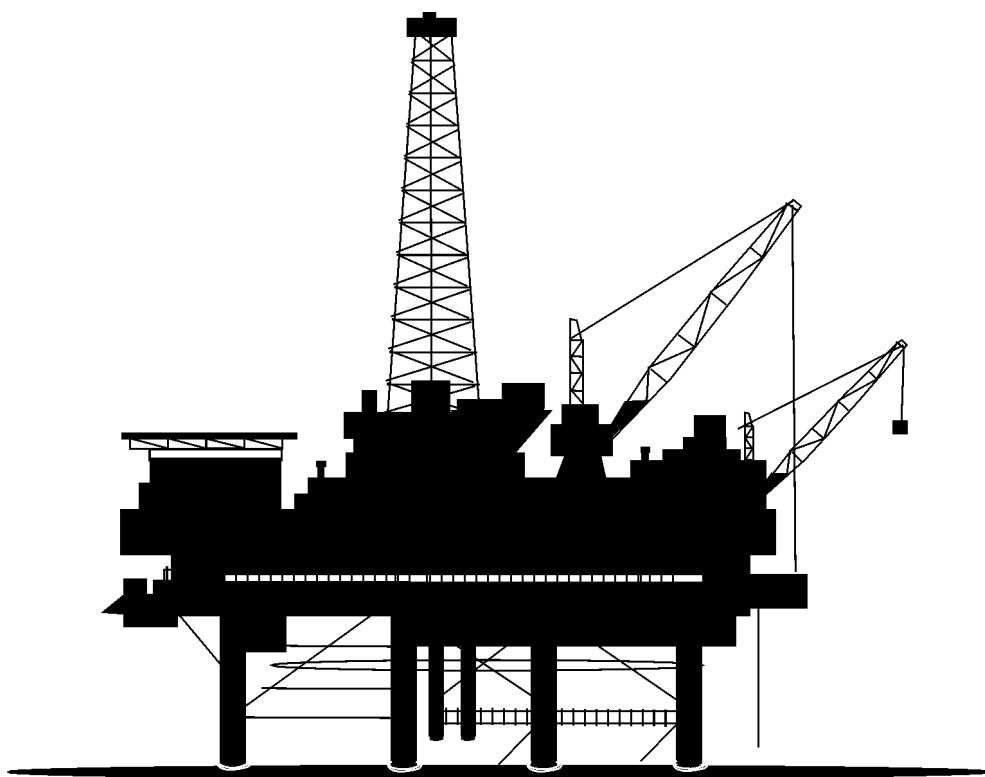


Environmental Impacts of Synthetic Based Drilling Fluids



Environmental Impacts of Synthetic Based Drilling Fluids

Authors

J.M. Neff
Battelle Ocean Sciences
Duxbury, Massachusetts

S. McKelvie
Rudall Blanchard Associates
London, England

R.C. Ayers, Jr.
Robert Ayers & Associates
Houston, Texas

Prepared under MMS
Purchase Order 15240
by
Robert Ayers & Associates
P. O. Box 272706
Houston, Texas 77277-2706

Published by

DISCLAIMER

This report was prepared under contract between the Minerals Management Service (MMS) and Robert Ayers & Associates, Inc. This report has been technically reviewed by the MMS, and it has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the MMS, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. It is, however, exempt from review and compliance with the MMS editorial standards.

REPORT AVAILABILITY

Extra copies of this report may be obtained from the Public Information Office (Mail Stop 5034) at the following address:

U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Region
Public Information Office (MS 5034)
1201 Elmwood Park Boulevard
New Orleans, Louisiana 70123-2394

Telephone: (504) 736-2519 or
1-800-200-GULF

CITATION

Suggested citation:

Neff, J.M., S. McKelvie and R.C. Ayers, Jr. 2000. Environmental impacts of synthetic based drilling fluids. Report prepared for MMS by Robert Ayers & Associates, Inc. August 2000. U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 2000-064. 118 pp.

ACKNOWLEDGMENTS

We would like to thank Dr. Mary Boatman and Ms. Katherine Valltos of MMS who respectively served as Project Officer and Contracting Officer for this project. The Scientific Review Board members for the project were Mr. Joseph Daly and Dr. Carol Daniels of EPA, Dr. James P. Ray of Equilon and Dr. John Veil of Argonne National Laboratory. The authors are grateful to the UK Offshore Operators Association for allowing access to its member companies seabed survey data in the UK sector of the North Sea. We would also like to thank Mr. John Candler and Mr. Stephen Rabke of M-I Drilling Fluids, Dr. John Hall of Baroid Drilling Fluids, and Dr. Joseph Smith and Dr. Heide Mairs of ExxonMobil who reviewed the draft document and provided many useful comments. Sound Environmental Solutions, Inc. prepared the final documentation in the standard MMS format. We would like to thank Jean Mathur for her efforts in this endeavor.

EXECUTIVE SUMMARY

Synthetic based drilling fluids (SBF) are a relatively new class of drilling muds that are particularly useful for deepwater and deviated hole drilling. They were developed to combine the technical advantages of oil based drilling fluids (OBF) with the low persistence and toxicity of water based drilling fluids (WBF). In an SBF, the continuous liquid phase is a well-characterized synthetic organic compound. A salt brine usually is dispersed in the synthetic phase to form an emulsion. The other ingredients of an SBF include emulsifiers, barite, clays, lignite, and lime. SBFs contain the same metals as WBFs. All are tightly complexed with the barite and clay fractions of the mud and have a low bioavailability and toxicity.

Bulk SBFs usually are not discharged to the ocean. However, drill cuttings generated during drilling with SBFs may be treated to remove SBFs and discharged to the ocean. The cuttings contain a small amount, usually 5 to 15 percent, adhering SBFs. During drilling of each of 21 wells in the UK Sector of the North Sea in the late 1990s, 150 to 3000 metric tons of cuttings containing 11 to 300 metric tons of SBF were discharged to the ocean.

The SBF base fluid (or synthetic) may be a hydrocarbon, ether, ester, or acetal. Synthetic hydrocarbons include normal (linear) paraffins (LPs), linear- α -olefins (LAOs), poly- α -olefins (PAOs), and internal olefins (IOs). Most drilling in the Gulf of Mexico currently is with WBFs. When WBFs are not suitable and OBFs are not selected, IO and LAO SBFs are used almost exclusively.

SBF cuttings are "oil-wet" and, when discharged to the ocean, tend to clump together in large particles that settle rapidly to the sea floor. Ester SBF cuttings are more easily dispersed than PAO SBF cuttings. If the concentration of base fluid on cuttings is reduced to less than about 5 percent, the cuttings will disperse more effectively and a cuttings pile will be less likely to accumulate on the bottom.

Because of rapid settling, SBF cuttings do not disperse in the water column and do not increase water column turbidity. The cuttings settle in a very heterogeneous pattern on the bottom near the platform, the direction from the platform of deposition depending on current direction and speed at different depths in the water column. Cuttings piles occasionally are observed in shallow water, but rarely are higher than 1 m. Cuttings piles rarely occur in deep-water or high energy marine environments.

Several field studies have shown that the highest concentrations of SBF cuttings usually are located in sediments within about 100 m of the platform. However, SBF cuttings may be deposited 1 to 2 km from the discharge point. Base fluid concentrations as high as 200,000 mg/kg dry wt have been observed in sediments. Concentrations in sediments usually are less than 10,000 mg/kg at distances of more than 200 m from the discharge. Base fluid concentrations in sediments usually decrease with time after completion of drilling and cuttings discharges. However, the rate of decrease is difficult to document because of the heterogeneous distribution of cuttings in sediments.

Concentrations of synthetic base fluids in sediments may decrease with time after discharge by resuspension, bed transport, and mixing, or by biodegradation. Base fluids are designed to be biodegradable under conditions that occur in offshore marine sediments. Sediment-dwelling bacteria and fungi are able to use synthetics as a source of nutrition, releasing simple non-toxic metabolic degradation products. Several laboratory methods have been developed to measure the rate of biodegradation of base fluids in sediments. The different methods give widely different results.

Biodegradation of synthetic base fluids in sediments results in a decrease in sediment oxygen concentration. If the initial base fluid concentration is high enough, the sediments become anoxic. Therefore, ideally, synthetics should be biodegradable under both aerobic and anaerobic conditions. The rate-limiting step in loss of base fluid from sediments in which concentrations are high enough to cause anoxia usually is the rate of anaerobic biodegradation.

The available laboratory biodegradation tests show that base fluids are much more biodegradable under aerobic than under anaerobic conditions. The different synthetics also vary considerably in biodegradability. The laboratory biodegradation tests most widely accepted in North Sea countries rate the aerobic and anaerobic biodegradation rates of synthetic base fluids in the following order: ester>LAO≈IO>PAO>acetal>ether. Esters, LAOs, and possibly IOs biodegrade anaerobically at a rate significantly faster than that of the mineral oils used in OBFs. A field study at a platform in the Atlantic Ocean west of Ireland where a mixed linear paraffin/LAO/PAO SBF was used showed that the linear paraffin and LAO were biodegraded rapidly, but the PAO was degraded slowly, if at all. More than 90 percent of the paraffin and LAO were lost in two years. Simulated seabed tests with intact sediment cores performed in Norway show that esters, LAOs, and IOs, but not acetals and PAOs, biodegrade under simulated natural conditions more rapidly than mineral oils. Rapid biodegradation of some base fluids, particularly esters, in sediments may produce anoxia, resulting in changes in benthic community structure and function, the organic enrichment effect.

The toxicity of synthetic base fluids and SBFs have been examined in water column and sediment toxicity tests. Water column toxicity tests with mysids (*Americamysis (Mysidopsis) bahia*) and the suspended particulate phase of SBFs have shown that SBFs have a much lower toxicity than OBFs. The SBFs pass the test criterion median lethal concentration of 30,000 mg/L suspended particulate phase. SBF base fluids and most ingredients and degradation products also exhibit low toxicity. Water column tests performed in Europe with a marine microalga and a copepod also show that base fluids have a low toxicity that passes local acceptance criteria. Solid phase toxicity tests with benthic amphipods or bivalve mollusks also show a low order of toxicity of synthetics.

Bioaccumulation tests have been performed with several synthetic base fluids. In all but a few tests, they were not bioavailable. In a few cases, bivalve mollusks appeared to bioaccumulate small amounts; however, it was uncertain whether the animals were retaining SBF particles in the gills and gut or had actually assimilated the synthetic into their tissues. It is unlikely that synthetics are very bioavailable, based on their physical/chemical properties.

Several field studies have been performed to monitor the biological effects of SBF cuttings discharges on the benthic environment. The studies show that where base fluids accumulate to high concentrations in sediments, adverse effects in benthic communities are evident. The usual pattern of response in sediments is a decrease in the number of taxa of marine animals in the sediments, accompanied by little change or even an increase in the number of individuals present. This change results in a decrease in species diversity. The change in benthic community structure is considered an organic enrichment effect. Microbial degradation of the base fluid in sediments results in oxygen depletion and hypoxia or anoxia. Sensitive species are eliminated and are replaced by tolerant, opportunistic species. Population size of the opportunists may increase to a high biomass as the fauna use the elevated microbial production as food. Recovery of affected benthic substrates occurs when synthetic concentrations decline to levels that are low enough that the sediments can become re-oxygenated.

The information about SBFs discussed in this review was used as the basis for a qualitative risk assessment for SBF cuttings discharges from a platform in deep continental slope waters of the northern Gulf of Mexico. It was assumed that drill cuttings containing about 10 percent adhering LAO or IO SBF would be discharged during drilling. The SBF cuttings settle rapidly through the water column and accumulate in sediments down-current from the discharge. At continental slope depths, cuttings would be distributed over a large area of sediments. An upper-bound estimate of 1 hectare (10,000 m²) of sea floor would initially contain more than 1000 mg/kg of synthetic. The estimated biodegradation half-life of the IO or LAO at this approximate deposition density in sediment would be in the 65 to 104 day range. At this degradation rate, the affected area (>1000 mg/kg SBF) would decrease by about 75 percent per year to an area of about 625 m² after two years.

Concentrations of base fluid in solution in the water column are unlikely to exceed about 1 mg/L at any time during cuttings discharges. Because of the low toxicity of LAOs and IOs to water column organisms, there is no risk of direct toxicity of the settling SBF cuttings to water column organisms. The SBF cuttings clump together and settle rapidly through the water column. This generates little increased water column turbidity and phytoplankton communities are unlikely to be significantly affected by the SBF cuttings plume.

Biological effects of the SBF cuttings will be restricted to the sediments near the platform where base fluid concentrations accumulate to more than approximately 1,000 mg/kg. Synthetics are unlikely to accumulate to concentrations that are directly toxic to the benthic fauna. Changes in benthic communities in sediments where SBF cuttings accumulate to high concentrations probably will include a decrease in the number of taxa and biological diversity and either a decrease or an increase in the total number of individuals of benthic fauna present. These benthic community responses often are associated with a decrease in oxygen concentration in surficial layers of sediments. They are typical responses to organic enrichment of the sediments. An increase in the concentration of biodegradable organic matter (the base fluid and other organic constituents of the SBF) in sediments stimulates growth of resident bacterial and fungal consortia that degrade the organic matter and consume available oxygen.

With the depletion of sediment oxygen, the resident microbiota use alternative electron acceptors to oxidize the organic matter, producing hydrogen sulfide, ammonia, and possibly methane as waste products. Some species of benthic fauna are sensitive to low oxygen concentrations or high concentrations of hydrogen sulfide or ammonia and are eliminated from the community. Other species can tolerate these chemical changes and they may colonize the affected substrate in large numbers. Total biomass and benthic production may actually increase in the affected sediments.

The slope benthos are not adapted to rapid sediment deposition and may be buried and smothered by accumulation of SBF cuttings on the sea floor. Accumulation of cuttings to a depth of more than a centimeter probably would be sufficient to smother most of the smaller slope benthic fauna.

It is probable that within three to five years of cessation of SBF cuttings discharges, concentrations of synthetic in sediments will have fallen to low enough levels and oxygen concentrations will have increased enough throughout the previously affected area that complete recovery will be possible. The rate of deep-water benthic ecosystem recovery will depend on the rate of recruitment and recolonization by the benthic fauna characteristic of the area. Because some species of deep-water benthic animals reproduce and grow slowly, complete recovery may require many years. However, ecological succession toward recovery is likely to begin shortly after completion of cuttings discharges and will be well advanced within three to five years when the synthetic material will have degraded to low concentrations.

TABLE OF CONTENTS

| | | |
|-----|--|------|
| | DISCLAIMER, REPORT AVAILABILITY, CITATION..... | iii |
| | ACKNOWLEDGMENTS..... | v |
| | EXECUTIVE SUMMARY..... | vii |
| | LIST OF FIGURES..... | xiii |
| | LIST OF TABLES..... | xv |
| 1.0 | INTRODUCTION..... | 1 |
| 2.0 | BACKGROUND..... | 1 |
| | 2.1 Offshore Drilling..... | 1 |
| | 2.2 Drilling Fluids..... | 1 |
| 3.0 | CHARACTERISTICS OF SYNTHETIC BASED FLUIDS..... | 4 |
| | 3.1 Base Chemicals..... | 4 |
| | 3.2 SBF Usage Trends..... | 7 |
| | 3.3 Synthetic Based Fluid Systems..... | 8 |
| 4.0 | FATE OF SYNTHETIC BASED DRILLING FLUIDS IN THE MARINE ENVIRONMENT..... | 11 |
| | 4.1 Discharge of SBF Cuttings..... | 11 |
| | 4.2 Evaporation of Chemicals from SBFs..... | 13 |
| | 4.3 Dispersion of SBFs..... | 15 |
| | 4.4 Accumulation of SBF Cuttings on the Sea Floor..... | 15 |
| | 4.5 Biodegradation of SBFs..... | 30 |
| 5.0 | BIOAVAILABILITY AND TOXICITY OF SBF CUTTINGS..... | 44 |
| | 5.1 Toxicity Tests..... | 45 |
| | 5.2 Water Column Tests..... | 46 |
| | 5.3 Solid Phase Toxicity Tests..... | 48 |
| | 5.4 Bioavailability of SBF Base Chemicals..... | 50 |
| 6.0 | BIOLOGICAL IMPACTS OF SBF CUTTINGS DISCHARGES..... | 52 |
| | 6.1 North Sea..... | 53 |
| | 6.2 Gulf of Mexico..... | 59 |
| | 6.3 Australia..... | 61 |
| 7.0 | DISCUSSION: ECOLOGICAL RISK ASSESSMENT..... | 62 |
| | 7.1 Problem Formulation..... | 63 |
| | 7.2 Exposure Assessment..... | 64 |
| | 7.3 Effects Assessment..... | 66 |
| | 7.4 Risk Characterization..... | 67 |
| 8.0 | REFERENCES..... | 69 |
| | APPENDIX ANNOTATED BIBLIOGRAPHY: SYNTHETIC BASED DRILLING MUDS..... | 79 |

LIST OF FIGURES

| | | |
|------------|---|----|
| Figure 1. | Relationship between water depth and maximum concentrations of SBF base chemical in surface sediments near drilling platforms in the UK Sector of the North Sea..... | 23 |
| Figure 2. | Average concentration of ester in surface sediments at different distances from a platform in 150 m of water shortly after completion of drilling..... | 26 |
| Figure 3. | Average concentrations of LAO in surface sediments at different distances from a platform in 92 m of water. Survey 1 was immediately after drilling; Survey 2 was a year later..... | 29 |
| Figure 4. | Average concentration of PAO in surface sediments at different distances from a platform in 55 m of water shortly after completion of drilling..... | 29 |
| Figure 5. | Biodegradation pathways of selected SBF base chemicals..... | 32 |
| Figure 6. | Biodegradation of SBFs in SOAEFD tests after 120 days..... | 37 |
| Figure 7. | Half life of various SBFs in NIVA simulated seabed studies..... | 40 |
| Figure 8. | Relationship between redox potential and diversity for NIVA seabed simulation studies..... | 43 |
| Figure 9. | Relationship between concentration of ester SBF in sediments and numbers of taxa and individuals of benthic fauna in sediments near a platform in the North Sea shortly after drilling..... | 57 |
| Figure 10. | Relationship between concentration of ester SBF in sediments and numbers of taxa and individuals of benthic fauna in sediments near a platform in the North Sea 1 year after drilling..... | 57 |
| Figure 11. | Relationship between concentration of linear paraffin in sediments and numbers of taxa and individuals of benthic fauna in sediments near a platform in the North Sea shortly after drilling..... | 58 |
| Figure 12. | Relationship between concentration of linear paraffin SBF in sediments and numbers of taxa and individuals of benthic fauna in sediments near a platform in the North Sea..... | 58 |
| Figure 13. | Relationship between concentration of PAO base chemical in sediments and numbers of taxa and individuals in sediments near a well in the Gulf of Mexico 2 years after drilling. | 60 |

LIST OF TABLES

| | |
|--|----|
| Table 1. Names and chemical structures of several synthetic base chemicals..... | 5 |
| Table 2. Trade names and SBF base chemical compositions of some representative SBFs currently available from three drilling mud suppliers for offshore drilling in the United States..... | 7 |
| Table 3. Typical concentration ranges of the major additives in SBFs..... | 8 |
| Table 4. Major ingredients of a typical PAO drilling mud (SBF) compared to a typical mineral oil based mud (OBF)..... | 8 |
| Table 5. Examples of several emulsifiers used in SBF systems..... | 9 |
| Table 6. Comparison of the concentrations of metals in water based drilling muds and in a typical oil based drilling mud..... | 10 |
| Table 7. The viscosity and aromatic hydrocarbon concentration in several types of OBFs and SBFs..... | 11 |
| Table 8. Retention of SBF base material on drill cuttings produced during offshore drilling in the Gulf of Mexico with IO and PAO based synthetic drilling fluids..... | 12 |
| Table 9. Estimated masses of drill cuttings and SBFs discharged to the ocean during discharge of SBF cuttings from 18 wells in the UK Sector of the North Sea..... | 13 |
| Table 10. Concentrations of organic chemicals in vapors over different types of SBF base chemicals heated to 60 to 70°C in the laboratory..... | 14 |
| Table 11. Comparison of average organic vapor concentrations in laboratory and field studies of evaporation from OBFs, WBFs, and SBFs..... | 14 |
| Table 12. Summary of field studies of the fates and effects of SBF cuttings discharges to the ocean..... | 17 |
| Table 13. Dimensions of SBF cuttings piles near 12 single-well platforms drilled with SBFs in the UK Sector of the North Sea..... | 19 |
| Table 14. Concentrations of Petrofree LE (90% LAO and 10% ester) measured as TPH by gas chromatography in sediments near the Pompano Phase II subsea template in 565 m of water off Louisiana..... | 20 |
| Table 15. Concentrations of total petroleum hydrocarbons (used as a marker of SBF) and barium in surface sediments around a drilling rig in 131 m of water in the Gulf of Mexico 9 days, 8 months, and 24 months after drilling a well with PAO SBF..... | 22 |
| Table 16. Summary of SBFs used to drill the 21 wells monitored in the UK Sector of the North Sea..... | 22 |
| Table 17. Average and maximum concentrations of SBFs of different types in sediments within 100 m of wells drilled with SBFs in the UK Sector of the North Sea..... | 24 |
| Table 18. Concentrations of Ester SBF at different depths in sediments near a platform in 150 m of water shortly after completion of drilling (Year 1) a well and discharge of 3,304 metric tons of cuttings and 304 tons of ester SBF, and ten months later (Year 2)..... | 25 |

LIST OF TABLES (continued)

| | |
|--|----|
| Table 19. Concentrations of LAO SBF at different depths in sediments near a platform in 185 m of water shortly after completion of drilling of a well and discharge of 795 metric tons of cuttings containing 115 tons of LAO SBF..... | 26 |
| Table 20. Concentrations of ester at different depths in sediments near a platform in 186 m of water 19 months after completion of drilling of a well and discharge of 1,062 metric tons of cuttings and 67 tons of ester SBF..... | 27 |
| Table 21. Relationship between water depth, mass of cuttings discharged, and SBF type and distance to maximum SBF concentration in sediments and maximum distance to nontoxic (<1000 mg/kg) SBF concentration in sediments..... | 28 |
| Table 22. Aerobic biodegradation (percent of theoretical oxygen demand: ThOD) of acetal SBF base chemical in several biodegradation tests at several initial concentrations..... | 34 |
| Table 23. Biodegradation rate, measured as the percent reduction in concentration, of several SBF base chemicals based on different biodegradation test protocols..... | 35 |
| Table 24. Anaerobic biodegradation rates of several SBF and OBF base chemicals and possible SBF degradation products as measured with the ISO/DIS 11734 anaerobic biodegradation test..... | 36 |
| Table 25. Rates of loss (biodegradation plus washout) of ester and IO SBF base chemicals in a modified SOAEFD solid phase test. Percent loss in 28 days and half-life (days) are given..... | 38 |
| Table 26. Percent degradation after 120 days and half life (days) of ester SBF base chemical determined with the SOAEFD solid phase biodegradation test at ambient seawater temperatures (6 to 16°C).... | 38 |
| Table 27. Percent degradation after 120 days and half life (days) of ester SBF base chemical at different temperatures determined with the SOAEFD solid phase biodegradation test..... | 39 |
| Table 28. Summary of results of five NIVA simulated seabed SBF biodegradation studies..... | 40 |
| Table 29. Average half-lives of SBF cuttings in simulated seabed chambers containing intact sediments and benthic communities during a 187-day incubation..... | 41 |
| Table 30. Effect of SBF concentration in NIVA simulated seabed biodegradation test chambers on the half-life of the synthetic base chemical..... | 41 |
| Table 31. Effects of SBF cuttings layered (1.4 to 1.8 mm) on natural sediments in NIVA simulated seabed chambers on characteristics of benthic communities after 187 days..... | 42 |
| Table 32. Effect of incubation temperature on the biodegradation of ester and LAO cuttings in sediments from northern (-0.5°C) and southern (6-8°C) Norway..... | 43 |
| Table 33. Toxicity test requirements for SBFs in North Sea countries..... | 45 |
| Table 34. The 96-hour median lethal concentration (LC ₅₀) of the suspended particulate phase (SPP) of several SBFs to mysids (<i>Americamysis (Mysidopsis) bahia</i>)..... | 46 |

LIST OF TABLES (continued)

| | |
|---|----|
| Table 35. Acute toxicity to mysids <i>Americamysis (Mysidopsis) bahia</i> of the suspended particulate phase (SPP) of several SBF base chemicals or chemical intermediates..... | 47 |
| Table 36. Acute toxicity of unused SBFs and SBF base chemicals to the microalga <i>Skeletonema costatum</i> and the copepod <i>Acartia tonsa</i> in water column toxicity tests performed according to North Sea protocols..... | 48 |
| Table 37. Acute Toxicity of an unused laboratory PAO SBF and a used field PAO SBF to three species of marine organisms..... | 48 |
| Table 38. Mean LC ₅₀ s of oils and SBF base chemicals in sediments for the marine amphipods <i>Ampelisca abdida</i> and <i>Corophium volutator</i> in standard 10-day sediment toxicity tests (ASTM E1367-92)..... | 49 |
| Table 39. Acute toxicity as LC ₅₀ of SBF base chemicals and whole fresh (unused) SBFs to the amphipod <i>Corophium volutator</i> and the bivalve mollusk <i>Abra alba</i> , based on sediment toxicity tests performed according to North Sea protocols..... | 49 |
| Table 40. Measured or estimated values for log octanol/water partition coefficient (log K _{ow}) of several SBF base chemicals..... | 51 |
| Table 41. Ester concentrations and benthic community characteristics near the Ula Well 7/12-9 in the Norwegian Sector of the North Sea..... | 54 |
| Table 42. PAO and barium concentrations and benthic infaunal parameters in sediments near a well site in 39 m of water 2 years after discharge of 354 barrels of PAO SPF..... | 60 |
| Table 43. Concentrations of LAO/ester SBF, benthic macrofauna, and demersal megafauna (mostly fish) along four transects extending to 90 m from a drilling template in 565 m of water in the Gulf of Mexico..... | 61 |

ENVIRONMENTAL IMPACTS OF SYNTHETIC BASED DRILLING FLUIDS

1.0 INTRODUCTION

Synthetic based drilling fluids (SBFs) are a relatively new class of drilling muds that are particularly useful for deepwater and deviated hole drilling. They were developed to provide an environmentally superior alternative to oil based drilling fluids (OBFs). Although the technical and economic benefits of using these fluids in the deepwater Gulf of Mexico are clear, the environmental impacts of discharged drill cuttings produced during use of SBFs are not well understood.

The U.S. Minerals Management Service (MMS) has the responsibility of ensuring that U.S. deepwater oil and gas reserves are developed safely and with a minimum of environmental impact. Therefore, MMS has a special interest in the environmental behavior of SBFs. As a result, MMS has commissioned this review of existing data on the environmental effects associated with discharges of SBF cuttings from offshore drilling locations. This review summarizes information published in the scientific literature as well as reports performed for oil and drilling fluid companies, industry associations, and government agencies. The available information has been incorporated into an ecological risk assessment framework for use by the MMS.

2.0 BACKGROUND

2.1 Offshore Drilling

Drilling fluids or drilling muds are an essential component of the rotary drilling process used to drill for oil and gas on land and in offshore environments. The most important functions of drilling fluids are to transport cuttings to the surface; to balance subsurface and formation pressures preventing a blowout; and to cool, lubricate, and support part of the weight of the drill bit and drill pipe (Neff et al. 1987; Darley and Gray 1988). During drilling, the drilling fluid is pumped from the mud tanks down the hollow drill pipe and through nozzles in the drill bit. The flowing mud sweeps the crushed rock cuttings from beneath the bit and carries them back up the annular space between the drill pipe and the borehole or casing to the surface. The mud is then passed through solids control equipment (an integrated system of shale shaker screens and hydrocyclones) to remove the cuttings. It is then circulated back to the mud tanks where the cycle is repeated.

Drill cuttings are particles of crushed rock produced by the grinding action of the drill bit as it penetrates into the earth (Neff et al. 1987). Drill cuttings range in size from clay-sized particles to coarse gravel and have an angular configuration. Their chemistry and mineralogy reflect that of the geologic strata being penetrated by the drill. Drill cuttings contain small amounts of liquid and solid drilling fluid components, in addition to formation solids. SBF cuttings discharged offshore in the Gulf of Mexico contain an average of 12 ± 4.8 weight percent adhering SBF base chemical (Annis 1997). Although the drill cuttings themselves are considered toxicologically inert, there is concern that any adhering drilling fluid ingredients may be toxic, particularly if the cuttings are produced during drilling with OBFs or SBFs.

2.2 Drilling Fluids

Over the long history of offshore development of oil and gas resources, a large number of different chemical formulations of drilling fluids have been used. The different types of drilling fluids can be separated into two basic types: water based fluids (WBFs) and non-aqueous based fluids (NABFs). WBFs, used in most offshore drilling operations in U.S. waters, consist of water (fresh or salt), barite, clay, caustic soda, lignite, lignosulfonates and/or water-soluble polymers. WBFs may also contain low concentrations of specialty chemicals added to solve some particular problem that is affecting mud properties (e.g. tributylphosphate to control foaming, ammonium bisulfite to remove oxygen, sodium bicarbonate to remove excess calcium ions). Diesel fuel, mineral oil, or another insoluble organic liquid may be added to a WBF at a concentration of a few percent to improve the lubricity of the mud in difficult formations. The oil is dispersed in the water phase and the cuttings remain water-wet (Hudgins 1991). The

compositions, environmental fates, and toxicological and ecological effects in the marine environment of WBFs have been studied in great detail, particularly in the U.S. The results of these studies are the topic of several reviews (National Research Council 1983; Neff 1987; Neff et al. 1987; Hinwood et al. 1994).

In NABFs, the continuous phase is a liquid hydrocarbon mixture or other insoluble organic chemical. NABFs also contain barite, clays, emulsifiers, water, calcium chloride, lignite, and lime. Water or a saline brine (usually containing CaCl_2), at a concentration of 10 to 50 percent, is dispersed into the hydrocarbon phase to form a water-in-organic phase emulsion with water droplets less than 1 μm in diameter (Hudgins 1991; Norwegian Oil Industry Association Working Group 1996). This emulsion is called an invert emulsion because water is dispersed in the organic phase, and formation solids that come in contact with the NABF become oil-wet. NABFs are more expensive than WBFs; however, they may be used in difficult drilling situations where their technical advantages are required. NABFs are used frequently to (Norwegian Oil Industry Association Working Group 1996):

- drill troublesome, hydratable shales;
- drill deep, hot wells where WBFs might be unstable;
- drill salt, anhydrite, gypsum, and mixed salt zones;
- drill and core hydrocarbon-bearing formations near the bottom of wells;
- drill through hydrogen sulfide (H_2S) and carbon dioxide (CO_2) containing formations;
- increase lubricity to decrease torque and drag when drilling a directional well;
- minimize the likelihood of differential sticking of the drill pipe in the hole;
- serve as a packer fluid for corrosion control; and
- serve as a workover fluid where water might damage the formation.

There are three types of NABFs, based on the chemical composition of the base fluid in the mud. These are oil-based fluids (OBFs), enhanced mineral oil based fluids (EMOBFs), and synthetic based fluids (SBFs). OBFs contain diesel fuel or conventional mineral oil as the continuous phase. They are the least expensive NABFs and were the only ones in use until the late 1980s. Mineral oils were developed as low-toxicity replacements for diesel fuel in the OBF in an attempt to reduce the environmental impacts of discharge of OBF-contaminated drill cuttings (Dicks et al. 1986/87). OBFs have been used extensively in the North Sea, in Canadian offshore waters, and in several other offshore development areas in the world. Cuttings containing adsorbed OBFs were routinely discharged to offshore waters of the North Sea until the early 1990s when such discharges were severely restricted. For example, in the UK Sector of the North Sea, 75 percent of the 333 wells drilled in 1991 were drilled with OBFs, resulting in the discharge of an estimated 11,000 metric tons of oil to the ocean (Munro et al. 1998b). In 1995, less than 30 percent of 342 wells were drilled with OBFs. The environmental effects of OBF cuttings being discharged in the North Sea have been thoroughly studied (Davies et al. 1989; Kingston 1987, 1992; Olsgard and Gray 1995).

EMOBFs contain an enhanced mineral oil as the continuous phase. Enhanced mineral oils are conventional paraffinic mineral oils that have been hydrotreated or otherwise purified to remove all aromatic hydrocarbons. Enhanced mineral oils generally contain less than about 0.25 percent total aromatic hydrocarbons and less than 0.001 weight percent total polycyclic aromatic hydrocarbons (Jacques et al. 1992; Meinhold 1999). One of the enhanced mineral oils evaluated by Jacques et al. (1992) contained less than 1 mg/L benzene. Aromatic hydrocarbons, including polycyclic aromatic hydrocarbons, are considered to be the most toxic components of OBFs. Although EMOBFs are less toxic than OBFs, EPA does not permit the discharge of EMOBF cuttings to U.S. territorial waters.

The base fluid or continuous phase of an SBF is a water insoluble synthetic organic material. The EPA (EPA 1996) defines a "synthetic material", as applied to synthetic based drilling fluids, as:

“A material produced by the reaction of a specific purified chemical feedstock, as opposed to the traditional base fluids such as diesel and mineral oil which are derived from crude oil solely through physical separation processes. Physical separation processes include fractionation and distillation and/or minor chemical reactions such as cracking and hydro processing. Since they are synthesized by the reaction of purified compounds, synthetic materials suitable for use in drilling fluids are typically free of polycyclic aromatic hydrocarbons (PAHs) but tests sometimes report levels of PAH up to 0.001 weight percent PAH expressed as phenanthrene.”

The Norwegian regulatory authority defines a SBF as (Norway 1997):

“A drilling fluid where the base fluid consists of non water soluble organic compounds and where neither the base fluid nor the additives are of petroleum origin.”

During drilling with WBFs, both cuttings and mud may be discharged to the sea. On the other hand, discharge of OBFs and WBFs containing free oil and the associated cuttings is prohibited in U.S. offshore waters. As a result, when the relatively expensive OBFs are used in U.S. waters, they are taken ashore after well completion and restored for future use. The cuttings usually are transported to an onshore disposal site; in some situations, it is possible to suspend the cuttings in water and inject them down a disposal well.

OBFs were used for more than 20 years in the North Sea, and the cuttings were frequently discharged to the environment. In 1992, the Paris Commission set down maximum discharge levels of 10 percent mineral-oil-on-cuttings, with a further stipulation of a 1 percent threshold for all North Sea drilling operations after January 1997 (Munro et al. 1997c). The 1 percent oil on cuttings threshold is not economically attainable with current technology; consequently, the oil and gas industry has developed more environmentally acceptable alternative drilling fluids that retain the favorable drilling properties of OBFs.

The need to drill increasingly difficult deviated and deep-water wells, coupled with the desire to discharge cuttings, led to the development of SBFs. SBFs are designed to be less toxic and degrade faster than OBFs, and they yield mud systems similar to OBFs in drilling performance (Friedheim and Conn 1996). Furthermore, synthetics have certain technical and human health advantages over most mineral oils and diesel fuel. For example, they are less volatile than OBFs and their vapors are free of aromatic compounds (Candler, et al. 1996). Thus, the use of SBFs can reduce vapor inhalation by workers in closed, poorly ventilated areas on the drilling platform.

An SBF was used for the first time to drill a well in the Norwegian Sector of the North Sea in 1990. The first well drilled with an SBF in the UK Sector was in 1991, and in the Gulf of Mexico in 1992 (Friedheim and Conn, 1996; Fechhelm et al. 1999). By September 1994, 169 wells had been drilled with SBFs in the North Sea. In 1995, 49 wells were drilled with SBFs in the Norwegian Sector of the North Sea, resulting in the discharge to the ocean of an estimated 5,500 metric tons of SBF on cuttings (Norway 1997).

SBFs can greatly enhance drilling performance over WBFs for difficult wells. Burke and Veil (1995) compared costs of wells drilled with SBFs to comparable wells drilled with WBFs. Drilling times were reduced by 50 to 60 percent, and well costs were generally cut in half for the SBF wells. In these cases, the SBF cuttings were discharged to the ocean. If cuttings can not be discharged, however, the added cost of transportation to shore for land-based disposal may make the use of SBFs cost-prohibitive. Burke and Veil (1995) also point out that when SBFs are used instead of WBFs, the total quantity of waste discharged is greatly reduced. This is due primarily to the fact that only SBF cuttings are discharged, whereas both WBFs and cuttings are discharged.

In many cases, SBFs do not appear to have better drilling properties than OBFs, although they are much more expensive than OBFs. However, if the discharge of cuttings associated with SBFs is allowed and the discharge of cuttings associated with OBFs is prohibited, the higher cost of the SBF usually is more than offset by the cost of onshore disposal of OBF cuttings.

SBFs have a clear advantage over OBFs in deep water. Fast drilling rates are especially important in deep water where expensive drilling rigs with high day rates must be used. Both OBFs and SBFs increase the rate of penetration as compared to WBFs and can reduce drilling time. However, wells drilled with OBFs usually take longer because of delays associated with handling and offloading OBF cuttings to barges.

Another potential problem in deep-water drilling results from the relatively long time the mud is exposed to low temperatures. As the mud cools, gas hydrates may form and interfere with mud circulation. While both SBFs and OBFs inhibit gas hydrate formation, SBFs may be more effective (Carlson and Hemphill 1994; Zevallos et al. 1996). Natural gas is less soluble in SBFs than in most OBFs, making it easier to detect gas kicks.

For deep-water drilling operations, SBFs systems promote good hole cleaning and cuttings suspension properties. They also suppress gas hydrate formation, and exhibit improved conditions for well control compared to most WBF

systems. The rheological properties of SBFs provide good carrying capacity for cuttings, improving cuttings transport in long, cold deep-water risers.

The scientific literature clearly documents that ocean discharge of WBFs and the associated cuttings has little or no adverse, long-term biological impact in the water column or on the seafloor (National Research Council 1983; Neff 1987; Hinwood et al. 1994). Other studies, mostly performed in the North Sea, show that discharge of OBF cuttings may cause persistent adverse biological effects at the seafloor within at least 1 km of the platform (Kingston 1992; Olsgard and Gray 1995). Because of their low toxicity and persistence, SBFs are thought to have environmental impacts intermediate between those of WBFs and OBFs. In some cases, however, SBFs may have environmental impacts similar to those of OBFs. Therefore, there is considerable debate in the U.S. and North Sea countries about how best to regulate discharge of SBF cuttings.

EPA recognizes that SBFs and EMOBFs are new classes of drilling fluids, but the national effluent limitations guidelines (ELGs) do not currently address them (Veil and Daly 1999). EPA Region VI permits discharge of cuttings associated with SBFs in the Western Gulf of Mexico provided they meet discharge limitations for cuttings associated with WBFs. The discharge of cuttings associated with EMOBFs is prohibited.

EPA intends to modify the ELGs to include requirements for discharge of SBF cuttings, but needs more information. An industry consortium of operators and mud suppliers is working with EPA to develop the new environmental and operational information needed to modify the ELGs (Veil and Daly 1999; Veil et al. 1999). This effort includes a multi-year field study to evaluate seafloor impacts of SBF cuttings in the Gulf of Mexico. The field study is scheduled to begin in 2000. Both the MMS and the U.S. Department of Energy are participating with the industry consortium in the field study.

3.0 CHARACTERISTICS OF SYNTHETIC BASED FLUIDS

3.1 Base Chemicals

Synthetic base fluids may be classified into four general categories:

- synthetic hydrocarbons,
- ethers,
- esters, and
- acetals.

The chemistry of these basic classes of synthetic base materials is discussed in the following and example chemical structures are shown in Table 1.

3.1.1 Synthetic Hydrocarbons

Polymerized olefins are the most frequently used synthetic hydrocarbons in SBFs today. Polymerized olefins include linear alpha olefins (LAOs), poly alpha olefins (PAOs), and internal olefins (IOs) (Friedheim and Conn 1996). Linear alkyl benzenes (LABs) originally were included in this class of SBF base chemicals. LAB muds were used to drill 33 wells in the UK Sector of the North Sea before September 1994. However, because they contain a benzene molecule, they have been reclassified as environmentally unacceptable and are no longer used (Friedheim and Conn 1996). They never have been used in U.S. offshore waters.

Linear paraffins (LP) (also sometimes called n-paraffins) sometimes are included in this class; however, they usually are prepared from a petroleum feedstock. Synthetic linear paraffins are available commercially for use in SBFs, but are not widely used because of their cost. Synthetic paraffins are produced by the low-pressure Fischer-Tropsch synthesis, involving catalytic hydrogenation of carbon monoxide. Because EPA classifies synthetic paraffins as SBFs, synthetic LP cuttings are permitted for offshore discharge in the Gulf of Mexico.

Table 1. Names and chemical structures of several synthetic base chemicals.

| TYPE | CHEMICAL STRUCTURE |
|---------------------------------------|--|
| Synthetic Hydrocarbons | |
| Linear Alpha Olefin (LAO) | $\text{CH}_3 - (\text{CH}_2)_n - \text{CH} = \text{CH}_2$ |
| Poly Alpha Olefin (PAO) | $\text{CH}_3 - (\text{CH}_2)_n - \text{C} = \text{CH} - (\text{CH}_2)_m - \text{CH}_3$ $\quad \quad \quad \backslash$ $\quad \quad \quad (\text{CH}_2)_p - \text{CH}_3$ |
| Internal Olefin (IO) | $\text{CH}_3 - (\text{CH}_2)_m - \text{CH} = \text{CH} - (\text{CH}_2)_n - \text{CH}_3$ |
| Linear Alkyl Benzene (LAB) | $\text{CH}_3 - \text{CH} - (\text{CH}_2)_n - \text{CH}_3$ $\quad \quad \quad \backslash$ $\quad \quad \quad \text{C}_6\text{H}_5$ |
| Other Synthetic Base Chemicals | |
| Ether | $\text{CH}_3 - (\text{CH}_2)_n - \text{O} - (\text{CH}_2)_n - \text{CH}_3$ |
| Ester | $\text{CH}_3 - (\text{CH}_2)_n - \text{C} = \text{O}$ $\quad \quad \quad \backslash$ $\quad \quad \quad \text{O} - (\text{CH}_2)_m - \text{CH}_3$ |
| Acetal | $\text{CH}_3 - (\text{CH}_2)_n - \text{O} \quad \text{O} - (\text{CH}_2)_n - \text{CH}_3$ $\quad \quad \quad \backslash \quad /$ $\quad \quad \quad \text{CH} - (\text{CH}_2)_m - \text{CH}_3$ |

Linear Alpha Olefins

LAOs are produced by the polymerization of ethylene. Ethylene (C_2H_4), the smallest unsaturated hydrocarbon, is oligomerized by heating in the presence of a catalyst and triethyl aluminum to produce LAOs with different hydrocarbon chain lengths (Friedheim and Conn 1996; Lee 1998). Each LAO molecule has a single, double bond in the alpha position (between the first and second carbon in the chain) (Table 1). LAOs have molecular weights ranging from 112 (C_8H_{16}) to 260 ($\text{C}_{20}\text{H}_{40}$). The LAO mixture is distilled to produce different molecular weight blends. The physical-chemical properties of the mixtures can be altered systematically by changing the chain lengths and branching of the LAO molecules. Typical LAO mixtures used in SBFs are LAO $\text{C}_{14}\text{C}_{16}$ (a blend of $\text{C}_{14}\text{H}_{28}$ and $\text{C}_{16}\text{H}_{32}$ LAOs) and LAO $\text{C}_{16}\text{C}_{18}$. In a typical LAO, about 28 percent of the molecules contain branching; most branches are methyl groups ($-\text{CH}_3$) (Rabke et al. 1998).

Poly Alpha Olefins

PAOs are manufactured in a four- to five-step process: 1) polymerization of ethylene to form a series of linear alpha olefins; 2) distillation to isolate LAOs of the desired chain length; 3) oligomerization of the LAOs to produce PAOs; 4) hydrogenation to saturate the PAOs (sometimes); and 5) distillation to isolate PAOs with the desired physical-chemical properties (Friedheim and Conn 1996). Typical LAOs used to manufacture PAOs include 1-octene (C_8H_{16}) and 1-decene ($\text{C}_{10}\text{H}_{20}$) (Burke and Veil 1995). PAOs may be hydrogenated, producing alkanes for some applications (Friedheim and Pantermuehl 1993). However, the unsaturated PAO is more biodegradable than

the saturated alkane; therefore, unsaturated PAOs are preferred to the saturated congeners in applications where PAO cuttings may be discharged to the ocean.

Depending on the chain length of the LAOs and the nature of the oligomerization reactions, PAOs can be produced with varying degrees of branching and carbon chain lengths (Lee 1998). In a typical PAO SBF, more than 90 percent of the molecules have branching (Rabke et al. 1998). The PAO fluid may contain a mixture of several PAOs from C_8H_{16} to $C_{30}H_{62}$ and sometimes to $C_{40}H_{82}$ (Vik et al. 1996a; Rabke et al. 1998). The average PAO is $C_{20}H_{42}$ (Eicosane) with a molecular weight of 282.6 and an aqueous solubility less than 1 $\mu\text{g/L}$.

Internal Olefins

IOs are formed by isomerization of LAOs in the presence of heat and a suitable catalyst. Isomerization shifts the double bond from the alpha position to a position between two internal carbons (Friedheim and Conn 1996; Lee 1998) (Table 1). Isomerization of a LAO decreases its pour point and flash point. Commercial IOs usually have a chain length of 16 ($C_{16}H_{32}$) or 18 ($C_{18}H_{36}$) carbons, and usually contain more than 20 percent internal branching (Vik et al. 1996a; Rabke et al. 1998). As for LAOs and PAOs, the IO mixture may be hydrogenated to produce saturated hydrocarbons; however, they are still referred to as LAOs, PAOs, and IOs.

In today's market, LAOs and IOs usually are preferred over PAOs. LAOs and IOs often are used in blends that are designed to achieve a balance among the physical properties important to the drilling operation (e.g. viscosity, pour point, flash point, etc.).

3.1.2 Ethers

Alcohols with different chain lengths are condensed and partially oxidized to produce mono- and di-ethers. Ethers are saturated hydrocarbons with an oxygen atom in the center (Table 1). Hydrocarbon chain lengths and branching are selected to optimize drilling properties and minimize toxicity (Candler et al. 1993). Ethers are more stable both chemically and biologically than esters or acetals. Ether SBFs have a high hydrolytic stability. This is an advantage during drilling, but results in low biodegradability following ocean disposal of SBF cuttings (Friedheim and Conn 1996). At one time, ethers were used frequently in the North Sea; before September 1994, ether or acetal SBFs were used to drill 13 wells in the UK Sector of the North Sea (Friedheim and Conn 1996). However, they are no longer used in the North Sea. Ethers have never been used in U.S. offshore waters.

3.1.3 Acetals

Acetals are dialkylethers that are closely related to ethers (Slater et al. 1995). They are formed by the acid-catalyzed reaction of an aldehyde with an alcohol or carbonyl compound (One mole of aldehyde and two moles of alcohol) (Patel 1998). A typical acetal in a SBF has the formula, $C_{20}H_{42}O_2$, and has a molecular weight of 314.3 (Vik et al. 1996a). Acetals are relatively stable under neutral and basic conditions, but may revert back to the aldehyde and alcohol under acidic conditions. At one time, acetals were used frequently in the North Sea; however, they are not used today. Acetals have never been used in U.S. waters.

3.1.4 Esters

Esters are formed by the reaction of a carboxylic acid with an alcohol under acidic conditions (Norman 1997). The ingredients of esters used in SBFs include fatty acids (carboxylic acids) with 8 to 24 carbons and alcohols with different chain lengths. 2-Ethylhexanol ($C_8H_{18}O$, molecular weight 130.2) is the alcohol used most frequently; however, mono- and poly-hydric alcohols (glycerols) may also be used. The fatty acids usually are derived from natural vegetable or fish oils. They also can be made by oxidation of the terminal double bond of LAOs (Friedheim and Pantermuehl 1993). An example of ester used in SBFs is a mixture of C_8 through C_{14} fatty acid esters of 2-ethylhexanol. The original Petrofree SBF system consisted of a mixture of five homologous fatty acid esters, of which the main component was 2-ethylhexyl dodecanoate (Schaanning et al. 1996). A typical ester has a molecular weight of 396.4 and the chemical formula, $C_{26}H_{52}O_2$ (Vik et al. 1996a). Esters are somewhat polar and more water-soluble than would be expected from their molecular weights. Chain length and branching of the fatty acids and alcohol are modified to optimize viscosity, pour point, and hydrolytic stability (Friedheim and Pantermuehl 1993;

Norman 1997). Esters also may be mixed with synthetic hydrocarbons (LAO, IO, or PAO) in an SBF to attain some particular drilling performance characteristic. Esters are relatively stable under neutral conditions, but may undergo hydrolysis and revert back to the acid and alcohol under basic or acidic conditions. Esters are commonly used in the North Sea and have been used extensively in the Gulf of Mexico.

3.2 SBF Usage Trends

A large number of trade name SBF products are available from drilling fluid suppliers in the U.S and Europe. Examples of some of the SBFs available from three U.S. suppliers are summarized in Table 2. The products listed are the ones used in most SBF drilling mud packages for offshore drilling in the Gulf of Mexico. Additional products from these and other suppliers are available in the U.S. and elsewhere in the world.

Table 2. Trade names and SBF base chemical compositions of some representative SBFs currently available from three drilling mud suppliers for offshore drilling in the United States.

| Trade Name | SBF Base Chemical | Supplier |
|---------------------------|---|--------------------|
| ISO-TEQ | IO (C ₁₄ – C ₂₀ blend) | Baker Hughes INTEQ |
| NX-3500 | Ester | Baker Hughes INTEQ |
| BG-550 | Ester | Baker Hughes INTEQ |
| PT-3500 ^a | Iso-Paraffin | Baker Hughes INTEQ |
| ALPHA-TEQ | LAO (C ₁₄ – C ₁₆ blend) | Baker Hughes INTEQ |
| NOVAPLUS | IO (C ₁₆ – C ₁₈ blend) | M-I |
| ECOGREEN | Ester | M-I |
| NOVATEC | LAO (C ₁₄ – C ₁₈ blend) | M-I |
| PARADRIL ^a | Paraffin | M-I |
| PETROFREE SF | IO (C ₁₆ – C ₁₈ blend) | Baroid |
| PETROFREE | Ester | Baroid |
| PETROFREE LE ^b | LAO (C ₁₄ – C ₁₈ blend) | Baroid |
| XP-07 ^a | Linear Paraffin | Baroid |

^a These SBFs contain synthetic paraffins. EPA currently does not permit discharge of drilling fluids cuttings containing petroleum-derived paraffins.

^b PETROFREE LE originally was a blend of LAO and ester. The ester was phased out in 1997.

