Important Synonyms and Trade Names

Silicone

Chemical and Physical Properties

Property	Component	Product [3]
Molecular Weight	Depends on R- and n	NA
Boiling Point	NA	NA
Melting Point	NA	NA
Specific Gravity	NA	.84-.88 @ 60° F
Solubility in Water	Insoluble [3]	Insoluble
Solubility in Organics	Soluble in oil	Soluble in oil
Vapor Pressure	NA	10.2 mm Hg @ 100° F
Vapor Density (Air = 1)	ND	NA
Physical State (Phase)	Liquid	Liquid
Viscosity	NA	368 cst @ 60° F
Chemical Reactivity in the Environment	NA	NA

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component	Product
Autoignition Temperature	NA	NA
Flash Point	NA	140° F [3]
Upper Explosive Limit	None	NA
Lower Explosive Limit	None	NA
Air Toxicity	NA	NA
OSHA TLV	NA	Kerosene = 100 ppm [3]

Notes: NA = Not Available

The most important health and safety concerns for this product offshore are due to the solvent component. See Profile 21 for Naphtha solvents for more information.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 55 gal.
Maximum = 550 gal.

Transport Container(s): 5, 55, and 500 gal. totes (steel and/or HDPP).

Storage Methods: Shipping containers on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

A polysiloxane spill was not modeled.

Aquatic Toxicity Levels

The available literature for polysiloxane toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Carcinus maenus (marine crustacean): LC50 (9-days) = 10,000 ppm (4)
Artemia sallina (marine crustacean): LC50 (9-days) = 20,000 ppm (4)

Fish

Scorpaena porcus (marine fish): LC50 (9-days) = 1,000 ppm (4)

Benthos (Sediment)

*Nereis diversicolor (*marine worm): LC50 (9-days) = 2,000 ppm (4)
Mytilus edulis (marine bivalve): LC50 (9-days) = 2,000 ppm (4)

Risk Characterization

Although no spill model was done for polysiloxanes (silicone), comparison with other materials can give perspective to its possible environmental impact. Products containing polysiloxanes are dissolved in mixed solvents, including naphtha solvents. Naphtha solvents are discussed in Profile 21. Although these toxicity concentrations are for different species (i.e., fish and crustaceans), comparing the lowest toxicity concentration for polysiloxane (listed above) to the lowest toxicity concentrations for naphtha solvents in Profile 21, shows that they can be up to about five orders of magnitude less toxic than the solvent in which they are dissolved.

Modeling of polysiloxanes spills is mathematically similar to that for amides/ imidazolines. Therefore the distribution of polysiloxane concentrations in the marine environment following a spill would be the same order of magnitude as the modeled concentration. Comparing a toxicity concentration of 1,000 ppm (1,000,000 ppb) 9-day LC50 to these concentrations in Table 44 shows that no predicted exposure concentrations in a grid block around a spill of polysiloxanes would exceed this toxicity level. These comparisons indicate that polysiloxanes would pose minimal threat to the marine environment in the event of a spill.

References

(1) Mallinckrodt Baker, Inc. (1997)
(2) University of Southern Mississippi (1996)
(3) Nalco/Exxon Energy Chemical, L.P. (1992)
(4) Aubert (1985)

Profile 4

GLUTARALDEHYDE (Component of X-CIDE 0102 and EC6111A)

Summary

X-CIDE 0102 and EC6111A are water solutions containing glutaraldehyde. They are production-treating chemicals used to control the growth of bacteria in production gathering and treatment systems. Glutaraldehyde, as the active ingredient, is profiled here. If discharged to the marine environment, it will ultimately be removed by biological degradation. Environmental concerns include potential aquatic toxicity impacts.

Background Information

Fate in the Environment

Glutaraldehyde is the dialdehyde of glutaric acid and is soluble in seawater. When spilled in seawater, glutaraldehyde solution will rapidly mix into the water column where oceanographic and meteorological forces will disperse it. The magnitude of these forces determines how rapidly glutaraldehyde disperses through the water column.

Glutaraldehyde will ultimately be removed from seawater by biological degradation. Below toxic concentrations, it is degraded by bacteria. Glutaraldehyde has been shown to degrade by more than 50% in less than 5 days in a standard BOD test. (1) Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Glutaraldehyde is used in produced water streams and treatment vessels and will partition to produced waters. Thus produced waters will contain residual concentrations of glutaraldehyde. The produced waters containing the glutaraldhyde may either be discharged to the marine environment or injected under ground.

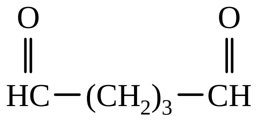
Other Components

Water

CAS Number (Glutaraldehyde)

111-30-8

Chemical Formula (Glutaraldehyde)



$$\overset{O}{\overset{\|}{HC}}-(CH_2)_3-\overset{O}{\overset{\|}{CH}}$$

Important Synonyms and Trade Names

1,5 Pentanedial

Chemical and Physical Properties

Property	Component (2)	Product (1), (3)
Molecular Weight	100.13	NA
Boiling Point	187-189° C	213° C (1)
Melting Point	NA	- 7° F (1)
Specific Gravity	NA	1.06 – 1.07@ 60° F
Solubility in Water	Soluble	Soluble
Solubility in Organics	Benzene and Alcohols	Alcohol
Vapor Pressure	NA	16 mm Hg @ 20° C (1)
Vapor Density (Air = 1)	NA	Heavier than air
Physical State (Phase)	Liquid	Liquid
Viscosity	NA	3.4 cp @ 69° F (1)
Chemical Reactivity in the Environment	Biodegrades	Biodegrades

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component	Product
Autoignition Temperature	NA (5)	NA
Flash Point	NA (5)	> 93° C (3)
Upper Explosive Limit	NA (5)	NA
Lower Explosive Limit	NA (5)	NA
Air Toxicity	NA	NA
OSHA PEL	None Established (5)	None Established (5)

Notes: NA = Not Available

It is corrosive to the eyes on contact, with possible permanent damage depending on exposure time. It can cause moderate skin irritation, can be fatal if ingested, and can cause severe respiratory tract irritation.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 55 gal.
Maximum = 500 gal.

Transport Container(s): 5, 55, and 500 gal. totes (steel and/or HDPP)

Storage Methods: Shipping containers on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Glutaraldehyde was modeled as Scenario 11 (surface release) and Scenario 12 (bottom release).

Surface Release

Results are shown in Tables 30 to 31 and Figures 23 to 24. The surface release of dissolved glutaraldehyde solution is dispersed nearly symmetrically, but less often to the northwest.

Bottom Release

Results are shown in Tables 32 to 33 and Figures 25 to 26. The bottom release of dissolved glutaraldehyde solution is dispersed primarily along-shelf with the prevalent direction of the currents at that level.

Aquatic Toxicity Levels

The available literature for glutaraldehyde toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Artemia salina (brine shrimp, marine crustacean): LC50 (96-hr.) values range between 10 and 840 ppm; values cannot be compared with other LC50 values, as they were determined through use of concentrations of treated mud diluted with seawater. (4)

Fish

O*ncorhynchus tshawytscha* (Chinook salmon, marine fish): high mortality at 62 mg/L. (5)

Benthos

Crangon crangon (brown shrimp, marine crustacean): LC50 (96-hr.) values range between 6 and 2,200 ppm; these values were not determined for glutaraldehyde alone, but were determined using treated mud diluted with seawater, which contains glutaraldehyde (Hudgins and Petrotech Consultants, Inc. 1991).

Risk Characterization

The lowest toxic concentration values found for glutaraldehyde were gathered from toxicity tests done on mud containing glutaraldehyde. A 96-hr LC50 of 6 ppm (6,000 ppb) was reported. Examination of Tables 30 and 31 (surface release) and 30 and 31 (bottom release) indicate that no unit grid cell area in either spill model scenario was exposed to a concentration greater than 6,000 ppb. The highest average concentration affecting an entire unit grid block for the surface release was 10 ppb and the highest average concentration affecting an entire unit grid block for the bottom release was 100 ppb.

References

(1) NalcoExxon Energy Chemical, L.P. (1998)
(2) CRC Handbook of Chemistry and Physics (1985-1986)
(3) Baker Petrolite and Baker Hughes Co. (1997)
(4) Hudgins and Petrotech Consultants, Inc. (1991)
(5) Fitzpatrick et al. (1995)

Table 30

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 11. Dissolved concentration of glutaraldehyde (surface release) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1.0	49,941,388.0	523,079,648.0	3,987.0	12,904.0
10.0	5,837,298.0	83,019,576.0	1,363.0	5,141.0
100.0	-	6,161,592.0	-	1,400.0
1,000.0	-	-	-	-
10,000.0	-	-	-	-
100,000.0	-	-	-	-
1,000,000.0	-	-	-	-

Table 31

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 11. Dissolved concentration of glutaraldehyde (surface release) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	3.04E+07	1.27E+07	6.75E+07	6.16E+06	0
10H-100H	0.1-1.0	2.29E+08	1.12E+08	6.82E+08	7.75E+07	0
100H-1,000H	1.0-10.0	7.08E+08	2.12E+08	1.27E+09	3.64E+08	0
1,000H-10,000H	10.0-100.0	2.57E+08	8.32E+07	5.52E+08	1.26E+08	0
10,000H-100,000H	100.0-1,000.0	2.79E+07	8.74E+06	8.56E+07	1.14E+07	0
> 100,000H	> 1,000.0	2.83E+06	5.94E+05	4.22E+06	1.62E+06	0
> 1H	> 0.01	1.26E+09	3.15E+08	2.32E+09	8.20E+08	0
> 10H	> 0.1	1.22E+09	3.10E+08	2.26E+09	8.02E+08	0
> 100H	> 1.0	9.96E+08	2.37E+08	1.73E+09	6.28E+08	0
> 1,000H	> 10.0	2.88E+08	8.38E+07	5.78E+08	1.67E+08	0
> 10,000H	> 100.0	3.08E+07	8.63E+06	8.72E+07	1.43E+07	0
> 100,000H	> 1,000.0	2.83E+06	5.94E+05	4.22E+06	1.62E+06	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 32

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 12. Dissolved concentration of glutaraldehyde (bottom release) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	25,619,236	196,845,920	2,856	7,916
10	3,891,531	26,267,824	1,113	2,892
100	324,294	1,945,766	321	787
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 33

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 12. Dissolved concentration of glutaraldehyde (bottom release) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	2.38E+07	2.60E+07	2.61E+08	8.76E+06	0
10H-100H	0.1-1.0	1.60E+08	7.63E+07	4.99E+08	7.52E+07	0
100H-1,000H	1.0-10.0	4.27E+08	1.94E+08	1.26E+09	1.23E+08	0
1,000H-10,000H	10.0-100.0	1.41E+08	7.71E+07	6.01E+08	5.19E+07	0
10,000H-100,000H	100.0-1,000.0	1.99E+07	6.36E+06	4.31E+07	1.17E+07	0
> 100,000H	> 1,000.0	2.28E+06	4.72E+05	3.57E+06	1.30E+06	0
> 1H	> 0.01	7.75E+08	3.15E+08	2.41E+09	3.15E+08	0
> 10H	> 0.1	7.51E+08	3.07E+08	2.35E+09	3.05E+08	0
> 100H	> 1.0	5.91E+08	2.63E+08	1.91E+09	1.93E+08	0
> 1,000H	> 10.0	1.64E+08	8.21E+07	6.43E+08	6.71E+07	0
> 10,000H	> 100.0	2.22E+07	6.47E+06	4.48E+07	1.36E+07	0
> 100,000H	> 1,000.0	2.28E+06	4.72E+05	3.57E+06	1.30E+06	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

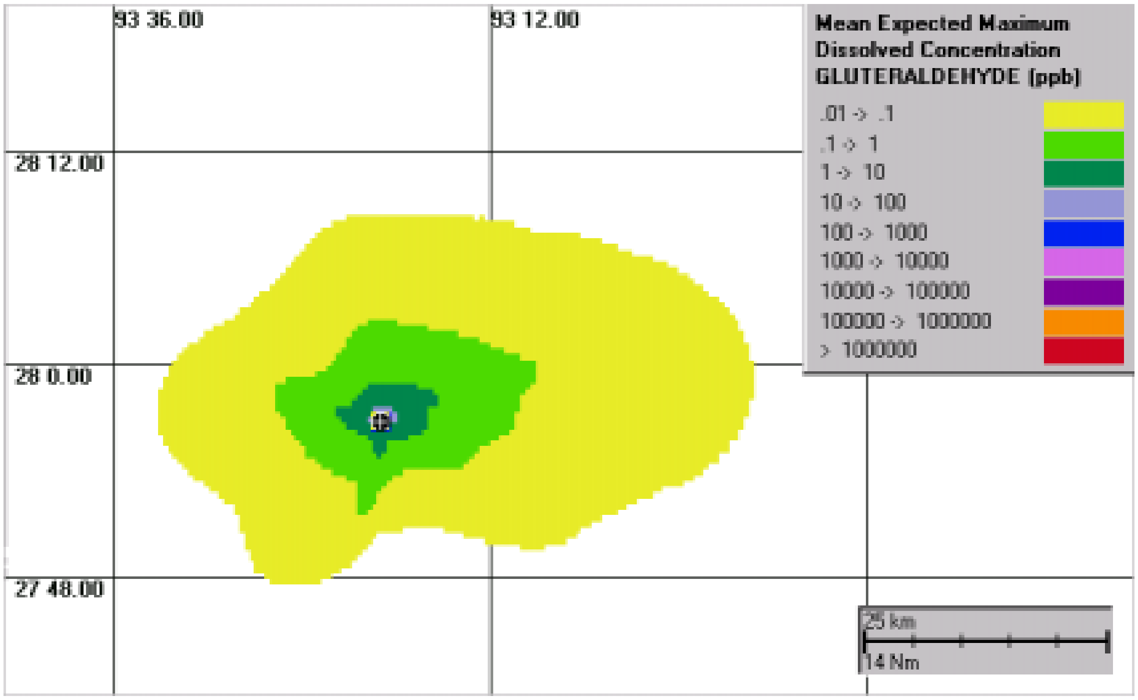


Figure 23. Peak exposure concentration (ppb) of glutaraldehyde (surface release) dissolved in the water at each location: averaged over all simulations (Scenario 11).

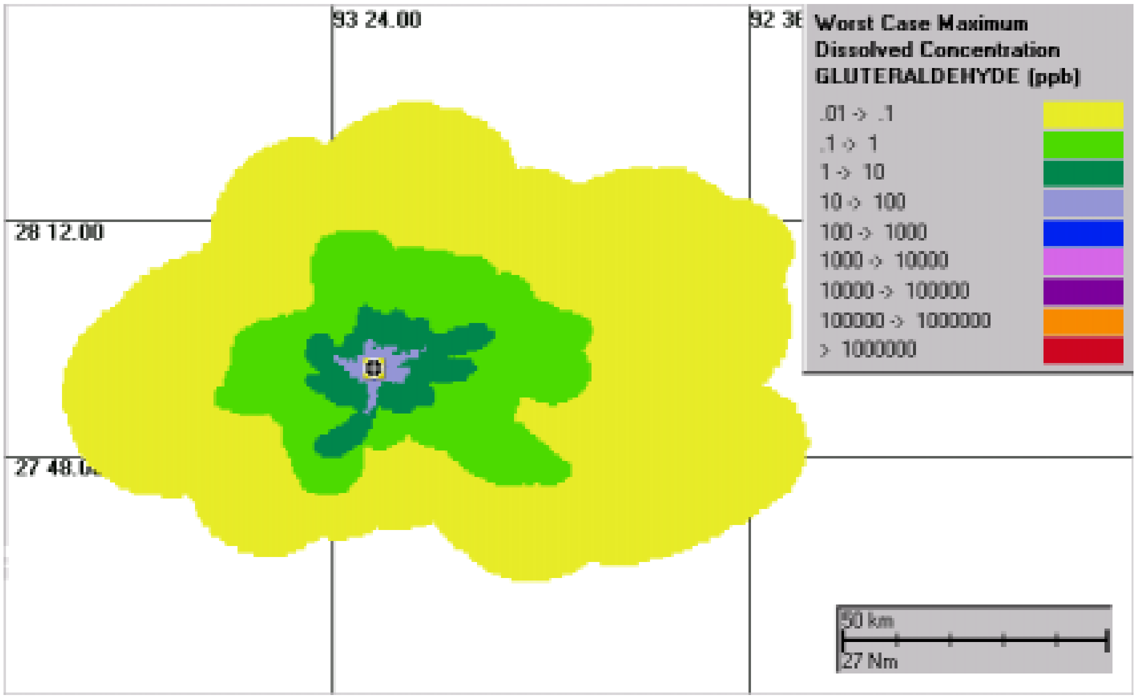


Figure 24. Peak exposure concentration (ppb) of glutaraldehyde (surface release) dissolved in the water at each location: worst case of all simulations (Scenario 11).

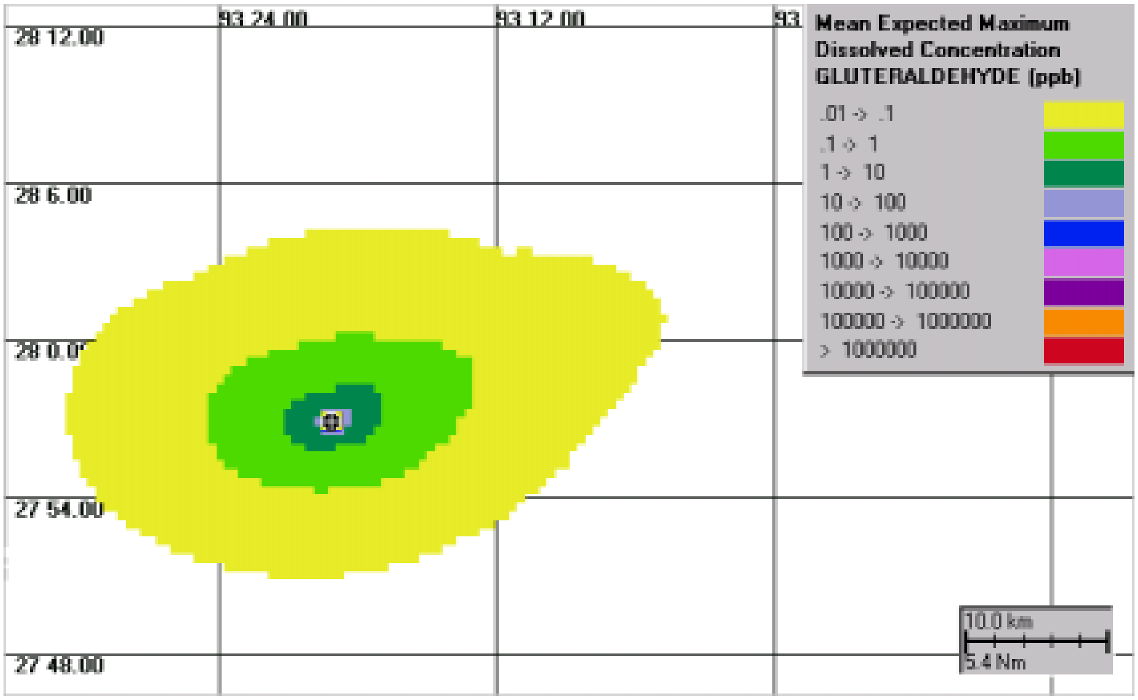


Figure 25. Peak exposure concentration (ppb) of glutaraldehyde (bottom release) dissolved in the water at each location: averaged over all simulations (Scenario 12).

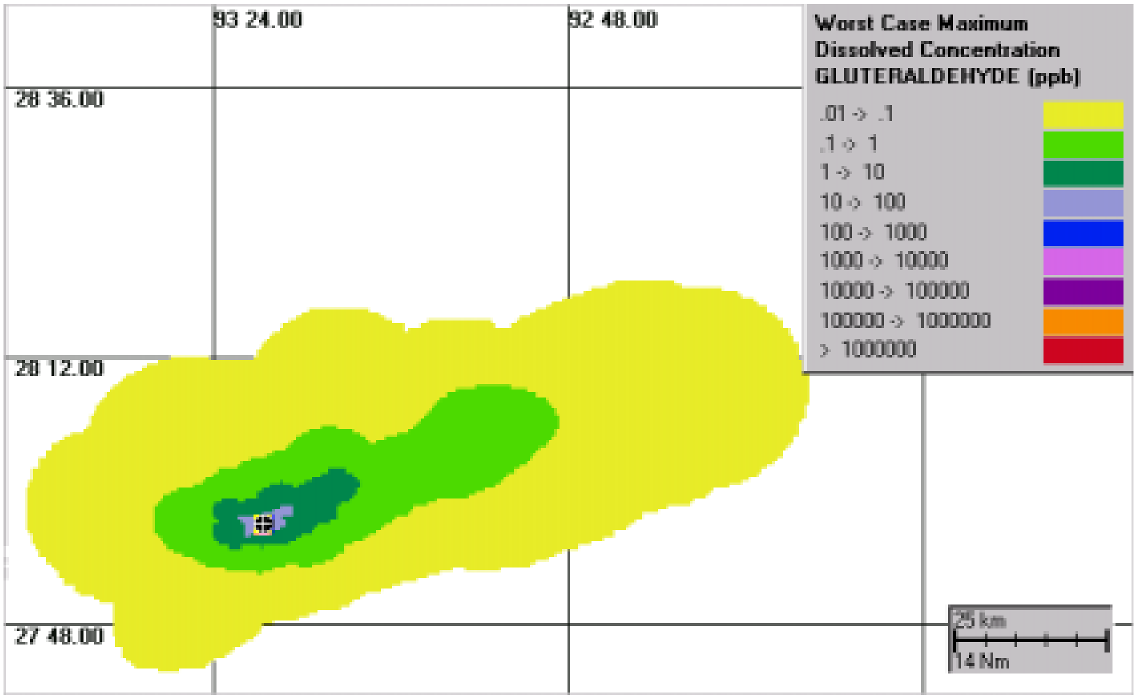


Figure 26. Peak exposure concentration (ppb) of glutaraldehyde (bottom release) dissolved in the water at each location: worst case of all simulations (Scenario 12).

Profile 5

QUATERNARY AMMONIUM COMPOUNDS (Component of Product A)

Summary

Product A is a water solution containing a quaternary ammonium chloride. It is a production-treating chemical used to control corrosion in production gathering and treatment systems. A quaternary ammonium chloride, one of the active ingredients, is profiled here. If discharged to the marine environment, it will ultimately be removed by biological degradation. Environmental concerns include possible aquatic toxicity.

Background Information

Fate in the Environment

Quaternary ammonium compounds are salts of substituted ammonium hydroxide bases. They are soluble in water or a mixture of alcohol and water depending on their composition. When spilled in seawater, Product A solution will rapidly mix into the water column where oceanographic and meteorological forces will disperse it through the water column. The magnitude of these forces determines how rapidly it spreads through the water column.

In the water column, Product A separates into an alcohol component and a quaternary component. The alcohol component of Product A will dissolve in the water column and the quaternary component will dissolve or disperse in the water column as tiny droplets. Quaternary ammonium compounds will ultimately be removed from the environment by biological degradation. Although quaternary ammonium compounds are also used to control bacteria, at low concentrations they are degraded by bacteria. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Product A is used in produced water streams and treatment vessels to protect against corrosion. It is designed to adsorb to the internal surfaces of piping and vessels, react with active corrosion sites and form a protective layer. Product A is designed to disperse into the produced water that carries it to the surfaces to be treated. Therefore, produced waters will contain residual concentrations of quaternary ammonium compounds. The produced waters containing the residual treating chemical may either be discharged to the marine environment or injected under ground for disposal.

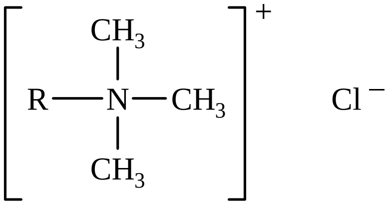
Other Components

Water, methanol, isopropyl alcohol, acetic acid, ethoxylated nonylphenol and amides/imidazolines.

CAS Number (Quaternary Ammonium)

NA

Chemical Formula (Quaternary Ammonium)



$$\left[R-N(CH_3)_3 \right]^+ \quad Cl^-$$

Important Synonyms and Trade Names

NA

Chemical and Physical Properties

Property	Component	Product (1)
Molecular Weight	NA	NA
Boiling Point	NA	ND
Melting Point	NA	ND
Specific Gravity	NA	.926 @ 25° C
Solubility in Water	Slightly soluble	Soluble
Solubility in Organics	Soluble in alcohols and hydrocarbons	NA
Vapor Pressure	NA	> 1
Vapor Density (Air = 1)	NA	> 1
Physical State (Phase)	NA	Liquid
Viscosity	NA	8.5 cps
Chemical Reactivity in the Environment	None	None

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component	Product (1)
Autoignition Temperature	NA	NA
Flash Point	NA	17º C
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity	NA	NA
OSHA PEL	NA	NA

Notes: NA = Not Available

The solvent for Product A is methanol and it comprises over 40% of the product. Most of the reported health and safety effects of this product are due to methanol. See Profile 15 for methanol.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 550 gal.
Maximum = 3,000 gal.

Transport Container(s): 55 gal. drums and/or 500 gal. HDPP plastic totes.

Storage Methods: In shipping containers or steel or plastic bulk tanks on the production platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Quaternary ammonium compounds for Product A were modeled as Scenario 14a.

Results for all of Product A's components are shown in Figures 37 to 42 and areas exposed above threshold concentrations of quaternary ammonium compounds are shown in Table 34 and Table 35.

The active ingredients of the miscible organic solution – amides/imidazolines, and quaternary ammonium chloride – are modeled as insoluble particulate representing liquid droplets (Figures 27 to 28 and Tables 34 to 35). Thus, all concentrations are in that form. The particulate disperses only by current transport and diffusion in this simulation. If the active ingredient were dissolved, it would disperse at the same rate to similar concentrations. As noted above, after the model runs were made, the corrosion inhibitor mixture was corrected slightly to include 11.2% quaternary ammonium chloride instead of 15% quaternary ammonium chloride. Thus, the model runs were made with slightly more chemical mass spilled (165 gal.) than the corrected composition (144 gal.) would indicate. Thus, the corrected results would be 87% of the concentrations predicted by the model.

Aquatic Toxicity Levels

The available literature for quaternary ammonium chloride toxicity was reviewed and is shown below. (2)

Algae and Invertebrates

Unspecified crustacean: LC50 = 0.9 ppm. (2)

Artemia salina (brine shrimp, marine crustacean): LC50 (96-hr.) = 10 ppm. (2)

Risk Characterization

The lowest toxicity concentration found for quaternary ammonium compounds was 0.9 ppm (900 ppb) 96-hr LC50. Comparing this concentration with toxicity thresholds presented in Table 34 shows that no predicted exposure concentration in a unit grid cell area would be greater than 1,000 ppb for either average or worst case concentration distributions.

References

(1) Supplier’s MSDS for Product A (See Appendix B)
(2) Hudgins and Petrotech Consultants, Inc. (1991)

Table 34

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 14a. Particulate concentration of miscible organic solution (amides/imidazolines and quaternary ammonium chloride) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	62,588,932	506,865,248	4,463	12,702
10	6,810,181	95,342,824	1,472	5,509
100	-	10,701,712	-	1,846
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 35

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 14a. Particulate concentration of miscible organic solution(amides/imidazolines and quaternary ammonium chloride) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	3.96E+07	1.90E+07	1.06E+08	4.22E+06	0
10H-100H	0.1-1.0	3.01E+08	1.48E+08	8.58E+08	9.63E+07	0
100H-1,000H	1.0-10.0	8.51E+08	2.40E+08	1.58E+09	5.20E+08	0
1,000H-10,000H	10.0-100.0	3.54E+08	1.27E+08	9.67E+08	1.97E+08	0
10,000H-100,000H	100.0-1,000.0	3.90E+07	8.16E+06	5.71E+07	2.24E+07	0
100,000H-10^6H	1,000-10,000	3.81E+06	7.51E+05	5.19E+06	1.89E+06	0
10^7H-10^8H	10,000-100,000	1.07E+05	1.88E+05	3.46E+05	0	75
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	1.59E+09	3.78E+08	2.80E+09	1.09E+09	0
> 10H	> 0.1	1.55E+09	3.72E+08	2.79E+09	1.05E+09	0
> 100H	> 1.0	1.25E+09	3.02E+08	2.55E+09	8.16E+08	0
> 1,000H	> 10.0	3.97E+08	1.26E+08	1.01E+09	2.30E+08	0
> 10,000H	> 100.0	4.29E+07	8.05E+06	6.03E+07	2.63E+07	0
> 100,000H	> 1,000.0	3.91E+06	6.73E+05	5.19E+06	2.27E+06	0
> 1,000,000H	> 10,000	1.07E+05	1.88E+05	3.46E+05	0	75
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

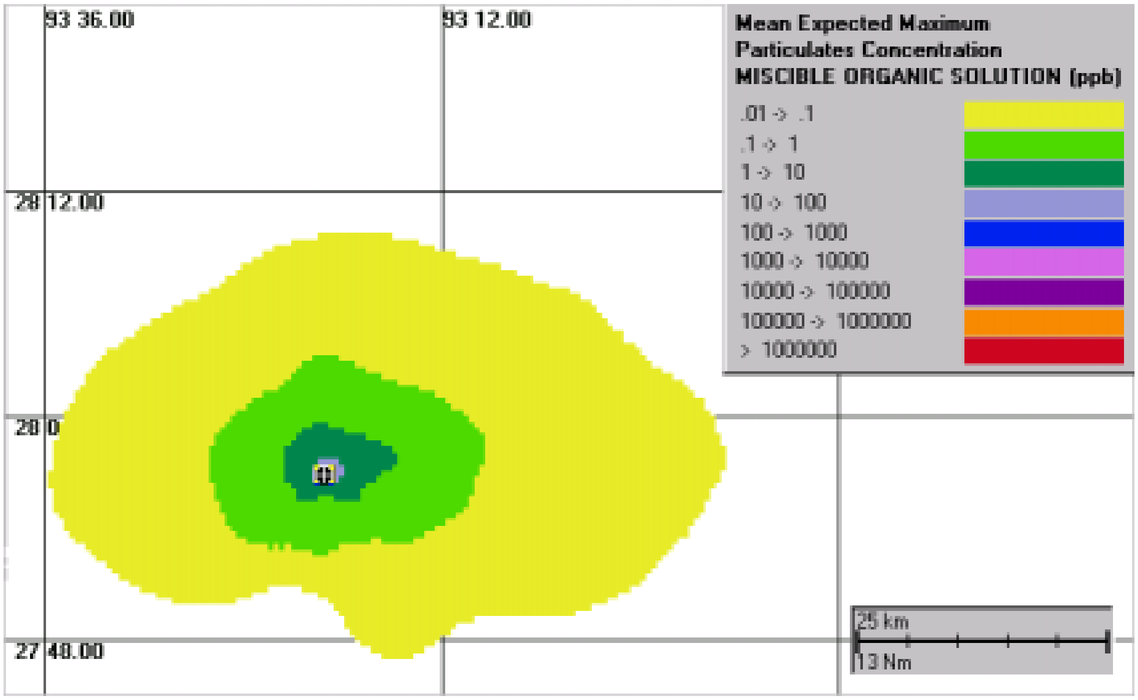


Figure 27. Peak exposure concentration (ppb) of miscible organic solution (amides/imidazolines and guaternary ammonium chloride) as particulate in the water at each location: averaged over all simulations (Scenario 14a).

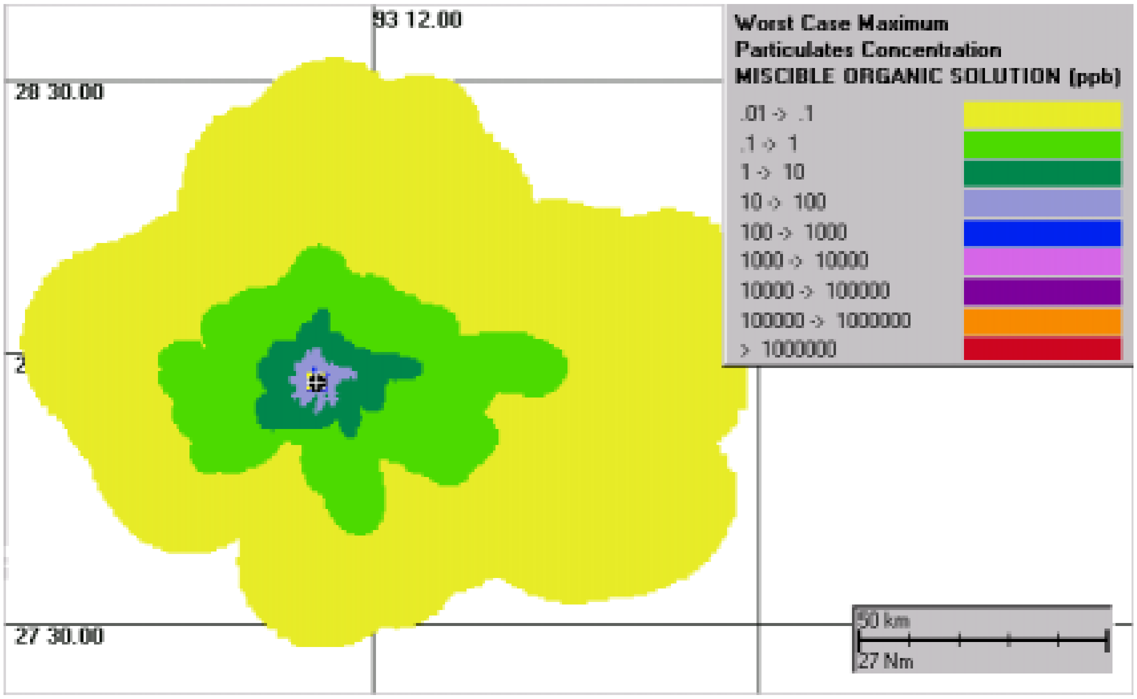


Figure 28. Peak exposure concentration (ppb) of miscible organic solution (amides/imidazolines and guaternary ammonium chloride) as particulate in the water at each location: worst case of all simulations (Scenario 14a).

Profile 6

Tetrakishydroxymethyl Phosphonium Sulfate (THPS)
(Component of Magnicide 535)

Summary

Magnicide 535 is a water solution containing Tetrakishydroxymethyl Phosphonium Sulfate (THPS). It is a production-treating chemical used to control the growth of bacteria in production gathering and treatment systems. Tetrakishydroxymethyl phosphonium sulfate (THPS), the active ingredient, is profiled here. If discharged to the marine environment, it will ultimately be removed by reaction with oxygen. Environmental concerns include possible aquatic toxicity.

Background Information

Fate in the Environment

Tetrakishydroxymethyl phosphonium sulfate (THPS) is soluble in seawater. It degrades to THPO (trishydroxymethylphosphine oxide) in the presence of oxygen. Subsequently, it degrades to phosphate ion and water. Its value as a biocide is based not only on efficiency, but also on its ability to be rapidly removed from the environment by oxidation.

When spilled in seawater, THPS solution will rapidly mix into the water column where oceanographic and meteorological forces provide the mixing energy to disperse it through the water column. The magnitude of these forces determines how rapidly THPS will spread through the water column.

When THPS mixes with oxygenated seawater it will begin to degrade by reacting with the oxygen in seawater to form THPO. Within a few hours, the THPS will be gone from the environment. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

THPS is used in produced water streams and treatment vessels and partitions to the produced water. The produced water contains residual concentrations of THPS when discharged to the marine environment or injected under ground.

Other Components

Water

CAS Number (THPS)

55566-30-8

Chemical Formula (THPS)

$(C_4H_{10}O_4)_2SO_4$

Important Synonyms and Trade Names

Tolcide

Chemical and Physical Properties

Property	Component [(1)]	Product [(2)]
Molecular Weight	406.3	NA
Boiling Point	NA	NA
Melting Point	- 43° C	28° F
Specific Gravity	1.37 @ 20° C	1.164 @ 60° F
Solubility in Water	Soluble	Soluble
Solubility in Organics	NA	NA
Vapor Pressure	NA	NA
Vapor Density (Air = 1)	NA	> 1
Physical State (Phase)	Liquid	Liquid
Viscosity	31 cps 25° C	21.1 cps @ 77° F
Chemical Reactivity in the Environment	Reacts with oxygen	Reacts with oxygen

Notes: NA = Not Available

The component supplied by the manufacturer is a 75% solution in water. The data presented for the product here were taken from an MSDS for a 35% solution in water. When the spill models were planned, an MSDS was not available for this product, and a 20% solution was modeled because it was the most common concentration applied offshore.

Health and Safety Properties and Effects

Property	Component [(1)]	Product [(2)]
Autoignition Temperature	Non Flammable	Non Flammable
Flash Point	Non Flammable	Non Flammable
Upper Explosive Limit	Non Flammable	Non Flammable
Lower Explosive Limit	Non Flammable	Non Flammable
Air Toxicity	ND	ND
OSHA PEL	ND	ND

Notes: ND =Not Determined

THPS can cause significant eye irritation and ingestion can cause significant irritation to the digestive tract. Inhalation is expected to cause significant irritation to the lungs, upper respiratory tract and nose.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 55 gal.
Maximum = 500 gal.

Transport Container(s): 5, 55, and 500 gal. totes (steel and/or HDPP).

Storage Methods: Shipping containers on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

THPS was modeled as Scenario 13. The exposure concentrations presented below are derived from the results of this modeling.

Results are shown in Figures 29 and 30 and Tables 36 and 37. The dissolved THPS solution is dispersed nearly symmetrically, but less often to the northwest.

In the modeling, the degradation half-life is assumed (25-days). However, as noted above, the intermediate product THPO, generated with a half-life of 6-hours, is reportedly much less toxic than THPS. Thus, the THPS concentrations calculated by the model are for THPS and its products. Comparison of this total concentration to LC50s for THPS would overestimate toxicity to the degree that the THPO is less toxic.

Aquatic Toxicity Levels

The available literature for THPO and THPS toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates for THPO
Skeletonema costatum (marine algae): EC50 = 2,090 mg/L (3)
Daphnia magna (freshwater crustacean): LC50 (acute) = > 1,000 mg/L (3)
Acartia tonsa (marine copepod crustacean): NOEC > 1,000 mg/L (3)

Fish for THPO
Onchorynchus mykiss (rainbow trout, freshwater fish): LC50 = > 500 mg/L (3)

Benthos (Sediment) for THPO
Mytilus edulis (marine bivalve mollusk): EC50 > 872 mg/L (3)

Fish
Oncorhynchus mykiss (rainbow trout, freshwater fish): LC50 (96-hr) = 119 mg/L (3)

Benthos (Sediment)
Crangon crangon (brown shrimp, marine crustacean): LC50 (96-hr) = 340 mg/L (3)

Risk Characterization

The lowest toxicity concentration found for THPS was 119 mg/L (approximately 119 ppm or 119,000 ppb) for a fresh water species. Comparing this concentration with the modeled concentrations presented in Table 36 shows that no predicted exposure concentration in a unit grid cell area would be greater than 119,000 ppb for either average or worst case concentration distributions. In fact, the highest concentration modeled for a complete unit grid cell area was 100 ppb.

The biocide THPS degrades to THPO with a half-life of approximately 6 hours. The degradation rate is dependent on oxygen concentration, temperature, THPS concentration, and the presence of catalysts, such as heavy metals. This reaction ensures that THPS will exist in the environment for only a short time.

References

(1) Albright and Wilson Americas Inc. (1997)
(2) Baker Petrolite and Baker Hughes Co. (1998)
(3) Downward et al. (1997)

Table 36

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 13. Dissolved concentration of THPS in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1.0	38,915,324.0	447,196,256.0	3,520.0	11,931.0
10.0	3,891,531.0	67,453,368.0	1,113.0	4,634.0
100.0	-	5,837,298.0	-	1,363.0
1,000.0	-	-	-	-
10,000.0	-	-	-	-
100,000.0	-	-	-	-
1,000,000.0	-	-	-	-

Table 37

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 13. Dissolved concentration of THPS in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	2.41E+07	1.04E+07	5.58E+07	5.84E+06	0
10H-100H	0.1-1.0	2.02E+08	1.09E+08	8.33E+08	4.38E+07	0
100H-1,000H	1.0-10.0	6.01E+08	1.87E+08	1.12E+09	3.23E+08	0
1,000H-10,000H	10.0-100.0	2.03E+08	6.56E+07	4.41E+08	1.09E+08	0
10,000H-100,000H	100.0-1,000.0	2.24E+07	7.05E+06	6.68E+07	1.01E+07	0
> 100,000H	> 1,000.0	2.26E+06	4.93E+05	3.24E+06	6.49E+05	0
> 1H	> 0.01	1.05E+09	2.70E+08	1.99E+09	6.80E+08	0
> 10H	> 0.1	1.03E+09	2.66E+08	1.94E+09	6.62E+08	0
> 100H	> 1.0	8.28E+08	2.00E+08	1.42E+09	5.28E+08	0
> 1,000H	> 10.0	2.27E+08	6.59E+07	4.62E+08	1.36E+08	0
> 10,000H	> 100.0	2.46E+07	6.96E+06	6.84E+07	1.23E+07	0
> 100,000H	> 1,000.0	2.26E+06	4.93E+05	3.24E+06	6.49E+05	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

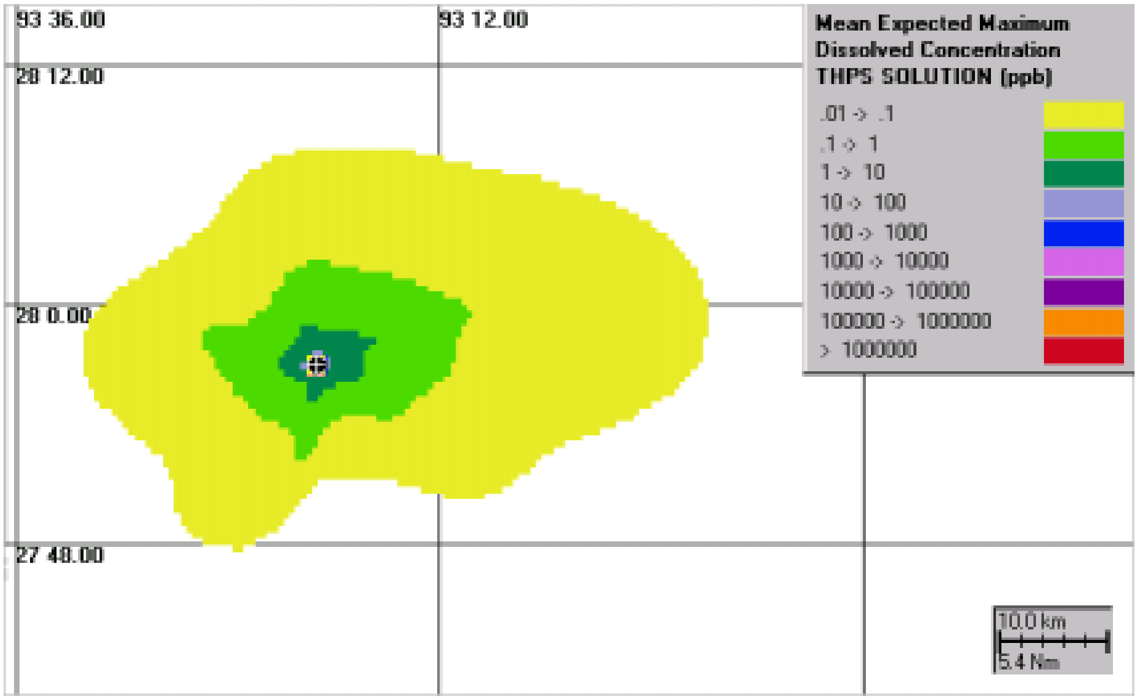


Figure 29. Peak exposure concentration (ppb) of THPS dissolved in the water at each location: averaged over all simulations (Scenario 13).