In today's market, concerns about toxicity, biodegradation rates, environmental impacts, and costs have essentially eliminated all SBFs except olefins and esters from use in offshore drilling. Olefins are less costly than esters, more stable at higher temperatures, less viscous at low temperature, and more adaptable to deep water drilling environments. Olefins usually are preferred if only drilling properties are considered. However, esters are much more biodegradable than olefins, giving the impression that they are more environmentally compatible than olefins.

WBFs still are the most frequently used drilling muds in U.S. offshore waters. In deep water or difficult drilling situations where WBFs are not suitable, IOs and LAOs are used. PAOs and esters were used in the past, but rarely are used today. Most operators drilling in offshore waters of the Gulf of Mexico "rent" complete SBF packages from drilling fluid companies. Formulation, monitoring physical/chemical properties, and recycling of the SBF is performed by the drilling fluid company on a contract basis.

3.3 Synthetic Base Fluid Systems

The SBF base material usually represents about 30 to 90 percent of the total volume of the complete mud (Rushing et al. 1991) and about 20 to 40 percent of the mass of the mud (Kenny 1993). All SBF systems contain emulsifiers, wetting agents, thinners, weighting agents, and gelling agents. Relative proportions of the different ingredients vary depending on the SBF type and the chemistry, geology, and depth of the formation being drilled (Table 3 and 4). The major ingredients are similar for all SBF systems. The relative amounts of different ingredients in the SBF are varied to address drilling conditions.

Table 3. Typical concentration ranges of the major additives in SBFs. Modified from McKee et al. (1995).

| Additive | Concentration in Drilling Mud | |
|----------------------|-------------------------------|------------------------------|
| | Pounds/Barrel | Kilograms/meter ³ |
| Emulsifier | 9.0 – 14.0 | 25.7 – 39.9 |
| Rheological Modifier | <1.0 – 2.0 | 2.9 – 5.7 |
| Fluid Loss Additive | 1.0 – 8.0 | 2.9 – 22.8 |
| Lime | 6.0 – 9.0 | 17.1 – 25.7 |
| Organophilic Clay | 5 – 8 | 15.0 – 21.0 |
| Wetting Agent | 0 – 1.0 | 0 – 2.9 |

Table 4. Major ingredients of a typical PAO drilling mud (SBF) compared to a typical mineral oil based mud (OBF). Concentrations (except for density) are pounds per barrel and kilograms per meter³ (in parentheses). Modified from Rushing et al. (1991).

| Component | Concentration in Drilling Mud | |
|---------------------------|-------------------------------|-----------------|
| | Poly- α -Olefin Mud | Mineral Oil Mud |
| Base Liquid/Water Ratio | 70/30 | 80/20 |
| Density (lb/gal & kg/L) | 11.0 (1.32) | 7.43 (0.89) |
| Base Liquid | 163.4 (470) | 217.0 (620) |
| Water | 83.5 (238) | 64.3 (183) |
| CaCl ₂ | 36.6 (104) | 8.58 (24) |
| Emulsifier | 5.0 (14) | 1.9 (5) |
| Wetting Agent | 2.0 (6) | 1.0 (3) |
| Lime (CaCO ₃) | 6.0 (17) | --- |
| Hot Lime (CaO) | --- | 2.0 (6) |
| Organophilic Clay | 2.0 (6) | 10.0 (28) |
| Rheology Modifier | --- | 4.0 (11) |
| Barite | 164.5 (469) | --- |

SBFs and OBFs share many of the same ingredients (Table 4). Water (usually in the form of a concentrated calcium chloride brine) is emulsified in the SBF base material to increase viscosity. The synthetic/water volume ratio is varied to alter mud viscosity and usually ranges from 55/45 to perhaps as high as 96/4 (McKee et al. 1995; Friedheim and Patel 1999). The brine promotes dehydration of shales in the formation being drilled. It is dispersed in the oil phase to form an inverted emulsion (a water-in-SBF emulsion). The solids in the SBF, including formation solids (cuttings), are “SBF-wet”.

Emulsifiers, which often are metal soaps of fatty acids, are added to the SBF to aid in forming and maintaining the inverted emulsion. The emulsifier (surfactant) packages used in SBFs often are different from those used in OBFs. They are modified to be compatible with the physical/chemical properties of the organic base phase of the mud (Friedheim et al. 1991). Wetting agents are added to ensure the solids in the mud are SBF-wet. Wetting agents include polyamines, fatty acids, and oxidized tall oils. Lime is added to make calcium soaps that aid in emulsification of water in the SBF. Rheology modifiers and organophilic clays are added to aid in suspending drill cuttings in the mud.

Barite (barium sulfate) is used to increase the weight of the drilling mud, counteracting formation pressure and thus preventing a blowout. The amount of barite added to the mud usually increases as both the depth of the well and formation pressure increase. A typical 11.5 lb SBF may contain about 230 lb/bbl (660 g/L) barite (Friedheim and Patel 1999). Barite has an extremely low solubility in sea water and so is used frequently as a conservative tracer of the dispersion and fate of discharged drilling fluids (Hartley 1996).

Of the major ingredients of SBFs, other than the base fluids themselves, emulsifiers and wetting agents (detergents or surfactants) are of greatest environmental concern because of their potential toxicity (Rye et al. 1997). The exact compositions of commercial emulsifiers and wetting agents are proprietary. Some common surfactant products used in SBFs and their generic compositions and use concentrations are summarized in Table 5.

Table 5. Examples of several emulsifiers used in SBF systems. Some related SBF chemicals are included.

| Product | Function | Composition | Typical Concentration in SBF (lb/bbl) |
|----------------|--------------------------|--|--|
| Novamul | Primary emulsifier | Fatty acid/solvent blend | 6 – 10 |
| Novawet | Wetting agent | Imidazoline | 1 – 2 |
| Novathin | Thinner/conditioner | Fatty acid blend | 0.5 – 2 |
| Novamod | Organic gelling agent | Polymerized fatty acids | 1 – 4 |
| Ez Mul NTE | Emulsifier/wetting agent | Polyaminated fatty acid in ester carrier fluid | 6 – 12 |
| Le Mul | Emulsifier | Fatty acid blend in synthetic carrier fluid | 6 – 10 |
| Le Supermul | Emulsifier | Polyaminated fatty acid in synthetic carrier fluid | 2 – 4 |
| Omni-Tec | Emulsifier | Fatty acids/synthetic blend | 4 – 8 |
| Omni-Mul | Emulsifier | Polyamide/synthetic blend | 8 – 16 |
| Omni-Coat | High Temp Emulsifier | Polyolefin/sulfonate blend | 1 |

Alkylphenol polyethoxylates were widely used in the past as lubricants, detergents, and emulsifiers in WBFs and NABFs (Getliff and James 1996). Their use has been phased out in most locations because of the high toxicity of some of their degradation products, particularly nonylphenol and octylphenol. These products usually are dissolved or dispersed in the base synthetic fluid. Because of their hydrophobic/hydrophilic structure, they concentrate at the synthetic/brine interface, stabilizing the brine dispersion in the synthetic fluid and helping to make other mud ingredients and formation solids synthetic-wet.

The thermal stability of emulsifiers controls the upper temperature at which SBFs and OBFs can operate down-hole (Growcock et al. 1994). The thermal threshold for degradation of several emulsifiers is in the range of 130°F to 520°F (54.4°C to 270°C). Rheology modifiers have similar thermal stability to emulsifiers. Most SBF based fluids are stable to greater than 425°F (218°C). Thermal degradation products of emulsifiers and rheology modifiers could contribute to the toxicity of some SBFs.

Several metals are present in WBFs, OBFs, and SBFs. The metals are associated with dispersed cuttings and the solid additives (barite and clays), not with the continuous phase (water, oil, or synthetic), in drilling fluids. Metals concentrations in whole WBFs and OBFs are roughly similar (Table 6), depending mainly on the quality of barite and clays used to formulate the fluids. No data are available for the metals concentration in an SBF, but concentrations should be similar to those in OBFs. Aluminum and barium in drilling muds are from clays and barite, respectively. The other metals are associated primarily with the clay minerals and barite fractions and are present primarily as insoluble sulfide salt inclusions in clay and barite lattices (Neff et al. 1987). All the metals in drilling fluids are in solid or complexed forms. They have a low bioavailability and toxicity to marine organisms (Neff et al. 1989b,c). Metals do not contribute to the toxicity of drilling muds.

Table 6. Comparison of the concentrations of metals in water based drilling muds and in a typical oil based drilling mud (Neff et al. 1987; Fillio et al. 1987). Concentrations are mg/kg dry wt (ppm).

| Metal | Water-Based Mud | Oil-Based Mud |
|--------------|------------------------|----------------------|
| Aluminum | 10,800 | 52,000 |
| Barium | 720 – 449,000 | 487,000 |
| Cadmium | 0.16 – 54.4 | 0.39 – 12 |
| Chromium | 0.1 – 5,960 | 190 – 1,350 |
| Iron | 0.002 – 27,000 | 76,300 |
| Lead | 0.4 – 4,226 | 100 – 290 |
| Mercury | 0.017 – 10.4 | Not Reported |
| Zinc | 0.06 – 12,270 | 160 – 2,100 |

The viscosity of most SBF base materials (other than the olefins) is higher than that of diesel and mineral oils (Table 7). The high viscosity of some SBF base materials may limit the amount of barite that can be added to the mud and, therefore, the mud weight. This may limit the use of higher viscosity SBF base fluids in wells in which high mud weights are needed.

SBF base materials are synthesized in such a way as to avoid inclusion of aromatic hydrocarbons. This was done because aromatic hydrocarbons are considered to be major contributors to the toxicity of WBFs and OBFs (Neff et al. 1987; Kingston 1992). Because the base materials do not contain aromatic hydrocarbons, the complete SBF mud systems usually do not contain aromatic hydrocarbons (Table 7). However, crude oil may contaminate the mud, introducing aromatic hydrocarbons when drilling through hydrocarbon-bearing formations.

Table 7. The viscosity and aromatic hydrocarbon concentration in several types of OBFs and SBFs. Modified from Meinhold (1999).

| Base Fluid | Viscosity (cst @ 40°C) | Aromatic Hydrocarbons (%) |
|--|------------------------|---------------------------|
| Diesel | 3 – 4 | 25 |
| Conventional Mineral Oil | 2 – 3 | 1 – 7 |
| Purified Paraffin Oil | 2 – 3 | <1 |
| Enhanced Mineral Oil | 1.7 – 3 | <0.01 – <0.2 |
| Ester ~ C ₂₆ | 5 – 6 | 0 |
| Ester ~ C ₂₀ | 6.0 | 0 |
| Acetal C ₂₀ | 6.0 | 0 |
| Poly alpha olefin C ₂₀ | 5 – 7 | 0 |
| Linear alpha olefin C ₁₄ -C ₁₆ | 2.1 | 0 |
| Linear alpha olefin C ₁₆ -C ₁₈ | 3.1 | 0 |
| Internal olefin C ₁₆ -C ₁₈ | 3.1 | 0 |

4.0 FATE OF SYNTHETIC BASED DRILLING FLUIDS IN THE MARINE ENVIRONMENT

4.1 Discharge of SBF Cuttings

SBF cuttings are either permitted for offshore disposal or under active regulatory evaluation in much of the world. Cuttings produced during use of SBFs contain small amounts of adhering SBF. This is the route by which SBFs reach the ocean. Drilling fluid is circulated down the drill pipe continuously during drilling. It returns to the surface through the annular space between the drill pipe and well wall or casing, carrying drill cuttings in suspension. On the platform, the SBF is passed through equipment designed to remove drill cuttings and then is pumped into the mud pits from which it is pumped back down the hole. SBFs may be processed through mesh screens on shale shakers, hydrocyclones, and centrifuges to remove cuttings. In the Gulf of Mexico, most SBFs are processed through two or more shale shakers with different mesh size screens; hydrocyclones and centrifuges usually are not required (Annis 1997). Upon completion of drilling a well, the used SBF is transported to shore where it is cleaned and reformulated to make new SBF. Bulk discharge of SBFs to the ocean is not permitted in U.S., North Sea, and Australian waters.

The amount of SBF retained on cuttings following processing is highly variable. It depends on the grain size of the cuttings particles, the type of SBF, the efficiency of the cuttings processing equipment, and geologic characteristics of the formation being drilled (Annis 1997). As a general rule, if comparable cuttings-cleaning equipment is being used, the amount of SBF adhering to cuttings increases as cuttings particle size decreases and SBF viscosity increases.

Several studies have been performed on the concentration of SBF, OBF, or WBF on processed cuttings discharged to the ocean. Annis (1997) measured the percent SBF on cuttings from 54 wells drilled in the Gulf of Mexico. A total of 738 cuttings samples, drilled with PAO or IO, were analyzed. The average retention of synthetic base material on cuttings was 12.0 ± 4.8 percent. An average of 12.8 percent PAO was retained on cuttings, compared to 9.2 percent IO (Table 8). The primary shale shaker removes primarily coarse cuttings from the SBF; the secondary shale shaker removes finer-grained cuttings. The centrifuge removes the finest cuttings. Retention of IO and PAO on cuttings was highest for the secondary shale shakers and lowest for the primary shale shaker or centrifuge (Table 8). The U.S. EPA is considering requiring a best management practice involving treatment of effluents from the

shale shakers by centrifugation. The wet cuttings from the primary and secondary shale shakers would be directed to a cuttings dryer. The cuttings dryer is a two-stage centrifuge system. The coarse cuttings particles are separated in the first stage and discharged to the ocean. The liquid from the first stage passes to the second, higher speed centrifuge system that removes the finer particles from the waste stream.

Table 8. Retention of SBF base material on drill cuttings produced during offshore drilling in the Gulf of Mexico with IO and PAO based synthetic drilling fluids. From Annis (1997).

| Synthetic Type | Discharge Stream | Number of Samples | Ave. Synthetic Retained (% ± S.D.) |
|----------------|------------------|-------------------|------------------------------------|
| IO | Primary Shaker | 48 | 7.2 ± 3.2 |
| | Secondary Shaker | 48 | 11.3 ± 4.0 |
| | Centrifuge | 5 | 8.7 ± 1.5 |
| | All Streams | 101 | 9.2 ± 4.1 |
| PAO | Primary Shaker | 116 | 10.8 ± 5.0 |
| | Secondary Shaker | 116 | 15.1 ± 4.2 |
| | Centrifuge | 5 | 9.5 ± 1.5 |
| | All Streams | 237 | 12.8 ± 5.1 |
| Both | Primary Shaker | 164 | 9.7 ± 4.8 |
| | Secondary Shaker | 164 | 14.0 ± 4.5 |
| | Centrifuge | 10 | 9.1 ± 1.5 |
| | All Streams | 338 | 11.8 ± 5.1 |

In the mid-1990s, the UK government established a seabed monitoring program of single-well sites drilled with SBF. Twenty-one sites have been monitored to date. The distribution of SBFs in sediments around the discharge sites was monitored shortly after completion of drilling and approximately one year later. The operators provided estimates of the mass discharges of drill cuttings and SBFs discharged from 18 of the platforms; information from the other 3 wells is not available. The volume of SBF discharged with cuttings from the 18 wells ranged from 11 to 730 metric tons (Table 9). Estimated weight percent SBFs on cuttings are approximate because of differences in the methods used to estimate drilling fluid and cuttings weights actually discharged to the ocean.

The mass of mud on cuttings can be estimated by mass balance (amount of mud used minus amount recovered and estimated amount lost to the formation equals amount discharged on cuttings), or by retort or other chemical analysis of the concentration of SBF base fluid on cuttings samples. Retorting entails heating a known weight of cuttings in a retort to vaporize the liquids (water and SBF base fluid). The liquids are condensed and their volume measured in a graduated receiver (Annis 1997).

The concentration of barium in cuttings also can be used to estimate the mass of drilling fluid solids (high in barium) adhering to cuttings. Frequently, a distinction is not made between the mass of SBF base chemical and the mass of total SBF (base chemical and all other mud ingredients) on the cuttings. The different analytical methods give different results; the mass balance method is particularly subject to error because of the difficulty in accurately estimating the volume of drilling fluid lost to the geological formations being drilled.

Weight percent SBF on cuttings varied from 4.6 to 80 percent (Table 9). The highest loading was on ether SBF cuttings from a platform in 95 m of water. The operator assumed that all ether SBF not recovered was discharged to the ocean, which may not have been true. The operator may have underestimated SBF losses to the formation.

Excluding the single well drilled with an ether SBF system, the average percent SBF on cuttings discharged to the UK Sector of the North Sea ranged from 7.4 percent for n-paraffin SBFs to 10.5 percent for linear alpha olefin SBFs.

Table 9. Estimated masses of drill cuttings and SBFs discharged to the ocean during discharge of SBF cuttings from 18 wells in the UK Sector of the North Sea. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| SBF Type | Cuttings Discharged (metric tons) ¹ | SBF Discharged (metric tons) ¹ | % Mud on Cuttings |
|--------------------------|--|---|-------------------|
| n-Paraffin (Linear | 381 | 30 | 7.9 |
| Paraffin) | 1,000 | 70 | 7.0 |
| | 926 | 78 | 8.4 |
| | 198 | 13 | 6.6 |
| | 961 | 44 | 4.6 |
| | 145 | 11 | 7.6 |
| | 1,068 | 51 | 4.8 |
| | 1,418 | 179 | 12.6 |
| Average | | | 7.4 ± 2.3 |
| Linear- α -Olefin | 901 | 76 | 8.4 |
| | 795 | 115 | 14.5 |
| | 1,920 | 165 | 8.6 |
| Average | | | 10.5 ± 2.8 |
| Linear Alkylbenzene | 413 | 42 | 10.2 |
| | 655 | 65 | 9.9 |
| | 1,055 | 88 | 8.3 |
| Average | | | 9.5 ± 0.93 |
| Ether | 914 | 730 | 79.9 |
| Ester | 512 | 53 | 10.4 |
| | 1,062 | 67 | 6.3 |
| | 3,304 | 304 | 9.2 |
| Average | | | 8.6 ± 1.7 |

ⁱ Amounts of drilling fluids and cuttings discharged are commonly expressed in barrels (volumetric units) or metric tons (gravimetric units). In most cases there are insufficient data available to convert from volumetric to gravimetric units. For example, to convert a cuttings discharge given in metric tons to barrels, one needs the density of the SBF and the concentration of the SBF in the cuttings (the density of dry cuttings is fairly constant and equal to about 2.6 g/cc). However, there can be a wide variation in the density of whole drilling fluids and the concentration of the fluid in the discharged cuttings. Typically, one metric ton of SBF cuttings would be equal to 2.5-3 barrels.

4.2 Evaporation of Chemicals from SBFs

Because drilling fluids are heated during use by elevated temperatures in the geologic formation being drilled, their temperature in the mud tanks and shale shakers are well above ambient. During drilling, drilling mud and cuttings temperatures usually range from about 50°C to 70°C (Candler et al. 1996). At these temperatures, some of the

organic chemicals in the muds evaporate and are dispersed in the vapor phase over the mud tanks or shale shakers. These vapor losses are of importance mainly because of their toxicity through inhalation to personnel working near the mud storage and treatment systems on the platform.

In laboratory evaporation studies, organic vapor concentrations over different SBF base chemicals heated to 60°C to 70°C ranged from 0.5 to 37 mg/L (parts per million) (Table 10). PAOs produced the lowest concentrations of vapors; LAOs produced the highest concentrations. Emissions from esters were variable, probably due to variability in the amount of hydrolysis and release of 2-ethylhexanol (the most common alcohol building block for esters) in the different samples. Vapors from olefin based SBFs included decene (C₁₀H₂₀), that is the LAO building block for C₂₀ and C₃₀ PAOs, ethylene, that is the building block for LAOs, and low molecular weight volatile alkanes and alkenes derived from SBF base chemical synthesis or degradation.

Table 10. Concentrations of organic chemicals in vapors over different types of SBF base chemicals heated to 60 to 70°C in the laboratory. From Candler et al. (1996).

| Synthetic Fluid Type | Sample Temperature (°C) | Vapor Concentration (ppm) |
|--|-------------------------|---------------------------|
| LAO (C ₁₄ C ₁₆) | 60 – 70 | 15 – 37 |
| LAO (C ₁₆ C ₁₈) | 70 | 6.9 |
| IO (C ₁₆ C ₁₈) | 60 | 7.3 |
| PAO (C ₂₀ C ₃₀) | 60 | 0.62 – 0.78 |
| Ester F | 70 | 23.0 |
| Ester H | 70 | 2.9 |
| Ester PJ | 70 | 1.2 |
| Ester PU | 70 | 0.5 |

SBFs released much smaller amounts of vapors than diesel or mineral oil based drilling fluids in both laboratory and field studies (Table 11) (Candler et al. 1996). A water-miscible glycol fluid produced vapor concentrations similar to those of the SBFs. Overall, the amounts of base organic chemicals and their degradation products lost by evaporation from the drilling mud system are very small.

Table 11. Comparison of average organic vapor concentrations in laboratory and field studies of evaporation from OBFs, WBFs, and SBFs.

| Base Fluid | Average Vapor Concentration | |
|----------------------|-----------------------------|---------------------|
| | Laboratory Studies (ppm) | Field Studies (ppm) |
| Diesel | 310 | 42.0 |
| Mineral Oil | 166 | 340.0 |
| Synthetic Fluids | 9 | 0.3 |
| Water-Soluble Glycol | 8 | 1.0 |

4.3 Dispersion of SBFs

When discharged to the ocean, NABF cuttings tend to clump together in discrete masses that settle rapidly to the bottom (Delvigne, 1996; Brandsma 1996). Water cannot easily penetrate the oleophilic mass of cuttings, so they do not disperse efficiently.

Growcock et al. (1994) estimated the dispersibility of several SBFs by mixing a SBF sample with seawater and allowing the solids to settle for 10 minutes before measuring organic matter (representing the SBF base chemical) in the aqueous phase. The relative dispersibility of different drilling mud systems measured this way was:

Ester > Di-Ether >> Linear alkyl benzene > PAO > Low-Toxicity Mineral Oil

This order of decreasing dispersibility correlates fairly well with increasing hydrophobicity of the organic phase of the fluids, as indicated by estimated average log octanol/water partition coefficients ($\log K_{ow}$). IOs and LAOs, the most commonly used synthetics today, should lie between esters and PAOs in dispersibility.

Getliff et al. (1997) reported that low-viscosity SBFs, such as LAO SBFs, allow better separation of the drilling fluid from the cuttings on the shale shaker screens. Cuttings with lower concentrations of adhering SBFs have a lesser tendency than cuttings containing high concentrations of SBFs to clump, and dispersion is greater as the SBF cuttings settle through the water column. When cuttings containing 5 percent LAO or less (measured by retort analysis) were discharged, they dispersed in the water column and no cuttings pile accumulated on the bottom.

Thus, SBFs, particularly esters and low viscosity LAOs and IOs, are somewhat more dispersible than OBFs in seawater. Higher dispersibility allows the synthetic-contaminated cuttings to disperse and dilute in the water column as the cuttings settle to the bottom, decreasing the concentration and increasing the areal extent of cuttings accumulation on the seafloor. Increasing the dispersibility of SBF cuttings may decrease the magnitude of biological effects in sediments. Effective dispersion of SBF cuttings in the water column is not likely to have biologically significant adverse effects on water column organisms. WBFs and WBF cuttings, which do disperse in the water column, do not cause adverse effects in water column organisms (National Research Council 1983).

4.4 Accumulation of SBF Cuttings on the Sea Floor

Because most SBF and OBF cuttings do not disperse efficiently in the water column following discharge, they settle rapidly through the water column and accumulate on the bottom near the platform discharge site. Usually, the cuttings discharge on a platform is located in the upper water column within 10-20 m of the sea surface. However, sometimes cuttings are shunted to or near the bottom from fixed platforms (Cordah 1998). The effect of shunting is to decrease the area of the sea floor over which cuttings accumulate and to increase the mass of cuttings deposited per unit area near the well site.

Cuttings discharges have been monitored for more than 20 years in the UK Sector of the North Sea (United Kingdom Offshore Operators Association and United Kingdom Department of Trade and Industry, 1997). Cuttings piles were documented around approximately 60 multiwell platforms, from which most wells were drilled with OBFs, in the deeper central and northern parts of the UK Sector of the North Sea. Cuttings piles near multi-well platforms that discharged OBF cuttings were up to 26 m high, but most were less than 10 m high (Cordah 1998). A typical cuttings pile footprint was less than 50 m in diameter and therefore occupied less than 2,000 m² of sea floor. Cuttings piles usually did not form near platforms in the southern, shallower areas of the North Sea; the deposited cuttings were resuspended and dispersed over a wide area by storm-driven currents.

Several monitoring programs have been performed to document the distribution and fate of SBF cuttings in sediments near offshore exploration and production platforms and, in some cases, to assess the effects of cuttings accumulations on benthic communities. Field studies that included both chemical and biological assessments are summarized in Table 12. Accumulation and fates of SBF cuttings in sediments are discussed in the paragraphs that follow; biological effects of SBF cuttings discharges are discussed later in this review under **Biological Effects of SBF Cuttings Discharges**.

As part of the SBF cuttings discharge studies in the UK Sector, seabed surveys were performed to document the presence of cuttings piles on the seabed near some of the single-well drilling operations listed in Table 9. The height and area of cuttings piles varied widely (Table 13). Cuttings pile heights ranged from not evident (no visible pile) to 3 m. Height was not measured at any site in both years 1 and 2, so temporal changes can not be inferred. The area of the SBF cuttings piles varied from not evident to 94,250 m² (0.9 km²). The depth of penetration of SBF cuttings into bottom sediments was 0.25 m or less in all cases. There was no discernable relationship between the height and area of cuttings piles on the one hand and SBF type, water depth, or mass of cuttings discharged on the other. This may be due to insufficient sampling to characterize these factors. It is probable that discharge depth, rate and total mass of discharge, and tidal, residual, and storm currents are the main determinants of the dimensions of cuttings piles near offshore platforms.

IO cuttings were discharged to the Timor Sea off northern Australia from a platform in 27 m of water (McIlroy 1998). After completion of drilling, SBF cuttings were observed mixed with the sandy sediments at the site and as small, discrete mounds. A storm shortly after completion of drilling apparently had dispersed the cuttings over a wide area at this shallow-water drilling site. Similar observations were made by Terrens et al. (1998) near a drilling platform in about 70 m of water in the Bass Strait of Australia, a high-energy marine area off the southeast coast. A video survey of the sea floor near the platform revealed patches of ester based SBF cuttings interspersed with clean sediments. The cuttings accumulations were not thick enough to obscure ripples in the sediment. The cuttings patches were not evident at a distance of 200 m from the platform.

In another study, the dimensions of the cuttings pile were mapped with a 3D sonar imaging system following drilling of a well in 88 m of water with ether SBF in the UK sector of the North Sea (Hartley 1996). Cuttings were distributed in surface sediments in a ring around the well site. The maximum height of the cuttings pile was less than 1 m and cuttings accumulations above the original seabed level extended out to 10 to 15 m from the drill site. It is probable that most of the accumulated cuttings in the pile were deposited during spudding of the well before hookup to the riser. However, high concentrations of the ether SBF base chemical were detected in the cuttings pile, indicating that some of the pile was derived from cuttings discharges from the platform.

SBF cuttings piles also appear to be small at deep-water drilling sites. The fate of SBF cuttings was monitored near a drilling rig in 565 m of water south of the Mississippi River in the northern Gulf of Mexico (Galloway et al. 1998; Fechhelm et al. 1999). Discharges from the rig included 7700 bbls of WBF cuttings, 5150 bbls of SBF cuttings, and an estimated 7695 bbls of Petrofree LE (a SBF base material containing 90 percent LAO and 10 percent ester).

The sea floor near the drilling template was surveyed with a remotely operated vehicle (ROV). There was no evidence of cuttings piles of the sizes reported for the UK Sector of the North Sea. Instead, there was a thin veneer of cuttings dispersed over much of the bottom in a patchy distribution near the drilling template. Maximum cuttings accumulations appeared to be 20 to 25 cm thick in some locations. The largest deposits of large, chunk-like cuttings were detected a short distance southwest of the template. These cuttings accumulations probably were derived from direct drilling returns to the sea bottom during initial drilling with WBF before the riser was installed. There was no clear gradient of SBF-cuttings concentrations with distance from the rig site.

Drilling fluid and cuttings discharges at the site occurred between May 1996 and March 1997, and again in February and March 1998. Sediment samples were collected at different distances and directions from the template for analysis of SBF base chemicals in July 1997 and March 1998. Highest concentrations of LAO were detected in surficial (0 – 2 cm) sediments northeast of the drilling site (Table 14). They probably were carried to the northeast from the rig by the prevailing mid-water ocean currents. The highest LAO concentration measured in 1997 was 165,000 mg/kg in surficial sediment from a location 75 m northeast of the template. In March 1998, surficial sediment from the same location contained 198,000 mg/kg LAO. In July 1997, LAO concentrations in surficial sediments from other locations near the rig site ranged from 180 to 47,000 mg/kg; in March 1998, LAO concentrations in surficial sediments were lower (except for the one high value), ranging from 89 to 49,000 mg/kg (depth distribution). The mean concentration of LAO in surficial sediments (all sampling stations combined) was 4,000 mg/kg in 1997 and 2,000 mg/kg in 1998.

Table 12. Summary of field studies of the fates and effects of SBF cuttings discharges to the ocean. All studies are discussed in the text.

| SBF Type | Water Depth (m) | Cuttings Discharge | Field Surveys | SBF Fates | SBF Effects | Reference |
|--------------------------|-----------------|--------------------|---------------------------------|---|---|--|
| North Sea | | | | | | |
| Ester | 30 | 477 mt | 4 (pre, 1, 4, & 11 months) | <200 m, ester concentrations to 4,700 mg/kg at 4 mos., still detected after 11 mos. >200 m, esters near background. Est. $t_{1/2}$ ~ 133 d. | At 4 mos., sediments to 75 m anaerobic. Benthic fauna diminished <200 m, minor effects >200 m. Evidence of some recovery <200 m after 11 mos. | Daan et al. 1996 |
| Ester | 67 | 96.5 mt | 3 (at end of drilling, 1 & 2 y) | <200 m accumulation of high conc. of ester. Decrease after 1 & 2 years. | Impoverished fauna <100 m, no impacts >200 m, recovery after 1 year. | Smith & Hobbs 1993; Smith & May 1991; Smith & Moore 1991 |
| Unknown (probably ester) | Not reported | 115 mt | 1 Post-drilling | Low SBF to 2 km of site. | Benthic fauna normal. | Bakke et al. 1996 |
| Ester | Not reported | 46 m ³ | 1 Post-drilling | Most ester close to site, low concentrations to 500 m | Benthic fauna highly diverse, minor effects to 500 m | Bakke et al. 1996 |
| Ether | Not reported | 544 mt | 1 Post-drilling | Elevated concentration to 2 km down-current. | Benthic fauna near site had reduced diversity. Effects to 1 km down-current, 250 m in other directions | Bakke et al. 1996 |
| PAO | Not reported | 55 mt | 1 Post-drilling | SBF low but detected to 2 km from site. | Benthic fauna affected to 500 m from site. | Bakke et al. 1996 |
| Ester | 150 | 304 mt | 2 (post-drilling & 1 year) | Highest ester concentration 8,400 mg/kg at 25 m after drilling dropped to 1800 mg/kg after 1 year. Some contamination to 200 m. | Numbers of individuals increased, species numbers and diversity decreased at stations with highest ester conc. | UKOOA (unpub) |
| Linear Paraffin | 95 | 13 | 1 Post-drilling | Uneven distribution in sediment to 1,600 mg/kg at 70 m. | Abundance of benthic fauna and no. of taxa decreased with increasing SBF conc. | UKOOA (unpub) |

Table 12. Summary of field studies of the fates and effects of SBF cuttings discharges to the ocean. (continued)

| SBF Type | Water Depth (m) | Cuttings Discharge | Field Surveys | SBF Fates | SBF Effects | Reference |
|------------------------------|------------------|----------------------|--|--|--|------------------------------------|
| North Sea (continued) | | | | | | |
| Linear Paraffin | Not reported | 57.5 mt | 1 Post-drilling | Highest LP concentration, 28,000 mg/kg at 210 m from site. Distribution of SBF very uneven. | Abundance of benthic fauna high at most heavily contaminated sites, but number of taxa low. Organic enrichment effect. | UKOOA (unpub) |
| Ireland | | | | | | |
| LP/LAO/PAO | 380 | Not reported | 3 (at end of drilling, 1 & 2 y) | Highest SBF concentration 2,550 mg/kg within 100 m of site. Substantial decline in SBF in 2 years. | Some sediment anoxia. LP and LAO degraded by 90 % in 2 years. Little or no degradation of PAO in 2 years. | Gardline 1998 |
| Gulf of Mexico | | | | | | |
| PAO | 39 | 45 mt (est.) | 3 (9d, 8m, & 2y after drilling) | SBF and Ba unevenly distributed in sediments to 134,000 mg/kg at 50 m. SBF concentration declined to max of 19,000 mg/kg at 2 y. | After 2 y, no effects on benthic fauna more than 50 m from site. Decreased numbers of individuals and taxa at contaminated stations <50 m. | Candler et al. 1995 |
| Unknown (probably IO) | 33 – 61 (3 rigs) | 94-2,390 bbl | 10-25 mos. After drilling | Highest SBF conc. 1,900-23,000 mg/kg at 50 m. | Contaminated sediments anoxic. Sediments not toxic. | Continental Shelf Associates, 1998 |
| LAO/Ester | 565 | 7,700 bbl | Shortly after drilling | Very patchy SBF distribution to a max. of 198,000 mg/kg at 75 m. | Increase in numbers of benthic fauna but decrease in taxa at most heavily contaminated locations. Fish attracted to site. | Gallaway et al. 1998 |
| Australia | | | | | | |
| Ester | 70 | 2,000 m ³ | 5 (pre-drilling to 11 mos after drilling). | Ester conc. declined rapidly from max of 12,000 mg/kg after drilling to 200 mg/kg 6 mos later. | Change in benthic community structure within 100 m of platform shortly after drilling with recovery within 4 mos. | Terrens et al. 1998 |

In 1997, LAO concentrations in subsurface (2 – 5 cm) sediments were lower than those in surficial sediments at all but one station (along the most heavily contaminated northeast transect) (Table 14). In March 1998, LAO concentrations in subsurface sediments from several stations were equal to or higher than those in surficial sediments from the same stations. These results suggest that SBF cuttings mixed downward into the site sediments in the year after the first drilling activities. Average LAO concentrations in the 2 – 5 cm layer of sediments were 782 mg/kg in 1997 and 1,000 mg/kg in 1998.

Table 13. Dimensions of SBF cuttings piles near 12 single-well platforms drilled with SBFs in the UK Sector of the North Sea. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| SBF | Depth (m) | Cuttings (Tonnes) | Max. Height of Cuttings Pile (m) | | Max. Depth* of Cuttings Pile (m) | | Area of Pile (m ²) | |
|-------|-----------|-------------------|----------------------------------|-----|----------------------------------|------|--------------------------------|--------|
| | | | Y1 | Y2 | Y1 | Y2 | Y1 | Y2 |
| n-Par | 80 | 381 | NA | 0.6 | 0.15 | 0.14 | 94,250 | 3,770 |
| | 123 | 926 | 1.0 | 0.5 | NA | 0.15 | 5,025 | 5,025 |
| | 118 | 1,303 | NE | NA | 0.05 | NA | NE | NA |
| LP | 90 | 145 | NA | 3.0 | 0.05 | 0.10 | NA | 2,800 |
| | 90 | 961 | 2.0 | NA | 0.15 | 0.10 | 8,800 | 8,800 |
| | 140 | 869 | NE | NA | NA | NA | 40,000 | NA |
| | 100 | 1,418 | NA | 0.5 | 0.25 | 0.24 | NA | 40,000 |
| LAO | 78 | NA | 0.3 | NA | 0.09 | NA | 2,800 | NA |
| | 92 | 1,920 | NA | 1.0 | NA | 0.27 | 6,830 | 27,330 |
| | 55 | NA | NE | NE | NA | NA | NA | NA |
| Ester | 186 | 1,062 | NA | 0.0 | NA | 0.14 | NA | 0 |
| | 150 | 3,304 | NA | 0.2 | 0.17 | 0.17 | 62,800 | NE |

NA Not analyzed

NE Not evident

* Depth of penetration into bottom sediment

This study showed that SBF cuttings are distributed very heterogeneously in surface and subsurface sediments around deep-water drilling sites. This extremely uneven distribution of cuttings on the bottom is caused by clumping of the hydrophobic SBF-coated cuttings. They settle through the water column as large clumps of solids, rather than as a finely-dispersed rain of particles, as some WBF cuttings do. The sediment samples containing the highest concentrations of SBF base chemical apparently are “pure” SBF cuttings with little or no admixture of bottom sediments. The locations of discrete SBF cuttings accumulations on the bottom is controlled by the direction and velocity of water currents at different depths in the water column. At the Pompano II site, bottom currents were toward the southwest; therefore, mud and cuttings discharged during initial spudding of the wells settled to the southwest of the template. However, SBF cuttings discharged from the drilling rig passed through a zone of mid-water currents moving toward the northeast. Most of the discharged cuttings accumulated to the northeast of the platform. An estimated area of 6,700 m² of sediments (nearly 65 percent of which was northeast of the template) contained 10,000 mg/kg or more of LAO at the time of the July 1997 and March 1998 surveys.

Candler et al. (1995) monitored the accumulation and fate of a PAO SBF in sediments near a platform in 131 m of water in the Gulf of Mexico. Field surveys were performed 9 days, 8 months, and 24 months after completion of drilling. Accumulation of SBF in sediments was monitored as total petroleum hydrocarbons (TPH) and barium. There was a good correlation between concentrations of the two SBF tracers. SBF (as TPH) and barium were very unevenly distributed in sediments near the platform over time (Table 15). Shortly after drilling, highest SBF concentrations in sediments were 100 m north (38,470 mg/kg) and 50 m south (134,428 mg/kg) of the platform. After eight months, the highest SBF concentration in sediments was 25 m west (25,747 mg/kg) of the discharge

point. Two years after drilling, 19,110 mg/kg of SBF was measured in surface sediments 25 m south of the platform site. These four sediment samples were the only ones containing more than 10,000 mg/kg SBF. Surface sediments containing more than 1,000 mg/kg SBF were located 50, 100, and 200 m north, 50 and 100 m south, 25 and 50 m to the west, and 25 m to the east of the discharge site nine days after completion of drilling. After eight months and two years, sediments containing more than 1,000 mg/kg SBF were restricted to within 50 m of the drilling site. Between nine days and two years after drilling, SBF and barite concentrations decreased in sediments collected from more than 25 m from the discharge and fluctuated erratically in sediments 25 m from the discharge site. The total estimated area of sea floor contaminated with 1,000 to 10,000 mg/kg SBF decreased by 86 percent from 43,984 m² shortly after drilling to 5,891 m² two years later.

Table 14. Concentrations of Petrofree LE (90% LAO and 10% ester) measured as TPH by gas chromatography in sediments near the Pompano Phase II subsea template in 565 m of water off Louisiana. Concentrations in excess of 1,000 mg/kg (ppm) have been rounded to the nearest 1,000 ppm. From Gallaway et al. (1998).

| Transect Direction | Distance From Template (m) | 11 – 12 July 1997 | | 13 – 14 March 1998 | |
|--------------------|----------------------------|---------------------------------------|---------------|--------------------|---------------|
| | | Depth of Sediment Layer (centimeters) | | | |
| | | 0 – 2 | 2 – 5 | 0 – 2 | 2 – 5 |
| NE (45°) | 0 | 2,000 | 15 | 12,000 | 1,000 |
| | 25 | 3,000 | 9,000 | 21,000 | 23,000 |
| | 50 | 47,000 | 58,000 | 6,000 | 39,000 |
| | 75 | 165,000 | 8,000 | 198,000 | 86,000 |
| | 90 | --- | --- | 6,000 | 30,000 |
| | Mean | 54,000 | 19,000 | 49,000 | 30,000 |
| SE (135°) | 0 | 312 | 4 | 2,000 | 2,000 |
| | 25 | 7,000 | 68 | 2,000 | 5,000 |
| | 50 | 986 | 33 | 4,000 | 524 |
| | Mean | 3,000 | 35 | 3,000 | 3,000 |
| SW (225°) | 0 | 3,000 | 59 | 89 | 103 |
| | 25 | 10,000 | 3,000 | 691 | 77 |
| | 50 | 2,000 | 309 | 603 | 5,000 |
| | 75 | 2,000 | 13 | 6,000 | 209 |
| | 90 | 2,000 | 528 | --- | --- |
| | Mean | 4,000 | 782 | 2,000 | 1,000 |
| NW (315°) | 0 | 5,000 | 2,000 | 5,000 | 4,000 |
| | 25 | 15,000 | 1,000 | 8,000 | 11,000 |
| | 50 | 180 | 38 | 6,000 | 3,000 |
| | Mean | 7,000 | 1,000 | 6,000 | 6,000 |

Continental Shelf Associates (1998) monitored SBF cuttings accumulation and distribution on the bottom around three platforms in 33 to 61 m of water in the central Gulf of Mexico. Between one and five wells had been drilled from the three platforms, and 94 to 2390 barrels of SBF (apparently an IO) on cuttings had been discharged. The wells were completed 10 to 25 months before the survey.

The only sediments containing high concentrations of SBF (measured as total petroleum hydrocarbons with NOVAPLUS as a standard) were located 50 m northwest of the platforms. The three sediment samples contained 1900 mg/kg, 6500 mg/kg, and 23,000 mg/kg dry weight total petroleum hydrocarbons. All other sediment samples contained low (10 to 170 mg/kg dry wt) or non-detectable concentrations of total petroleum hydrocarbons. Several of the sediment samples, including the ones containing high concentrations of total petroleum hydrocarbons, smelled of hydrogen sulfide or looked anoxic. The sediment sample containing the highest concentration of total petroleum hydrocarbons had an Eh at a depth of 2.0 cm of -387 mV, indicating strongly reducing conditions. Bottom waters at 2 of the sites were hypoxic (~ 1.4 mg/L O_2 concentration) possibly contributing to sediment anoxia. Traces of PAHs, probably of petroleum origin, were detected in several of the sediment samples. This study showed a very limited contamination of sediments with SBFs near SBF cuttings discharges. Sediment anoxia in the area may have been natural, but probably was exacerbated by accumulation of SBFs.

Similar observations were made in the UK sector of the North Sea. The UK government established a program of seabed monitoring of single well sites drilled with SBFs. In the UK, seabed surveys can be requested by the government as part of an approval to drill a well. The goal of the program was to select five well sites for each key SBF system, whenever possible. At each well site, two surveys were requested, the first survey to be undertaken as soon as possible after cessation of drilling, and the second approximately one year later. To date, the majority of surveys have been completed and results reported to the government via the respective operators.

Data on SBF concentrations in sediments were collected near 21 well sites; full data sets (results from two surveys and additional information about the amount of cuttings discharged, etc.) are available for 17 sites. The wells were drilled with SBFs containing seven different base materials (Table 16). Water depths ranged from 55 to 186 m. Discharged cuttings contained approximately 4.6 to 14.5 weight percent adhering SBF (Table 10). The mass of SBF discharged with cuttings from individual wells ranged from 11 to 730 metric tons.

There was some variation among the well sites in terms of location (water depth, sediment type, and current regime) and drilling program (hole depth and mass of mud and cuttings discharged to the sea). In addition, the survey design was not consistent for all wells, survey timing (particularly the timing of the second survey) and station arrangement varying among the different operators. These combined factors have made it difficult to draw clear conclusions from the combined data sets concerning the amounts and concentrations of SBFs in sediments and the rate of change in SBF concentrations with time after completion of drilling.

Average concentrations of SBFs in sediments within 100 m of the wells shortly after completion of drilling ranged from 98 to 52,858 mg/kg, measured by gas chromatography as the specific SBF base chemical type (Table 17). Maximum concentrations of SBFs in sediments within 100 m of the different platforms ranged from 282 to 217,513 mg/kg in Year 1 and 118 to 228,474 mg/kg in Year 2. Approximately one year after drilling, average SBF concentrations in sediments (from 18 sites) ranged from 164 to 34,049 mg/kg. Mean concentrations of SBFs in sediments declined between the first and second survey at eight drilling sites and increased at 11 drilling sites. The declines occurred at two each of the rigs discharging linear paraffin, linear alkyl benzene, or ester SBFs, and one each of platforms discharging n-paraffins or LAO. The variability in the concentrations of SBFs in sediments within 100 m of platforms between the first and second field surveys probably is due to the extremely heterogeneous distribution of SBF cuttings in the sediments and the difficulty in exactly reoccupying the same sampling locations on the two surveys.

Because of the variability in the data, it is not possible to draw any firm conclusions about rates of biodegradation, dilution, or washout of different types of SBF cuttings from sediments. The overall impression is that the rate of loss of SBFs, other than esters, from sediments was low. Ester concentrations in sediments near rigs using ester SBFs were lower than concentrations of other SBFs near the platforms using other SBFs. This observation lends support to the hypothesis that esters biodegrade rapidly in sediments.

There was no clear relationship between concentrations of SBFs in sediments and water depth (Table 17), mass of cuttings discharged, or mass of SBFs discharged (Table 16). There was a trend for SBF cuttings concentrations in sediments near discharging platforms to decrease as water depth increased (Figure 1). However, the regression was not significant ($r^2 = 0.106$).

Table 15. Concentrations of total petroleum hydrocarbons (used as a marker of SBF) and barium in surface sediments around a drilling rig in 131 m of water in the Gulf of Mexico 9 days, 8 months, and 24 months after drilling a well with PAO SBF. Concentrations are mg/kg. From Candler et al. (1995).

| Distance & Direction | Total Petroleum Hydrocarbons (mg/kg) | | | Barium (mg/kg) | | |
|----------------------|--------------------------------------|----------|-----------|----------------|----------|-----------|
| | 9 Days | 8 Months | 24 Months | 9 Days | 8 Months | 24 Months |
| 25 m North | 256 | 158 | 822 | 586 | 1,181 | 2,478 |
| 50 m North | 1,855 | 2,850 | 450 | 1,925 | 4,521 | 1,603 |
| 100 m North | 39,470 | 187 | 383 | 39,608 | 1,413 | 1,884 |
| 200 m North | 1,460 | 297 | 87 | 5,641 | 2,693 | 1,392 |
| 2000 m North | 76 | ND | ND | 681 | 644 | 901 |
| 25 m East | 1,020 | 197 | 560 | 540 | 1,679 | 2,771 |
| 50 m East | 62 | 190 | ND | 466 | 1,791 | 1,796 |
| 100 m East | 153 | 95 | 55 | 1,118 | 1,285 | 1,461 |
| 200 m East | 84 | ND | 20 | 766 | 600 | 990 |
| 2000 m East | 24 | ND | ND | 569 | 559 | 822 |
| 25 m South | 203 | 7,283 | 19,110 | 803 | 8,230 | 17,993 |
| 50 m South | 134,428 | 727 | 3,620 | 47,437 | 2,700 | 8,415 |
| 100 m South | 2,010 | 562 | 720 | 4,618 | 2,483 | 3,227 |
| 200 m South | 378 | 270 | 280 | 1,282 | 2,005 | 1,720 |
| 2000 m South | 26 | ND | ND | 642 | 639 | 883 |
| 25 m West | 2,827 | 25,747 | 8,330 | 4,256 | 14,670 | 32,634 |
| 50 m West | 2,610 | 498 | 1,080 | 1,887 | 3,652 | 4,024 |
| 100 m West | 494 | 108 | 60 | 1,929 | 1,296 | 1,373 |
| 200 m West | 80 | 24 | 20 | 542 | 848 | 1,081 |
| 2000 m West | 34 | ND | 46 | 594 | 808 | 871 |

ND Not detected.

Table 16. Summary of SBFs used to drill the 21 wells monitored in the UK Sector of the North Sea. Ranges of water depths and mud and cuttings discharge masses also are given. With permission of the operators through the United Kingdom Offshore Operators Association.

| Mud Type | No. Wells | Water Depth (meters) | Cuttings Discharged (metric tons) | Mud Discharged (metric tons) |
|-----------------|----------------|----------------------|-----------------------------------|------------------------------|
| n-Paraffin | 3 | 80 – 140 | 381 – 1,000 | 30 – 7 |
| Linear Paraffin | 6 ^a | 78 – 100 | 145 – 1,418 | 11 – 179 |
| PAO | 1 ^a | 55 | NA | NA |
| LAO | 4 ^a | 55 – 185 | 795 – 1,920 | 76 – 165 |
| LAB | 3 | 92 – 130 | 413 – 1,056 | 42 – 88 |
| Ether | 1 | 95 | 914 | 730 |
| Ester | 3 | 130 – 186 | 512 – 3,304 | 53 – 304 |

^a Incomplete data available for one site.

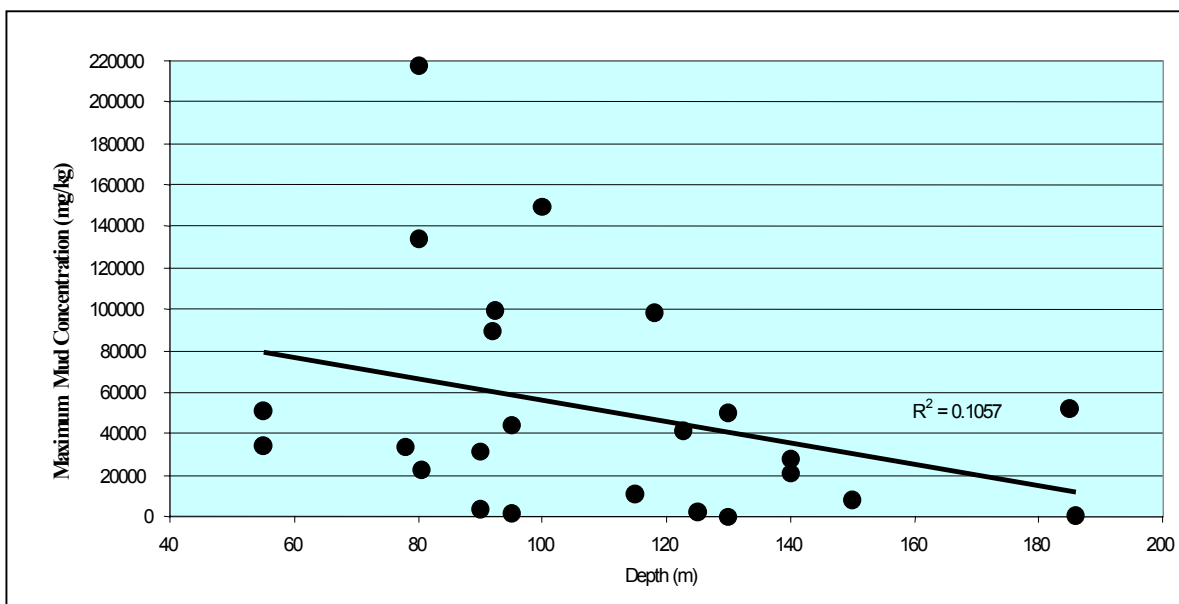


Figure 1. Relationship between water depth and maximum concentrations of SBF base chemical in surface sediments near drilling platforms in the UK Sector of the North Sea.

If the mass of cuttings discharged is the main factor controlling the concentrations of SBF cuttings in sediments within 100 m of drilling rigs, a regression of mass of cuttings discharged versus the normalized (per 100 tons of cuttings discharge) concentration of SBFs in sediments should yield a statistically significant positive slope. Mean normalized concentrations of SBFs in sediments (mg/kg/100 tons of cuttings discharged) immediately after drilling ranged from 54 mg/kg to 138,492 mg/kg. There was no correlation with the mass of cuttings discharged. The amount of cuttings accumulating in sediments is dependent on a complex interaction of discharge rate and mass, water depth, current structure of the water column, and the type of SBF and cuttings.

In most cases, SBF cuttings do not penetrate and mix deeply into surface sediments near the platform. SBF concentrations usually are higher in the surface layer (0 – 2 cm) of sediments than in deeper layers (2 – 5 cm and 5 – 8 cm) (Tables 18, 19, and 20). At one site (Table 19), the concentration of LAO in sediments at the well site (0 m from the discharge) shortly after completion of drilling increased from 7876 mg/kg at the surface to 25,023 mg/kg at a depth in the sediment of 5 to 8 cm. This could have been caused by a decrease with drilling depth in the concentration of SBF on cuttings discharged during drilling.

Approximately a year after completion of drilling, concentrations of SBF in the surface layer of sediments often decrease; however, concentrations at greater depths in the sediment core may increase or decrease (Table 18). Temporal changes in SBF concentrations below the sediment surface probably are controlled by the amount of sediment reworking (by bioturbation and current-induced bed transport) and biodegradation. After more than a year, SBF concentrations at all depths in sediment may decline to low values, particularly if ester SBF cuttings were discharged (Table 20).

The area of sea floor near a platform discharging SBF cuttings that becomes contaminated with measurable concentrations of SBFs varies widely from one site to another. The approximate area of SBF cuttings piles around drilling rigs in the UK Sector of the North Sea ranges from less than 2800 m² to 94,250 m² (Table 13). The cuttings are not evenly distributed in sediments around the rig. Most cuttings settle in the direction of the net current flow (integrated for the full water column) (Figure 2). In the example from a single-well platform in the UK Sector of the North Sea in Figure 2, the highest measured ester concentration was in surface sediment from 25 m southwest of the rig.

Table 17. Average and maximum concentrations of SBFs of different types in sediments within 100 m of wells drilled with SBFs in the UK Sector of the North Sea. Concentrations of SBF are mg/kg. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| Mud Type | Water Depth (m) | Number of Samples | Mean SBF Concentration | | Maximum SBF Concentration | |
|--------------------------|-----------------|-------------------|------------------------|---------------|---------------------------|----------------|
| | | | Year 1 | Year 2 | Year 1 | Year 2 |
| n-Paraffin | 80 | 47 | 42,302 | 15,956 | 217,513 | 228,474 |
| | 140 | 30 | 1,611 | 1,827 | 21,218 | 159,045 |
| | 123 | 24 | 5,713 | 28,796 | 41,338 | 110,570 |
| Average | 114 | -- | 16,542 | 15,526 | 93,356 | 166,030 |
| Linear Paraffin | 95 | 52 | 277 | 298 | 1,603 | 1,282 |
| | 90 | 36 | 3,657 | 4,191 | 31,371 | 33,551 |
| | 78 | 21 | 11,266 | ND | 33,942 | ND |
| | 90 | 22 | 653 | 9,992 | 3,219 | 68,023 |
| | 80 | 33 | 21,670 | 19,531 | 133,638 | 43,337 |
| | 100 | 31 | 52,858 | 29,409 | 149,640 | 58,866 |
| Average | 89 | -- | 15,064 | 12,684 | 58,902 | 41,012 |
| Poly- α -Olefin | 55 | 15 | 16,815 | 25,937 | 51,232 | 75,050 |
| Linear- α -Olefin | 55 | 16 | 8,045 | 13,945 | 34,533 | 63,888 |
| | 80 | 40 | 5,449 | 20,466 | 22,440 | 44,945 |
| | 185 | 21 | 16,642 | ND | 52,139 | ND |
| | 92 | 16 | 45,510 | 8,756 | 99,365 | 52,622 |
| Average | 103 | -- | 18,912 | 14,389 | 52,119 | 53,818 |
| Linear Alkyl | 115 | 17 | 2,990 | 24,501 | 11,071 | 104,152 |
| Benzene | 140 | 18 | 23,074 | 16,279 | 50,024 | 60,244 |
| | 92 | 16 | 36,329 | 34,049 | 89,732 | 91,529 |
| Average | 112 | -- | 20,798 | 24,943 | 50,276 | 85,308 |
| Ether | 95 | 25 | 392 | 1,246 | 44,260 | 94,150 |
| Ester | 140 | 17 | 98 | 164 | 282 | 1,848 |
| | 186 | 25 | 388 | 334 | 719 | 1,375 |
| | 150 | 32 | 1,492 | 473 | 8,389 | 1,785 |
| Average | 155 | -- | 659 | 324 | 3,130 | 1,669 |

Table 18. Concentrations of Ester SBF at different depths in sediments near a platform in 150 m of water shortly after completion of drilling (Year 1) a well and discharge of 3,304 metric tons of cuttings and 304 tons of ester SBF, and ten months later (Year 2). Concentrations are mg/kg dry wt. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| Location (Distance/Direction) | Year | 0 – 2 cm | 2 – 5 cm | 5 – 8 cm |
|-------------------------------|------|----------|----------|----------|
| 0 | 1 | 4,020 | 1,935.0 | 23.5 |
| | 2 | 15 | 5.4 | 15.1 |
| 25 m North | 1 | 1,578 | 1,767.0 | 1,081.0 |
| | 2 | 470 | 107.0 | 13.7 |
| 25 m Northeast | 1 | 1,604 | 10.3 | 13.3 |
| | 2 | 133 | 2.1 | 14.6 |
| 25 m Southeast | 1 | 2,631 | 0.9 | --- |
| | 2 | 400 | 83.1 | 2.1 |
| 25 m South | 1 | 2,262 | 19.4 | 11.9 |
| | 2 | 1,785 | 485.0 | 17.9 |
| 25 m Southwest | 1 | 8,389 | 17.0 | 2.4 |
| | 2 | 1715 | 459.0 | 32.9 |
| 25 m West | 1 | 1,055 | 8.4 | 0.4 |
| | 2 | 588 | 380.0 | 20.5 |
| 25 m Northwest | 1 | 4,318 | 196.0 | 0.2 |
| | 2 | 1,239 | 427.0 | 57.7 |
| 50 m North | 1 | 1,304 | 1,613.0 | --- |
| | 2 | 453 | 0.4 | --- |
| 50 m South | 1 | 1,334 | 1.8 | --- |
| | 2 | 543 | 146.0 | --- |
| 50 m Southwest | 1 | 1,243 | 1.4 | --- |
| | 2 | 629 | 687.0 | 17.8 |
| 50 m Northwest | 1 | 2,371 | 105.0 | --- |
| | 2 | 471 | 206.0 | 60.5 |
| 75 m West | 1 | 136 | 8.7 | --- |
| | 2 | 184 | 16.9 | --- |

Table 19. Concentrations of LAO SBF at different depths in sediments near a platform in 185 m of water shortly after completion of drilling of a well and discharge of 795 metric tons of cuttings containing 115 tons of LAO SBF. Concentrations are mg/kg dry wt. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| Location (Distance/Direction) | 0 – 2 cm | 2 – 5 cm | 5 – 8 cm |
|-------------------------------|----------|----------|----------|
| 0 | 7,876.0 | 13,965.0 | 25,023 |
| 50 m North | 9,766.0 | 954.0 | --- |
| 50 m Northeast | 44,515.0 | 842.0 | --- |
| 50 m East | 48,042.0 | 17,375.0 | 2,804 |
| 50 m Southeast | 50,908.0 | 542.0 | --- |
| 50 m South | 40,125.0 | 28,669.0 | --- |
| 50 m Southwest | 7,798.0 | 38.2 | --- |
| 50 m Northwest | 5,266.0 | 503.0 | --- |
| 100 m Southeast | 2.9 | 2.8 | --- |

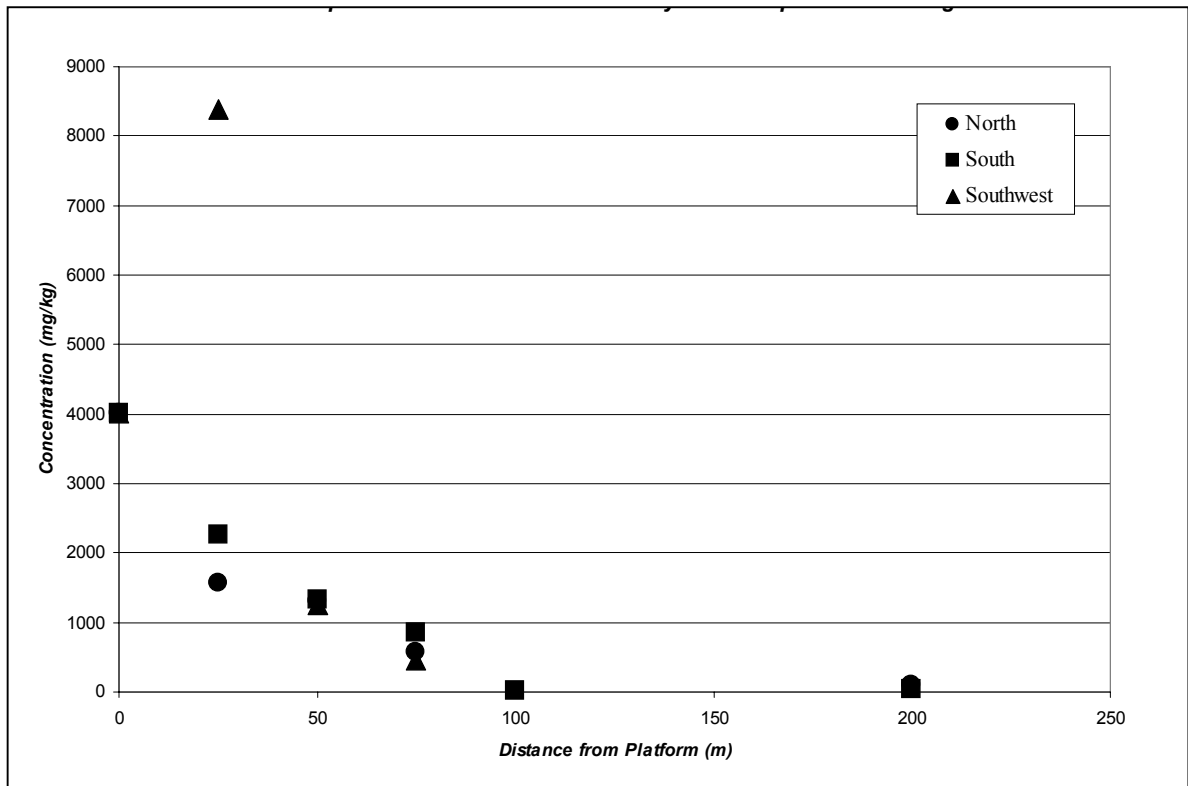


Figure 2. Average concentration of ester in surface sediments at different distances from a platform in 150 m of water shortly after completion of drilling.

The distance from the rig to the highest concentration of SBF cuttings on the bottom varies depending on distance from the discharge to the seafloor, the net water current speed, and cuttings density. For example, the highest concentration of Petrofree SBF in surface sediments near a drilling rig in 565 m of water off Louisiana was located 75 m northeast of the drilling template (Table 14). Lower concentrations of SBF accumulated in sediments closer to and farther from and in different directions from the rig. Midwater currents at the site were toward the northeast, explaining the distribution of cuttings on the bottom.

The studies of SBF discharges to the UK Sector of the North Sea reveal a complex pattern of SBF distribution around drilling rigs. Shortly after drilling, the highest concentrations of SBF in sediments were located 0 m to 224 m from the rig (Table 21). Approximately one year after completion of drilling, the highest SBF concentrations in sediments were located 5 m to 153 m from the former drilling sites. The distance from the rig sites to sediment SBF concentrations below about 1,000 mg/kg ranged from 40 m to about 500 m from the rigs. Many surface sediment samples from closer to the rigs contained less than 1,000 mg/kg SBF. Thus, the average radius around the rigs where sediment SBF concentrations were greater than 1,000 mg/kg was less than the maximum distances.

Table 20. Concentrations of ester at different depths in sediments near a platform in 186 m of water 19 months after completion of drilling of a well and discharge of 1,062 metric tons of cuttings and 67 tons of ester SBF. Concentrations are mg/kg dry wt. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| Location (Distance/Direction) | 0 – 2 cm | 2 – 5 cm | 5 – 8 cm |
|-------------------------------|----------|----------|----------|
| 0 | 1,070.0 | 644.0 | 33.8 |
| 25 m North | 289.0 | 7.8 | --- |
| 25 m East | 418.0 | 17.2 | 2.8 |
| 25 m South | 570.0 | 161.0 | 36.3 |
| 25 m West | 943.0 | 50.3 | --- |
| 50 m North | 1,295.0 | 41.3 | --- |
| 50 m Northeast | 1,375.0 | 682.0 | --- |
| 50 m East | 5.4 | 7.1 | 6.7 |

The uneven distribution of average SBF concentrations around a rig can be seen in Figure 3. In this example, 1,055 metric tons of cuttings and 88 tons of LAO SBF were discharged; the highest average concentration of SBF in surface sediments was located 90 m from the platform shortly after drilling and 110 m from the platform a year later. A year after drilling was completed, there also was a high concentration of LAO in surface sediments 300 m from the rig site. Low concentrations of LAO were detected in sediments from 500 m and 1,200 m from the rig. In two other examples (Figures 2 and 4), ester and PAO concentrations in sediments were highest 20 to 25 m southwest and northwest, respectively, from the rig and SBF concentrations in sediments declined sharply with distance from the rig sites. SBF concentrations in sediments were below 1000 mg/kg in all directions from the rig 75 m and 50 m, respectively, from the platforms.

Accumulation of SBF cuttings in sediments was monitored near a rig in approximately 380 m of water off the west coast of Ireland (Gardline 1998). Field surveys were performed shortly after completion of drilling and one and two years later. The well was drilled with a commercial mud formulation containing linear paraffins, LAOs, and PAOs.

Table 21. Relationship between water depth, mass of cuttings discharged, and SBF type and distance to maximum SBF concentration in sediments and maximum distance to nontoxic (<1000 mg/kg) SBF concentration in sediments. With permission of the operators through the United Kingdom Offshore Operators Association (UKOOA).

| Mud Type | Water Depth (m) | Cuttings Disch. (mt) | Max Conc. | Distance to Maximum (m) | | Distance to < 1000 mg/kg ^a |
|----------|-----------------|----------------------|-----------|-------------------------|--------|---------------------------------------|
| | | | | Year 1 | Year 2 | |
| Ester | 130 | 512 | 282 | 106 | 37 | 43 |
| | 150 | 3,304 | 8,389 | 25 | 25 | 200 |
| | 186 | 1,062 | 719 | 0 | 50 | 100 |
| Ether | 95 | 914 | 44,260 | 74 | 30 | 497 |
| PAO | 55 | ND | 51,232 | 20 | 20 | 200 |
| LAO | 55 | ND | 35,533 | 7 | 7 | 50 |
| | 80 | 901 | 22,440 | 25 | 10 | 168 |
| | 185 | 795 | 52,139 | 100 | ND | 500 |
| LP | 78 | ND | 33,942 | 50 | ND | 200 |
| | 80 | 1,068 | 133,638 | 77 | 153 | 496 |
| | 90 | 145 | 3,219 | 224 | 50 | 497 |
| | 90 | 961 | 31,371 | 30 | 80 | 500 |
| | 95 | 198 | 1,603 | 70 | ND | 80 |
| | 100 | 1,418 | 149,640 | 50 | 25 | 500 |
| n-Par. | 80 | 381 | 217,513 | 50 | 50 | 500 |
| | 123 | 926 | 41,338 | 40 | 5 | 500 |
| | 140 | 1,000 | 21,218 | 50 | 50 | 300 |
| LAB | 92 | 1,055 | 89,732 | 96 | 77 | 501 |
| | 115 | 413 | 11,071 | 105 | 78 | 498 |
| | 130 | 655 | 50,024 | 94 | 94 | 500 |

^a Concentration of OBF in sediments that is considered the threshold for effects on benthic community structure (Berge 1996).

Shortly after completion of drilling, SBF were detected at concentrations of 21 to 2550 mg/kg in sediments within 100 m of the drilling site. After one and two years, SBF had spread at low concentrations as far as 500 m from the drilling site. The highest concentrations in sediments within 50 m of the site had declined to 1110 mg/kg after one year and 520 mg/kg after two years. Careful examination of the gas chromatograms of sediment samples revealed that linear paraffins and LAOs were degraded rapidly, but PAOs were degraded slowly, if at all. After two years, there was a 90 percent reduction in the concentration of LAOs in sediments, but almost no reduction in the concentration of PAOs. This study provides the strongest evidence to date of the limited biodegradability of PAOs in field sediments.

Studies in the North Sea, Gulf of Mexico, and offshore Australia and Ireland show that SBF cuttings accumulate in a very irregular pattern in sediments around a drilling rig. The modeled footprint, maximum thickness, and SBF concentration in the cuttings pile around the platform seem, in most cases to be less than those predicted when OBF cuttings are discharged (Brandsma 1996). Highest concentrations of SBF in sediments often are lower than the concentration of SBF in the cuttings at the time of discharge, suggesting that some SBF desorbs from the cuttings during their fall through the water column (Getliff et al. 1997). Sometimes, SBF base chemical concentrations in sediments are as high as or higher than reported average concentrations on discharged cuttings, suggesting either that some cuttings are discharged containing high concentrations of adsorbed SBF or that some sediment samples represent undiluted clumps of SBF cuttings.

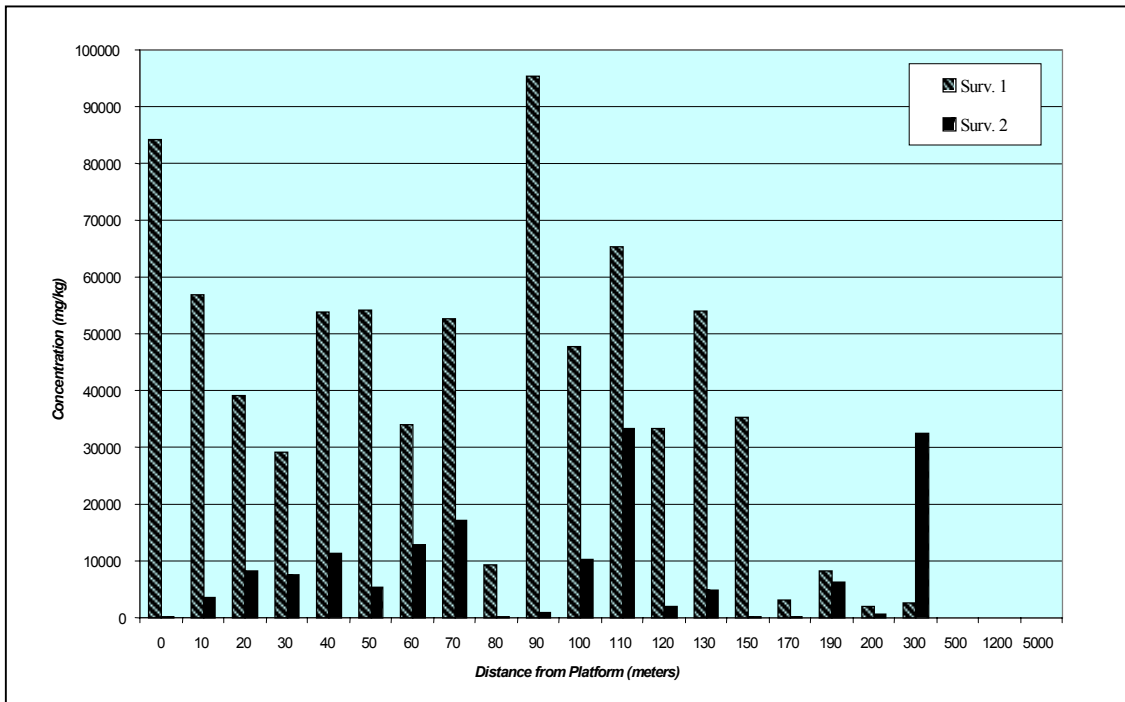


Figure 3. Average concentrations of LAO in surface sediments at different distances from a platform in 92 m of water. Survey 1 was immediately after drilling; Survey 2 was a year later.

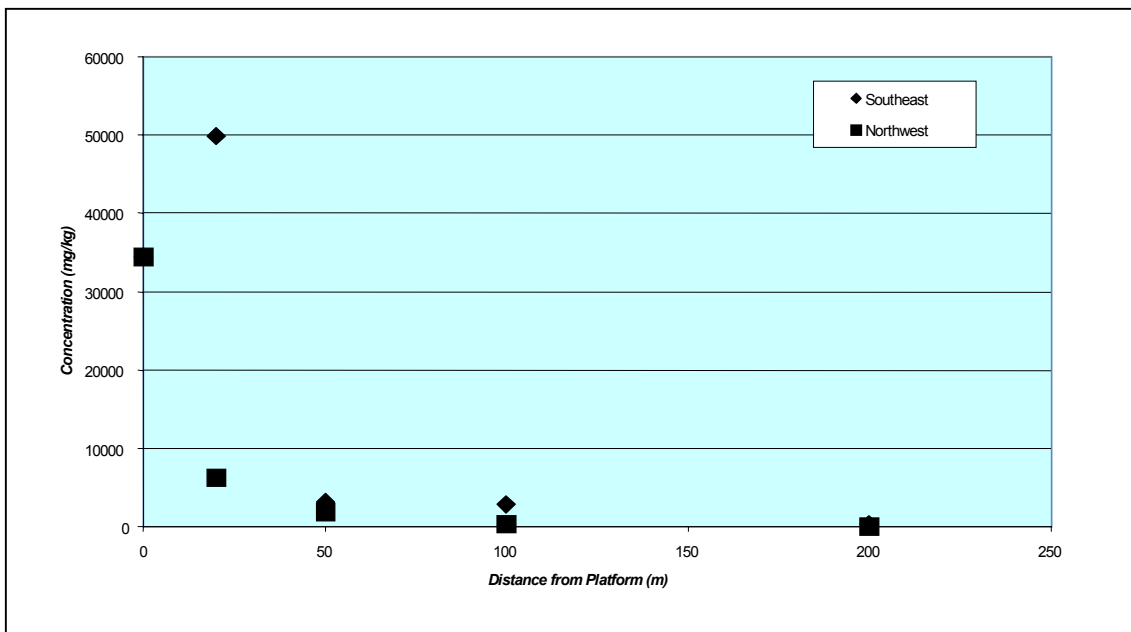


Figure 4. Average concentration of PAO in surface sediments at different distances from a platform in 55 m of water shortly after completion of drilling.

Brandsma (1996) modeled the initial deposition of low toxicity mineral oil OBF cuttings discharges from platforms in different water depths in the North Sea. Subsequent resuspension and bottom transport were not considered. The maximum initial thickness of OBF cuttings on the sea floor following a simulated discharge of 300 m³ OBF cuttings ranged from 0.1 to 15.5 cm, depending on water depth and concentration of oil on cuttings. Maximum estimated oil concentrations in surficial sediments shortly after OBF cuttings discharges ranged from 106 to 196,000 mg/kg. The maximum radius of oil accumulation in sediments to more than 100 mg/kg was 172 m.

Field studies have shown a greater dispersal of OBF cuttings than those predicted by Brandsma (1996). Around platforms in the North Sea where OBF cuttings were discharged, the maximum distance from the discharge site to a concentration of 1,000 mg/kg oil in sediments usually has ranged from 500 to 1,000 m (Davies et al. 1983; Kingston 1992). Concentration above 10 mg/kg oil in sediments often extended out to 8 to 12 km from the platform. In all but one case in the North Sea studies discussed above, concentrations of SBF dropped below 50 mg/kg and in most cases below 10 mg/kg, within 1.2 km of the discharge point. Candler et al. (1995) estimated that the area of sediment near six platforms in the North Sea containing 1,000 to 10,000 mg/kg total petroleum hydrocarbons (from discharged OBF cuttings) ranged from 78,542 m² to 107,996 m² 0 to five years after completion of drilling. By comparison, the area of sea floor containing 1000 to 10,000 mg/kg SBF ranged between 5,891 and 43,984 mg/kg zero to two years after completion of drilling with a PAO SBF from a platform in 131 m of water in the Gulf of Mexico.

4.5 Biodegradation of SBFs

OBFs, particularly those made with diesel fuel, are highly persistent in sediments. Grahl-Nielsen et al. (1989) reported little change over five years in the area of sea bottom near a single exploratory well in the North Sea that contained 1,000 to 10,000 mg/kg OBF from the discharge of OBF cuttings. One of the objectives in developing environmentally acceptable alternatives to OBFs was to produce a drilling fluid that would provide the drilling performance of an OBF, but would degrade rapidly following discharge to the ocean. Environmental authorities of North Sea countries have hypothesized that rapid degradation will minimize environmental impacts of SBF cuttings discharges, speeding ecosystem recovery (Vik et al. 1996a).

The main mechanism of degradation of SBF base materials is through microbial metabolism of the SBF base chemicals to harmless byproducts. Natural populations of sediment-dwelling bacteria, fungi, and protists are able to biodegrade some hydrocarbons and related oxygen-containing organic chemicals (e.g., esters, ethers, acetals) and use the carbon fragments as a source of nutrition (Figure 5).

Hydrocarbons vary in their susceptibility to biodegradation. The solubility and bioavailability to microbes of paraffins and olefins decreases sharply with increasing carbon chain length and molecular weight. As a result, high molecular weight, insoluble SBF base chemicals, such as PAOs, are less bioavailable and biodegradable than lower molecular weight, slightly soluble base chemicals, such as IOs (Friedheim and Conn 1996). As a general rule, linear hydrocarbons are more easily biodegraded than branched or aromatic hydrocarbons (Atlas 1995). Biodegradation rate of linear paraffins decreases as chain length increases. Branching of hydrocarbon chains tends to slow biodegradation. Carbon-carbon double bonds and internal oxygen atoms (e.g., esters) are more readily attacked by microbes than carbon-carbon single bonds. Hydrocarbons are biodegraded mainly by oxidation; therefore, biodegradation of SBF base materials and other hydrocarbons is much more rapid in the presence of oxygen (aerobic) than in its absence (anaerobic). This could be due to the absence of primary nutrients (inorganic nitrogen and phosphorous) rather than the absence of oxygen in the sediments (Scherrer and Mille 1989).

A normal alkane (e.g., linear paraffin) or an alkene (e.g., LAO, IO, and PAO) is oxidized by microbes to an alcohol; the alcohol is oxidized further, through a 1,2-diol or ketone intermediate, to a fatty acid (Figure 5). Two atoms of oxygen are consumed for each atom of fatty acid formed. Fatty acids are storage and structural nutrients for all plants and animals. The fatty acids derived from oxidation of SBF base chemicals are oxidized two carbons at a time through β -oxidation. The resulting acetate (CH₃COOH) molecules are incorporated into the energy and synthetic pathways of the microorganism. Thus, SBF base chemicals are biodegraded completely under aerobic conditions, with the reduction (incorporation into biochemical substrate) of a large amount of oxygen. Aerobic biodegradation of SBFs may deplete the oxygen in sediments, rendering the sediments anaerobic, if loading of the

sediments with biodegradable organic matter from SBF cuttings is high and aeration of sediments is slow. Field studies of OBF cuttings discharges have indicated that sediments may become anaerobic if they contain 1000 mg/kg or more of mineral oil (Vik et al. 1996a).

In the absence of oxygen (anaerobiosis), SBF base chemicals are dehydrogenated to alcohols that are converted through a ketone or aldehyde intermediate to fatty acids (Getliff et al. 1997; Candler et al. 1999). These initial degradation reactions are very inefficient under anaerobic conditions, and their rate probably limits the overall net rate of SBF biodegradation in marine sediments (Steber et al. 1995). Carbon-carbon double bonds and ester linkages are more easily oxidized than carbon-carbon single bonds by marine anaerobic bacteria. Thus, esters and unsaturated SBF base chemicals would be expected to biodegrade more rapidly than paraffins, linear alkyl benzenes, ethers, and acetals in anoxic sediments. Under anaerobic conditions, fatty acid oxidation also is inefficient. Alternatives to oxygen (e.g., NO_3^{-1} , SO_4^{-2} , and CO_2) are used by the microbes to oxidize fatty acids, producing byproducts, such as hydrogen sulfide, ammonia, and methane, that are toxic to some sediment-dwelling marine organisms. Sulfate is abundant in seawater (~ 29 mM) and marine sediments; therefore, it is the dominant terminal electron acceptor for microbial oxidation of SBF base chemicals in anoxic marine sediments (Getliff et al. 1997). OBF cuttings piles in the North Sea contained 30 to 879 mg/kg sulfide, indicating that the OBFs were being degraded anaerobically by sulfate reducing bacteria (Cordah 1998). Methanogenesis (reduction of CO_2 to CH_4) occurs only when most of the available sulfur has been reduced to sulfide. Sulfate reducing bacteria are more aggressive than methanogens, and olefins and esters should biodegrade more rapidly in marine sediments than indicated by anaerobic biodegradation tests, most of which are based on methanogenesis (Friedheim and Pantermuehl 1993).

Regulatory agencies may require proof of rapid biodegradation before approving ocean disposal of SBF cuttings (Vik et al. 1996a). Measurement of biodegradation rates of SBFs is difficult because of the large number of environmental and chemical variables that affect degradation rate. The most important environmental factors affecting biodegradation rate of SBFs in sediments are temperature, oxygen concentration, and seafloor energy. Several types of biodegradation tests have been developed or modified to evaluate the biodegradation of SBFs. They include:

- standard laboratory tests,
- solid phase tests, and
- simulated seabed tests.

4.5.1 Standard Laboratory Tests

Although most European regulatory agencies require that drilling fluids pass a biodegradability test in order to be permitted for ocean disposal, there is no agreement on an environmentally acceptable biodegradation rate or how to measure it and extrapolate the results to predict impacts of SBF cuttings deposits in seafloor sediments. Laboratory biodegradation tests vary widely in specific details and environmental realism. The different test methods produce widely different results. Biodegradation test protocols vary in three key aspects:

- **Aerobic/anaerobic** – Standard test procedures are usually designed to be either aerobic or anaerobic. Anaerobic conditions are likely to occur in the central part of cuttings piles or in subsurface sediment layers; aerobic conditions are likely to occur in the surface layers of the transition zone where SBF concentrations are low.
- **Water soluble/non-water soluble** - Most test procedures are designed for water-soluble materials. There is no agreed standard protocol for SBFs, which are essentially insoluble.
- **Freshwater/seawater** – Several biodegradation tests are performed in fresh water; test water salinity may affect test results, in part due to effects of dissolved salts on emulsion stability. Freshwater tests use a bacterial inoculum, whereas seawater tests rely on natural bacterial populations in the seawater used in the tests. The difference in the number and types of bacteria in the freshwater and seawater tests is the main reason that test results are different. Results of freshwater tests may not be relevant to marine SBF disposal.

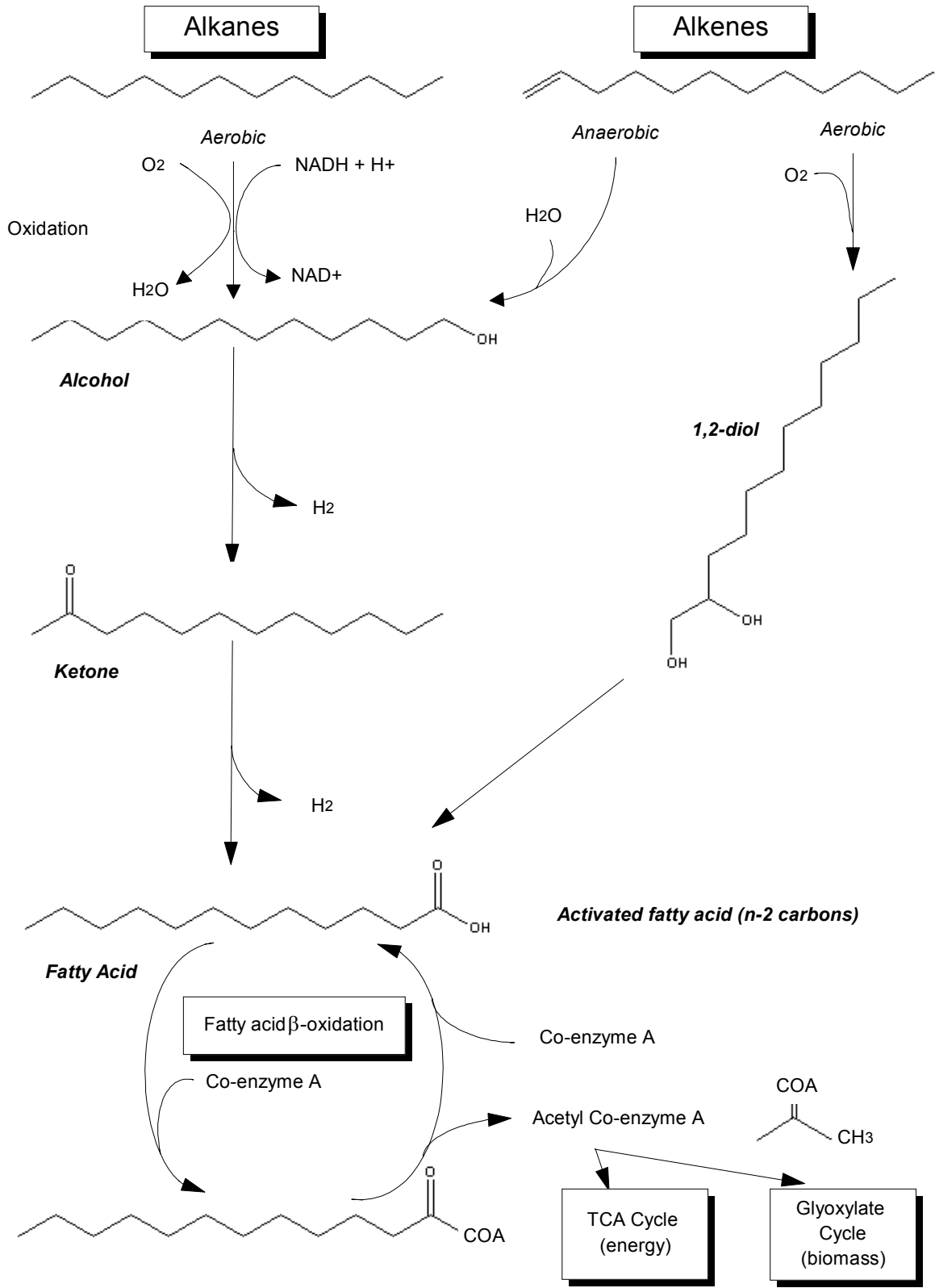


Figure 5. Biodegradation pathways of selected SBF base chemicals. From Getliff et al. (1997).

Several laboratory biodegradability tests have been proposed or used to estimate the rate of biodegradation of SBF base chemicals in marine sediments. Most are based on standard tests for water-soluble, non-volatile organic chemicals (OECD 1995). They lack environmental realism. Modifications to the tests have been developed to better measure the biodegradation of insoluble, solid materials, such as SBFs, or to measure anaerobic biodegradation. The different biodegradation tests can provide an initial evaluation of the potential biodegradability of a chemical in marine sediments.

To our knowledge, laboratory biodegradation tests have not been applied to whole used SBF cuttings, the material discharged to the ocean. It is quite likely that if intact, used SBFs on cuttings will degrade at a different rate in ocean sediments than the SBF base chemical in a laboratory biodegradation test. Some ingredients of the SBF, such as emulsifier, may increase the effective SBF-water interface surface area in the drilling mud and thereby increase the bioavailability of the SBF base chemical to sediment and seawater bacteria. This would have the effect of increasing the biodegradation rate under both aerobic and anaerobic conditions.

McKee et al. (1995) performed anaerobic biodegradation tests with a laboratory formulated LAO SBF and the LAO alone. The SBF was an 11 lb/gal SBF with a synthetic/water ratio of 75/25. After 70 days of anaerobic incubation, the complete SBF had biodegraded by 53.1 percent, whereas the SBF base chemical had biodegraded by 41 percent. However, there was no difference in the degradation rates of a LAO base chemical and a LAO SBF in simulated seabed tests (Schaanning 1995a).

Laboratory biodegradation test methods include the following (Slater et al. 1995, Candler et al. 1999):

- **OECD 301 B** – The test substance is incubated in a freshwater nutrient medium with an inoculum of sewage sludge bacteria. Biodegradation is measured as the production of CO₂.
- **OECD 301 D** – The test substance is incubated in a completely full closed bottle with a freshwater nutrient medium and a bacterial inoculum. Biodegradation is measured as oxygen consumption.
- **OECD 306** – This is the seawater modification of the OECD 301 D closed bottle respirometric test. Natural seawater, containing a natural community of marine bacteria, is used without addition of sewage bacteria. Because no bacterial inoculum is used, results of the OECD 306 test can not be compared to those of the OECD 301 D test.
- **BODIS** – This test measures biochemical oxygen demand (BOD) of insoluble substances. It is similar to the OECD 301 D test, except that a headspace of air about 1/3 of the volume of the closed bottle is left. The freshwater suspension of SBF is spiked with nutrients and sludge bacteria, and the bottle is sealed and shaken to maintain oxygen saturation in the aqueous phase. Biodegradation is measured as oxygen consumption in the closed bottle system.
- **Marine BODIS** – This test is a modification of the freshwater BODIS test and the OECD 306 test. The SBF base chemical is incubated in a closed bottle 2/3 full of natural seawater containing indigenous bacteria and supplemented with primary nutrients. Biodegradation is measured as oxygen consumption.
- **ISO/DIS 11734** – This is an anaerobic biodegradation test that is performed in a closed bottle with an oxygen-free gas in the headspace. Anaerobic bacteria are provided in activated sewage sludge. Nutrients are dissolved in the freshwater medium. Biodegradation rate is measured as an increase in gas pressure in the headspace from methanogenic production of CO₂ and CH₄. A seawater variation of this test is being developed in which biodegradation by indigenous sulfate reducing bacteria is measured as the increase in the concentration of hydrogen sulfide in the bottle.

For all test protocols, the theoretical oxygen demand (ThOD) is estimated from the amount of carbon in the chemical being evaluated. The measured oxygen consumption (or CO₂ or H₂S production) is divided by the theoretical values to estimate percent degradation of the SBF chemical.

These methods give different and highly variable estimates of the biodegradation potential for SBF base chemicals. For example, Vik et al (1996b) report that some SBFs can be classified as ‘readily biodegradable’ (i.e. percent biodegradation >60) based on the BODIS freshwater test but have a low biodegradation rate in the marine BODIS test.

Steps are being taken to identify the most appropriate biodegradation test procedures. The Oslo and Paris Commission (OSPAR) commissioned several laboratories to compare the various available protocols and to develop a harmonized protocol for the North Sea countries. The study concluded that all methods tested yielded comparable results when testing an ester and an ether SBF (Elf Akuamiljo 1996). However, reproducibility of the methods was poor for the less biodegradable ether SBF.

A comparison of several biodegradation tests shows that they gave markedly different estimates of aerobic biodegradation for acetal SBF base chemical (Table 22). Measured biodegradation (usually in 28 days) varied with test method, water salinity, and concentration of acetal used. Estimated biodegradation ranged from 5 percent to 86 percent of the ThOD. The proposed acceptability criterion for biodegradation in North Sea countries is 60 percent of the ThOD; therefore, acetal passes some tests and not others.

Table 22. Aerobic biodegradation (percent of theoretical oxygen demand: ThOD) of acetal SBF base chemical in several biodegradation tests at several initial concentrations. Most tests were run for 28 days. From Slater et al. (1995).

| Test Method | Acetal Concentration (mg/L) | Percent Biodegradation |
|-----------------------|-----------------------------|------------------------|
| BODIS Freshwater | 10 | 86 |
| BODIS Freshwater | 40 | 50 |
| BODIS Seawater | 10 | 19.5 |
| BODIS Seawater | 40 | 8 |
| OECD 301 B Freshwater | 10 | 78.6 |
| OECD 301 B Freshwater | 20 | 62.8 |
| OECD 301 D Freshwater | 0.5 | 73 |
| OECD 301 D Freshwater | 2.5 | 21 |
| OECD 306 Seawater | 0.5 | 35 |
| OECD 306 Seawater | 2 – 2.5 | 5 |
| OECD 306 Seawater | 10 | 9.4 |

Freshwater tests consistently gave higher estimates of biodegradation than seawater tests did (Table 22). This may be an artifact of the protocols. In the freshwater tests, the incubation medium is dosed with an inoculum of activated sludge bacteria; in the marine tests, only bacteria indigenous to the natural sea water medium are included. The abundance of hydrocarbon-degrading bacteria and fungi is much higher in marine sediments than in sea water, so the seawater tests probably greatly underestimate the biodegradation potential SBF base chemicals in marine sediments.

Biodegradation rate decreased as acetal concentration in the tests was increased. Concentrations of base chemicals in SBF cuttings accumulations on the ocean floor usually are much higher than concentrations used in the tests, making interpretation of test results difficult. It is uncertain which test provides the most environmentally realistic results.

The results of biodegradability tests with several SBF base chemicals using several of the more common laboratory protocols are summarized in Table 23. The OECD 306 test (OECD 1995) currently is the standard test for OSPAR, and the BODIS test (ISO 1990), modified for seawater, is an accepted standard for the Norwegian State Pollution Authority. The results of these biodegradation tests indicate that aerobic and anaerobic biodegradation rates of synthetics occur in the following order: ester>LAO≈IO>PAO> acetal>ether.

Table 23. Biodegradation rate, measured as the percent reduction in concentration, of several SBF base chemicals based on different biodegradation test protocols. The duration of the ISO/DIS 11734 tests is included in parentheses.

| Test | Ester | LAO | IO | PAO | Ether | Acetal |
|---|-----------------------------------|----------------------|---|---|-------|--------|
| Anaerobic (freshwater) ISO/DIS 11734 | 83 (35d) 56 (56d) | 41 (70d) 53 (70d) | 47 (5d) 28 (56d) 55 (70d) 35 (120d) 38 (120d) | 0.6 (50d) 15 (50d) 14 (70d) 40 (140d) 46 (140d) | | |
| Aerobic (28d-Freshwater) OECD 301 D | 69 70 | 70 84 | 70 | 13 29 43 50 | | |
| Aerobic (28d-Marine) OECD 306 | 69 93 81 15 81 71* | | 76 72 68 68 | 55 52 47 1 52 | 6* | 14 |
| Marine BODIS | 55 96 66* | 66 | 80 | 44 70 | 5* | 14 |
| Marine CO ₂ Evolution | 66* | | | | 6* | 6* |
| Marine CO ₂ Headspace | 68* | | | | 5* | |

Sources: Baroid Drilling Fluids; McKee et al. 1995; Baker Hughes INTEQ; M-I Drilling Fluids; Zevallos et al. 1996; Slater et al. 1995; Steber et al. 1995; Vik et al 1996a; Elf Akuamiljo 1996

* Mean value.

As a general rule, SBF base chemicals are more biodegradable under aerobic than anaerobic conditions (Tables 23 and 24). The anaerobic test is a freshwater test and so results should be compared to those from a freshwater aerobic test. All the SBF base chemicals evaluated by Norman (1997) and Steber et al. (1994) have measurable aerobic and anaerobic biodegradability. Aerobic and anaerobic biodegradation rates are greatest for esters, followed by IOs. Mineral oils are less biodegradable than SBF base chemicals, particularly under anaerobic conditions.

Considering the high concentrations of SBFs measured in surficial sediments within 100 m of some offshore platforms discharging SBF cuttings (Table 17), it is probable that most SBF biodegradation will occur under anaerobic conditions after sediment oxygen concentration is reduced to low levels by the initial aerobic biodegradation of the SBF cuttings. In low energy environments where cuttings dispersion at the seafloor is a minor factor, anaerobic degradation of SBF cuttings probably is the rate-limiting step in recovery of benthic marine ecosystems contaminated with SBF cuttings. Although olefin and ester SBF base chemicals can be biodegraded anaerobically in the laboratory, degradation rates usually are much slower than aerobic degradation rates. Anaerobic biodegradation rates of SBF and OBM base chemicals and a few potential SBF base chemical degradation products range from essentially zero (alkylbenzene) to 83 percent in 35 days (ester) (Table 24).

Table 24. Anaerobic biodegradation rates of several SBF and OBF base chemicals and possible SBF degradation products as measured with the ISO/DIS 11734 anaerobic biodegradation test. Biodegradation is measured as net gas (CH₄ + CO₂) production. Values are means from five replicate tests for each chemical. From Steber et al. (1995).

| Test Chemical | Test Duration (Days) | Mean Degradation (±CI) (% of Organic Carbon) |
|--|----------------------|---|
| Fatty Acid Ester I | 35 | 82.5 ± 13.9 |
| Fatty Acid Ester II | 35 | 83.7 ± 13.1 |
| Linear- α -Olefin (C _{16/18}) | 84 | 22.4 ± 19.5 |
| Linear- α -Olefin (C ₁₄) | 98 | 48.3 ± 15.5 |
| Poly- α -Olefin I | 70 | 14.4 ± 20.3 |
| Poly- α -Olefin II | 50 | 0.6 ± 16.2 |
| Acetal | 70 | 12.6 ± 19.2 |
| Alkyl Benzene | 50 | - 1.5 ± 12.2 |
| Mineral Oil A | 35 | 3.9 ± 11.0 |
| Mineral Oil B | 28 | 5.4 ± 8.2 |
| Mineral Oil C | 28 | 5.8 ± 6.7 |
| Olelyl Alcohol | 84 | 88.6 ± 14.8 |
| 2-Ethyl Hexanol | 84 | 78.8 ± 21.4 |
| Dioctyl Ether | 42 | 12.3 ± 10.8 |
| Dihexadecyl Ether | 42 | 1.4 ± 12.5 |

Anaerobic biodegradation rate is highest for esters, followed by LAOs (Table 24). In general, SBF base chemicals, other than ester, do not biodegrade anaerobically at a substantially higher rate than mineral oils used in OBFs. Alkylbenzenes are not biodegraded under anaerobic conditions. Of the possible degradation products, alcohols are highly biodegradable, and ethers are resistant to anaerobic biodegradation. Biodegradation rate seems to be inversely related to molecular weight (directly related to aqueous solubility) of LAOs and PAOs. The C₁₄ LAO is more biodegradable than the C_{16/18} LAO. The aerobic biodegradability of PAOs decreases with increasing molecular weight (Friedheim and Pantermuehl 1993). Candler et al. (1999) ranked both aerobic and anaerobic biodegradability of drilling fluid base chemicals from most to least biodegradable as:

ester>>LAO>IO>>PAO>mineral oil.

In addition, the rate of anaerobic biodegradation of PAOs and possibly other sparingly soluble olefins tends to increase with incubation time. Mean percent degradation of different PAOs after 50, 70, and 133 days of anaerobic incubation are 0.6 percent, 14.4 percent, and 80 percent, respectively (Friedheim and Pantermuehl 1993; Steber et al. 1995). The anaerobic bacteria in the inoculum may require a long acclimation period before they can metabolize PAOs efficiently. The bacteria may also need to synthesize and secrete biosurfactants to solubilize the olefins so they can be biodegraded. Another possibility is that colonization by opportunistic species of olefin-degrading microbes is required before degradation rate can increase.

4.6 Solid Phase Biodegradation Tests

A solid phase biodegradation test was developed at the Scottish Office, Agriculture, Environment and Fisheries Department (SOAEFD) Marine Laboratory to evaluate and compare degradation rates of various SBFs and OBFs. The test was designed to simulate both aerobic and anaerobic conditions that are present in a cuttings pile on the sea floor. In the SOAEFD test, a base fluid is mixed with sieved marine sediment to produce concentrations of 100, 500 and 5,000 mg/kg base fluid in sediment. The exposure concentrations are intended to resemble measured

concentrations of OBF base mineral oils in sediment samples collected 1,000-3,000 m, 200-1,000 m, and 200 m, respectively from a platform discharging OBF cuttings. The test chambers are maintained in a flowing seawater trough for 120 days. The chambers are sampled for chemical analysis after 0, 28, 56, and 120 days. The base chemical is measured in the sediment samples by gas chromatography. Degradation rates and degradation half times are estimated. The test provides a measure of the loss of base fluids from all mechanisms, not just biodegradation. Reference tests may be performed with mineral oil (poorly biodegradable) and a vegetable oil (e.g., olive oil: readily biodegradable).

There is a large difference in the degradation rates among the various SBF base chemicals (Figure 6) (Munro et al. 1997a). The ester had the highest degradation rate followed by the LAO. The IO and paraffin were comparable to the mineral oil at 5,000 ppm, but degraded faster than the mineral oil at the lower concentrations. Degradation rates of the PAO and acetal were similar to the mineral oil, though the mineral oil appeared to degrade somewhat faster at the 100 ppm concentration.