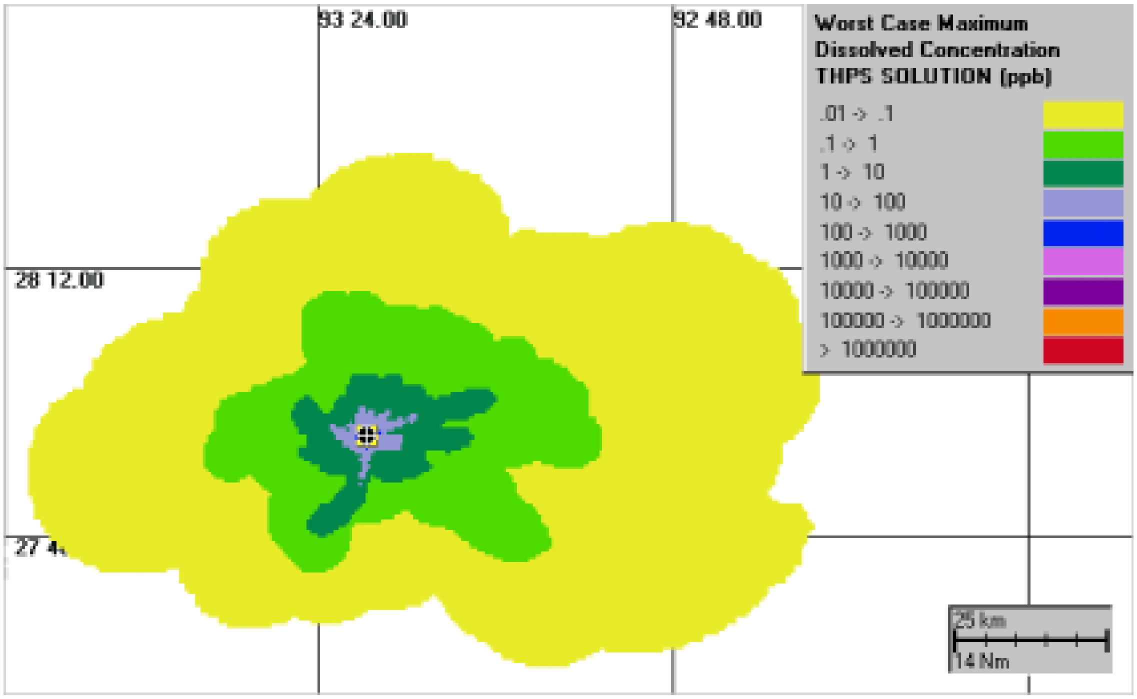


Figure 30. Peak exposure concentration (ppb) of THPS dissolved in the water at each location: worst case of all simulations (Scenario 13).

Profile 7

ZINC BROMIDE
(Component of a Zinc Bromide/Calcium Bromide Completion Fluid)

Summary

Zinc bromide is a solid inorganic salt. It is used as a constituent in completion, stimulation, and workover chemicals. Its ions are natural constituents of seawater and, at higher concentrations, zinc ion reacts with various other constituents of seawater to form insoluble compounds. Bromide ion will ultimately dilute to ambient seawater concentrations. Environmental concerns about this chemical are its potential aquatic toxicity.

Background Information

Fate in the Environment

When spilled in seawater, zinc bromide solution will rapidly disperse in seawater. In solution, it is present as separate zinc and bromide ions. Zinc ion reacts with the hydroxide ion in seawater to form insoluble zinc hydroxide. During and after reaction, oceanographic and meteorological forces will act to dilute zinc ion and bromide ion to normal seawater concentrations. The magnitude of these forces determines how rapidly these ions spread through the water column.

Fate in the Process System

Zinc bromide is used in stimulation and workover work on wells. It is placed in wells to hold pressure on the formation during casing perforation and during setting of packers and tubing in wells. During these operations, some of it will be lost to the formation. In some wells, the zinc bromide will remain in the annulus between the tubing and the casing and serve as a packer fluid. Ultimately, the zinc bromide will leave the well or production system as waste. Normally it will end up as part of the produced water stream. The produced water will ultimately be disposed of overboard into the marine environment or injected under ground.

Other Components

Water, Calcium Bromide

CAS Number (Zinc Bromide)

7699-45-8

Chemical Formula (Zinc Bromide)

$ZnBr_2$ (Zn^{+2} and Br^{-1} in water solution)

Important Synonyms and Trade Names

Zinc Dibromide

Chemical and Physical Properties

Property	Component [(1)]	Product [(2)]
Molecular Weight	225.18	NA
Boiling Point	697º C	275º F
Melting Point	394º C	ND
Specific Gravity	4.22	2.3
Solubility in Water	Complete (100%)	Soluble
Solubility in Organics	ND	ND
Vapor Pressure	Not Applicable (1)	17.5 mm Hg @ 68º F
Vapor Density (Air = 1)	7.8	ND
Physical State (Phase)	Solid (granular powder) @ standard conditions	Liquid solution
Viscosity	NA	NA
Chemical Reactivity in the Environment	Reacts with hydroxide in seawater	Reacts hydroxide in seawater

Notes: NA = Not Available; ND = Not Determined

The only health hazard found for the component, is skin irritation due to improper handling. See Appendix B for Product MSDS sheet.

Health and Safety Properties and Effects

Property	Component (1)	Product (2)
Autoignition Temperature	NA	ND
Flash Point	NA	ND
Upper Explosive Limit	NA	ND
Lower Explosive Limit	NA	ND
Air Toxicity	None Established (1)	NA
OSHA PEL	None Established (1)	NA

Notes: NA = Not Available; ND = Not Determined

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 45,000 gal.
Maximum = Varies with well design.

Transport Container(s): Steel bulk tanks provided by supplier or cargo tanks on boats.

Storage Methods: In bulk tanks on the drilling rig or on the supplier’s boat.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Zinc bromide was modeled as spill scenario 4. The exposure concentrations presented below are derived for the results of this modeling.

Results are shown in Figures 31 and 32 and Tables 38 and 39. The zinc bromide is spilled as a dissolved solution. Zinc may react with constituents of seawater to form a precipitate, some of which would settle to the sediment if the particulates become large enough to overcome turbulence. The model does not include these precipitation reactions. Thus, the dissolved concentrations may be construed as total concentrations (of zinc bromide, molecular weight 225 g/mole), with the assumption that the zinc precipitate does not settle significantly.

In the concentration plot, the high concentrations near shore (not part of the symmetric plume around the spill size) are an artifact of the compression of mass into a shallow water column, as the current data from offshore aimed the modeled mass in the shoreward direction. If detailed actual currents were available, shoreward transport would, by physical laws, be balanced by offshore transport, and there would be no increase in concentration towards shore.

Aquatic Toxicity Levels

The available literature for zinc bromide toxicity was reviewed. No data were found for zinc bromide. The following results are for zinc ion.

Algae and Invertebrates

Daphnia magna (freshwater crustacean) LC50 (48-hr) = 1.22 mg/L. (3)
Ceriodaphnia dubia (freshwater crustacean) LC50 (48-hr) = 0.5 mg/L. (3)

Fish

Pimelphales promelas (fathead minnow, freshwater fish) LC50 (7-days) = 0.78 mg/L. (3)

Risk Characterization

No marine toxicity data were found for zinc bromide. In seawater, zinc bromide chemically changes to zinc hydroxide or zinc carbonate. If toxicity tests on seawater were available the effect of precipitated zinc compounds would automatically be part of the bioassay test. The fresh water toxicity data listed above indicates that zinc ion has significant toxicity. It ranges from 0.5 mg/l (approximately 0.5 ppm or 500 ppb) 48-hr LC50 to 1.22 mg/l (approximately 1,220 ppb) 48-hr LC50. While 100% of the zinc bromide will not dissociate into zinc ion, a conservative comparison of these concentrations to the toxicity thresholds presented in Table 38 shows that significant areas are exposed to concentrations of zinc bromide greater than 500 ppb. On average, zinc bromide concentrations from a spill of the simulated volume would exceed 1ppm for at least one hour in an area of 11 million m^2 (11 km^2, volume of 11 million m^2 x 114 m deep = 1,254 million m^3) around the spill site. This indicates that, based on fresh water toxicity studies, there could be an adverse impact of a zinc bromide spill. For the most sensitive species tested, the dose required to cause 50% of the test organisms in freshwater to die in 48 hours is 24,000 ppb-hrs (500 ppb x 48 hours). From Table 39, an area of approximately 100 million m^2 (100 km^2, volume of 11,400 million m^3) around the spill site would be exposed to a dosage of 24,000 ppb-hrs or greater. However, based on the reaction of zinc bromide in seawater vs. freshwater (i.e., zinc ion reacts with hydroxide ion in seawater to form insoluble zinc hydroxide within minutes of mixing), and the absence of marine toxicity data, it is not possible to definitively determine the potential toxicity posed by the accidental release of zinc bromide under modeled conditions.

The potential for marine environmental impacts are affected by the chemical fate of zinc in seawater. The nominal concentration of zinc in seawater is 0.01 mg/L. (4) Dilution of zinc bromide spilled in the seawater would eventually reduce the zinc concentration to this level. Dissolved zinc is removed from the water column by reaction with hydroxide ion and carbonate ion in seawater. At the pH of seawater, the equilibrium concentration of zinc ion is 2 mg/L. Assuming that zinc above that concentration would precipitate, the potential impact zone is likely much smaller than the model results indicate. Dilution would further reduce this zinc concentration within a short period of time, certainly less than the 14 days modeled in spill scenario 4. The solid precipitate formed by chemical reaction would initially become suspended solids in the water column and eventually settle onto the sediment. A direct assessment of the potential impact of a zinc bromide spill on the marine environment would require toxicity data on marine organisms exposed to both zinc ion added to seawater and insoluble zinc compounds, studies of reaction products of zinc ion with seawater, and modeling of important chemical processes in the spill scenario.

References

(1) Mallinckrodt Baker Inc. (1996a)
(2) M-I Drilling Fluids (1998a)
(3) Magliette et al. (1995)
(4) CRC Handbook of Chemistry and Physics (1985-1986)

Table 38

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 4. Dissolved concentration of zinc bromide in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	3,176,494,592	25,957,097,472	31,798	90,898
10	542,861,248	3,883,581,952	13,145	35,159
100	88,856,904	834,720,448	5,318	16,300
1,000	11,026,006	152,742,752	1,873	6,973
10,000	324,294	17,511,886	321	2,361
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 39

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 mg/m^3-hours (0.01 ppb-hours): Scenario 4. Dissolved concentration of zinc bromide in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	9.11E+08	3.99E+08	2.56E+09	2.47E+08	0
10H-100H	0.1-1.0	3.73E+09	1.35E+09	7.60E+09	9.69E+08	0
100H-1,000H	1.0-10.0	1.04E+10	2.99E+09	2.06E+10	1.68E+09	0
1,000H-10,000H	10.0-100.0	1.35E+10	3.23E+09	2.76E+10	3.86E+09	0
10,000H-100,000H	100.0-1,000.0	5.57E+09	2.14E+09	1.17E+10	2.03E+09	0
100,000H-10^6H	1,000-10,000	5.96E+08	4.13E+08	3.23E+09	1.81E+08	0
10^7H-10^8H	10,000-100,000	1.54E+08	1.17E+08	9.89E+08	4.03E+07	0
10^8H-10^9H	100,000-1,000,000	1.58E+07	9.76E+06	6.93E+07	4.22E+06	0
> 10^9H	> 1,000,000	8.85E+05	1.54E+06	5.33E+06	0.00E+00	21
> 1H	> 0.01	3.49E+10	3.96E+09	4.79E+10	1.91E+10	0
> 10H	> 0.1	3.40E+10	3.78E+09	4.67E+10	1.89E+10	0
> 100H	> 1.0	3.03E+10	3.26E+09	4.26E+10	1.79E+10	0
> 1,000H	> 10.0	1.98E+10	2.76E+09	3.02E+10	1.53E+10	0
> 10,000H	> 100.0	6.34E+09	2.41E+09	1.53E+10	2.44E+09	0
> 100,000H	> 1,000.0	7.66E+08	4.42E+08	3.64E+09	2.70E+08	0
> 1,000,000H	> 10,000	1.71E+08	1.28E+08	1.06E+09	4.46E+07	0
> 10,000,000H	> 100,000	1.66E+07	1.13E+07	7.47E+07	4.22E+06	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

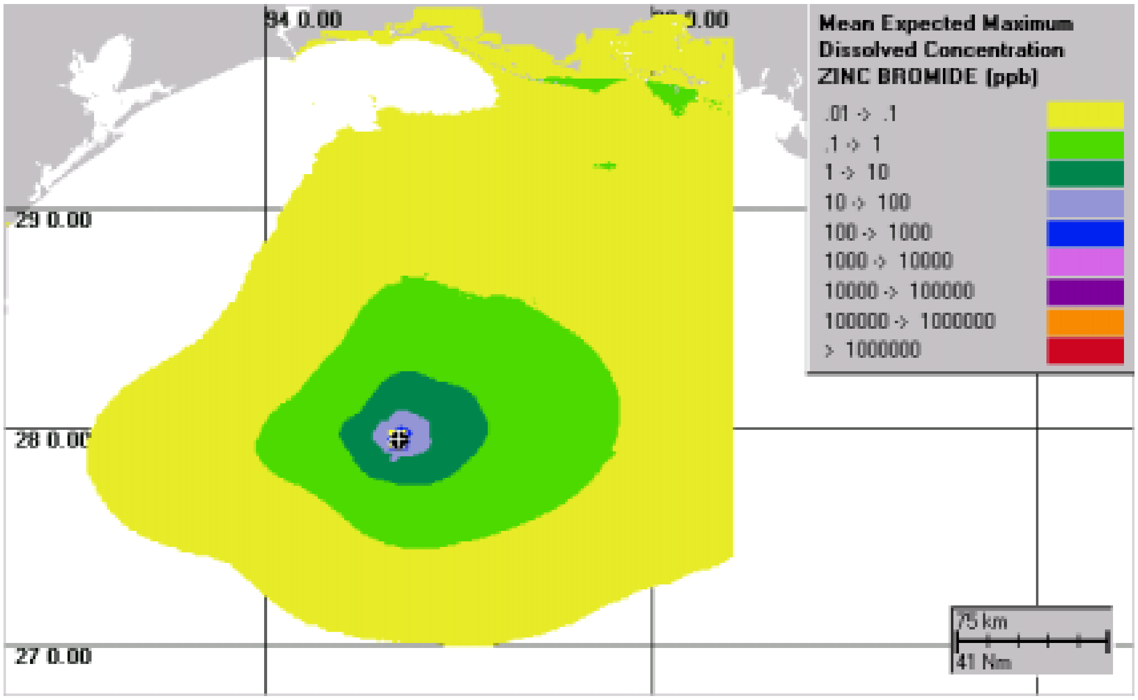


Figure 31. Peak exposure concentration (ppb) of zinc bromide dissolved in the water at each location: averaged over all simulations (Scenario 4).

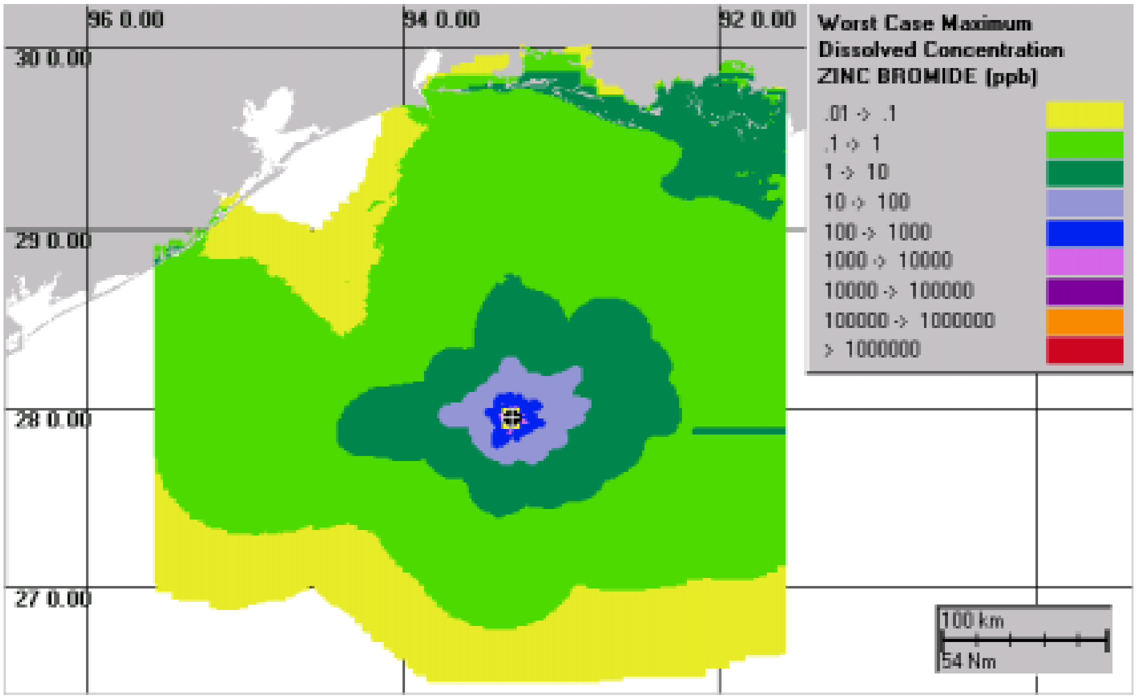


Figure 32. Peak exposure concentration (ppb) of zinc bromide dissolved in the water at each location: worst case of all simulations (Scenario 4).

Profile 8

CALCIUM BROMIDE
(Component of a Zinc Bromide/Calcium Bromide Completion Fluid)

Summary

Calcium bromide is a solid inorganic salt. It is used as a constituent in Completion, stimulation, and workover chemicals. Its ions are natural constituents of seawater. At higher concentrations, calcium ion reacts with various other constituents of seawater to form insoluble compounds. Bromide ion will ultimately dilute to seawater concentrations. This chemical is unlikely to pose potential aquatic toxicity.

Background Information

Fate in the Environment

When spilled in seawater, calcium bromide solution will rapidly disperse in seawater. In solution, it is present as separate calcium and bromide ions. Calcium ion reacts with the carbonate system in seawater to form insoluble calcium carbonate. At equilibrium with seawater, the calcium ion concentration will be reduced to 400 mg/L (1). During and after reaction, oceanographic and meteorological forces will act to dilute calcium ion and bromide ion back to normal seawater concentrations. The magnitude of these forces will determine how rapidly these ions spread through the water column.

Fate in the Process System

Calcium bromide is used in stimulation and workover on wells. It is placed in wells to hold pressure on the formation during casing perforation and during setting of packers and tubing in wells. During these operations, some of it will be lost to the formation. In some wells, the calcium bromide will remain in the annulus between the tubing and the casing and serve as a packer fluid. Ultimately, the calcium bromide will leave the well or production system as waste (i.e., it will normally end up as part of the produced water stream). The produced water will ultimately be disposed of overboard into the marine environment or injected under ground.

Other Components

Water, Zinc Bromide

CAS Number (Calcium Bromide)

7789-41-5

Chemical Formula (Calcium Bromide)

$CaBr_2 \bullet 2H_20$ (In water solution: Ca^{+2}, Br^{-1})

Important Synonyms and Trade Names

None

Chemical and Physical Properties

Property	Component (2)	Product (3)
Molecular Weight	235.92	NA
Boiling Point	No information found	275º F
Melting Point	No information found	ND
Specific Gravity	No information found	2.3
Solubility in Water	Complete	Soluble
Solubility in Organics	Insoluble	ND
Vapor Pressure	NA	17.5 mm Hg @ 68º F
Vapor Density (Air = 1)	NA	ND
Physical State (Phase)	Solid (crystals or granules) @ standard conditions	Liquid solution
Viscosity	NA	NA
Chemical Reactivity in the Environment	Reacts with carbonate in seawater	Reacts with carbonate in seawater

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component	Product (3)
Autoignition Temperature	NA	ND
Flash Point	NA	ND
Upper Explosive Limit	NA	ND
Lower Explosive Limit	NA	ND
Air Toxicity	None Established (2)	NA
OSHA PEL	None Established (2)	NA

Notes: NA = Not Available; ND = Not Determined

The only health hazard found for the component is skin irritation due to improper handling. See Appendix B for Product MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 45,000 gal.
Maximum = Varies with well design.

Transport Container(s): Steel bulk tanks provided by supplier or cargo tanks on boats.

Storage Methods: In bulk tanks on the drilling rig or on boats.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

No spill model was run for calcium bromide.

Aquatic Toxicity Levels

The available literature for calcium bromide toxicity was reviewed and the results from relevant studies are shown below.

Fish

Puntius conchonius (freshwater fish) LC50 (24-96 hr) = 2,791 mg/L. (4)

Benthos (Sediment)

Planorbarius corneus (freshwater snail) EC50 (6 week test) = 50% survival or cell number reduction > 1,202 ppm; concentration reduced fecundity. (5)

Crangon crangon (brown shrimp, marine crustacean) LC50 (96-hr) > 1,000 ppm. (6)

Risk Characterization

Calcium bromide exists in water solution as calcium ions and bromide ions. Both calcium ions and bromide ions are natural constituents of seawater. A toxicity level of 1,000 ppm (1,000,000 ppb) 96-hr LC50 for one marine species was found for calcium bromide. The spill model results for calcium bromide would be mathematically similar to the model results for zinc bromide, as the model simply dilutes and disperses the ions and no degradation is assumed. Using the results of the zinc bromide spill modeling and assuming a similar amount was spilled, Table 38 can be used to approximate a potential impact for calcium bromide. As may be seen in Table 38, 10,000 ppb is not exceeded over the area of a model grid cell. This concentration is two orders of magnitude lower than the 96-hr LC50 concentration.

The chemical fate of calcium in seawater will also affect the potential for impact on the marine environment. The nominal concentration of calcium in seawater is 400 mg/L(1). Dilution alone would ultimately reduce the calcium concentration to this level. However the nominal concentration of calcium in seawater is determined by reaction with carbonates. At the pH of seawater, this equilibrium reaction acts to maintain the calcium ion concentration at 400 mg/L. This means that there are two forces acting to dilute the calcium ion in seawater: dilution and reaction. The solid precipitate formed by chemical reaction would initially become suspended solids in the water column and eventually settle on to the sediment.

References

(1) CRC Handbook of Chemistry and Physics (1985-1986)
(2) Mallinckrodt Baker Inc. (1996b)
(3) M-I Drilling Fluids L.L.C. (1998a)
(4) Pant and Gill (1984)
(5) Mazuran et al. (1999)
(6) Hudgins and Petrotech Consultants, Inc. (1991)

Profile 9

AMMONIUM CHLORIDE (Single Component)

Summary

Ammonium chloride is a solid inorganic salt. It is used as a constituent of several different types of completion, stimulation, and workover chemicals. Other ammonium compounds are also used (i.e., ammonium hydroxide). If discharged to the marine environment, it will ultimately be removed by biological activity. The major environmental concern associated with this chemical is its potential aquatic toxicity.

Background Information

Fate in the Environment

When ammonium chloride dissolves in seawater, it immediately undergoes several reactions, dissociating into ammonium and chloride ions. Chloride ions are a major natural constituent of seawater. The ammonium ions further react with the hydroxide in seawater to form the undissociated molecule ammonium hydroxide (NH_4OH), the predominant ammonium species in seawater. A small fraction of the ammonium hydroxide dissociates into ammonium ions and hydroxide ions. Thus, the concentration of ammonium dissolved in seawater is the sum of the ammonium hydroxide and the ammonium ion concentrations. Ammonium is very soluble in seawater. It can decompose into ammonia gas and water and the ammonia gas can escape into the atmosphere.

Fate in the Process System

Ammonium chloride is used in stimulation and workover work on wells, and will be lost to the formation during this activity. When the well is returned to production, most of the ammonium chloride will be returned as part of the produced stream, and becomes a component of the produced water. The produced water is ultimately disposed of overboard into the seawater or is injected under ground.

Other Components

None

CAS Number (Ammonium Chloride)

12125-02-9

Chemical Formula (Ammonium Chloride)

NH_4Cl

Important Synonyms and Trade Names

Sal Ammoniac; Ammonium Muriate

Chemical and Physical Properties

Property	Component (1)	Product
Molecular Weight	53.49	Same as Component
Boiling Point	520º C	Same as Component
Melting Point	338º C	Same as Component
Specific Gravity	1.53	Same as Component
Solubility in Water	29.7g / 100g water @ 0º C	Same as Component
Solubility in Organics	Trace solubility in organic solvents	Same as Component
Vapor Pressure	1.0 mm Hg @ 160º C	Same as Component
Vapor Density (Air = 1)	1.9	Same as Component
Physical State (Phase)	Solid (powder) @ standard conditions	Same as Component
Chemical Reactivity in the Environment	Reacts with hydroxide in seawater to form undissociated ammonium hydroxide	Same as Component

Health and Safety Properties and Effects

Property	Component (1)	Product
Autoignition Temperature	NA	Same as Component
Flash Point	NA	Same as Component
Upper Explosive Limit	NA	Same as Component
Lower Explosive Limit	NA	Same as Component
Air Toxicity	20 mg/m^3 STEL (4)	Same as Component
OSHA PEL	NA (5)	Same as Component

Notes: NA = Not Available

There is no identified danger for fire or explosion. Contact with skin, eyes, or respiratory tract can cause irritation. Ingestion or inhalation of ammonium chloride can cause coughing, difficulty in breathing, nausea, vomiting, or diarrhea.

Use and Handling Properties (assumed to be similar to Potassium Chloride)

Storage Volumes Offshore (deep water): Typical = varies with well depth.
Maximum = 11,000 lbs.

Transport Container(s): 50 lb. paper sacks on pallets.

Storage Methods: In sacks on pallets (usually in the offshore drilling rig's mud room).

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

A spill of ammonium chloride was not modeled.

Aquatic Toxicity Levels

The toxicity information below is for ammonium chloride. The available literature for ammonium chloride toxicity was reviewed and the results from relevant studies are shown below. Freshwater toxicity values are reported as total ammonia and marine toxicity values are reported as unionized ammonia. Unionized ammonia can be absorbed through gill tissues and is more toxic to fish species. The relationship between unionized and total ammonia concentration can be calculated empiricaly if the pH, temperature and salinity of the water is known. The general relationship between unionized and total ammonia concentrations results in total ammonia concentrations higher than unionized ammonia concentrations, therefore the use of unionized ammonia toxicity data may result in a conservative risk estimate.

Fish

Pimephales promelas (fathead minnow - freshwater species) LC50 = 3.55 mg/L .(2)
Scophthalmus maximum (turbot - saltwater species) LC50 (4-6 weeks) = 2.6 mg/L.(3)
Sparus aurata (gilthead seabream - saltwater species) LC50 (4-6 weeks, 6-136 g fish) = 2.6 mg/L. (3)
Sparus aurata (gilthead seabream - saltwater species) LC50 (4-6 weeks, 0.4-3 g fish) = 2.6 mg/L. (3)
Salmo salar (Atlantic salmon - saltwater species) LC50 (4-6 weeks) = 0.24-0.34 mg/L. (3)

Risk Characterization

Although a spill of ammonium chloride was not modeled, it would be mathematically similar to a spill of potassium chloride. A potassium chloride spill was modeled in Spill Scenario 3. Both chemicals are highly soluble. Potassium chloride is not volatile and degrades slowly, whereas ammonium is volatile and biodegradable (as a nutrient for plants and bacteria). Thus, the modeled dilution of potassium chloride over-estimates the concentrations that would result from an ammonium chloride spill.

Unlike potassium ion, ammonium ion reacts with seawater components. Such reactions distribute the ammonium between the chemical species ammonium ion ($NH4^+$) and ammonium hydroxide (NH_4OH). The effect of this distribution is accounted for in toxicity testing because the same distribution occurred in the test solutions.

Marine LC50 toxicity values range between 0.24 and 2.6 mg/L(approximately 0.24 ppm to 2.6 ppm or 240 ppb to 2,600 ppb). Using these concentrations and the modeling results in Table 42 it is apparent that, on average, a complete unit grid area of 5.5 million m^2 would be expected to exceed a concentration of 100 ppb, but the area exceeding 1,000 ppb would be less than one grid cell. Thus, the toxic effect levels could be exceeded. The maximum concentration under worst case environmental conditions would exceed 1,000 ppb over an area of 5.8 million m^2.

Table 43 shows the dose that water column organisms would be exposed to, calculated as integrations of concentration over time. The toxicity test for the most sensitive species indicates a 50% lethal concentration of 240 ppb for 4 to 6 weeks. Calculating the lethal dose that the test species were exposed to one finds a dose of 240 x 4 x 7 x 24 = 161,280 ppb-hrs. From Table 43, the area where this dose would be exceeded is approximately 3 million m^2. Given that biodegradation and volatilization of ammonium are not accounted for in the potassium chloride simulation results used for this analysis, potential impacts of ammonium chloride spills should be evaluated in future research.

References

(1) Mallinckrodt Baker, Inc. (1999a)
(2) Versteeg and Shorter (1992)
(3) Person-Le Ruyet et al. (1997)
(4) American Conference of Governmental Industrial Hygienists (1994-1995)
(5) U.S. Department of Health and Human Services (1994)

Profile 10

SODIUM HYDROXIDE (Single Component)

Summary

Sodium hydroxide is a strong base used as a drilling fluid chemical. It is used to adjust the pH of drilling fluids and cause clays to hydrate and thicken. It also acts to dissolve lignite which is soluble in water only above pH 8. In this manner it aids in creating the viscosity necessary for the mud to lift cuttings. High pH facilitates this process. If discharged into the marine environment, it will initially affect the pH of the water. Eventually chemical reaction with the natural buffering system will adjust the seawater to its original concentrations. The most important potential impact of this chemical is associated with the health and safety of the workers. Accidental discharge of amounts used offshore will not result in significant localized impacts to the environment.

Background Information

Fate in the Environment

When spilled on the seawater surface, sodium hydroxide will dissolve into the water column. Such mixing releases the heat of solution, which can heat and agitate the receiving water. This release of energy helps to mix the sodium hydroxide into the seawater where oceanographic and meteorological forces provide additional mixing energy to disperse it through the water column. Immediately on mixing with seawater, the hydroxide reacts with the carbonate equilibrium system, which acts to maintain the pH of the seawater. Since all the reaction products are natural components of seawater, ultimately the seawater will return to its natural state. The concentration of the various carbonate chemical species and the hydroxide ion concentration are determined by the carbon dioxide concentration in the atmosphere. Exchanges of carbon dioxide with the atmosphere act to convert the hydroxide ion component of the sodium hydroxide into carbonate ion and water. The sodium component of sodium hydroxide becomes part of the natural concentration of sodium ion in seawater.

Fate in the Process System

Sodium hydroxide is a component of drilling fluid, usually water-based fluids. It will eventually exit the system as a waste in one of three ways: clinging to cuttings that are disposed of; as excess drilling fluid that is disposed of; or at the completion of the well when all the remaining drilling fluid is disposed of. Outside the territorial seas, waste drilling fluids are discharged to the sea. Inside the territorial seas, waste drilling fluids are sent to landfills for disposal.

Other Components

None

CAS Number (Sodium Hydroxide)

1310-73-2

Chemical Formula (Sodium Hydroxide)

NaOH

Important Synonyms and Trade Names

Caustic Soda; Lye

Chemical and Physical Properties

Property	Component (1), (2), (3)	Product
Molecular Weight	40	Same as Component
Boiling Point	2,130° C	Same as Component
Melting Point	318.4° C	Same as Component
Specific Gravity	2.13	Same as Component
Solubility in Water	42 g/100 ml @ 0° C	Same as Component
Solubility in Organics	Alcohol and glycol	Same as Component
Vapor Pressure	NA	Same as Component
Vapor Density (Air = 1)	NA	Same as Component
Physical State (Phase)	Solid	Same as Component
Chemical Reactivity in the Environment	Reacts with seawater buffering system	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component	Product (2), (3)
Autoignition Temperature	Non combustible (7)	Same as component
Flash Point	Non combustible (7)	Same as component
Upper Explosive Limit	Non combustible (7)	Same as component
Lower Explosive Limit	Non combustible (7)	Same as component
Air Toxicity	TLV 2 mg/m^3 Ceiling (8)	NA
OSHA PEL	2 mg/m^3 Ceiling (8)	NA

Notes: NA = Not Available

Sodium hydroxide is a strong base that can cause eye and skin burns. Contact with the product is severely irritating to the eyes, skin, and respiratory tract and may cause severe injury. It is reactive with water, and contact with water or moisture may generate sufficient heat to ignite combustible materials. (2)

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 100,000 lbs.
Maximum = 150,000 lbs.

Transport Container(s): 50 lb. paper sacks on pallets.

Storage Methods: In sacks on pallets (usually in drilling rig mud room).

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

A sodium hydroxide spill was modeled as spill scenario 2. The exposure concentrations presented below are derived for the results of this modeling.

Results are shown in Figures 33 and 34 and Tables 40 to 41. The sodium hydroxide begins as particulate, but dissolves so quickly the particulate concentration is not relevant. In the dissolved concentration plots (Figures 33 and 34), the high concentrations near shore (not part of the symmetric plume around the spill size) are an artifact of the compression of mass into a shallow water column, as the current data from offshore aimed the modeled mass in the shoreward direction. If detailed actual currents were available, shoreward transport would, by physical laws, be balanced by offshore transport, and there would be no increase in concentration towards shore.

As the molecular weight of NaOH is 40, and the concentration of hydroxide ion in seawater is 2.5×10^{-8}, 1,000 mg $NaOH/m^3$ (~1 ppm) might be considered a threshold of significance. The average exposed area with peak concentration above 1 ppm is 5.2 km^2, with an approximate volume of 590 million m^3. This is a much more significant volume than expected for the acid spill (because of the larger mass assumed spilled).

Aquatic Toxicity Levels

The available literature for sodium hydroxide was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Daphnia magna (water flea, freshwater crustacean): TLM (Threshold Limit Median) =15 ppm (4)

Mysidopsis bahia (mysid shrimp, marine crustacean): LC50 (96-hr SPP test) 163,000 - 1,000,000 ppm; concentrations ranged from 0-5 lbs. per barrel in EPA muds 2, 3, 5, 6, 7, 8 (5)

Fish

Lepomis macrochirus (bluegill, freshwater fish): LC50 (96-hr) = 32.3 ppm (6)

Risk Characterization

None of the toxicity data for sodium hydroxide are directly relevant to this study. The only seawater toxicity study is for ion muds containing sodium hydroxide. This data is relevant for mud discharges, but not for spills of sodium hydroxide, since in muds sodium hydroxide reacts with other mud constituents. Assuming that sodium hydroxide is more toxic to freshwater organisms, since marine species are used to higher pH values and seawater is buffered by the carbonate system, using freshwater toxicity results in this study results in conservatively high predicted impacts.

Fresh water toxicity ranges from 15 ppm to 32.3 ppm (15,000 ppb to 32,300 ppb). Using these concentrations and the modeling results in Table 40, under average environmental conditions, no complete unit grid cell area would be expected to exceed a concentration of 1,000 ppb, indicating that the impact would be localized around the spill site in most cases.

Under worst case environmental conditions; i.e., with minimal dispersion rates and assuming no buffering, the maximum modeled concentration would exceed 10,000 ppb over an area of 6.8 million m^2. Table 41 shows dose or integrations of concentration over time. The lowest toxicity level was 15,000 ppb for 96 hours of exposure. The dose that the test species was exposed to was 15,000 x 96 = 1,440,000 ppb-hrs. This dose level was not exceeded over a unit grid cell area under any environmental conditions, including worst case. Comparison of Tables 40 and 41 shows that 109 m^2 exceeded 1,000 ppb under worst case conditions (Table 40) and this same area could receive a dose of 1,000 ppb-hrs (Table 41). Thus, the average exposure time to concentrations above 1,000 ppb was 1 hour (i.e., the maximum dose was 1,000 ppb-hrs). Therefore, the dose to the environment from this spill was three orders of magnitude lower than the dose required to produce the toxic effect.

References

(1) CRC Handbook of Chemistry and Physics (1985-1986)
(2) M-I Drilling Fluids L.L.C. (1998b)
(3) Baker Hughes Inteq (1994a)
(4) Hudgins and Petrotech Consultants, Inc. (1991)
(5) Jones et al. (1986)
(6) Bailey (1984)
(7) U.S. Department of Health and Human Services (1994)
(8) Mallinckrodt Baker Inc. (1998)

Table 40

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 2. Dissolved concentration of sodium hydroxide in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	1,779,835,008	13,390,407,680	23,802	65,286
10	325,263,968	2,280,958,720	10,175	26,945
100	47,022,724	487,407,968	3,869	12,456
1,000	5,188,709	88,856,904	1,285	5,318
10,000	-	6,810,181	-	1,472
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 41

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01-hours (0.01 ppb-hours): Scenario 2. Dissolved concentration of sodium hydroxide in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	8.39E+08	3.55E+08	1.71E+09	1.32E+08	0
10H-100H	0.1-1.0	3.95E+09	1.41E+09	7.74E+09	6.32E+08	0
100H-1,000H	1.0-10.0	1.11E+10	3.29E+09	2.65E+10	1.69E+09	0
1,000H-10,000H	10.0-100.0	9.59E+09	1.98E+09	1.56E+10	4.65E+09	0
10,000H-100,000H	100.0-1,000.0	2.81E+09	1.39E+09	9.05E+09	1.02E+09	0
> 100,000H	> 1,000.0	3.26E+08	1.40E+08	1.14E+09	1.89E+08	0
> 1H	> 0.01	2.86E+10	3.74E+09	4.15E+10	1.57E+10	0
> 10H	> 0.1	2.77E+10	3.56E+09	4.06E+10	1.56E+10	0
> 100H	> 1.0	2.38E+10	2.95E+09	3.60E+10	1.48E+10	0
> 1,000H	> 10.0	1.27E+10	2.08E+09	1.79E+10	8.92E+09	0
> 10,000H	> 100.0	3.13E+09	1.49E+09	1.02E+10	1.24E+09	0
> 100,000H	> 1,000.0	3.26E+08	1.40E+08	1.14E+09	1.89E+08	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

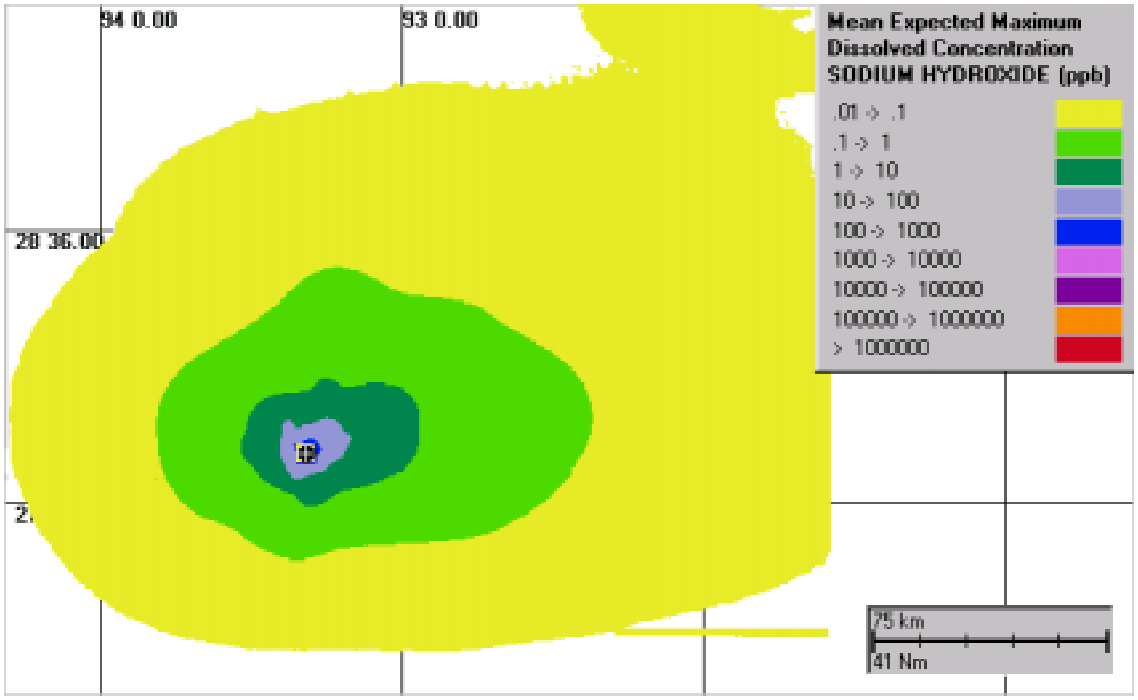


Figure 33. Peak exposure concentration (ppb) of sodium hydroxide as dissolved in the water at each location: mean case of all simulations (Scenario 2).

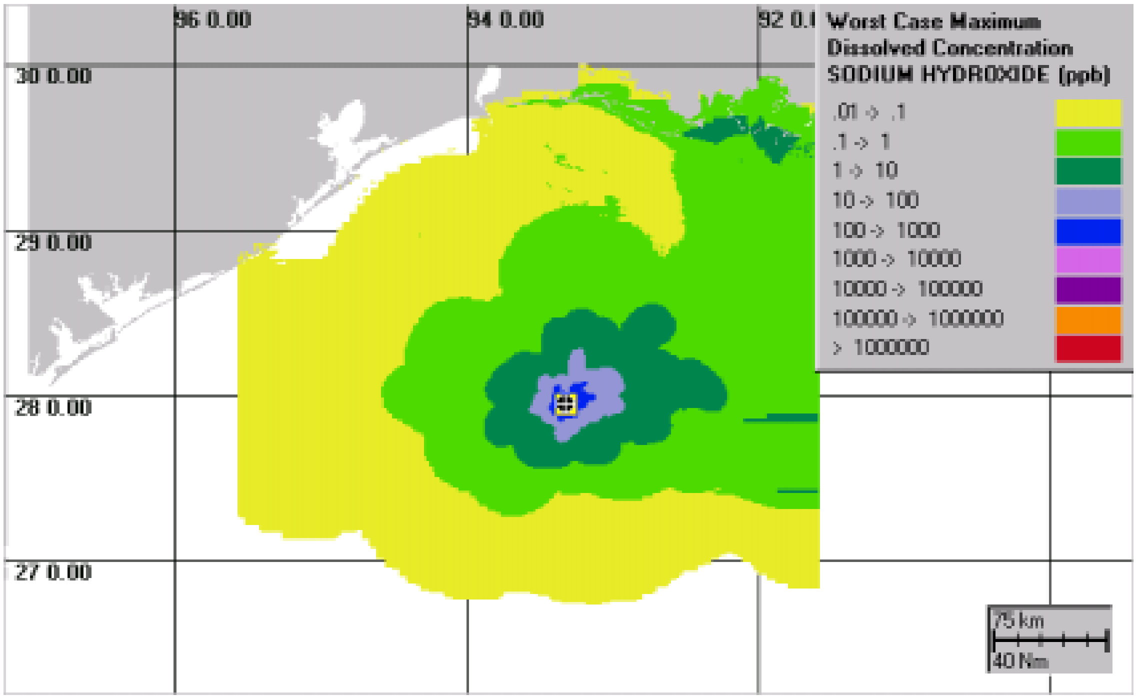


Figure 34. Peak exposure concentration (ppb) of sodium hydroxide dissolved in the water at each location: worst case of all simulations (Scenario 2).