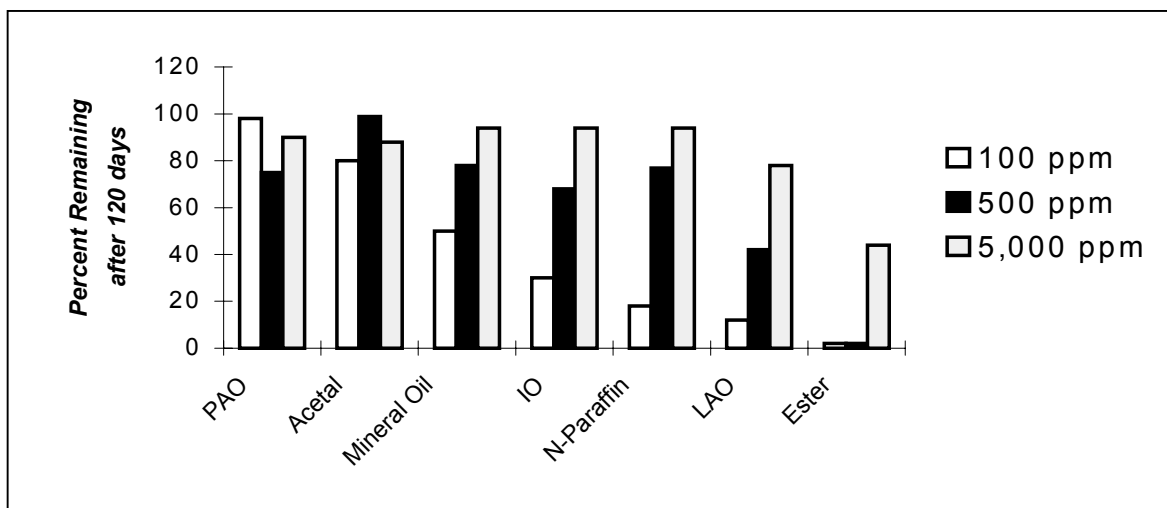


Figure 6. Biodegradation of SBFs in SOAEFD Tests after 120 days. From Munro et al. (1997a).

Sediment characteristics influence the rate of biodegradation of SBF base chemicals. The half-life of an ester was 10.2 days in mud sediments, compared to 37.3 days in sand sediments (Stagg et al. 1996). Fine-grained sediments are more likely than sandy sediments to contain a larger, more diverse bacterial community. In the solid phase biodegradation system, fine sand sediments become anaerobic more rapidly than mud and mud/sand sediments (Munro et al. 1997b, 1998b; Moffat et al. 1998). Below the upper 5 mm of sediment in the test chambers, redox potential declines to below 0 mV within about 14 days in the presence of 500 mg/kg olive oil, ester, or LAO.

The SOAEFD test was designed to reflect environmental conditions better than existing laboratory biodegradation tests. Because it measures disappearance of base fluid rather than actual biodegradation, the SOAEFD solid-phase test overestimates biodegradation. On the other hand, even this test probably underestimates disappearance rates that would occur in the field. Other important factors, such as high seabed currents, bed transport, and bioturbation, are not considered. A modified version of the SOAEFD solid-phase test was used to examine the degradation of an ester and an IO under estuarine conditions similar to those encountered in nearshore waters of Nigeria (Munro et al. 1997b). The sediment was coarse silt from an estuarine environment. Brackish water at 25°C was recirculated through the test chambers. Olive oil was used as a positive biodegradable control and some sediments were poisoned with phylatol as abiotic controls. The test chambers contained 120 mg/kg of test material. In 28 days, there was a loss of 40.5 to more than 96.6 percent of the SBF base material or olive oil from the chambers (Table 25). Estimated half-lives ranged from 2.7 to 57.3 days. The olive oil and the ester were both lost at about 25°C.

Ester degradation was about twice as fast at 25°C as at 12°C. IOs were lost more slowly than esters, but loss rates (biodegradation plus washout) were high (91 to 94 percent after 35 days). IO loss from poisoned chambers was much slower than from non-poisoned chambers, showing that most of the loss from the non-poisoned chambers was

by biodegradation. The differences were small for esters, suggesting either that loss of ester from sediments was from dissolution (esters are more water-soluble than other SBF base chemicals) or chemical (abiotic) hydrolysis). Concentrations of 2-ethylhexanol, a degradation product of ester, were highest in the water of ester chambers that were poisoned and lowest in unpoisoned chambers maintained at 25°C. This suggests either that the ester bond is easily hydrolyzed abiotically, or that biocide-resistant bacteria in the sediments were hydrolyzing the esters and bacteria were biodegrading the alcohol in the water. Abiotic degradation probably is not as important as biodegradation in removing esters from sediments.

Munro et al. (1998a) also evaluated other factors affecting the biodegradation rate of ester SBF base chemicals in sediments. The SOAEFD protocol was used to examine ester biodegradation over 245 days at initial concentrations of 15,000 and 50,000 mg/kg and degradation rate during 120 days at temperatures between -1 and 20°C.

Table 25. Rates of loss (biodegradation plus washout) of ester and IO SBF base chemicals in a modified SOAEFD solid phase test. Percent loss in 28 days and half-life (days) are given. From Munro et al. (1997c).

| Test Chemical | Percent Loss in 28 Days | Half-Life (days) |
|--------------------------|-------------------------|------------------|
| Olive Oil | 100 | 2.7 |
| Ester (25°C) | 99.6 | 2.8 |
| Ester (12°C) | 93.2 | 4.4 |
| Internal Olefin (1) | 90.3 | 8.1 |
| Internal Olefin (2) | 88.4 | 9.2 |
| Poisoned Ester | 84.3 | 12.8 |
| Poisoned Internal Olefin | 40.5 | 57.3 |

At 120 days, percent loss of ester from test chambers was inversely related to initial nominal concentration of ester. Percent degradation in 201 days decreased from 98 percent at 100 mg/kg, to 10 percent at 50,000 mg/kg (Table 26). After 245 days, ester loss was 31 percent at a nominal concentration of 15,000 mg/kg ester and 20 percent at 50,000 mg/kg ester. A poisoned 50,000 mg/kg ester treatment lost only 4 percent of the ester in 245 days. Half-lives of ester in sediments ranged from 11 days (100 mg/kg ester) to 495 days (50,000 mg/kg ester). The half-life for the 500,000 mg/kg treatment was 391 days when estimated by a zero order kinetic model. These results strongly suggest that the main pathway of ester degradation is by sediment microbiota.

Table 26. Percent degradation after 120 days and half life (days) of ester SBF base chemical determined with the SOAEFD solid phase biodegradation test at ambient seawater temperatures (6 to 16°C). Estimated half-lives are based on first order reaction kinetics. From Munro et al. (1998a).

| Initial Ester Concentration (mg/kg) | Percent Degradation at 120 Days | Half Life in Sediments (days) |
|-------------------------------------|---------------------------------|-------------------------------|
| 100 | 98 | 11 |
| 500 | 98 | 21 |
| 5,000 | 56 | 99 |
| 15,000 | 29 | 198 |
| 50,000 | 10 | 495 |

There was a strong link between the rate of degradation and temperature. The half-life of the ester, at an initial concentration of 500 mg/kg, decreased from 136 days at -1°C to 16 days at 20°C (Table 27). Percent of ester lost after 120 days increased from 66 percent at -1°C to 99 percent at 20°C . Ester degraded much more slowly at an initial nominal concentration of 5000 mg/kg than at an initial concentration of 500 mg/kg. At an initial concentration of 5,000 mg/kg, degradation at 120 days increased from 18 percent at 4°C to 54 percent at 20°C , and half-life decreased from 385 days to 112 days. Mineral oil at an initial concentration of 500 mg/kg showed only minimal degradation at 2°C and 40 percent degradation at 20°C after 120 days.

Table 27. Percent degradation after 120 days and half life (days) of ester SBF base chemical at different temperatures determined with the SOAEFD solid phase biodegradation test. From Munro et al. (1998a).

| Substrate and Temperature | Percent Degradation at 120 Days | Half Life in Sediments (days) |
|--|---------------------------------|-------------------------------|
| Ester -1°C | 66 | 75 |
| Ester 2°C | 73 | 64 |
| Ester 4°C | 71 | 67 |
| Ester 12°C | 98 | 22 |
| Ester 20°C | 99 | 16 |
| 5,000 mg/kg Ester 4°C | 18 | 385 |
| 5,000 mg/kg Ester 20°C | 54 | 112 |
| Mineral Oil 2°C | 6.5 | Regression Insignificant |
| Mineral Oil 20°C | 40 | 136 |

4.7 Simulated Seabed Studies

Simulated seabed studies are required for the introduction and use of all new drilling fluids in Norway (Vik et al. 1996a). These studies have been performed by the Norwegian Institute of Water Research (NIVA). The NIVA simulated seabed chambers are intended to more accurately simulate offshore conditions for biodegradation than the standard laboratory and solid phase tests. Groups of exposure chambers are filled with 25 cm of homogenized intertidal marine sediment from outer Oslofjord. The natural benthic fauna and flora are not removed. Homogenization may destroy some of the fauna, so recent tests have been performed with intact sediments cores that are placed in the chambers with minimal disturbance. The sediments in the chambers are covered with a 15-cm layer of natural seawater from Oslofjord. At the initiation of the test, cuttings from an offshore platform are diluted with clean sediment and layered on the sediment in the chambers; the usual depth of cuttings is 1 to 2 mm.

Concentrations are measured as mg SBF/cm² of sediment in the chamber. Tests are run for up to 160 days. At different times during and at the end of the test, chambers are sampled for SBF, barite, and benthic fauna. Barite is used as a conservative marker of the SBF cuttings. The amount of SBF washout from the chambers can be estimated by normalizing SBF concentrations to barite concentrations. Each study compares several types of SBF cuttings. There may be some limitations on comparisons among studies due to minor adjustments in procedures or possibly as a result of seasonal variation in the benthic fauna present.

The organic phase of the different mud cuttings samples disappeared through biodegradation, washout, and bioturbation from the chambers at different rates (Table 28). Ester SBF cuttings degraded most rapidly, followed by LAO and IO SBF cuttings. The lowest losses were for mineral oil and PAO cuttings. The ester was completely degraded at the end of the experiment, and there was a white mat of sulfate reducing bacteria on the surface of the sediment, indicating anaerobic conditions. Sediments in the other exposures did not become anaerobic during the tests.

Table 28. Summary of results of five NIVA simulated seabed SBF biodegradation studies. Test substances were SBF or mineral oil cuttings from offshore platforms. Biodegradation is expressed as percent disappearance from test chambers after 28 and 160 days. Regression analysis of loss-rate data were used to estimate the half-lives (days) of SBFs in marine sediments. From Vik et al. (1996a,b).

| Mud/Cuttings Tested | Biodegradation (Disappearance) % | | Mean Half-Life $t_{1/2}$ (Days) |
|---------------------|----------------------------------|----------------|------------------------------------|
| | After 28 Days | After 160 Days | |
| Ester | 46 | 97 | 24 |
| LAO | 38 | 38 | 54 |
| IO | 17 | 66 | 104 |
| Acetal | 12 | 39 | 200 |
| PAO | 11 | 43 | 207 |
| Mineral Oil | 23 | 44 | 311 |

Mean estimated half lives for the organic phase of SBF cuttings ranged in different tests and for different SBF base chemicals from 24 days to 311 days (Table 28; Figure 7). Estimated half-lives for mineral oil were highly variable, possibly because of heterogeneous distribution of the hydrocarbon mixture in sediments. Based on estimated half-lives, degradation rate can be ranked from highest to lowest as:

ester>LAO>IO>acetal≈PAO≈mineral oil.

Overall, the SOAEFD and NIVA tests gave roughly equivalent results.

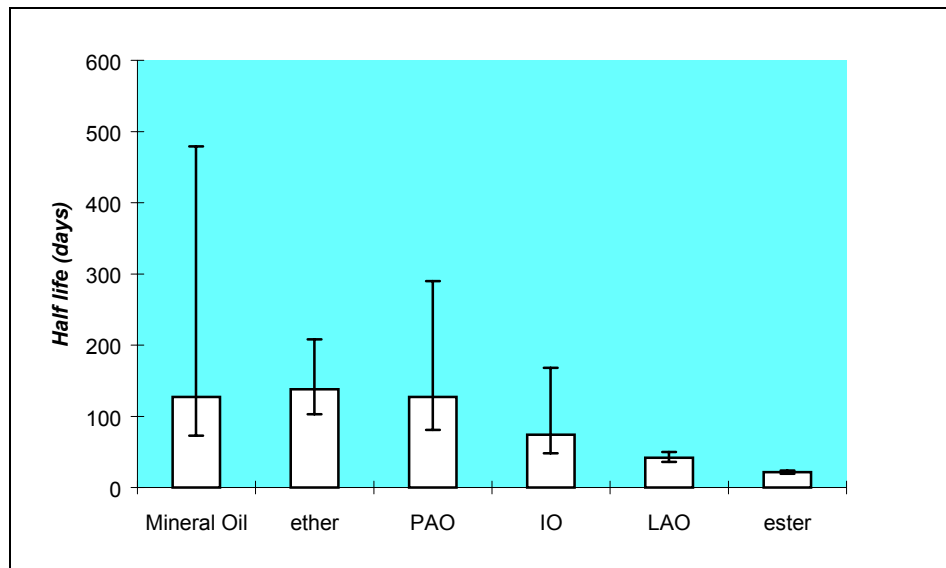


Figure 7. Half-life of various SBFs in NIVA simulated seabed studies. Bars denote confidence limits.

Schaanning et al. (1996) obtained similar results when intact sediment cores rather than homogenized sediments were used in the chambers. Sediment cores were collected from 200 m in Oslofjord and had intact benthic communities. Chambers were incubated for up to 187 days. SBF/barium normalization was used to estimate the

fraction of SBF loss from chambers that was caused by biodegradation. In this system, ester and mineral oil biodegraded more quickly, and LAO degraded more slowly than in the homogenized sediment chambers (Table 29). However, the differences were small, suggesting that the benthic fauna (some of which are lost during homogenization) play only a minor role in biodegrading SBF cuttings. The two esters degraded at slightly different rates. The more degradable Anco Green is a mixture of isopropyl esters of saturated and unsaturated fatty acids in the C₁₄ to C₂₀ range. Petrofree was a mixture of five homologous fatty acid esters based on 2-ethylhexyl dodecanoate. Some petrofree formulations may contain other SBF base chemicals such as LAO or PAO.

Table 29. Average half-lives of SBF cuttings in simulated seabed chambers containing intact sediments and benthic communities during a 187-day incubation. Biodegradation rate was estimated from SBF/barium concentration ratios. From Schaanning et al. (1996).

| Drilling Mud/Cuttings | Half-Life for Loss (days) | |
|-----------------------|---------------------------|----------------|
| | Total Loss | Biodegradation |
| Ester (Anco Green) | 16.6 | 17.9 |
| Ester (Petrofree) | 22.2 | 22.0 |
| LAO | 51.2 | 55.9 |
| IO | 73.7 | 104.0 |
| Mineral Oil | 105.0 | 158.0 |

Part of the variation in the results of the NIVA simulated seabed studies is the effect of SBF concentration on biodegradation rate, as has been observed for other biodegradation test methods. Degradation rate decreases as the concentration of SBF added to the sediments in the test chambers increases (Table 30).

Table 30. Effect of SBF concentration in NIVA simulated seabed biodegradation test chambers on the half-life of the synthetic base chemical. From Schaanning et al. (1996).

| SBF Base Chemical | Concentration (mg/cm ²) | Half-Life (days) |
|-------------------|-------------------------------------|------------------|
| Ester | 2.4 – 4.2 | 21.4 |
| | 13.1 – 18.5 | 83.0 |
| PAO | 4.3 | 127.0 |
| | 6.5 – 9.9 | 207.0 |

The ether SBF and mineral oil OBF (Figure 7) had a lag phase of approximately 60 days before degradation began (Schaanning 1996). A similar lag in the start of biodegradation was identified during the OSPAR Ring Test Studies for all methods used (Elf Akuamiljo 1996). During the lag period, the sediment bacterial community may be changing to include more hydrocarbon-degraders and the hydrocarbon degraders may be adapting to metabolizing the SBF base chemicals (Atlas 1995).

In some of the simulated seabed studies, effects of thin layers of SBF cuttings on the benthic fauna in the test chambers were examined (Schaanning et al., 1996). Fauna were enumerated at the beginning and end of the tests. Two ester SBFs had the greatest impacts on the benthic fauna in the chambers (Table 31). Exposure to a thin layer of ester II (Petrofree) resulted in a substantial decrease in the number of species and individuals in the chambers and low diversity indices. Mineral oil was less harmful than ester II to the benthic fauna; Ester I (Anco Green) and IO were essentially without effects on the benthic fauna in the exposure chambers and effects of LAO were minor.

Table 31. Effects of SBF cuttings layered (1.4 to 1.8 mm) on natural sediments in NIVA simulated seabed chambers on characteristics of benthic communities after 187 days. From Schaanning et al. (1996).

| SBF Cuttings | No. Species | No. Individuals | Diversity (H) | Diversity (ES ₁₀₀) |
|--------------|-------------|-----------------|---------------|--------------------------------|
| Control | 36 – 39 | 281 – 856 | 2.97 – 3.65 | 17.74 – 22.94 |
| Ester I | 14 – 35 | 283 – 809 | 2.20 – 2.31 | 11.12 – 13.66 |
| Ester II | 4 – 6 | 32 – 83 | 0.87 – 1.90 | --- |
| IO | 30 – 36 | 588 – 647 | 2.70 – 3.33 | 13.89 – 19.71 |
| LAO | 22 – 26 | 308 – 338 | 2.88 – 3.16 | 14.33 – 16.44 |
| Mineral Oil | 18 – 20 | 226 – 309 | 2.51 | 13.18 – 13.65 |

The harmful effects of the SBF cuttings on benthic fauna, as measured by diversity indices, were correlated to sediment redox potential (Eh), an indication of oxygen availability in sediments (Figure 8). Sediments with an Eh approaching 0 mV are hypoxic. The lowest Eh values were produced by the esters that are highly biodegradable. The other SBF base chemicals and mineral oil biodegrade slowly and did not markedly decrease sediment Eh.

Organic enrichment of sediments often produces a reduction in the number of species and a marked increase in the abundance of a few stress-tolerant species (Pearson and Rosenberg 1978). This was observed in the NIVA simulated seabed chambers dosed with ester SBF cuttings. In the Petrofree chambers, most species of benthic fauna were eliminated or their numbers were greatly reduced compared to controls. The abundance of a pollution-tolerant polychaete increased. It represented more than half the individuals in the Petrofree chambers. Several of the species that disappeared from the sediments are known to be intolerant of low oxygen concentrations in sediment pore water.

There were changes in the activity of oxidative enzymes (glutathione reductase and catalase) in the tissues of polychaete worms *Hediste (Nereis) diversicolor* following exposure to SBF cuttings (Schaanning et al. 1996). The enzyme activity responses indicated that the worms exposed to Anco Green (ester), LAO, and IO cuttings were experiencing oxidative stress, probably resulting from a decrease in oxygen concentration in the sediments. The worms did not survive exposure to Petrofree (ester). Benthic invertebrates in the NIVA chambers were adversely affected by a reduction in sediment oxygen concentration caused by organic loading of the sediments with SBF base chemicals, not by the toxicity of the chemicals.

The NIVA chambers also were used to evaluate the effect of temperature on biodegradation rate of ester and LAO cuttings (Schaanning et al. 1997). Chambers contained sediment from northern Norway (water temperature – 1.35°C) and from Oslofjord (water temperature 6 to 8°C) and were maintained at –0.5°C and 7°C, respectively, for the 89-day duration of the exposure.

The small temperature difference had little effect on the biodegradation rate of ester and LAO cuttings (Table 32). Biodegradation rate was slightly lower in arctic than in the warmer-water sediments. Biodegradation rate decreased as the concentration of ester or LAO layered on the sediment increased. The effect of SBF concentration was greatest for the ester in the cold-water chambers.

Average oxygen consumption (an indication of microbial biodegradation) of the sediments was similar in all treatments. Cumulative oxygen consumption was higher in the Oslofjord than in the Porsangen sediments. However, oxygen consumption in the arctic chambers initially was lower than that in the Oslofjord chambers. Oxygen consumption increased with time in the arctic chambers, but remained relatively constant in the Oslofjord chambers. This result suggests that the microbial community in the arctic chambers required a period of acclimation before they could degrade the SBF base chemicals. Redox potential decreased in all chambers, indicating a depletion of oxygen. The lowest Eh was 0 in Oslofjord sediments treated with ester. The decline in redox potential was greater for ester treatments than for LAO treatments but temperature effects were minimal.

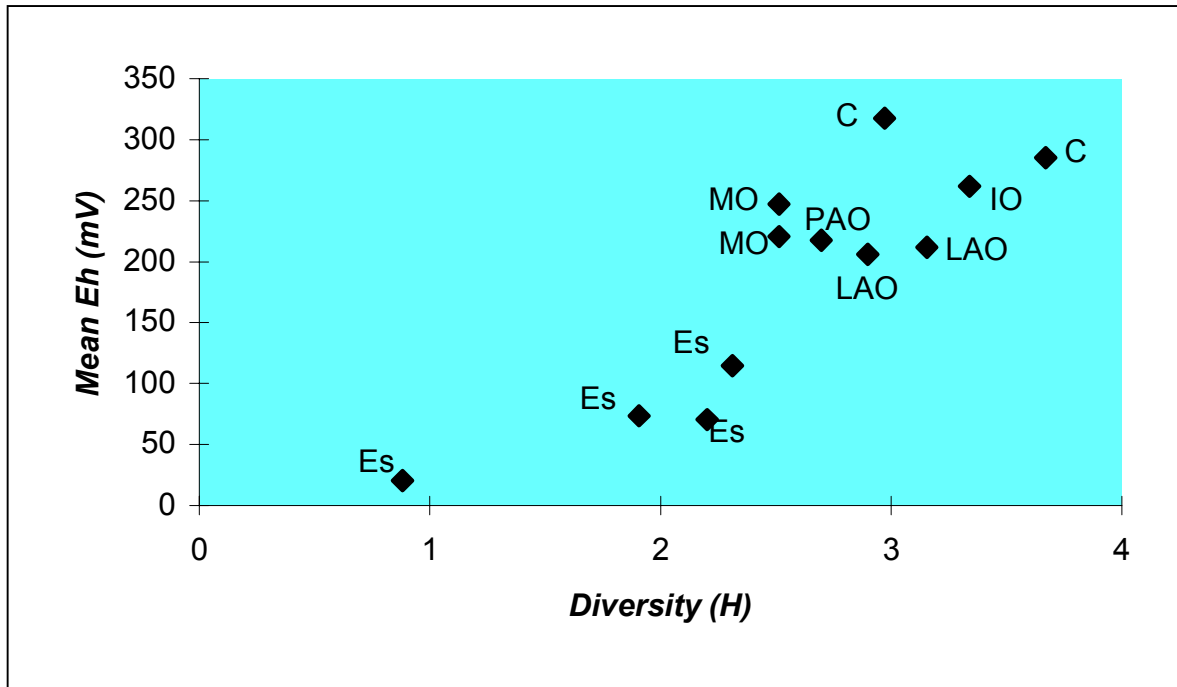


Figure 8. Relationship between redox potential and diversity for NIVA seabed simulation studies (C=control, MO=mineral oil, Es=ester, PAO, IO, LAO = olefins). From Schaanning et al. (1996)

Table 32. Effect of incubation temperature on the biodegradation of ester and LAO cuttings in sediments from northern (-0.5°C) and southern (6-8°C) Norway. Percent biodegradation is based on the SBF/barium ratio. From Schaanning et al. (1997).

| Location | SBF Cuttings | Dose (mg/cm ²) | % Biodegradation | Half-Life (Days) |
|--------------------|--------------|----------------------------|------------------|------------------|
| Oslofjord (6-8°C) | Ester | 0.5 | 99 | --- |
| | | 5.0 | 61 | 57 |
| | | 20.0 | 26 | 198 |
| | LAO | 0.5 | 100 | --- |
| | | 5.0 | 56 | 65 |
| | | 20.0 | 26 | 206 |
| Porsangen (-0.5°C) | Ester | 0.5 | 92 | --- |
| | | 5.0 | 59 | 58 |
| | | 20.0 | 16 | 340 |
| | LAO | 0.5 | 75 | --- |
| | | 5.0 | 40 | 92 |
| | | 20.0 | 26 | 205 |

Benthic fauna were more abundant and diverse in Oslofjord sediments than in Porsangen sediments. However, number of species, number of individuals, and species diversity did not vary much with SBF type and exposure

concentration, indicating that the differences observed were characteristic of the arctic and temporal benthic communities. This study shows that temperature has little effect on the rate of biodegradation and biological effects of ester and LAO cuttings in sediments. Biodegradation occurred even at -0.5°C . The temperature of bottom water in the deep waters (~ 1000 m) of the northern Gulf of Mexico remain at about 5°C year-round. Thus, the results of the NIVA studies are relevant to conditions in deep waters of the Gulf of Mexico. As discussed previously, SBF base chemical concentrations in surface sediments near offshore discharges quite frequently are much higher initially than 20 mg/cm^2 , the highest concentration used in the NIVA tests, especially within about 200 m of the discharge. Degradation rates in heavily contaminated surface sediments are likely to be substantially slower than those estimated in NIVA tests.

5.0 BIOAVAILABILITY AND TOXICITY OF SBF CUTTINGS

Environmental impacts that may result from the discharge of drilling fluids and cuttings to the ocean are of two types: effects on water-column (pelagic) ecosystems; and effects on sea-bottom (benthic) ecosystems (National Research Council 1983; Neff 1987; Hinwood et al. 1994). Following discharge to the ocean, WBFs and WBF cuttings mix with and disperse in the ambient seawater. The large individual cuttings particles sink rapidly to the seafloor. The WBF plume, containing the clay sized particles, entrains seawater as it descends and eventually reaches the seafloor or becomes neutrally buoyant (Brandsma et al. 1980; Brandsma and Sauer 1983). The salts in seawater cause clay particles to flocculate as the mud dilutes. Some of the larger flocculated mud particles may settle near the well site; however, except in relatively shallow waters, most of the mud particles disperse over a wide area and accumulate in sediments at low concentrations.

On the other hand, OBF and SBF cuttings are “oil wet” and so do not mix efficiently with the receiving waters (Growcock et al. 1994; Getliff et al. 1997). They tend to clump, with the large clumps settling quickly to the bottom. The tendency for cuttings to clump increases as the concentration of SBF on the cuttings increases. The average concentration of SBF base chemical on SBF cuttings discharged to the Gulf of Mexico is about 10 percent. Cuttings containing this concentration of adhering SBF will clump and sink rapidly to the bottom. Cuttings containing 5 percent LAO do not clump. They are likely to disperse readily in the water column over a large area and not form a cuttings pile on the sea floor (Getliff et al. 1997).

Because of the differences in behavior of WBF and SBF cuttings, water column organisms are likely to be exposed to drilling mud components near platforms discharging WBF and WBF cuttings. Water column exposure will be minimal near platforms discharging OBF or SBF cuttings. Concentrations of WBF cuttings are likely to be lower than those of SBF cuttings in sediments within about 100 m of the cuttings discharge. Pelagic and benthic organisms may be affected by WBF discharges, but only benthic organisms are likely to be affected by SBF cuttings discharges.

Many studies of environmental impacts of WBF discharges have shown that mud toxicity to water column organisms is low, unless the mud contains high concentrations of diesel (added to WBF for lubricity) or hexavalent chromium (added to temperature stabilize chrome lignosulfonate) (Neff 1987; Hinwood et al. 1994). No adverse effects have been documented or are expected in pelagic organisms exposed in open waters of the outer continental shelf and slope to discharged WBF and WBF cuttings (National Research Council 1983).

The effects of SBF cuttings on pelagic organisms are expected to be even less than those of WBFs because of the low toxicity of SBFs (similar to or lower than the toxicity of WBFs; see below) and the reduced exposure time due to rapid settling of SBF cuttings clumps and particles out of the water column. Brandsma (1996) used model results and toxicity data to show that acute toxic effects in the water column are unlikely, even with OBFs.

Biological effects of SBF cuttings on the benthos are expected to be similar to or greater than those of WBFs and WBF cuttings. The mass of SBF discharged to the ocean per well is much less than the mass of WBF discharged per well, because the drilling fluid itself is not discharged and cuttings are cleaned before discharge (Veil and Daly 1999). The toxicity of WBFs and SBFs is low enough that they probably represent only a small direct toxic threat to marine organism living on or in sediments near the platform. However, SBF cuttings may harm benthic communities by production of anoxia in sediments through microbial biodegradation if SBF cuttings concentrations

in sediments are high enough (Olsgard and Gray 1995). WBFs and WBF cuttings do not usually cause sediment anoxia because they contain only low concentrations of biodegradable organic chemicals. However, they may harm benthic communities by burial and smothering, or they may alter sediment texture, rendering the local benthic environment less suitable for some species of benthic fauna and better for others (Neff 1987). Thus, biological effects of SBF cuttings discharges are likely to be greater than effects of WBF and WBF cuttings discharges in the immediate vicinity (within 50 to 100 m) of platforms where SBF cuttings are likely to accumulate to high concentrations.

5.1 Toxicity Tests

In many countries that are developing offshore oil and gas resources, discharge permits require performance of toxicity tests with drilling fluid ingredients and whole drilling fluids (Jones et al. 1996). North Sea countries usually require toxicity testing of individual drilling fluid ingredients; the EPA requires testing of whole drilling fluids. Two types of toxicity tests may be performed: water column tests and solid-phase (sediment) tests. They are intended to assess the potential risks from drilling fluid discharges to pelagic and benthic organisms, respectively.

Historically, the EPA has required performance of a water column test with the SPP of WBF and mysids *Americamysis (Mysidopsis) bahia*, small shrimp-like crustaceans (EPA 1999a,b). The median lethal concentration at 96 hours (96h LC₅₀) of the WBF must be equal to or greater than 30,000 mg/L (3% by volume) of the SPP, or the WBF is not permitted for ocean disposal.

EPA has determined that water column toxicity of SBF cuttings is likely to be low, for the reasons discussed above, and has proposed a solid-phase test to evaluate the potential environmental impacts of SBF cuttings discharges. In the solid-phase test under consideration, survival of benthic amphipods *Leptocheirus plumulosus* is measured during a 10-day exposure to sediments containing an SBF base chemical or SBF cuttings (ASTM, 1992). The median lethal concentration of SBF base chemical in sediment should be greater than 2,600 mg/kg dry wt, the LC₅₀ to *L. plumulosus* of a C_{16/18} IO base chemical.

In North Sea countries, toxicity tests are required for unused SBF base chemicals (Norwegian Oil Industry Association, 1996). Information about the UK offshore chemicals notification scheme and hazard ratings for several drilling and production chemicals used on the UK continental shelf can be found on the internet at <http://www.cefas.co.uk/OCNS/frame.HTM>.

The recommended test organisms include a microalga, a copepod, a bivalve mollusk, and a benthic amphipod (Table 33). The toxicity tests with the first two marine organisms are water column tests; the last two are solid phase tests. The tests are performed according to standard toxicity test protocols (McKee et al. 1995). Acceptance criteria vary from 20 mg/kg to 1000 mg/kg or mg/L for the different tests.

Table 33. Toxicity test requirements for SBFs in North Sea countries. From Norwegian Oil Industry Association (1996).

| Taxon | Species | Lowest Acceptable EC ₅₀ /LC ₅₀ |
|------------------|-----------------------------|--|
| Microscopic Alga | <i>Skeletonema costatum</i> | EC ₅₀ >1000 mg/L |
| Copepod | <i>Acartia tonsa</i> | LC ₅₀ >2000 mg/L |
| Bivalve Mollusk | <i>Abra alba</i> | EC ₅₀ >20 mg/kg |
| Amphipod | <i>Corophium volutator</i> | LC ₅₀ >1000 mg/kg |

EC₅₀ The concentration producing a defined sublethal effect in 50 percent of the exposed population.

LD₅₀ The concentration producing 50 percent mortality in the exposed population.

5.2 Water Column Tests

In the water column toxicity test used in the U.S., mysids are exposed to several dilutions of the SPP of a WBF (EPA, 1999). The SPP is prepared by mixing one part drilling fluid with nine parts seawater and allowing the phases to separate for a short period of time. The aqueous phase is collected for use in the bioassay. Mysids (*Americamysis (Mysidopsis) bahia*) are considered among the most sensitive marine animals to a wide variety of chemical contaminants (Suter and Rosen 1988). They are widely used for effluent testing in the U.S. The median lethal concentration at 96 hours (96h LC₅₀) of the SPP of different SBFs to mysids ranges from about 200,000 mg/L to 1,000,000 mg/L SPP (Table 34).

Table 34. The 96-hour median lethal concentration (LC₅₀) of the suspended particulate phase (SPP) of several SBFs to mysids (*Americamysis (Mysidopsis) bahia*). A LC₅₀ for a low toxicity oil based mud is included for comparison. Toxicity concentrations are mg/L (ppm) SPP.

| SBF Base Fluid | LC ₅₀ (mg/L) | Reference |
|----------------------------|-------------------------|---|
| Ester | 1,000,000 | Baroid Drilling Fluids (unpublished) |
| Linear- α -Olefin | 794,450 | McKee et al. 1995 |
| Internal Olefin | 56,500 – 1,000,000 | Baker Hughes-INTEQ (unpublished), MI Drilling Fluids (unpublished) |
| Poly- α -Olefin | 209,316 – 1,000,000 | MI Drilling Fluids (unpublished), Friedheim et al. 1991 |
| Low Toxicity Oil Based Mud | 13,200 | Friedheim et al. 1991 |

Because the SPP represents a one to nine dilution of the drilling fluid, SPP toxicity values should be divided by 10 to obtain a toxicity value for the whole-mud dissolved/suspended particulate fraction. All the SBFs tested passed the mysid acute toxicity test. The low toxicity oil based mud did not pass the test. The acceptance criterion is LC₅₀>30,000 mg/L SPP.

Several SBF base chemicals or chemical precursors also have been tested in the mysid SPP water column test (Table 35). In most cases, the toxicity of SBF base chemicals and precursors decreases (LC₅₀ increases) as molecular weight of the chemical increases. This undoubtedly is because as molecular weight increases, the aqueous solubility and bioavailability of most organic chemicals decreases. Most of the SBF base fluids or precursors pass the SPP toxicity criterion of 30,000 mg/L. Low molecular weight olefins (e.g., polypropene (MW 170) and C₁₄ – C₁₆ IO in Table 35) do not pass. However, when these base fluids are combined with other ingredients into an SBF, the SBF itself passes (Table 34).

Of the major SBF precursors, low molecular weight alcohols are the most toxic to mysids. During drilling, a small amount of the esters in an ester SBF may hydrolyze, releasing free alcohols and fatty acids. During cuttings discharge, if low molecular weight alcohols are present in the associated SBF, they could partition into the water as the SBF cuttings settle through the water column. However, duration of exposure of water column organisms to potentially toxic concentrations of alcohols is not likely to be great enough to elicit toxic responses.

Growth rate of estuarine minnows *Fundulus grandis* was not affected by exposure for 30 days to a suspension of 1 percent, 5 percent and 8.4 percent PAO on cuttings in a flow-through toxicity test system (Jones et al. 1991). A

low aromatic mineral oil base mixture on cuttings also did not adversely affect growth of the fish. Chronic exposure to synthetic-wet and oil-wet cuttings suspensions did not harm this marine fish.

Table 35. Acute toxicity to mysids *Americamysis (Mysidopsis) bahia* of the SPP of several SBF base chemicals or chemical intermediates. Median lethal concentrations are mg/L SPP. From Patel (1998).

| SBF Base Chemical Type | Chemical | 96h LC ₅₀ (mg/L) |
|------------------------|--|-----------------------------|
| Poly- α -Olefin | Polypropene (MW 170) | 10,800 |
| | Polypropene (MW 198) | 30,000 |
| | Decene Dimer (MW 290) | 574,330 |
| | Polypropene (MW 310) | 914,650 |
| | Polybutene (MW 320) | >1,000,000 |
| | Polypropene (MW 400) | >1,000,000 |
| Internal Olefin | C ₁₄ – C ₁₆ IO | <30,000 |
| | C ₁₅ – C ₁₈ IO | 119,658 |
| | C ₁₆ – C ₁₈ IO | 321,000 |
| Ether | Dibutyl Ether | >10,000 |
| | Dihexyl Ether | 61,659 |
| | Dioctyl Ether | 156,880 |
| Esters | Methyl Laurate | <10,000 |
| | Isopropyl Palmitate | 271,701 |
| | Isopropyl Oleate | 52,319 |
| | C ₁₀ – C ₁₄ Alcohols | <10,000 |
| | C ₁₆ Alcohol | 30,158 |

Suspensions of SBF base chemicals or unused mud also are not very toxic to the water column organisms used for toxicity testing in the North Sea countries (Table 36). The exposure medium for these tests is prepared by mixing the SBF base chemical or unused mud with seawater for 16 hours and allowing the phases to separate for 4 hours. The test medium contains dissolved and finely dispersed components of the SBF base chemical or mud. Because SBFs and mud systems prepared with them have low aqueous solubilities, these water column preparations are not toxic to marine plants and animals. Acutely toxic concentrations range from 2,000 mg/L to greater than 100,000 mg/L, compared to acceptance criteria of 1,000 to 2,000 mg/L (Table 33). The alga is more sensitive to the SBF base chemicals than to the whole unused muds; the copepod is insensitive to both. This is not always the case. The acute toxicities of a C₁₆/C₁₈ IO base fluid and a complete IO SBF to the alga *Isochrysis* sp. are 16,700 mg/L and 11,500 mg/L, respectively (McIlroy 1998). The acute toxicity of the two IO preparations to the tropical shrimp *Penaeus monodon* is >79,000 mg/L and 9100 mg/L, respectively.

Unused laboratory-formulated drilling fluids often are used in aquatic toxicity tests. These muds often have a different acute toxicity than used drilling fluids and cuttings of the same generic type (Neff et al. 1987). Friedheim and Pantermuehl (1993) reported that a laboratory PAO SBF was more toxic than a field PAO SBF to three species of marine organisms in water column tests performed according to Norwegian protocols (Table 37). The laboratory mud was a 10 pound/gallon 75/25 PAO/water mud; the used field mud was a 15.5 pound/gallon 80/20 PAO/water mud from a North Sea well. Although the laboratory mud was much more toxic than the field mud, both PAO SBFs

passed the acceptance criteria for the different bioassays. Thus, toxicity tests with SBF base chemicals and freshly prepared, unused SBFs may substantially overestimate the toxicity of the whole used SBF cuttings discharged to the ocean.

Table 36. Acute toxicity of unused SBFs and SBF base chemicals to the microalga *Skeletonema costatum* and the copepod *Acartia tonsa* in water column toxicity tests performed according to North Sea protocols. Endpoints are the concentration causing 50% reduction in growth rate (cell division) in the microalga and 50% mortality in the copepod. Concentrations are mg/L. From Vik et al. (1996a).

| SBF | Fraction | <i>Skeletonema</i> | <i>Acartia</i> |
|--------------------------|---------------|--------------------|----------------|
| Ester | Unused Mud | 34,000 – 145,600 | >50,000 |
| | Base Chemical | 60,000 | 50,000 |
| Acetal | Unused Mud | >300,000 | >50,000 |
| | Base Chemical | >100,000 | >100,000 |
| Poly- α -Olefin | Unused Mud | 82,400 | >50,000 |
| | Base Chemical | 3,900 | >50,000 |
| Internal Olefin | Base Chemical | 2,050 | >10,000 |
| Linear- α -Olefin | Unused Mud | >10,000 | >10,000 |

Table 37. Acute Toxicity of an unused laboratory PAO SBF and a used field PAO SBF to three species of marine organisms. Exposure media represent the dissolved/finely dispersed fraction of the muds. Acceptability criteria are included for comparison. LC₅₀/EC₅₀ is in mg/L. From Friedheim and Pantermuehl (1993).

| Species | Mud | Toxicity (EC ₅₀ /LC ₅₀) | Acceptability Limit (EC ₅₀ /LC ₅₀) |
|------------------------------------|-------|--|---|
| Alga <i>Skeletonema costatum</i> | Lab | 2,100.0 | ≥ 1000 |
| | Field | 50,300.0 | ≥ 1000 |
| Barnacle <i>Balanus improvisus</i> | Lab | >69,000.0 | ≥ 1000 |
| | Field | 240,000.0 | ≥ 1000 |
| Mussel <i>Mytilus edulis</i> | Lab | 5.0 | ≥ 1.0 |
| | Field | 14.6 | ≥ 1.0 |

5.3 Solid Phase Toxicity Tests

Solid phase toxicity tests measure the toxicity of chemicals or solid mixtures to sediment-dwelling marine animals. Because SBF cuttings usually do not disperse in the water column following discharge, but instead settle quickly through the water column and to the sea bottom, solid phase tests are better than water column tests for predicting the biological impacts of SBF cuttings discharges to the ocean. Most marine solid phase tests use amphipod crustaceans that live in and sift through or ingest sediments for food, or bivalve mollusks that live in sediments and either ingest sediment or filter food from the sediment/water interface. The standard marine amphipod solid phase toxicity test (ASTM E1367-92) has been modified to evaluate the acute toxicity of SBFs to benthic amphipods and to discriminate between the toxicity of OBFs and SBFs (Still and Candler 1997; Rabke et al. 1998; Rabke and Candler 1998, 1999). Various modifications of the protocols produced average LC₅₀s for IO C₁₆/C₁₈ SBF base chemical added to formulated sediment ranging from 407 mg/kg dry wt to 2944 mg/kg.

In the test protocol currently being evaluated by EPA, the SBF base chemical is mixed at five concentrations into formulated sediments. Concentrations are mg of base chemical per kg of dry sediment. Test SBF base chemical/sediment mixtures are added to exposure chambers with seawater. Amphipods *Leptocheirus plumulosus* are added to each chamber and the exposure is continued for 96 hours, at which time the number of survivors in each chamber is counted. The mean LC₅₀ for IO C₁₆/C₁₈ SBF base chemical in sediment using this protocol was 3480 mg/kg (CV 36%). The mean LC₅₀ of a diesel fuel run concurrently was 534 mg/kg (CV 19%). Candler et al. (1997) obtained similar results in 10-day sediment bioassays with the amphipods *Ampelisca abdida* and *Corophium volutator* (Table 38). The two SBF base chemicals evaluated, IO and PAO, were less toxic than the enhanced mineral oil and diesel fuel formerly used as OBF base chemicals.

The amphipod *Corophium volutator* and the bivalve mollusk *Abra alba* are used in many North Sea countries to evaluate the toxicity of SBF base chemicals and unused drilling muds to sediment-reworking benthic marine animals. The acute toxicities of the base chemicals and whole, unused muds usually are similar and LC₅₀s usually are higher than the acceptability criteria (Table 39). The SBFs are less toxic than OBFs in sediment bioassays.

Table 38. Mean LC₅₀s of oils and SBF base chemicals in sediments for the marine amphipods *Ampelisca abdida* and *Corophium volutator* in standard 10-day sediment toxicity tests (ASTM E1367-92). LC₅₀ and 95% CI concentrations are mg/kg dry wt. From Candler et al. (1997).

| Drilling Mud Base Chemical | Mean LC ₅₀ (95% Confidence Interval) | |
|----------------------------|---|----------------------------|
| | <i>Ampelisca abdida</i> | <i>Corophium volutator</i> |
| Enhanced Mineral Oil | 557 (493 – 630) | 7,146 (5,708 – 8,945) |
| Diesel Fuel | 879 (695 – 1112) | 840 (690 – 1,008) |
| Internal Olefin | 3,121 (2,503 – 3,893) | >30,000 (ND) |
| Poly- α -Olefin | 10,680 (7,665 – 18,599) | >30,000 (ND) |

ND Not determined.

Table 39. Acute toxicity as LC₅₀ of SBF base chemicals and whole fresh (unused) SBFs to the amphipod *Corophium volutator* and the bivalve mollusk *Abra alba*, based on sediment toxicity tests performed according to North Sea protocols. LC₅₀ concentrations are mg/kg dry wt. Acceptability criteria are >1000 for *Corophium* and >20 mg/kg for *Abra* (Table 33).

| SBF | <i>Corophium volutator</i> | <i>Abra alba</i> | Reference |
|-------------------|----------------------------|------------------|-----------------------|
| Ester Base Chem. | NA | >100,000 | Vik et al. 1996a |
| Acetal Mud | NA | ~1,500 | Vik et al., 1996a |
| Acetal Base Chem. | NA | 549 | Vik et al., 1996a |
| PAO Mud | >10,000 | 7,000 | Vik et al., 1996a |
| PAO Mud | >10,000 | 572 | Friedheim & Conn 1996 |
| PAO Base Chem. | NA | 7,900 | Vik et al. 1996a |
| IO Mud | 7,131 | 303 | Friedheim & Conn 1996 |
| IO Base Chem. | 7,100 | 300 | Vik et al. 1996a |
| LAO Mud | 1,021 | NA | Vik et al. 1996a |
| LAO Mud | 1,268 | 277 | Friedheim & Conn 1996 |

SBFs and SBF ingredients exhibit a low overall acute toxicity in water column and solid phase tests with a variety of marine plants and animals. LC_{50} s nearly always are higher (less toxic) than acceptability criteria. However, acutely toxic concentrations of many SBFs in solid phase tests are lower than concentrations of SBF base chemicals measured in surface sediments near (within about 100 m) of offshore platforms discharging SBF cuttings. Therefore, it is uncertain if SBF cuttings are eliciting direct toxic responses in benthic marine animals near SBF cuttings discharges.

Solid phase toxicity tests have not been performed to date with authentic SBF cuttings from a platform or with SBF-contaminated sediments collected from the sea floor near a discharging platform. As part of a recent joint EPA/Industry screening survey of SBF cuttings deposition in offshore waters of the Gulf of Mexico, benthic amphipods (*Leptocheirus plumulosus* and *Ampelisca abdida*) were exposed to sediments collected near platforms discharging SBFs (Continental Shelf Associates, 1998). Survival among the amphipods ranged from 62 to 98 percent and was comparable to survival among amphipods exposed to reference sediments.

Although the sediments collected for toxicity testing contained 0.67 to 0.91 percent total organic carbon, none contained measurable concentrations of total petroleum hydrocarbons (used to estimate concentrations of SBF base chemicals). Some of the sediments were anoxic and this may have contributed to the slightly less than control survival in a few sediment samples. Field studies (discussed below) seem to indicate that much of the harmful effects of high concentrations of SBF cuttings in sediments is caused by nutrient enrichment and resulting oxygen depletion in the contaminated sediments rather than by direct toxicity of the SBF base chemicals themselves.

5.4 Bioavailability of SBF Base Chemicals

A concern about SBF base chemicals, particularly in North Sea countries is that they may bioaccumulate in tissues of marine organisms, possibly tainting demersal marine animals of commercial value (Rushing et al. 1991; Vik et al., 1996a). Demersal fish are able to bioaccumulate petroleum hydrocarbons from OBF cuttings (Payne et al. 1989; Stagg and McIntosh 1996).

A chemical may bioaccumulate in the tissues of marine organisms if the organisms are exposed to bioavailable forms of the chemical in the ambient water, sediment, or food. A chemical is bioavailable if it is in a form that can move through or bind to the surface coating (e.g., skin, gill epithelium, gut lining, cell membrane) of an organism (Newman and Jagoe 1994). Bioavailability of nonpolar (un-ionizable) organic chemicals, such as SBF base chemicals, to marine organisms depends on the physical and chemical forms of the compounds. Organic chemicals in true solution in sea water usually are much more bioavailable than organic chemicals that are present in complexed, adsorbed, or solid forms. SBF base chemicals in discharged SBF cuttings are present in the marine environment in true solution, complexed with dissolved or particulate organic matter, adsorbed to the surface of cuttings and sediment particles, occluded within "oil-wet" particles, and possibly in the tissues of marine organisms in contact with the SBF cuttings. The SBF base chemicals in the different phases are exchangeable but, at any given moment, only a small fraction of the total SBF base chemicals (depending on aqueous solubility) is in solution in sediment pore water or the overlying water column.

Nonpolar organic chemicals, such as SBF base chemicals, usually have a low aqueous solubility and a high solubility in the lipids of plants and animals. They are classed as hydrophobic or lipophilic compounds. The rate and extent of bioaccumulation of hydrophobic compounds by marine organisms depends on the relative affinities of the chemical for the ambient water phase and the tissue lipid phase. The relative affinities are approximated by the octanol/water partition coefficient (K_{ow}) for the chemical. K_{ow} is used as a surrogate for lipid/water partition coefficient because solubility of many nonpolar organic compounds in octanol and biological lipids is similar and there are published values for K_{ow} for a large number of nonpolar organic chemicals of environmental concern (Chiou et al., 1982; Connell, 1993). At equilibrium, the rates of absorption into and desorption from the lipid phase of the plant or animal are equal. Because of the relationship between $\log K_{ow}$ and bioconcentration, it is possible to predict the equilibrium bioconcentration factor (BCF: concentration in tissues/concentration in solution in ambient water) for a particular nonpolar organic compound from its K_{ow} .

Many linear regressions between $\log K_{ow}$ and $\log BCF$ have been performed with different numbers and classes of nonpolar organic chemicals spanning different ranges of $\log K_{ow}$ (Isnard and Lambert 1988; Schüürmann and Klein

1988; Nishihara et al. 1993). Hydrophobic chemicals with a log K_{ow} less than about 3 to 3.5 may bioaccumulate rapidly but not to high concentrations in tissues of marine organisms, particularly if they are readily biodegradable (ECETOC, 1996). Hydrophobic chemicals with a log K_{ow} greater than about 6.5 to 7 do not bioaccumulate effectively from the water, because their solubility in both the water and lipid phases is very low (Chessels et al. 1993). Large hydrophobic molecules with a linear chain length of more than about 4.3 nm, an effective cross-section of about 1.0 nm, or a molecular weight greater than about 600 daltons may not be able to permeate biological membranes and so are not bioavailable (Opperhuizen 1986; Connell 1993).

Log K_{ow} values for several SBF base chemicals have been measured or estimated in order to predict their bioavailability to marine organisms (Table 40). Esters are moderately soluble and have a low log K_{ow} . They probably are bioavailable; however, they are readily biodegradable and probably do not bioaccumulate to biologically significant concentrations in tissues of marine animals. The liver and gut enzymes involved in fat metabolism in marine animals can hydrolyze ester bonds and convert the resulting alcohols and fatty acids to low molecular weight organic nutrients. Food chain transfer is significant only for hydrophobic chemicals with log K_{ow} s greater than about 5 (Thomann 1989). Therefore, esters are not readily bioaccumulated from food and will not biomagnify in marine food chains.

Table 40. Measured or estimated values for log octanol/water partition coefficient (log K_{ow}) of several SBF base chemicals.

| SBF Base Chemical | Log K_{ow} | Reference |
|--------------------------|--------------|-----------------------|
| Ester | 1.69 | Growcock et al. 1994 |
| Acetal | 11.8 | Vik et al. 1996a |
| Linear- α -Olefin | >6.43 | McKee et al. 1995 |
| Internal Olefin | 8.57 | Zevallos et al. 1996 |
| Internal Olefin | >9.0 | ERT Ltd, 1994a |
| Poly- α -Olefin | 11.2 – 13.7 | Vik et al. 1996a |
| Poly- α -Olefin | >10.0 | Leuterman 1991 |
| Poly- α -Olefin | 15.4 | Friedheim et al. 1991 |
| Poly- α -Olefin | 14.9 – 15.7 | Schaanning, 1996 |
| Poly- α -Olefin | 11.2 | Zevallos et al. 1996 |

Olefins and paraffins of the sizes found in SBF base chemicals are relatively large linear chains that do not permeate membranes efficiently. They have high log K_{ow} s, mostly higher than 9 (Table 40), indicating extremely low aqueous solubility and low potential to bioaccumulate. There is an inverse relationship between log K_{ow} and aqueous solubility. For example, octadecane (C_{18} n-paraffin) has a log K_{ow} of 9.32 and an aqueous solubility of 4×10^{-7} mg/L. Bioaccumulation of highly hydrophobic chemicals, such as SBF olefins, occurs very slowly, if at all. Equilibration in marine animals may require more than a year of continuous exposure (Hawker and Connell 1985, 1986). This is longer than the life span of most benthic organisms. Olefins, which are readily biodegraded by aerobic microorganisms, probably are readily metabolized in the tissues of marine animals. As a result, acetate is produced, which is an important organic nutrient for all tissues. Therefore, it is unlikely that bioaccumulation of SBF base chemicals represents an environmentally important risk to marine organisms in the vicinity of offshore SBF cuttings discharges.

There have been a few laboratory investigations of bioaccumulation of SBF base chemicals by marine organisms. Rushing et al. (1991) exposed estuarine mud minnows *Fundulus grandis* to substrates of cuttings containing 1.0, 5.0 and 8.4 percent of a laboratory-prepared PAO SBF in a flow through seawater bioassay system. The SBF was an 11.0 pound/gallon mud with a PAO/water ratio of 70/30. At several times up to 30 days, fish were sampled and analyzed for PAO in the gut and whole tissues. No PAO was detected in tissues of the fish. One fish contained a small amount of PAO in its gut, indicating that the fish had ingested some SBF cuttings. In a parallel experiment performed with low-aromatic mineral oil cuttings, the fish did bioaccumulate a small amount of petroleum hydrocarbons in their tissues.

Marine mussels *Mytilus* spp. have been used extensively to monitor bioavailable chemicals in coastal estuarine and marine waters, including chemicals discharged from offshore oil and gas platforms (Goldberg et al. 1978; Johnsen et al. 1998). They filter large volumes of water, bioaccumulating chemicals from it. They have only a limited ability to metabolize and excrete accumulated organic chemicals and so tend to bioaccumulate them to high concentrations in soft tissues. Mussels were used by ERT (1994b) and McKee et al. (1995) to measure the bioavailability of an IO and a LAO SBF base chemical, respectively.

In both studies, the bivalves were exposed to “saturated solutions” of the base chemicals in seawater. It is probable that the exposure water contained dispersed droplets of the base chemicals. In both studies, the bivalves rapidly accumulated the SBF chemical in soft tissues. When returned to clean seawater, the mussels equally rapidly released the accumulated chemicals from their tissues. Lipid normalized BCFs (concentration per unit weight of tissue lipid/concentration in exposure water) were estimated for both base chemicals. Lipid-normalized log BCFs for the C₁₆ and C₁₈ IO base chemicals were 5.37 and 5.38, respectively. The log BCF for the LAO was 4.84.

Similar results were obtained for acetal, PAO, and hydrogenated paraffin oil (Vik et al. 1996a). BCFs usually are expressed on a wet tissue weight/water volume basis. If the BCF is expressed on this basis, it is apparent that the bioaccumulation of these highly hydrophobic chemicals is much less than predicted by published regression relationships between log K_{ow} and log BCF. The rapid uptake and release of these chemicals by the mussels suggests that the mussels actually were filtering and retaining droplets (or particles) of SBF base chemical in their gills and digestive tracts. The SBF base chemicals were not assimilated into the tissues of the mussels and were released back to the water when the mussels were returned to clean water.

Schaanning et al. (1996) added marine polychaete worms *Hedeste (Neries) diversicolor* to NIVA simulated seabed sediment chambers containing sediments contaminated with two ester, one internal olefin, one linear alpha olefin, or a mineral oil base chemical. After about 160 days, no worms survived in one ester treatment, having succumbed to low oxygen concentrations. In the other ester treatment, the worms contained high concentrations of esters in their tissues. The tissue esters were different from those in the base chemical formulation and resembled those in the tissues of worms from control chambers. They probably were natural fatty acid esters. Thus, there was no bioaccumulation of ester SBF base chemicals by the worms.

At the end of the six-month exposure period, worms exposed to sediments containing IO SBF base chemical, contained 2.37 to 49.5 mg/kg wet wt IO in their tissues. Worms exposed to the LAO contaminated sediments contained 3.56 to 7.77 mg/kg LAOs. However, a comparison of the SBF/barium ratio in exposure sediments and whole worm tissues revealed that all or most of the SBF was not assimilated into the worm tissues. It probably was in the digestive tract of the worms. It is possible that a small amount of SBF was bioaccumulated by the worms during six months exposure to contaminated sediments. These studies show that SBF base chemicals have a very low bioavailability to marine organisms. There is little or no risk that these chemicals will bioaccumulate to potentially harmful concentrations in tissues of benthic animals or be transferred through marine food chains to important fishery species.

6.0 BIOLOGICAL IMPACTS OF SBF CUTTINGS DISCHARGES

This information on the physical/chemical properties of SBF base chemicals and whole muds, their fates in the ocean, biodegradation rates, toxicities, and potential for bioaccumulation provides a good initial basis for predicting their effects on marine organisms and ecosystems following SBF cuttings discharges to the ocean. However, field studies are essential to validate predictions from laboratory studies (Limia 1996; Norman 1997). Field studies often

are required in the North Sea to document the environmental fates and effects of cuttings discharges. Most field studies are designed to provide the information needed to monitor the fate and persistence of SBF cuttings on the sea floor. Relatively few studies also have documented the effects of and recovery from SBF cuttings accumulations in the bottom on biological communities living on or in bottom sediments.

For example, all of the 19 field studies performed in offshore oil fields in the Norwegian Sector of the North Sea in 1994 included monitoring of physical and chemical characteristics of bottom sediments, but sediment macrofauna were monitored in only eight of the field studies (Bakke et al. 1996). Field studies on the fates and persistence of SBF cuttings in the marine environment were reviewed above. Biological effects field studies are reviewed below.

6.1 North Sea

The most comprehensive field survey published to date on the biological impacts of SBF cuttings discharges was undertaken for a well drilled with an ester based mud in the Dutch sector of the North Sea (Daan et al. 1996; Limia 1996). Water depth at the drilling location was approximately 30 m, with spring tidal current speeds of approximately 0.6 m/s. The drilling program for the well produced a discharge of 248.7 metric tons of WBF and 477.2 tons of ester SBF (containing 180.5 tons of esters). The esters in the SBF included 2-ethylhexanol esters of octanoic, decanoic, dodecanoic, tetradecanoic, and hexadecanoic acids.

Sampling included a baseline survey and post-drilling sampling 1, 4, and 11 months after completion of drilling. Sediments were collected along transects at distances of 75, 125, 200, 500, 1,000 and 3,000 m primarily down current from the discharge point.

Two zones of physical and biological impacts were identified: within 200 m of the discharge and greater than 200 m from the discharge. At the time of the first two post-drilling surveys, ester concentrations in sediments out to 200 m from the rig were highly variable, suggesting a patchy distribution of cuttings on the sea floor. Concentrations in individual replicates ranged from 1.7 to nearly 4,700 mg/kg dry wt total esters. Ester concentrations in sediments collected at distances greater than 200 m from the rig were at or near background. By the time of the third post-drilling survey 11 months after completion of drilling, ester concentrations in sediments from stations within 200 m of the rig had dropped to the range of 1.6 to 84.2 mg/kg. The estimated half-life of esters in the nearfield sediments was 133 days, with a 95 percent decrease in concentration requiring an estimated 580 days. The loss of esters from sediments was due to a combination of biodegradation by sediment bacteria and redistribution and dilution of surficial sediments.

At the time of the baseline survey, sediments out to about 200 m from the drilling site were composed of fine sand and silt. At greater distances, the sediments gradually changed to coarse sand. The dominant benthic animal in sediments within 200 m of the drilling site was the echinoderm *Echinocardium cordatum*. Between 20 and 23 different species of benthic fauna were recorded at each station. Distribution of different species was related to sediment grain size.

Biological results of the first post-drilling survey were not reported. At the time of the second post-drilling survey, sediments within 75 m of the rig site were anaerobic and smelled of hydrogen sulfide. Living *E. cordatum*, the dominant species in the pre-drilling survey, were completely absent from sediment samples collected within 500 m of the rig site. They were present at the 3,000 m station. The total abundance of benthic fauna was low at stations within 200 m of the rig site, and increased with distance farther away. Abundance of the opportunistic polychaete worm *Capitella capitata* was high at stations 75 and 125 m from the well site; they were absent from stations more than 200 m away. No effects on species richness were observed at stations between 500 and 3,000 m from the rig.

At the time of the third post-drilling survey, 11 months after drilling, surficial sediments out to 200 m from the rig site still were more or less anaerobic. Abundance of individuals and species still was low at the 75-m stations, but had risen to levels higher than in the pre-drilling survey at greater distances from the discharges. Although effects still were evident one year after drilling, there was definite evidence of ecosystem recovery, particularly at stations more than 75 m from the discharge.

Similar observations were made near a well drilled with an ester SBF in the Norwegian Sector of the North Sea (Smith and Moore 1990; Cranmer and Sande 1991; Gjos et al. 1991; Smith and May 1991; Smith and Hobbs 1993).

The areal extent of ester accumulation and biological effects was less than in the Dutch Sector, probably because of greater water depth (67 m) and faster currents (Table 41). Immediately after drilling, there was a severely affected zone of sediments within 100 m of the well site. Ester concentrations in sediments were in the range of 360 to 85,300 mg/kg; metals concentrations also were elevated. The benthic fauna were severely impoverished. Only 16 individuals of four taxa were found in the sediments containing 85,300 mg/kg ester. The impoverished fauna at the 50 and 100-m stations were dominated by the opportunist polychaete *Capitella capitata*. Between 100 and 200 m from the well site, benthic conditions improved and there was no evidence of biological effects at distances of 200 m or greater.

One year after drilling, the zone of chemical and biological disturbance within 100 m of the well site had disappeared from most of the area, indicating recovery of the local benthic ecosystem (Table 41). However, some cuttings still were present in isolated patches on the sea floor. Two of the five replicate sediment samples collected 500 m SW of the well site contained cuttings and had an odor of esters; the other three samples showed no evidence of cuttings contamination. These samples contained a large number of animals, dominated by a few opportunistic species.

The initial effects of ester SBF cuttings discharges at the two sites were similar to those observed for OBF cuttings discharges from other platforms (Olsgard and Gray 1995). The initial effects in both cases were attributed primarily to sediment anoxia caused by biodegradation of organic matter (esters or oil) in the cuttings and to clogging of sediment pore spaces with organic residues. The organic enrichment and resulting sediment anoxia had the effect of eliminating anoxia/H₂S-sensitive species, allowing colonization by large numbers of tolerant, opportunistic species (Pearson and Rosenberg 1978). Recovery began when sediment organic matter was depleted and redox potential increased. Recovery of the benthos from ester SBF cuttings discharge was much more rapid than that following OBF discharges, because of the rapid aerobic and anaerobic biodegradation of the esters.

Table 41. Ester concentrations and benthic community characteristics near the Ula Well 7/12-9 in the Norwegian Sector of the North Sea. From Gjøset al. (1991).

| Location (m) | Mean Ester Conc. (mg/kg) | No. Taxa | No. Individuals | Shanon-Weiner Diversity |
|--------------------------------------|--------------------------|----------|-----------------|-------------------------|
| 1990, Two Days After Drilling | | | | |
| 50 SW | 85,300 | 4 | 16 | 1.50 |
| 100 SW | 46,400 | 7 | 167 | 0.96 |
| 200 SW | 208 | 52 | 290 | 4.52 |
| 500 SW | 0.98 | 50 | 308 | 4.53 |
| 800 SW | 0.42 | 57 | 284 | 4.72 |
| 1200 SW | 0.38 | 56 | 308 | 4.54 |
| 2500 SW | 0.26 | 51 | 316 | 4.64 |
| 5000 SW | 0.30 | 56 | 336 | 4.50 |
| 100 SE | 360 | 35 | 234 | 3.39 |
| 200 SE | 97 | 52 | 290 | 4.66 |
| 500 SE | 2.44 | 51 | 255 | 4.75 |
| 1200 SE | 0.25 | 47 | 224 | 4.58 |
| Ref A | --- | 56 | 385 | 4.59 |
| Ref. B | --- | 53 | 368 | 4.33 |

Table 41. Ester concentrations and benthic community characteristics near the Ula Well 7/12-9 in the Norwegian Sector of the North Sea. (continued)

| Location (m) | Mean Ester Conc. (mg/kg) | No. Taxa | No. Individuals | Shanon-Weiner Diversity |
|--------------------------------------|--------------------------|----------|-----------------|-------------------------|
| 1991, One Year After Drilling | | | | |
| 50 SW | 0.21 | 51 | 379 | 4.30 |
| 100 SW | 0.22 | 44 | 370 | 4.24 |
| 200 SW | 1.34 | 38 | 212 | 4.31 |
| 500 SW | 0.43 | 43 | 625 | 2.61 |
| 800 SW | 0.18 | 49 | 365 | 4.36 |
| 1200 SW | 0.31 | 53 | 322 | 4.71 |
| 2500 SW | 0.39 | 45 | 230 | 4.54 |
| 5000 SW | 0.36 | 52 | 334 | 4.49 |
| 100 SE | 11.68 | 52 | 408 | 4.41 |
| 200 SE | 0.34 | 57 | 395 | 4.37 |
| 500 SE | 5.28 | 52 | 367 | 3.98 |
| 1200 SE | 0.18 | 41 | 259 | 4.28 |
| Ref A | 0.25 | 48 | 340 | 4.18 |
| Ref. B | --- | 58 | 329 | 4.73 |

In 1994, 19 monitoring surveys were performed near platforms discharging SBF to offshore waters of the Norwegian Sector of the North Sea (Bakke et al. 1996). Eight of these surveys included observations of benthic communities near platforms. A total of 115 metric tons of an unidentified SBF (probably ester) was discharged from the Frøy platform in 1994, shortly before the survey. Low concentrations of SBF base chemical could be detected in sediments out to 2 km of the well site. The benthic fauna appeared normal, and there was no evidence of disturbance from the drilling and discharge activities.

A total of 1950 metric tons of barite and 46 m³ of ester SBF were discharged from the Yme Gamma Platform shortly before the field survey (Bakke et al. 1996). Ester was detected in sediments from the four stations closest to the discharge and in two stations down-current to a distance of 500 m from the platform. Concentrations were low. Elevated concentrations of barium, but not other metals, were detected at most stations. The benthic fauna was highly diverse throughout the field; there were minor effects of the discharges to a distance of 500 m from the platform.

Fifteen wells were drilled with WBF at the Troll East platform (Bakke et al., 1996). No OBF or SBF discharges were reported. The benthic fauna in sediments near the platform had a high diversity, and there were no signs of effects of the WBF discharges. Minimal or no benthic biological effects of WBF and WBF cuttings discharges have been documented in the North Sea, Gulf of Mexico, northwestern Atlantic, and California (Ferbrache 1983; National Research Council 1983; Neff 1987; Neff et al. 1989a; Daan and Mulder 1993; Hyland et al. 1994).

A total of 8331 metric tons of WBF and 544 tons of ether SBF were discharged from the Bragge Platform prior to the 1994 field survey (Bakke et al. 1996). Elevated concentrations of SBF base chemical were detected in sediments up to 2 km down current from the platform. Barium concentrations had increased gradually in the sediments of the area since 1992. The benthic community near the platform had a reduced diversity. Effects of the drilling fluid accumulations on the benthos were detected to 1 km down current of the discharge and to a maximum of 250 m in other directions.

No information was available on the types or quantities of SBF drilling muds discharged from Sleipner West in 1994 (Bakke et al. 1996). Concentrations of hydrocarbons and metals in sediments near the platform were low. The benthic fauna had a high diversity, and there was no evidence of an effect on the benthos of drilling activities.

A total of 4,456 metric tons of drilling chemicals, containing 3,025 tons of barite and 55 tons of a PAO SBF was discharged from the Tordis Platform in 1994 (Bakke et al. 1996). Elevated barium concentrations were distributed uniformly in sediments around the platform. Concentrations of SBF base chemical in sediments were low, but could be detected to 2 km from the platform. There was a gradient of benthic community structure in sediments across the field that was not there at the time of the baseline survey. Benthic faunal disturbance was detected at three stations out to 500 m from the platform.

Three of the monitoring programs around platforms discharging SBF cuttings to offshore waters of the UK Sector of the North Sea included measurement of the number of taxa and number of species of benthic fauna at some stations (data provided by the UKOOA with permission of the offshore operators). As discussed above, SBF base chemicals, and presumably the cuttings to which they were adsorbed, were distributed in a very patchy pattern in sediments near the platforms. There were no clear gradients of SBF with distance from the platforms. Therefore, SBF concentrations in sediment were compared to biological parameters in this review, without consideration of distance from the discharge, in an attempt to identify possible biological effects of the SBF accumulations.

Ester concentrations up to 4020 mg/kg were detected in sediments that were monitored for benthic fauna near a platform shortly after drilling with ester SBF (Figure 9). Numbers of individuals of benthic fauna were not correlated with sediment ester concentrations. In fact, highest abundances of benthic fauna were in sediments with the highest ester concentrations. However, the sediments with the highest concentrations of esters and largest numbers of benthic animals had the fewest taxa, indicating that the surviving fauna of ester-contaminated sediments consisted of a few opportunistic species. A year after drilling, the pattern had not changed, although the maximum concentration of ester in sediment had declined to 543 mg/kg (Figure 10). The two most heavily contaminated sediments had the lowest numbers of taxa, but some of the largest numbers of individuals. In both surveys, the most heavily contaminated sediments were from 0 to 50 m from the well site.

Benthic faunal surveys were performed shortly after completion of drilling with linear paraffin SBFs on two platforms in the UK Sector of the North Sea. At the first platform, the number of individuals of benthic fauna in sediments declined with increasing linear paraffin concentrations in sediments (Figure 11). A total of 64 individuals representing 27 taxa were present per 0.2 m² in sediments containing 1603 mg/kg linear paraffin, compared to 686 individuals, representing 83 taxa, in a sediment sample containing 10 mg/kg linear paraffin. All the sediments, except those containing the highest linear paraffin concentration, contained an abundant, diverse benthic fauna. There was no evidence of the organic enrichment effect in the benthic community. The limited data from this survey suggest that biological effects in an abundant, diverse benthic community may occur where the concentration of linear paraffin in sediment does not exceed about 500 mg/kg. The benthic fauna were much less abundant and diverse in sediments at the second linear paraffin SBF cuttings discharge site (Figure 12).

The biological response was intermediate between that at the other linear paraffin discharge site and at the ester discharge site. The number of individuals was highest in sediments from three of the four stations with the highest linear paraffin concentrations (102 to 202 individuals/0.2 m²); at the fourth station, both number of individuals and number of taxa were low.

The number of taxa varied from 6 to 14 in the 4 heavily contaminated sediments, compared to 10 to 20 taxa in sediments containing less than 100 mg/kg linear paraffin. The most heavily contaminated sediments may be showing the organic enrichment effect, larger numbers of individuals dominated by a few opportunistic species. The naturally low biological diversity of the benthic fauna at the site may have obscured effects of the drilling discharges, or the resident community, possibly already adapted to environmental stress, may have been less sensitive than the community at the other linear paraffin SBF cuttings site to SBF cuttings.

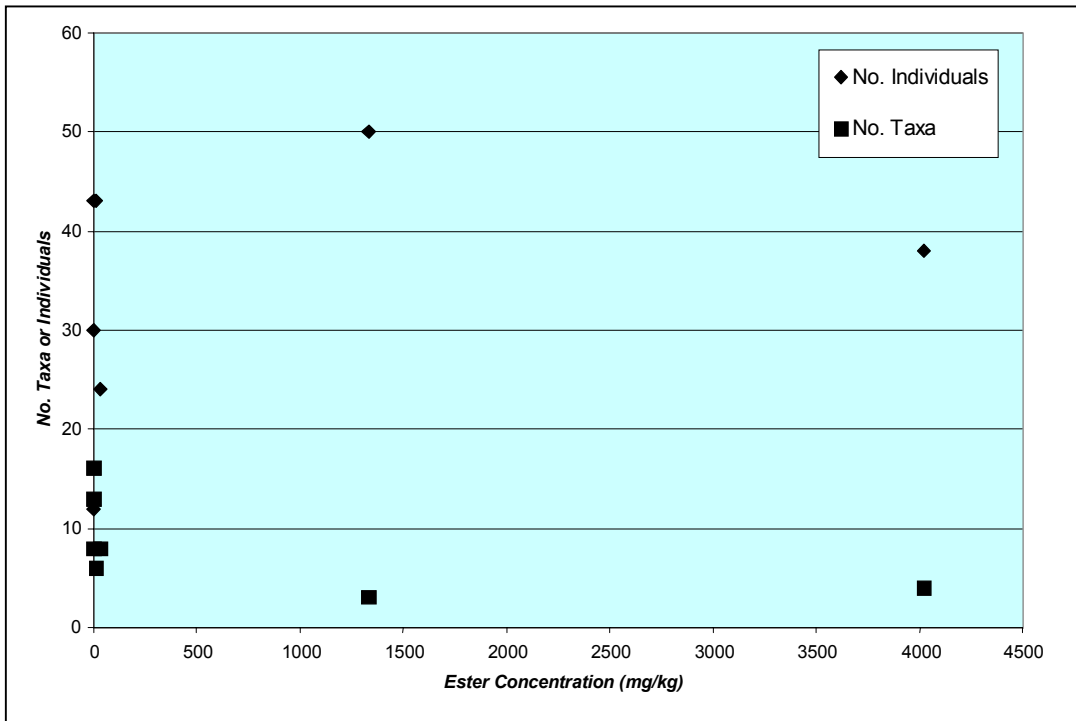


Figure 9. Relationship between concentration of ester SBF in sediments and numbers of taxa and individuals of benthic fauna in sediments near a platform in the North Sea shortly after drilling.

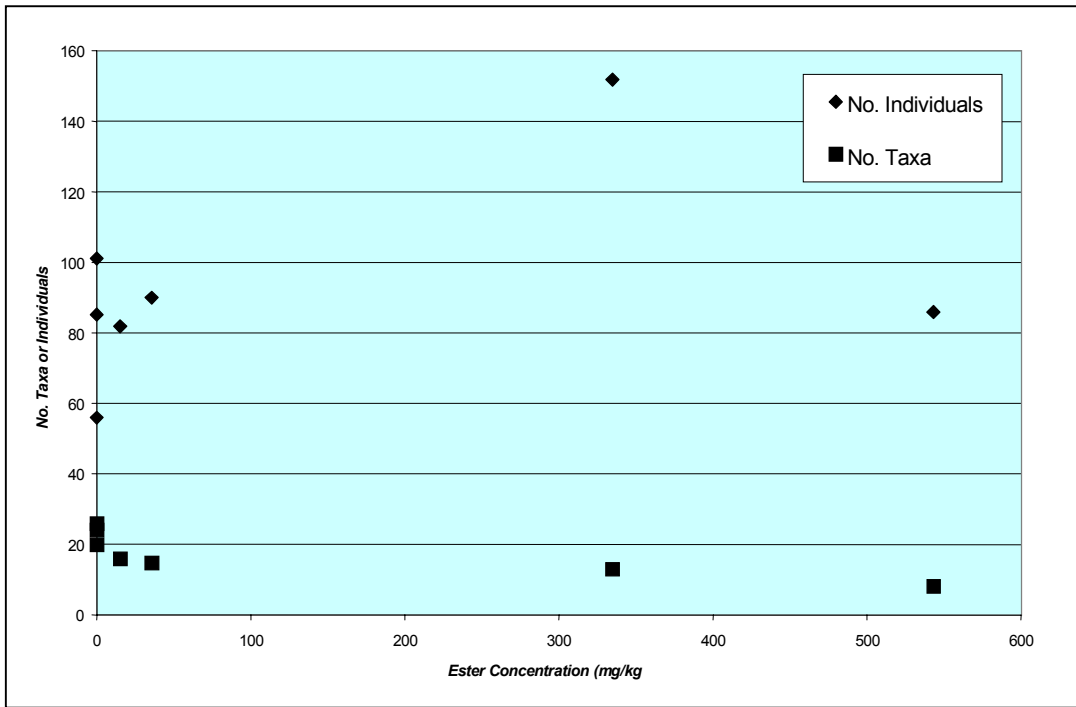


Figure 10. Relationship between concentration of ester SBF in sediments and numbers of taxa and individuals of benthic fauna in sediments near a platform in the North Sea 1 year after drilling.

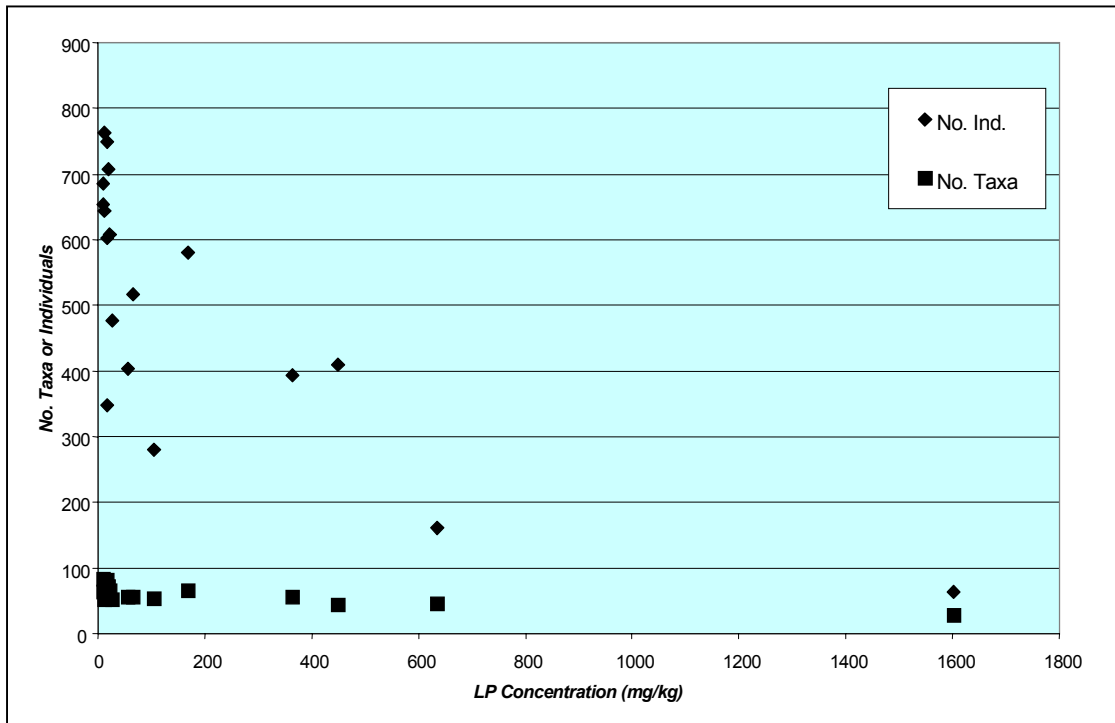


Figure 11. Relationship between concentration of linear paraffin in sediments and numbers of taxa and individuals of benthic fauna per 0.2 m² of sediment near a platform in the North Sea.

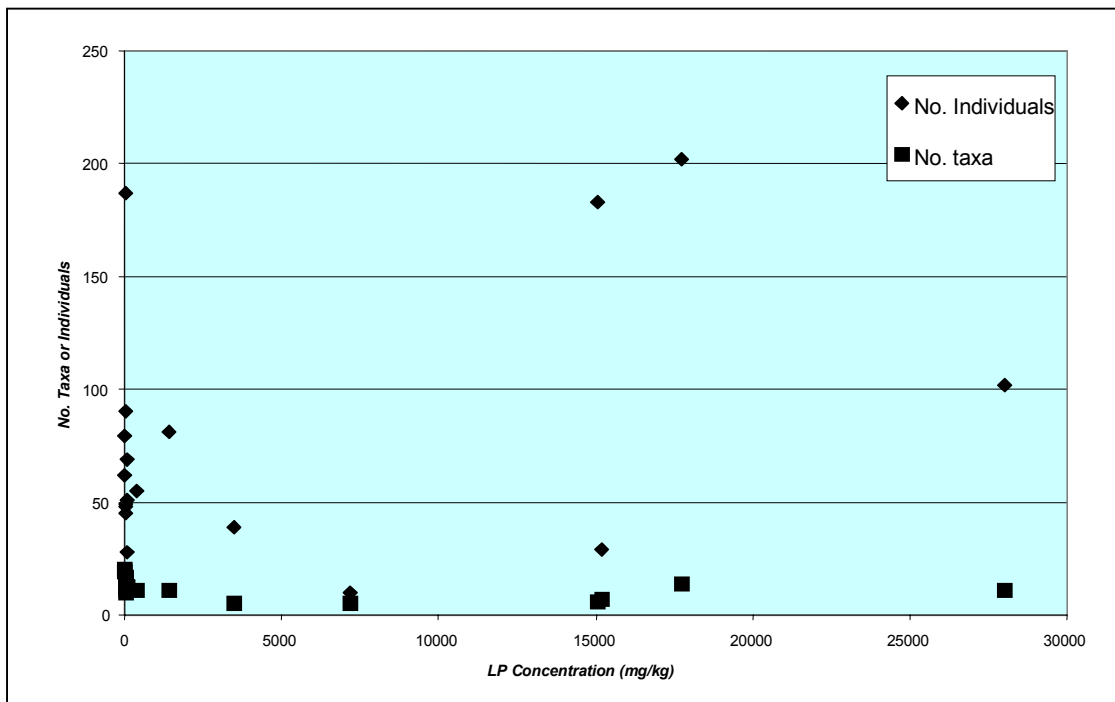


Figure 12. Relationship between concentration of linear paraffin SBF in sediments and numbers of taxa and individuals of benthic fauna in 0.2 m² of sediment near a platform in the North Sea.

6.2 Gulf of Mexico

The physical and biological effects of SBF cuttings discharges were studied at a drilling site in 39 m of water in the northwestern Gulf of Mexico (Candler et al. 1995). WBF was used to drill the first 3,400 ft of the well. A PAO SBF was used to drill from 3400 to 8050 ft. A total of 441 bbls of cuttings (approximately 200 metric tons) and 354 bbls of associated SBF were discharged. EPA (1999a) estimated that the discharge included 45 metric tons of PAO SBF.

Three field surveys, 9 days, 8 months, and 24 months after completion of mud and cuttings discharges were performed at the site. Samples for benthic community analysis were collected only on the 24-month survey. During all three surveys, sediment samples were collected at 25, 50, 100, 200, and 2000 m along transects in the four compass directions from the well site.

PAO in sediments was measured as total petroleum hydrocarbons (TPH) by infrared spectroscopy. The method is subject to interference from natural hydrocarbons and non-hydrocarbon chemicals and so provides a conservative (upper bound) estimate of PAO concentrations. Barium also was measured in sediments as a tracer of drilling mud accumulation and distribution. TPH concentrations in sediments ranged from 24 to 134,428 mg/kg 9 days after drilling, and not detected to 25,747 mg/kg after 8 months (Table 15). TPH concentrations above 1000 mg/kg in sediments extended to 200 m from the well site 9 days after drilling and to 50 m from the well site after 8 months.

Two years after completion of drilling, sediment TPH concentrations ranged from not detectable to 19,110 mg/kg (Tables 15 and 42). Concentrations above 1000 mg/kg were in sediments 25 and 50 m south and west of the well site. After 2 years, only 7 percent of the SBF originally discharged was found within this 200 m radius, suggesting substantial degradation and dispersion in the two years after discharge.

Sediment barium concentrations showed a similar concentration and distribution trend. Background (2000-m stations) barium concentrations in sediments were 500 to 800 mg/kg. Highest concentrations ranged from 47,437 mg/kg nine days after drilling to 14,670 mg/kg after eight months, and 32,634 mg/kg after 24 months (Table 42). The TPH and barium data show the patchy distribution of WBF and SBF in sediments around the well site. The overall trend was for concentrations of drilling mud ingredients in sediments to decrease with time after drilling.

A total of 106 taxa of benthic invertebrates were identified in sediments near the drill site two years after completion of drilling. The benthic community was typical of those in shallow waters of the western Gulf of Mexico and included 42.5 percent polychaetes, 24.5 percent crustaceans, 19.8 percent mollusks, and 5 percent echinoderms. The benthic community apparently was unaffected by the drilling discharges (two years after drilling) at all stations east and north of the well site and at stations more than 50 m south and west of the well site (Table 42). At three of the four stations 25 and 50 m south and west of the well site, sediments contained 3,620 to 19,110 mg/kg TPH, 8415 to 32,634 mg/kg barium, and had reduced numbers or taxa and individuals of benthic fauna. Sediments containing more than about 3000 mg/kg TPH had depauperate benthic communities (Figure 13). Species diversity was lower in sediments at these stations than at the other stations. Community evenness was about the same at all stations, indicating that effects on benthic fauna were evenly distributed among species of benthic fauna.

In general, the results of this monitoring study were similar to those around SBF-discharging platforms in the North Sea. Effects on benthic communities were restricted to a small area down current from the discharge. The benthos were sampled only once in the Gulf of Mexico study, so it is not possible to determine if there was ecosystem recovery taking place. However, the temporal patterns of PAO concentrations in sediments, suggest that ecological recovery was likely.

Impacts of SBF cuttings discharges on deep-water benthic ecosystems are largely unknown. The only study to date that included some observations of bottom fauna near a deep-water discharge site was at the Pompano II platform in 565 m of water. As discussed above, discharges from the rig included 7,700 bbls of WBF cuttings, 5,150 bbls of SBF cuttings, and an estimated 7,695 bbls of a mixed 90% LAO/10% ester SBF. SBF concentrations reached a maximum in surficial sediments (0 – 2 cm) of 198,000 mg/kg 75 m northeast of the drilling template. In most areas, drill cuttings accumulated as a thin layer on bottom sediments.

Table 42. PAO and barium concentrations and benthic infaunal parameters in sediments near a well site in 39 m of water 2 years after discharge of 354 barrels of PAO SPF. From Candler et al. (1995).

| Parameter | 3 Affected Stations | 13 Remaining Stations | 4 Reference Stations |
|--|---------------------|-----------------------|----------------------|
| PAO (mg/kg TPH) | 3620 – 19,110 | ND – 1080 | ND – 46 |
| Barium (mg/kg) | 8415 – 32,634 | 990 – 4024 | 822 – 901 |
| Number of Taxa/0.2 m ² | 8 – 22 | 26 – 38 | 27 – 32 |
| Number of Individuals/0.2 m ² | 17 – 141 | 162 – 280 | 152 – 219 |
| Shannon Weiner Diversity | 1.69 – 2.25 | 2.32 – 3.15 | 2.49 – 2.86 |
| Evenness | 0.73 – 0.92 | 0.65 – 0.87 | 0.73 – 0.82 |

ND Not detected.

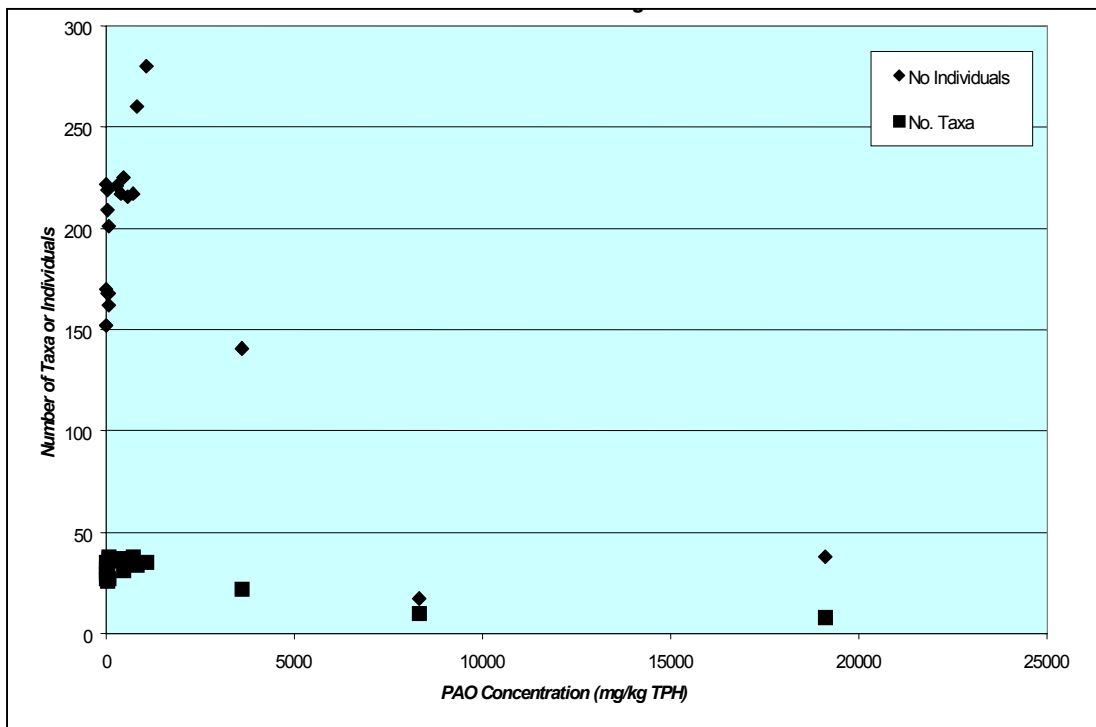


Figure 13. Relationship between concentrations of PAO base chemical in sediments and numbers of taxa and individuals per 0.2 m² of sediment near a well in the Gulf of Mexico 2 years after drilling. From Candler et al. (1995).

Sediments for benthic faunal analysis were collected with a remotely operated vehicle (ROV) from stations 25, 50, and 75 m northeast and 25, 50, 75, and 90 m southwest of the template. A total of 2,100 macrofaunal animals were collected; polychaetes were most abundant, followed by gastropod mollusks. The abundance of benthic fauna was significantly higher in sediments along the northeastern transect (highest SBF concentrations in sediment) than in sediments along the southwestern transect (Table 43).

There was a larger number of individuals but a smaller number of taxa of benthic fauna in the more heavily contaminated sediments northeast of the template than in cleaner sediments southwest of the template, suggesting an organic enrichment effect. Much of the difference in abundance of benthic fauna in sediments along the northeast transect than along the southwest transect was due to polychaetes, which were present in sediments from the northeast transect at a density of more than 85,000/m², compared to a density of 16,600/m² in sediments from the southwest transect. However, copepods, nematodes, polychaetes, and gastropods all were more abundant in sediments along the northeast transect than in sediments along the southwest transect.

Table 43. Concentrations of LAO/ester SBF, benthic macrofauna, and demersal megafauna (mostly fish) along four transects extending to 90 m from a drilling template in 565 m of water in the Gulf of Mexico. From Fechhelm et al. (1999).

| Parameter | Transect Direction from Template | | | |
|--|----------------------------------|-------|-------|-------|
| | NE | SE | SW | NW |
| Mean SBF, 0–2 cm (mg/kg) | 49,000 | 3,000 | 2,000 | 6,000 |
| Mean SBF, 2–5 cm (mg/kg) | 30,000 | 3,000 | 1,000 | 6,000 |
| No. Macrofauna | 1,761 | --- | 339 | --- |
| No. Taxa Macrofauna | 8.0 | --- | 12 | --- |
| Macrofauna Density (no/cm ²) | 15.7 | --- | 2.3 | --- |
| No. Megafauna | 18.0 | 15 | 7.0 | 22 |
| Megafauna Density (no/ha) | 1,475 | 1,389 | 875 | 2,037 |

Demersal megafauna (mostly fish) were counted from videotapes taken along each transect. Seven fish taxa were identified and counted. Numbers and densities of demersal fish observed along the 4 transects were similar. The densities were higher than observed at other locations at similar depths in the northern Gulf of Mexico. The fish may have been attracted to the Pompano drilling template or disturbed sediments nearby. Neither benthic fauna nor demersal fish abundance seems to have been adversely affected by the discharge of SBF cuttings.

6.3 Australia

Results similar to those reported in other regions have been reported for the Fortescue Field, located in 70 m of water in the Bass Strait off southeast Australia (Terrens et.al. 1998). Twenty-one wells were drilled at Fortescue with WBF between 1983 and 1985. Eighteen additional wells were drilled there between October 1994 and September 1996. Most of this drilling also was performed with WBF; however, the long-reach, high-angle sections of 7 wells required the use of SBFs. During the entire 1994 – 1996 program, approximately 20,000 m³ of WBF, 5,000 m³ of cuttings, and 2,000 m³ of ester SBF on cuttings were discharged to the Bass Strait. The fate of these discharges was monitored during five seabed surveys undertaken between August 1995 (pre SBF cuttings discharges) and August 1997 (11 months after completion of SBF cuttings discharges).

Sediments were sampled at 4 stations 100 to 2000 m along a transect southwest of the platform (the direction of the prevailing water currents) and 100 m south of the platform. Sediments in the vicinity of Fortescue are medium to coarse sands, indicating a high-energy environment. The highest ester concentration in sediments (12,000 mg/kg) was in sediment collected 100 m southwest of the platform shortly after completion of drilling with SBF. Six months later, the concentration of ester in sediment from this station had declined to 200 mg/kg. Sediment from the station 100 m south of the platform contained 1810 mg/kg ester shortly after SBF discharge and 260 mg/kg 6 months later. Most other stations did not contain measurable concentrations of ester (<0.2 mg/kg) at any time. Thus, esters from SBF cuttings were not persistent in sediments from this high-energy environment. Barium concentration increased in sediments (maximum concentration 795 mg/kg) up to 1 km southwest of the platform during SBF cuttings discharges. Barium concentrations remained elevated in sediments 100 m from the platform for at least 1 year after completion of drilling.

Impacts of the drilling fluids and cuttings discharges on benthic faunal communities was limited to within 100 m of the platform with recovery evident within 4 months after completion of drilling. During the time of SBF cuttings discharges, numbers of nematodes and crustaceans decreased and numbers of polychaetes increased in sediments 100 m southwest of the platform. Total abundance of benthic fauna remained nearly constant and benthic faunal diversity declined. These effects are typical of an organic enrichment effect (Pearson and Rosenberg 1978). Within 4 months after completion of drilling, benthic biological parameters had returned to pre-drilling conditions. Recovery was attributed to a combination of ester biodegradation and the active physical seabed dispersion processes in the eastern Bass Strait.

7.0 DISCUSSION: ECOLOGICAL RISK ASSESSMENT

Ecological risk assessment methods are being used with increasing frequency to predict or forecast the consequences of human activities, particularly releases of toxic chemicals, to the environment. An ecological risk assessment is performed in four steps, the two most important of which are an exposure assessment and a biological effects assessment (EPA, 1992, 1998; Suter, 1993). In the exposure assessment, estimates of the rates of release of the chemicals of concern to the environment are converted to estimates of doses of the chemicals of concern (COCs) to valued ecosystem components. The effects assessment interprets the estimated doses in terms of biological effects on valued ecosystem components. The same risk assessment procedures are integral to the evaluation of the ecological effects (injury to biological resources) from historic or ongoing activities or acute events, such as in-place pollutants, effluent discharges, and accidental releases of oil or hazardous materials (EPA, 1997). The objective of a risk assessment for SBF cuttings discharges is to characterize the likelihood and nature, magnitude, and duration of adverse ecological effects resulting from permitted discharges to the ocean of SBF cuttings.

The first step in a risk assessment for SBF cuttings is problem formulation, also called hazard definition (Suter 1993). It involves identification of valued ecosystem components at risk (resources at risk) and effects of concern, and includes a description of the environment under investigation and the source terms (rate of release of the COCs from their sources).

In the exposure assessment, the source terms are converted into estimates of exposure or dose of the COCs to valued ecosystem components. The effects assessment interprets the estimated exposure in terms of biological effects (injury) on valued ecosystem components. The final step is a risk characterization that integrates the results of the exposure and effects assessment to obtain an estimate of the probability (the risk) of different levels of effects that are or will result from the exposure (Suter 1993).

This risk assessment relies on the extensive information on the composition and environmental fates and effects of SBF cuttings described in earlier sections of this review. The nature of the available data precludes a quantitative estimate of risk. Therefore, the risk characterization is qualitative, and focuses on potential ecological effects of SBF cuttings discharges to deep offshore waters (the continental slope) of the Gulf of Mexico.

7.1 Problem Formulation

7.1.1 Resources at Risk

The Gulf of Mexico is a semi-enclosed, subtropical sea with a surface area of approximately 1.5 million km² (MMS, 1997). The continental slope has a hill and basin topography and extends from the edge of the continental shelf in 120 to 200 m of water to a depth of about 2800 m (Phillips and James 1988). The continental slope of the western and central Gulf of Mexico has an area of about 120,000 km². It currently is the site of substantial exploration for and development of oil and gas resources.

The benthic environment of the continental slope of the northern Gulf of Mexico generally is characterized by a more stable physical/chemical regime than the shallower shelf environments: uniform low temperatures, high salinity, and usually high dissolved oxygen concentrations. In most locations, the slope fauna has a high species richness and diversity, but low energy and biomass production, characterized by zoogeographic variation and small-scale patchiness (Jumars 1976; Rex 1983; Gallaway 1988; Grassle 1991).

One of the most important factors regulating community structure and production in the slope benthos is the slow rain of organic nutrient particles from above. Biological production in surface waters of the continental slope of the Gulf of Mexico is much less than in coastal and continental shelf waters, accounting in part for the lower productivity of the slope benthos (Pequegnat 1983). Because sediment deposition rates on most parts of the slope are very low, most benthic fauna of the slope are not well adapted to tolerate high sediment fluxes and deposition rates. The benthos could be sensitive to increased fluxes of particulate matter associated with SBF cuttings discharges from offshore oil and gas exploration and development.

On the slope off Louisiana and Texas, there is a large number of hydrocarbon seeps that support unique biological communities (MacDonald 1992). Chemosynthetic communities consist of assemblages of large sessile marine animals that are dependent on chemosynthetic bacteria as their primary food source. The bacteria subsist on petroleum hydrocarbons and H₂S seeping from the sea floor. Sediments in areas of chemosynthetic communities often are covered with a white or orange mat of anaerobic bacteria, primarily *Beggiatoa* spp., indicating that the underlying sediments are anoxic (MacDonald and Schroeder 1993). Most of the chemosynthetic communities discovered to date occur on the slope in water depths from 500 to 2,200 m. It is not clear if the chemosynthetic communities are sensitive to sediment deposition from SBF cuttings discharges. They probably would not be sensitive to the organic enrichment effects of SBF cuttings observed in shelf sediments.

7.1.2 Effects of Concern

The main environmental concern resulting from discharge of SBF cuttings to deep offshore waters of the Gulf of Mexico is that the cuttings may accumulate on the sea floor and adversely affect the benthic communities living there. As discussed above, adverse effects on benthic communities may occur as a result of the toxicity of SBF cuttings ingredients, organic enrichment of sediments from biodegradation of organic matter in the SBF cuttings, direct smothering of benthic fauna by the accumulation of cuttings solids on the sea floor, and alteration of sediment texture and physical/chemical properties, rendering the sediments less suitable for some species and more suitable for others.

An important factor in the potential effects of SBF cuttings on benthic communities is the rate of ecosystem recovery following cessation of cuttings discharge. The rate of ecosystem recovery depends on the persistence of impact-causing SBF cuttings ingredients in sediments, and the rate of recruitment to or recolonization of benthic habitats. Some benthic animals reproduce and grow slowly (Grassle 1977; MacDonald 1993), which may slow ecosystem recovery of the slope benthos, should it be adversely affected by SBF cuttings discharges.

7.1.3 Chemicals of Concern

Most drilling on the deep-water slope of the northern Gulf of Mexico probably will be performed with WBFs and SBFs. Although several types of SBFs have been used in the past in the Gulf of Mexico, it is probable that most future drilling with SBFs in the deep-water gulf will be with IOs and possibly also LAOs. The focus of this risk

assessment will be on SBFs. Bulk SBFs are not permitted for discharge to offshore waters of the Gulf of Mexico. However, drill cuttings, usually containing an average of about 10 percent SBF base chemical (Table 8), may be discharged to the ocean.

IOs and LAOs are synthetic olefins (hydrocarbons with one or more double bonds) (Table 1). LAOs used in SBFs are linear and branched C₈ to C₂₀ olefins with the double bond in the terminal (alpha) position. Molecular weights range from about 112 to 280. LAOs have low aqueous solubilities.

IOs are prepared from LAOs by isomerization. Commercial IOs used for drilling fluid formulation usually have carbon chain lengths of 16 to 18. The double bond is between two internal carbons.

SBFs contain several other ingredients, including an emulsifier, wetting agents, rheology modifiers, organophilic clay, lime, and barite (Tables 3 and 4). The clay and barite may contain several metals of potential environmental concern (Table 6). The metals are mostly in very insoluble, immobile forms in the mineral matrices of the clay and barite. The only ingredient of SBF of environmental concern, other than the SBF base chemical, is the emulsifier. Emulsifiers probably interact with the SBF base chemical to increase its bioavailability and biodegradability.

7.1.4 Discharge of SBF Cuttings

During drilling, SBFs are circulated down-hole where they pick up cuttings produced by the grinding action of the drill bit on the formation solids. The drilling mud containing suspended cuttings is passed through treatment devices to remove the cuttings from the mud. The SBF is returned to the mud pits for recirculation down-hole. Cuttings containing adhering SBF are discharged more or less continuously to the ocean during drilling, which may occur about 50 percent of the time.

Discharge statistics from 18 wells drilled in the UK sector of the North Sea indicate that about 400 to 3000 metric tons of cuttings containing 11 to 700 tons of SBF may be discharged to the ocean during drilling of a well (Table 9). Because of the adherent SBF base chemicals, the cuttings are hydrophobic and clump together after discharge to the ocean. The clumps of SBF cuttings, being denser than seawater, settle rapidly to the sea floor. The cuttings accumulate on the sea floor near the discharge point, the distance from and distribution around the discharge depending on water depth, current speeds, and density and degree of clumping of the cuttings.

7.2 Exposure Assessment

Because SBF cuttings containing several percent adhering SBF do not disperse effectively in the water column following discharge, they settle rapidly as clumps of solids through the water column and accumulate on the bottom near the platform discharge site. The rate of settling of SBF cuttings through the water column and the areal extent and concentrations of cuttings accumulating on the bottom depend on the density and size distribution of settling particles, water depths, and the three dimensional water current regime in the water column.