Profile 11

POTASSIUM CHLORIDE (Single Component)

Summary

Potassium chloride is a solid inorganic salt. It is used as a constituent in several different types of completion, stimulation, and workover chemicals. It is a natural constituent of seawater and, if discharged to the marine environment, it will ultimately dilute to seawater concentrations. Potassium is an essential nutrient in low concentrations, (1) and its potential toxicity is low.

Background Information

Fate in the Environment

When spilled in seawater, potassium chloride will rapidly dissolve in seawater. In solution, it dissociates into potassium and chloride ions. Both ions are normal constituents of seawater, and oceanographic and meteorological forces will act to dilute them to normal seawater concentrations. The magnitude of these forces determines how rapidly potassium chloride spreads through the water column.

Because potassium ion is one of the three common nutrients for plants, some of it is needed in the environment, but an excess can cause toxicity in some marine organisms. (1) For example, if an excess exists after an accidental discharge, a short-term impact may occur.

Fate in the Process System

Potassium chloride is used in stimulation and workover work on wells, and it will be lost to the formation during this process. When the well is returned to production status, most of the potassium chloride will be recycled as part of the produced stream, thus becoming part of the produced water. The produced water will ultimately be disposed of overboard into the marine environment or injected under ground.

Other Components

None

CAS Number (Potassium Chloride)

7447-40-7

Chemical Formula (Potassium Chloride)

KCl (K^{+1}, Cl^{-1} in water solution)

Important Synonyms and Trade Names

Muriate of Potash

Chemical and Physical Properties

Property	Component [(2)]	Product
Molecular Weight	74.55	Same as Component
Boiling Point	1,500º C (sublimes)	Same as Component
Melting Point	770º C	Same as Component
Specific Gravity	1.984	Same as Component
Solubility in Water	28.1 g / 100g water @ 0º C (3)	Same as Component
Solubility in Organics	Soluble in ether and glycol	Same as Component
Vapor Pressure	NA	Same as Component
Vapor Density (Air = 1)	NA	Same as Component
Physical State (Phase)	Solid (powder) @ STP	Same as Component
Chemical Reactivity in the Environment	Non-reactive	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component (3)	Product
Autoignition Temperature	NA	NA
Flash Point	NA	NA
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Airborne Exposure Limits (PEL)	15 mg/m^3 total dust, 5 mg/m^3 respirable fraction for nuisance dusts	Same as Component
Airborne Exposure Limits (ACIGH TLV)	10 mg/m^3 total dust containing no asbestos and < 1% crystalline silica for Particulates Not Otherwise Classified	Same as Component

Notes: NA = Not Available

High concentrations of dust may cause irritation to the eyes. Ingesting large quantities can cause can cause vomiting and lead to weakness and circulatory problems. Contact of dust with moist skin can cause irritation.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 11,000 lbs.
Maximum = varies with well depth and perforated interval.

Transport Container(s): 50 lb. sacks on pallets

Storage Methods: In sacks on pallets (usually in the offshore drilling rig’s mud room)

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Potassium chloride was modeled as spill scenario 3. The exposure concentrations presented below are derived from the results of this modeling.

Results are shown in Figures 35 to 36 and Tables 42 to 43. As for sodium hydroxide, the potassium chloride begins as particulate, but dissolves so quickly the particulate concentration is instantaneous. Thus, dissolved concentrations are of interest. The more likely directions for the plume to move are along-shelf, as indicated by the east-west stretching of the concentration plots. (This pattern is evident in the results for most scenarios.)

Aquatic Toxicity Levels

The available literature for potassium chloride toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Mysidopsis bahia (mysid shrimp, marine crustacean) (tested in drilling mud): LC50 (96-hr SPP test) = 27,000 ppm (6)

Mysidopsis bahia (mysid shrimp, marine crustacean): Predicted LC50 (48-hr) Deficiency = 115 mg/l; Excess = 790 mg/l (1).

Fish

Puntius conchonius (freshwater fish): LC50 (24 - 96 hr.) = 368.5 mg/L; concentrations resulted in elevated blood glucose, and decreased amino acid nitrogen, muscle water content erythrocyte count, and hemoglobin (4)

Pimephales promelas (fathead minnow, freshwater fish): LOEC (7-day, survival) = 1,000 mg/L (5)

Pimephales promelas (fathead minnow, freshwater fish) NOEC (7-day, survival) = 500 mg/L (5)

Pimephales promelas (fathead minnow, freshwater) LOEC (7-day, growth) = 500 mg/L(5)

Risk Characterization

Most of the toxicity data found for potassium chloride is not directly relevant to this study. One reference is to studies done in drilling mud, and all but one of the others are tests on freshwater species. Pillard et al. (2000) gives relevant data for a marine species. Since potassium is an essential nutrient for some marine species, his work determined both deficiency toxicity and excess toxicity for potassium ion. The deficiency toxicity is not relevant here. The excess toxicity reported is 790 mg/l (approximately 790 ppm or 790,000 ppb). Using this concentration and the results report in Table 42 it is apparent that the lowest predicted exposure concentration in any unit grid cell area would be at least three orders of magnitude lower than the toxic concentration.

References

(1) Pillard (2000)
(2) CRC Handbook of Chemistry and Physics (1985-1986)
(3) Mallinckrodt Baker Inc. (1999b)
(4) Pant and Gill (1984)
(5) Pickering et al. (1996)
(6) Jones et al. (1986)

Table 42

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 3. Dissolved concentration of potassium chloride in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	316,832,480	2,227,764,992	10,042	26,629
10	50,589,980	451,412,000	4,013	11,987
100	5,513,003	86,911,128	1,325	5,260
1,000	-	5,837,298	-	1,363
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 43

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 mg/m^3-hours (0.01 ppb-hours): Scenario 3. Dissolved concentration of potassium chloride in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	2.65E+08	2.51E+08	1.84E+09	7.91E+07	0
10H-100H	0.1-1.0	1.12E+09	9.81E+08	6.31E+09	3.64E+08	0
100H-1,000H	1.0-10.0	3.63E+09	1.58E+09	9.16E+09	1.76E+09	0
1,000H-10,000H	10.0-100.0	2.39E+09	8.49E+08	5.92E+09	9.33E+08	0
10,000H-100,000H	100.0-1,000.0	3.19E+08	1.38E+08	1.00E+09	1.18E+08	0
100,000H-10^6H	1,000-10,000	1.47E+07	3.07E+06	2.43E+07	7.62E+06	0
10^7H-10^8H	10,000-100,000	1.29E+07	4.18E+06	2.67E+07	5.44E+06	0
10^8H-10^9H	100,000-1,000,000	3.22E+06	1.30E+06	6.64E+06	7.92E+05	0
> 10^9H	> 1,000,000	3.65E+05	8.42E+04	5.82E+05	1.51E+05	0
> 1H	> 0.01	7.75E+09	2.58E+09	1.76E+10	4.90E+09	0
> 10H	> 0.1	7.48E+09	2.42E+09	1.64E+10	4.75E+09	0
> 100H	> 1.0	6.36E+09	1.74E+09	1.22E+10	4.20E+09	0
> 1,000H	> 10.0	2.74E+09	9.27E+08	6.33E+09	1.14E+09	0
> 10,000H	> 100.0	3.50E+08	1.40E+08	1.04E+09	1.51E+08	0
> 100,000H	> 1,000.0	3.12E+07	6.44E+06	5.35E+07	1.65E+07	0
> 1,000,000H	> 10,000	1.65E+07	5.56E+06	3.39E+07	6.38E+06	0
> 10,000,000H	> 100,000	3.59E+06	1.38E+06	7.23E+06	9.43E+05	0
> 100,000,000H	> 1,000,000	3.65E+05	8.42E+04	5.82E+05	1.51E+05	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

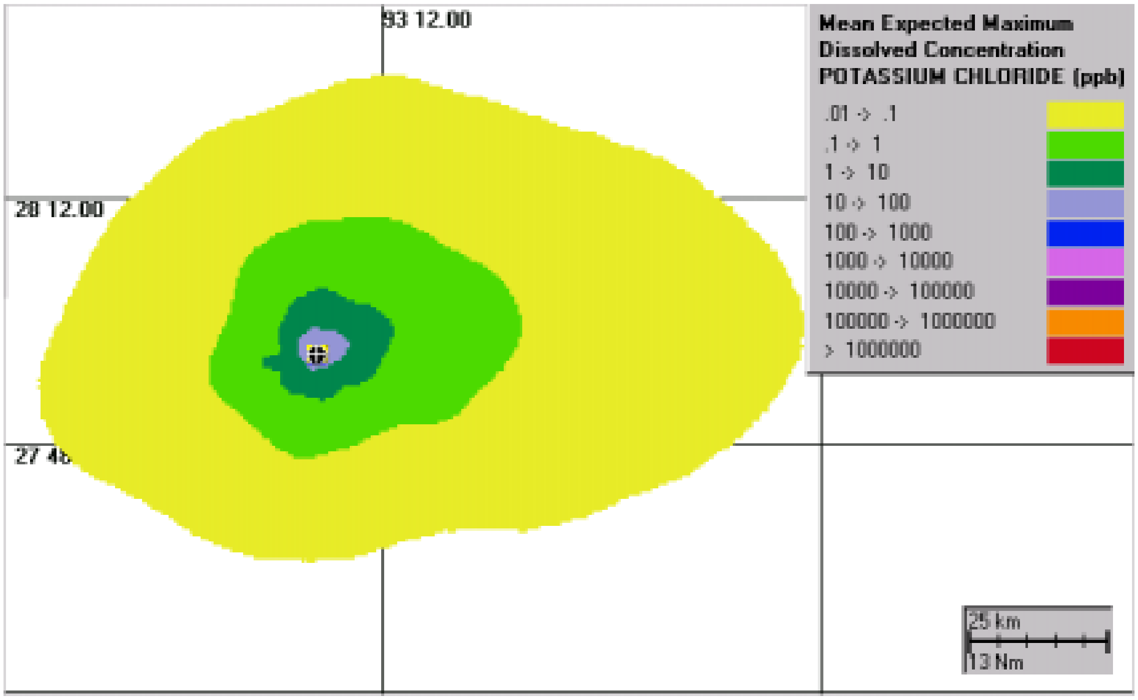


Figure 35. Peak exposure concentration (ppb) of potassium chloride dissolved in water at each location: averaged over all simulations (Scenario 3).

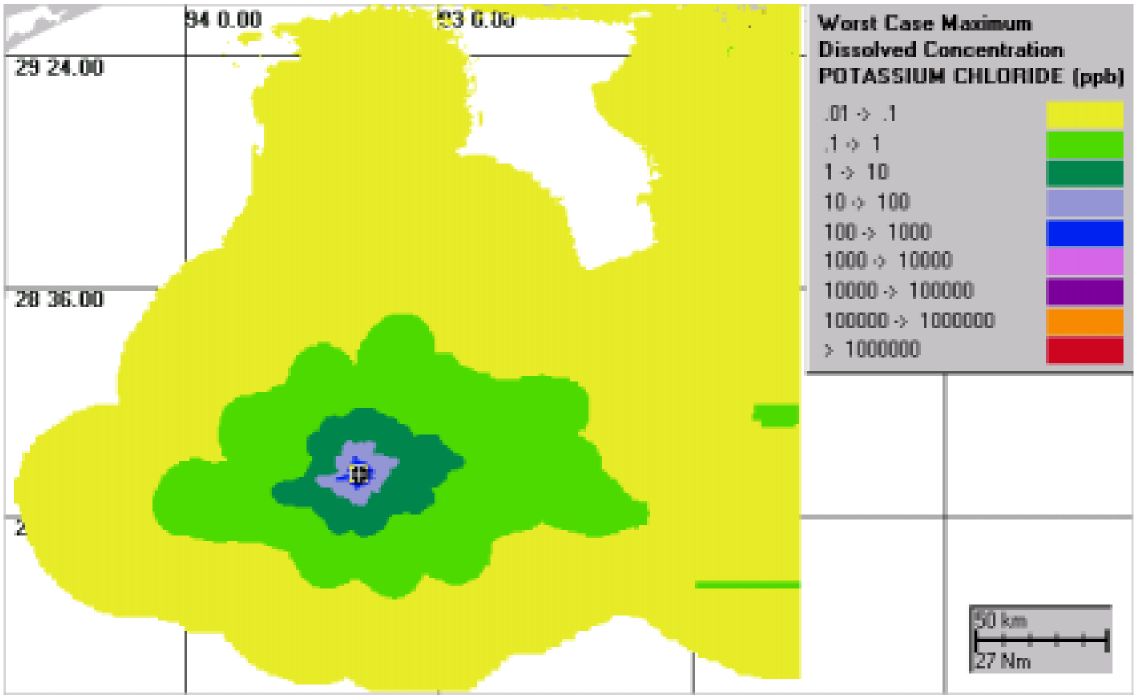


Figure 36. Peak exposure concentration (ppb) of potassium chloride dissolved in the water at each location: worst case of all simulations (Scenario 3).

Profile 12

AMIDES / IMIDAZOLINES (Component of Product B)

Summary

Product B is an oil-soluble mixture containing an amide/imidazoline, which comprises less than 5% of Product B. Product B is a production-treating chemical used to control corrosion in production gathering and treatment systems. If discharged to the marine environment, it will ultimately be removed by biological degradation. A lack of aquatic toxicity data preclude conclusions about the possible toxic impacts of amides/imidazolines.

Background Information

Fate in the Environment

Imidazolines are nitrogen containing organic compounds with a five-member ring structure. Amides are organic compounds containing a carbon double bonded to an oxygen and bonded to an $-NH_2$ radical. These functional groups are frequently in the same molecule for compounds used as corrosion inhibitors. They may be soluble in either water/alcohol mixtures or in an organic solvent. When spilled in seawater, Product B solution will spread on the water surface and the hydrocarbon solvent portion of the product will either evaporate or be dispersed in the water column, separating from the amine compound. Once separated from the solvent, the amine component will be dispersed in the water column as liquid droplets or will dissolve in the water. Oceanographic and meteorological forces will disperse it through the water column and the magnitude of these forces determines how rapidly amides/imidazolines spread through the water column. Ultimately, the amide/imidazoline component will be removed from the environment through biological degradation. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Product B is used in produced streams and treatment vessels to protect against corrosion. It will mix with the oil phase and be distributed throughout the system. It is designed to adsorb to the internal surfaces of piping and vessels, react with active corrosion sites, and form a protective layer. Residual amounts of it will disperse into the produced water, but the majority of it will leave the system in the crude oil sales line. Therefore, produced waters will contain residual concentrations of amide/imidazoline compounds, and the produced waters containing the residual treating chemical may either be discharged to the marine environment or injected under ground for disposal.

Other Components

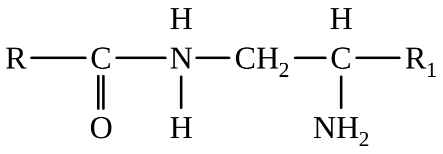
Heavy Aromatic Naphtha, Isopropyl Alcohol, Ethoxylated Amine, Fatty Acid Dimers, and Polyglycol

CAS Number (Amides/Imidazolines)

NA

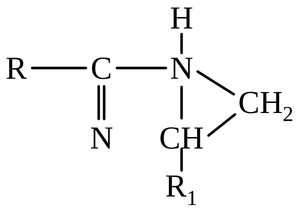
Chemical Formula (Amides/Imidazolines)

Amide



$$R-\underset{\overset{\|}{O}}{C}-\overset{H}{\underset{H}{N}}-CH_2-\overset{H}{\underset{NH_2}{C}}-R_1$$

Imidazoline



This varies with the specific compound. The basic imidazoline structure is a five-membered ring containing two nitrogen atoms that are attached to two of the bonds of a carbon atom between them. One of the nitrogen atoms may also be bonded to a carbonyl group. The ring also has an alkyl radical attached.

Important Synonyms and Trade Names

NA

Chemical and Physical Properties

Property	Component	Product [(1)]
Molecular Weight	NA	NA
Boiling Point	NA	ND
Melting Point	NA	ND
Specific Gravity	NA	0.918 @ 60° F
Solubility in Water	NA	Insoluble
Solubility in Organics	Soluble in alcohols and hydrocarbons	Soluble in oil
Vapor Pressure	NA	1.144 psia (Reid)
Vapor Density (Air = 1)	NA	> 1
Physical State (Phase)	NA	Dark brown liquid with aromatic odor
Viscosity	NA	NA
Chemical Reactivity in the Environment	None	None

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component	Product [(1)]
Autoignition Temperature	NA	NA
Flash Point	NA	32º C
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity	NA	NA
OSHA PEL	NA	NA

Notes: NA = Not Available

No health hazards were found for the component; however, the formulation that carries this material contains alcohols and aromatic solvents that have potential health and safety effects to human health. See Appendix B for Product MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 550 gal.
Maximum = 3,000 gal.

Transport Container(s): 55 gal. drums, 500 gal. HDPP plastic totes.

Storage Methods: In shipping containers or steel or plastic bulk tanks on the production platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Amide/Imidazoline compounds in Product B were modeled as part of Scenario 15t. The total concentrations of all ingredients in Product B, including amides/imidazolines and amines, were modeled together. It is assumed that these materials behave similarly in the environment. The amides/imidazolines portion is approximately 60% of the total concentration of amine-amide/imidazoline ingredients, which in turn were assumed in the modeling as 30% of the total product. The exposure concentrations presented below are derived from the results of model scenario 15t (see Section 7.8) by applying a factor 0.18 to the resulting concentrations. See discussion of spill modeling for Product B above.

The amides/imidazolines are highly surface active (as are the compounds in naphtha), and would predominantly exist as particulates, either alone (as suspended droplets) or adsorbed to suspended sediments. Because suspended sediment concentrations in the open Gulf of Mexico are low, most of the mass remains as “droplets.” Thus, concentrations for amides/imidazolines are shown in scenario 15t (droplets) in Tables 44 and 47.

Aquatic Toxicity Levels

The available literature for amide/imidazoline toxicity was reviewed. No data were found except that presented for amides/imidazolines by Hudgins. (2)

Algae and Invertebrates

Unspecified crustacean: LC50 = 2.0 ppm (96-hr). (2)

Risk Characterization

Only one source of toxicity data was found for amides/imidazolines. A toxicity of 2.0 ppm (2,000 ppb) was reported. After adjusting the modeled concentrations for scenario 15t by a factor of 0.18 (the fraction of the chemical that was amides/imidazolines) and comparing the resulting concentrations to the reported toxicity value, it is apparent that less than one unit grid cell area would contain exposure concentrations exceeding 180 ppb (listed as 1,000 ppb of total Product B in Table 44), even under worst case environmental conditions. Table 47 shows dose or integrations of concentration over time. The toxicity test found a 50% lethal concentration of 2,000 ppb for a 96-hr exposure. The 50% lethal dose was 2,000 x 96 = 192,000 ppb-hrs. This dose is not exceeded over a grid cell area (Table 47).

References

(1) Supplier's MSDS for Product B (See Appendix B)
(2) Hudgins and Petrotech Consultants, Inc. (1991)

Table 44

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 15t. Concentration of amides/imidazolines in naphtha (modeled as naphthalene) as droplets in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	143,338,400	1,039,346,176	6,755	18,189
10	19,781,944	217,600,352	2,509	8,323
100	1,621,471	33,726,588	718	3,277
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 45

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 15t. Dissolved concentration of amides/imidazolines in naphtha (modeled as naphthalene) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	2,918,648	145,932,704	964	6,816
10	-	5,513,003	-	1,325
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 46

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 15t. Concentration of amides/imidazolines in naphtha (modeled as naphthalene) adsorbed to suspended sediments in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	-	45,401,244	-	3,802
10	-	324,294	-	321
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 47

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 15t. Particulate concentration of amides/imidazolines in naphtha (modeled as naphthalene) in all subtidal habitats.

Exposure Range	**Dose (1) (ppb-hours)**	**Mean (m^2)**	**Std. Dev. (m^2)**	**Maximum (m^2)**	**Minimum (m^2)**	**% runs @ 0**
1H-10H	0.01-0.1	6.58E+07	3.56E+07	1.96E+08	1.65E+07	0
10H-100H	0.1-1.0	4.48E+08	1.87E+08	1.04E+09	1.74E+08	0
100H-1,000H	1.0-10.0	1.03E+09	2.51E+08	1.77E+09	6.29E+08	0
1,000H-10,000H	10.0-100.0	5.23E+08	1.52E+08	1.03E+09	3.17E+08	0
10,000H-100,000H	100.0-1,000.0	8.50E+07	2.59E+07	2.11E+08	3.53E+07	0
100,000H-10^6H	1,000-10,000	9.33E+06	2.19E+06	1.56E+07	5.19E+06	0
10^7H-10^8H	10,000-100,000	1.12E+06	4.48E+05	1.84E+06	4.32E+05	0
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	2.16E+09	4.64E+08	3.55E+09	1.32E+09	0
> 10H	> 0.1	2.09E+09	4.40E+08	3.36E+09	1.28E+09	0
> 100H	> 1.0	1.65E+09	3.20E+08	2.51E+09	1.10E+09	0
> 1,000H	> 10.0	6.18E+08	1.58E+08	1.13E+09	4.01E+08	0
> 10,000H	> 100.0	9.55E+07	2.53E+07	2.20E+08	4.51E+07	0
> 100,000H	> 1,000.0	1.05E+07	2.00E+06	1.65E+07	6.49E+06	0
> 1,000,000H	> 10,000	1.12E+06	4.48E+05	1.84E+06	4.32E+05	0
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 48

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 15t. Dissolved concentration of amides/imidazolines in naphtha (modeled as naphthalene) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	3.96E+07	2.67E+07	1.26E+08	3.24E+05	0
10H-100H	0.1-1.0	2.85E+08	1.92E+08	1.08E+09	6.10E+07	0
100H-1,000H	1.0-10.0	7.32E+08	3.04E+08	1.61E+09	2.50E+08	0
1,000H-10,000H	10.0-100.0	1.92E+08	8.21E+07	4.61E+08	6.00E+07	0
10,000H-100,000H	100.0-1,000.0	7.36E+06	4.87E+06	2.85E+07	9.73E+05	0
100,000H-10^6H	1,000-10,000	2.57E+05	5.42E+05	3.89E+06	0	79
10^7H-10^8H	10,000-100,000	3.85E+04	2.07E+05	1.95E+06	0	97
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	1.26E+09	5.12E+08	2.99E+09	4.50E+08	0
> 10H	> 0.1	1.22E+09	4.92E+08	2.90E+09	4.34E+08	0
> 100H	> 1.0	9.32E+08	3.34E+08	2.03E+09	3.53E+08	0
> 1,000H	> 10.0	2.00E+08	8.46E+07	4.72E+08	6.16E+07	0
> 10,000H	> 100.0	7.65E+06	4.79E+06	2.85E+07	9.73E+05	0
> 100,000H	> 1,000.0	2.95E+05	5.65E+05	3.89E+06	0	79
> 1,000,000H	> 10,000	3.85E+04	2.07E+05	1.95E+06	0	97
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 49

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 15t. Concentration of amides/imidazolines in naphtha (modeled as naphthalene) adsorbed to suspended sediments in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	2.79E+06	1.61E+07	1.17E+08	0	93
10H-100H	0.1-1.0	1.96E+07	8.53E+07	5.19E+08	0	91
100H-1,000H	1.0-10.0	4.82E+07	1.84E+08	1.01E+09	0	50
1,000H-10,000H	10.0-100.0	5.93E+07	2.04E+08	1.36E+09	0	47
10,000H-100,000H	100.0-1,000.0	8.96E+07	1.58E+08	9.09E+08	0	47
100,000H-10^6H	1,000-10,000	7.53E+06	3.07E+07	2.13E+08	0	85
10^7H-10^8H	10,000-100,000	2.98E+07	1.06E+08	7.35E+08	0	85
10^8H-10^9H	100,000-1,000,000	5.60E+07	1.22E+08	8.27E+08	0	85
> 10^9H	> 1,000,000	1.13E+09	1.14E+09	2.82E+09	0	85
> 1H	> 0.01	1.44E+09	1.39E+09	4.25E+09	0	47
> 10H	> 0.1	1.44E+09	1.38E+09	4.24E+09	0	47
> 100H	> 1.0	1.42E+09	1.36E+09	4.14E+09	0	47
> 1,000H	> 10.0	1.37E+09	1.33E+09	3.63E+09	0	47
> 10,000H	> 100.0	1.31E+09	1.29E+09	3.17E+09	0	47
> 100,000H	> 1,000.0	1.22E+09	1.22E+09	2.94E+09	0	85
> 1,000,000H	> 10,000	1.21E+09	1.36E+09	4.38E+09	0	85
> 10,000,000H	> 100,000	1.18E+09	1.26E+09	3.65E+09	0	85
> 100,000,000H	> 1,000,000	1.13E+09	1.14E+09	2.82E+09	0	85

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

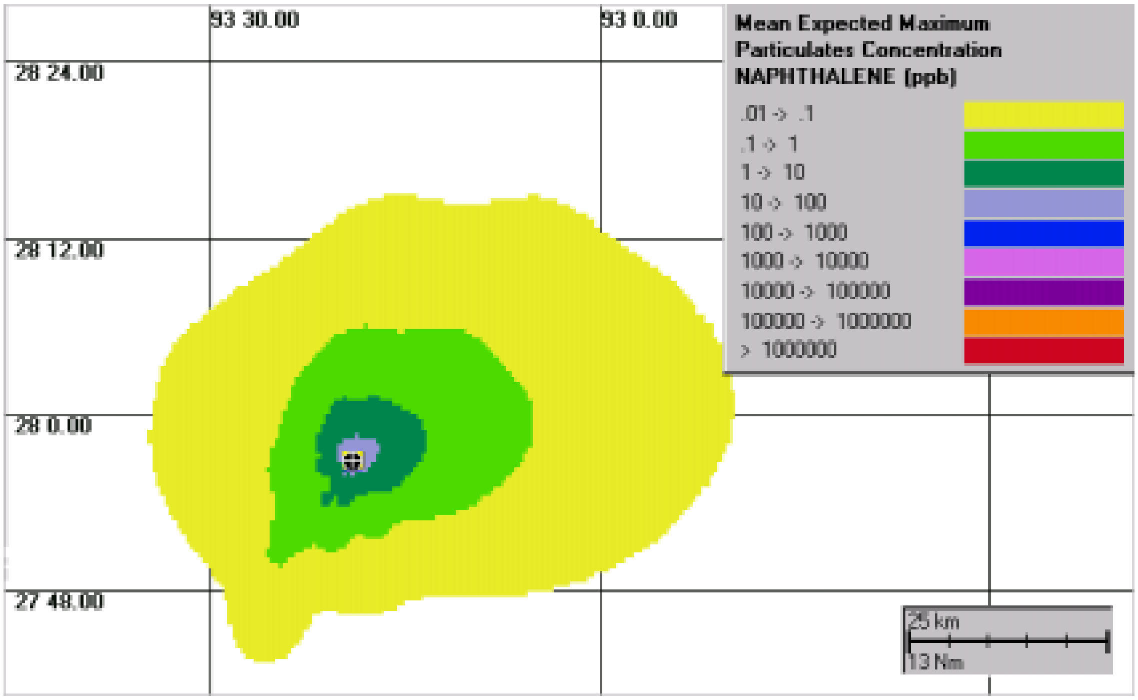


Figure 37. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) as pure liquid droplets at each location: averaged over all simulations (Scenario 15t).

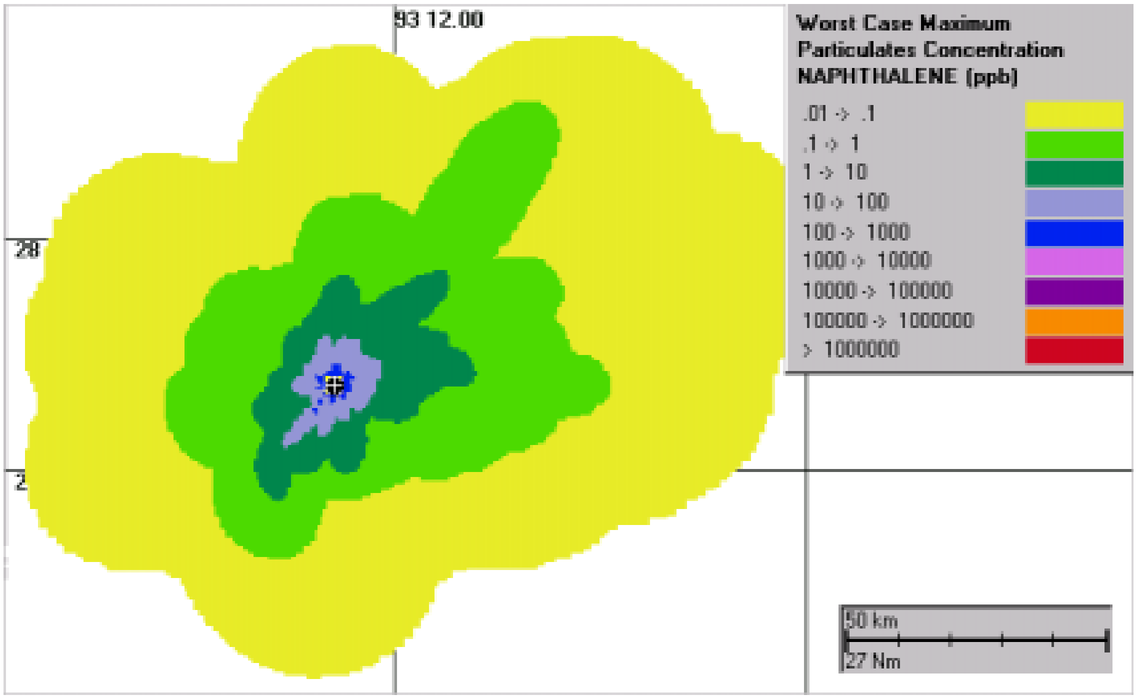


Figure 38. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) as pure liquid droplets in the water at each location: worst case of all simulations (Scenario 15t).

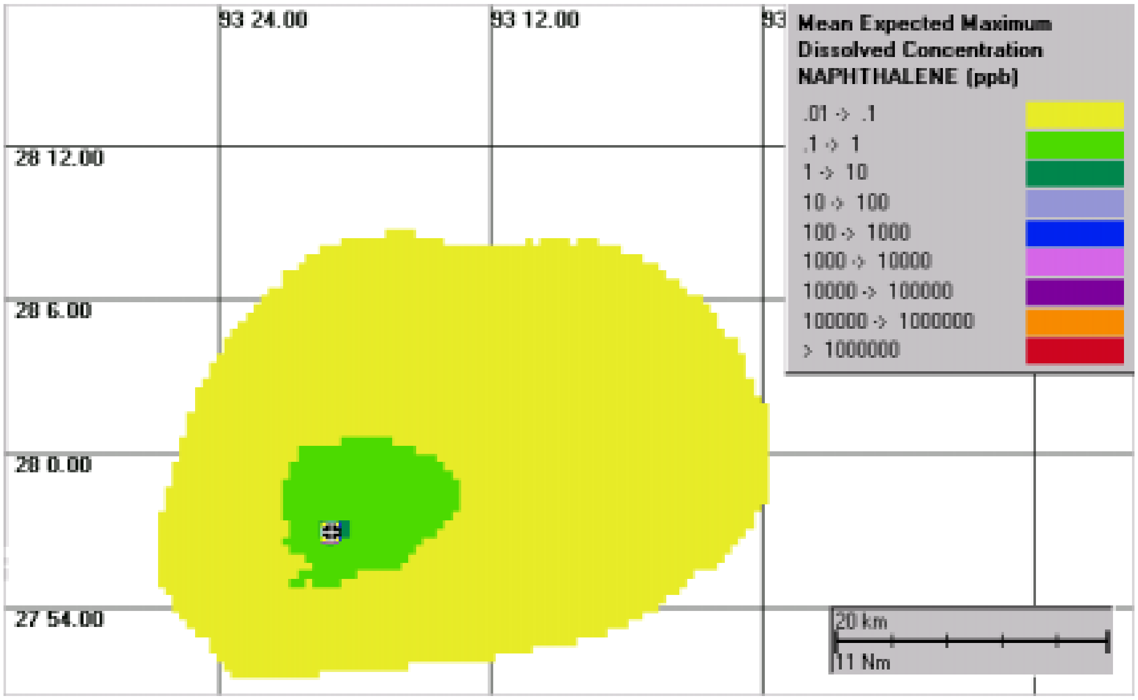


Figure 39. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) dissolved in the water at each location: averaged over all simulations (Scenario 15t).

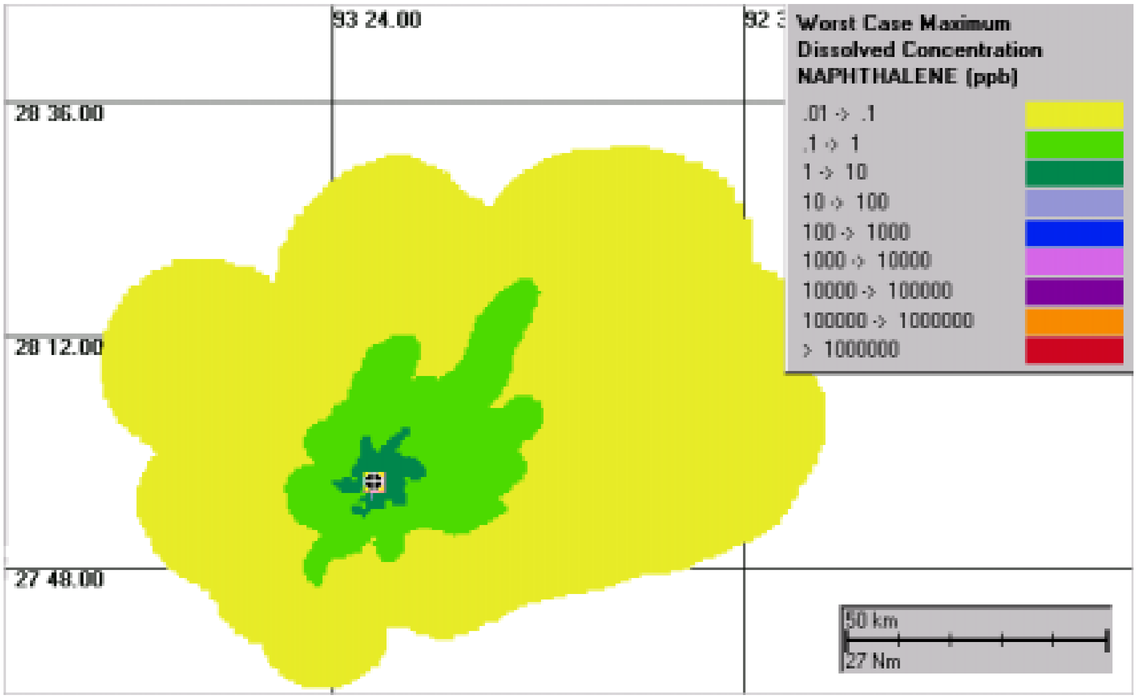


Figure 40. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) dissolved in the water at each location: worst case of all simulations (Scenario 15t).

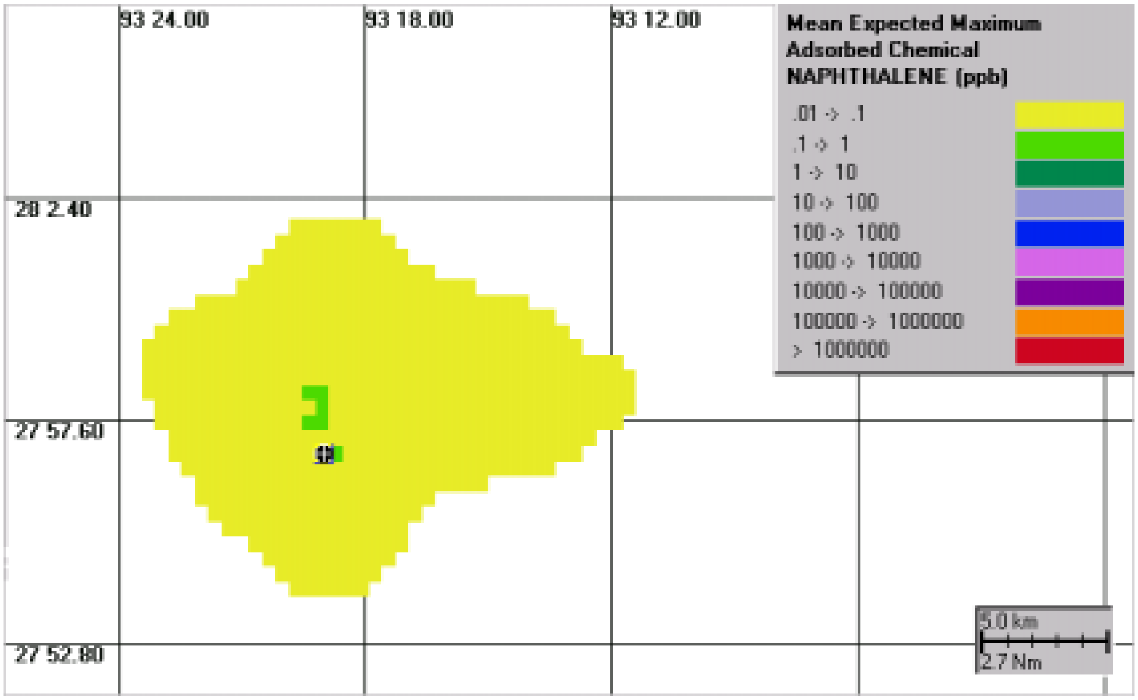


Figure 41. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) adsorbed to suspended sediment in the water at each location: averaged over all simulations (Scenario 15t).

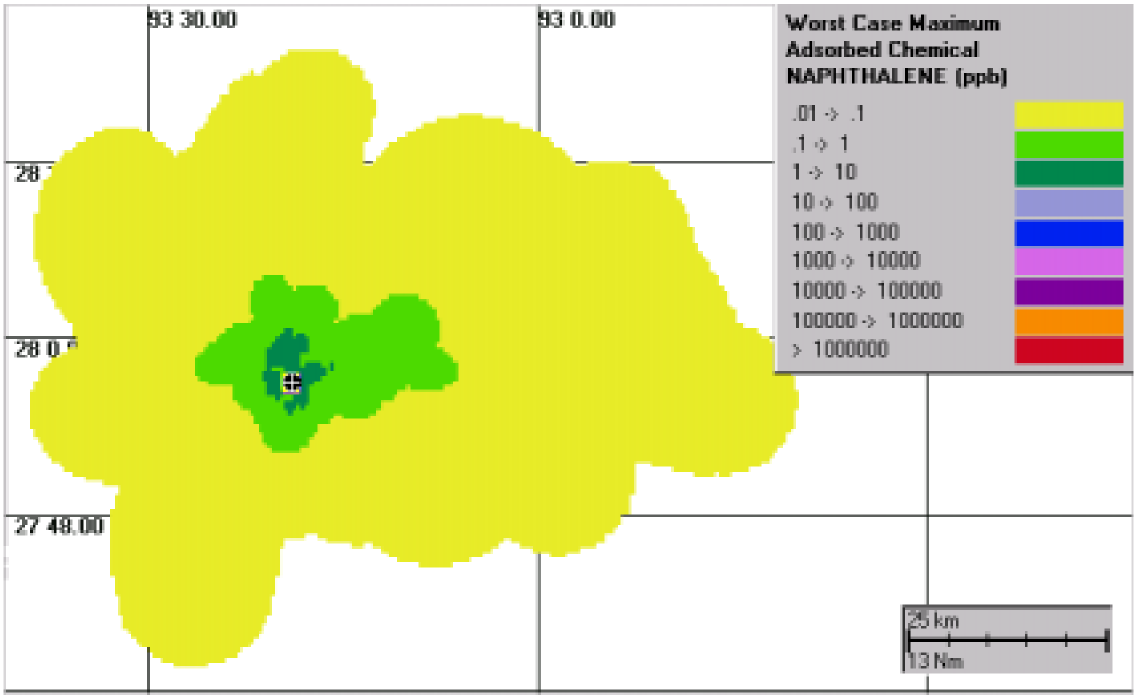


Figure 42. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) adsorbed to suspended sediment in the water at each location: worst case of all simulations (Scenario 15t).

Profile 13

AMINES AND AMINE SALTS (Component of Product B)

Summary

Product B is an oil-soluble mixture containing an amine, in this case an ethoxylated amine. It is a production-treating chemical used to control corrosion in production gathering and treatment systems. An ethoxylated amine, one of the major active ingredients, is profiled here. The ethoxylated amine typically is less than 5% of the total product. If discharged to the marine environment, it will ultimately be removed by biological degradation. There are few environmental concerns associated with ethoxylated amines.

Background Information

Fate in the Environment

Amines and amine salts (the reaction product of an amine and an acid) are nitrogen-containing organic compounds, which are essentially ammonium compounds (NH_4^+) with one or more of the hydrogens replaced by organic radicals. They may be soluble in either water/alcohol mixtures or in an organic solvent. In Product B, the amine component contains an ethoxylated radical (a radical also containing carbon-oxygen bonds). When spilled in seawater, Product B solution will spread on the water surface and the hydrocarbon solvent portion of Product B (such as naphtha and alcohols) will either evaporate or be dispersed in the water column. When the solvent evaporates or dissolves the amine component will be dispersed in the water column as liquid droplets, or will be dissolved. Oceanographic and meteorological forces will disperse it through the water column and the magnitude of these forces determines how rapidly the amine component will spread through the water column. Ultimately, the amine component will be removed from the environment through biological degradation. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Product B is used in produced streams and treatment vessels to protect against corrosion. It will mix with the oil phase and be distributed throughout the system. It is designed to adsorb to the internal surfaces of piping and vessels, react with active corrosion sites, and form a protective layer. Residual amounts will disperse into the produced water but the majority will leave the system as part of the crude oil (i.e., commercially sold product). Therefore, produced waters will contain residual concentrations of amine and amine salt compounds. Produced waters containing the residual treating chemicals may either be discharged to the marine environment or injected under ground for disposal.

Other Components

Heavy Aromatic Naphtha, Isopropyl Alcohol, Amides/Imidazolines, Fatty Acid Dimers, and Polyglycol

CAS Number (Amines and Amine Salts)

Varies, one example (not a component of Product B) being diethylenetriamine 111-40-0

Chemical Formula (Amines)

$CH_3(CH_2)_{11}NH_2$

Important Synonyms and Trade Names

NA

Chemical and Physical Properties

Property	Component	Product [(1)]
Molecular Weight	NA	NA
Boiling Point	NA	ND
Melting Point	NA	ND
Specific Gravity	NA	0.918 @ 60° F
Solubility in Water	NA	Insoluble
Solubility in Organics	Soluble in alcohols and hydrocarbons	Soluble in oil
Vapor Pressure	NA	1.144 psia (Reid)
Vapor Density (Air = 1)	NA	> 1
Physical State (Phase)	NA	Dark brown liquid with aromatic odor
Viscosity	NA	NA
Chemical Reactivity in the Environment	None	None

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component	Product [(1)]
Autoignition Temperature	NA	NA
Flash Point	NA	32º C
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity	NA	NA
OSHA PEL	NA	NA

Notes: NA = Not Available

No health hazards were found for the component; however, the formulation that carries this material contains alcohols and aromatic solvents that have potential health and safety effects to human health. See Appendix B for Product MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 550 gal.
Maximum = 3,000 gal.