Because of the rapid descent of the cuttings, very little SBF base chemical dissolves or is dispersed in the water column. Brandsma (1996) estimated the maximum concentrations of petroleum in the water column during discharge of OBF cuttings in the North Sea. The maximum oil concentration in the water column was about 1 mg/L when the discharge was of OBF cuttings containing 5 percent oil. It is probable that SBF base chemical concentrations in the water column following discharge of SBF cuttings would be similar to the predicted oil concentrations. By comparison, the acute toxicity of the suspended particulate phase of IO base chemicals ranges from less than 30,000 mg/L to 321,000 mg/L (Table 35).

The acute toxicity of IO and LAO base chemicals to marine algae and copepods is 2,050 mg/L to more than 10,000 mg/L (Table 36). Thus, there is no risk of a toxic response in water column organisms from exposure to SBF cuttings settling through the water column. An increase in surface water turbidity from suspended cuttings particles could affect phytoplankton production on a highly localized scale. However, turbidity plumes are likely to be small and transitory because of the rapid settling of SBF cuttings.

Brandsma (1996) modeled the initial accumulation of OBF cuttings on the bottom following discharge of 300 m³ OBF cuttings containing 0.3 to 19.6 percent oil to the North Sea from platforms in 30 to 250 m of water. He

estimated the area of sea floor that would be contaminated to a depth of 4 cm or 10 cm with more than 1000 mg/kg of oil. 1000 mg/kg oil was considered to be the threshold for significant benthic biological effects of oil from OBF cuttings accumulations (Berge 1996).

The estimated seabed area containing more than 1000 mg/kg oil in the 4-cm sediment layer ranged from 0 to 9.5 hectares (0 to 95 km²) depending on the oil content of the cuttings. If the OBF cuttings were mixed in sediments to a depth of 10 cm, the area containing more than 1000 mg/kg oil decreased to 0 to 7.4 hectares. The largest areas of high estimated oil concentrations in sediments were associated with discharges of cuttings containing the highest concentrations of oil. Settling and deposition of SBF cuttings probably would be similar to that of OBF cuttings.

In the simulated discharges of OBF cuttings containing 15.8 and 19.6 percent oil, the smallest area of sediments containing more than 1000 mg/kg oil (1.6 to 1.9 hectares assuming a mixing depth of 4 cm) was at the deepest site (250 m). The predicted area of sediments containing more than 1000 mg/kg oil was reduced to 1.2 hectares when the concentration of oil in the discharged cuttings was reduced to 5.1 percent. If modeled mixing depth in sediment was increased to 10 cm, oil concentration in sediments did not exceed 1000 mg/kg.

At the deeper end of the range of continental slope depths in the Gulf of Mexico, it is highly likely that the area of deposition of SBF cuttings on the bottom will be much greater than predicted by Brandsma (1996). SBF concentrations in sediments greater than 1000 mg/kg are likely to cover a smaller area, if concentrations exceed 1000 mg/kg at all. Current speeds and directions at different depths in the water column will be the main determinant of the area of SBF cuttings deposition and the distance from the platform within which high concentrations of cuttings in sediments will occur.

There is a long history of WBF use offshore in the Gulf of Mexico. However, drilling is more rapid and costs are lower with SBFs than with WBFs, particularly if SBF cuttings can be discharged (Burke and Veil, 1995). It is highly likely that SBFs will largely replace WBFs in the deep-water Gulf of Mexico where drilling costs are high. Even though WBFs are used for the upper portions of wells, SBFs probably will be used for the more difficult sections or when problems requiring the special properties of SBFs are encountered. Thus, the amount of SBF cuttings discharged per well in the deep Gulf of Mexico will probably be similar to the amount of SBF cuttings discharged per well offshore in the North Sea and other outer continental shelf and slope areas of the world.

For the risk assessment, we have assumed a conservative upper-bound estimate that 1 hectare of sea floor near a drilling site on the continental slope will contain surficial sediments with more than 1000 mg/kg SBF immediately following discharge of SBF cuttings from the platform. Over time, the area of sea floor sediments containing more than 1000 mg/kg SBF base chemical will decrease through biodegradation and sediment resuspension and transport. The rate of resuspension and transport probably will be very low at the water depths characteristic of the continental slope. Vertical mixing in sediments by bioturbation also is unlikely to contribute much to diluting SBF cuttings concentrations in surficial sediments. Thus, the main mechanism of loss of SBF from deep-water sediments will be biodegradation.

Although laboratory and simulated seabed studies have shown that SBF base chemicals are biodegradable under aerobic and sometimes anaerobic conditions, results from field monitoring studies are mixed and equivocal. Thus, it is uncertain if SBFs, particularly PAOs (Gardline, 1998), biodegrade faster than low-toxicity mineral oils under field conditions, particularly if the SBF concentration in sediments is high (Figure 6). Esters definitely do biodegrade in offshore sediments, causing localized sediment anoxia.

In deposition scenarios modeled by Brandsma (1996), a concentration of 1000 mg/kg oil in a 4-cm sediment layer corresponded to a deposition density of 74.2 g/m² (7.42 mg/cm²). At this concentration, PAO base chemical had a biodegradation half-life in the NIVA simulated seabed test of 207 days (Table 30). The degradation half-life for IO and LAO base chemicals at this approximate deposition density in sediment would be 65 to 104 days (Table 28). Thus, the area of sediments containing more than 1000 mg/kg SBF base chemical will decrease substantially within one year after SBF cuttings discharge. A conservative estimate of the decrease in the "affected area" is 75 percent/year if LAO or IO cuttings are discharged. If this assumption is used, the area of sediments containing more than 1000 mg/kg SBF decreases from 10,000 m² immediately after completion of cuttings discharge, to 2500 m² after one year and 625 m² after two years.

7.3 Effects Assessment

As discussed above, biological effects in benthic communities from deposition of SBF cuttings may be caused by toxicity of the drilling fluid ingredients, effects of sediment anoxia caused by biodegradation of organic chemicals in the SBF cuttings, direct burial by drill cuttings solids, and changes in texture and physical/chemical properties of the sediments. The sensitivity of benthic fauna of the continental slope of the Gulf of Mexico to these effects of cuttings deposition is largely unknown. Therefore, it is not possible to predict which of these effects is likely to contribute most to any possible adverse effects of SBF cuttings deposition on benthic communities.

IO and LAO base chemicals and SBFs had a low to moderate toxicity in solid-phase tests (Tables 38 and 39). In most cases the acute toxicity of the SBFs was well above 1000 mg/kg dry sediment. The test species were amphipods and bivalve mollusks. The dominant benthic fauna in slope sediments are polychaetes. Polychaetes vary widely in sensitivity to chemical toxicity. Some species, such as *Capitella*, are tolerant to many environmental stresses, and may replace other species in SBF-contaminated sediments (Gjøs et al. 1991; Daan et al. 1996). When SBF concentrations in sediments exceed about 1000 mg/kg, SBF toxicity may contribute to effects of SBF cuttings on the benthos.

In the UK sector of the North Sea, concentrations of linear paraffin SBF above about 500 mg/kg in sediments were associated with decreases in abundance and diversity of benthic fauna (data from UKOOA). Near a well site in the Gulf of Mexico, sediments containing more than about 3000 mg/kg of PAO SBF (measured as total petroleum hydrocarbons) supported only depauperate benthic communities (Candler et al. 1995).

Field surveys of impacts of SBF cuttings discharges on benthic environments usually document accumulation of SBF cuttings in sediments near the discharge site and, in some cases changes in the composition and diversity of the benthic fauna in sediments containing the highest concentrations of SBFs. When effects are observed, changes in benthic communities usually include a decrease in the number of taxa and biological diversity and either a decrease or an increase in the total number of individuals of benthic fauna present. Often, the species composition of the benthic community is different in SBF-contaminated and clean sediments. These benthic community responses often are associated with a decrease in oxygen concentration in surficial layers of sediments. These community changes are typical responses to organic enrichment of the sediments (Pearson and Rosenberg 1978). An increase in the concentration of biodegradable organic matter in sediments stimulates growth of resident bacterial and fungal consortia that degrade the organic matter and consume available oxygen. With the depletion of sediment oxygen, the resident microbiota use alternative electron acceptors to oxidize the organic matter, producing hydrogen sulfide, ammonia, and possibly methane as waste products. Some species of benthic fauna are sensitive to low oxygen concentrations or high concentrations of hydrogen sulfide or ammonia and are eliminated from the community; other species can tolerate these chemical changes and they may colonize the affected substrate in large numbers.

Organic enrichment appears to be the main mechanism of adverse impact of OBF and SBF cuttings on benthic communities. Field studies of OBF cuttings discharges have indicated that sediments may become anaerobic if they contain 1000 mg/kg or more of mineral oil (Vik et al., 1996a). Biodegradability of SBFs is similar to or greater than that of diesel fuel or mineral oils (Table 28). Esters (the most biodegradable SBF) may cause sediment anoxia at concentrations well below 1000 mg/kg (Daan et al. 1996). IO and LAO SBFs did not cause sediment anoxia in NIVA simulated seabed tests (Schaanning et al. 1996), but may in the field if concentrations in sediments exceed about 1000 mg/kg. There was a good correlation in NIVA seabed simulation biodegradation studies with SBF between benthic faunal diversity and sediment redox potential (Figure 8), suggesting that oxygen depletion by SBF biodegradation in sediments contributes to effects of SBF cuttings on benthic communities.

Effects of burial with SBF cuttings solids on continental slope benthic fauna are not known. Natural sedimentation rates in slope sediments are very low in most locations, usually just a fraction of a millimeter per year. Cuttings piles up to about 1 m high accumulated on sediments near SBF cuttings discharge sites in the UK Sector of the North Sea (Table 13). The piles occupied areas of up to about 95,000 m². Following drilling with SBFs and discharge of SBF cuttings from a rig in 565 m of water in the northern Gulf of Mexico, there was a thin veneer of cuttings dispersed over much of the bottom in a patchy distribution near the drilling template (Gallaway et al. 1998; Fechhelm et al. 1999). Maximum cuttings accumulation appeared to be 20 to 25 cm thick in some locations. It is

probable that discharges to deeper slope waters of the Gulf will not accumulate to a depth of more than a few centimeters on sediments.

Shallow water benthic animals are able to migrate upward through several centimeters of sediment following burial (Maurer et al. 1986). Small benthic fauna typical of deep-water sediments can not migrate as far as larger macrofauna. Deep-sea benthic fauna, acclimated to sediments with a very low net deposition rate, probably can not migrate vertically for more than a few centimeters. Because of the patchy distribution of SBF cuttings on the bottom, particularly in deeper waters, it is likely that burial effects will be highly localized.

7.4 Risk Characterization

SBF cuttings may accumulate to potentially harmful concentrations in sediments near a drilling rig on the continental slope of the Gulf of Mexico over an area of as much as 10,000 m² (1 hectare: about 0.04 percent of a lease block, 3x3 miles). The distribution of the cuttings on the bottom is likely to be extremely patchy, with small patches of high concentrations interspersed with areas with little or no SBF cuttings accumulation. Where SBFs accumulate to concentrations above about 1000 mg/kg, benthic faunal communities are likely to be adversely affected, primarily by effects of organic enrichment. Species sensitive to low oxygen or high concentrations of sulfide or ammonia may be eliminated. The number of taxa present in surficial sediments will decrease, but the number of individuals of the species remaining may increase. Opportunistic species, not present in benthic communities in nearby clean sediments, may colonize the contaminated sediments. Thus, benthic production may not change much or may even increase. Unless IO or LAO reach very high concentrations in sediments, sediment redox potential is unlikely to drop low enough to eliminate all the benthic macrofauna, as sometimes happens following OBF discharges (Kingston, 1992; Olsgard and Gray 1995).

IO and LAO that have accumulated in the sediments near the well will biodegrade slowly. If esters were used, they probably would degrade rapidly in the sediments, as has been shown for several shallow-water SBF cuttings discharge sites. Sediment resuspension and transport are unlikely to contribute much to the decrease in the concentration of SBFs in deep-water sediments. Benthic communities will recover as SBF concentrations in sediments decrease and sediment oxygen concentrations increase. It is probable that within three to five years of cessation of SBF cuttings discharges, concentrations of SBFs in sediments will have fallen to low enough levels and oxygen concentrations will have increased enough throughout the previously affected area that complete recovery will be possible. The rate of deep-water benthic ecosystem recovery then will depend on the rate of recruitment and recolonization by the benthic fauna characteristic of the area. Because some species of deep-water benthic animals reproduce and grow slowly, complete recovery may require many years. However, ecological succession toward recovery is likely to begin shortly after completion of cuttings discharges and be well advanced within three to five years when SBFs have degraded to low concentrations

8.0 REFERENCES

- Annis, M.R. 1997. Retention of synthetic-based drilling material on cuttings discharged to the Gulf of Mexico. Report for the American Petroleum Institute (API) *ad hoc* Retention on Cuttings Work Group under the API Production Effluent Guidelines Task Force. American Petroleum Institute, Washington, DC. August 29, 1997. Various pages.
- ASTM (American Society for Testing and Materials). 1992. Standard guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. ASTM E1367-92. American Society for Testing and Materials, Philadelphia, PA.
- Atlas, R.M. 1995. Petroleum biodegradation and oil spill bioremediation. *Mar. Pollut. Bull.* 31:178-182.
- Bakke, T., J.S. Gray, R.G. Lichtentaler and K.H. Palmork. 1996. Environmental surveys in the vicinity of petroleum installations on the Norwegian shelf. Report for 1994. Rapport 96:15. Statens Forurensningstilsyn (SFT), Oslo, Norway.
- Berge, J.A. 1996. The effect of treated drill cuttings on benthic recruitment and community structure: main results on an experimental study on a natural seabed. Pages 41-63 In: The Physical and Biological Effects of Processed Oily Drill Cuttings (Summary Report). E&P Forum, London.
- Brandsma, M.G. 1996. Computer simulations of oil-based mud cuttings discharges in the North Sea. Pages 25-40 In: The Physical and Biological Effects of Processed Oily Drill Cuttings (Summary Report). E&P Forum, London.
- Brandsma, M.G., L.R. Davis, R.C. Ayers, Jr. and T.C. Sauer, Jr. 1980. A computer model to predict the short-term fate of drilling discharges in the marine environment. Proceedings of Symposium, Research on Environmental Fate and Effects of Drilling Fluids and Cuttings, January 21-24, 1980, Lake Buena Vista, Florida. Volume I, pp. 588-608.
- Brandsma, M.G. and T.C. Sauer, Jr. 1983. The OOC model: prediction of short-term fate of drilling mud in the ocean. part 1: model description. Proceedings of MMS Workshop on An Evaluation of Effluent Dispersion and Fate Models for OCS Platforms, February 7-10, 1983, Santa Barbara, California, Minerals Management Service, Contract No. 14-21-0001-29122, pp. 58-84.
- Burke, C.J. and J.A. Veil. 1995. Synthetic-based drilling fluids have many environmental pluses. *Oil Gas J.* 93:59-64.
- Candler, J., M. Churan and L. Conn. 1996. Laboratory and field measurements of vapors generated by organic materials in drilling fluids. SPE 35866. Pages 831-843 In: The Third International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc. Richardson, TX.
- Candler, J., R. Hebert and A.J.J. Leuterma. 1997. Effectiveness of a 10-day ASTM amphipod sediment test to screen drilling mud base fluids for benthic toxicity. SPE 37890. In: 1997 SPE/EPA Exploration and Production Environmental Conference. Dallas, TX, 3-5 March 1997. Society of Petroleum Engineers, Inc. Richardson, TX. 19 pp.
- Candler, J.E., S. Hoskin, M. Churan, C.W. Lai and M. Freeman. 1995. Seafloor monitoring for synthetic-based mud discharged in the Western Gulf of Mexico. SPE 29694. Pages 51-69 In: SPE/EPA Exploration & Production Environment Conference. Houston, TX, 27-29 March 1995. Society of Petroleum Engineers, Inc. Richardson, TX.

- Candler, J.E., S.P. Rabke and J.J. Leuterman. 1999. Predicting the potential impact of synthetic-based muds with the use of biodegradation studies. SPE 52742. In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. SPE., Inc. Richardson, TX. 17 pp.
- Candler, J.E., J.H. Rushing, and A.J.J. Leuterman. 1993. Synthetic-based mud systems offer environmental benefits over traditional mud systems. SPE 25993. Pages 485-499 In: SPE/EPA Exploration & Production Environmental Conference. San Antonio, TX, 7-10 March 1993. Society of Petroleum Engineers, Inc. Richardson, TX.
- Carlson, T. and T. Hemphill. 1994. Meeting the challenges of deepwater Gulf of Mexico drilling with non-petroleum ester-based drilling fluids. SPE 287349. Pages 669-682 In: SPE International Petroleum Conference & Exhibition of Mexico, Veracruz, Mexico, Oct. 10-13, 1994. Society of Petroleum Engineers, Richardson, TX.
- Chénard, P.G., F.R. Engelhardt, J. Blane and D. Hardie. 1989. Patterns of oil-based drilling fluid utilization and disposal associated with waters on the Canadian offshore frontier lands. Pages 119-136 In: F.R. Engelhardt, J.P. Ray, and A.H. Gillam, Eds., *Drilling Wastes*. Elsevier Applied Science, London.
- Chessels, M., D.W. Hawker and D.W. Connell. 1993. Influence of solubility in lipid on bioconcentration of hydrophobic compounds. *Ecotoxicol. Environ. Saf.* 23:260-273.
- Chiou, C.T., D.W. Schmedding and M. Manes. 1982. Partitioning of organic compounds in octanol-water systems. *Environ. Sci. Technol.* 16:4-10.
- Connell, D.W. 1993. The octanol-water partition coefficient. Pages 311-320 In: P. Calow, ed., *Handbook of Ecotoxicology*. Vol. 2. Blackwell Scientific Pub., London.
- Continental Shelf Associates, Inc. 1998. Joint EPA/Industry screening survey to assess the deposition of drill cuttings and associated synthetic based mud on the seabed of the Louisiana Continental Shelf, Gulf of Mexico. Prepared for: API Health & Environmental Sciences Dept., Washington, DC. Data Report. Continental Shelf Associates, Inc., Jupiter, FL. 58 Pages plus appendices.
- Cordah. 1998. Review of drill cuttings piles in the North Sea. Report for the Offshore Decommissioning Communications Project. Cordah Environmental Consultants, Aberdeen, Scotland. 90 pp.
- Cranmer, G.J. and A. Sande. 1991. Summer Report of Seabed Studies to Verify Degradation of Petrofree Ester. Summary Seabed Survey Results from Well 7/12-9 and 2/7-22. BP Exploration. (Cited by Vik et al. 1996a).
- Daan, R., K. Booij, M. Mulder and E.M. van Weerlee. 1996. Environmental effects of a discharge of drill cuttings contaminated with ester-based drilling muds in the North Sea. *Environ. Toxicol. Chemistry.* 15:1709-1722.
- Daan, R. and M. Mulder. 1993. A study of possible environmental effects of WBM cuttings discharge in the North Sea, one year after termination of drilling. NIOZA-Rapport 1993-16. Netherlands Institute for Sea Research, Texel, The Netherlands. 17 pp.
- Darley, H.C.H. and G.G. Gray. 1988. *Composition and properties of drilling and completion fluids*. Fifth Edition. Gulf Publishing Co., Houston, TX. 643 pp.
- Davies, J., J. Addy, R. Blackman, J. Blanchard, J. Ferbrache, D. Moore, H. Sommerville, A. Whitehead and T. Wilkinson. 1983. Environmental effects of oil based mud cuttings. Joint Working Group of: UKOOA Clean Seas and Environmental Committee; Dept. of Energy; Dept. of Agriculture and Fisheries of Scotland; and Ministry of Agriculture Fisheries and Food. 24 pp.

- Davies, J.M., D.R. Bedborough, R.A.A. Blackman, J.M. Addy, J.F. Appelbee, W.C. Grogan, J.G. Parker and A. Whitehead. 1989. Environmental effect of oil-based mud drilling in the North Sea. Pages 59-90 In: F.R. Engelhardt, J.P. Ray, and A.H. Gillam, eds., *Drilling Wastes*. Elsevier Applied Science Publishers, London.
- Delvigne, G.A.L. 1996. Laboratory investigations on the fate and physicochemical properties of drill cuttings after discharge into the sea. Pages 16-24 In: *The Physical and Biological Effects of Processed Oily Drill Cuttings* (Summary Report). E&P Forum, London.
- Dicks, B., T. Bakke, and I.M.T. Dixon. 1986/87. Oil exploration and production: impact on the North Sea. *Oil Chem. Pollut.* 3:289-306.
- ECETOC (European Chemical Industry Ecology and Toxicology Centre). 1996. The role of bioaccumulation in environmental risk assessment: the aquatic environment and related food webs. European Chemical Industry Ecology and Toxicology Centre, Brussels, Belgium.
- Elf Akuamiljo 1996. Biodegradability of chemical substances in seawater. Results of all four OSPARCOM ring tests. Elf Akuamiljo at Institute des Amenagements Regionaux et de l'Environnement. November 1996.
- EPA (Environmental Protection Agency). 1992. Framework for ecological risk assessment. EPA/630/R-92/001. Risk Assessment Forum, U.S. Environmental Protection Agency, Washington, DC.
- EPA (Environmental Protection Agency). 1996. Oil and gas extraction point source category; final effluent limitations guidelines and standards for the coastal subcategory; final rule. Part III. 40 CFR Part 435. *Federal Register*. 61(242):66086,66120-66122.
- EPA (Environmental Protection Agency). 1997. Ecological risk assessment guidance for Superfund: process for designing and conducting ecological risk assessments. interim final. EPA 540-R-97-006. U.S. Environmental Protection Agency, Solid Waste and Emergency Response, Washington, DC.
- EPA (Environmental Protection Agency). 1998. Guidelines for ecological risk assessment. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC. EPA/630/R/002F. April 1998.
- EPA (Environmental Protection Agency). 1999a. Environmental Assessment of Proposed Effluent Limitations Guidelines and Standards of Synthetic-Based Drilling Fluids and Other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category. EPA-821-B-98-019. U.S. Environmental Protection Agency, Office of Water, Washington, DC. February 1999.
- EPA (Environmental Protection Agency). 1999b. Effluent limitations guidelines and new source performance standards for synthetic-based and other non-aqueous drilling fluids in the oil and gas extraction point source category; proposed rule. Part III. 40 CFR Part 435. *Federal Register*. 64(22):5488-5554.
- ERT (Environment & Resource Technology Ltd). 1994a. Bioaccumulation potential of ISO-TEQ base fluid. ERT 94/209. Report to Baker Hughes INTEQ, Houston, TX.
- ERT (Environmental & Resource Technology Ltd.). 1994b. Bioconcentration assessment report. Assessment of the bioconcentration factor (BCF) of ISO-TEQ base fluid in the blue mussel *Milts eludes*. ERT 94/061. Report to Baker Hughes INTEQ, Houston, TX.
- Fechhelm, R.G., B.J. Galaxy and J.M. Farmer. 1999. Deepwater sampling at a synthetic drilling mud discharge site on the Outer Continental Shelf, Northern Gulf of Mexico. SPE 52744. Pages 509-513 In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers. Richardson, TX.
- Ferbrache, J. 1983. A review of the available literature on the marine benthic effects resulting from the discharge of water based mud and cuttings. Report to the UKOOA Oil Base Mud Workgroup, Great Britain.

- Fillio, J.P., TA Hamacker, S.M. Koraido, R.G. Stefanacci, J.T. Tallon and D. Wesolowski. 1987. Production waters associated with the production, processing, transmission, and storage of natural gas: a literature study. Technical Report GRI-87/0126 to the Gas Research Institute, Chicago, IL.
- Friedheim, J.E. and H.L. Conn. 1996. Second generation synthetic fluids in the North Sea: are they better? IADC/SPE 35061. Pages 215-228 In: IADC/SPE Drilling Conference. New Orleans, 12-15 March 1996. Society of Petroleum Engineers, Inc. Richardson, TX.
- Friedheim, J.E., G.J. Hans, A. Park, and C.R. Ray. 1991. An environmentally superior replacement for mineral oil drilling fluids. SPE 23062. Pages 299-311 In: The Offshore Europe Conference. Aberdeen, 3-6 September 1991. Society of Petroleum Engineers, Inc. Richardson, TX.
- Friedheim, J.E. and R.M. Pantermuehl. 1993. Superior performance with minimal environmental impact: a novel nonaqueous drilling fluid. SPE/IADC 25753. Pages 713-726 In: 1993 SPE/IADC Drilling Conference. Amsterdam, 23-25 February 1993. Society of Petroleum Engineers, Inc. Richardson, TX.
- Friedheim, J.E. and A. Patel. 1999. Technical solutions for environmental problems: novel drilling formulations to minimize environmental impact. SPE 52741. In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers, Inc. Richardson, TX.
- Galloway, B.J. (Ed.). 1988. Northern Gulf of Mexico Continental Slope Study. Final Report: Year 4. Volume II. Synthesis Report. OCS Study MMS 88-0053. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Office, New Orleans, LA. 318 pp.
- Galloway, B.J., R.G. Fechhelm, G.F. Hubbard and S.A. MacLean. 1998. Opportunistic sampling at a synthetic drilling fluid discharge site on the continental slope of the northern Gulf of Mexico: The Pompano Development, 13-14 March 1998. Report to BP Exploration, Inc., Houston, TX. LGL Ecological Research Associates, Inc. Bryan, TX. Various pages.
- Gardline Surveys. 1998. Environmental survey of the sediments around the drilling locations at Eire 18/20-1 and 18/20-B wells. September 1998. Report for Enterprise Oil plc.
- Getliff, J.M. and S.G. James. 1996. The replacement of alkyl-phenol ethoxylates to improve the environmental acceptability of drilling fluid additives. SPE 35982. Pages 713-719 In: International Conference on Health, Safety & Environment. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc., Richardson, TX.
- Getliff, J., A. Roach, J. Toyo and J. Carpenter. 1997. An overview of the environmental benefits of LAO based drilling fluids for offshore drilling. Report from Schlumberger Dowell. 10 pp.
- Gjøs, N., F. Orelid, T. Øfsti, J. Smith and S. May. 1991. Ula well site 7/12-9 environmental survey 1991. Senter for Industriforskning, rapport nr 91 02 16-3.
- Goldberg, E.D., V.T. Bowen, J.W. Farrington, G. Harvey, J.H. Martin, P.L. Parker, R.W. Riseborough, W. Robertson, E. Schneider and E. Gamble. 1978. The mussel watch. *Environ. Conserv.* 5:101-125.
- Grahl-Nielsen, O., S. Sporstøl, C.E. Sjøgren and F. Orelid. 1989. The five-year fate of sea-floor petroleum hydrocarbons from discharged drill cuttings. Pages 667-684 In: F.R. Engelhardt, J.P. Ray, and A.H. Gillam, Eds., *Drilling Wastes*. Elsevier Applied Science, London.
- Grassle, J.F. 1977. Slow recolonization of deep-sea sediment. *Nature*, London 265:618-619.
- Grassle, J.F. 1991. Deep-sea benthic biodiversity. The ocean bottom supports communities that may be as diverse as those of any habitat on earth. *Bio-Science* 41:464-469.

- Growcock, F.B., S.L. Andrews and T.P. Frederick. 1994. Physicochemical properties of synthetic drilling fluids. IADC/SPE 27450. Pages 181-190 In: 1994 IADC/SPE Drilling Conference. Dallas, TX, 15-18 February 1994. International Association of Drilling Contractors/Society of Petroleum Engineers, Inc. (IADC/SPE). Richardson, TX.
- Hartley, J.P. 1996. Environmental monitoring of offshore oil and gas drilling discharges – A caution on the use of barium as a tracer. *Mar. Pollut. Bull.* 32:727-733.
- Hawker, D.W. and D.W. Connell. 1985. Relationships between partition coefficient, uptake rate constant, clearance rate constant, and time to equilibrium for bioaccumulation. *Chemosphere* 14: 1205-1219.
- Hawker, D.W. and D.W. Connell. 1986. Bioconcentration of lipophilic compounds by some aquatic organisms. *Ecotoxicol. Environ. Saf.* 11:184-197.
- Hinwood, J.B., A.E. Poots, L.R. Dennis, J.M. Carey, H. Houridis, R.J. Bell, J.R. Thomson, P. Boudreau and A.M. Ayling. 1994. Drilling activities. Pages 123-207 In: J.M. Swan, J.M. Neff, and P.C. Young, eds., *Environmental Implications of Offshore Oil and Gas Development In Australia – Findings of an Independent Scientific Review*. Australian Petroleum Production and Exploration Association, Canberra, Australia.
- Hudgins, C.M. 1991. Chemical usage in north sea oil and gas production and exploration operations. Report prepared for Oljeindustriens Landsforening (OLF). The Norwegian Oil Industry Association, Environment Committee, Stavanger, Norway.
- Hyland, J., D. Hardin, M. Steinhauer, D. Coats, R. Green and J. Neff. 1994. Environmental impact of offshore oil development on the outer continental shelf and slope off Point Arguello, California. *Mar. Environ. Res.* 37:195-229.
- Isnard, P. and S. Lambert. 1988. Estimating bioconcentration factors from octanol-water partition coefficient and aqueous solubility. *Chemosphere* 17:21-34.
- ISO. 1990. BOD test for insoluble substances - Two phase closed bottle test. ISO Protocol TC/147, SC5/WG4 N14.
- Jacques, D.F., H.E. Newman, Jr. and W.B. Turnbull. 1992. A comparison of field drilling experience with low-viscosity mineral oil and diesel muds. IADC/SPE 23881. Pages 341-354 In: 1992 IADC/SPE Drilling Conference. New Orleans, Louisiana, February 18-21, 1992. IADC/SPE Drilling Conference. Richardson, TX.
- Johnsen, S., T.I. Røe and G. Durell. 1998. Dilution and bioavailability of produced water compounds in the northern North Sea. A combined modeling and field study. SPE 46269. In: 1998 SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezuela, 7-10 June 1998. Society of Petroleum Engineers, Inc. Richardson, TX. 11 pp.
- Jones, F.V., C. Hood, and G. Moiseyenko. 1996. International methods of evaluating the discharge of drilling fluids in marine environments. SPE 46825. In: 1998 SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezuela, 7-10 June 1998. Society of Petroleum Engineers, Inc. Richardson, TX. 18 pp.
- Jones, F.V., J.H. Rushing and M.A. Churan. 1991. The chronic toxicity of mineral oil-wet and synthetic liquid-wet cuttings on an estuarine fish, *Fundulus grandis*. SPE 23497. Pages 721-730 In: The First International Conference on Health, Safety and Environment. The Hague, The Netherlands, 10-14 November 1991. Society of Petroleum Engineers, Inc. Richardson, TX.

- Jumars, P.A. 1976. Deep-sea species diversity: does it have a characteristic scale? *J. Mar. Res.* 34:217-246.
- Kenny, P. November 8, 1993. Ester-based muds show promise for replacing some oil-based muds. *Oil Gas J.* 91:88-91.
- Kingston, P.F. 1987. Field effects of platform discharges on benthic macrofauna. *Phil. Trans. Roy. Soc. London* B316:545-565.
- Kingston, P.F. 1992. Impact of offshore oil production installations on the benthos of the North Sea. *ICES J. Mar. Sci.* 49:45-53.
- Lee, B. 1998. The use of synthetics in well drilling fluids for the offshore oil field. American Chemical Society, Div. of Fuel Chemistry. Preprints of Sympotia 43(2):233-237.
- Leuterman, A.J.J. 1991. Environmental considerations in M-I product development. Novasol/Novadril. M-I Drilling Fluids Co., Houston, TX.
- Limia, J.M. 1996. Seabed surveys: the best means to assess the environmental impact of drilling fluid discharges? SPE 36048. Pages 803-813. Society of Petroleum Engineers, Inc. Richardson, TX.
- MacDonald, I.R. 1992. Chemosynthetic ecosystem study literature review and data synthesis. Volumes I-III. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 92-0033 – 92-0035.
- MacDonald, I.R. 1993. Presentation at the Thirteenth Gulf of Mexico Information Transfer Meeting. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA.
- MacDonald, I.R. and W.W. Schroeder. 1993. Chemosynthetic ecosystem studies interim report. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. OCS Study MMS 93-0032. 110 pp.
- Maurer, D., R.T. Keck, J.C. Tinsman, W.A. Leathem, C. Wethe, C. Lord and T.M. Church. 1986. Vertical migration and mortality of marine benthos in dredged material: a synthesis. *Internat. Rev. Ges. Hydrobiol.* 71:49-63.
- McIlroy, W. 1998. Review of BHP's experience into the persistence of drilling fluids pollutants. Pages 121-134 In: International Workshop on Drilling Fluids Ecotoxicology and Biodegradation. Curtin University, Perth, Western Australia, 8-9 October 1998.
- McKee, J.D.A., K. Dowrick, and S.J. Astleford. 1995. A new development towards improved synthetic based mud performance. SPE/IADC 29405. Pages 613-621 In: 1995 SPE/IADC Drilling Conference. Amsterdam, 28 February-2 March 1995. SPE/IADC Drilling Conference. Society of Petroleum Engineers, Richardson, TX.
- Meinhold, A.F. 1999. Framework for a comparative environmental assessment of drilling fluids used offshore. SPE 52746. Pages 515-524 In: 1999 SPE/EPA Exploration and Production Environmental Conference. Society of Petroleum Engineers, Inc. Richardson, TX.
- MMS (Minerals Management Service). 1997. Gulf of Mexico OCS Oil and Gas Lease Sales 169, 172, 175, 178, and 182. Central Planning Area. Final Environmental Impact Statement. OCS EIS/EA MMS 97-0033. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA.
- Moffat, C.F., P.D. Munro and R.M. Stagg. 1998. Development of a solid-phase test for the comparison of the biodegradation rates of synthetic mud base fluids. Pages 14-32 In: International Workshop on Drilling Fluids Ecotoxicology and Biodegradation. Western Australia, 8-9 October 1998.

- Munro, P.D., N.A. Brown, B. Roddie and C.F. Moffat. 1998a. Degradation of an ester-type synthetic mud base fluid in a solid-phase test system: effect of concentration and temperature. Marine Laboratory, Aberdeen Report No. 12/98. Fisheries Research Services, Marine Laboratory. Aberdeen. Scotland. 22 pages plus charts.
- Munro, P.D., B. Croce, C.F. Moffat, N.A. Brown, A.D. McIntosh, S.J. Hird and R.M. Stagg. 1998b. Solid-phase test for comparison of degradation rates of synthetic mud base fluids used in the off-shore drilling industry. *Environmental Toxicology and Chemistry*. 17(10):1951-1959.
- Munro, P.D., C.F. Moffat, L. Couper, N.A. Brown, B. Croce, and R.M. Stagg. 1997a. Degradation of synthetic mud base fluids in a solid-phase test system. Fisheries Research Services Report No 1/97. Scottish Office Agriculture, Environment and Fisheries Department, Marine Laboratory. Aberdeen, Scotland. 9 pp.
- Munro, P.D., C.F. Moffat, and R.M. Stagg. 1997b. Biodegradation of base fluids used in synthetic drilling muds in a solid-phase test system. SPE 37861. Pages 1-9 *In*: 1997 SPE/UKOOA European Environmental Conference. Aberdeen, Scotland, 15-16 April 1997. Society of Petroleum Engineers, Inc. Richardson, TX.
- Munro, P.D., L. Webster, N.A. Brown, C.F. Moffat, and R.M. Stagg. 1997c. Investigation into the degradation of synthetic drilling fluids in a solid-phase test using a closed, brackish water system. Fisheries Research Services Report No 8/97. Fisheries Research Services. Aberdeen. 13 pages plus figures.
- National Research Council. 1983. Drilling discharges in the marine environment. National Academy Press, Washington. 180 pp.
- Neff, J.M. 1987. Biological effects of drilling fluids, drill cuttings and produced waters. Pages 469-538 *In*: D.F. Boesch and N.N. Rabalais, eds., Long-term Effects Of Offshore Oil And Gas Development. Elsevier Applied Science Publishers, London.
- Neff, J.M., M.H. Bothner, N.J. Maciolek, and J.F. Grassle. 1989a. Impacts of exploratory drilling for oil and gas on the benthic environment of Georges Bank. *Mar. Environ. Res.* 27:77-114.
- Neff, J.M., R.J. Breteler, and R.S. Carr. 1989b. Bioaccumulation, food chain transfer, and biological effects of barium and chromium from drilling muds by flounder (*Pseudopleuronectes americanus*) and lobster (*Homarus americanus*). Pages 439-460 *In*: F.R. Engelhardt, J.P. Ray, and A.H. Gillam, eds. Drilling Wastes. Elsevier Applied Science Publishers, London.
- Neff, J.M., R.E. Hillman, and J.J. Waugh. 1989c. Bioaccumulation of trace metals from drilling mud barite by benthic marine animals. Pages 461-480 *In*: F.R. Engelhardt, J.P. Ray, and A.H. Gillam, eds. Drilling Wastes. Elsevier Applied Science Publishers, London.
- Neff, J.M., N.N. Rabalais, and D.F. Boesch. 1987. Offshore oil and gas development activities potentially causing long-term environmental effects. Pages 149-174 *In*: D.F. Boesch and N.N. Rabalais, eds. Long-term Effects of Offshore Oil and Gas Development. Elsevier Applied Science Publishers, London.
- Newman, M.C. and C.H. Jagoe. 1994. Ligands and the bioavailability of metals in aquatic environments. Pages 39-61 *In*: J.L. Hamelink, P.F. Landrum, H.L. Bergman, and W.H. Benson, Eds. Bioavailability. Physical, Chemical, and Biological Interactions. Lewis Publishers, Boca Raton, FL.
- Nishihara, T., S. Saito, and M. Matsuo 1993. Mechanism in bioconcentration of organic chemicals in fish and its structure-activity relationship. *Jap. J. Toxicol. Environ. Hlth.* 39:494-508.
- Norman, M. 1997. Esters - the only synthetic option for the next millennium? Presented at the 5th International [IBC] Conference of Minimizing the Environmental Effects of Drilling Operations. Aberdeen, Scotland. 13 pp.

- Norway. 1997. Synthetic drilling fluids. Proposal for a definition of synthetic drilling fluids and experiences on the Norwegian Continental Shelf. SEBA 97/5/5-E. Presented by Norway at the Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Sea-Based Activities (SEBA). Biarritz, France, 17-21 February 1997. 6 pp.
- Norwegian Oil Industry Association Working Group. 1996. Criteria for selection and approval of drilling fluids: with respect to effects on human workers and marine ecological systems. Norwegian Oil Industry Association, Stavanger, Norway. 70 pp.
- OECD (Organization for Economic Co-Operation and Development). 1995. Detailed Review Paper on Biodegradability Testing. Environmental Monograph No. 98. OECD Series on the Test Guidelines Programme, No. 2. Organization for Economic Co-operation and Development, Paris.
- Olsgard, F. and J.S. Gray. 1995. A comprehensive analysis of the effects of offshore oil and gas exploration and production on the benthic communities of the Norwegian continental shelf. *Mar. Ecol. Prog. Ser.* 122:277-306.
- Opperhuizen, A. 1986. Bioconcentration of hydrophobic chemicals in fish. Pages 304-315 *In*: T.M. Poston, and R. Purdy, Eds., *Aquatic Toxicology and Environmental Fate: Ninth Volume*. ASTM STP 921. American Society for Testing and Materials, Philadelphia, PA.
- Patel, A.D. 1998. Choosing the right synthetic-based drilling fluids: drilling performance versus environmental impact. SPE 39508. Pages 1-14 *In*: The First SPE India Oil and Gas Conference and Exhibition. New Delhi, 17-19 February 1998. Society of Petroleum Engineers, Inc. Richardson, TX.
- Payne, J.F., J. Kiceniuk, A. Rahimtula, U. Williams, L. Fancey, W. Melvin and R.A. Addison. 1989. Bioaccumulation of polycyclic aromatic hydrocarbons in flounder (*Pseudopleuronectes americanus*) exposed to oil-based drill cuttings. Pages 427-438 *In*: F.R. Engelhardt, J.P. Ray, and A.H. Gillam, eds., *Drilling Wastes*. Elsevier Applied Science Publishers, London.
- Pearson, T.H. and R. Rosenberg. 1978. Macrobenthos succession in relation to organic enrichment and pollution of the marine environment. *Oceanogr. Mar. Biol. Ann. Rev.* 16: 229-311.
- Pequegnat, W.E. 1983. The ecological communities of the continental slope and adjacent regimes in the northern Gulf of Mexico. Final report to U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA. (Contract No. AA851-CT1-12).
- Phillips, N.W. and B.M. James (eds.). 1988. Offshore Texas and Louisiana marine ecosystems data synthesis. Volume II: Synthesis Report. OCS Study MMS 88-0067. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Office, New Orleans, LA. 477 pp.
- Rabke, S.P. and J.E. Candler. 1998. Reducing potential seafloor impacts from synthetic-based muds with acute benthic toxicity testing. Presented at the 5th Annual International Petroleum Environmental Conference. Albuquerque, New Mexico, October 20-23, 1998. 16 pages plus appendix and charts.
- Rabke, S.P. and J.E. Candler. 1999. Maximizing the discriminatory power for non-aqueous fluids using modified *Leptocheirus plumulosus* sediment toxicity test method. Poster, SETAC Annual Meeting, Philadelphia, PA, Nov. 14-18, 1999. Manuscript from M-I L.L.C, Houston, TX.
- Rabke, S.P., J. Candler and C. Trial. 1998. Development of acute benthic toxicity testing for monitoring synthetic-based muds discharged offshore. Presented at the IBC Conference on Monitoring the Environmental Effects of Offshore Drilling. Houston, TX. 26 pp.
- Rex, M.A. 1983. Geographic patterns of species diversity in deep-sea benthos. Pages 453-472 *In*: G.T. Rowe, ed., *Deep-Sea Biology*. John Wiley & Son, New York.

- Rushing, J.H., M.A. Churan and F.V. Jones. 1991. Bioaccumulation from mineral oil-wet and synthetic liquid-wet cuttings in an estuarine fish, *Fundulus grandis*. SPE 23350. Pages 311-320 In: The First International Conference on Health, Safety and Environment. The Hague, The Netherlands, 10-14 November 1991. Society of Petroleum Engineers, Inc. Richardson, TX.
- Rye, H., T. Nordtug, A. Tobiesen and A. Østeorøt. 1997. Drilling and well chemicals and their environmental impacts. A survey of amounts, ecotoxicological properties, dispersion and impacts in the marine environment. Paper in "Chemistry in the Oil Industry," 6th International Symposium. Ambleside, the Lake District, UK, 14-17 April, 1997. The Royal Society of Chemistry, UK. London. 21 pp.
- Schaanning, M.T. 1995a. Biodegradation of Ultidril base fluid and drilling mud on cuttings deposited in benthic chambers. Norwegian Institute for Water Research, NIVA Report 0-95018, Oslo, Norway. March 20, 1995.
- Schaanning, M.T. 1995b. Evaluation of overall marine impact of the Novadril mud systems. NIVA Report 0-95018. Norwegian Institute for Water Research. Oslo, Norway.
- Schaanning, M.T. 1996. Environmental fate of synthetic drilling fluids from offshore drilling operations. NIVA rapport nr. 3429-96. Norwegian Institute for Water Research. Oslo, Norway.
- Schaanning, M., K. Hylland, R. Lichtenthaler and B. Rygg. 1996. Biodegradation of *Anco Green* and *Novaplus* drilling muds on cuttings deposited in benthic chambers. Report SNO 3475-96. Norwegian Institute for Water Research. Oslo, Norway. 77 pages plus appendix.
- Schaanning, M., R. Lichtenhaler and B. Rygg. 1997. Biodegradation of esters and olefins in drilling mud deposited on Arctic soft-bottom communities in a low-temperature mesocosm. Report SNO 3760-97. Norwegian Institute for Water Research. Oslo, Norway. 57 pages plus appendices.
- Scherrer, P. and G. Mille. 1989. Biodegradation of crude oil in an experimentally polluted peaty mangrove soil. *Mar. Pollut. Bull.* 20:430-432.
- Schüürmann, G. and W. Klein. 1988. Advances in bioconcentration prediction. *Chemosphere* 17: 1551-1574.
- Slater, M., M.H. Hille, and A. Molversmyr. 1995. Commonly used biodegradation techniques for drilling fluid chemicals, are they appropriate? SPE/IADC 29376. Pages 387-397 In: 1995 SPE/IADC Drilling Conference. Amsterdam, 28 February-2 March 1995. SPE/IADC Drilling Conference. Richardson, TX.
- Smith, J. and G. Hobbs. 1993. Ula wellsite 7/12-9 environmental survey 1992. Report FSC/RC/15/92. Field Studies Council Research Centre, UK.
- Smith, J. and S.J. May. 1991. Ula wellsite 7/12-9 environmental survey 1991. Report FSC/RC/13/91. Field Studies Council Research Centre, UK.
- Smith, J. and J.J. Moore. 1990. Ula wellsite 7/12-9 environmental survey, May 1990. Report FSC/RC/15/90. Field Studies Council Research Centre, UK.
- Stagg, R.M., B. Croce, A.D. McIntosh, C. Moffat and S. Hird. 1996. Biodegradation of base-oils used in synthetic drilling muds in an experimental solid-phase sediment system. Fisheries Research Services Report No 3/96. Scottish Office Agriculture, Environment and Fisheries Department, Marine Laboratory. Aberdeen. 40 pp.
- Stagg, R.M. and A. McIntosh. 1996. The effects of drill cuttings on the dab (*Limanda limanda*). Pages 79-103 In: The Physical and Biological Effects of Processed Oily Drill Cuttings. E&P Forum Report No. 2.61/202. E&P Forum, London. April 1996.
- Steber, J., C.P. Herold H. KGaA, and J.M. Limia. 1994. Solving fluid biodegradation in seabed drill cuttings pile. *Offshore*. 57-60.

- Steber, J, C.P. Herold and J.M. Limia. 1995. Comparative evaluation of anaerobic biodegradability of hydrocarbons and fatty derivatives currently used as drilling fluids. *Chemosphere*. 31(4):3105-3118.
- Still, I. and J. Candler. 1997. Benthic toxicity testing of oil-based and synthetic-based drilling fluids. In: Eighth International Symposium on Toxicity Assessment, Perth, Western Australia. May 25-30.
- Suter, G.W. II. 1993. Ecological risk assessment. Lewis Press, Boca Raton, FL. 538 pp.
- Suter, G.W. II and A.E. Rosen. 1988. Comparative toxicology for risk assessment of marine fishes and crustaceans. *Environ. Sci. Technol.* 22:548-556.
- Terrens, G.W., D. Gwyther, M.J. Keough and R.D. Tait. 1998. Environmental assessment of synthetic based drilling mud discharges to Bass Strait, Australia. SPE 46622. Pages 1-14 In: 1998 SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezuela, 7-10 June 1998. Society of Petroleum Engineers, Inc. Richardson, TX.
- Thomann, R.V. 1989. Bioaccumulation model of organic chemical distribution in aquatic food chains. *Environ Sci. Technol.* 23:699-707.
- United Kingdom Offshore Operators Association and United Kingdom Department of Trade and Industry. 1997. Synopsis of review of drill cuttings piles on the United Kingdom Continental Shelf. Agenda Item 5. SEBA 97/5/3-E. Presented by the United Kingdom at the Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Sea-Based Activities (SEBA). Biarritz, France, 17-21 February 1997. 3 pp.
- Veil, J.A., C.J. Burke and D.O. Moses. 1996. Synthetic-based muds can improve drilling efficiency without polluting. *Oil & Gas Journal*. 94(10):49-54.
- Veil, J.A. and J.M. Daly. 1999. Innovative regulatory approach for synthetic-based drilling fluids. SPE 52737. In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers, Inc. Richardson, TX. 5 pp.
- Veil, J.A., J.M. Daly and N. Johnson. 1999. EPA speeds regs for offshore synthetic-based mud. *Oil and Gas Journal*. 97(37): 78-85.
- Vik, E.A., S. Dempsey and B.S. Nesgard. 1996a. Evaluation of available test results from environmental studies of synthetic based drilling muds. Version 4. Aquateam Report Number: 96-010. OLF Project. Acceptance Criteria for Drilling Fluids. Aquateam-Norwegian Water Technology Centre A/S. Oslo, Norway. 127 pp.
- Vik, E.A., B.S. Nesgard, J.D. Berg, S.M. Dempsey, D.R. Johnson, L. Gawel and E. Dalland. 1996b. Factors affecting methods for biodegradation testing of drilling fluids for marine discharge. SPE 35981. Pages 697-711 In: International Conference on Health, Safety & Environment. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc. Richardson, TX.
- Zevallos, M.A.L., J. Candler, J.H. Wood and L.M. Reuter. 1996. Synthetic-based fluids enhance environmental and drilling performance in deepwater locations. SPE 35329. Pages 235-242 In: SPE International Petroleum Conference & Exhibition of Mexico. Villahermosa, Tabasco, Mexico, 5-7 March 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

APPENDIX

ANNOTATED BIBLIOGRAPHY: SYNTHETIC BASED DRILLING MUDS

Annis, M.R. Retention of synthetic-based drilling material on cuttings discharged to the Gulf of Mexico. Report for the American Petroleum Institute (API) *ad hoc* Retention on Cuttings Work Group under the API Production Effluent Guidelines Task Force. American Petroleum Institute, Washington, DC. August 29, 1997. Various pages.

Abstract: *The purpose of this study is to gather and analyze data from Gulf of Mexico wells on the amount of synthetic-based drilling material retained on drill cuttings (geologic formation). A quantity of drilling fluid adheres to drill cuttings that have been separated and discharged from a mud system. Data from 54 wells drilled in the Gulf of Mexico using synthetic-based drilling fluids were compiled to examine data on the retention of synthetic-based drilling material on cuttings that were discharged. The compiled data yielded 738 individual data points. Poly alpha olefin (PAO) and internal olefin (IO) were the two synthetic-based drilling materials for which data were available. On average, the synthetic based drilling material, or base material, comprised 12.0% by weight of the discharge stream (wet weight) with a standard deviation of 4.8. On average, 12.8% of PAO and 9.2% of IO are retained on cuttings following washing.*

Avanti Corporation. 1997. Bioaccumulation of synthetic-based drilling fluids. Report for U.S. Environmental Protection Agency Office of Science and Technology, Washington, DC. Contract 68-C5-0035. Avanti Corporation. Annandale, VA. 16 pp.

Abstract: *The available scientific literature on possible bioaccumulation of base oils from synthetic-based drilling fluids was reviewed. Octanol/water partition coefficients were used as an indication of bioaccumulation potential. Polyalpha olefins and internal olefins have log P_{ow} of 8.57 to 15.4, indicating high hydrophobicity and low aqueous solubility. High log P_{ow} chemicals do not bioaccumulate efficiently, if at all. Esters have a log P_{ow} of 1.69, and could show very limited bioaccumulation. A 10-day uptake, 20-day depuration test yielded a log bioconcentration factor (BCF) for an internal olefin of 5.37 (C_{16} forms) or 5.38 (C_{18} forms). Bioaccumulation of polyalpha olefins could not be demonstrated.*

Avanti Corporation. 1997. Biodegradability of synthetic-based drilling fluids. Report for U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC. Contract 68-C5-0035. Avanti Corporation. Annandale, VA. 20 pp.

Abstract: *The findings of field studies that have been conducted on diesel and mineral oils, and the limited data from field studies of synthetic fluids, show that the major impact of synthetic fluids as drilling fluid components adherent to discharged cuttings will be organic enrichment. This conclusion suggests that, other than the simple quantity of material discharged, the biodegradability of these materials is the single most important factor in assessing their potential environmental fate and effects. Methods for measuring biodegradation of synthetic drilling fluids give highly variable results, and are not relevant to the conditions under which discharged materials will be found (i.e., a largely anoxic, marine sediment matrix). Seabed simulation protocols most closely mimic receiving water conditions. The most important biodegradation data appear to be those that can be obtained from further field studies.*

Avanti Corporation. 1997. Seabed survey review and summary. Report for U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC. EPA Contract 68-C5-0035. Avanti Corporation. Annandale, VA. 51 pp.

Abstract: *Field studies of fates and effects of WBM and SBM were reviewed. There is little information upon which to base any broad conclusions about the potential extent of impacts from SBM. It appears that the area of biological impacts may range from as little as 50 m to as much as 500 m from the platform shortly after discharges cease to as much as 200 m a year later. Ester SBMs appear to be more readily biodegraded in North Sea studies than ether SBM; the Gulf of Mexico study suggests PAO also are less biodegradable than ester SBM. Also, although esters appear to be readily biodegraded, one study indicates the persistence of uncharacterized "minor" impacts on*

benthos after SBM levels have fallen to reference levels. These limited data, however, are not entirely adequate as a basis for any reliable projections concerning the potential nature and extent of impacts from discharges of SBM. Based on basic SBM and marine sediment chemistry, the level of nutrient enrichment from these materials, and the ensuing development of benthic anoxia, resultant adverse benthic community impacts are expected. The extent and duration of these impacts are much more speculative. Severe effects seem likely within 200 m of the discharge; impacts as far as 500 m have been demonstrated. The initiation of benthic recovery seems likely within a year, although it also seems unlikely that it will be complete within one year. The relative impacts of the various types of SBM is completely speculative given the highly limited marine sediment applicability of available laboratory methods for assessing biodegradability and the paucity of field data for laboratory field correlations.

Blanchet, D., A. Audibert and J.F. Argillier. 1998. Anaerobic biodegradability of oil base fluid for invert emulsion drilling fluids. IADC/SPE 39386. Pages 799-806 In: 1998 IADC/SPE Drilling Conference. Dallas, TX, 3-6 March 1998. IADC/SPE Drilling Conference. Richardson, TX.

Abstract: Environmental legislation restricts the use of oil based muds, especially in the North Sea, including their discharge in the form of oily cuttings. Different synthetic based muds (SBM) are proposed for replacing refined oils as the base fluid. These are low toxicity mineral oils, poly or mono α -olefins, acetals, and esters. Controversial data exist concerning their biodegradability under aerobic or anaerobic conditions. Both conditions are representative of offshore drilling activities since the oil present in the cuttings deposited on the seabed can be degraded on the surface through an oxygen-dependent process and in the center of the pile through anaerobic process. For examination of the easy and ultimate anaerobic biodegradability, the ECETOC screening test is generally employed. This procedure was here improved to evaluate the variability due to the digester sludge. The disappearance of the initial substrate is evaluated by gas chromatography analysis that gives information on the alteration of the base oil chemical structure. The potential for anaerobic biodegradability of an oleic acid ester is compared to an α olefin (C_{12} - C_{14}) and fructose used as a reference substrate. A substantial biodegradation of the oleic acid ester is observed; more than 80% of ultimate biodegradation to CO_2 and CH_4 and total primary biodegradability with no accumulation of the corresponding fatty acids. This attests the easy anaerobic biodegradability of the oleic acid ester. In the same conditions, the test performed with the α olefin presents a low-pressure evolution and low CH_4 production confirming the poor anaerobic biodegradability of this type of compounds.

Bodepudi, V., J.M. Wilson and A. Patel. 1998. Drilling fluid type affects elastomer selection. Oil and Gas Journal. 96(43):75-79.

Abstract: The authors discuss the interactions of SBMs with elastomers used in drilling and identify factors to consider in evaluating the compatibility of different SBMs and elastomers. SBMs are selected based on toxicity, biodegradability, thermal stability, viscosity, cost, required performance, and type of application. SBMs can alter properties of elastomers used in down-hole tools. Elastomers to be used in wells drilled with SBMs should be evaluated for their compatibility with the mud.

Burke, C.J. and J.A. Veil. 1995. Potential environmental benefits from regulatory consideration of synthetic drilling muds. ANL/EAD/TM-43. Environmental Assessment Division, Argonne National Laboratory under Contract with the Department of Energy. 28 pp.

Abstract: When drilling exploration and production wells for oil and gas, drillers use specialized drilling fluids, referred to as "muds," to help maintain well control and to remove drill cuttings from the hole. Historically, either water-based muds (WBMs) or oil-based muds (OBMs) have been used for offshore wells. Recently, in response to U.S. Environmental Protection Agency (EPA) regulations and drilling-waste discharge requirements imposed by North Sea nations, the drilling industry has developed several types of synthetic-based muds (SBMs) that combine the desirable operating qualities of OBMs with the lower toxicity and environmental impact qualities of WBMs. This report describes the operational, environmental, and economic features of all three types of muds and discusses potential EPA regulatory barriers to wider use of SBMs.

Burke, C.J. and J.A. Veil. 1995. Synthetic drilling muds: environmental gain deserves regulatory confirmation. SPE 29737. Pages 457-468 In: SPE/EPA Exploration & Production Environment Conference. Houston, TX, 27-29 March 1995. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *Efficient drilling technology is essential to meet the needs of the oil industry. Both the challenges of new oil provinces, especially in offshore waters, and the demands for efficient environmental protection have driven the development of new technology. Drilling mud is a key factor influencing drilling technology used in modern drilling operations. New oil industry developments involve directional and horizontal drilling as well as drilling in frontier areas at greater and greater depths. Such capabilities and conditions demand careful attention to the selection and engineering of efficient mud systems.*

Spent drilling fluids and drill cuttings are among the most significant waste streams from exploration and development activities in the oil and gas industry; they pose a serious and costly disposal problem for offshore operators who must barge spent mud and cuttings to shore for land disposal if they do not meet U.S. Environmental Protection Agency (EPA) discharge limitations or permit requirements. Suppliers of mud systems have responded to this problem. Since 1990, several non-toxic, biodegradable synthetic-based muds (SBMs) with desirable performance and environmental characteristics have entered the market. However, EPA regulations apply mud technology that was available when the regulations were developed, namely water- and oil-based muds (WBMs and OBMs). While EPA requirements appear to have been a major driver behind the development of SBM, now concern is focused on the inhibiting effect of discharge limitations on use of alternative mud technologies.

This paper examines and describes SBM systems recently developed as substitutes for conventional drilling muds. Initially, background information on drilling mud is presented to provide an overview. The paper identifies the advantages and disadvantages of alternative drilling muds and assesses their comparative environmental impact and cost/benefit. The paper also characterizes the regulatory factors that affect the introduction and widespread use of innovative alternative mud technology. Finally, the paper assesses the approach of EPA in administering effluent limitations guidelines (ELGs) and its impact on innovative technology development. It recommends areas of further study and suggests regulatory process improvements to encourage the development and use of alternative mud technologies. The recommendations include:

- *The term “synthetic based fluid” should be clearly and simply defined to include low-toxicity SBM products being developed; and*
- *The static sheen test, as it applies to SBMs, should be replaced or amended with other analytical procedures to ensure the absence of free oil in SBMs. The static sheen test does not effectively determine the presence of contaminants in SBMs because the continuous phase of SBMs is lighter than water and could cause a film on the water.*

Burke, C.J. and J.A. Veil. 1995. Synthetic-based drilling fluids have many environmental pluses. Oil and Gas Journal. 93(48):59-64.

Abstract: *The authors review the properties and benefits of synthetic-based drilling muds used offshore. SBMs have several quantitative benefits compared to WBMs; less waste is produced from a recyclable product; increased use of horizontal drilling reduces the areal extent and the environmental impacts of offshore oil and gas operations; reduced drilling time results in reduced emissions from drilling power sources; and improved drilling performance reduces waste-generating incidents such as pipe stuck in hole and the use of diesel pills, thereby further reducing waste and pollution production. SBMs have several quantifiable benefits compared to OBMs; low toxicity and reduced irritant properties improve worker safety; elimination of diesel as a mud base reduces pollution hazard and risks and improves worker safety.*

Campbell, J.A. 1998. An E&P industry perspective on acceptability criteria for the marine discharge of cuttings drilled with synthetic based drilling. SPE 46704. Pages 1-5 In: 1998 SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezuela, 7-10 June 1998. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *This paper discusses the issues that the oil and gas exploration and production industry (the E&P industry) considers to be of importance in the development of acceptability criteria for the marine discharge of cuttings from drilling with synthetic-based drilling fluids. Synthetic-based drilling fluids are used to improve performance when drilling through sensitive formations, under extremes of temperature and pressure, and when drilling highly deviated wells. Synthetic-based drilling fluids are designed to have improved environmental behaviour, particularly with respect to persistence, compared with conventional oil-based drilling fluids.*

Drilled cuttings must be removed periodically from the drilling rig due to limitations on storage capacity. Drilling operations are often carried out under conditions in which technical and logistical factors make zero discharge operations highly impractical. As a result, marine discharge, subject to appropriate controls, is a management option that must be considered for cuttings from drilling with synthetic drilling fluids.

The E&P industry supports the use of scientific criteria based on consideration of persistence in the receiving environment, toxicity and potential for bioaccumulation to determine the acceptability of marine discharge of drilled cuttings. Consistent with that support, industry associations and individual operators are cooperating with regulators to develop practical laboratory testing protocols and monitoring programs. Progress has been made towards developing practical laboratory techniques to assess the relative degradation rates of different base fluids under conditions relevant to the seabed environment. However, new methods for measuring biodegradation rates should be validated according to accepted procedures before adoption as the basis for regulatory controls.

Practical and robust testing methods are needed to implement acceptability criteria and to provide for the development of new drilling fluid technology. The relationship of acceptability criteria and practical test methods to the complex natural seabed environment needs to be established to provide a reasonable basis for relating test results to environmental effects. The seabed surveys and laboratory studies now underway or recently completed will provide valuable insight into this issue. Based upon these factors, the E&P industry recommends that:

- 1. Acceptability criteria for marine discharge of drilled cuttings from drilling with synthetic-based drilling fluids (1) be developed based on consideration of environmental risk factors such as persistence, toxicity and bioaccumulation, and (2) be implemented by means of practical and robust test methods.*
- 2. Agreement be pursued on clearly defined criteria for the acceptability of synthetic-based drilling fluid materials for discharge to facilitate the development of new and environmentally acceptable drilling fluid technology.*
- 3. Criteria for marine discharge provide for exceptions for essential use on a site-specific basis, considering technical drilling requirements, safety, assessment of environmental risk and the practicality and environmental effects of zero discharge alternatives.*

Candler, J., M. Churan and L. Conn. 1996. Laboratory and field measurements of vapors generated by organic materials in drilling fluids. SPE 35866. Pages 831-843 In: The Third International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *In an era of increasing awareness of worker health issues, one of the key concerns in exploration activities is the exposure of wellsite personnel to vapors generated by organic materials in drilling fluids. Areas on the drilling location with the highest exposure potentials are the shale shakers and mud pits. These areas are often enclosed in rooms and ventilated to prevent unhealthy levels of vapors from accumulating. In continuing efforts to minimize health risks, new products are evaluated to minimize the volatility of organic materials used in drilling fluids.*

This study presents a laboratory technique for measuring vapors generated from organic materials in drilling fluids. Using this technique, data are presented comparing the volume of vapors generated from diesel oils, mineral oils,

synthetic fluids, and a water-miscible glycol. Synthetic fluids generated 0.62 to 37 ppm (average 9 ppm) vapors at 60-70°C. The dominant vapor from ester-based fluid was 2-ethylhexanol. Field data collected from the shaker and mud pit areas of drilling operations was used to validate the laboratory study to field conditions. Vapor concentrations at the shale shaker during synthetic fluid processing was 0.3 ppm, much lower than vapor concentrations during used of oil-based fluids. The potential health effects of the collected vapors were considered low for synthetic-based fluids.

Candler, J., R. Hebert, and A.J.J. Leuterman. 1997. Effectiveness of a 10-day ASTM amphipod sediment test to screen drilling mud base fluids for benthic toxicity. SPE 37890. In: 1997 SPE/EPA Exploration and Production Environmental Conference. Dallas, TX, 3-5 March 1997. Society of Petroleum Engineers, Inc. Richardson, TX. 19 pp.

Abstract: *The introduction of synthetic-based drilling fluids has challenged both industry and the Environmental Protection Agency to investigate benthic toxicity testing. The need for a synthetic-based mud screening tool has been highlighted by the recommendation by the Coastal Effluent Limitation Guidelines that benthic testing to be included in offshore general permits. Outside of the oilfield, development of solid phase testing of dredged material has led to standardized benthic testing protocols accepted by the EPA. ASTM E1367-92, used with *Ampelisca abdita* and *Corophium volutator* on sediments spiked with various base fluids, was able to distinguish synthetic-based muds from oil-based muds. It is demonstrated in this paper that analysis of other test species using ASTM E1367-92, and additional testing with *A. abdita*, can lead to rapid development of a benthic screening tool for incorporation into the next round of offshore general permits. This should promote the continued positive development of synthetic-based drilling fluid technology.*

Candler, J.E., S. Hoskin, M. Churan, C.W. Lai and M. Freeman. 1995. Seafloor monitoring for synthetic-based mud discharged in the Western Gulf of Mexico. SPE 29694. Pages 51-69 In: SPE/EPA Exploration & Production Environment Conference. Houston, TX, 27-29 March 1995. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *Synthetic-based muds have been used to simultaneously improve drilling and environmental performance. The fate and effects of synthetic-based mud discharges in the marine environment have been issues of concern with the drilling industry and governmental agencies. Most of the environmental data on synthetic-based muds have been generated under laboratory conditions. This study uses field-collected data to investigate the fate and effects of a polyalphaolefin synthetic-based drilling fluid.*

The first well drilled in the Gulf of Mexico using synthetic-based mud was completed in June 1992. Approximately 441 bbl of cuttings and 354 bbl of synthetic-based mud were discharged over a 9-day period. Three sampling trips made to the discharge location over a 2-year period (June 1992 shortly after completion of drilling, February 1993, and June 1994) to collect sediment samples for chemical and biological analysis. The sediment samples were analyzed for synthetic base chemicals (as total petroleum hydrocarbons, TPH, by infrared analysis) and barium. On the third trip, infaunal samples also were taken.

In June 1992, shortly after completion of drilling, TPH concentrations in sediments near the platform ranged from background levels of 24 to 76 mg/kg 2,000 m from the discharge to a high of 134,428 mg/kg 50 m to the south of the discharge. The distribution of the SBM in sediments was very uneven, but correlated well with concentrations of barium. The highest concentration of barium in sediments was 47,437 mg/kg 50 m south of the platform. Two years later, sediment TPH concentrations had declined to not detectable at the 2,000-m stations to 19,110 mg/kg at a station 25 m south of the drilling site. Concentrations were below 1,000 mg/kg at all stations further than 50 m from the discharge site. Barium concentrations still were elevated in sediments from several stations.

Two years after discharges of synthetic-based cuttings were completed, an area within 50 m of the discharge point continued to exhibit alterations in the benthic community not normally associated with water-based mud discharges. Sediments from 25 m and 50 m south and 25 m west of the discharge site had benthic communities with fewer taxa, numbers of individuals, and lower diversity than sediments from other sampling locations. The study indicates that poly alpha olefin synthetic-based mud exhibits significant improvements over oil-based mud in terms of removal of organic contamination and minimization of adverse effects on the benthic community.

Candler, J.E., S.P. Rabke and J.J. Leuterma. 1999. Predicting the potential impact of synthetic-based muds with the use of biodegradation studies. SPE 52742. In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers, Inc. Richardson, TX. 17 pp.

Abstract: *The use of synthetic based muds (SBMs) can improve drilling performance and reduce the volume of pollution generated by offshore drilling operations. Investigations into the environmental impact of SBMs to date have concentrated on the seafloor. The biodegradation rate of an SBM is an important factor in determining the overall environmental performance. Laboratory biodegradation tests are an inexpensive alternative to conducting field studies. However, most of the tests have been designed for water-soluble compounds and reproducible results are difficult to obtain with regularity for hydrophobic materials like SBMs. For this study, a variety of base fluids were tested using the SOAEFD (Scottish Office of Agriculture, Environment and Fisheries Department) solid-phase test. Several biodegradation test protocols were compared. The conclusions of the study were:*

- *Biodegradation is a technology control that can be used to minimize potential impacts associated with SBM use.*
- *Other environmental parameters than biodegradation are also important and no one parameter will be able to universally identify the best SBM technology.*
- *The conservative approach to ensuring that end users minimize their long-term liability is to assume that under some discharge conditions base fluids will need to biodegrade under both aerobic and anaerobic conditions and that a minimum performance level will need to be required for both aerobic and anaerobic conditions.*
- *Use of biodegradation as a performance requirement for SBMs has experienced the challenges of environmental microbiology.*
- *The suggested design goals for a BAT biodegradation test are: maximum discriminatory power; practicality of implementation; ranking of known test substances as expected; and ecological relevance.*
- *Anaerobic biodegradation test have offered the highest discriminatory power to date.*
- *Most biodegradation tests (including the SOAEFD solid-phase test) used to date on SBMs are subject to % coefficients of variability greater than 30 for some base fluids.*
- *Closed-bottle tests are less expensive, faster, and more practical than the solid-phase test.*
- *The underlying chemical model for biodegradation performance is documented in the scientific literature.*
- *The aerobic test results have not always matched the predicted performance of the predictive model.*
- *The anaerobic test results match the predictive model in the case of ester, olefin, and paraffin (mineral oil) performance.*
- *The NIVA test appears to rank the base fluids more consistently than the SOAEFD test.*
- *For the SOAEFD protocol, the ranking of test materials appears to be an artifact of the testing conditions.*
- *The NIVA test has the most ecological relevance.*
- *The SOAEFD solid-phased test approaches biodegradation from field conditions but suffers from testing artifacts.*
- *Closed-bottle tests are ecologically relevant because they measure aerobic and anaerobic degradation.*

- *Field studies may, over time, help improve and validate the ecological relevance of the test method selected.*
- *Continued development of closed-bottle techniques and solid-phase tests is justified.*
- *Due to lack of time, closed-bottle and solid-phase tests need to be tested quickly so that decisions can be made in a timely manner.*

Candler, J.E., J.H. Rushing and A.J.J. Leuterma. 1993. Synthetic-based mud systems offer environmental benefits over traditional mud systems. SPE 25993. Pages 485-499 In: SPE/EPA Exploration & Production Environmental Conference. San Antonio, TX, 7-10 March 1993. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *This paper addresses critical issues concerning the regulation of synthetic-based fluids in Outer Continental Shelf waters. Synthetic-based muds were not envisioned when discharge criteria were formulated a decade ago. It is critical that the U.S. Environmental Protection Agency investigate this new category, since the original permit language and discharge criteria may inhibit the utilization of this new technology and prevent the realization of volume reduction that can be achieved using synthetic-based muds.*

To date, the EPA has not addressed the use of inhibitive mud systems as a control technology for reducing the quantity of pollutants. Drilling through shale formations is an integral part of drilling wells in the Gulf of Mexico. Solving problems associated with these formations can benefit the EPA, industry, and the environment. The use of synthetic-based muds offers greater waste reducing capabilities than water-based muds. They also permit drilling in areas that now require oil-based mud to combat troublesome shales. Compared to hauling oil-based mud, synthetic-based muds offer significant non-water quality advantages in the areas of air pollution, worker safety, reduction of potential spills, and reduction in landfill usage.

Carlson, T. and T. Hemphill. 1994. Meeting the challenges of deepwater Gulf of Mexico drilling with non-petroleum ester-based drilling fluids. SPE 28739. Pages 669-682 In: SPE International Petroleum Conference & Exhibition of Mexico. Veracruz, Mexico, 10-13 October 1994. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *The search for recoverable hydrocarbons in the Gulf of Mexico has moved into increasingly deeper waters. Since its introduction in the Gulf of Mexico in 1993, the ester-based drilling fluid system has been used on five deepwater wells. This paper describes the applications of the ester-based system and its ability to handle the special challenges of deepwater drilling in the Gulf of Mexico. Ester-based drilling fluids have proven to be top performers in tow of the most difficult drilling environments known today: extended reach and deepwater drilling.*

Chapman, P.J. 1997. Thin layer chromatographic analysis for detection of crude oil contamination in synthetic- and enhanced mineral oil-based muds. Draft report from Gulf Ecology Division (NHEERL), U.S. EPA, Gulf Breeze, FL. 5 pp.

Abstract: *This is a draft protocol for determining crude oil in SBM by thin-layer chromatography. Organic matter is extracted from the SBM with a volatile organic solvent, applied to a silicon-coated TLC plate with fluorescent indicator. The plate is developed with suitable organic solvents and bands of aromatic hydrocarbons (indicative of petroleum) are quantified by comparison to the fluorescence intensity of standards developed concurrently.*

Churan, M., J.E. Candler, and M. Freeman. 1997. Onsite and offsite monitoring of synthetic-based drilling fluids for oil contamination. SPE 37906. Pages 179-192 In: 1997 SPE/EPA Exploration and Production Environmental Conference. Dallas, TX, 3-5 March 1997. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *The development of synthetic-based drilling fluids (SBMs) has generated the need for new analytical techniques to identify oil contamination and to distinguish SBMs from oil-base muds (OBMs). In response to this need, laboratory techniques using gas chromatography/mass spectrometry (GC/MS) and field techniques using portable gas chromatography with a flame ionization detector (GC/FID) have been developed and successfully*

applied to SBM in the North Sea, Gulf of Mexico, and other global locations. This paper describes the analytical techniques and equipment used to monitor SBMs and reviews field case histories where contamination of SBM was identified.

The two methods have been evaluated with PAO, LAO, IO, and ester synthetic base fluids and drilling muds. The GC/MS method has lower detection limits than the GC/FID method. The GC/MS method has been used on more than 2000 samples from more than 200 wells in the U.S. Gulf of Mexico, Norway, UK, Holland, Australia, Mexico, and Germany. These methods have been successful in identifying contamination, most notably from crude oil, in SBMs. Hydrocarbon contamination from oil-based drilling muds also has been detected.

Cobby, G.L. and R.J. Craddock. 1999. Western Australian Government decision - making criteria involved in the regulation of drilling fluids offshore. APPEA Journal. 39(Part 1):600.

Abstract: Traditional regulatory regimes have focused upon the regulation of classes of drilling fluids based on their chemical category. The Western Australian Department of Minerals and Energy (WADME) has developed an alternative approach to the regulation of drilling fluids offshore. This alternate approach is based on an objective case-by-case assessment of each drilling proposal. The WADME assesses the likelihood and consequence (environmental risk) of potential environmental events associated with the total drilling proposal in determining the acceptability of that proposal.

This approach uses a framework of assessment criteria to assist in decision making. These criteria include the environmental sensitivity of the well location; the oceanographic conditions and the potential for cuttings accumulation; the type and quantity of the proposed drilling fluid and cuttings; the method of cuttings disposal; the environmental performance of the drilling fluid under standard test protocols and the technical justification for the proposed use of the drilling fluids. This framework offers a more holistic assessment of the potential environmental impacts of a drilling proposal. This paper considers each criterion in this assessment and introduces cuttings pile removal as a topic for discussion.

Collins, G.J. and W.W. White. 1995. Improved practices, synthetic mud drive record 24-hy drilling. World Oil. May 1995:35-39.

Abstract: Revised and improved drilling practices resulted in an increased rate of penetration (ROP), improved hole cleaning, decreased circulating time, fewer instances of stuck pipe, and reduced total drilling days. In the central Gulf of Mexico, a total-project concept helped Marathon drill back-to-back record 24-hr footages. Methods and philosophy described in this article allow drillers to choose optimum technologies, tools, materials and service performance for achieving optimum or lowest cost per foot rather than always using low bid.

Continental Shelf Associates, Inc. 1998. Joint EPA/Industry screening survey to assess the deposition of drill cuttings and associated synthetic based mud on the seabed of the Louisiana Continental Shelf, Gulf of Mexico. Prepared for: API Health & Environmental Sciences Dept., Washington, DC. Data Report. Continental Shelf Associates, Inc., Jupiter, FL. 58 Pages plus appendices.

Abstract: A joint oil industry coalition sponsored a screening survey in the northwestern Gulf of Mexico to gain preliminary information on SBM cuttings deposition, SBM concentrations in marine sediments near platforms that recently have discharged SBM cuttings, nearfield sediment anoxia, characteristics of benthic communities near SBM cuttings discharges, and the toxicity of sediments near platforms.

Field sampling was preformed in August 1997 around three platforms off Louisiana: Grand Isle 95A, South Marsh Island 57C, and South Timbalier 148 E-3. Sediment sampling was preformed at each platform in a radial grid at distances of 50, 150, and 2,000 m from the platform. Sediment grab samples were collected at each station for analysis of SBM-associated hydrocarbons, total organic carbon, polycyclic aromatic hydrocarbons, sediment grain size, presence of drill cuttings, odor, visual characteristics, and, at selected stations oxidation-reduction potential. Grab samples for macroinfaunal analysis were collected at the Grand Isle and Marsh Island platforms, and grab samples for sediment toxicity testing were collected at selected stations around all three platforms.

Hydrographic profiles at the three platforms indicated the presence of a pycnocline in this area of the Gulf during August. Deep water in much of the area was hypoxic. A near-bottom nephroid layer was detected around the platforms. The bottom water hypoxia and nephroid layer are widespread during the summer off Louisiana.

SBM-hydrocarbons were detected in some sediment samples near the platforms. A sediment sample from GI 95A Station 1 contained 3% TOC and 11,000 mg/kg wet weight SBM-hydrocarbons. Sediment in this sample had an *eH* of -380 mV, characteristic of an anoxic sediment.

Sediment toxicity was determined with the amphipods *Leptocheirus plumulosus* and *Ampelisca abdida*. Survival of the amphipods in all sediment samples was about 91% and 86%, respectively, indicating no toxicity. The sediment samples used for bioassays did not contain measurable concentrations of SBM-hydrocarbons.

Daan, R., K. Booij, M. Mulder and E.M. van Weerlee. 1996. Environmental effects of a discharge of drill cuttings contaminated with ester-based drilling muds in the North Sea. *Environmental Toxicology and Chemistry*. 15(10):1709-1722.

Abstract: A field-monitoring program has been carried out to assess the environmental effects associated with drill cutting discharges at a drilling location in the North Sea, after drilling with ester-based muds. The study included a baseline survey just before drilling started and three postdrilling surveys, 1, 4, and 11 months after termination of drilling. During these surveys, ester concentrations and macrofauna densities were determined at distances between 75 and 3,000 m from the well. For the first and second postdrilling surveys, ester concentrations ranged between 2 and 4,700 mg·kg⁻¹ dry sediment. During the third survey, esters were detected up to 200 m from the platform, with concentrations between 1 and 250 mg·kg⁻¹ dry sediment. Between 500 and 3,000 m, ester concentrations were below detection level. The half-life was estimated at 133 d. This value reflects the composite effects of biodegradation and sediment relocation. During the second postdrilling survey, a reduced abundance as well as a reduced species richness of the macrofauna was observed up to 200 m from the well. Also, the presence of *Capitella capitata* was an obvious sign of disturbed sediment conditions in this area. A few species showed abundance gradients over the whole sampling transect and occurred in reduced abundance up to 500 or 1,000 m compared to the 3,000-m reference station. The third postdrilling survey clearly revealed effects at 75 to 200 m from the well. Although the results of the present study show that effects had not completely disappeared after 1 year, there are signs of recovery of the macrobenthos, because a reasonable number of species had recolonized the area in the vicinity of the well site, particularly at 200 m, in fairly high numbers.

de Groot, S.J. 1996. Quantitative assessment of the development of the offshore oil and gas industry in the North Sea. *ICES Journal of Marine Science*. 53:1045-1050.

Abstract: An overview is given of the development of the offshore oil and gas industry in the North Sea and the possible physical impact on the ecosystem in the short and long term. The order of magnitude of several activities (seismic exploration, drilling, platforms, pipelines, subsea facilities, and gas flaring) has been estimated on the basis of information from national authorities and the hydrocarbon industry.

Between 1964 and 1993, the U.K drilled a total of 1530 exploration wells, 997 appraisal wells, and 2256 production wells in the North Sea. The Netherlands drilled 559 exploration, 114 appraisal, and 314 production wells. Norway drilled 771 wells in the North Sea through 1993. Denmark has drilled more than 150 exploration wells and 69 development wells since 1983. An estimated 7 million m³ of cuttings was discharged to the North Sea from all the wells drilled there between 1964 and 1993.

Degouy, D., J.-F. Argillier, A. Demoulin, and F. Velghe. 1993. Biodegradable muds: an attractive answer to environmental legislations around offshore drilling. SPE 26737. Pages 507-514 In: Offshore European Conference. Aberdeen, Scotland, 7-10 September 1993. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: For many years, oil based muds have shown proof of efficiency towards hostile drilling cases especially water-sensitive shales or high temperature wells. However, their use is subjected to more and more constraints due to the fast evolution of environmental legislation. One of the possibilities to avoid this problem while keeping the advantages of oil muds consists in substituting mineral oils by biodegradable vegetable oils such as fatty acid esters.

The esters used in these new oil-based muds have an aerobic biodegradability of more than 85% after 4 weeks and an anaerobic biodegradability of more than 60% after 2 months.

An original formulation has been developed, presenting very good properties up to 140°C. Its performance is based on a proper choice of ester quality, emulsifying system and additives types, and on a severe control of lime concentration to avoid any risks of ester hydrolysis in conjunction to pH and temperature. Its behavior has been studied under bottomhole conditions, using a home made HT/HP flow loop, during aging. Contamination tests demonstrated the ability of ester-based muds to resist possible contamination i.e., sea water, drilled solids, cements during the drilling process.

Derkies, D.L. and S.H. Souders. 1993. Pollution prevention and waste minimization opportunities for exploration and production operations. SPE 25934. Pages 71-76 In: SPE/EPA Exploration & Production Environmental Conference. San Antonio, TX, 7-10 March 1993. Society of Petroleum Engineers. Richardson, TX.

Abstract: *In a continuing effort to encourage improvements in the management of exploration and production (E&P) wastes, the Office of Solid Waste (OSW) of the U.S. Environmental Protection Agency (EPA) is identifying practices and technologies that may contribute to pollution prevention and waste minimization when applied to E&P operations. The sources of this information include trade literature, product literature, and patents. Once identified, details of these practices and technologies may be compiled in a database where the information may be easily accessed and ultimately used in the development of outreach materials for industry.*

Several notable practices and technologies identified to date are discussed in this paper along with results of field trials where available. Although many have already been described in the literature, the intent of the authors is to present a brief overview of selected pollution prevention and waste minimization concepts in order to stimulate further investigation and discussion.

Det Norske Veritas. 1994. Gyda well site 2/1-9 environmental survey 1993. Det Norske Veritas Industry Technical Report nr. 95-3150.

SI. 1992. Gyda well site 2/1-9 environmental survey 1991. Senter for industriforskning rapport nr 91 01 16-3.

SINTEF. 1993. Gyda well site 2/1-9 environmental survey 1992. SINTEF rapport nr. STF27 SF93035.

Abstract: *These three papers provide the results of three field surveys undertaken after drilling the Gyda well offshore Norway with an ether SBM. The surveys found elevated concentrations of ether in sediments at distances up to 200 m from the discharge immediately after drilling. After one year, some samples showed a reduction of ether SBM but others showed an increase. Normalizing the concentration of ether relative to Ba in sediments suggested that there was little evidence for biodegradation after one year (Schaanning et al. 1996). After two years, concentrations of ether SBM in sediments had declined to very low levels (2-3 mg/kg).*

Elf Akuamiljo 1996. Biodegradability of Chemical Substances in Seawater. Results of all four OSPARCOM ring tests. Elf Akuamiljo at Institute des Amenagements Regionaux et de l'Environnement. November 1996

Abstract: *The objective of this study was to evaluate and compare different procedures for testing biodegradation of chemicals in seawater. The four procedures were suggested by members of the Oslo and Paris Commission (OSPAR) and included: OECD Guideline 306 Closed Bottle Test, Marine BODIS Test, Marine CO₂ Evolution Test, and Marine CO₂ Headspace Test. Four test substances were used, two of which were considered to be readily biodegradable (sodium benzoate and an ester based drilling fluid) and two that were less readily biodegradable (pentaerythritol and an ether drilling fluid). Each material was tested in 18 different laboratories.*

The four methods provided similar results for each of the four substances tested. The tests showed that the ester based drilling fluid was readily biodegradable over the 28 day test period. Percent degradation after 28 days ranged from 25 to 95% but was usually greater than 60%. However, the ether based drilling fluid was considered not biodegradable as the 60% biodegradation threshold set for the test was never achieved. Percent

biodegradation of the ether after 28 days was less than approximately 25% for all four tests.

Environmental Protection Agency. 1999. Development document for proposed effluent limitations guidelines and standards for synthetic-based drilling fluids and other non-aqueous drilling fluids in the oil and gas extraction point source category. EPA-821-B-98-021. Office of Water, Office of Science and Technology, Engineering and Analysis Division, U.S. Washington, DC. Various Pages.

Abstract: *This development document provides a comprehensive description of current and available practices for use and discharge of SBMs to the ocean from offshore platforms. This technical document is used as the basis and justification for recommended effluent limitations guidelines and new source performance standards for synthetic-based and other non-aqueous drilling fluids in the oil and gas extraction point source category (EPA, 1999). The document describes:*

- *the legal authority of EPA to regulate SBM discharge;*
- *the purpose and summary of the proposed regulation;*
- *a definition of SBM and associated waste streams;*
- *a description of the offshore oil industry in the Gulf of Mexico, with emphasis of drilling practices;*
- *a description of data and information gathering for the development document;*
- *selection of pollutant parameters to measure in SBM cuttings;*
- *drilling wastes characterization, control, and treatment;*
- *compliance cost and pollution reduction determination of drilling fluids and drill cuttings;*
- *non-water quality environmental impacts and other factors;*
- *options selection rationale; and*
- *references.*

Environmental Protection Agency. 1999. Effluent Limitations Guidelines and New Source Performance Standards for Synthetic-Based and Other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category; Proposed Rule. Part III. 40 CFR Part 435. Federal Register. 64(22):5488-5554.

Abstract: *EPA is proposing to amend the regulation by providing specific requirements for the discharge of synthetic-based drilling fluids (SBFs) and other non-aqueous drilling fluids. The waste streams that would be limited are drilling fluids and drill cuttings. Controlling the discharge of SBFs as proposed today would reduce the discharge of SBFs by 11.7 million pounds annually. Further, allowing rather than prohibiting the discharge of SBFs would substantially reduce non-water quality environmental impacts compared to the zero discharge option. EPA estimates that allowing discharge will reduce air emissions of the criteria air pollutants by 450 tons per year, decrease fuel use by 29,000 barrels per year of oil equivalent, and reduce the generation of oily drill cuttings wastes requiring offsite disposal by 212 million pounds per year.*

Environmental Protection Agency. 1999. Environmental Assessment of Proposed Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and Other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category. EPA-821-B-98-019. U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division. Washington, DC. Various Pages.

Abstract: This environmental assessment consists of an evaluation of the ecological and indirect human health impacts for the discharge of cuttings contaminated with synthetic-based drilling fluids (SBFs) with respect to discharges to water. In addition, this document describes the environmental characteristics of SBF drilling wastes (e.g., toxicity, bioaccumulation, biodegradation), the types of anticipated impacts, and the pollutant modeling results for water column concentrations, pore water concentrations, and human health effects via consumption of affected seafood. This document does not consider the potential non-water quality environmental effects associated with the proposed rule.

Modeled dilutions of SBM cuttings in the Gulf of Mexico indicate an initial dilution of 1,545-fold within one minute of discharge and a dilution of 35,234-fold within 11 minutes. Toxicities of synthetic base chemicals and drilling muds to benthic organisms have been evaluated. Diesel fuel and mineral oil usually are substantially more toxic than IO, and PAO. Olefin-type synthetic base fluids have log octanol/water partition coefficients ($\log K_{ow}$) generally higher than 9, indicating little or no potential to bioaccumulate in the tissues of marine animals. Esters have a $\log K_{ow}$ of about 1.69, indicating a limited potential to bioaccumulate. One IO containing 16 to 18 carbons was reported to bioaccumulate in mussels.

Environmental Protection Agency. 1996. Oil and Gas Extraction Point Source Category; Final Effluent Limitations Guidelines and Standards for the Coastal Subcategory; Final Rule. Part III. 40 CFR Part 435. Federal Register. 61(242):66086,66120-66122.

Abstract: This regulation establishes effluent limitations guidelines and new source performance standards (NSPS) for direct discharges based on "best practicable control technology currently available" (BPT), "best conventional pollutant control technology" (BCT), "best available technology economically achievable" (BAT), and "best available demonstrated control technology" (BADCT) for new sources.

Fechhelm, R.G., B.J. Gallaway and J.M. Farmer. 1999. Deepwater sampling at a synthetic drilling mud discharge site on the Outer Continental Shelf, Northern Gulf of Mexico. SPE 52744. Pages 509-513 In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers. Richardson, TX.

Abstract: Between 1992 and 1994, BP Exploration drilled ten wells from a single jacket at a depth of 393 meters in MMS Lease Block Viosca Knoll 989 (Pompano Phase I). Production began in October 1994. The second phase, utilizing a subsea template, was drilled between 1995 and 1997 at a depth of 565 meters in Mississippi Canyon Block 28, four miles downslope (Pompano Phase II). Both water based muds and synthetic muds were used. An additional well was drilled at Mississippi Canyon 28 in early 1998. This review describes the procedures used to survey the deepwater seafloor in July 1997 and March 1998 using a remote operated vehicle (ROV). Included are qualitative and quantitative sampling of the bottom sediment for chemical and benthic analyses using core samplers and videotransects for identification and enumeration of fish and large invertebrates.

The goals of this project were to document: the size and extent of the cuttings piles following two+ years of a multi-well development drilling program in the deep Gulf; the concentrations of synthetic based drilling fluids (SBFs) in sediments around the drilling template; and the appearance of the bottom sediments with respect to chemical activity and densities of macrofauna and megafauna at the same locations. The main purposes of the follow-up study were to compare findings with those seen earlier and to identify changes in the structure of the local macrofauna and megafauna biological communities since the July 1997 survey. In 1998, the highest average concentration of Petrofree LE in surface sediments was 49,000 mg/kg northeast of the platform. The highest concentration of Petrofree LE in the 2-5-cm depth interval of sediments was 30,000 mg/kg, also northeast of the platform. Megafauna and sediment macrofauna were more abundant at locations where large amounts of SBF were deposited. Results of both the 1997 and 1998 studies were compared to data collected at similar depths in the eastern and western Gulf during the MMS baseline studies conducted in the 1980s.

Fisk, J.V., R. Wood and J. Kirsner. 1996. Development and field trial of two environmentally-safe water-based fluids used sequentially to free stuck pipe. IADC/SPE 35060. Pages 205-213 In: 1996 International Association of Drilling Contractors & Society of Petroleum Engineers Drilling Conference. New Orleans, Louisiana, 12-15 March 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: Diesel-based spotting fluids have historically been used to free differentially-stuck pipe. Increasing environmental regulatory pressures have prompted the development of environmentally-acceptable water-based spotting fluids. In spite of their widespread application, these new fluids have had only sporadic success in freeing differentially-stuck pipe in the field.

An extensive laboratory research project was initiated to identify potential chemistries that could offer increased performance and maintain environmental acceptability. Literature review revealed that previous spotting fluid research had focused mainly on the spotting fluid providing lubrication between the drillpipe and mud filter cake. However, it was found that successful spotting fluids must not only provide lubrication, but also quickly invade mud filter cakes. Laboratory data also revealed that the best performing conventional spotting fluids were highly toxic to mysid shrimp. In accordance with the new findings, a two phase spot was developed. A field application is detailed that validated the concept of the two phase spot and its method of application.

Fraser, L. 1996. Synthetics winning approval in Gulf. The American Oil & Gas Reporter. 81-83 & 103.

Abstract: The composition of different SBMs is described. SBMs have several advantages over OBMs that would be negated if direct site discharge for SMB cuttings were to be discontinued. The costs for alternative disposal of drill cuttings would be prohibitive. If it is deemed that continued discharge of SBM cuttings is acceptable, the industry will be using synthetics for a long time to come. If, however, the opposite is concluded, synthetics will have little if any advantage to offer over cheaper highly refined mineral oils.

Friedheim, J.E. 1994. Drilling with synthetic fluids in the North Sea - an overview. Presented at the IBC Conference on "Drilling Technology". Aberdeen, November 1994. 13 Pages plus figures.

Abstract: Synthetic drilling fluids or "pseudo-oil" muds have been used in the North Sea for over four years. Generally speaking, all types of these fluids have been successful in a variety of drilling applications and share several performance benefits which often make them the preferred fluid even over oil-based muds. This paper briefly describes these mud systems and discusses their benefits as well as some limitations. Case histories focusing on the PAO (poly-alpha-olefin) based synthetic fluid will be used to illustrate the utility of these systems.

Friedheim, J.E. 1998. Area-specific analysis reflects impact of new generation fluid systems on deepwater exploration. IADC/SPE 47842. In: 1998 IADC/SPE Asia Pacific Drilling Conference. Jakarta, Indonesia, 7-9 September 1998. IADC/SPE Asia Pacific Drilling Technology. Society of Petroleum Engineers, Richardson, TX. 14 pp.

Abstract: The worldwide acceleration in deepwater exploration and the accompanying technical and environmental complications have been well documented in the literature. From a drilling fluids perspective, the demands intrinsic to deepwater drilling and completions are especially acute as operators must reconcile performance and economic objectives with unique technical and environmental obstacles. Beyond standard fluid criteria, mud systems designed for deepwater projects must also address such unique problems as shallow gas hazards/water flows; gas hydrate formations; lost circulation/lower fracture gradients and hole cleaning in the riser section.

This paper reviews the latest developments in synthetic and water-based mud systems geared specifically for deepwater drilling and completions. The inherent advantages and disadvantages of the various systems are reviewed. Moreover, to illustrate the technical and economic impact of latest generation fluid systems in deepwater projects, the author presents case studies from deepwater theaters worldwide. For example, an isomerized-olefin synthetic fluid was used to drill the 12 ¼ in section to total depth in 6,740 ft of water in the Gulf of Mexico. The well was drilled five days ahead of schedule and \$875,000 under budget. The rate of penetration were as high as 100 ft/hr. Use of the SBF resulted in very little trouble time during vertical and offset drilling.

Friedheim, J.E. and H.L. Conn. 1996. Second generation synthetic fluids in the North Sea: are they better? IADC/SPE 35061. Pages 215-228 In: IADC/SPE Drilling Conference. New Orleans, 12-15 March 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: At the beginning of the 1990s, three synthetic type materials were introduced - esters, ethers and polyalphaolefins. Now after heading towards the last half of this decade, a new generation of synthetics is gaining popularity - linear alpha olefins and isomerized olefins. Another base fluid, linear paraffin, which can be considered pseudo-oil rather than synthetic, is also making an impact. Each of these materials has similarities as well as differences both as base fluids and drilling muds.

North Sea applications of synthetic-based muds highlight the major aspects that not only delineate the first generation of fluids from the second but also the various fluids themselves. Each area- the United Kingdom, Norway, and the Netherlands - not only have different marketplaces, but also different emphasis on the many facets of environmental as well as health and safety concerns. This variance from country to country provided the impetus for the introduction of these various fluids.

This paper provides an overview of these second generation fluids and deals with their technical, environmental, and economical status as it relates to the North Sea drilling area. It will also discuss these second generation fluids in light of their predecessors and emphasize the differences. Details are provided on the chemistry of these second generation fluids and actual field data will be provided to illustrate their effectiveness.

First generation SBFs include: ester, PAO, ether, and acetal. Second generation SBFs include linear alkylbenzene (LAB), linear alpha olefin (LAO), internal olefin (IO), and linear paraffins (LP). The cost of the base fluids of the 2nd generation synthetics is lower. The lower viscosity of the 2nd generation synthetics allows these systems to be formulated and engineered more economically. The lower viscosity of the 2nd generation synthetics generally results in lower circulation pressures. The benefits of the lower viscosity may be offset by hole cleaning and lubrication concerns. Except for the esters, 2nd generation synthetics have demonstrated a greater ability to biodegrade. In general, 2nd generation synthetics exhibit higher aquatic toxicity than 1st generation synthetics. The final environmental fate of synthetic fluids will be determined by future seabed surveys.

Friedheim, J.E., G.J. Hans, A. Park and C.R. Ray. 1991. An environmentally superior replacement for mineral-oil drilling fluids. SPE 23062. Pages 299-311 In: The Offshore Europe Conference. Aberdeen, 3-6 September 1991. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: Environmental constraints have led to the development of an invert mud system that has excellent toxicity, health and safety aspects, and is biodegradable. This system is particularly suitable for North Sea use where discharges from drilling with mineral oil-base drilling fluids are limited. Based on a synthetic material as the continuous phase, this mud system gives the same high performance as that of mineral oil-base systems. This paper describes this novel mud system and focuses on the impact of its use in environmentally sensitive areas.

The ratio of synthetic liquid continuous phase and aqueous phase (S/W ratio) can vary from 90/10 to 50/50 with mud weights ranging from unweighted to 18.0 ppg. The rheology parameters can be altered with rheology modifiers to give increased low-shear-rate viscosities for enhanced hole cleaning capabilities. Huxley-Bertram HTHP viscometer data shows good stability of the system under downhole conditions. Additional work indicates this system has reduced gas solubility, better lubricity, and lower retention on cuttings when compared to mineral oil-based muds.

Favorable toxicity data, bioaccumulation studies, and biodegradation work have been compiled for both the synthetic material and mud system. U.K. toxicity tests give highly acceptable values. These results, along with the bioaccumulation data; have led the U.K. Department of Energy (DEN) to assign the system a Category 0 Classification under its Chemical Notification Scheme. Likewise, the Norwegian government agency (SFT) has agreed to permit this system to be used on a field trial basis. Currently, the U.S. Environmental Protection Agency (EPA) is considering its use, and subsequent discharge of cuttings, for Gulf of Mexico drilling.

In tests performed in the UK, a PAO-based fluid had an acute toxicity to shrimp of more than 18,000 mg/L. The complete PAO mud system had an acute toxicity of greater than 32,000 mg/L. Because of their high molecular weight and low solubility, PAOs do not bioaccumulate in marine organisms and have little effect on growth in fish.

Friedheim, J.E. and R.M. Pantermuehl. 1993. Superior performance with minimal environmental impact: a novel nonaqueous drilling fluid. SPE/IADC 25753. Pages 713-726 In: 1993 SPE/IADC Drilling Conference. Amsterdam, 23-25 February 1993. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *The first well utilizing a novel drilling fluid based on polyalphaolefin (PAO) chemistry has been drilled in the North Sea. In addition to excellent drilling performance, PAO drilling fluids exhibit low toxicity, low bioaccumulation, and are biodegradable. Success of the PAO mud has established the system as a viable synthetic-based alternative to oil-based muds.*

The non-aqueous PAO system was used to drill the 12.25-in. section of a well in the Central Basin of the North Sea. The interval from 6,300 to 15,067 ft (1,920 m to 4,592 m) was drilled at an angle of 55 deg. The formation consisted primarily of tertiary shales mixed with limestone stringers. Mud weight range was 15.0-15.5 ppg (1.8-1.86 s.g.).

Comparisons with oil-based muds used in this area of the North Sea indicated the PAO fluid helped increase penetration rates and reduce torque and drag. Other performance benefits included superior hole cleaning and no evidence of weight material sag. Additionally, cuttings discharged into the sea retained an average of 8.2 % PAO (82 g/kg dry retort solids). The PAO-contaminated cuttings dispersed quickly.

Comparisons with other non-aqueous alternatives such as ester and ether-based fluids show PAO systems provide better elastomer compatibility, lime and cement tolerance, surface handling, synthetic/water ratio flexibility, and temperature stability.

A field prepared used PAO mud had an acute toxicity to algae, barnacles, and bivalves of 50,000 mg/kg, 240,000 mg/kg, and 14.8 mg/kg. The PAO was not bioaccumulated by a marine fish. The PAO also degraded in laboratory tests under aerobic and anaerobic conditions.

Friedheim, J.E. and A. Patel. 1999. Technical solutions for environmental problems: novel drilling formulations to minimize environmental impact. SPE 52741. In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *The use of synthetic-base muds (SBM) has increased steadily since their introduction in the Gulf of Mexico early this decade. Research into SBM has centered on assessing the heavy environmental impact of cuttings discharges. This impact is potentially affected by various factors, not the least of which is the synthetic base fluid itself, related to the technical composition of the mud.*

New technology in the form of synthetic mud formulations further reduce the environmental impact of cuttings and their associated fluid. These novel formulations aid in pollution retention associated with the discharge of drill cuttings into the receiving environment. These new technologies include:

- *Unique emulsifiers that allow wellbore surfaces and cuttings to change from an oil-wet state to a water-wet state*
- *New synthetic-base materials that allow cuttings to disperse readily into the water column*
- *Novel brine phases that benefit the disposal of cuttings via land farming*

This paper discusses these approaches in formulating and engineering synthetic-base muds [that] can reduce the overall environmental impact of a drilling operation.

Gallaway, B.J., R.G. Fechhelm, G.F. Hubbard and S.A. MacLean. 1998. Opportunistic sampling at a synthetic drilling fluid discharge site on the continental slope of the northern Gulf of Mexico: The Pompano Development, 13-14 March 1998. Report to BP Exploration, Inc., Houston, TX. LGL Ecological Research Associates, Inc. Bryan, TX. Various pages.