Transport Container(s): 55 gal. drums, 500 gal. HDPP plastic totes.

Storage Methods: In shipping containers or steel or plastic bulk tanks on the production platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Amine compounds in Product B were modeled as part of spill scenario 15t. The amine portion was approximately 5% of the total. The exposure concentrations presented below are derived from the results of this modeling. The use of the total concentrations to represent the concentrations of amines is a conservative approach. See discussion of spill modeling for Product B above.

The amines are highly surface active, active (as are the compounds in naphtha), and would predominantly exist as particulates, either alone (as suspended droplets) or adsorbed to suspended sediments. Because suspended sediment concentrations in the open Gulf of Mexico are low, most of the mass remains as “droplets.” Thus, concentrations for amines are shown in scenario 15t (droplets) in Tables 50 and 53.

Aquatic Toxicity Levels

The available literature for amine toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Mysidopsis bahia (mysid shrimp, marine crustacean): LC50 (96 hr.) = 29,000 to 78,000 ppm (2)

Fish

Oncorhynchus mykiss (rainbow trout, freshwater fish): LC50 (96 hr.) 271 to 779 µg/L (3)
Pimephales promelus (fathead minnow, freshwater fish): LC50 (96hr.) = 0.07-47,000 mg/L (4)

Benthos

Mytilus edulis (blue mussel, marine bivalve mollusk) LC50 (96-hr.) < 250 mg/L (5)
Mytilus edulis (blue mussel, marine bivalve mollusk) NOEL = 100 mg/L (5)
Crassostrea gigas (Japanese oyster, marine bivalve mollusk) LC50 (96-hr.) < 250 mg/L(5)
Crassostrea gigas (Japanese oyster, marine bivalve mollusk) NOEL = 100 mg/L (5)

Risk Characterization

The lowest toxic concentration for marine species was found to be for benthic species exposed to concentrations in water; 250 mg/l (approximately 250 ppm or 250,000 ppb) as 96-hr LC50s for two species. Particulate (droplet) concentrations in the water (Table 50) did not exceed 50 ppb and sediment concentrations did not exceed 100 ppb (total Product B) over any unit grid cell area. These results show that the modeled concentrations are more than three orders of magnitude lower than the lowest toxic concentration.

References

(1) Supplier's MSDS for Product B (See Appendix B)
(2) Jones et al. (1986)
(3) Goodrich et al. (1991)
(4) Newsome et al. (1991)
(5) Knezovich and Crosby (1985)

Table 50

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 15t. Concentration of amides/imidazolines in naphtha (modeled as naphthalene) as droplets in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	143,338,400	1,039,346,176	6,755	18,189
10	19,781,944	217,600,352	2,509	8,323
100	1,621,471	33,726,588	718	3,277
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 51

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 15t. Dissolved concentration of amides/imidazolines in naphtha (modeled as naphthalene) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	2,918,648	145,932,704	964	6,816
10	-	5,513,003	-	1,325
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 52

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 15t. Concentration of amides/imidazolines in naphtha (modeled as naphthalene) adsorbed to suspended sediments in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	-	45,401,244	-	3,802
10	-	324,294	-	321
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 53

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 15t. Particulate concentration of amides/imidazolines in naphtha (modeled as naphthalene) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	6.58E+07	3.56E+07	1.96E+08	1.65E+07	0
10H-100H	0.1-1.0	4.48E+08	1.87E+08	1.04E+09	1.74E+08	0
100H-1,000H	1.0-10.0	1.03E+09	2.51E+08	1.77E+09	6.29E+08	0
1,000H-10,000H	10.0-100.0	5.23E+08	1.52E+08	1.03E+09	3.17E+08	0
10,000H-100,000H	100.0-1,000.0	8.50E+07	2.59E+07	2.11E+08	3.53E+07	0
100,000H-10^6H	1,000-10,000	9.33E+06	2.19E+06	1.56E+07	5.19E+06	0
10^7H-10^8H	10,000-100,000	1.12E+06	4.48E+05	1.84E+06	4.32E+05	0
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	2.16E+09	4.64E+08	3.55E+09	1.32E+09	0
> 10H	> 0.1	2.09E+09	4.40E+08	3.36E+09	1.28E+09	0
> 100H	> 1.0	1.65E+09	3.20E+08	2.51E+09	1.10E+09	0
> 1,000H	> 10.0	6.18E+08	1.58E+08	1.13E+09	4.01E+08	0
> 10,000H	> 100.0	9.55E+07	2.53E+07	2.20E+08	4.51E+07	0
> 100,000H	> 1,000.0	1.05E+07	2.00E+06	1.65E+07	6.49E+06	0
> 1,000,000H	> 10,000	1.12E+06	4.48E+05	1.84E+06	4.32E+05	0
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 54

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 15t. Dissolved concentration of amides/imidazolines in naphtha (modeled as naphthalene) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	3.96E+07	2.67E+07	1.26E+08	3.24E+05	0
10H-100H	0.1-1.0	2.85E+08	1.92E+08	1.08E+09	6.10E+07	0
100H-1,000H	1.0-10.0	7.32E+08	3.04E+08	1.61E+09	2.50E+08	0
1,000H-10,000H	10.0-100.0	1.92E+08	8.21E+07	4.61E+08	6.00E+07	0
10,000H-100,000H	100.0-1,000.0	7.36E+06	4.87E+06	2.85E+07	9.73E+05	0
100,000H-10^6H	1,000-10,000	2.57E+05	5.42E+05	3.89E+06	0	79
10^7H-10^8H	10,000-100,000	3.85E+04	2.07E+05	1.95E+06	0	97
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	1.26E+09	5.12E+08	2.99E+09	4.50E+08	0
> 10H	> 0.1	1.22E+09	4.92E+08	2.90E+09	4.34E+08	0
> 100H	> 1.0	9.32E+08	3.34E+08	2.03E+09	3.53E+08	0
> 1,000H	> 10.0	2.00E+08	8.46E+07	4.72E+08	6.16E+07	0
> 10,000H	> 100.0	7.65E+06	4.79E+06	2.85E+07	9.73E+05	0
> 100,000H	> 1,000.0	2.95E+05	5.65E+05	3.89E+06	0	79
> 1,000,000H	> 10,000	3.85E+04	2.07E+05	1.95E+06	0	97
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 55

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 15t. Concentration of amides/imidazolines in naphtha (modeled as naphthalene) adsorbed to suspended sediments in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	2.79E+06	1.61E+07	1.17E+08	0	93
10H-100H	0.1-1.0	1.96E+07	8.53E+07	5.19E+08	0	91
100H-1,000H	1.0-10.0	4.82E+07	1.84E+08	1.01E+09	0	50
1,000H-10,000H	10.0-100.0	5.93E+07	2.04E+08	1.36E+09	0	47
10,000H-100,000H	100.0-1,000.0	8.96E+07	1.58E+08	9.09E+08	0	47
100,000H-10^6H	1,000-10,000	7.53E+06	3.07E+07	2.13E+08	0	85
10^7H-10^8H	10,000-100,000	2.98E+07	1.06E+08	7.35E+08	0	85
10^8H-10^9H	100,000-1,000,000	5.60E+07	1.22E+08	8.27E+08	0	85
> 10^9H	> 1,000,000	1.13E+09	1.14E+09	2.82E+09	0	85
> 1H	> 0.01	1.44E+09	1.39E+09	4.25E+09	0	47
> 10H	> 0.1	1.44E+09	1.38E+09	4.24E+09	0	47
> 100H	> 1.0	1.42E+09	1.36E+09	4.14E+09	0	47
> 1,000H	> 10.0	1.37E+09	1.33E+09	3.63E+09	0	47
> 10,000H	> 100.0	1.31E+09	1.29E+09	3.17E+09	0	47
> 100,000H	> 1,000.0	1.22E+09	1.22E+09	2.94E+09	0	85
> 1,000,000H	> 10,000	1.21E+09	1.36E+09	4.38E+09	0	85
> 10,000,000H	> 100,000	1.18E+09	1.26E+09	3.65E+09	0	85
> 100,000,000H	> 1,000,000	1.13E+09	1.14E+09	2.82E+09	0	85

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

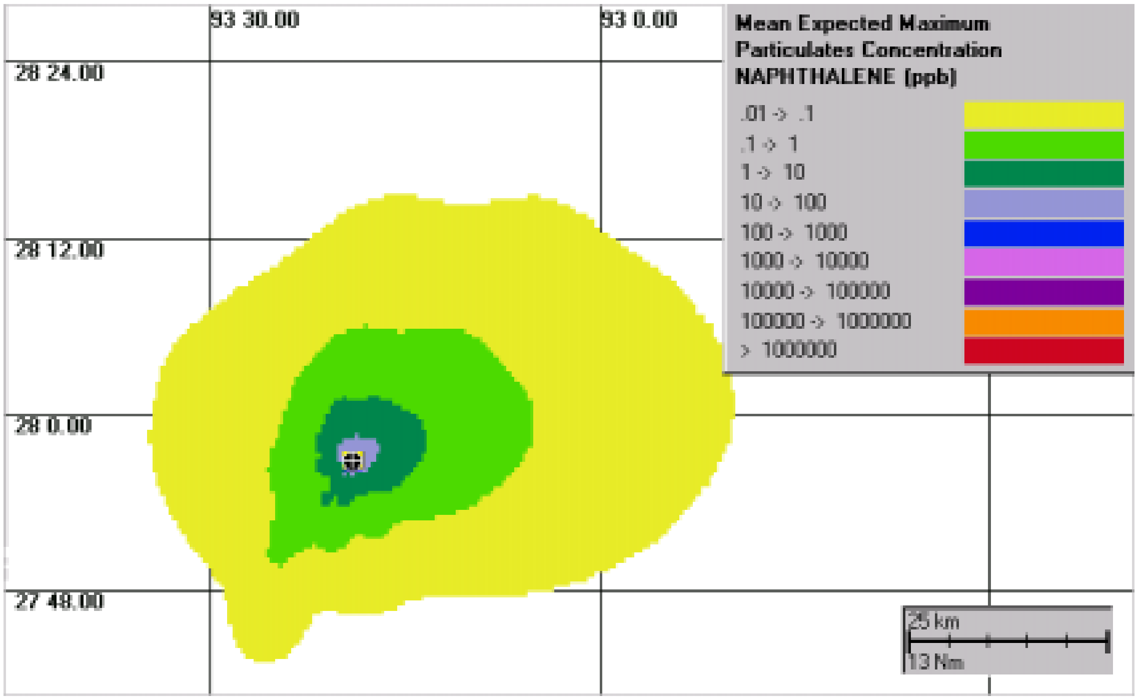


Figure 43. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) as pure liquid droplets at each location: averaged over all simulations (Scenario 15t).

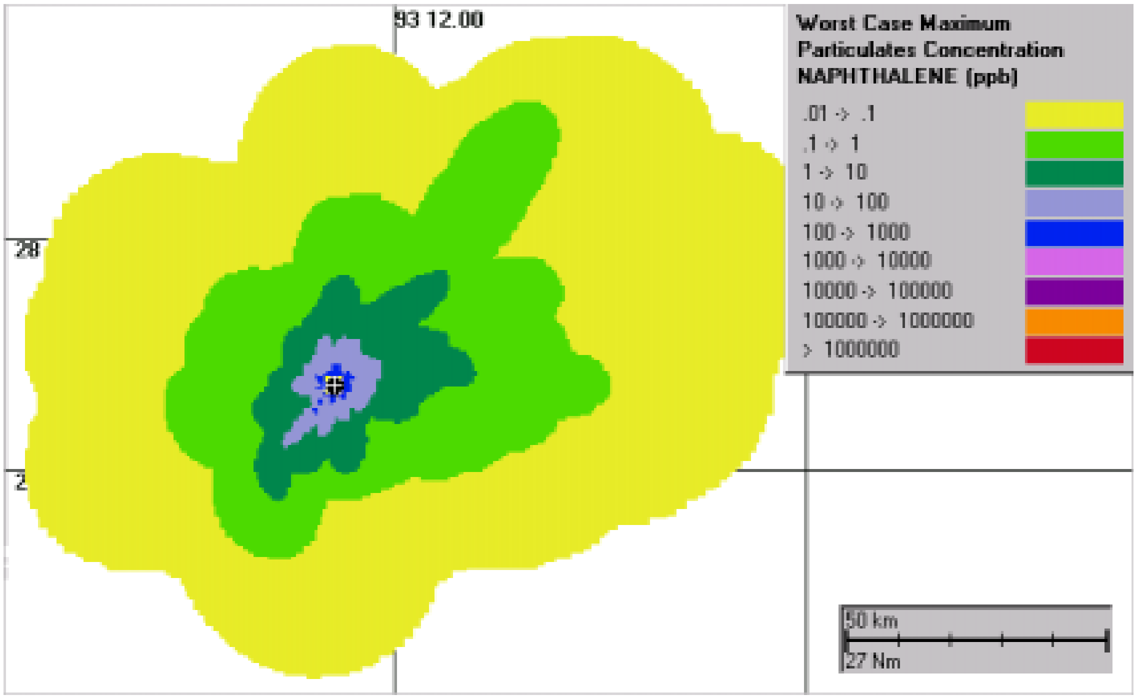


Figure 44. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) as pure liquid droplets in the water at each location: worst case of all simulations (Scenario 15t).

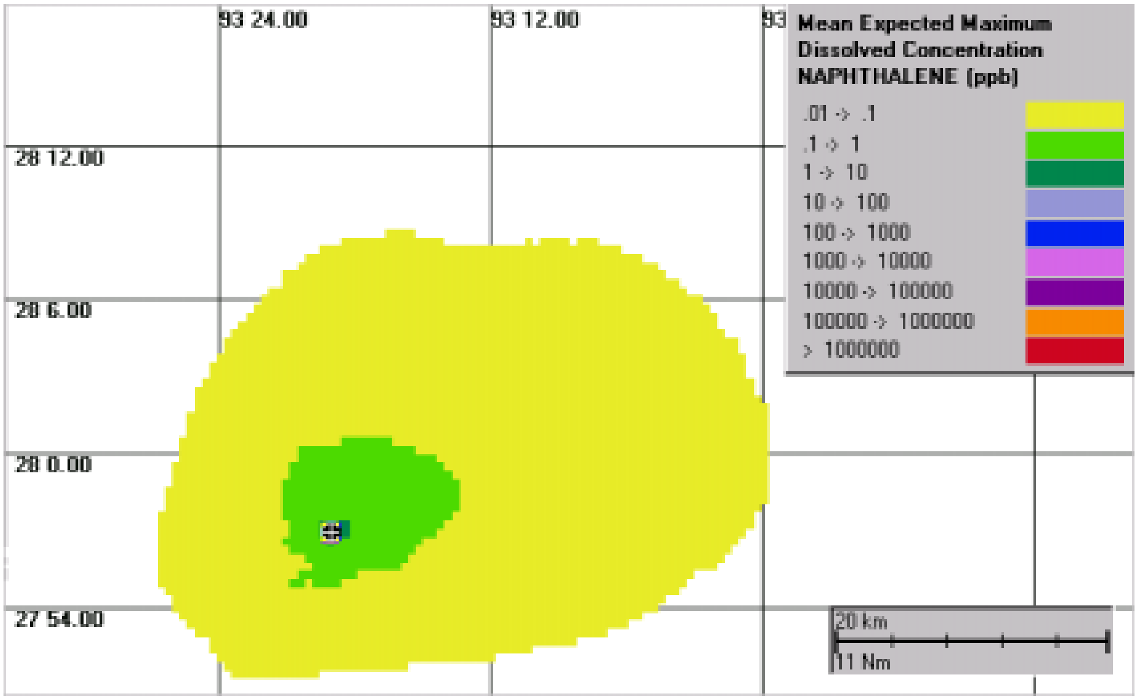


Figure 45. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) dissolved in the water at each location: averaged over all simulations (Scenario 15t).

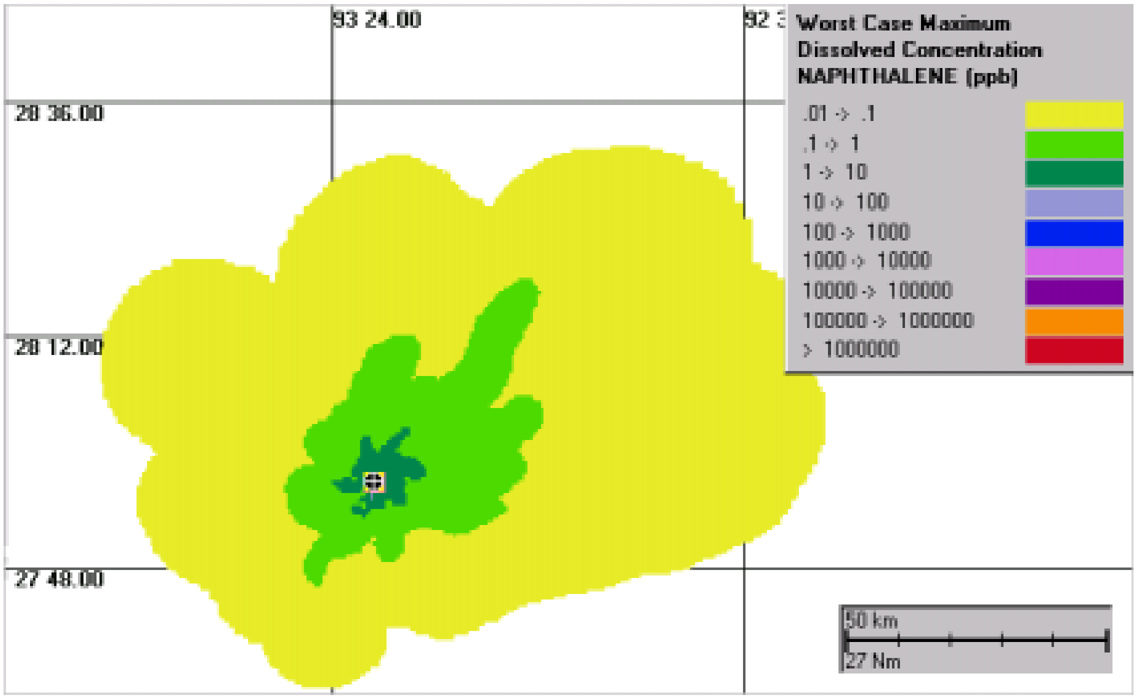


Figure 46. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) dissolved in the water at each location: worst case of all simulations (Scenario 15t).

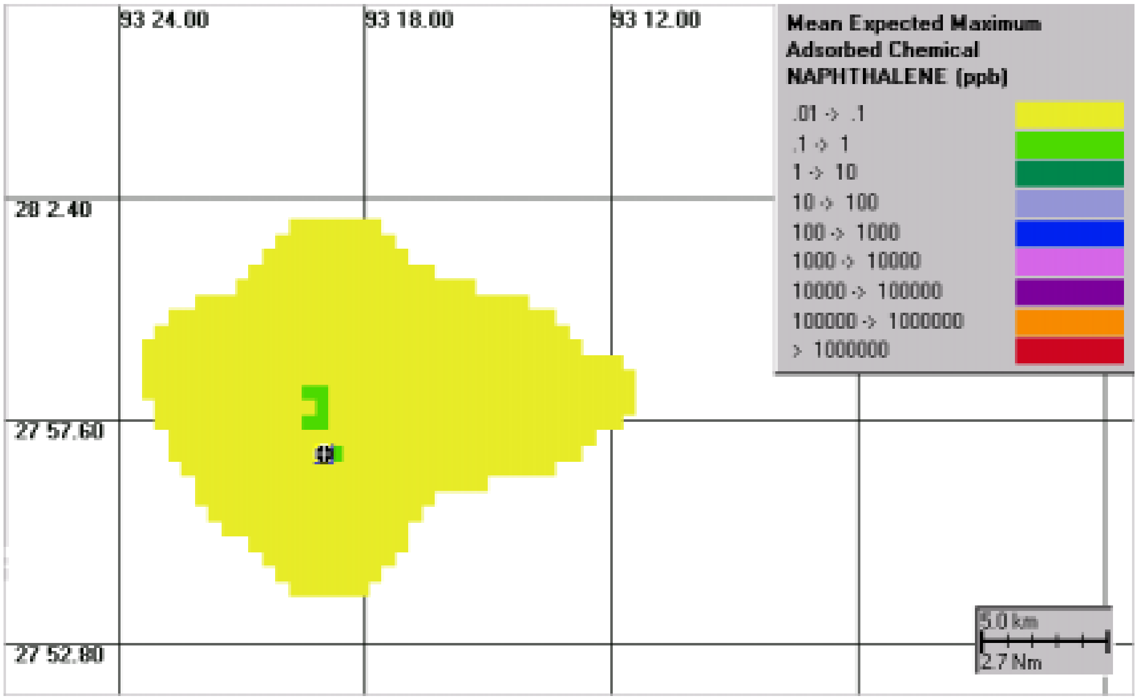


Figure 47. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) adsorbed to suspended sediment in the water at each location: averaged over all simulations (Scenario 15t).

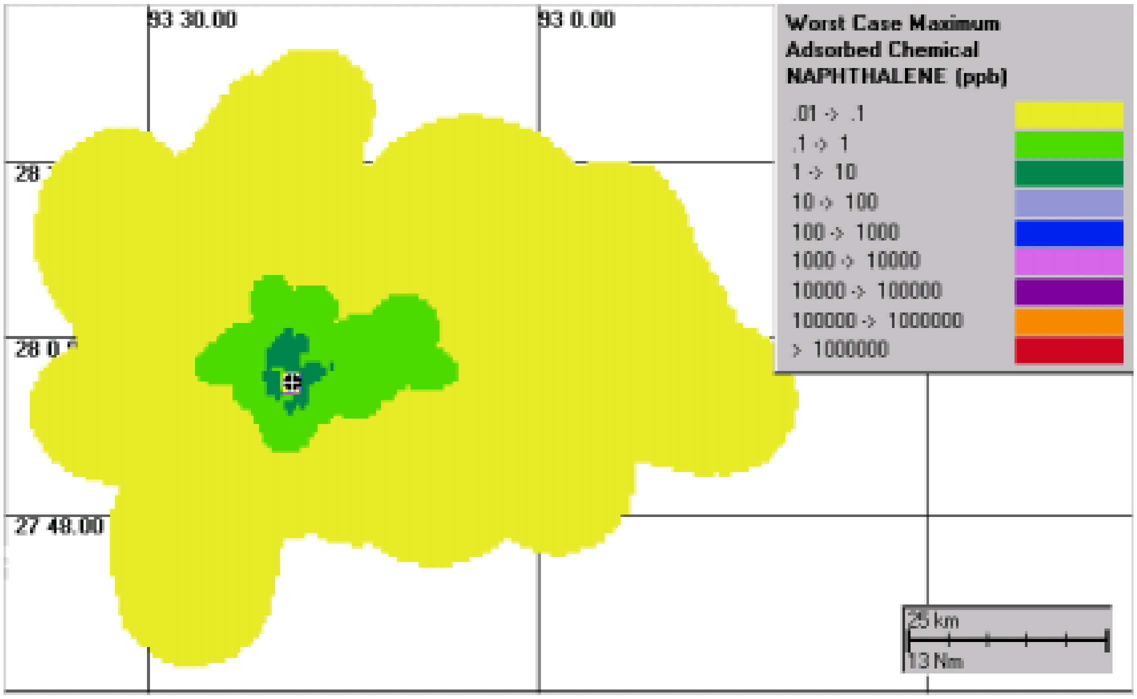


Figure 48. Peak exposure concentration (ppb) of amides/imidazolines (modeled as naphthalene) adsorbed to suspended sediment in the water at each location: worst case of all simulations (Scenario 15t).

Profile 14

LIGNITE (Single Component)

Summary

Lignite is a naturally occurring organic material used as a drilling fluid chemical. It is used as a filtrate reducer, a temperature stability agent, and a dispersant. If discharged to the marine environment, it will ultimately be removed by biological degradation.

Background Information

Fate in the Environment

Lignite is a naturally occurring organic material resulting from prehistoric decomposition of plant material that also contains some clay and silica impurities. It is supplied as a very fine powder material. If it is discharged into the marine environment in its pure form, it will disperse into the water column. It is not water soluble at low pH values, but is soluble at up to 20-22% in water depending on the source of the lignite at pH values above 8. Thus, the solubility is pH dependent, with more lignite dissolving at higher pH values. Once lignite is diluted enough in seawater, the normal seawater pH (i.e., normal range of 8 to 8.2) will dissolve it.

Fate in the Process System

Lignite is a component of water-based drilling fluids. Such fluids usually are formulated with pH values of 10 or higher, so that the lignite goes into solution. As an offshore well is drilled, drilling fluid is lost in one of three ways: (1) clinging to bits of formation (i.e., cuttings) removed from the well which are then disposed of; (2) as excess drilling fluid that is disposed during the drilling operation; or (3) when the well drilling has been completed, and all the remaining drilling fluid is disposed of. Outside the territorial seas, waste drilling fluids are discharged to the sea. Inside the territorial seas, waste drilling fluids are captured and sent ashore for disposal (i.e., to landfills).

Other Components

None

CAS Number (Lignite)

1415-93-6

Chemical Formula (Lignite)

No proven structure. A complex mixture of partially unsaturated structures containing oxygen and nitrogen functional groups.

Important Synonyms and Trade Names

Humic Acid

Chemical and Physical Properties

Property	Component [(1), (2)]	Product
Molecular Weight	Unknown	Same as Component
Boiling Point	ND	Same as Component
Melting Point	ND	Same as Component
Specific Gravity	1.6-1.8 @68° F	Same as Component
Solubility in Water	Insoluble	Same as Component
Solubility in Organics	NA	Same as Component
Vapor Pressure	NA	Same as Component
Vapor Density (Air = 1)	NA	Same as Component
Physical State (Phase)	Solid powder	Same as Component
Chemical Reactivity in the Environment	Biodegrades	Same as Component

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component	Product
Autoignition Temperature	ND (1)	Same as Component
Flash Point	309° C (PM closed cup) (1)	Same as Component
Upper Explosive Limit	ND (1)	Same as Component
Lower Explosive Limit	ND (1)	Same as Component
Air Toxicity	2 mg/m^3 TWA (1)	Same as Component
OSHA PEL	NA	Same as Component

Notes: NA = Not Available; ND = Not Determined

Health hazards for this chemical are related to the fact that it is a fine powder that can cause irritation to the skin, eyes, and throat. Explosive dust and air mixtures are possible. See Appendix B for MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 100,000 lbs.
Maximum = 150,000 lbs.

Transport Container(s): 50 lb. paper sacks on pallets.

Storage Methods: In sacks on pallets (usually in drilling rig mud room).

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

A lignite spill was modeled as Scenario 8. The exposure concentrations presented below are derived from the results of this modeling.

Results are shown in Figures 49 to 54 and Tables 56 to 61. Lignite is spilled as particulate, and takes some time to dissolve. Thus, both particulate and dissolved concentrations are of interest. Particulate also settles to the sediments, predominantly east and west of the spill site (along-shelf direction).

The extension to the southwest of the main concentration area is caused by a single rare event of southwest-directed current, which catches only a few Lagrangian particles representing the spilled mass in the model.

Aquatic Toxicity Levels

The available literature for lignite toxicity was reviewed and the results from relevant studies are shown below. The only literature found included data on lignite in a mud formulation, where the toxicity of lignite was calculated from mud component, matrix studies. (3)

Algae and Invertebrates

Mysidopsis bahia (marine shrimp): LC50 (96-hr. SPP test) = 163,000 to 654,000 ppm of processed lignite; concentrations of 3-10 lbs. per barrel in EPA mud 2,3,7,8. (3)
Mysidopsis bahia (marine shrimp): LC50 (96-hr SPP test) > 1,000,000 ppm causticized lignite. (3)

Risk Characterization

The only toxicity data found for lignite was measured on lignite in drilling mud and thus is not relevant to this study. In addition to its function as a drilling mud additive, lignite is used as a soil improver for agricultural crops, where it has shown no toxicity for terrestrial plants. Assuming the toxicity measured in mud is applicable, 163,000 ppm (163,000,000 ppb) is used to estimate the potential impact of a lignite spill. Using this concentration and the results reported in Tables 56, 57, and 58, it is apparent that the highest predicted exposure concentration in any unit grid cell area to is at least three orders of magnitude lower than the toxic concentration.

References

(1) M-I Drilling Fluids L.L.C. (1998c)
(2) Baker Hughes Inteq (1994b)
(3) Jones et al. (1986)

Table 56

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 8. Particulate concentration of lignite in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	442,331,936	3,293,261,312	11,866	32,377
10	110,260,440	622,636,096	5,924	14,078
100	21,727,708	144,635,552	2,630	6,785
1,000	3,567,237	20,430,532	1,066	2,550
10,000	324,294	2,270,060	321	850
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 57

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 8. Dissolved concentration of lignite in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	924,548,224	8,123,730,432	17,155	50,851
10	110,260,440	752,027,008	5,924	15,472
100	7,458,770	89,505,496	1,541	5,338
1,000	-	3,242,943	-	1,016
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 58

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 8. Mass loading of lignite onto sediments in all subtidal habitats.

Threshold (g/m^2)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	176,091,488	840,557,632	7,487	16,357
0.10	19,133,356	840,557,632	2,468	16,357
1.0	1,297,177	27,889,294	643	2,980
10	-	324,294	-	321
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-

Table 59

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 8. Particulate concentration of lignite in all subtidal habitats.

Exposure Range	Dose (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	1.49E+07	9.66E+07	9.61E+08	0.00E+00	63
10H-100H	0.1-1.0	1.28E+08	8.20E+08	8.15E+09	0.00E+00	57
100H-1,000H	1.0-10.0	5.69E+08	1.25E+09	8.80E+09	1.46E+07	0
1,000H-10,000H	10.0-100.0	2.41E+09	2.52E+09	9.65E+09	1.57E+08	0
10,000H-100,000H	100.0-1,000.0	4.40E+09	2.97E+09	1.10E+10	8.72E+07	0
> 100,000H	> 1,000.0	1.22E+09	1.91E+09	9.56E+09	3.21E+07	0
> 1H	> 0.01	8.74E+09	3.86E+09	1.66E+10	1.89E+09	0
> 10H	> 0.1	8.72E+09	3.85E+09	1.66E+10	1.89E+09	0
> 100H	> 1.0	8.60E+09	3.81E+09	1.65E+10	1.88E+09	0
> 1,000H	> 10.0	8.03E+09	3.72E+09	1.62E+10	1.43E+09	0
> 10,000H	> 100.0	5.61E+09	3.81E+09	1.55E+10	1.50E+08	0
> 100,000H	> 1,000.0	1.22E+09	1.91E+09	9.56E+09	3.21E+07	0

Table 60

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 8. Dissolved concentration of lignite in all subtidal habitats.

Exposure Range	Dose (1) ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	7.92E+08	2.35E+08	1.26E+09	1.07E+07	0
10H-100H	0.1-1.0	3.96E+09	1.05E+09	5.86E+09	7.77E+08	0
100H-1,000H	1.0-10.0	1.19E+10	2.44E+09	1.70E+10	1.29E+09	0
1,000H-10,000H	10.0-100.0	9.45E+09	2.28E+09	1.46E+10	1.42E+09	0
10,000H-100,000H	100.0-1,000.0	2.06E+09	1.50E+09	8.05E+09	2.25E+08	0
> 100,000H	> 1,000.0	2.82E+08	9.66E+08	9.78E+09	1.65E+07	0
> 1H	> 0.01	2.84E+10	3.33E+09	3.26E+10	3.74E+09	0
> 10H	> 0.1	2.76E+10	3.24E+09	3.18E+10	3.73E+09	0
> 100H	> 1.0	2.37E+10	3.00E+09	2.83E+10	2.95E+09	0
> 1,000H	> 10.0	1.18E+10	3.27E+09	2.02E+10	1.66E+09	0
> 10,000H	> 100.0	2.34E+09	1.88E+09	1.24E+10	2.44E+08	0
> 100,000H	> 1,000.0	2.82E+08	9.66E+08	9.78E+09	1.65E+07	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 61

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.0001 (g/m^2)-hours: Scenario 8. Mass loading of lignite onto sediments in all subtidal habitats.

Exposure Range	Dose (g/m^2)-hrs)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
10H-100H	0.1-1.0	3.00E+07	1.69E+07	7.95E+07	8.11E+06	0
100H-1,000H	1.0-10.0	7.29E+06	4.64E+06	2.69E+07	6.49E+05	0
1,000H-10,000H	10.0-100.0	2.92E+05	3.04E+05	1.30E+06	0.00E+00	37
10,000H-100,000H	100.0-1,000.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
> 100,000H	> 1,000.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
> 1H	> 0.01	3.76E+07	2.02E+07	9.34E+07	1.07E+07	0
> 10H	> 0.1	3.76E+07	2.02E+07	9.34E+07	1.07E+07	0
> 100H	> 1.0	7.58E+06	4.65E+06	2.76E+07	6.49E+05	0
> 1,000H	> 10.0	2.92E+05	3.04E+05	1.30E+06	0.00E+00	37
> 10,000H	> 100.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
> 100,000H	> 1,000.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100

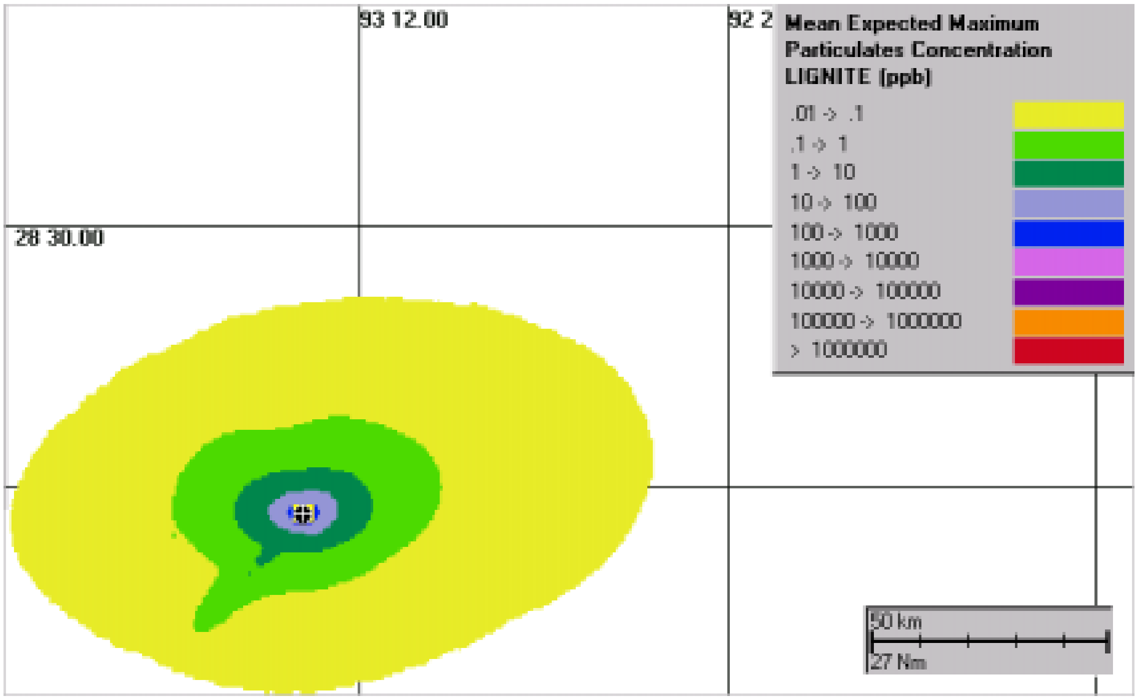


Figure 49. Peak exposure concentration (ppb) of lignite as particulate in the water at each location: averaged over all simulations (Scenario 8).

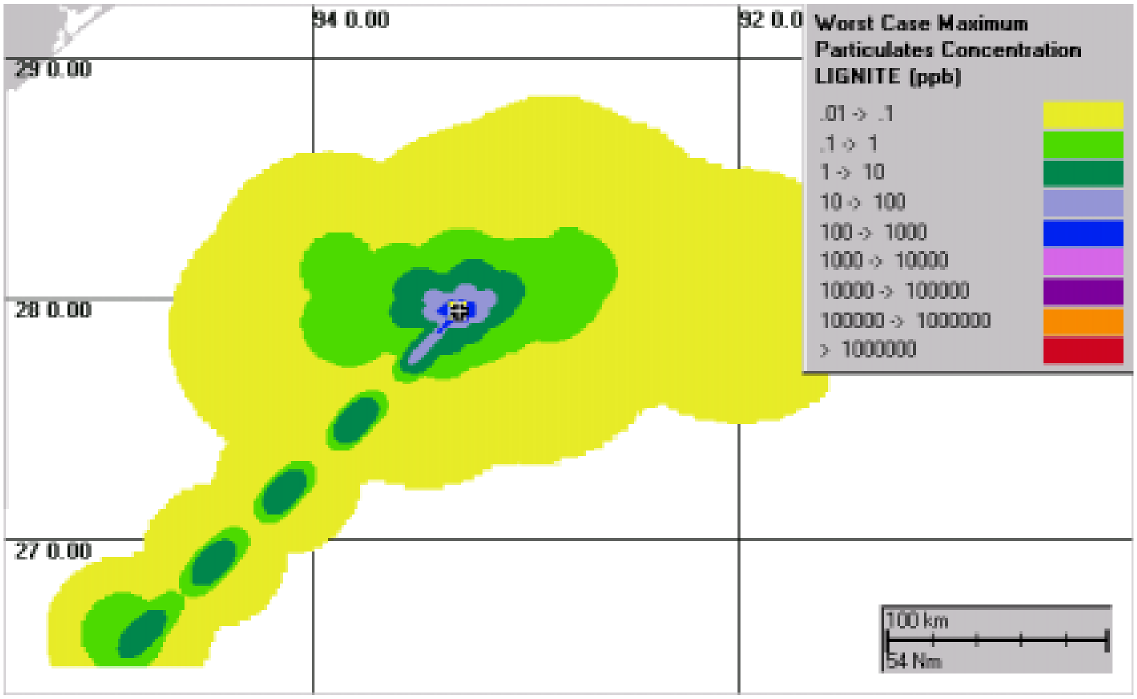


Figure 50. Peak exposure concentration (ppb) of lignite as particulate in the water at each location: worst case of all simulations (Scenario 8).

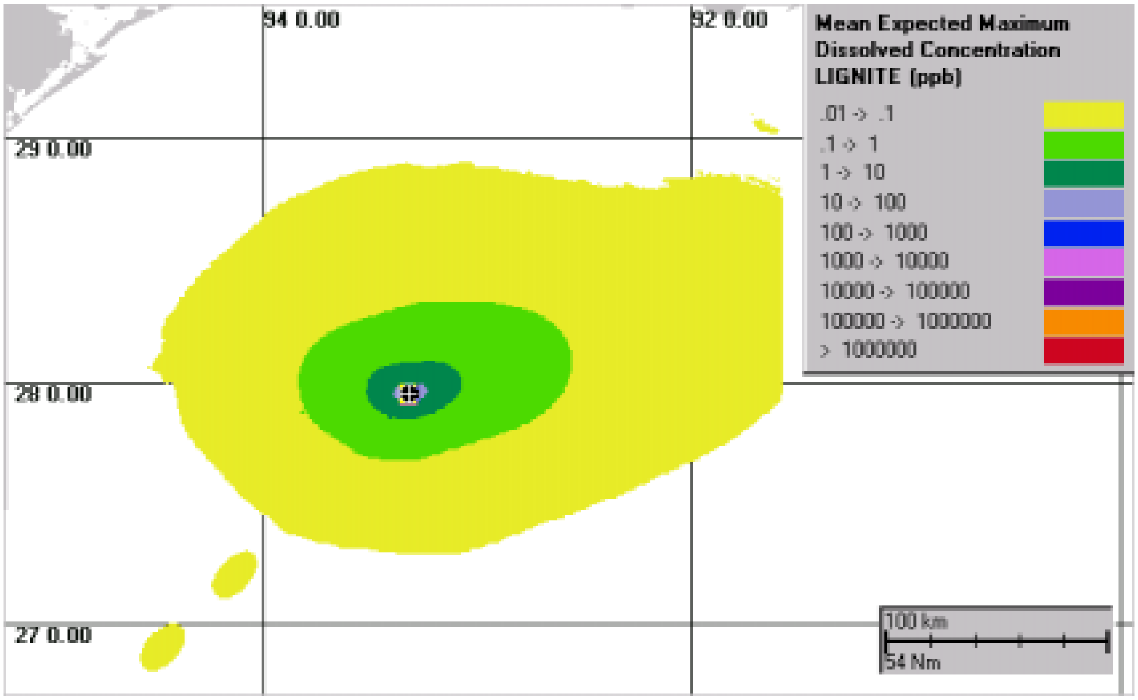


Figure 51. Peak exposure concentration (ppb) of lignite dissolved in the water at each location: averaged over all simulations (Scenario 8).

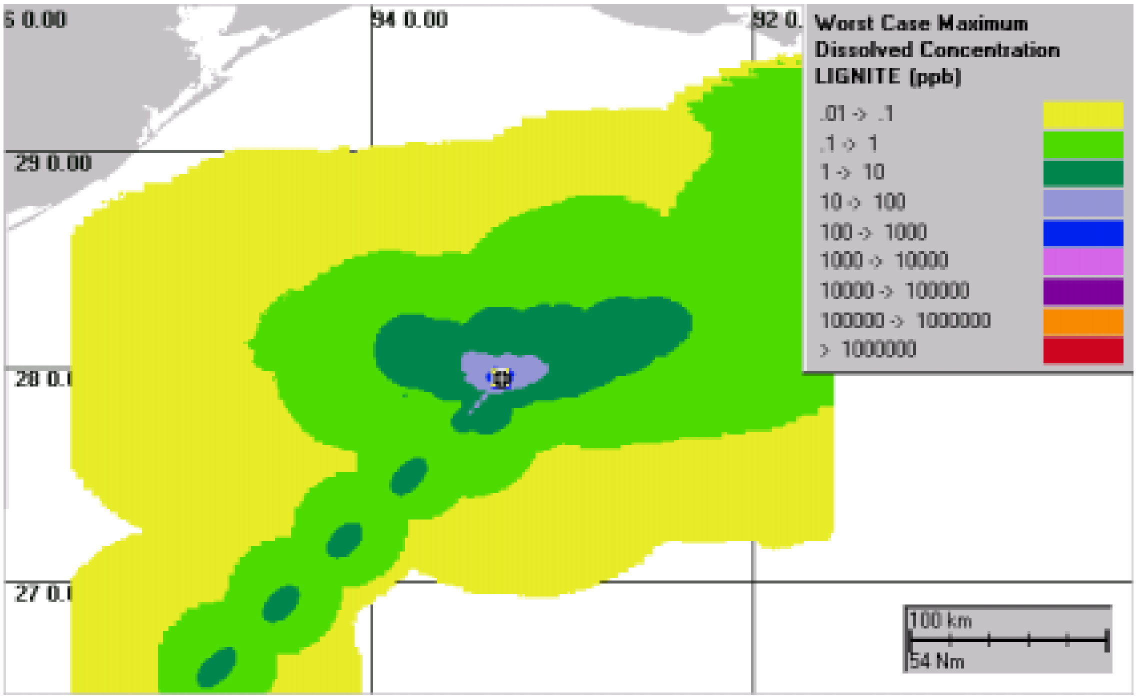


Figure 52. Peak exposure concentration (ppb) of lignite dissolved in the water at each location: worst case of all simulations (Scenario 8).

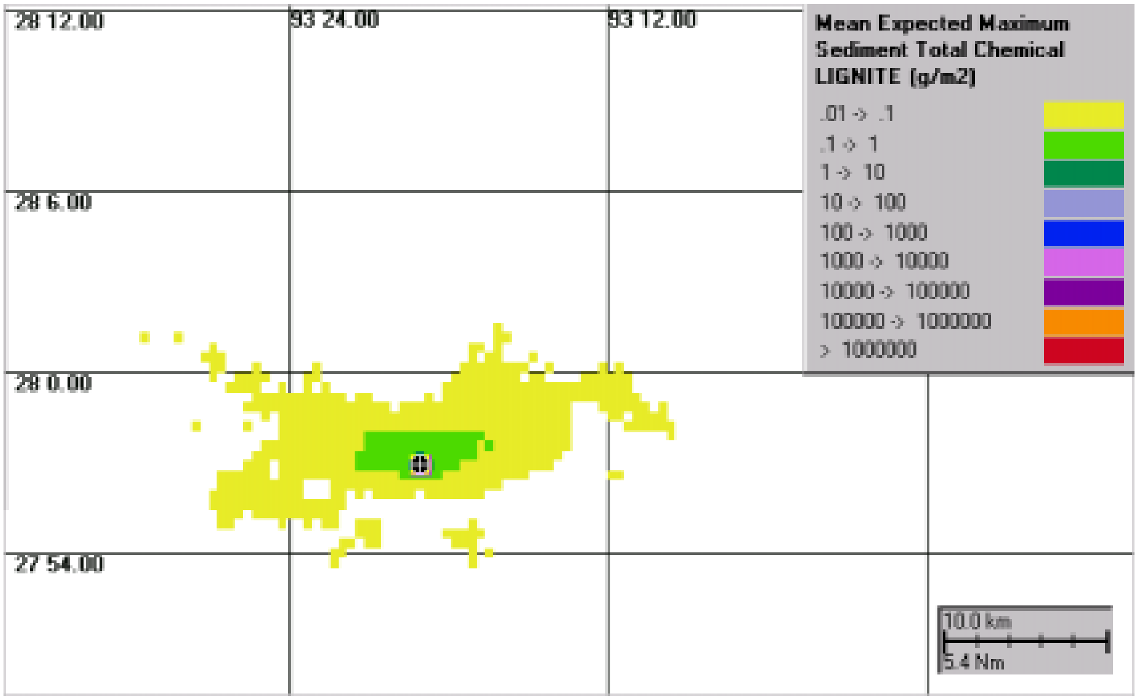


Figure 53. Peak exposure mass per unit area (g/m^2) of lignite in the sediment averaged over all simulations (Scenario 8).

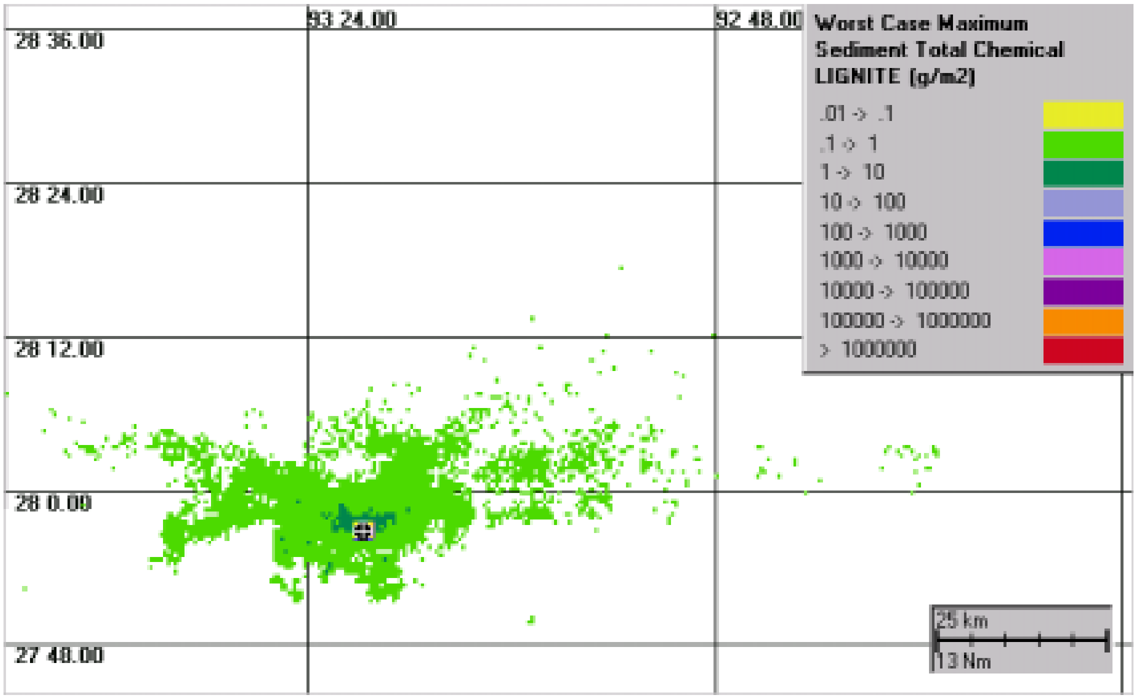


Figure 54. Peak exposure mass per unit area (g/m^2) of lignite in the sediment at each location: worst case of all simulations (Scenario 8).

Profile 15

METHANOL (Single Component)

Summary

Methanol is a single carbon alcohol, widely used as an industrial solvent. It is a production-treating chemical used primarily to prevent gas hydrate formation in gas gathering systems. If discharged to the marine environment, it will ultimately be removed by biological degradation. The most important potential impacts of this chemical are the human safety issues associated with its potential for fire and explosion offshore. Very high concentrations of methanol are required to produce measurable aquatic toxicity.

Background Information

Fate in the Environment

Methanol is an organic liquid. It is miscible in seawater at all proportions. When spilled on the seawater surface, methanol will rapidly mix into the water column where oceanographic and meteorological forces provide the mixing energy to disperse it through the water column. The magnitude of these forces determines how rapidly methanol spreads through the water column. In the water column, methanol will ultimately be removed from the environment by biological degradation. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Methanol is also volatile and a portion of the spilled methanol would be lost to the atmosphere, since methanol has a relatively high vapor pressure. Since alcohols are very soluble in water, the portion lost to volatilization will be less than that dissolved in the water.

In the atmosphere, oxidation of the methanol will occur.

Fate in the Process System

Methanol in the production system equilibrates with the gas, oil, and water phases and distributes between them. A large proportion of the methanol remains in the produced water and will be disposed of with the produced water, usually into the sea.

Other Components

None

CAS Number (Methanol)

67-56-1

Chemical Formula (Methanol)

CH_3OH

Important Synonyms and Trade Names

Methyl Alcohol; Wood Alcohol

Chemical and Physical Properties

Property	Component	Product
Molecular Weight	32.04 (2)	Same as Component
Boiling Point	64.5° C (2)	Same as Component
Melting Point	-94° C (2)	Same as Component
Specific Gravity	0.791 @ 20° C (2)	Same as Component
Solubility in Water	Miscible (2)	Same as Component
Solubility in Organics	Soluble in alcohol, other alcohol's, acetone, ether, benzene, and chloroform	Same as Component
Vapor Pressure	96 mm Hg @ 20° C (2)	Same as Component
Vapor Density (Air =1)	1.11 (1)	Same as Component
Physical State (Phase)	Liquid @ standard conditions (1)	Same as Component
Chemical Reactivity in the Environment	None	Same as Component

Health and Safety Properties and Effects

Property	Component (1)	Product
Autoignition Temperature	725° F (385° C)	Same as Component
Flash Point	12° C (closed cup)	Same as Component
Upper Explosive Limit	36.0%	Same as Component
Lower Explosive Limit	6.7%	Same as Component
Air Toxicity	200 ppm	Same as Component
OSHA PEL	200 ppm	Same as Component

The most important health and safety concern offshore is the danger of fire and explosion. However, this danger is no greater than that from the natural gas produced on the platform (i.e., if normal safety precautions are observed). Vapor toxicity also presents a potential health concern on offshore platforms. Although ingestion of methanol and large concentrations in vapor are reported to cause serious health effects, including blindness and death, protective measures used offshore limit exposure to these conditions. Chronic exposures to low levels of methanol are not expected to have serious health effects.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 7,500 gal.
Maximum = 100,600 gal.
(modeled in Scenario 9).

Transport Container(s): 550 gal. HDPP totes (typical).

Storage Methods: Shipping container or stationary bulk tank on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Methanol was modeled as Scenario 9. The exposure concentrations presented below are derived from the results of this modeling.

Results are shown in Tables 62 to 67 and Figures 55 to 60. Methyl alcohol (methanol) is buoyant in water, but also very soluble, and so dissolves quickly. Thus, droplets of methanol ("particulate") are short-lived in the water column, and surfaced methanol forms slicks for a very brief time. The plots for these are, therefore, patchy and blocky in appearance, and concentrations last only an hour or so. The dissolved concentration plume is much more extensive, and of interest in terms of potential toxic effects. There is also some partitioning of the methanol onto suspended sediments (adsorbed concentration).

Aquatic Toxicity Levels

The available literature for methanol toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Artemia salina (brine shrimp): LC50 (96-hr) = 10,000 mg/L (3)
Artemia salina (brine shrimp): LC50 (24-hr) = 10,000 mg/L; generated using most sensitive stage of species (72 hr) (4)
Rhodomonas baltica (marine microalgae): EC50 (4-hr) = 100,000 mg/L; significantly reduced survival at reported concentrations (5)
Tetraselmis chuii Butcher (marine microalgae): EC50 (4-hr) = 250,000 mg/L significantly reduced survival at reported concentrations (5)
Isochrysis aff. galbana (strain T-ISO) Parke (marine microalgae): EC50 (4-hr) = 250,000 mg/L significantly reduced survival at reported concentrations (5)
Nannochloropsis gaditana Lubian (marine microalgae): EC50 (4-hr) = 200,000 mg/L significantly reduced survival at reported concentrations (5)
Nannochloris atomus Butcher (marine microalgae): EC50 (4-hr) = 200,000 mg/L significantly reduced survival at reported concentrations (5)
Chaetoceros gracilis Schutt (marine microalgae): EC50 (4-hr) = 200,000 mg/L significantly reduced survival at reported concentrations (5)

Fish

Lepomis macrochiris (bluegill, freshwater fish): LC50 (96-hr) = 10,000 mg/L (6)
Salmo gairdneri (rainbow trout, freshwater fish): LC50 (96-hr) = 20,100 mg/L (6)
Pimephales promelas (fathead minnow, freshwater fish): LC50 (96-hr) = 28,100 mg/L (9)
Alburnas alburnas (bleak, freshwater fish): LC50 (96-hr) = 28,000 ppm (8)

Benthos

Mytilus edulis (blue mussel, marine bivalve mollusk): LC50 (96 hr) = 15,900 mg/L (7)
Mytilus edulis (blue mussel, marine bivalve mollusk): NOEC = 7,960 mg/L (7)
Nitroca spinipes (harpacticoid copepod, marine crustacean): LC50 (96 hr) = 12,539 mg/L (8)

Risk Characterization

Toxicity data on methanol were found for planktonic and benthic species. Data for fish were for freshwater species. The lowest 96-hr LC50 toxicity level found for benthic species was 12,539 mg/l (approximately 12,539 ppm or 12,539,000 ppb) 96-hr LC50. Using a concentration of 12,539,000 ppb and comparing it to the results in Table 64 it is apparent that the highest predicted exposure concentration in any grid unit cell area would be approximately two orders of magnitude lower than the toxic concentration.

References

(1) Air Products and Chemicals (1987)
(2) CRC Handbook of Chemistry and Physics (1986-1986)
(3) Price et al. (1974)
(4) Barahona-Gomariz et al. (1994)
(5) Canavate and Lubian (1994)
(6) Poirier et al. (1986)
(7) Helmstetter et al. (1996)
(8) Tarkpea and Svanberg (1982)
(9) Veith et al. (1983)

Table 62

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 9. Mass per unit area (g/m^2) of methyl alcohol as slicks in all subtidal habitats. Note that these slicks occur only instantaneously after the spill, as dissolution would be immediate.

Threshold (g/ m^2)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	27,565,000	35,348,068	2,962	3,354
0.10	11,674,594	35,348,068	1,928	3,354
1.0	3,891,531	26,267,824	1,113	2,892
10	-	10,053,124	-	1,789
100	-	1,945,766	-	787
1,000	-	-	-	-
10,000	-	-	-	-

Table 63

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 9. Concentration of methyl alcohol slicks and pure liquid droplets in all subtidal habitats. Note that these concentrations occur only instantaneously after the spill, as dissolution would be immediate.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	72,642,104	82,046,688	4,809	5,110
10	51,562,868	78,155,136	4,051	4,988
100	21,727,708	72,642,104	2,630	4,809
1,000	9,404,536	49,292,796	1,730	3,961
10,000	3,567,237	17,836,180	1,066	2,383
100,000	-	6,485,887	-	1,437
1,000,000	-	-	-	-

Table 64

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 9. Dissolved concentration of methyl alcohol in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	5,127,787,008	28,561,301,504	40,401	95,349
10	972,218,560	6,753,776,640	17,592	46,366
100	152,742,752	1,322,498,688	6,973	20,517
1,000	15,241,828	254,244,896	2,203	8,996
10,000	2,270,060	32,753,704	850	3,229
100,000	-	5,188,709	-	1,285
1,000,000	-	-	-	-

Table 65

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 9. Concentration of methyl alcohol adsorbed to suspended sediments in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	62,264,636	2,245,604,352	4,452	26,736
10	5,188,709	374,231,456	1,285	10,914
100	-	57,724,492	-	4,287
1,000	-	4,215,825	-	1,158
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 66

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 9. Dissolved concentration of methyl alcohol in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	8.23E+08	3.69E+08	2.15E+09	1.09E+08	0
10H-100H	0.1-1.0	3.67E+09	1.36E+09	6.63E+09	5.53E+08	0
100H-1,000H	1.0-10.0	1.01E+10	3.22E+09	2.00E+10	1.28E+09	0
1,000H-10,000H	10.0-100.0	1.16E+10	2.68E+09	1.86E+10	2.85E+09	0
10,000H-100,000H	100.0-1,000.0	5.97E+09	2.23E+09	1.30E+10	2.12E+09	0
> 100,000H	> 1,000.0	1.25E+09	5.90E+08	3.01E+09	3.85E+08	0
> 1H	> 0.01	3.34E+10	5.44E+09	4.42E+10	1.54E+10	0
> 10H	> 0.1	3.25E+10	5.25E+09	4.29E+10	1.52E+10	0
> 100H	> 1.0	2.89E+10	4.46E+09	3.74E+10	1.47E+10	0
> 1,000H	> 10.0	1.88E+10	3.25E+09	2.51E+10	1.16E+10	0
> 10,000H	> 100.0	7.22E+09	2.58E+09	1.52E+10	2.70E+09	0
> 100,000H	> 1,000.0	1.25E+09	5.90E+08	3.01E+09	3.85E+08	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 67

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 9. Concentration of methyl alcohol adsorbed to suspended sediments in all subtidal habitats.

Exposure Range	Dose [(1)] (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
10H-100H	0.1-1.0	7.13E+04	7.13E+05	7.13E+06	0.00E+00	99
100H-1,000H	1.0-10.0	2.50E+05	1.48E+06	1.17E+07	0.00E+00	96
1,000H-10,000H	10.0-100.0	3.42E+06	1.86E+07	1.28E+08	0.00E+00	96
10,000H-100,000H	100.0-1,000.0	1.63E+07	1.02E+08	8.46E+08	0.00E+00	96
> 100,000H	> 1,000.0	1.15E+09	5.68E+09	2.96E+10	0.00E+00	96
> 1H	> 0.01	1.17E+09	5.77E+09	2.99E+10	0.00E+00	96
> 10H	> 0.1	1.17E+09	5.77E+09	2.99E+10	0.00E+00	96
> 100H	> 1.0	1.17E+09	5.77E+09	2.99E+10	0.00E+00	96
> 1,000H	> 10.0	1.17E+09	5.77E+09	2.98E+10	0.00E+00	96
> 10,000H	> 100.0	1.17E+09	5.75E+09	2.98E+10	0.00E+00	96
> 100,000H	> 1,000.0	1.15E+09	5.68E+09	2.96E+10	0.00E+00	96

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

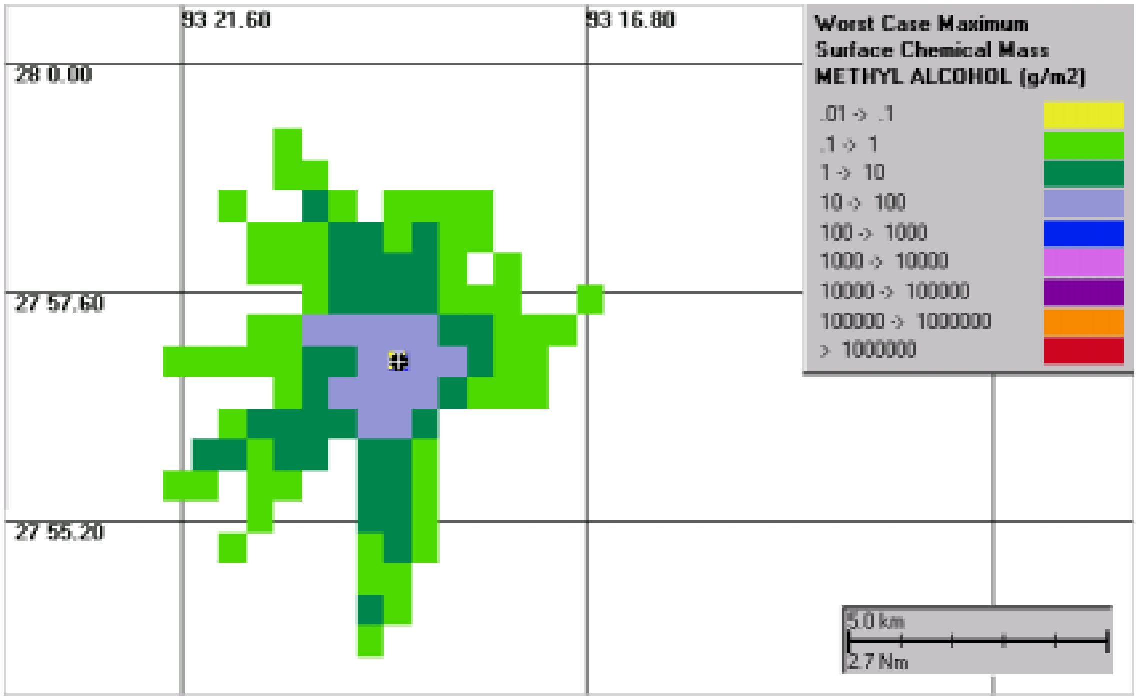


Figure 55. Peak exposure mass per unit area (g/m^2) of methyl alcohol as slicks on the water surface at each location: worst case of all simulations (Scenario 9).

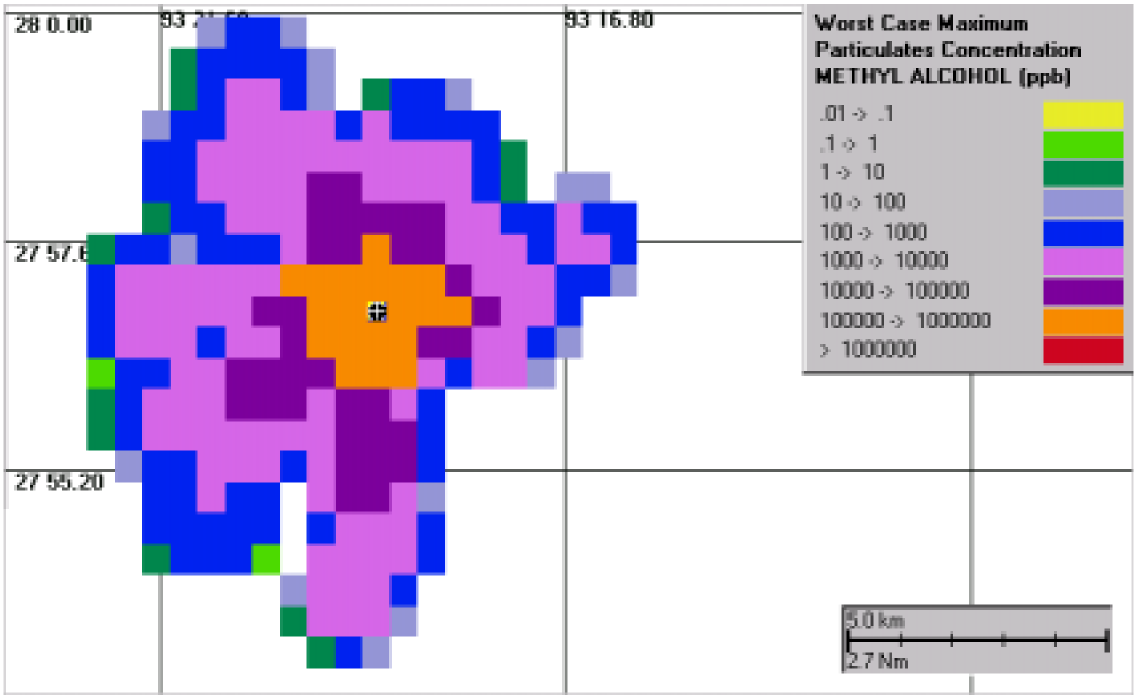


Figure 56. Peak exposure concentration (ppb) of methyl alcohol as slicks and pure liquid droplets in the water at each location: worst case of all simulations (Scenario 9).

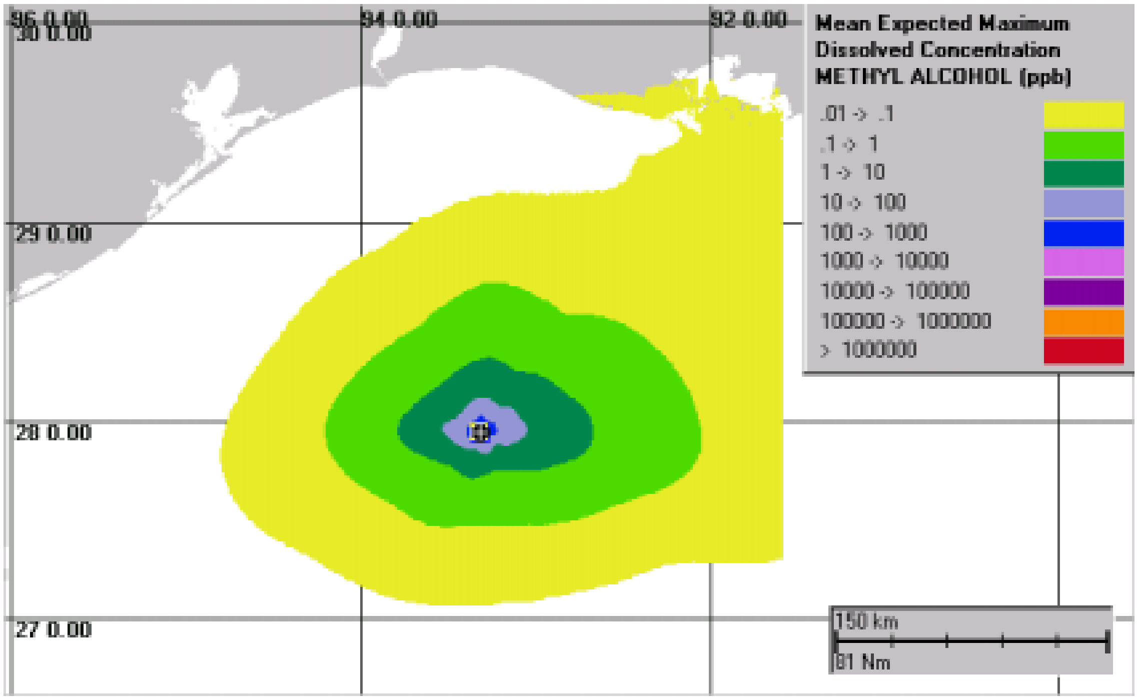


Figure 57. Peak exposure concentration (ppb) of methyl alcohol dissolved in the water at each location: averaged over all simulations (Scenario 9).

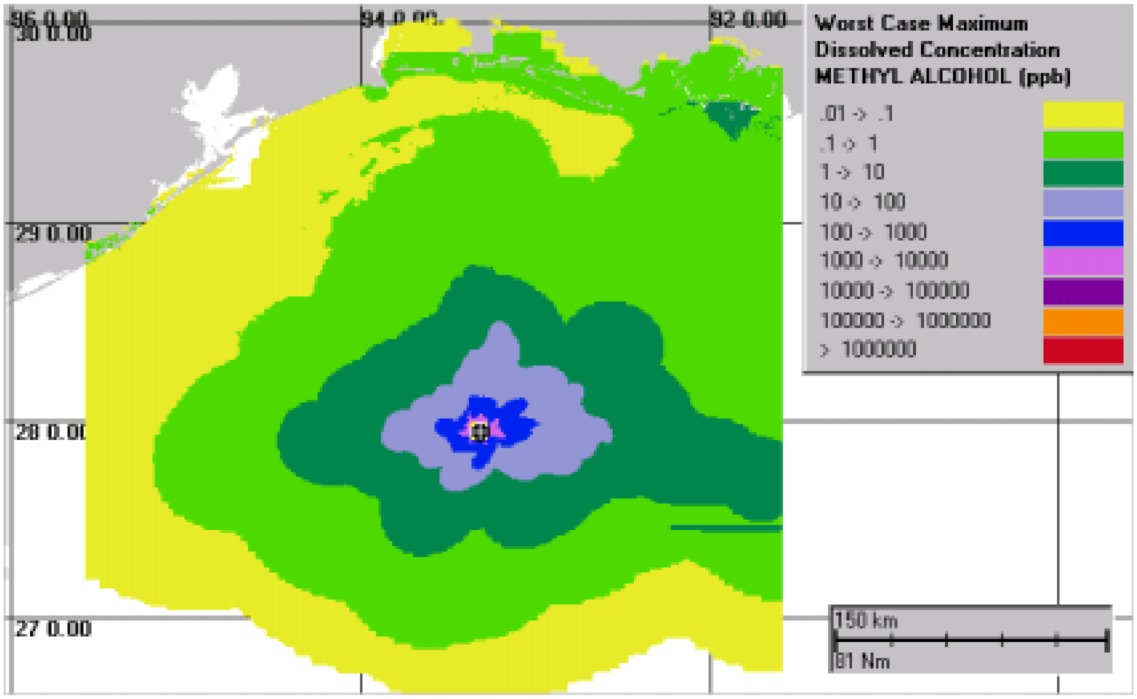


Figure 58. Peak exposure concentration (ppb) of methyl alcohol dissolved in the water at each location: worst case of all simulations (Scenario 9).

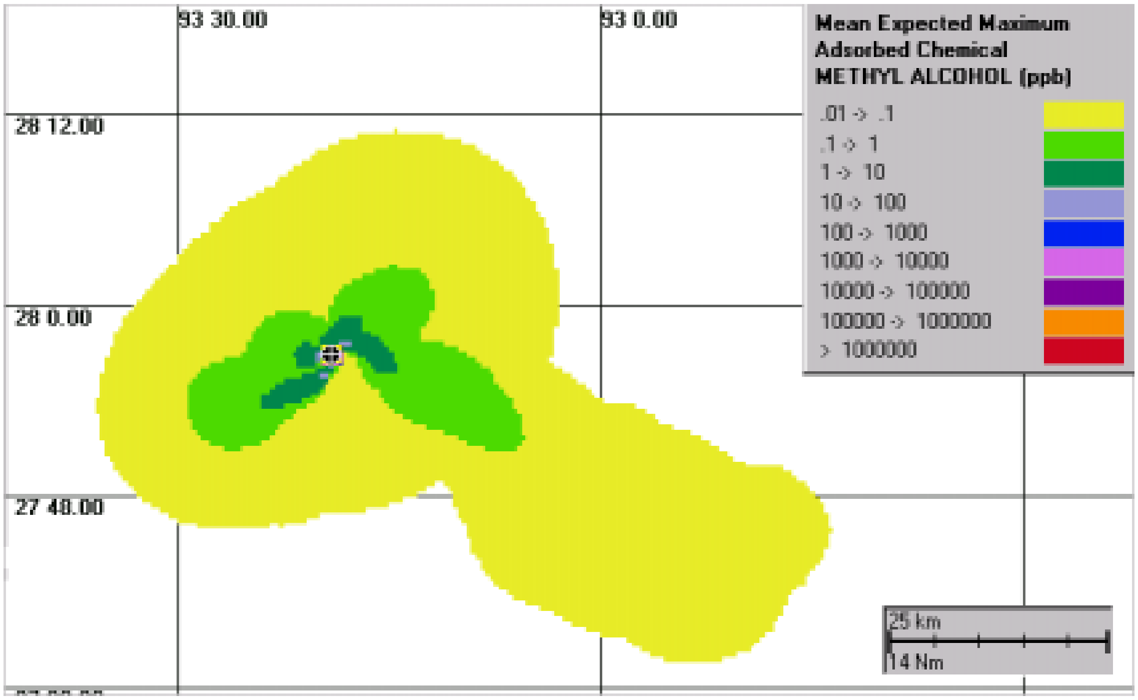


Figure 59. Peak exposure concentration (ppb) of methyl alcohol adsorbed to suspended sediment in the water at each location: averaged over all simulations (Scenario 9).

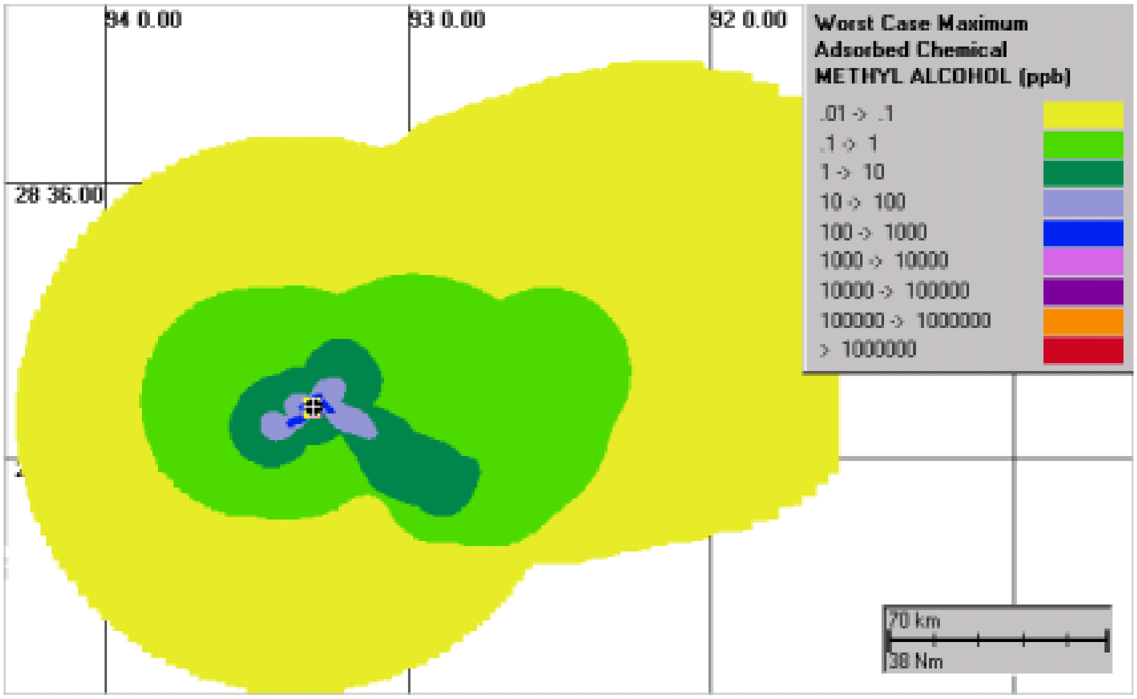


Figure 60. Peak exposure concentration (ppb) of methyl alcohol adsorbed to suspended sediment in the water at each location: worst case of all simulations (Scenario 9).

Profile 16

ETHYLENE GLYCOL (Single Component)

Summary

Ethylene glycol is a di-alcohol, widely used as an industrial solvent. It is a production-treating chemical used primarily to prevent gas hydrate formation in gas-gathering systems. If discharged to the marine environment, it will disperse through the water column and ultimately be removed by biological degradation.

Background Information

Fate in the Environment

Ethylene glycol is an organic liquid. It is miscible in seawater at all proportions. When spilled on the seawater surface, ethylene glycol will rapidly mix into the water column where oceanographic and meteorological forces provide the mixing energy to disperse it through the water column. The magnitude of these forces determines how rapidly ethylene glycol spreads through the water column. In the water column, ethylene glycol will ultimately be removed from the environment by biological degradation. If released below the seawater surface (i.e., bottom release), ethylene glycol will mix and disperse into the water column and the solution will be transported down current. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Ethylene glycol is added to production streams to prevent gas hydrate formation. Once in the production system, it equilibrates with the gas, oil, and water phases and distributes between them. While a proportion of the ethylene glycol normally remains in the produced water and may be disposed of with the produced water, it is also often recovered, recycled and reused.

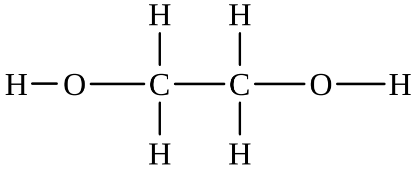
Other Components

None

CAS Number (Ethylene Glycol)

107-21-1

Chemical Formula (Ethylene Glycol)



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H}-\mathrm{O} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O}-\mathrm{H} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Important Synonyms and Trade Names

Ethylene Alcohol; Glycol; 1,2-Ethanediol

Chemical and Physical Properties

Property	Component (1)	Product
Molecular Weight	62.07	Same as Component
Boiling Point	197.6º C	Same as Component
Melting Point	-13º C	Same as Component
Specific Gravity	1.1 @ 20º C / 4º C	Same as Component
Solubility in Water	Miscible	Same as Component
Solubility in Organics	Soluble in alcohol, ether, and acetone (4)	Same as Component
Vapor Pressure	0.06 @ 20º C	Same as Component
Vapor Density (Air = 1)	2.14	Same as Component
Physical State (Phase)	Liquid (clear) @ standard conditions (1)	Same as Component
Viscosity	NA	Same as Component
Chemical Reactivity in the Environment	None	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component (1)	Product
Autoignition Temperature	398º C	Same as Component
Flash Point	111º C	Same as Component
Upper Explosive Limit	15.3% by Volume	Same as Component
Lower Explosive Limit	3.2% by Volume	Same as Component
Air Toxicity	50 ppm Ceiling (vapor)	Same as Component
OSHA PEL	50 ppm Ceiling	Same as Component

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = Depends on facility
Maximum = 110,000 gal.

Transport Container(s): 550 gal. HDPP totes (typical) or steel bulk tanks.

Storage Methods: Shipping container or stationary bulk tank on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Ethylene glycol was modeled as Scenario 10. The exposure concentrations presented below are derived from the results of this modeling.

Results are shown in Figures 66 to 69 and Tables 63 to 66. Ethylene glycol is denser than seawater and extremely soluble. Thus, there is a short-lived lens of ethylene glycol resting on the sediment following the hypothetical bottom release (from the umbilical). It dissolves quickly and disperses widely.

The extension to the southwest of the main concentration area is caused by a single rare event of southwest-directed current (same phenomenon as in the lignite scenario), which catches only a few Lagrangian particles representing the spilled mass in the model.

Aquatic Toxicity Levels

The available literature for ethylene glycol toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Ceriodaphnia dubia (water flea, freshwater crustacean): LC50 (48-hr) = 34,400 mg/L. (3)

Fish

Oncorhynchus mykiss (rainbow trout, freshwater fish): LC50 (96-hr) = 0.91 mol/L (56,483 mg/L). (2)

Pimephales promelas (fathead minnow, freshwater fish): LC50 (96-hr) = 1.1 mol/L (68,277 mg/L). (2)

Pimephales promelas (fathead minnow, freshwater fish): LC50 (96-hr) = 72,860 mg/L (3)

No toxicity data were found for ethylene glycol exposures to benthos in sediment.

Risk Characterization

No relevant marine toxicity data on ethylene glycol were found. The fresh water toxicity data listed above were found. Freshwater toxicity values range from 34,400 mg/L (approximately 34,400 ppm or 34,400,000 ppb) to 72,860 mg/L (approximately 72,860 ppm or 72,860,000 ppb). Assuming that it applies to marine waters the lowest toxicity concentration found was 34,400,000 ppb. Using this concentration and the results reported in Table 68 it is apparent that the highest predicted exposure concentration in any unit grid cell area would be an order of magnitude lower than the toxic concentration.

References

(1) Mallinckrodt Baker Inc. (1999c)
(2) Greene and Kocan (1997)
(3) Pillard (1995)
(4) CRC Chemical Handbook of Chemistry and Physics (1985-1986)

Table 68

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 10. Dissolved concentration of ethylene glycol in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	5,381,878,272	35,399,925,760	41,390	106,152
10	874,607,872	4,477,650,432	16,685	37,753
100	149,175,584	909,306,688	6,891	17,013
1,000	23,673,472	169,281,440	2,745	7,341
10,000	3,567,237	20,430,532	1,066	2,550
100,000	324,294	1,945,766	321	787
1,000,000	-	-	-	-

Table 69

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 10. Mass loading of ethylene glycol onto sediments in all subtidal habitats.

Threshold (g/m^2)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	3,242,943	3,242,943	1,016	1,016
0.10	2,918,648	3,242,943	964	1,016
1.0	1,621,471	3,242,943	718	1,016
10	324,294	1,945,766	321	787
100	-	1,297,177	-	643
1,000	-	-	-	-
10,000	-	-	-	-

Table 70

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 10. Dissolved concentration of ethylene glycol in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	6.84E+08	2.13E+08	1.69E+09	0.00E+00	1
10H-100H	0.1-1.0	2.62E+09	8.24E+08	5.60E+09	1.07E+07	0
100H-1,000H	1.0-10.0	7.38E+09	2.13E+09	1.57E+10	5.45E+07	0
1,000H-10,000H	10.0-100.0	1.35E+10	2.45E+09	1.94E+10	1.07E+08	0
10,000H-100,000H	100.0-1,000.0	7.84E+09	2.17E+09	1.38E+10	1.77E+08	0
> 100,000H	> 1,000.0	1.84E+09	1.72E+09	1.54E+10	3.20E+08	0
> 1H	> 0.01	3.38E+10	4.18E+09	4.34E+10	7.11E+08	0
> 10H	> 0.1	3.31E+10	4.04E+09	4.17E+10	7.11E+08	0
> 100H	> 1.0	3.05E+10	3.53E+09	3.62E+10	7.00E+08	0
> 1,000H	> 10.0	2.32E+10	2.89E+09	2.73E+10	6.46E+08	0
> 10,000H	> 100.0	9.68E+09	2.99E+09	1.80E+10	5.38E+08	0
> 100,000H	> 1,000.0	1.84E+09	1.72E+09	1.54E+10	3.20E+08	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 71

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.0001 (g/m^2)-hours: Scenario 10. Mass loading of ethylene glycol onto sediments in all subtidal habitats.

Exposure Range	Dose (g/m^2)-hrs)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
10H-100H	0.1-1.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
100H-1,000H	1.0-10.0	3.60E+05	2.76E+05	9.73E+05	0.00E+00	27
1,000H-10,000H	10.0-100.0	3.50E+05	2.75E+05	9.73E+05	0.00E+00	29
10,000H-100,000H	100.0-1,000.0	8.43E+04	1.57E+05	6.49E+05	0.00E+00	76
> 100,000H	> 1,000.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
> 1H	> 0.01	7.95E+05	3.95E+05	1.30E+06	0.00E+00	6
> 10H	> 0.1	7.95E+05	3.95E+05	1.30E+06	0.00E+00	6
> 100H	> 1.0	7.95E+05	3.95E+05	1.30E+06	0.00E+00	6
> 1,000H	> 10.0	4.35E+05	3.10E+05	1.30E+06	0.00E+00	23
> 10,000H	> 100.0	8.43E+04	1.57E+05	6.49E+05	0.00E+00	76
> 100,000H	> 1,000.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100

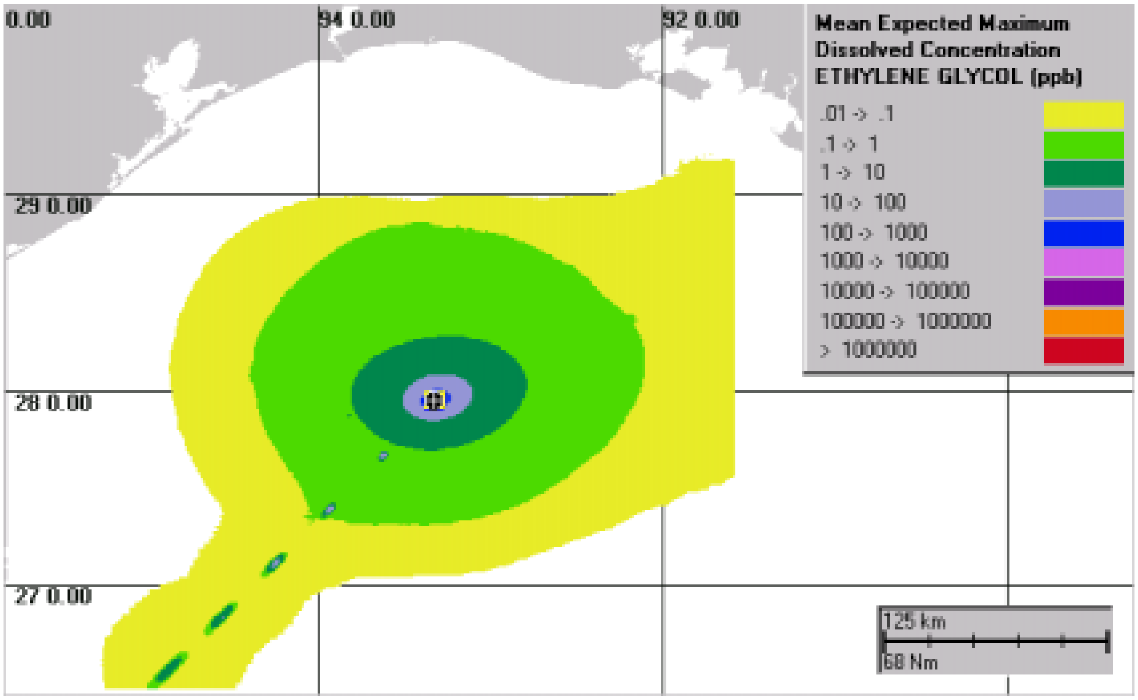


Figure 61. Peak exposure concentration (ppb) of ethylene glycol dissolved in the water at each location: averaged over all simulations (Scenario 10).

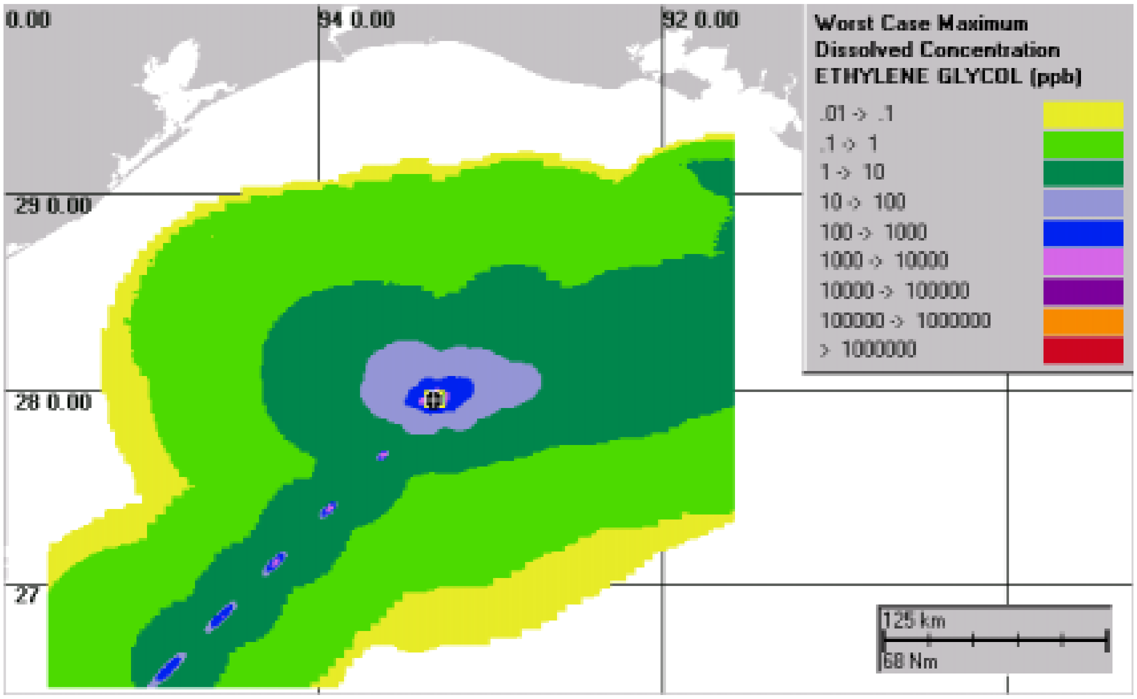


Figure 62. Peak exposure concentration (ppb) of ethylene glycol dissolved in the water at each location: worst case of all simulations (Scenario 10).

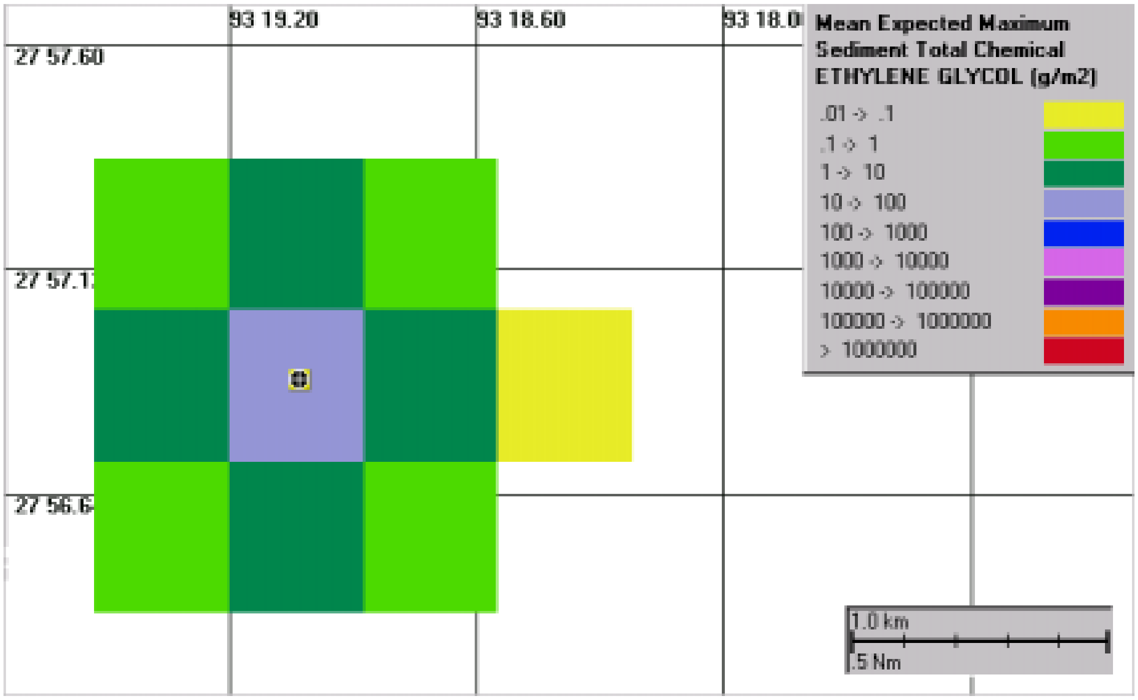


Figure 63. Peak exposure mass per unit area (g/m^2) of ethylene glycol in the sediment at each location: averaged over all simulations (Scenario 10).

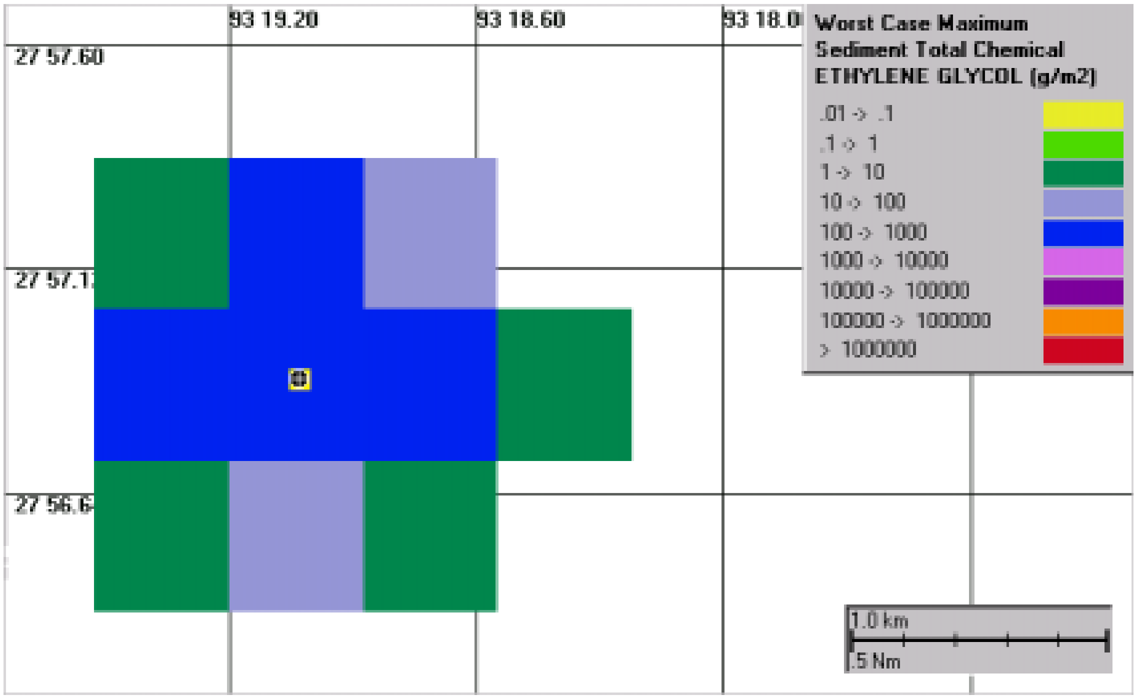


Figure 64. Peak exposure mass per unit area (g/m^2) of ethylene glycol in the sediment at each location: worst case of all simulations (Scenario 10).

Profile 17

TRIETHYLENE GLYCOL (Single Component)

Summary

Triethylene glycol is a complex alcohol consisting of three ethylene glycol units condensed into a single molecule. It is a production-treating chemical used primarily to prevent gas hydrate formation in gas-gathering systems. If discharged to the marine environment, it will disperse through the water column and ultimately be removed by biological degradation. Environmental concerns include potential aquatic toxicity.

Background Information

Fate in the Environment

Triethylene glycol is an organic liquid. It is miscible in seawater at all proportions. When spilled on the seawater surface, triethylene glycol will rapidly mix into the water column where oceanographic and meteorological forces provide the mixing energy to disperse it through the water column. The magnitude of these forces determines how rapidly triethylene glycol spreads through the water column. In the water column, triethylene glycol will ultimately be removed from the environment by biological degradation. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Triethylene glycol is added to production streams to prevent gas hydrate formation. Once in the production system it equilibrates with the gas, oil and water phases and distributes between them. While a proportion of the triethylene glycol normally remains in the produced water and may be disposed of with the produced water, it is also often recovered, recycled and reused.

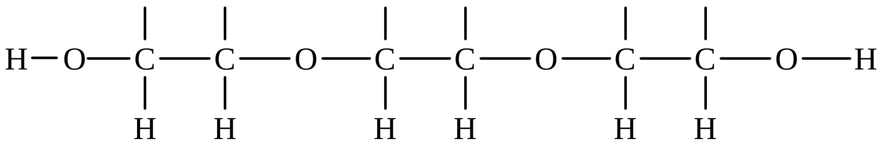
Other Components

None

CAS Number (Triethylene glycol)

112-27-6

Chemical Formula (Triethylene glycol)



$$H-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-H$$

Important Synonyms and Trade Names

TEG

Chemical and Physical Properties

Property	Component (1)	Product
Molecular Weight	150.20	Same as Component
Boiling Point	285º C	Same as Component
Melting Point	-5º C	Same as Component
Specific Gravity	1.1274 @ 15º C / 4º C	Same as Component
Solubility in Water	Miscible	Same as Component
Solubility in Organics	Soluble in alcohol and benzene (2)	Same as Component
Vapor Pressure	< 0.01 @ 20º C	Same as Component
Vapor Density (Air = 1)	5.17	Same as Component
Physical State (Phase)	Liquid (colorless) @ standard conditions	Same as Component
Viscosity	NA	Same as Component
Chemical Reactivity in the Environment	None	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component (1)	Product
Autoignition Temperature	398º C	Same as Component
Flash Point	111º C	Same as Component
Upper Explosive Limit	15.3% by Volume	Same as Component
Lower Explosive Limit	3.2% by Volume	Same as Component
Air Toxicity	50 ppm Ceiling (vapor)	Same as Component
OSHA PEL	50 ppm Ceiling	Same as Component

Triethylene glycol is mildly irritating to the eyes and skin and has a low order of acute oral toxicity for ingestion. However, small quantities of diethylene glycol byproduct are present in triethylene glycol that may cause kidney or liver damage if ingested and could be fatal.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = Depends on facility.
Maximum = 110,000 gal.

Transport Container(s): 550 gal. HDPP totes (typical) or steel bulk tanks.

Storage Methods: Shipping container or stationary bulk tank on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

A triethylene glycol spill was not modeled.

Aquatic Toxicity Levels

The available literature for triethylene glycol toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Daphnia magna (water flea, freshwater crustacean): LC50 (48-hr) = 35,000 µl/L. (2)
Daphnia magna (water flea, freshwater crustacean): LC50 (96-hr) = 10,000 ppm. (3)
Artemia salina (brine shrimp, marine crustacean): LC50 (96-hr) = 10,000 ppm. (3)

Fish

Carassius auratus (goldfish, freshwater fish): LC50 (96-hr) = 5,000 ppm. (3)

No toxicity data were located for triethylene glycol exposures to benthos in sediment.

Risk Characterization

Although no spill model was run for triethylene glycol, it is mathematically similar to ethylene glycol, if it were spilled in similar amounts. One source of marine toxicity data on triethylene glycol was found. The toxicity level was 10,000 ppm (10,000,000 ppb). Using this concentration and the results reported in Table 68 from the ethylene glycol spill model, it is apparent that the highest predicted exposure concentration in any unit grid cell area would be an order of magnitude lower than the toxic concentration.

References

(1) Mallinckrodt Baker Inc. (1996c)
(2) Le Blanc and Suprenant (1983)
(3) Hudgins and Petrotech Consultants, Inc. (1991)

Profile 18

SODIUM BISULFITE (Component of OSW3055)

Summary

OSW3055 is a water solution containing sodium bisulfite. It is a production-treating chemical used to remove oxygen from produced water and waterflood water. Sodium bisulfite, as the active ingredient, is profiled here. If discharged to the marine environment, it will ultimately be removed by chemical reaction with oxygen. Environmental concerns include the potential for sodium bisulfite to cause oxygen depletion in the seawater.

Background Information

Fate in the Environment

When spilled in seawater, OSW3055 will mix immediately into the surface where oceanographic and meteorological forces will provide the mixing energy to disperse it into the water column. The magnitude of these forces will determine how rapidly bisulfite spreads through the water column. Sodium bisulfite is very soluble in seawater and exists in water solution as sodium and bisulfite ions. In the presence of heavy metals naturally occurring in seawater, it reacts rapidly with oxygen to form sulfate and hydroxide ions, both major components of seawater. One part per million oxygen will react with 5 parts per million sodium bisulfite. The average peak concentrations resulting from a spill of OSW3055 will use up less than 0.2 ppm of the 6 to 8 ppm oxygen in seawater.

Fate in the Process System

Sodium bisulfite is used in produced water streams and treatment vessels and will partition to produced waters. Thus produced waters will contain residual concentrations of sodium bisulfite. The produced waters containing the sodium bisulfite may either be discharged to the marine environment or injected under ground.

Other Components

Water

CAS Number (Sodium Bisulfite)

7631-90-5

Chemical Formula (Sodium Bisulfite)

$NaHSO_3$

Important Synonyms and Trade Names

Sodium Acid Sulfite; Sulfurous Acid, Monosodium Salt; Sodium Hydrogen Sulfite

Chemical and Physical Properties

Property	Component (1)	Product (2)
Molecular Weight	104	NA
Boiling Point	NA	ND
Melting Point	150º C	NA
Specific Gravity	1.48	1.29 @ 60º F
Solubility in Water	Very soluble in water	Completely soluble
Solubility in Organics	Insoluble	Insoluble
Vapor Pressure	No information found	17.5 mm Hg @ 70º F
Vapor Density (Air = 1)	No information found	> 1
Physical State (Phase)	Solid (coarse white granules) @ standard conditions	Water solution
Viscosity	NA	ND
Chemical Reactivity in the Environment	Reacts with oxygen in seawater to form sulfate ion and hydroxide ion	See component

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component (1)	Product
Autoignition Temperature	NA	NA
Flash Point	NA	NA
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity	TLV 5 mg/m^3 TWA	NA
OSHA PEL	NA	NA

Notes: NA = Not Available

The most important human health and safety concern offshore is exposure to sulfite dust because of its potential air toxicity, and potential exposure to sulfur dioxide if the product is overheated (i.e., as a result of a fire).

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 55 gal.
Maximum = 500 gal.

Transport Container(s): 5, 55, and 500 gal. totes (steel and/or HDPP).

Storage Methods: Shipping containers on offshore platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Sodium bisulfite was modeled as Scenario 5. The exposure concentrations presented below are derived for the results of this modeling.

Results are shown in Figures 65 and 66 and Tables 72 and 73. The sodium bisulfite spill was modeled as sodium sulfite as a dissolved solution. On contacting seawater containing oxygen, the bisulfite ion will react to form sulfate ion, a common constituent of seawater. Dissociation and chemical changes in seawater would be complex, and modeling of this chemistry was not attempted. The sodium sulfite was simply diluted over time. Thus, the predicted concentrations are conservatively high.

Aquatic Toxicity Levels

None found

Risk Characterization

Although no toxicity test data could be found for sodium bisulfite, its chemical reactivity ensures that it will not persist in the environment for longer than a few minutes, limiting its potential toxicity. Table 72 shows that a 96-hr LC50 concentration for sodium bisulfite would have to be lower than 0.1 ppm in order to cause more than a minimal impact.

Bisulfite ion is used to remove oxygen from water streams. Stoichiometrically, 1 ppm oxygen will remove 5 ppm bisulfite. The oxygen content of seawater in the GOM ranges from 6 to 8 ppm (at the surface) and reaction with the bisulfite concentrations modeled will remove only 0.2 ppm of the available oxygen in seawater, thus will not significantly change the oxygen concentration. At standard conditions, this reaction takes less than 15 minutes.

References

(1) Mallinckrodt Baker Inc. (1999d)
(2) Baker Petrolite and Baker Hughes Co. (1996)

Table 72

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 5. Dissolved concentration of sodium bisulfite (modeled as sodium sulfite) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	72,966,400	661,874,944	4,819	14,515
10	8,431,654	122,583,688	1,638	6,247
100	324,294	14,593,240	321	2,155
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 73

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 mg/m^3-hours (0.01 ppb-hours): Scenario 5. Dissolved concentration of sodium bisulfite (modeled as sodium sulfite) in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	5.25E+07	4.88E+07	4.53E+08	1.30E+06	0
10H-100H	0.1-1.0	3.25E+08	2.00E+08	1.07E+09	1.21E+08	0
100H-1,000H	1.0-10.0	9.99E+08	3.11E+08	2.86E+09	5.71E+08	0
1,000H-10,000H	10.0-100.0	4.55E+08	1.71E+08	1.16E+09	2.51E+08	0
10,000H-100,000H	100.0-1,000.0	4.83E+07	1.33E+07	1.04E+08	2.63E+07	0
> 100,000H	> 1,000.0	4.78E+06	9.84E+05	7.46E+06	2.59E+06	0
> 1H	> 0.01	1.88E+09	4.69E+08	4.25E+09	1.26E+09	0
> 10H	> 0.1	1.83E+09	4.53E+08	4.19E+09	1.23E+09	0
> 100H	> 1.0	1.51E+09	3.50E+08	3.43E+09	1.01E+09	0
> 1,000H	> 10.0	5.08E+08	1.73E+08	1.21E+09	2.97E+08	0
> 10,000H	> 100.0	5.30E+07	1.32E+07	1.08E+08	2.98E+07	0
> 100,000H	> 1,000.0	4.78E+06	9.84E+05	7.46E+06	2.59E+06	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

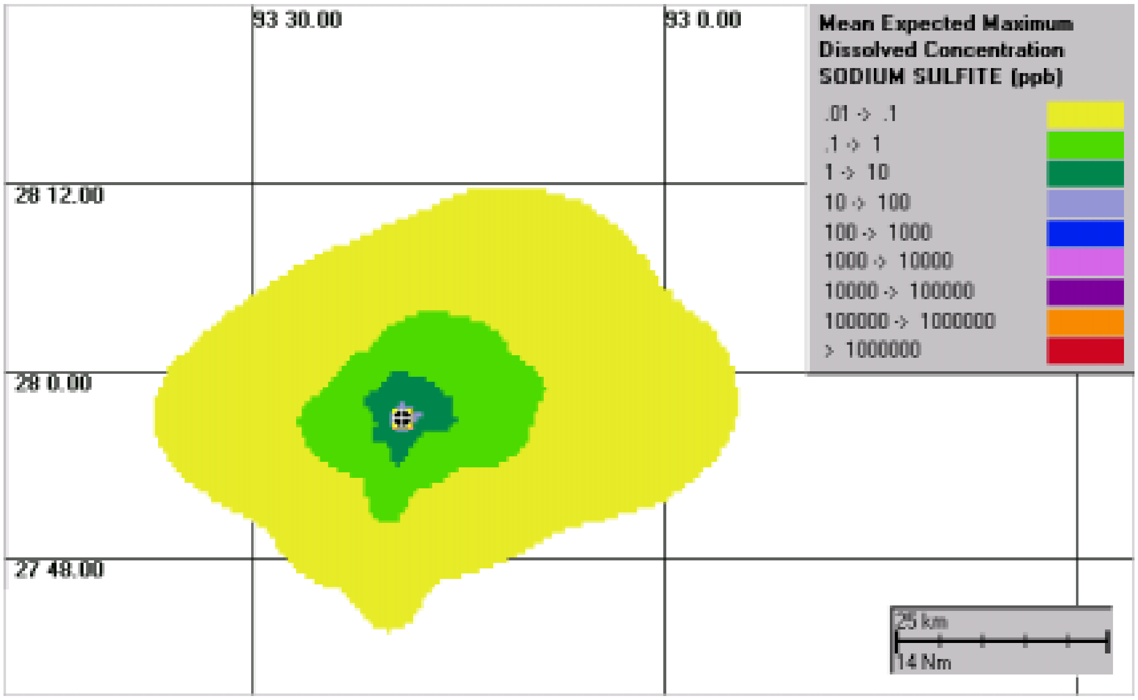


Figure 65. Peak exposure concentration (ppb) of sodium bisulfite (modeled as sodium sulfite) dissolved in the water at each location: averaged over all simulations (Scenario 5).

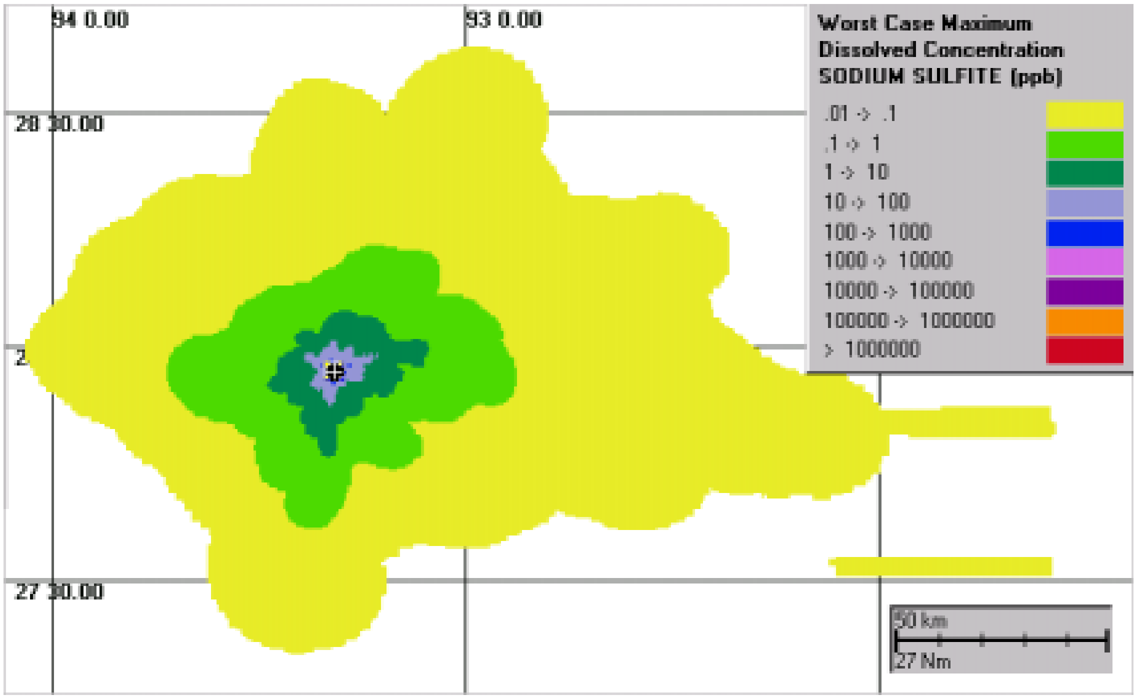


Figure 66. Peak exposure concentration (ppb) of sodium bisulfite (modeled as sodium sulfite) dissolved in the water at each location: worst case of all simulations (Scenario 5).

Profile 19

BARITE (Single Component)

Summary

Barite is a naturally occurring inorganic salt material mined in various locations throughout the world. It is used as a weighting agent to adjust the density of drilling fluids. Barite is supplied as a fine powder and is insoluble in water. If discharged to the marine environment, it will ultimately end up in the sediment where it is a natural constituent of many marine sediments.

Background Information

Fate in the Environment

Due to its high density and insolubility in seawater, barite will initially disperse into the water column and ultimately settle into marine sediment. Because of the product's small particle size, it will spread over a wide area.

Fate in the Process System

Barite is added to water-based drilling fluids in high concentrations by weight to give the drilling fluids the necessary density. As a well is drilled, drilling fluid is lost in one of three ways: (1) clinging to bits of the formation (i.e., cuttings) removed from the well, that are then disposed of; (2) as excess drilling fluid that is disposed during the drilling operation; or (3) when the well drilling has been completed, and all the remaining drilling fluid is to be disposed of. Outside the territorial seas, waste drilling fluids are discharged to the sea. Inside the territorial seas, waste drilling fluids are captured in waste tanks and sent ashore for disposal (i.e., to landfills).

Other Components

None

CAS Number (Barite)

7727-43-7

Chemical Formula (Barite)

$BaSO_4$

Important Synonyms and Trade Names

Barium Sulfate; Barium Salt of Sulfuric Acid; Baroid, Mil-Bar

Chemical and Physical Properties

Property	Component (1)	Product
Molecular Weight	233.39	Same as Component
Boiling Point	1,600º C	Same as Component
Melting Point	1,580º C	Same as Component
Specific Gravity	4.5 @ 15º C	Same as Component
Solubility in Water	Insoluble	Same as Component
Solubility in Organics	Insoluble (2)	Same as Component
Vapor Pressure	NA	Same as Component
Vapor Density (Air = 1)	NA	Same as Component
Physical State (Phase)	Solid Powder	Same as Component
Chemical Reactivity in the Environment	None	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component	Product (2)
Autoignition Temperature	NA	Same as Component
Flash Point	NA (3)	Same as Component
Upper Explosive Limit	NA (3)	Same as Component
Lower Explosive Limit	NA (3)	Same as Component
Air Toxicity	TLV 10 mg/m^3 total dust containing no asbestos and < 1% crystalline silica (1)	Same as Component
OSHA PEL (8)	15 mg/m^3 total dust, 5 mg/m^3 respirable dust (1)	Same as Component

Notes: NA = Not Available

Health hazards for this chemical are related to the fact that it is a fine powder that can cause mechanical irritation to the skin, eyes, and throat. See Appendix B for MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 4,000 tons
Maximum = 8,000 tons

Transport Container(s): 100 lb. paper sacks on pallets or in bulk boat tanks and transfer by blower to bulk tanks on the drilling rig.

Storage Methods: In sacks on pallets (usually in the drilling rig mud room) or in bulk tanks on the drilling rig.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

A barite spill was modeled as spill scenario 6 (shallow water) and 17 (deep water). The exposure concentrations presented below are derived from the results of this modeling.

Results are shown in Figures 67 to 70, 81 and 82 and Tables 74 to 79. Barite is an insoluble particulate, about 10 microns in diameter and with a very high density. Because of the small particle size, the particulate sinks only very slowly and disperses widely, with a bias along-shelf (the more frequent current directions). However, settling does occur, again primarily in the along-shelf direction, extending several hundred kilometers.

For scenario 17, a spill of barite in deep water (> 1,000 m), both single scenario and stochastic modeling were performed. Because of the depth of the water column (> 1,000 m), the plume does not mix vertically the entire distance to the bottom, as it does on the shelf. Thus, single scenarios were examined to evaluate the movement of the plume both horizontally and vertically over time.

Time series plots for an example spill on 1 January 1992 are in Figures 71 to 80. For this example spill date, the plume moved directly westward. For other example runs on different dates (not shown), the plume moved other directions, but underwent the same dispersion and vertical movement.

Barite, because of its small particulate size, will sink very slowly and disperse widely. This is evident in the plots of concentration over time after the spill. For example, after 1 week, the barite plume of > 1 mg/m^3 (~1ppb) has a radius of 50 km and is about 85 m thick, centered about 100 m below the surface. After 2 weeks, the barite plume of > 1 mg/m^3 (~1ppb) has a radius of about 100 km and is about 70 m thick, centered about 200 m below the surface. The direction and distance of horizontal movement is subject to the current field at the time of the spill. The dispersion rate is common to all the spill dates modeled.

In the example case (Figures 71 to 80), the plume eventually intersects the sediment on the continental slope at about 300 m depth. However, at that time (2 weeks after the spill), it is so dispersed that the sediment loading is extremely low, and lower than the threshold used in this analysis (for plotting).

Figures 81 to 82 and Tables 78 to 79 summarize the stochastic modeling results for spill scenario 17. The figures show the peak exposure concentration of barite as particulate in the water column and as a maximum in the vertical. Barite loading to the sediments is negligible as mass per unit area, because it is well dispersed before it ultimately reaches the sediments.

Tables 78 and 79 were prepared as follows. For the particulate in the water column, water volume exposed within ranges and above thresholds is tabulated. The peak exposure concentration is averaged over the vertical thickness of the plume. The plume where concentrations exceed about 1ppb does not extend over the entire water column, remaining about 100 m thick for a few weeks after the spill.

Scenario 17 may be considered a typical dispersion pattern for any non-reactive chemical. The high density of barite causes it to sink, but the small particle size causes it to sink slowly. More neutrally buoyant particulates and dissolved substances would not sink, but would disperse at about the same rate as the barite plume.

Aquatic Toxicity Levels

The available literature for barite toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Mysidopsis bahia (marine shrimp): LC50 (96-hr) > 1,000,000 ppm (non-toxic); (5) this value cannot be compared with other LC50 values, as it was determined through use of concentrations of treated mud diluted with seawater.

Mysidopsis bahia (marine shrimp): LC50 (96-hr SPP test) > 1,000,000 ppm; (6) concentrations ranged from 50 - 180 ppb in EPA muds 4, 5, and 6.

Cancer magister larvae (Dungeness crab, marine species): EC50 (96-hr) = 71.4 g/L; (4) concentrations caused cessation of larval swimming.

Pandalus danae larvae (coon-stripe shrimp, marine species): EC50 (96-hr) = 16.2 g/L; (4) concentrations caused cessation of larval swimming.

Benthos

Abra alba (marine mollusk): EC50 (5 days) = no toxicity; (4) no changes to fecal pellet production at concentrations up to 100,000 mg/kg in clean sediments.

Branchiostoma caribaeum (marine chordate): LC50 (168-hr) = no toxicity ; (7) toxicity to drilling muds found, but pure barite was non-toxic.

Risk Characterization

Toxicity data found for barite shows it to have very low toxicity. No conclusive LC50 values could be measured on barite. EC50 data was found on two marine species. The lowest EC50 was 16.2 g/l (approximately 16,200 ppm or 16,200,00 ppb) 96-hr EC50. Using this concentration and the results reported in Tables 74, 75, and 78, it is apparent that the highest predicted exposure concentration in any unit grid cell area would be at least two orders of magnitude lower than the toxic concentration. Both shallow water and deepwater spill models were run.

References

(1) Mallinckrodt Baker Inc. (1996d)
(2) Baker Hughes Inteq (1994c)
(3) Carls and Rice (1984)
(4) Clark and Patrick (1987)
(5) Hudgins and Petrotech Consultants, Inc. (1991)
(6) Jones et al. (1986)
(7) Stromgren et al. (1993)
(8) U.S. Department of Health and Human Services (1994)

Table 74

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 6. Particulate concentration of barite in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	46,451,613,696	104,086,855,680	121,598	182,022
10	10,299,490,304	65,495,502,848	57,258	144,388
100	1,449,644,672	11,351,220,224	21,481	60,110
1,000	281,160,800	2,013,692,800	9,460	25,318
10,000	45,076,948	464,059,232	3,788	12,154
100,000	6,161,592	72,642,104	1,400	4,809
1,000,000	-	6,161,592	-	1,400
10,000,000	-	-	-	-

Table 75

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 6. Mass loading of barite onto sediments in all subtidal habitats.

Threshold (g/m^2)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	11,548,906,496	11,548,906,496	60,631	60,631
0.10	11,548,906,496	11,548,906,496	60,631	60,631
1.0	3,943,911,424	11,548,906,496	35,431	60,631
10	-	11,548,906,496	-	60,631
100	-	177,064,352	-	7,507
1,000	-	-	-	-
10,000	-	-	-	-

Table 76

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 6. Particulate concentration of barite in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	6.29E+08	2.43E+08	1.45E+09	1.44E+08	0
10H-100H	0.1-1.0	1.76E+09	5.58E+08	3.17E+09	4.97E+08	0
100H-1,000H	1.0-10.0	3.10E+09	9.66E+08	5.82E+09	9.81E+08	0
1,000H-10,000H	10.0-100.0	6.26E+09	2.82E+09	2.67E+10	1.51E+09	0
10,000H-100,000H	100.0-1,000.0	1.20E+10	2.93E+09	1.60E+10	3.77E+09	0
> 100,000H	> 1,000.0	1.38E+10	5.03E+09	2.80E+10	7.52E+09	0
> 1H	> 0.01	3.76E+10	3.88E+09	5.86E+10	2.28E+10	0
> 10H	> 0.1	3.69E+10	3.74E+09	5.71E+10	2.26E+10	0
> 100H	> 1.0	3.52E+10	3.49E+09	5.46E+10	2.17E+10	0
> 1,000H	> 10.0	3.21E+10	3.14E+09	4.87E+10	2.01E+10	0
> 10,000H	> 100.0	2.58E+10	3.20E+09	3.39E+10	1.74E+10	0
> 100,000H	> 1,000.0	1.38E+10	5.03E+09	2.80E+10	7.52E+09	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 77

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 6. Particulate concentration of barite in all subtidal habitats.

Exposure Range	Dose (g/m^2)-hrs	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
10H-100H	0.1-1.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
100H-1,000H	1.0-10.0	0.00E+00	0.00E+00	0.00E+00	0.00E+00	100
1,000H-10,000H	10.0-100.0	1.82E+08	1.10E+08	6.02E+08	0.00E+00	1
10,000H-100,000H	100.0-1,000.0	1.92E+08	1.34E+08	6.64E+08	0.00E+00	1
> 100,000H	> 1,000.0	1.32E+07	1.59E+07	5.93E+07	0.00E+00	34
> 1H	> 0.01	3.88E+08	2.30E+08	1.25E+09	0.00E+00	1
> 10H	> 0.1	3.88E+08	2.30E+08	1.25E+09	0.00E+00	1
> 100H	> 1.0	3.88E+08	2.30E+08	1.25E+09	0.00E+00	1
> 1,000H	> 10.0	3.88E+08	2.30E+08	1.25E+09	0.00E+00	1
> 10,000H	> 100.0	2.06E+08	1.36E+08	6.64E+08	0.00E+00	1
> 100,000H	> 1,000.0	1.32E+07	1.59E+07	5.93E+07	0.00E+00	34

Table 78

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 17. Particulate concentration of barite in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	32,118,591,488	107,615,076,352	101,112	185,081
10	6,800,575,488	42,051,883,008	46,526	115,696
100	1,039,645,376	7,408,780,800	18,191	48,562
1,000	173,813,664	1,141,768,448	7,438	19,064
10,000	32,078,576	221,930,880	3,195	8,405
100,000	5,237,320	43,535,196	1,291	3,723
1,000,000	-	3,927,990	-	1,118
10,000,000	-	-	-	-

Table 79

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 17. Particulate concentration of barite in all subtidal habitats.

Exposure Range	Dose (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	1.0-10.0	1.14E+11	1.72E+10	1.67E+11	5.50E+10	0
10H-100H	10.0-100.0	6.93E+11	7.28E+10	8.19E+11	2.91E+11	0
100H-1,000H	100.0-1,000.0	1.46E+12	1.30E+11	1.87E+12	1.24E+12	0
1,000H-10,000H	1,000.0-10,000.0	5.51E+11	5.74E+10	7.88E+11	4.89E+11	0
10,000H-100,000H	10,000.0-100,000.0	2.20E+10	5.19E+09	3.18E+10	6.00E+09	0
> 100,000H	> 100,000.0	2.28E+08	1.06E+08	4.88E+08	0.00E+00	9
> 1H	> 1.0	2.84E+12	1.47E+11	3.44E+12	2.55E+12	0
> 10H	> 10.0	2.72E+12	1.45E+11	3.28E+12	2.44E+12	0
> 100H	> 100.0	2.03E+12	1.47E+11	2.52E+12	1.80E+12	0
> 1,000H	> 1,000.0	5.73E+11	5.32E+10	8.00E+11	5.12E+11	0
> 10,000H	> 10,000.0	2.22E+10	5.23E+09	3.18E+10	6.03E+09	0
> 100,000H	> 100,000.0	2.28E+08	1.06E+08	4.88E+08	0.00E+00	9

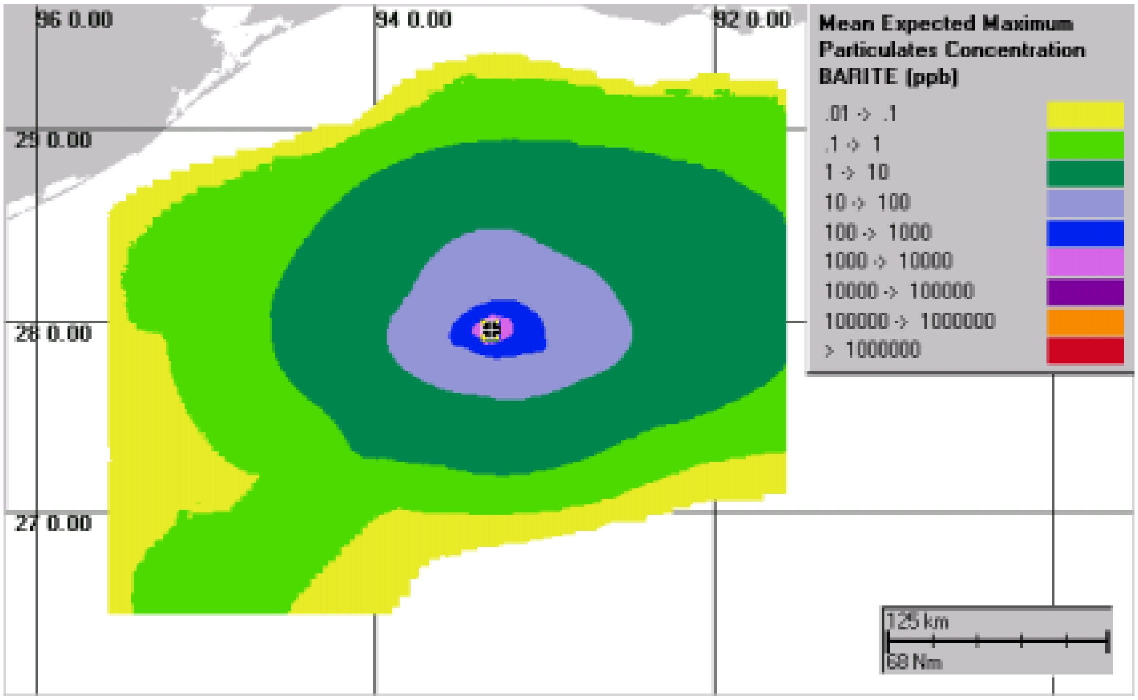


Figure 67. Peak exposure concentration (ppb) of barite as particulate in the water at each location: averaged over all simulations (Scenario 6).

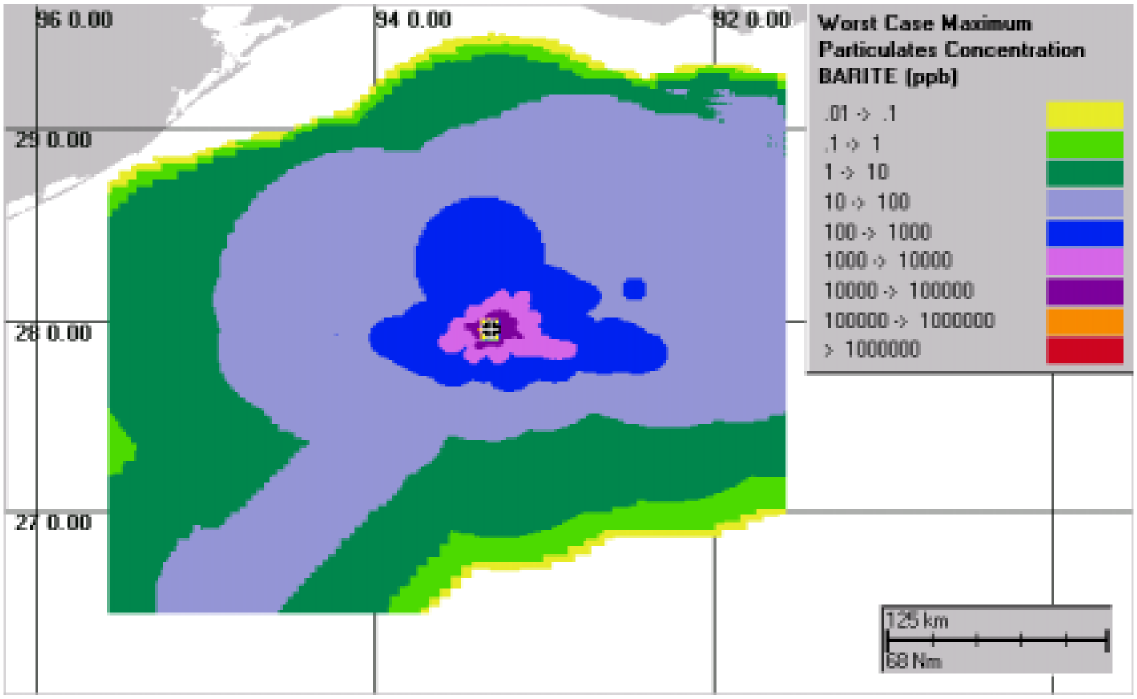


Figure 68. Peak exposure concentration (ppb) of barite as particulate in the water at each location: worst case of all simulations (Scenario 6).

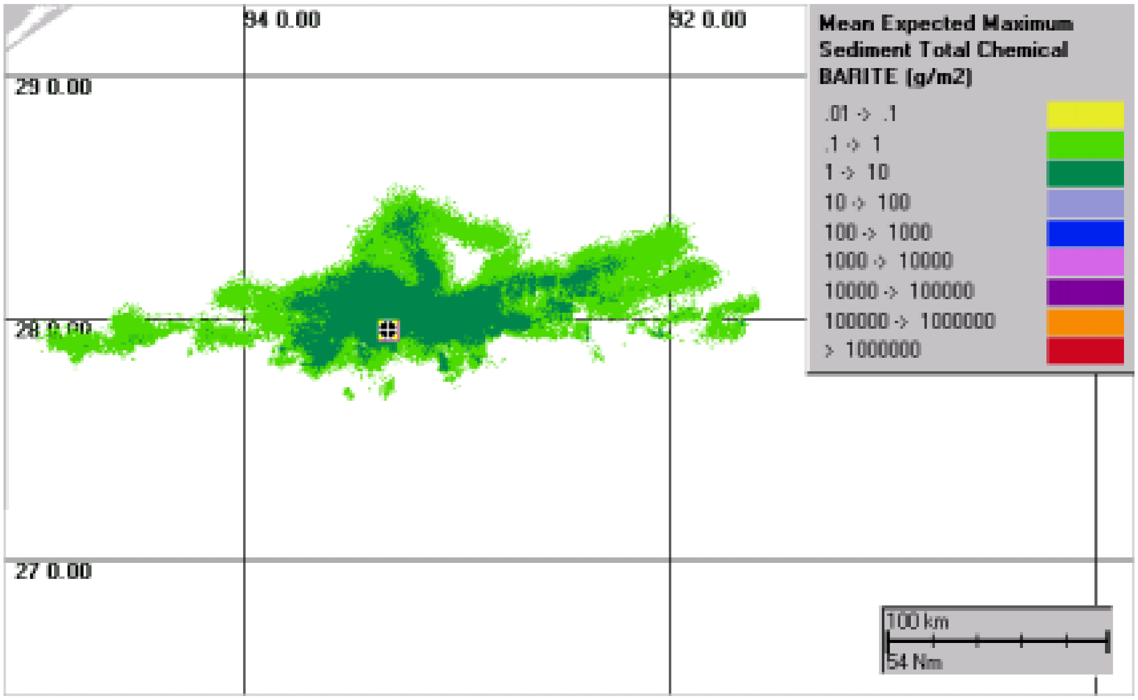


Figure 69. Peak exposure mass per unit area (g/m^2) of barite in the sediment at each location: averaged over all simulations (Scenario 6).

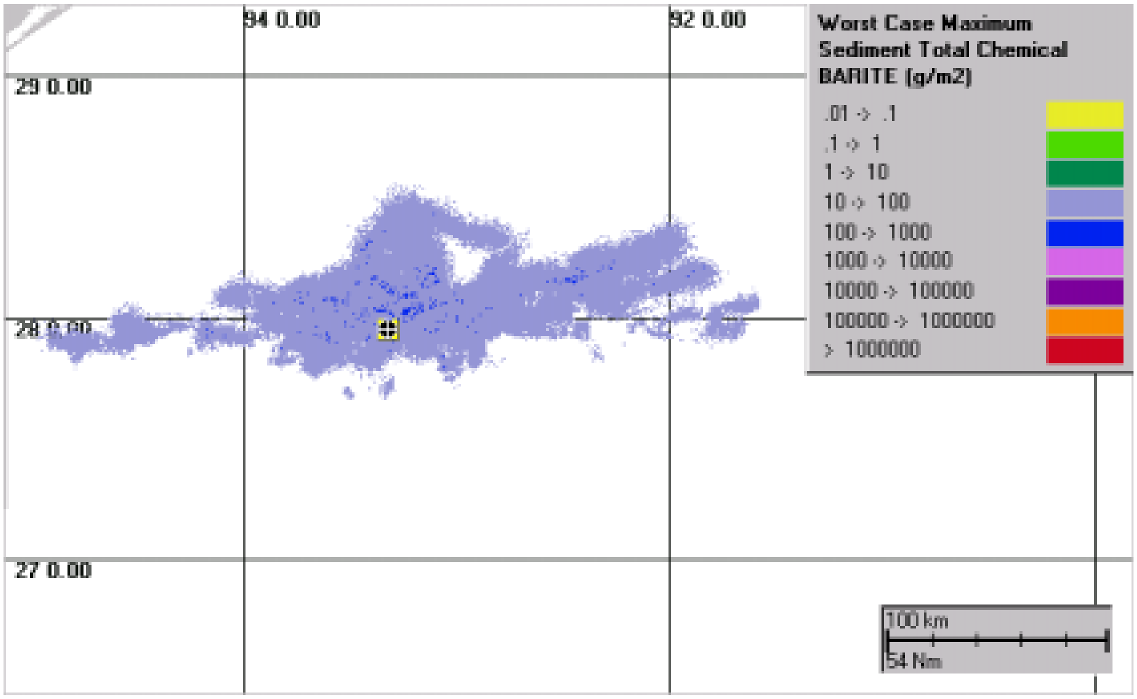


Figure 70. Peak exposure mass per unit area (g/m^2) of barite in the sediment at each location: worst case of all simulations (Scenario 6).

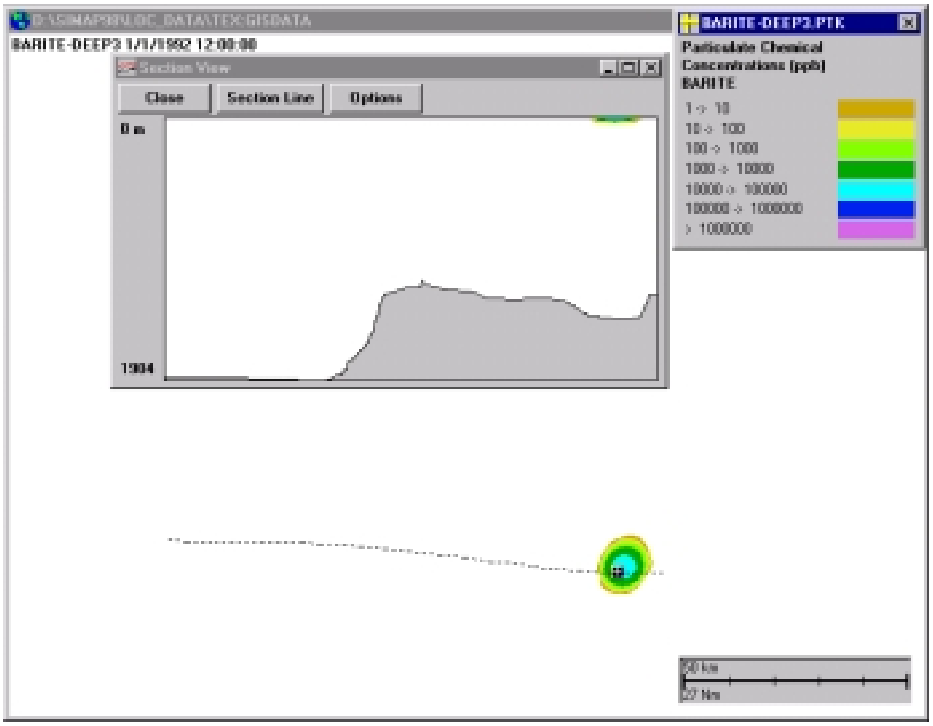


Figure 71. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 12:00 hours on 1 January 1992: 12 hours after the spill.

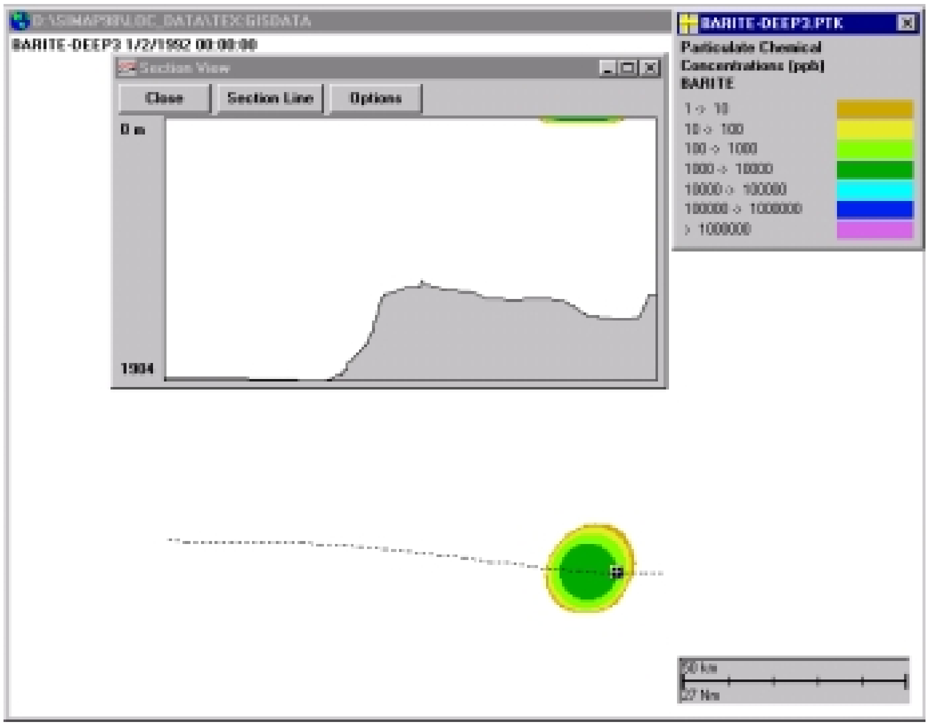


Figure 72. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 2 January 1992: 24 hours after the spill.

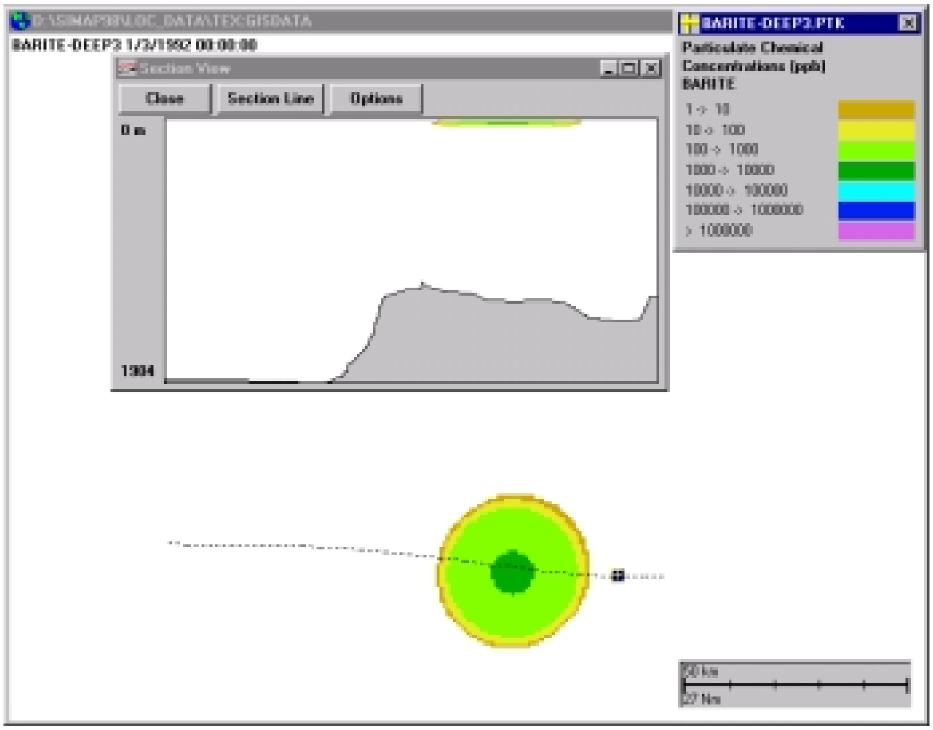


Figure 73. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 3 January 1992: 2 days after the spill.

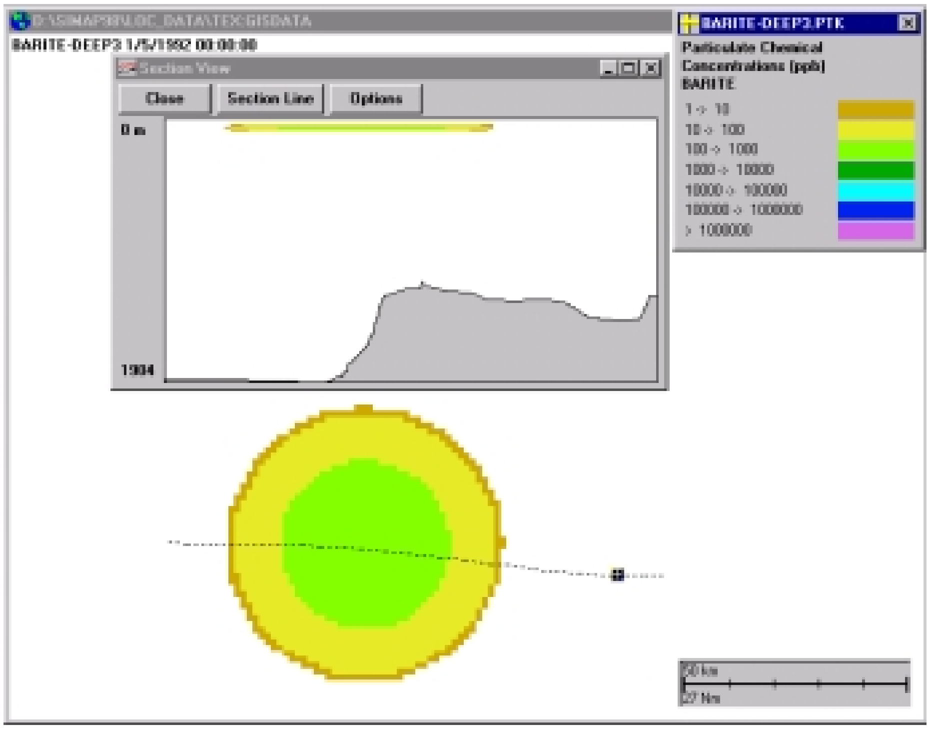


Figure 74. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 5 January 1992: 4 days after the spill.

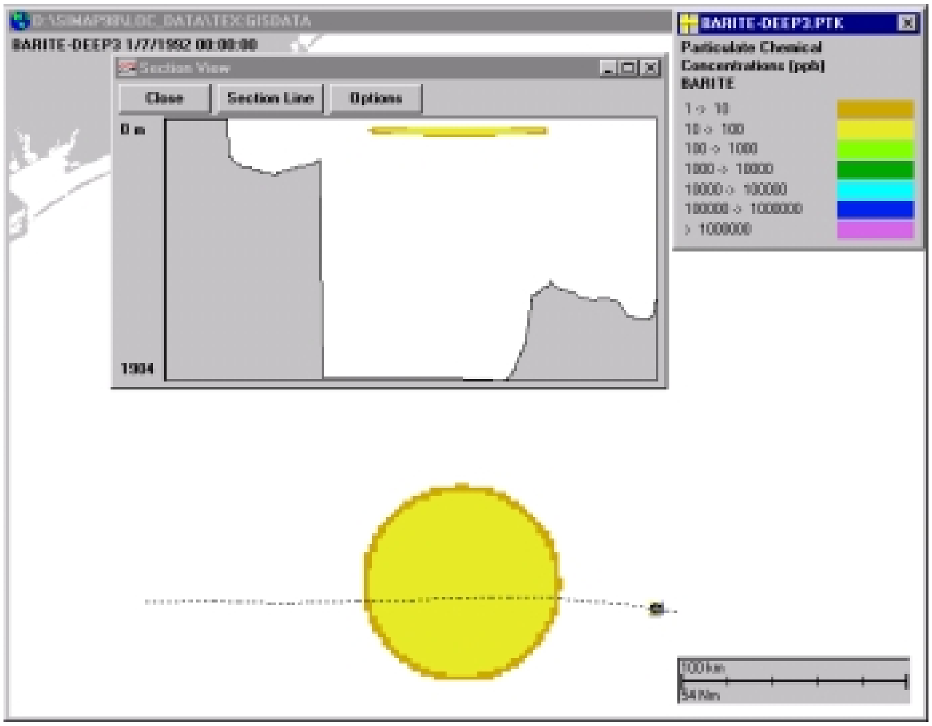


Figure 75. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 7 January 1992: 6 days after the spill.

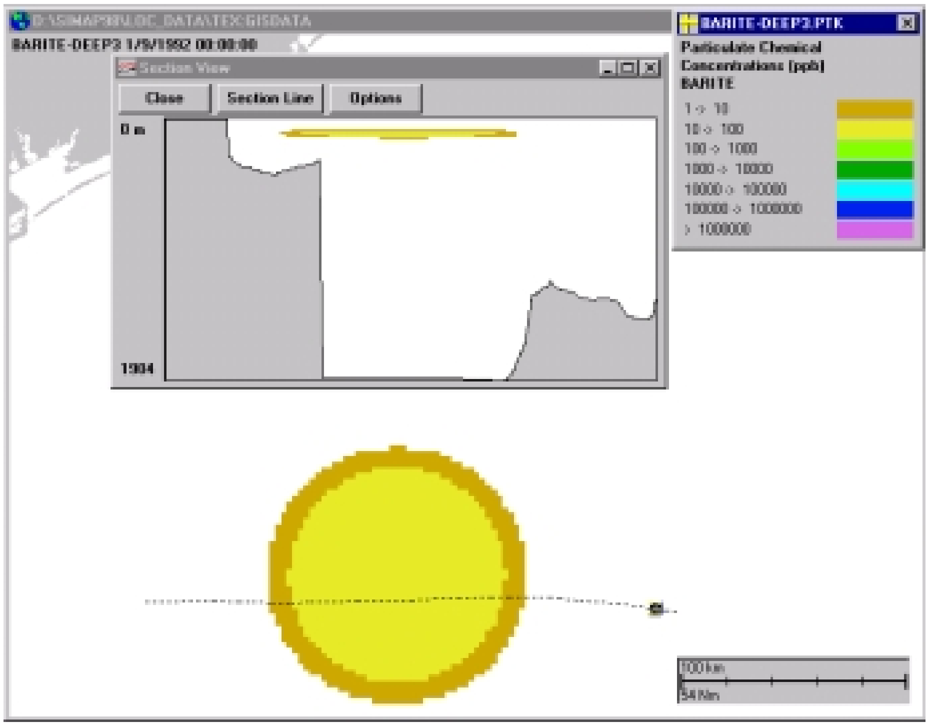


Figure 76. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 9 January 1992: 8 days after the spill.

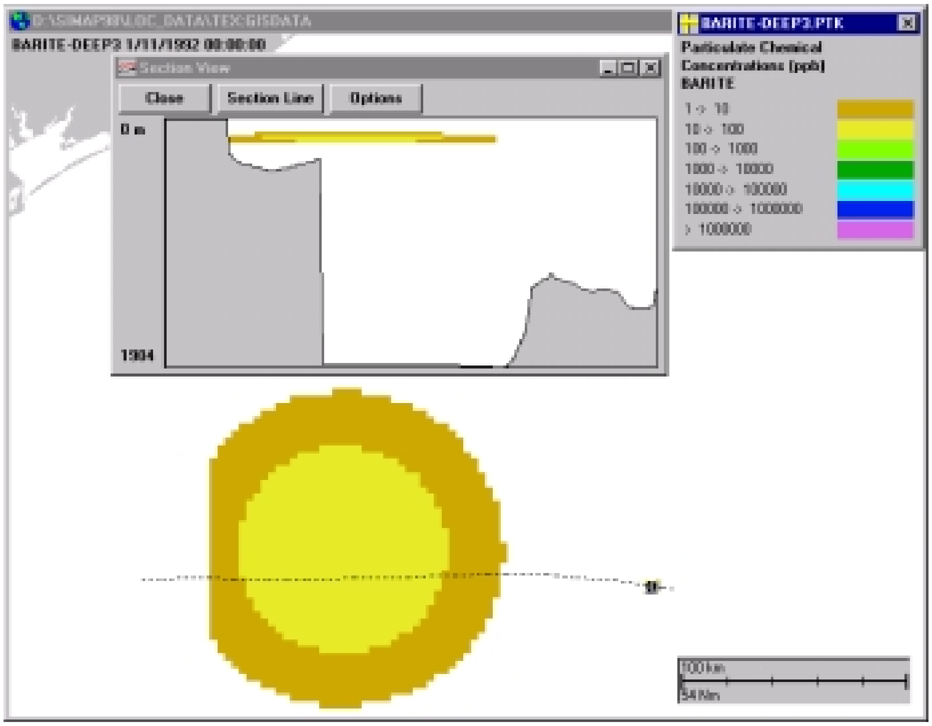


Figure 77. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 11 January 1992: 10 days after the spill.

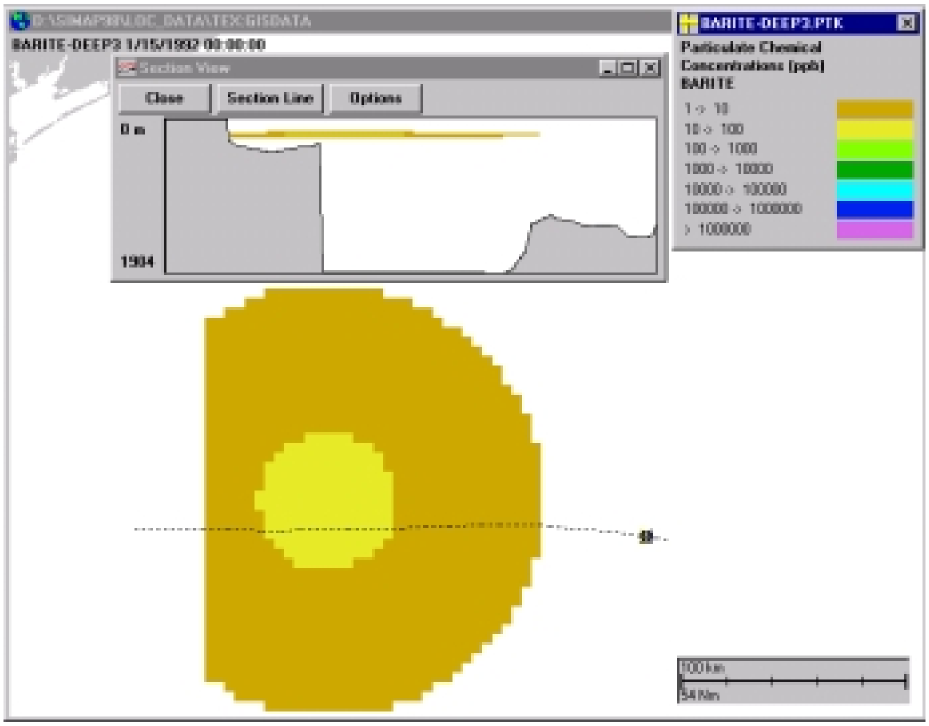


Figure 78. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 15 January 1992: 14 days after the spill.

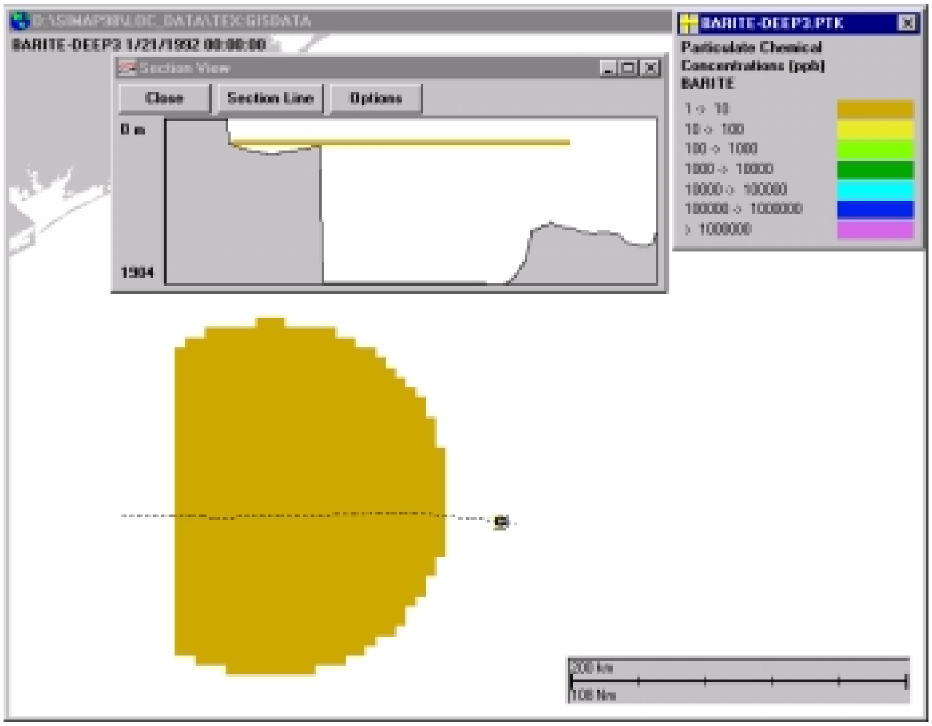


Figure 79. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 21 January 1992: 20 days after the spill.

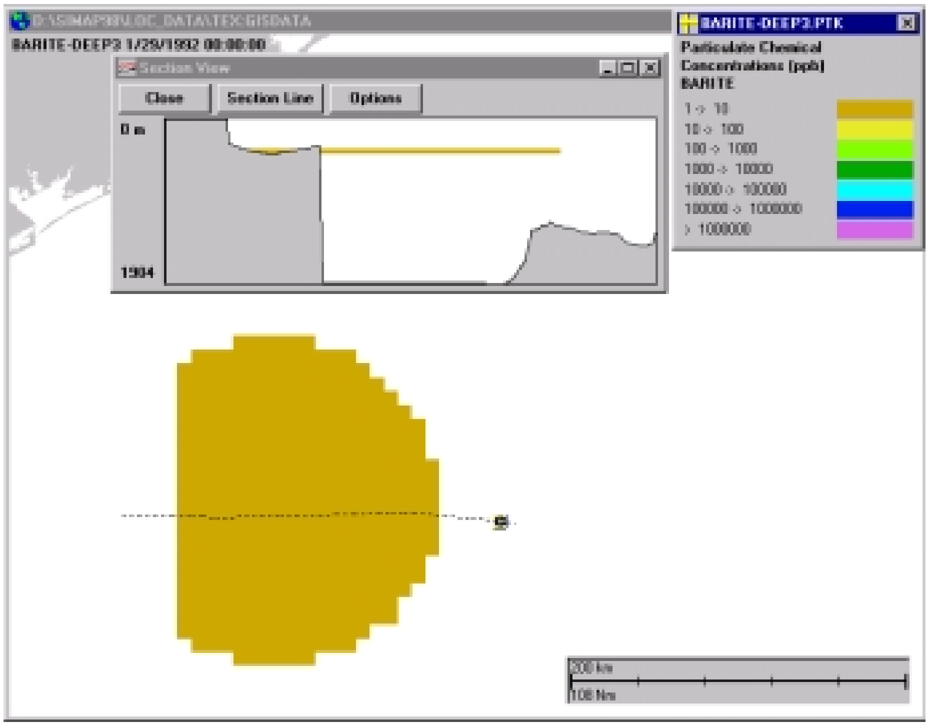


Figure 80. Particulate concentration of barite following a hypothetical surface release in the offshore Gulf of Mexico at 00:00 hours on 29 January 1992: 28 days after the spill.

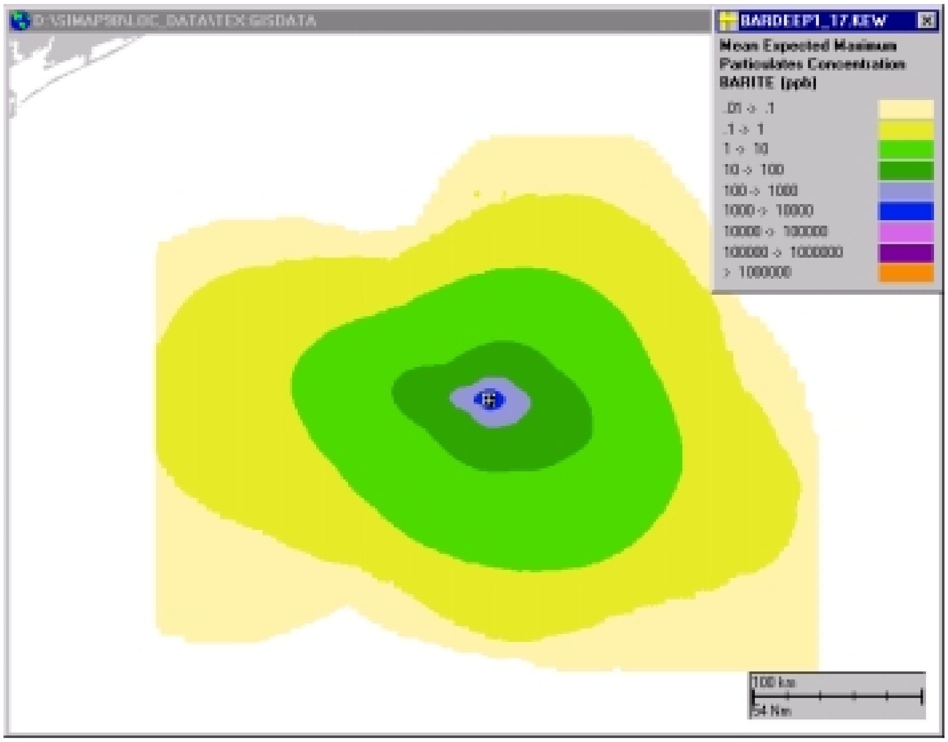


Figure 81. Peak exposure concentration (ppb) of barite as particulate in the water at each location: averaged over all simulations (Scenario 17).

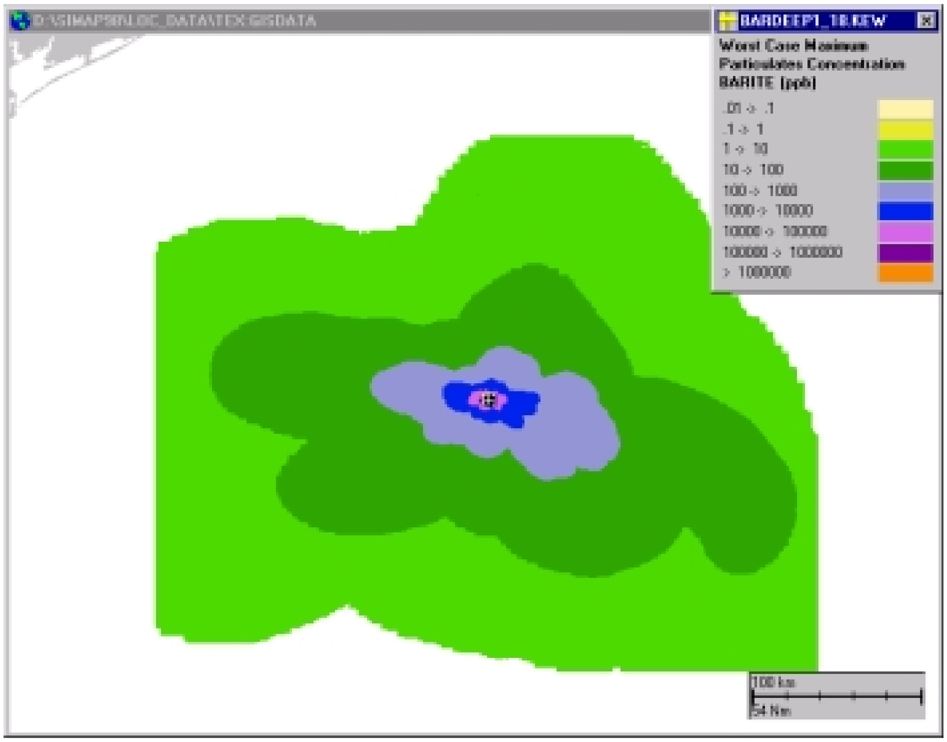


Figure 82. Peak exposure concentration (ppb) of barite as particulate in the water at each location: worst case of all simulations (Scenario 17).

Profile 20

LIGNOSULFONATE (Single Component)

Summary

Lignosulfonate is an organic salt material used as a drilling fluid chemical as a thinner or dispersant that adjusts the viscosity of the drilling fluid. It is made from nitrogen containing waste from the pulp and paper industry where wood is processed to make paper. It contains metal ions, usually chromium, and is supplied as a fine, water-soluble powder. If spilled in seawater, it will initially disperse into the water column and dissolve. Ultimately, it will be removed from the marine environment by biological action. An environmental concern associated with lignosulfonates is their potential toxicity due mainly to added metal ions.

Background Information

Fate in the Environment

Lignosulfonate is supplied as a fine, water-soluble powder. It is soluble in seawater, and, on being spilled, the lignosulfonate powder will disperse into the water column and dissolve. Ultimately, it will be removed from the marine environment by biological action. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Lignosulfonate is a component of water-based drilling fluids, which circulate through the drill string and bit and return to the mud pit. Eventually, drilling fluids become wastes. As a well is drilled, drilling fluid is lost to the environment in one of three ways: (1) clinging to bits of the formation removed from the well (cuttings) that are disposed of; (2) as excess drilling fluid that is disposed during the drilling operation; or (3) when the well drilling has been completed, and all the remaining drilling fluid is to be disposed. Outside the territorial seas, waste drilling fluids are discharged directly to the marine environment. Inside the territorial seas, waste drilling fluids are captured in cuttings boxes and are sent to landfills for disposal.

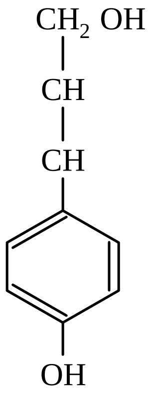
Other Components

None

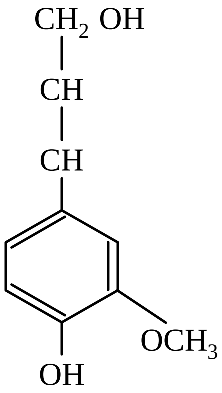
CAS Number

7440-47-3 (Chromium (III) compounds)

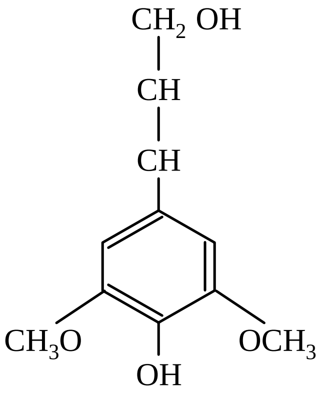
Chemical Formula



A

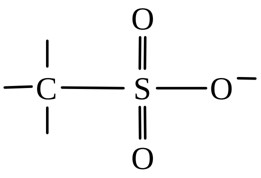


B



C

Lignosulfonates are low molecular weight polymers of various combinations of the monomers shown above which have been sulfonated. In the sulfonation process some of the alcohol groups (-OH) have been replaced by sulfonate groups ($-SO_3^{-1}$).



$$-\underset{|}{\overset{|}{C}}-\underset{\|\atop O}{\overset{O\atop\|}{S}}-O^-$$

Important Synonyms and Trade Names

UNI-CAL, SPERSENE, Q-BROXIN

Chemical and Physical Properties

Property	Component [1]	Product
Molecular Weight	NA	Same as Component
Boiling Point	NA	Same as Component
Melting Point	NA	Same as Component
Specific Gravity	1.2 – 1.4	Same as Component
Solubility in Water	Soluble	Same as Component
Solubility in Organics	Insoluble	Same as Component
Vapor Pressure	NA	Same as Component
Vapor Density (Air = 1)	NA	Same as Component
Physical State (Phase)	NA	Same as Component
Chemical Reactivity in the Environment	NA	Same as Component

Notes: NA = Not Available

Health and Safety Properties and Effects

Property	Component [(6)]	Product
Autoignition Temperature	450º C	Same as Component
Flash Point	153.9º C	Same as Component
Upper Explosive Limit	ND	Same as Component
Lower Explosive Limit	ND	Same as Component
Air Toxicity	0.5 mg/m^3 TLV for Chromium (III) compounds, respirable dust (1) 3 mg/m^3 TLV for PNOC, respirable dust (1)	Same as Component
OSHA PEL	0.5 mg/m^3 TWA for Chromium (III) compounds 5 mg/m^3 TWA for PNOC	Same as Component

Notes: ND = Not Determined; PNOC = Particulates Not Otherwise Classified

Health hazards for this chemical are related to the fact that it is a fine powder that can cause irritation to the skin, eyes, and throat. See Appendix B for MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 70 tons
Maximum = 100 tons

Transport Container(s): 50 lb. paper sacks on pallets.

Storage Methods: In sacks on pallets (usually in the drilling rig mud room).

Environmental and Toxicological Properties and Effects

Spill Model Results

A lignosulfonate spill was modeled as Scenario 7. The exposure concentrations presented below are derived for the results of this modeling.

Results are shown in Figures 83 to 85 and Tables 80 to 82. The DESCO/lignosulfonate begins as particulate, but dissolves so quickly the particulate concentration is instantaneous. Thus, dissolved concentrations are of interest. While DESCO and lignosulfonate are considered surface active, their partitioning behavior to suspended sediments has not been quantified. Thus, partitioning is assumed negligible in the model simulations. The dissolved concentrations may be considered as total concentrations of both dissolved and adsorbed material.

In the concentration plot, the high concentrations near shore (not part of the symmetric plume around the spill size) are an artifact of the compression of mass into a shallow water column, as the current data from offshore aim the modeled mass in the shoreward direction. If detailed actual currents were available, shoreward transport would, by physical laws, be balanced by offshore transport, and there would be no increase in concentration towards shore.

Aquatic Toxicity Levels

The available literature for lignite toxicity was reviewed and the results from relevant studies are shown below.

Algae and Invertebrates

Pandalus danae (coon-stripe shrimp, marine crustacean) larvae: LC50 (96 hr.) = 290 g/L. (2)
Mysidopsis bahia (mysid shrimp, marine crustacean): LC50 (96 hr.) = 506,000 ppm to > 1,000,000 ppm for chrome lignosulfonate muds with lignosulfonate concentrations of 3-15 lbs. per barrel in EPA muds 7 and 8. (5)
Mysidopsis bahia (mysid shrimp, marine crustacean): LC50 (96 hr.) 388,000 ppm to > 1,000,000 ppm for chrome-free lignosulfonate with lignosulfonate concentrations of 4-7.2 lbs. per barrel in EPA mud 7. (5)
Cancer magister (Dungeness crab, marine crustacean) larvae: LC50 (96 hr.) = 1.44 g/L(2)

Benthos

Crangon crangon (brown shrimp, marine crustacean) LC50 (96 hr.) = 3,300 ppm. (4)
Patria mineata (sea star, marine echinoderm) EC50 (48 hr.) = 5% WSF (Water Soluble Fraction) in embryo development test. (3)

Risk Characterization

Three of the toxicity data sources found for lignosulfonate are directly relevant to this study. The others are measured in tests on drilling muds. Toxicity values range from 290 mg/L (approximately 290 ppm or 290,000 ppb) 96-hr LC50 to 3,300 ppm (3,300,000 ppb) 96-hr LC50. Using 290,000 ppb and the results reported in Tables 80 and 81, it is apparent that the highest predicted exposure concentration in any unit grid cell area would be at least two orders of magnitude lower than the toxic concentration.

References

(1) Baker Hughes Inteq (1994d)
(2) Carls and Rice (1984)
(3) Chaffee and Spies (1982)
(4) Hudgins and Petrotech Consultants, Inc. (1991)
(5) Jones et al. (1986)
(6) M-I Drilling Fluids L.L.C. (1998d)

Table 80

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 7. Particulate concentration of DESCO/ lignosulfonate in all subtidal habitats. Note that these concentrations occur only within the first hour after the spill, as dissolution would be immediate.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	34,699,476	77,182,248	3,323	4,957
10	12,323,182	65,831,892	1,981	4,578
100	4,215,825	32,105,116	1,158	3,197
1,000	-	8,107,359	-	1,606
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 81

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 7. Dissolved concentration of DESCO/lignosulfonate in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
1	3,262,447,872	25,457,807,360	32,225	90,019
10	582,424,384	4,450,750,464	13,616	37,639
100	91,451,272	964,435,648	5,395	17,521
1,000	11,026,006	169,281,440	1,873	7,341
10,000	324,294	17,187,592	321	2,339
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 82

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 7. Dissolved concentration of DESCO/lignosulfonate in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	9.02E+08	4.22E+08	2.17E+09	1.07E+08	0
10H-100H	0.1-1.0	3.89E+09	1.50E+09	8.42E+09	6.67E+08	0
100H-1,000H	1.0-10.0	1.02E+10	3.17E+09	1.76E+10	1.62E+09	0
1,000H-10,000H	10.0-100.0	1.27E+10	2.93E+09	2.70E+10	3.18E+09	0
10,000H-100,000H	100.0-1,000.0	5.88E+09	2.21E+09	1.16E+10	2.15E+09	0
> 100,000H	> 1,000.0	8.13E+08	3.86E+08	2.19E+09	3.83E+08	0
> 1H	> 0.01	3.44E+10	4.69E+09	4.58E+10	1.82E+10	0
> 10H	> 0.1	3.35E+10	4.43E+09	4.41E+10	1.81E+10	0
> 100H	> 1.0	2.96E+10	3.47E+09	4.01E+10	1.74E+10	0
> 1,000H	> 10.0	1.94E+10	2.45E+09	2.97E+10	1.52E+10	0
> 10,000H	> 100.0	6.69E+09	2.41E+09	1.30E+10	2.58E+09	0
> 100,000H	> 1,000.0	8.13E+08	3.86E+08	2.19E+09	3.83E+08	0

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

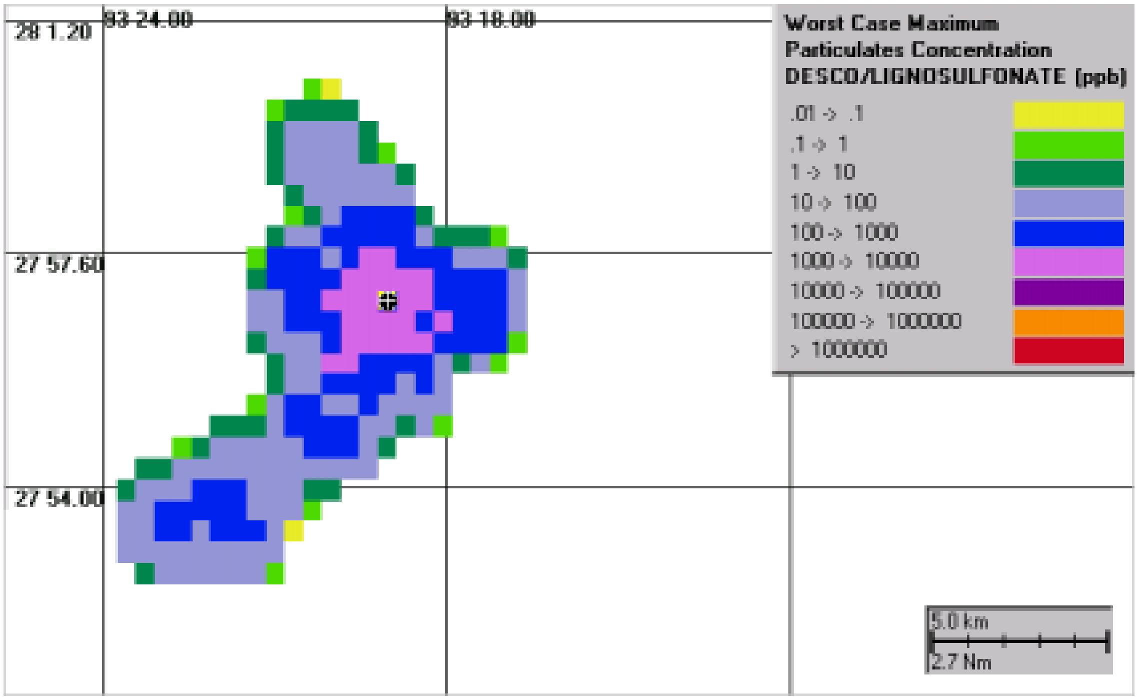


Figure 83. Peak exposure concentration (ppb) of DESCO/ lignosulfonate as particulate in the water at each location: worst case of all simulations (Scenario 7).

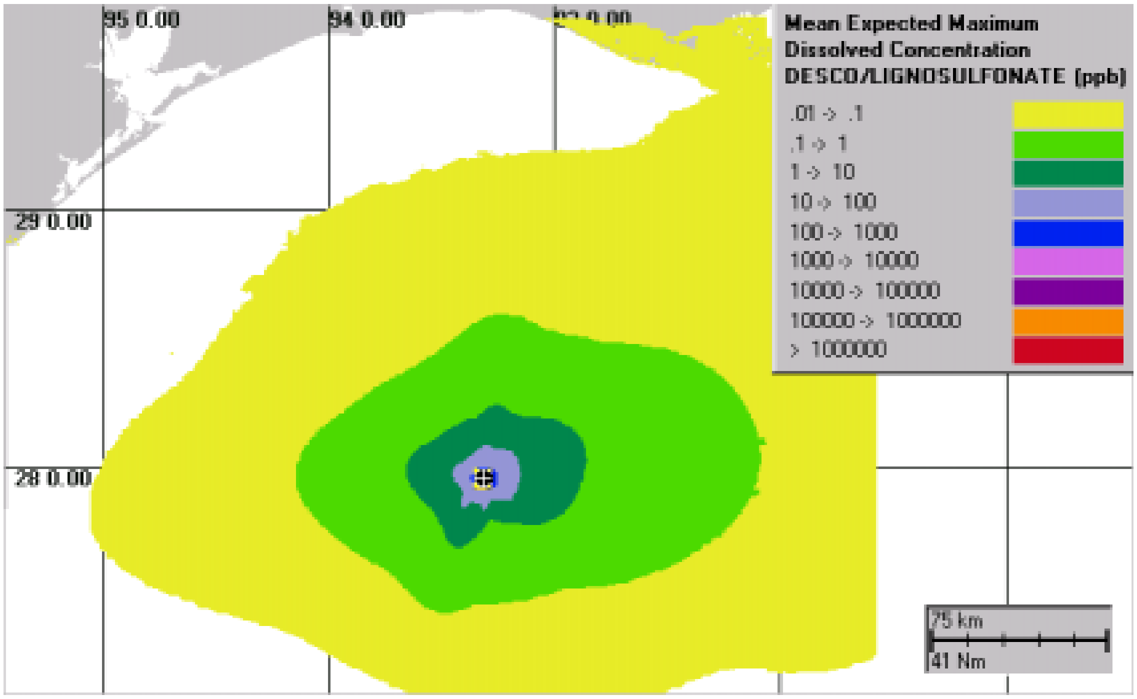


Figure 84. Peak exposure concentration (ppb) of DESCO/ lignosulfonate dissolved in the water at each location: averaged over all simulations (Scenario 7).

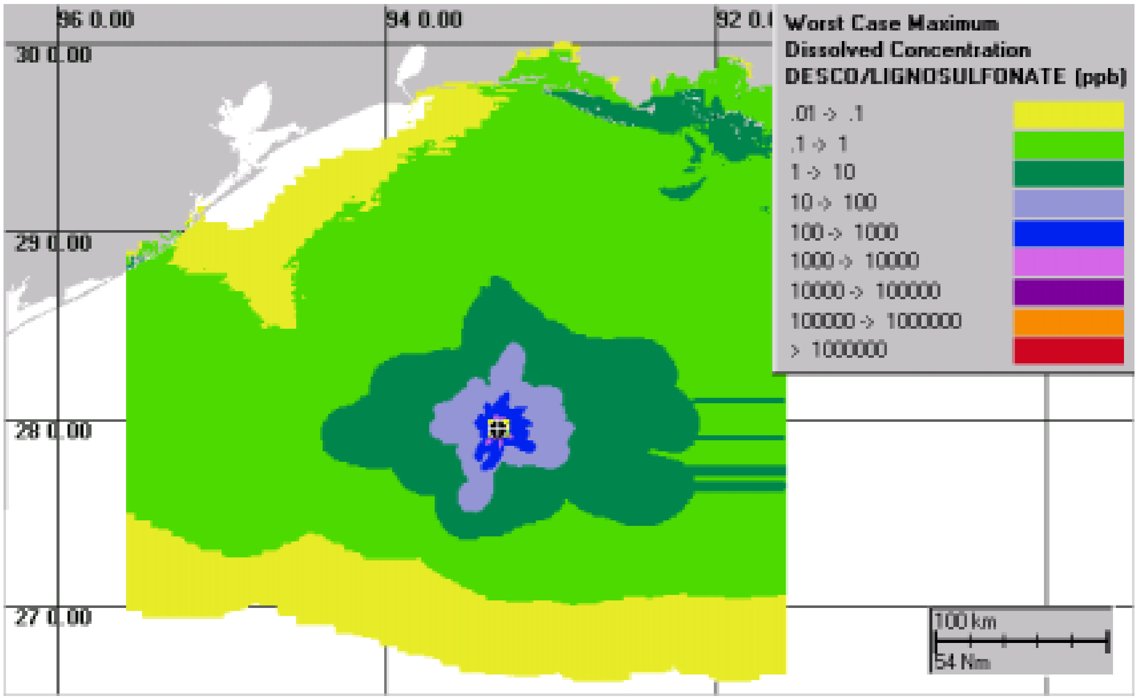


Figure 85. Peak exposure concentration (ppb) of DESCO/ lignosulfonate dissolved in the water at each location: worst case of all simulations (Scenario 7).

Profile 21

NAPHTHA, AROMATIC (Solvent for Oil Soluble Products)

Summary

Production-treating chemicals such as oil soluble corrosion inhibitors, emulsion breakers, oil/gas antifoaming chemicals, and other products, use aromatic naphthas as solvents. Product C, an oil soluble emulsion breaker, is one such product. The solvent portion of Product C, aromatic naphtha, is profiled here. A major component of aromatic naphtha is naphthalene. In the spill modeling of Product C, naphtha was assumed to have the properties of naphthalene for calculating distribution in the environment only. The main environmental impact of naphtha is its potential aquatic toxicity.

Background Information

Fate in the Environment

When spilled into the marine environment, Product C will spread on the surface of the water and some of the naphtha will be lost to the atmosphere. When the release to the environment is near the bottom (i.e., ocean floor), the product will rise rapidly to the surface and then spread on the surface. Oceanographic and meteorological forces will disperse the product into the water column as droplets, where some of it will partition to the water as soluble material. Dispersed droplets of Product C, and its naphtha component, will adhere to suspended solids and to sediment. Ultimately, naphtha will be lost to the atmosphere or biologically degraded. Table 26 (Section 7.0) presents the available degradation rates. The rates presented are instantaneous degradation rates. The half-life in days can be calculated by the following formula: 0.693/Degradation Rate = 1/2 life (days).

Fate in the Process System

Product C is used as an emulsion breaker to aid in the separation of emulsified water and solids from oil, so that the oil will meet sales specifications and the water can be removed for disposal. When applied to the produced stream, Product C will dissolve into the oil phase. Most of it will ultimately leave the treatment facility in the crude oil (i.e., commercially sold product). Small amounts of the chemical will be dispersed in the produced water, entering the produced water treatment system, and may be disposed of as a part of the produced water. In the Territorial Seas and the Outer Continental Shelf, produced water is disposed of into the sea, however, in other areas it is injected underground for disposal.

Other Components (Product)

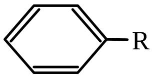
Alkyl benzenesulfonic acid

CAS Number (Naphtha)

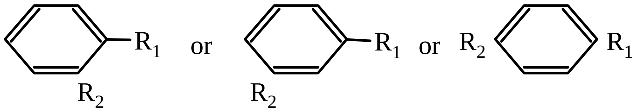
653 Aromatic Solvent (a standard solvent of this type) – 64742-94-5

Chemical Formula (Naphtha)

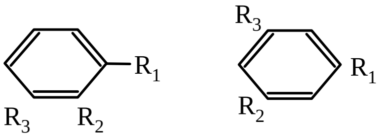
Common constituents of naptha include:



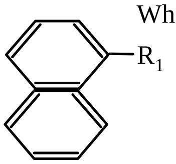
Substituted benzene
where R is 0 - 5



Where R is 0 - 3



Where R is 1 - 2



Where R is 0 - 3

653 Aromatic Solvent - a mixture of C9 to C11 aromatic hydrocarbons, primarily C10. Two constituents are naphthalene ($C_{10}H_8$) and 1,2,4-Trimethyl-Benzene

Important Synonyms and Trade Names

Heavy Aromatic Naphtha, HAN, Aromatic Solvent

Chemical and Physical Properties

Property	Component (1)	Product (2)
Molecular Weight	128.9 (naphthalene) 120.20 (trimethyl-benzene)	NA
Boiling Range	184-205º C	ND
Melting Point	NA	NA
Specific Gravity	0.90 @ 15.6º C	.93 (7.76 lbs./gal.)
Solubility in Water	Insoluble	Insoluble
Solubility in Organics	Soluble in hydrocarbons	Soluble in hydrocarbons
Vapor Pressure	0.5 mm Hg @ 20º C	2.0 psia @ 38º C
Vapor Density (Air = 1)	4.6	> 1
Physical State (Phase)	Liquid	Liquid
Viscosity	1.33 cst @ 25º C	NA
Chemical Reactivity in the Environment	None	None

Notes: NA = Not Available; ND = Not Determined

Health and Safety Properties and Effects

Property	Component (1)	Product (2)
Autoignition Temperature	443º C	ND
Flash Point	63º C (TCCC ASTM D 56)	20º C (TCC ASTM D 56)
Upper Explosive Limit	NA	NA
Lower Explosive Limit	NA	NA
Air Toxicity - TLV-STEL	100 ppm	250 ppm
OSHA PEL - TWA	NE	200 ppm

Notes: NA = Not Available; ND = Not Determined; NE = Not Established

Health hazards found for the component include effects on eyes, skin, respiratory tract, and gastrointestinal tract. Contact may cause permanent damage to the eyes. Inhalation of high concentrations may cause headache and nausea. Skin contact can result in toxic effects similar to those for inhalation. Ingestion may cause severe irritation or burns to the mouth and the gastrointestinal tract. See Appendix B for Product MSDS sheet.

Use and Handling Properties

Storage Volumes Offshore (deep water): Typical = 550 gal.
Maximum = 700 gal.

Transport Container(s): 55 gal. drums, 500 gal. steel or HDPP totes.

Storage Methods: In shipping containers on the platform or in steel or plastic bulk tanks on the platform.

Spill Modeling Results, Aquatic Toxicity, and Risk Characterization

Spill Model Results

Product C spill was modeled in spill scenario 16. The exposure concentrations presented below are derived from the results of this modeling. For Scenario 16t, the modeling assumed that all of Product C behaved physically as naphtha, using the physical-chemical properties of naphthalene. Since Product C is actually composed of only 60% naphtha, the naphtha values shown here are 60% of the results of Scenario 16t. See Section 7.0 for other modeling assumptions.

Results of scenario 16t are shown in Figures 86 to 92 and Tables 83 to 90. The alkylbenzene sulfonic acids are in a naphtha solution. If it is assumed that the active ingredients are transported with and have the same fate as the naphtha, scenario 16t (modeled as naphthalene) represents the concentrations of naphtha plus alkylbenzene sulfonic acids.

Scenario 16t (Figures 86 to 92 and Tables 83 to 90) shows the expected behavior of naphtha, with portions as suspended droplets (particulate), dissolved, and adsorbed to suspended sediments. Because the release is at the bottom, some of the naphtha solution is dispersed onto the sediments around the spill site, primarily along-shelf (along bathymetric contours). Dilution is by dispersion primarily, as there is little exposure to the atmosphere.

The naphtha represents 60% of the spilled mass and resulting concentrations in scenario 16t. Thus, consideration of the naphtha alone (scenario 16n) would be identical in pattern, with concentrations 60% of that shown in the figures for scenario 16t. (Thus, scenario 16n was not run.)

Since scenario 16t was a bottom release, such that the naphtha would not evaporate or volatilize appreciably, scenario 16t would be representative of the entire solution if the alkylbenzene sulfonic acids have a similar (low) solubility to naphtha. If alkylbenzene sulfonic acids are not at all soluble, the results of scenario 16a are more representative for that chemical. However, in comparing the patterns of the two scenarios in the figures, dissolution of alkylbenzene sulfonic acids does not change the results appreciably.

Aquatic Toxicity Levels

Algae and Invertebrates

No aquatic toxicity data were found for naphtha. Toxicity information found for naphthalene, a major constituent in most naphtha formulations, was used in this evaluation. The information found for naphthalene is listed below.

Plankton (Water Column)

Daphnia magna (water flea, freshwater crustacean): EC50 (48-hr) = 2,305 µg/L; end-point was immobility of test organisms (3)

Eurytemora affinis (marine copepod crustacean): concentration of 10 µg/L resulted in shortened lifespan and brood size (4)

Marine bacterioplankton: two to seven day growth test, 1 mg/L concentration resulted in reduced growth (5)

Benthos

Neanthes arenaceodentata (marine polychaete): TLM (96-hr) = 3.8 ppm (6)

Elasmopus pectenicrus (marine amphipod): LC50 (96-hr) > 3.0 ppm (7)

Chironomus attenuatus (freshwater insect): LC50 (24-hr) = 13 mg/L (8)

Tanytarsus dissimilis (freshwater insect): LC50 (24-hr) = 13 mg/L (8)

Risk Characterization

No marine toxicity data were found for naphtha. Naphthalene is a major constituent of naphtha and the properties of naphthalene were used to evaluate potential impact of naphtha. Data on toxicity to marine species included 96-hr LC50 data and effects data. Concentrations as low as 10 µg/L (approximately 10 ppb) were reported to cause shortened lifespan and reduced brood size in *Eurytemora affinis*. A two to seven day test at 1 mg/L (approximately 1 ppm or 1,000 ppb) resulted in reduced growth in marine bacterioplankton. Toxicity to one marine amphipod was 3 ppm (3,000 ppb) (96-hr LC50). Using 3,000 ppb and the results reported in Table 84, it is apparent that the highest predicted exposure concentration in any unit grid cell area would be at least two orders of magnitude lower than the toxic concentration.

References

(1) Exxon Company, U.S.A. (1999)
(2) Supplier's MSDS for Product C (See Appendix B)
(3) Muñoz and Tarazona (1993)
(4) Ott et al. (1978)
(5) Hudack and Furhman (1988)
(6) Rossi and Neff (1978)
(7) Lee and Nicol (1978)
(8) Darville and Wilhm (1983)

Table 83

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 16t. Concentration of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) as droplets in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	2,497,301,504	8,885,822,464	28,194	53,183
0.10	535,078,304	2,843,709,440	13,051	30,086
1.0	86,262,536	515,945,312	5,240	12,815
10	12,647,476	80,749,504	2,006	5,070
100	1,297,177	10,701,712	643	1,846
1,000	-	972,883	-	556
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 84

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 16t. Dissolved concentration of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	1,130,482,304	6,963,142,656	18,970	47,079
0.10	83,668,168	1,183,351,680	5,161	19,408
1.0	4,864,414	54,157,236	1,244	4,152
10	324,294	3,242,943	321	1,016
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 85

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 16t. Concentration of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) adsorbed to suspended sediments in all subtidal habitats.

Threshold (ppb)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	245,164,832	4,298,101,248	8,834	36,988
0.10	5,513,003	427,738,976	1,325	11,668
1.0	-	36,969,548	-	3,430
10	-	1,621,471	-	718
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-
100,000	-	-	-	-
1,000,000	-	-	-	-

Table 86

Areas (m^2) and distance (m) from the spill site exposed above the indicated threshold levels under average and worst case environmental conditions: Scenario 16t. Mass loading of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) onto sediments in all subtidal habitats.

Threshold (g/m^2)	Average (m^2)	Worst Case (m^2)	Average Radius (m)	Worst Case Radius (m)
0.01	-	608,043,136	-	13,912
0.10	-	1,621,471	-	718
1.0	-	-	-	-
10	-	-	-	-
100	-	-	-	-
1,000	-	-	-	-
10,000	-	-	-	-

Table 87

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 16t. Concentration of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) as droplets in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	7.79E+07	3.34E+07	2.14E+08	2.92E+07	0
10H-100H	0.1-1.0	4.72E+08	1.24E+08	9.20E+08	1.92E+08	0
100H-1,000H	1.0-10.0	9.36E+08	1.84E+08	1.51E+09	5.16E+08	0
1,000H-10,000H	10.0-100.0	4.64E+08	1.98E+08	1.14E+09	9.76E+07	0
10,000H-100,000H	100.0-1,000.0	7.51E+07	3.47E+07	2.29E+08	2.76E+07	0
100,000H-10^6H	1,000-10,000	6.46E+06	2.12E+06	2.35E+07	4.32E+06	0
10^7H-10^8H	10,000-100,000	9.20E+05	4.76E+05	3.24E+06	0	1
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	2.03E+09	3.98E+08	3.32E+09	1.12E+09	0
> 10H	> 0.1	1.95E+09	3.87E+08	3.21E+09	1.08E+09	0
> 100H	> 1.0	1.48E+09	3.48E+08	2.69E+09	8.36E+08	0
> 1,000H	> 10.0	5.46E+08	2.29E+08	1.30E+09	1.36E+08	0
> 10,000H	> 100.0	8.24E+07	3.57E+07	2.54E+08	3.41E+07	0
> 100,000H	> 1,000.0	7.38E+06	1.94E+06	2.43E+07	5.19E+06	0
> 1,000,000H	> 10,000	9.20E+05	4.76E+05	3.24E+06	0	1
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 88

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 16t. Dissolved concentration of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) in all subtidal habitats.

Exposure Range	Dose (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	4.69E+07	2.94E+07	2.04E+08	5.84E+06	0
10H-100H	0.1-1.0	2.71E+08	1.26E+08	6.78E+08	7.75E+07	0
100H-1,000H	1.0-10.0	7.15E+08	2.70E+08	1.61E+09	1.54E+08	0
1,000H-10,000H	10.0-100.0	2.11E+08	1.63E+08	9.75E+08	3.63E+07	0
10,000H-100,000H	100.0-1,000.0	6.92E+06	6.35E+06	5.51E+07	1.30E+06	0
100,000H-10^6H	1,000-10,000	2.92E+05	3.52E+05	2.27E+06	0	64
10^7H-10^8H	10,000-100,000	1.56E+05	2.64E+05	1.51E+06	0	80
10^8H-10^9H	100,000-1,000,000	0	0	0	0	100
> 10^9H	> 1,000,000	0	0	0	0	100
> 1H	> 0.01	1.25E+09	5.09E+08	3.22E+09	3.72E+08	0
> 10H	> 0.1	1.20E+09	4.93E+08	3.12E+09	3.50E+08	0
> 100H	> 1.0	9.33E+08	4.17E+08	2.59E+09	1.96E+08	0
> 1,000H	> 10.0	2.18E+08	1.66E+08	9.82E+08	4.22E+07	0
> 10,000H	> 100.0	7.36E+06	6.35E+06	5.58E+07	1.30E+06	0
> 100,000H	> 1,000.0	4.48E+05	4.29E+05	2.27E+06	0	31
> 1,000,000H	> 10,000	1.56E+05	2.64E+05	1.51E+06	0	80
> 10,000,000H	> 100,000	0	0	0	0	100
> 100,000,000H	> 1,000,000	0	0	0	0	100

Table 89

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.01 (mg/m^3)-hours (0.01 ppb-hours): Scenario 16t. Concentration of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) adsorbed to suspended sediments in all subtidal habitats.

Exposure Range	Dose (1) (ppb-hours)	Mean (m^2)	Std. Dev. (m^2)	Maximum (m^2)	Minimum (m^2)	% runs @ 0
1H-10H	0.01-0.1	2.53E+06	1.58E+07	1.47E+08	0	93
10H-100H	0.1-1.0	1.51E+07	6.54E+07	5.18E+08	0	90
100H-1,000H	1.0-10.0	2.76E+07	1.04E+08	5.90E+08	0	60
1,000H-10,000H	10.0-100.0	3.98E+07	1.33E+08	8.12E+08	0	56
10,000H-100,000H	100.0-1,000.0	5.29E+07	1.19E+08	6.95E+08	0	56
100,000H-10^6H	1,000-10,000	3.41E+05	9.84E+05	4.75E+06	0	98
10^7H-10^8H	10,000-100,000	3.24E+06	4.52E+06	1.43E+07	0	90
10^8H-10^9H	100,000-1,000,000	1.47E+07	1.81E+07	6.18E+07	0	89
> 10^9H	> 1,000,000	9.77E+08	1.15E+09	3.04E+09	0	89
> 1H	> 0.01	1.13E+09	1.29E+09	3.25E+09	0	56
> 10H	> 0.1	1.13E+09	1.29E+09	3.25E+09	0	56
> 100H	> 1.0	1.12E+09	1.27E+09	3.25E+09	0	56
> 1,000H	> 10.0	1.09E+09	1.25E+09	3.25E+09	0	56
> 10,000H	> 100.0	1.05E+09	1.22E+09	3.24E+09	0	56
> 100,000H	> 1,000.0	9.95E+08	1.17E+09	3.12E+09	0	56
> 1,000,000H	> 10,000	9.95E+08	1.17E+09	3.12E+09	0	89
> 10,000,000H	> 100,000	9.91E+08	1.17E+09	3.10E+09	0	89
> 100,000,000H	> 1,000,000	9.77E+08	1.15E+09	3.04E+09	0	89

(1) Peak exposure plots are included for all forms of chemical where concentrations exceed 0.01 mg/m^3 (~0.01 ppb) or mass loading exceeds 0.0001 g/m^2 for at least one hour (the time step) following the spill. These extremely low thresholds were used so that the entire fate of the chemical could be shown in the figures. The presence of these low concentration contours do not imply toxicological impact.

Table 90

Areas (m^2) impacted at each dosage level of exposure above a threshold of H=0.0001 (g/m^2)-hours: Scenario 16t. Mass loading of alkylbenzene sulfonic acids in naphtha (modeled as naphthalene) onto sediments in all subtidal habitats.

Exposure Range	**Dose (g/m^2)-hrs)**	**Mean (m^2)**	**Std. Dev. (m^2)**	**Maximum (m^2)**	**Minimum (m^2)**	**% runs @ 0**
1H-10H	0.01-0.1	1.59E+07	1.18E+07	5.35E+07	0	1
10H-100H	0.1-1.0	2.10E+06	3.24E+06	2.04E+07	0	33
100H-1,000H	1.0-10.0	0	0	0	0	100
1,000H-10,000H	10.0-100.0	0	0	0	0	100
10,000H-100,000H	100.0-1,000.0	0	0	0	0	100
> 100,000H	> 1,000.0	0	0	0	0	100
> 1H	> 0.01	1.80E+07	1.40E+07	6.19E+07	0	1
> 10H	> 0.1	2.10E+06	3.24E+06	2.04E+07	0	33
> 100H	> 1.0	0	0	0	0	100
> 1,000H	> 10.0	0	0	0	0	100
> 10,000H	> 100.0	0	0	0	0	100
> 100,000H	> 1,000.0	0	0	0	0	100

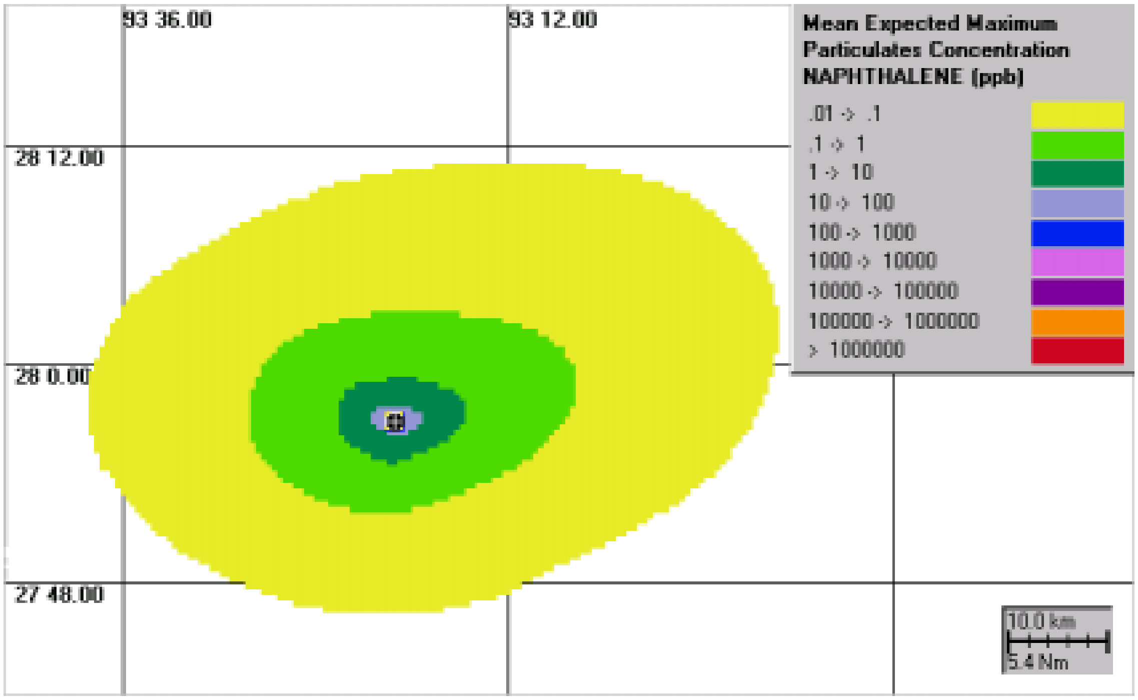


Figure 86. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) as pure liquid droplets in the water at each location: averaged over all simulations (Scenario 16t).

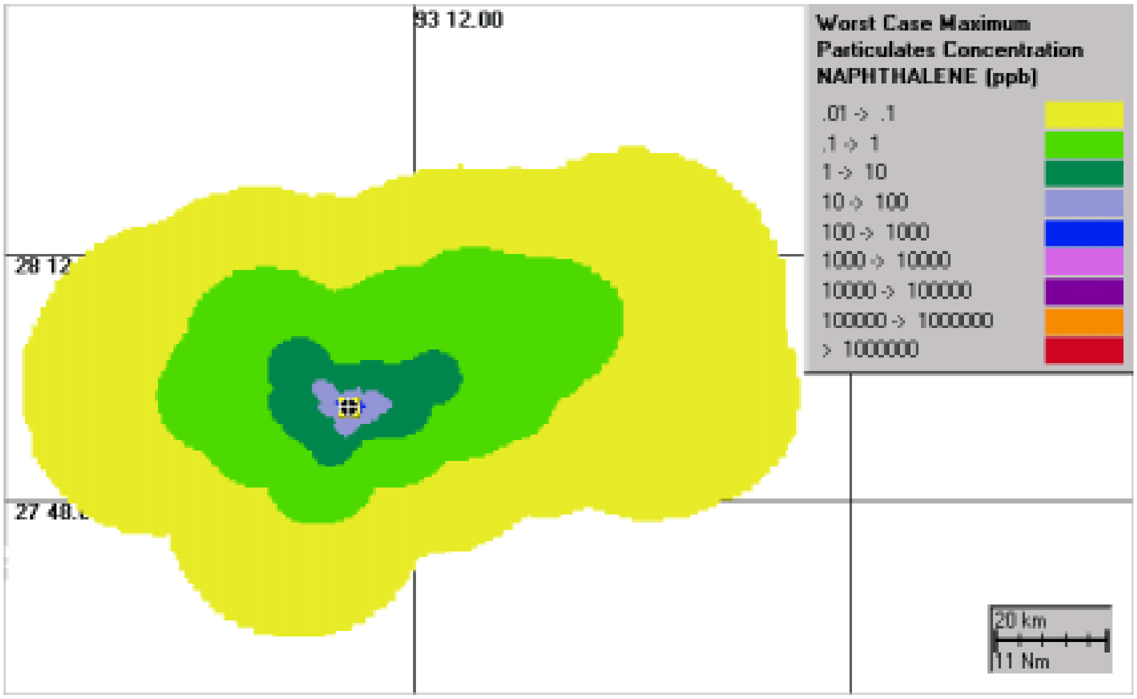


Figure 87. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) as pure liquid droplets in the water at each location: worst case of all simulations (Scenario 16t).

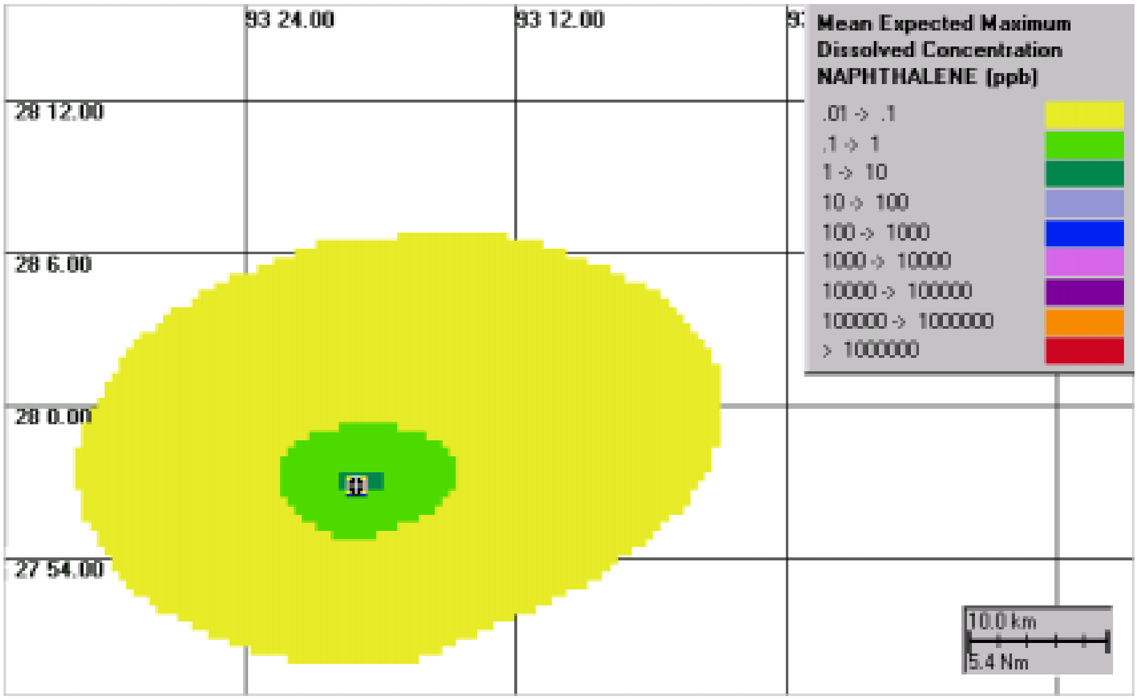


Figure 88. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) dissolved in the water at each location: averaged over all simulations (Scenario 16t).

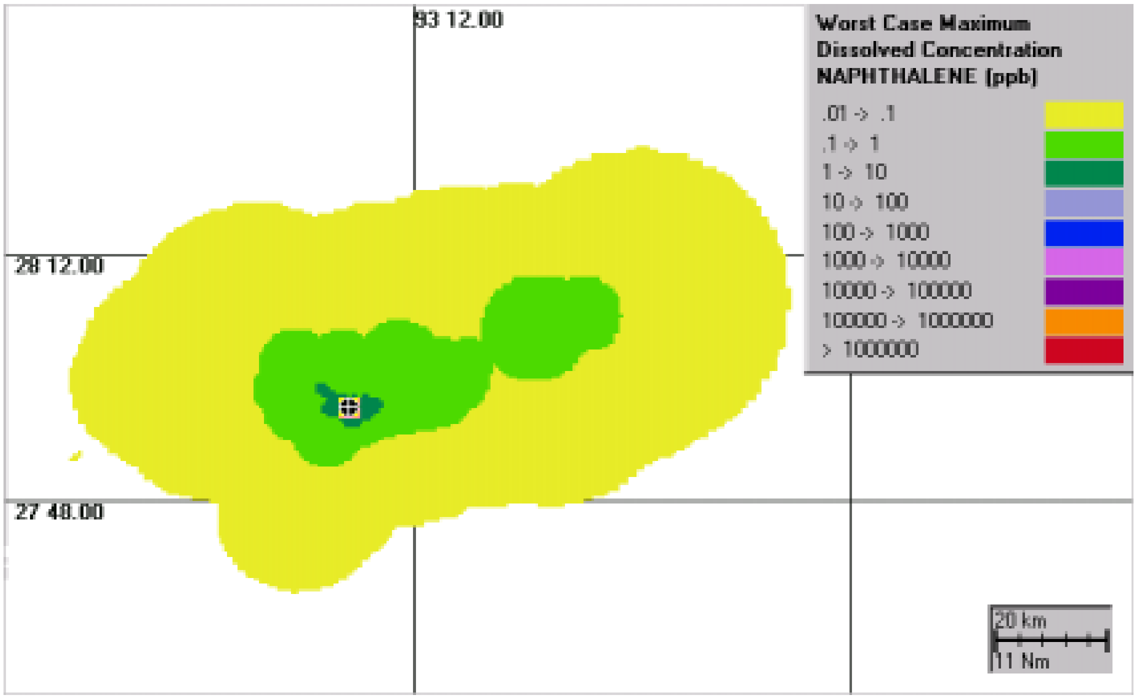


Figure 89. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) dissolved in the water at each location: worst case of all simulations (Scenario 16t).

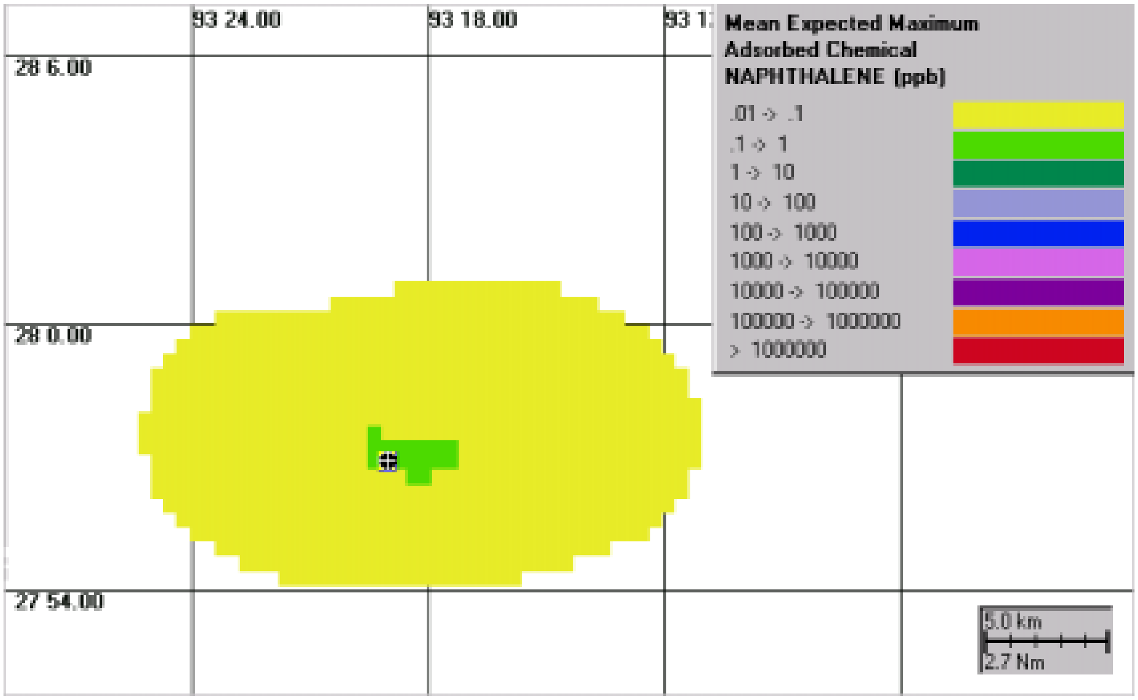


Figure 90. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) adsorbed to suspended sediment in the water at each location: over all simulations (Scenario 16t).

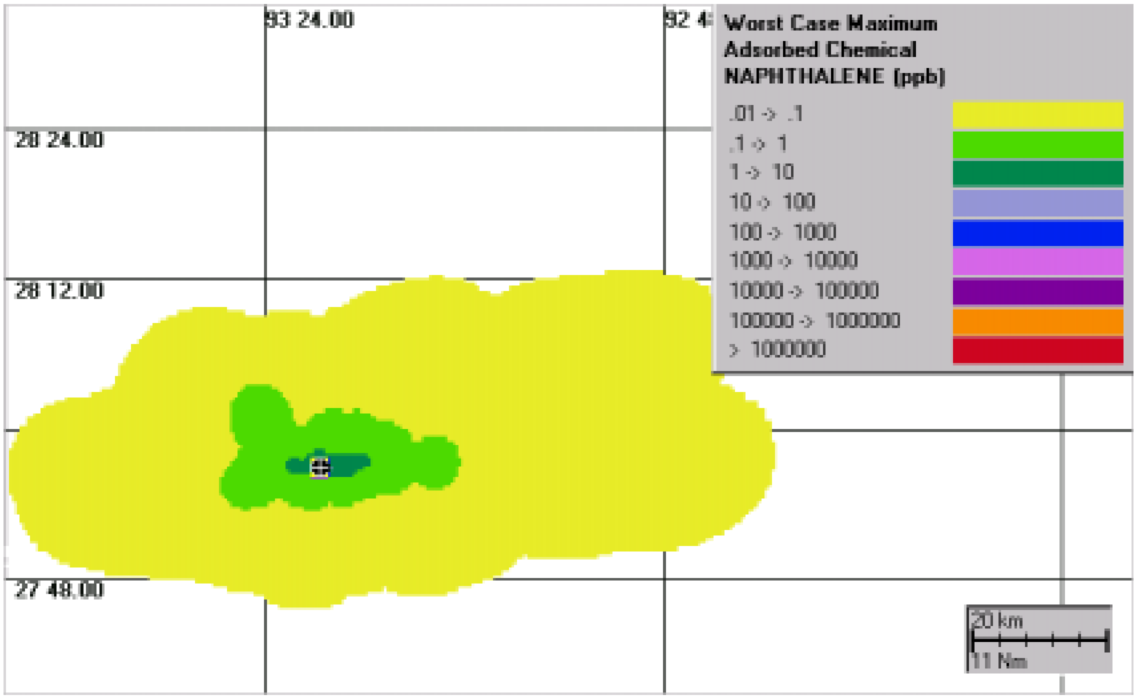


Figure 91. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) adsorbed to suspended sediment in the water at each location: worst case of all simulations (Scenario 16t).

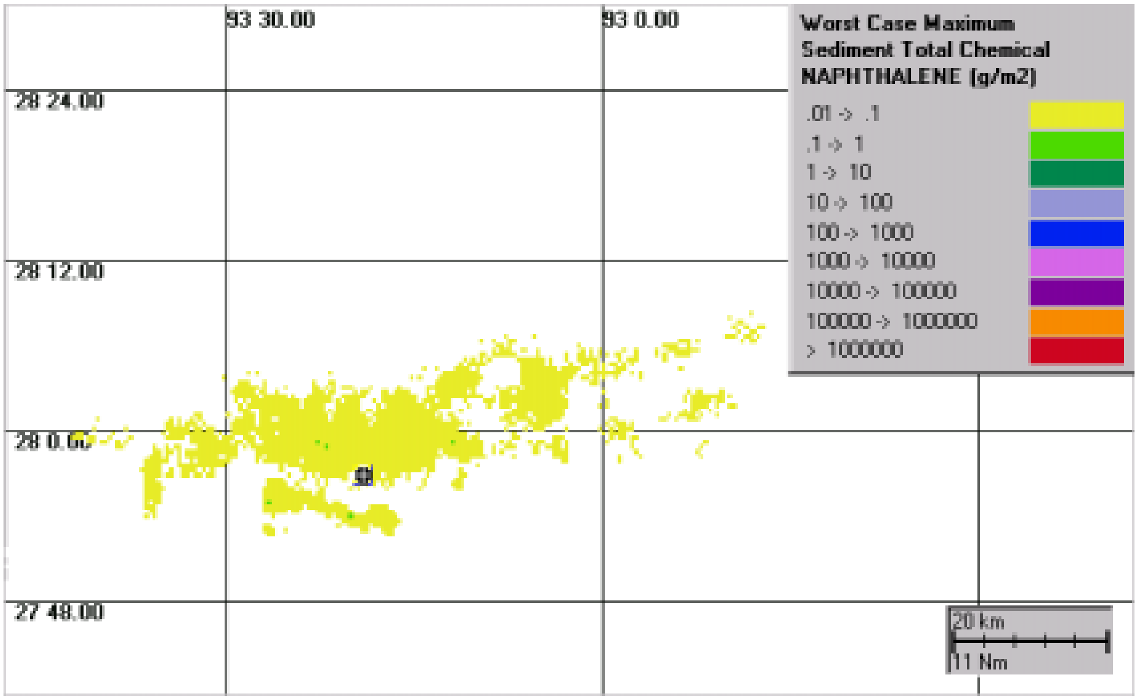


Figure 92. Peak exposure concentration (ppb) of alkylbenzene sulfonic acids (modeled as naphthalene) in the sediment at each location: worst case of all simulations (Scenario 16t).

Summary

Chemicals perform critical functions during drilling; cementing; well completion, stimulation, and workover processes; and producing processes. In offshore operations, chemicals fall naturally into four major classes: (1) drilling fluid chemicals, (2) cementing chemicals, (3) completion, stimulation, and workover chemicals and (4) Production-treating chemicals.

The liquid and solid drilling fluid chemicals used in the highest quantity in the GOM are:

- *Shale Control Inhibitors* (liquid)– 1,210,000 gal. (shallow water); 763,000 gal. (deep water)
- *Weighting Materials* – 326,000,000 lbs. (shallow water); 372,000,000 lbs. (deep water)
- *Shale Control Inhibitors* (solid) – 6,660,000 lbs. (shallow water); 14,100,000 lbs. (deep water)

The cementing chemicals used in the highest quantity in the GOM are:

- *Basic Cements* – 203,000,000 lbs. (shallow water); 18,500,000 lbs. (deep water)
- *Silica* – 14,100,000 lbs. (shallow water); 1,780,000 lbs. (deep water)
- *Extenders/density-reducers* – 3,890,000 lbs. (shallow water); 365,000 lbs. (deep water)

Except for the chemically inert substances such as sand and ceramic proppants the completion, stimulation and workover chemicals used in the highest quantity in the GOM are the following acids and brine solutions:

- *Water-based Completion Fluids* – 16,200,000 gal. (shallow water); 760,000 gal. (deep water), specific chemical amounts were: 9,100,000 gal. of calcium chloride (shallow water); 425,600 gal. (deep water) and 4,700,000 gal. sodium chloride (shallow water); 218,000 gal. (deep water)
- *Hydrochloric Acid* – 2,500,000 gal. solution containing 2,800,200 lbs. HCl (shallow water); 94,112 gal. solution containing 103,260 lbs. HCl (deep water)
- *Ammonium Chloride Overflush* – 2,300,000 gal. of 5% solution containing 988,500 lbs. of ammonium chloride (shallow water); 87,400 gal. of solution containing 37,000 lbs. of ammonium chloride (deep water)

The production-treating chemicals used in the highest quantity in the GOM are:

- Hydration Inhibition Chemicals (Methanol) – 200,000,000 gal. (total)
- Corrosion Inhibitor – 2,500,000 gal. (total)
- Hydration Inhibition Chemicals (Glycols) – 5,200,000 gal. (total)

As part of this study, the types and volumes of hazardous substances used, handled, and stored in offshore E&P operations were identified. Hazardous chemicals were defined as those substances listed in the U.S. Code of Federal Regulations (CFR) – Chapter 40, Protection of the Environment, Part 116, that designates hazardous substances per the Clean Water Act. Only eight hazardous substances were found to be stored in amounts exceeding reportable quantities; sodium hydroxide, potassium hydroxide, zinc bromide, diethylamine, toluene, xylene, and naphthalene.

Twenty-one chemicals were selected for detailed study based on volume estimates, screening-level toxicity data and professional judgement. For each of the selected chemicals a detailed chemical profile was developed to obtain a more definitive characterization of their use, storage, and potential for environmental impact. In addition, spill scenarios were developed and modeled for seventeen of the twenty-one profiled chemicals using Applied Science Associates' (ASA) chemical spill model CHEMMAP.

As part of the risk characterization, the results of the modeling effort were integrated with the toxicity data collected for the chemical profiles. The results of this analysis indicate a potential for impact from a release of either zinc bromide or ammonium chloride. The modeled impacts for zinc bromide were predicted based on a 45,000 gal. release to the environment, a predicted maximum exposure concentration of greater than 1ppm for at least one hour in an area of 11 million m^2 (11 km^2, volume of 11 million m^2 x 114 m deep = 1,254 million m^3) around the spill site and an acute 48-hr LC50 toxicity threshold for *Ceriodaphnia dubia* (freshwater crustacean) of 0.5 mg/L. While a spill of ammonium chloride was not modeled, a review of the chemical's structure and properties indicate that it would behave similarly to potassium chloride. Utilizing the modeled maximum predicted exposure concentrations of potassium chloride as a

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The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.