Abstract: *BP Exploration, Inc., installed an offshore oil and gas platform (Pompano Phase I) in 393 meters of water on the continental slope of the Gulf of Mexico in Lease Block Viosca Knoll 989 in 1994. Ten wells were drilled from the platform in 1994. The template for Pompano Phase II was installed four miles downslope from Pompano Phase I*

in 565 m of water in Mississippi Canyon Block 28 in 1995. Drilling at this site occurred between October 1995 and the summer of 1997.

Although water-based drilling fluids were used in most of the Pompano Phase II drilling operations, a synthetic-based drilling fluid, Baroid Petrofree LE, was used during drilling of six wells. Drill cuttings containing an estimated 6,057 bbls of Petrofree LE were discharged to the ocean. An additional 1,672 bbls of Petrofree were discharged with cuttings during drilling of another well in February and March, 1998. Two benthic surveys, in July 1997 and March 1998, were performed to determine the fates and possible effects of the discharged SBF-cuttings.

The objectives of the study were to document:

- the size and extent of any associated cuttings pile following 2 years of a multiwell development drilling program in the deep Gulf;
- the general appearance of the bottom as related to chemical activity and biodegradation processes;
- concentrations of Petrofree-LE (the SBM used) in sediments around the Pompano Phase II subsea drilling template; and
- densities of macrofauna and megafauna at some locations near the platform.

Sediment sampling was performed by ROV at 15 locations between 25 and 90 m up-current, down-current, and across-current from the template. Video surveys were performed to determine densities of megafauna.

Cuttings piles on the order of meters to tens of meters high were not present; maximum accumulations were on the order of 20 to 25 cm. Surface sediments near the template appeared to have a thin veneer of cuttings. The appearance of the bottom suggested intense chemical activity and active biodegradation. Concentrations of Petrofree-LE in sediments ranged up to 198,000 ppm within 50 to 75 m of the template. However, there were no gradients of sediment SBM concentrations with distance or direction from the site. 87% of surficial sediment samples contained 1,000 ppm or more SBM; only 40% of subsurface (2-5 cm) sediments contained 1,000 ppm or more of SBM.

High densities of macrofauna and megafauna were observed at the study site as compared to baseline information. Organic enrichment from SBM discharges or from organisms falling from submerged platform structures may have provided the energy need for the high productivity. The fatty acid esters in the synthetic base chemicals were contributing to bacterial enrichment of the sediments that served as food for the benthic fauna. There is an indication of a return of the benthic community to predrilling composition with time after the discharges.

Getliff, J.M. and S.G. James. 1996. The replacement of alkyl-phenol ethoxylates to improve the environmental acceptability of drilling fluid additives. SPE 35982. Pages 713-719 In: International Conference on Health, Safety & Environment. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc., Richardson, TX.

Abstract: Alkyl-Phenol ethoxylates (APEO) are a class of surfactants which have been used widely in the drilling fluid industry. The popularity of these surfactants is based on their cost effectiveness, availability and the range of hydrophilic-lipophilic balance values obtainable. Studies have shown that APEOs exhibit estrogenic effects and can cause sterility in some male aquatic species. This may have subsequent human consequences and such problems have led to a banning of their use in some countries and agreements to phase out their use e.g. PARCOM recommendation 92/8.

The use of APEOs as additives in detergents, lubricants and stuck-pipe release agents for drilling fluid applications is discussed. The effectiveness of products formulated with APEOs is directly compared with alternative products that are non-persistent and less damaging to aquatic species. Lubricity measurements using standard and in-house designed equipment and washing tests to compare the efficiency of surfactants are explained and product performance results presented.

The results show that alternatives to products containing APEOs are available and that in some cases they show a better technical performance. Linear alcohol ethoxylate (LAEO) surfactants and their degradation products are less toxic than APEOs to marine organisms. LAEOs are completely biodegradable to CO₂ and water in natural waters.

Getliff, J., A. Roach, J. Toyo, and J. Carpenter. 1997. An overview of the environmental benefits of LAO based drilling fluids for offshore drilling. Report from Schlumberger Dowell. 10 pp.

Abstract: Linear alpha olefins (LAO), used as the synthetic phase in some SBFs, have a low aqueous solubility and low toxicity to marine organisms. Impacts on benthic environments of LAO-contaminated cuttings discharges are caused by the physico-chemical environmental changes caused by the deposition and degradation of cuttings on the seabed (e.g., sedimentation and smothering, biological oxygen demand, and hydrogen sulfide production). The linear structure of LAO favors its microbial degradation. It is readily degraded under aerobic (60.3% at 2 mg/L) and anaerobic conditions (41% at 100 mg/L). The unsaturated bond in the molecule is sensitive to microbial attack. Under aerobic conditions, initial oxidation occurs at the terminal carbon group, resulting in the formation of an organic acid. One atom of oxygen is incorporated into the oxidized hydrocarbons producing an alcohol that is converted to a fatty acid through a ketone intermediate. Two-carbon (acetate) fragments are then removed from the fatty acid by cyclic β -oxidation. Acetate is used for nutrition by the microbes. Degradation requires oxygen. When LAO degradation occurs in surficial sediments, oxygen in the sediments may be depleted. Under anaerobic conditions, sulfate-reducing bacteria may degrade the LAO, producing hydrogen sulfide as a byproduct from the abundant sulfate in marine sediments.

LAO drilling fluids have a lower viscosity than other synthetic fluids allowing more complete separation of the drilling mud from the cuttings. This allows discharge of cuttings containing very low concentrations of LAO. The cuttings are more readily dispersed in the water column and settle over a wider area at lower concentrations. Sediment biota exposed to these more highly dispersed cuttings accumulations recover more rapidly than those exposed to high concentrations of SBF cuttings.

Gjos, N. et al. 1991. Ula well site 7/12-9 environmental survey 1991. Senter for Industriforskning, rapport nr 91 02 16-3.

Smith, J. and J.J. Moore. 1990. Ula wellsite 7/12-9 environmental survey, May 1990. Report FSC/RC/15/90. Field Studies Council Research Centre, UK.

Smith, J. and S.J. May. 1991. Ula wellsite 7/12-9 environmental survey 1991. Report FSC/RC/13/91. Field Studies Council Research Centre, UK.

Smith, J. and G. Hobbs. 1993. Ula wellsite 7/12-9 environmental survey 1992. Report FSC/RC/15/92. Field Studies Council Research Centre, UK.

Abstract: These four papers summarize the results of field surveys following the drilling at the Ula wellsite using an ester SBM. Immediately after drilling there were significant impacts within 100 m of the discharge where initial concentrations of ester in sediment were high (46,400 to 85,300 mg/kg). The highest barium concentrations in sediments were 1,720 to 3,770 mg/kg. There was no evidence of impacts at greater than 200 m from the discharge where concentrations of ester in sediment were lower (208 mg/kg). Recovery appeared to be relatively rapid as no impacts were evident 1 or 2 years after drilling when concentrations of ester in sediment had declined to less than 1 mg/kg. The authors did note that sample replication was a problem because of the position fixing system used and suggested that this could affect estimation of recovery times.

Growcock, F.B., S.L. Andrews, and T.P. Frederick. 1994. Physicochemical properties of synthetic drilling fluids. IADC/SPE 27450. Pages 181-190 In: 1994 IADC/SPE Drilling Conference. Dallas, TX, 15-18 February 1994. International Association of Drilling Contractors/Society of Petroleum Engineers, Inc. (IADC/SPE). Richardson, TX.

Abstract: Synthetic-based muds (SBMs) were developed as environmentally friendly alternatives to conventional petroleum-derived oil-based muds (OBMs). Although each synthetic fluid is chemically unique, the physico-chemical properties of the SBMs exhibit some common trends. SBMs are safer to work with, more biodegradable and more dispersible in seawater than conventional OBMs. On the other hand, SBMs are more viscous at low temperatures, thin more with increasing temperature, have lower thermal stability and do not dehydrate shales as readily as conventional OBMs. By adjusting the emulsifier package in each mud, these properties may be brought more in line with those of conventional OBMs.

Hartley, J.P. 1996. Environmental monitoring of offshore oil and gas drilling discharges - a caution on the use of barium as a tracer. *Marine Pollution Bulletin*. 32(10):727-733.

Abstract: *Commonly used methods for extracting barium from marine sediments are inefficient when high concentrations of barium sulfate are present in samples. Comparative data on sea-bed barium concentrations around a single exploration well are presented to highlight the influence of different extraction methods which can result in 2-3 order of magnitude differences in levels recorded. This suggests that in many monitoring studies the value of barium as a tracer of discharged drilling wastes and thus as an aid to the interpretation of survey data is reduced. The environmental management implications of these findings are explored and a holistic and more collaborative approach to environmental effects monitoring is advocated.*

Jacques, D.F., H.E. Newman, Jr., and W.B. Turnbull. 1992. A comparison of field drilling experience with low-viscosity mineral oil and diesel muds. IADC/SPE 23881. Pages 341-354 In: 1992 IADC/SPE Drilling Conference. New Orleans, Louisiana, February 18-21, 1992. IADC/SPE Drilling Conference. Richardson, TX.

Abstract: *Diesel has been the most widely used base-oil for oil muds. Mineral oil muds have found some application where operators wished to drill with an oil mud but wanted lower aromatic exposure to workers and the environment. Regulations have now been established that increase the difficulty of using diesel in drilling muds. From a human health, safety, and environmental issues perspective, alternates to diesel mud have merit. This paper will describe laboratory and field performance data comparing diesel oil muds with a low-viscosity, low-aromatic, low-toxicity oil or enhanced mud oil (EMO), an improvement over the early mineral oils. The physical compositional, environmental, and human health differences between diesel and the EMO muds have improved rate of penetration over diesel muds when used under similar conditions by 23 to 54%.*

Jones, F.V., J.H. Rushing, and M.A. Churan. 1991. The chronic toxicity of mineral oil-wet and synthetic liquid-wet cuttings on an estuarine fish, *Fundulus grandis*. SPE 23497. Pages 721-730 In: The First International Conference on Health, Safety and Environment. Hague, The Netherlands, 10-14 November 1991. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *One of the major factors concerning oil-wet cuttings discharges is the long-term effect on the aquatic environment. This study investigates the survival and growth of the mud minnow, *Fundulus grandis*, when exposed to different concentrations of mineral oil-wet and synthetic liquid-wet cuttings in flow-through bioassay chambers.*

The test fluids were a low aromatic mineral oil-based mud (MOBM) and a synthetic liquid-based mud (SBM). Each test fluid was added to a container of dried water-based cuttings which contained minimum hydrocarbons. The fluid and cuttings were mixed to obtain the desired test concentrations. The study tested three concentrations (1%, 5%, and 8.4% by dry weight) of each fluid on the cuttings.

Growth rates during the 30-day period were modest with fish in 1% MOBM losing weight. The highest percent growth rates were obtained with fish cultured in 5% SBM and the controls. However, overall growth was not significantly different between treatments. Mean growth did show a significant difference between controls and 5% SBM, and other treatments.

Jones, F.V., C. Hood, and G. Moiseychenko. 1996. International methods of evaluating the discharge of drilling fluids in marine environments. SPE 46825. In: 1998 SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezuela, 7-10 June 1998. Society of Petroleum Engineers, Inc. Richardson, TX. 18 pp.

Abstract: *Restrictions on the discharge of drilling mud and cuttings around the world are governed by standards, norms, laws and regulations designed to provide protection to the surrounding marine environment. Operations have been ongoing in waters off the American coasts and the North Sea for the longest period of time and both areas have developed the most detailed set of restrictions and testing of both the discharges and the chemicals used in drilling.*

Since the late 1970's, offshore operations have expanded throughout the world in Africa, South America, the Middle East, Asia, and in other areas. In many instances these countries have developed their own standards and requirements for discharges either through individual country laws or through international standards (i.e., the Baltic Sea Convention). Methodologies used to evaluate drilling fluids and their discharges include; biotesting (of both whole mud and the individual chemicals), chemical restrictions and analysis, oil content, biodegradability to name but a few.

How best to evaluate these discharges around the world has become problematic. The cost of testing fluids for each new venture is both costly, time consuming, and in many instances unwarranted. However, each region and country has the right and legal and moral obligation to assure that any industrial activity off their coast is controlled and the environment proven safe from these activities.

This paper discusses the various methods and methodologies that have been used around the world to evaluate drilling fluids and their approval for discharges. The paper describes the positive and negative aspects of these methods and compares results from three major offshore areas where operations are currently being conducted; U.S., North Sea, and Russia. Other area methodologies and restrictions are discussed also. Potential environmental impacts of drilling fluid and cuttings discharges are evaluated by toxicity tests. There is disagreement about whether individual drilling mud chemicals or whole drilling muds should be tested. In the U.S., whole muds are tested with mysids. In the North Sea countries and Russia, drilling mud chemicals and in some cases, whole drilling muds, are tested with several species at different trophic levels in the marine food web. Chronic tests may be included.

Kenny, P. November 8, 1993. Ester-based muds show promise for replacing some oil-based muds. Oil and Gas Journal. 91(45):88-91.

Abstract: Ester-based drilling muds have several advantages over oil-based muds that may make them suitable replacements for OBM in some applications in the Norwegian North Sea. There is substantial cost savings if synthetic-based mud cuttings can be discharged to the ocean. However, ester-based muds have a toxicity to marine organisms similar to that of the standard low-toxicity oil-based muds. The source of the toxicity of ester-based muds is not known, but is thought to be due to some of the additives (e.g., emulsifiers) in the mud.

Kenny, P., M. Norman, A.M. Friestad, and B. Risvik. 1996. The development and field testing of a less hazardous and technically superior oil based drilling fluid. SPE 35952. Pages 527-535 In: International Conference on Health Safety and Environment. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *This paper describes the development and subsequent field results of a new invert emulsion, low toxicity, oil based drilling fluid (LTOBM). The new fluid was developed in response to the anticipated increased usage of LTOBM, and primary considerations in the development were those of working conditions, the environment, technical performance and economics.*

Developments in invert emulsion drilling fluids have, over recent years, been concentrated in the areas of reducing environmental impact, and improving technical performance. LTOBM have, as a result of this, been largely replaced by synthetic based drilling fluids (SBM), which exhibit similar, or improved technical performance, whilst claiming to have reduced environmental impact. This development focus has resulted in very few changes being made to LTOBM since the replacement of diesel by low toxicity mineral oil.

The occupational health hazards involved in using SBM have, however, proven to be similar, or occasionally worse, than with LTOBM. Such health problems can be mainly attributed to two components; the base fluid and lime, the latter being a major contributor to skin irritation problems, and the former to both skin irritation, and inhalation problems. There has been a lack of occupational health studies carried out with respect to the use of SBM compared to LTOBM.

This paper describes the laboratory testing conducted, and results obtained during the development, where several base fluids were screened, along with a multitude of fluid additives, prior to obtaining the optimal formulation. The final fluid was designed for use on high temperature high pressure wells and extended reach wells, as well as more

"normal wells". The laboratory data presented is supported by field data from the successful use of the system as a worker friendly, high performance, LTOBM drilling fluid.

Base oils for LTOBMs tested in solid-phase bioassays with the clam *Abra alba* had acute toxicities in the range of 10 to 576 mg/kg. The complete mud systems had toxicities of 92 to 290 mg/kg.

Kingston, P.F. 1992. Impact of offshore oil production installations on the benthos of the North Sea. ICES Journal of Marine Science. 49:45-53.

Abstract: *Input of contaminants into the sea associated with offshore oil drilling and production include accidental spillage, discharge of cuttings and discharge of production water. Of these, oil discharged on drilling cuttings is by far the greatest source of oil pollution in the North Sea from these operations, having peaked in 1985 at 25,880 tonnes. The response to the seabed fauna to these inputs has been shown to follow established patterns in which there may be high individual abundance of a few species close to the source of contamination (organic enrichment effect) or a reduced number of individuals with few species close to the installation (smothering or toxic effect). Diversity shows a similar pattern to species richness, both are low in the immediate vicinity of the installation, and, in most cases, attaining preoperational levels within 2000 m. High levels of hydrocarbon contamination have also been shown to be concentrated around installations. There are indications that a fall in diversity can be expected when total hydrocarbon concentrations in the sediment reach 50-60 ppm. There is also increasing evidence to suggest that for some areas where there has been intensive drilling/production activity with OBM (e.g. Shetland Basin), there has been a significant rise in hydrocarbon levels in the sediment at distances between 5 and 10 km from installations.*

Lee, B. 1998. The use of synthetics in well drilling fluids for the offshore oil field. American Chemical Society, Div. Of Fuel Chemistry. Preprints of Symposia 43(2):233-237.

Abstract: *As Gulf of Mexico offshore drilling moves into deeper waters and into more demanding conditions in terms of the depth and type of wells (deviated or horizontal), drilling muds providing higher lubricity and better hole stability are needed. Previously, oil based muds (OBMs) that are primarily based on diesel oil met this need. However, the on-site discharge of cuttings from wells drilled using OBMs was banned in the early 1990s. Synthetic based muds (SBMs) were introduced that are prepared using synthetically derived base fluids. SBMs were developed to provide an environmentally safe alternative drilling mud that would meet both the severe drilling mud requirements and the need for cuttings discharge into the ocean. These base fluids are chemically synthesized from the reaction of specific purified chemical feedstocks to give readily characterized products. The synthetic fluids used in the Gulf of Mexico today are linear alpha olefins (LAOs), isomerized olefins (IOs), poly alpha olefins (PAOs) and esters. A description of their chemistry, the benefits they provide and the regulatory issues surrounding their use is discussed.*

Lie, H.N., J.R. Hasle, and K. Thorbjornsen. 1994. Modelling and monitoring of drilling discharges in the Barents Sea. Pages 121-130 In: Proceedings: Environmental Modelling Seminar. Trondheim, Norway, 17-19 August 1994. SINTEF Group, Trondheim, Norway.

Abstract: *Modelling and monitoring of seabed distribution of drill cuttings and drilling mud has been performed as part of the environmental programme for exploration well 7219/8-1s in the Western Barents Sea in 1992. Modelling prior to drilling was based on experience well data and historical current measurement from the region. The modelling was repeated after drilling, based on measured discharge quantities and particle sizes, and measured current during the drilling period, giving less local sedimentation and distribution over a much wider area. According to the modelling only 1% of the drilling mud baryte would settle within 1,000 m from the drilling platform, resulting in a very thin sediment layer (0.05 m). 53% of the baryte would spread more than 10 km. The modelling results were confirmed by sediment analyses, which showed that the drilling discharges increased the sediment barium content by 10 % at distance 250 - 1,000 m from the platform, corresponding to a 0.5 m baryte top layer. Reason for the wide distribution and limited local sedimentation may be tidal current dominance and large water depth (373 m).*

Limia, J.M. 1996. Seabed surveys: the best means to assess the environmental impact of drilling fluid discharges? SPE 36048. Pages 803-813. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *Laboratory biodegradation tests were compared to field surveys for assessing the persistence, biodegradation, and effects of discharged SBM in the benthic environment. The currently approved biodegradation test protocols do not produce consistent nor relevant information about the biodegradability of drilling fluids under the conditions found in marine sediments. It is desirable to have industry acceptance of a biodegradation test similar to the "solid biodegradation test" designed by the Scottish Office of Agriculture and Fisheries Department. The generation of anoxia in marine sediments, following the discharge of organic matter, depends on the amount discharged (concentration in the sediment), rather than its biodegradation rate. The rapid biodegradation of esters, even under these anaerobic conditions, means that its residence time in the sediment is short. Thus, recovery of the impacted area can be expected within a year. Seabed surveys, properly conducted, are still the ultimate tool to assess the environmental impact of the discharge of drilling cuttings. In the seabed survey presented here, the intensity and extension of the impact were detected and also the degree of recovery.*

The well was drilled in 30 m of water with Petrofree, an ester-based SBM. A total of 180 metric tons of ester was discharged with cuttings during drilling. The discharge was at about 1 m below the sea surface to maximize mud and cuttings dispersion. One month after completion of discharges, ester concentrations in surficial sediments collected between 75 and 200 m from the discharge ranged from 20 to 300 mg/kg dry sediment. Sediments were resampled four months after the discharges and contained higher concentrations of ester than the 1-month samples did: 20 to 800 mg/kg. This was attributed to dispersion of the cuttings pile. Surface sediments from 75 m from the platform were anoxic and the total faunal abundance was low. Sediments from stations 500 to 3,000 m from the discharge had normal benthic communities. After 11 months, concentrations of ester in sediments had decreased to the range of 10 to 250 mg/kg. The estimate half-life of ester in site sediments was estimated at 133 days. The benthic community at 75 m stations, although still affected by the discharges, showed signs of significant recovery, compared to 4-month samples.

Limia, J.M. 1999. Silica micro-encapsulation: a technology for the elimination of the environmental impact of cuttings discharges. SPE 52747. 1999 SPE/EPA Exploration and Production Environmental Conference, Austin, TX. Society of Petroleum Engineers, Richardson, TX. Pp. 525-529.

Abstract: *A new approach is required in order to eliminate the environmental impact of the discharge of cuttings contaminated with invert emulsion drilling fluids. Up to now, much emphasis has been given to the inherent environmental characteristics of the fluids themselves (toxicity, biodegradability, etc.) but little or no attention has been dedicated to the mechanisms of environmental impact.*

The main mechanism of impact of the discharge of drilled cuttings is the organic enrichment of the marine sediment. Organic enrichment is a situation derived from the accumulation of organic matter in concentrations exceeding the "processing capacity" of the receiving environment (the oxygen demand exceeds the supply).

Silica micro-encapsulation will eliminate the possibility of organic enrichment as well as the direct toxic effects of the fluids coating the discharged cuttings. Once the oil attached to the cuttings is encapsulated, the cuttings become water wetted, which leads to their dispersion in the water column (as is the case with water based mud cuttings). The dispersion of the cuttings will minimize the load of fluid in the sediment. In addition, the encapsulated oil is not bio-available, therefore these cuttings will not have an oxygen demand which will prevent organic enrichment.

McIlroy, W. 1998. Review of BHP's experience into the persistence of drilling fluids pollutants. Pages 121-134
In: International Workshop on Drilling Fluids Ecotoxicology and Biodegradation. Curtin University, Perth, Western Australia, 8-9 October 1998.

Abstract: *Field studies were performed in Australian waters to determine the effects of discharges of WBM and SBM. It is evident that there are changes to the local environment as a result of drilling fluid and cuttings discharge. Despite the fluid system employed (i.e., water based or synthetic based) most impacts were noted to occur within 200 m of the wellhead location. The water-based mud system employed in the high energy environment of the Otway Basin showed no persistence one year following the drilling program. Within three months, fluid discharge impacts for contaminants and fauna diversity were confined to within 100 m. SBM discharged to the Timor Sea showed little*

persistence one year after drilling, yet some contaminants were still evident within 200 m of the wellhead. There was some evidence of smothering of benthic fauna at both sites, however, a storm caused a major disturbance to the benthic community at the Timor Sea site, making it impossible to determine effects of the SBM discharge.

McIntyre, J. 1997. Memorandum from Jamie McIntyre, Avanti Corp, to Joseph Daly, U.S. EPA/EAD, regarding summary statistics for synthetic based fluid (SBF) retention data. 20 pp.

Abstract: Graphs showing percent retention of SBM on cuttings, based on studies of the API Retention-On-Cuttings Work Group are summarized. Percent retention varies from less than 5 to more than 20 percent and seems in some cases to increase with well depth.

McIntyre, J. 1997. Memorandum from Jamie McIntyre, Avanti Corp, to Joseph Daly, U.S. EPA/EAD, regarding addendum summary statistics for SBF retention data.

Abstract: Data from the API Retention-On-Cuttings Working Group on retention of synthetic base mud components on cuttings is presented in tabular and graphic formats. Effects of drilling depth on SBM retention on cuttings was evaluated. There is an inconsistent relationship between drilling depth and retention of SBM on cuttings.

McKee, J.D.A., K. Dowrick and S.J. Astleford. 1995. A new development towards improved synthetic based mud performance. SPE/IADC 29405. Pages 613-621 In: 1995 SPE/IADC Drilling Conference. Amsterdam, 28 February-2 March 1995. SPE/IADC Drilling Conference. Society of Petroleum Engineers, Richardson, TX.

Abstract: This paper describes a new synthetic based drilling fluid (SBM) which is able to emulate oil based mud performance while complying with environmental legislation. Comparisons with oil based mud in the laboratory show that the system can provide similar performance at low synthetic:water ratio, high mud weight, high temperature and in the presence of contaminants. The laboratory results are supported by field data which demonstrate that the system can be managed like mineral oil based mud, giving good rates of penetration with minimum mud maintenance and low retention of the synthetic base fluid on cuttings discharged to the sea.

Marine toxicity, bioaccumulation and biodegradation data has been compiled for the SBM and the synthetic base fluid. Acute toxicity to phytoplankton and zooplankton was greater than 10,000 mg/L. The suspended particulate phase of the SBM had a toxicity to mysids of 794,000 mg/L. A solid-phase test with the amphipod *Corophium volutator* gave an acute toxicity of 1,021 mg/kg. The base fluid has a high log K_{ow} and does not bioaccumulate. It degrades rapidly under both aerobic and anaerobic conditions. Based on these results, the system has been accepted for use in UK and Norwegian waters, subject to sea bed surveys following its use in trial wells. In the UK, the system has been placed in provisional Group E of the revised Offshore Chemical Notification Scheme (OCNS) product categorization. For operations in the United States, the mysid shrimp 96 hour LC_{50} toxicity test result significantly exceeds the limit required for use in the Western Gulf of Mexico outer continental shelf.

Meinhold, A.F. 1999. Framework for a comparative environmental assessment of drilling fluids used offshore. SPE 52746. Pages 515-524 In: 1999 SPE/EPA Exploration and Production Environmental Conference. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: In Response to effluent limitation guidelines promulgated by the United States Environmental Protection Agency, industry has developed alternatives to the water and oil-based drilling muds used offshore. These synthetic-based muds, (SBMs), enhanced mineral oils (EMOs) and purified paraffin oils have lower toxicity and lesser environmental impacts than diesel and conventional mineral oil-based muds (OBMs). EPA is developing new guidelines for the discharge of these fluids and associated cuttings. The decision about allowing or disallowing the discharge of cuttings with small amounts of associated SBMs, EMOs and purified paraffin oils should not be based solely on potential environmental impacts, especially those such as bioaccumulation or biodegradation that may not be directly connected to effects on populations or ecosystems. Regulatory decisions about drilling fluid discharges should consider potential impacts associated with the alternatives; including occupational accidents and chemical exposures, impacts associated with disposal, air emissions, and transportation risks. Because these new fluids are expensive, industry will not continue to use them if the cuttings cannot be discharged offshore. The alternative to allowing the discharge of these new drilling fluids is the continuing use of OBMs in difficult drilling situations. This

paper develops a framework and a comparative environmental assessment for the discharge of drilling fluids, to help support a risk-based, integrated approach to regulatory decision making.

Meinhold, A.F. 1998. Framework for a comparative environmental assessment of drilling fluids. Prepared for: National Petroleum Technology Office, Office of Fossil Energy, U.S. Department of Energy, Tulsa, OK. Contract number DE-AC02-98CH10886. Energy Science and Technology Division, Department of Applied Science, Brookhaven National Laboratory. Upton, NY. 77 pp.

Abstract: *This report develops a framework for a comparative risk assessment for the discharge of SBMs and EMOs, to help support a risk-based, integrated approach to regulatory decision making. The framework will help identify potential impacts and benefits associated with the use of SBMs, EMOs, WBMs and OBMs; identify areas where additional data are needed; and support early decision-making in the absence of complete data. As additional data become available, the framework can support a full quantitative comparative assessment. Detailed data are provided to support a comparative assessment in the areas of occupational and public health impacts.*

Moffat, C.F., P.D. Munro, and R.M. Stagg. 1998. Development of a solid-phase test for the comparison of the biodegradation rates of synthetic mud base fluids. Pages 14-32 In: International Workshop on Drilling Fluids Ecotoxicology and Biodegradation. Western Australia, 8-9 October 1998.

Abstract: *A solid-phase test was developed to assess the fate in marine sediment of synthetic mud base fluids (SMs) used in the off-shore drilling industry. The test comprised a series of glass jars containing marine sediment that had been homogeneously mixed with a test fluid. The jars were placed in either fiberglass troughs supplied with a continuous flow of seawater or glass aquarium tank with a restricted and/or recirculated seawater supply. The test was conducted at water temperatures varying between -1°C and 25°C. Periodically, triplicate or duplicate jars were sacrificed and, following solvent extraction, the concentration of the test fluid remaining in the sediment was determined by gas chromatography with flame ionization detection. Test fluids included a range of SMs, a mineral oil, used as an example of a recalcitrant mixture, and olive oil, a readily biodegraded material. Additional controls included poisoned samples, to allow an estimation of abiotic losses, and sediments without any test fluid added so as to provide background data. Determination of the redox potential at 5 mm intervals provided a depth profile for individual jars while microbiological activity was estimated by enumeration of culturable aerobic and anaerobic bacteria both in surface and sub-surface sediment samples. Furthermore, determination of the ability of bacteria to grow on each test fluid as the sole carbon source was assessed using the Sheen-screen. Variations in sediment type, temperature and the salinity of the water were investigated.*

The results to date show that the solid-phase test is able to reproducibly distinguish between easily degradable and poorly degradable fluids under a range of conditions. The test is convenient to set-up and has been run continuously for up to 240 days. Temperature regulation is readily achieved in the aquarium tanks permitting more detailed investigations of the influence of temperature on the degradation of SMs. The test, however, performs equally well using ambient seawater where there is a temperature variation both over a 24 hour period and over the duration of a long-term experiment. Estimated half-lives for degradation of esters and internal olefins, tested by these methods were 2.8 to 9.2 days, with esters more biodegradable than internal olefins. Poisoned ester and internal olefin systems had half-lives of 12.8 and 57.3 days, respectively, indicating the importance of sediment microbiota in degrading SBMs.

Munro, P.D., N.A. Brown, B. Roddie, and C.F. Moffat. 1998. Degradation of an ester-type synthetic mud base fluid in a solid-phase test system: effect of concentration and temperature. Marine Laboratory, Aberdeen Report No. 12/98. Fisheries Research Services, Marine Laboratory. Aberdeen. Scotland. 22 pages plus charts.

Abstract: *A solid phase test was used to compare the degradation of an ester-type synthetic mud base fluid at a range of concentrations and temperatures. Visual changes in the sediment, a darkening below the surface layer and, in the case of the higher concentrations of test compound, the formation of a white microbial mat on the surface, were accompanied by changes in the redox potential and number of bacteria in the sediment. The rate of bacterial growth increased with temperature, though similar maximum numbers were obtained after seven days at -1°C and at two days at 20°C. The half-life of olive oil at an initial concentration of 50,000 ppm was 27 days. Ester degraded more slowly. Based on first-order reaction kinetics, which may grossly underestimate the rate, the half-life of the*

ester was 433 and 630 days at initial concentrations of 15,000 and 50,000 ppm, respectively. There was no loss of ester in poisoned treatments. Ester degradation was temperature sensitive. At an initial concentration of 500 ppm, the half-life was 16 days at 20°C and 88 days at -1°C. Similar temperature effects were observed at higher ester concentrations.

Munro, P.D., B. Croce, C.F. Moffat, N.A. Brown, A.D. McIntosh, S.J. Hird, and R.M. Stagg. 1998. Solid-phase test for comparison of degradation rates of synthetic mud base fluids used in the off-shore drilling industry. *Environmental Toxicology and Chemistry*. 17(10):1951-1959.

Abstract: A solid-phase degradation test has been developed to assess the fate in marine sediment of synthetic mud base fluids used in the off-shore drilling industry. The degradation rate of an ester-type drilling fluid was investigated at three nominal concentrations in a fine sand. A naturally occurring triester, olive oil, was used as a positive control and a traditional mineral oil served as an example of a poorly degradable substance. Two synthetic drilling fluids, an ester and a blend of n-alkanes with polyalpha olefin and linear-alpha olefin, were compared in a mud and a coarse sand to examine the effect of different sediments on degradability. Glass jars, containing marine sediment that had been homogeneously mixed with test fluid, were placed in troughs in a continuous flow of seawater. Periodically, triplicate jars were sacrificed and, following solvent extraction, the concentration of test fluid remaining in the sediment was determined by gas chromatography with flame ionization detection. The test was able to reproducibly distinguish between easily degradable and poorly degradable fluids. The rate of degradation was concentration dependent; the half-life of the ester increased from 11 days to 198 days as the nominal concentration increased from 100 mg/kg to 5,000 mg/kg. The ester was more rapidly degraded than the blended synthetic drilling fluid and degradation was slower in sand compared with mud.

Munro, P.D., C.F. Moffat, L. Couper, N.A. Brown, B. Croce, and R.M. Stagg. 1997. Degradation of synthetic mud base fluids in a solid-phase test system. Fisheries Research Services Report No 1/97. Scottish Office Agriculture, Environment and Fisheries Department, Marine Laboratory. Aberdeen, Scotland. 9 pp.

Abstract: A solid-phase test was used to compare the degradation rates of synthetic mud base fluids used in the offshore drilling industry. Six base fluids were evaluated: a polyalpha olefin, a linear alpha olefin, an internal olefin, an n-paraffin, an acetal, and an ester. Anaerobic reducing conditions developed in all sediments, except those poisoned with biocide, within 7 days. The number of bacteria capable of growth on the olive oil control or ester as sole carbon source was 100-fold greater than the number capable of growth on any of the other base fluids. Losses of ester were greater than those of any other base fluid. The linear alpha olefin was consistently the second most degradable at all concentrations tested. At a nominal concentration of 100 ppm, highly significant losses of the ester, LAO, IO, and n-paraffin were observed. The study showed that many of the synthetic base fluids currently used in drilling operations in the North Sea are no more degradable than a traditional, low-toxicity mineral oil.

Munro, P.D., C.F. Moffat, and R.M. Stagg. 1997. Biodegradation of base fluids used in synthetic drilling muds in a solid-phase test system. SPE 37861. Pages 1-9 In: 1997 SPE/UKOOA European Environmental Conference. Aberdeen, Scotland, 15-16 April 1997. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: A solid-phase biodegradation test designed to assess the fate in marine sediment of base fluids used in synthetic drilling muds in the offshore drilling industry was evaluated. The test was intended to provide conditions for degradation which more closely parallel those encountered in the marine sedimentary environment, with respect to temperature, microbial flora, anaerobic characteristics and other physico chemical conditions, than existing biodegradation tests.

The basic experimental design consisted of sets of glass jars filled with marine sediment which had been homogeneously mixed with synthetic mud base fluid. The jars were maintained in fiber-glass troughs through which a continuous laminar flow of seawater was passed. At set times, triplicate jars were removed, the entire contents of each jar mixed thoroughly and, following solvent extraction, the concentration of base fluid remaining in the sediment was determined by gas chromatography with flame ionization detection.

The biodegradation rates of two synthetic mud base fluids, an ester and a blend of n-alkanes, poly-alpha olefin and linear-alpha olefin, were compared. A naturally occurring triester, olive oil, was used as a positive biodegradable control. A mud, a sand and a 1:1 (wt/wt) mixture of mud and sand were used to examine the effect of particle size on biodegradability.

The test was able to reproducibly distinguish between easily biodegradable and poorly biodegradable synthetic mud base fluids. In this system, biodegradation rates for the ester were faster than for the blended fluid. The rapid metabolism of the ester resulted in a depletion of oxygen, a drop in the oxidation-reduction potential and the occurrence of sulphide events in the sediments. Biodegradation of the ester was significantly slower in sand compared to mud, while no measurable biodegradation of the blended fluid took place in the sand. The results indicate that some synthetic drilling fluids may be poorly degraded. The implications for the perceived environmental friendliness of these fluids are discussed.

Munro, P.D., L. Webster, N.A. Brown, C.F. Moffat, and R.M. Stagg. 1997. Investigation into the degradation of synthetic drilling fluids in a solid-phase test using a closed, brackish water system. Fisheries Research Services Report No 8/97. Fisheries Research Services. Aberdeen. 13 pages plus figures.

Abstract: *A modified version of the solid-phase test for estimation of the degradation rate of synthetic drilling fluids was used to examine the degradation of an ester and an internal olefin under conditions similar to those encountered in Nigeria. The sediment was a coarse silt from an estuarine environment. The sea water in the tanks was diluted with fresh water to simulate brackish conditions and the temperature was maintained at 25°C. A closed, recirculating water system was used. Olive oil was used as a positive biodegradable control. Some sediment was poisoned with a broad-spectrum biocide in order to determine abiotic losses of test fluid and clean sediment was included as a background control. Degradation of the ester was compared at 25°C and 12°C. Furthermore, samples of tank water were analyzed for the presence of the ester and one of its primary degradation products, 2-ethyl hexan-1-ol.*

Similar half-lives, 2.7 and 2.8 days, were obtained for the degradation of the olive oil and the ester, respectively, at 25°C and an initial nominal concentration of 100 mg/kg. The half-life of the ester at 12°C was slightly greater at 4.4 days. The mean half-life of the internal olefin was 8.7 days, similar results being obtained from duplicate tanks. This confirmed that there was no tank effect.

Losses of ester from the poisoned sediment at 25°C were not significantly different from those from the unpoisoned ester-dosed sediment at 12°C. Analysis of the tank water revealed that losses from the poisoned sediment could not be accounted for by washout of the parent compound. However, higher concentrations of one of the primary degradation products of the ester were detected in the tank water in the case of the poisoned sediment than in the equivalent unpoisoned treatment. This suggested that either, there was a population of non-culturable, biocide-resistant bacteria which degraded the ester or, abiotic hydrolysis of the ester occurred.

Muschenheim, D.K. and T.G. Milligan. 1996. Flocculation and accumulation of fine drilling waste particulates on the Scotian Shelf (Canada). *Marine Pollution Bulletin*. 32(10):740-745.

Abstract: *Concentrations of suspended particles (from drilling mud and cuttings) were measured at different depths in the water column, including just above the bottom at several distances from a drilling rig on Sable Banks, Nova Scotia. Water-based and oil-based muds were used and water-based muds and water- and oil-based cuttings were discharged. During and shortly after discharges, suspended particulate concentrations in the benthic boundary layer were elevated above background, due to suspended clay-size mud and cuttings particles. The turbidity persisted long enough to have possible adverse effects on local populations of scallops.*

National Energy Board, Canada - Newfoundland Offshore Petroleum, and Canada - Nova Scotia Offshore Petroleum Board. 1996. Offshore waste treatment guidelines. National Energy Board; Canada - Newfoundland Offshore Petroleum; Canada - Nova Scotia Offshore Petroleum Board. Canada. 19 pp.

Abstract: *In order to minimize the quantity of oil discharged into the marine environment, operators should use water-based or synthetic-based muds if possible. The use of oil-based muds will require specific approval. Synthetic-*

based drilling muds remaining from a drilling mud change-over or drilling program completion should be recovered and recycled, or transferred to shore in a manner approved by the Chief Conservation Officer. If re-injection is not technically or economically feasible, drill solids associated with water-based and synthetic-based drilling muds may be discharged at the drill site without treatment.

Norman, M. 1997. Esters - the only synthetic option for the next millennium? Presented at the 5th International [IBC] Conference of Minimizing the Environmental Effects of Drilling Operations. Aberdeen, Scotland. 13 pp.

Abstract: *Physical/chemical properties, toxicity and health effects, and biodegradation of synthetic-based drilling muds were reviewed. The focus was on biodegradation. Laboratory data, simulated seabed studies, and actual seabed surveys show a rapid biodegradation of esters. Seabed survey results for both polyalpha olefin and ACETAL show that a considerable amount have disappeared after 2 years. The rate of disappearance is slower than for esters. The effect on the microflora is, however, much less dramatic. The SOAEFD test results are generally more conservative than real life. The method needs further optimization in order to be a decision making tool for discharge of synthetic drilling fluids. Experimental errors should be avoided in future experiments.*

Norway. 1997. Synthetic drilling fluids. Proposal for a definition of synthetic drilling fluids and experiences on the Norwegian Continental Shelf. SEBA 97/5/5-E. Presented by Norway at the Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Sea-Based Activities (SEBA). Biarritz, France, 17-21 February 1997. 6 pp.

Abstract: *The Norwegian authorities define a synthetic based drilling fluid as "a drilling fluid where the base fluid consists of non water soluble organic compounds and where neither the base fluid nor the additives are of petroleum origin." Current regulatory practices in Norway are reviewed and a recommendation is made to hold a workshop to harmonize the regulations of different North Sea countries with respect to SBM discharges to the ocean.*

Norwegian Oil Industry Association Working Group. 1996. Criteria for selection and approval of drilling fluids: with respect to effects on human workers and marine ecological systems. Norwegian Oil Industry Association, Stavanger, Norway. 70 pp.

Abstract: *Extensive legislation regarding the acceptance of discharges to the marine environment has existed for some years. Acceptance criteria regarding the work environment has been less clear. Therefore, an increased focus on human health effects in relation to drilling fluids was also required. The dangerous properties and a method of documentation and testing should be identified. Based on this, the project attempted to define acceptance criteria to avoid future negative health effects on personnel exposed to drilling fluids and a more competent evaluation pertaining to marine environment.*

To prepare the basis for the recommendations in this report, two consultant reports were compiled. A report regarding the marine environment was prepared by Aquateam (1), and a report regarding human health effects was prepared by the Statoil Research Center (2). The conclusions in these reports are of an advisory nature.

Oliver, G.A. and S.J. Fisher. 1998. The persistence and effects of non-water based drilling fluids on Australia's North West Shelf, progress findings from three seabed surveys. Pages 65-93 In: International Workshop on Drilling Fluids Ecotoxicology and Biodegradation. Curtin University, Perth, Western Australia, 8-9 October 1998.

Abstract: *The effects and persistence of low toxicity oil-based drilling mud contaminated drill cuttings discharged into the marine environment was investigated at three locations on Western Australia's North West Shelf (NWS), namely the North Rankin 'A' (NRA) drilling platform, the Wanaea 6 production well, and the Lynx 1a exploration well. For the multiple-well drilling operation at NRA, acute biological effects were restricted to within 400 m in the direction of the prevailing current. High total petroleum hydrocarbon (TPH) concentrations within the NRA cuttings pile persisted between 1991 and 1993. Away from the cuttings pile itself, a consistent downward trend in total petroleum hydrocarbons was evident, indicating an approximate half life of one year for surface sediments. A survey at the Wanaea 6 site, undertaken 11 months after the completion of drilling, indicated relatively low residual*

hydrocarbon concentrations (<200mg/kg) below the cuttings discharge point. After three years, biological effects appeared to be limited to within 100 m of the cuttings discharge point, with background levels of TPH and trace metals occurring at 1200 m in the direction of the prevailing current. Dramatic reductions in TPH and barium concentrations occurred in the 12 month period between the completion of drilling and the follow up survey at Lynx 1a. The reductions are attributed to sediment dispersal mechanisms which appear to play a major role in reducing sediment TPH and trace metal concentrations in mid shelf depths (70-80m) on the NWS. The installation and presence of subsea production facilities may result in sediment redistribution and changed dispersal mechanisms, complicating the interpretation of contaminants within sediment samples.

Ooi, B.-H. 1994. Marine environmental monitoring program. SPE 27166. Pages 593-602 In: The Second International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Jakarta, Indonesia, 25-27 January 1994. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *In the drilling for and production of crude oil and gas offshore, it is necessary to assess the effects of such activities on the marine environment. Environmental monitoring programs are conducted to collect data for assessing the effects and determining the degree of impact. They provide the bases for implementing appropriate measures to mitigate the impact. Esso Production Malaysia Inc. (SPMI) has since its early years of operation in Malaysia in the seventies, conducted several monitoring studies to gauge the impact of its operations on marine waters. The studies entail physical, chemical and biological aspects, and use of the benthic community to track short and long term effects. This paper describes the Seligi Environmental Monitoring Program commissioned by EPMI, and discusses observations made from it.*

Painter, H.A. 1995. Detailed review paper on biodegradability testing. OCDE/GC(95)43. Environment Monograph No 98. OECD Series on the Test Guidelines Programme. Number 2. Environment Directorate, Organisation for Economic Co-operation and Development. Paris.

Abstract: *A literature search was made to investigate developments and advances in methods for determining biodegradability over the last decade or so. The literature reviewed did not indicate that there was a real need to develop fundamentally new OECD Test Guidelines for biodegradation tests. Several approaches for measuring or estimating biodegradation rates are described, some of which may be suitable for evaluating biodegradation of synthetic-base drilling fluids.*

Park, S., D. Cullum, and A.D. McLean. 1993. The success of synthetic-based drilling fluids offshore Gulf of Mexico: a field comparison to conventional systems. SPE 26354. Pages 405-418 In: The 68th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers. Houston, TX, 3-6 October 1993. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *The first wells have been successfully completed offshore Gulf of Mexico using a new synthetic-based drilling fluid. Polyalphaolefin (PAO), the synthetic base used for these fluids, is unique to the drilling fluids industry at this time. The environmental benefits of PAO-based synthetic systems over conventional oil-based fluids and some water-based fluids has already been presented in prior papers. However, the practical benefits gained from utilizing PAO as an alternative to conventional systems can now be documented after a series of highly successful field tests in the Gulf of Mexico.*

The non-aqueous PAO system has been used on several wells in the Gulf of Mexico to drill problematic formations previously drilled with either inhibitive water-based or oil-based fluids. Wells with angles up to 86° and formations from 4500 ft to 18300 ft have been successfully drilled. Direct comparisons can be made regarding performance benefits of PAO-based synthetic systems versus water-based and oil-based systems previously used to drill in the same location. Benefits in hole stability, cuttings, integrity, lubrication, and gauge wellbores, all leading to increased penetration rates and subsequent reduction in drilling days, can be seen.

This paper reviews the results of the first field tests with PAO synthetic systems in the Gulf of Mexico concentrating on the practical aspects of drilling rather than the detailed environmental information which has been covered in prior literature.

Patel, A.D. 1998. Choosing the right synthetic-based drilling fluids: drilling performance versus environmental impact. SPE 39508. Pages 1-14 In: The First SPE India Oil and Gas Conference and Exhibition. New Delhi, 17-19 February 1998. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *Environmental issues have created ever-moving targets for drilling fluids, or muds. Environmental regulations are diverse, complex, and have a tremendous impact on drilling operations, economically as well as logistically. In order to successfully meet these regulatory constraints, synthetic-based muds are becoming increasingly popular as substitutes for conventional oil-based muds. Continual evolution of synthetic-based muds (SBMs) and the increasing diversity of synthetic base fluids (SBFs) have made the selection of environmentally acceptable synthetic fluids increasingly complex requiring knowledge of chemical composition and structure effects on toxicity, biodegradability, and performance.*

Examination of the SBFs, the synthetic base fluids, provides insight into the environmental and performance issues that affect the selection and drilling performance of the SBMs, the mud. The toxicity, biodegradability, and bioaccumulation of SBMs depend on the molecular composition and structure of the base fluid. In general, the degree of branching affects the biodegradability and the molecular weight affects the toxicity of synthetics derived from similar chemistry. The thermal stability and performance characteristics of the SBMs depend on the chemical composition of the base fluid and emulsifiers used in the SBMs. The final choice of the SBF depends on the application and environmental requirements for a particular area; however, synthetic hydrocarbon-based fluids have shown to be overall best in cost vs performance.

Petersen, S.P., B. Kruse, and K. Jensen. 1991. Degradation of low toxicity drilling mud base oil in sediment cores. Marine Pollution Bulletin. 22(9):452-455.

Abstract: *The removal of low toxicity base oil originating from drilling mud, was tested in sediment cores. The sediment was contaminated with 200 mg kg⁻¹ dry wt low toxic drilling base oil, and the amount of oil was determined using micro steam distillation and GC. The removal time in the upper centimeter of the sediment was estimated to be 147 days and the velocity constant to be 1.4 mg total PHC/kg dry sediment/day. No degradation could be seen in the underlying sediment, where the oil content remained constant or increased slightly due to bioturbation during the test period of 66 days.*

Petrazzuolo, Gary. 1997. Memorandum from *Avanti* Corporation, to Joseph Daly, U.S. EPA/OST/EAD, regarding review of the "Simulated Seabed" NIVA protocols for assessing potential impacts from discharges of cuttings from synthetic drilling fluid systems. 5 pp.

Abstract: *This memorandum presents a review, analysis, and evaluation of the NIVA protocols. The general experimental design of the NIVA protocols are presented first followed by an analysis and evaluation of the general and synthetic fluid-specific design considerations. The NIVA protocols afford the ability to undertake an experimental approach to ecological-scale investigation because the complexity that the system can provide affords observations of complicated, inter-related ecological processes and phenomena. Because of this complexity, the NIVA protocols are a less attractive approach to expend resources.*

Phillips, C., J. Evans, W. Hom, and J. Clayton. 1998. Long-term changes in sediment barium inventories associated with drilling-related discharges in the Santa Maria Basin, California, USA. Environmental Toxicology and Chemistry. 17(9):1653-1661.

Abstract: *Nine-year (1986-1995) records of barium (Ba) concentrations in surficial, subsurface, and suspended sediments near offshore oil and gas platforms in the Santa Maria Basin, California, USA, were analyzed to evaluate temporal trends related to drilling activities. These trends provide important information on the long-term effects of drilling discharges on geochemical conditions. Drilling during the 1986 through 1989 (phase II) monitoring period resulted in significant changes in Ba concentrations in suspended particles and surficial sediments, whereas the relatively shorter 1993 through 1994 (phase III) drilling operations resulted in only minor increases in Ba concentrations in suspended sediments. Residual excess Ba was present in some sediments within 500 m of the platforms at concentrations up to an order of magnitude above background. These elevated levels probably were associated with cuttings particles deposited near the base of the platforms. Calculated excess Ba in sediments within 500 m of the platforms represented 6 to 11 % of the total Ba discharged during the two drilling periods.*

Rabion, A., F. Perie, A.G.M. Basseres, and C. Zurdo. 1997. Biodegradation of synthetic muds: oxidative pretreatments. SPE 37862. In: 1997 SPE/UKOOA European Environmental Conference. Aberdeen, Scotland, 15-16 April 1997. Society of Petroleum Engineers, Inc. Richardson, TX. 7 pp.

Abstract: *This report describes a simple pretreatment to enhance olefin-based pseudo-oil-based mud biodegradation under bottom of the sea conditions. The suggested treatment involves the oxidation of cuttings with diluted nitric acid prior to liquid-solid separation, sea-water neutralization of the mud, and biodegradation. Saturated hydrocarbons such as polyalphaolefins contained in cuttings were not degraded under the proposed reaction conditions. Comparison of oxidized and untreated olefins-impregnated cuttings clearly demonstrates that oxidized cuttings biodegrade more rapidly than untreated ones. Furthermore, we demonstrate that oxidized cuttings allowed for an enhanced evolution of carbon dioxide as compared to unsoiled sediments. In addition it was shown that olefins have an inhibitory effect upon the sediment mineralization and that overall CO₂ evolution is significantly lower with untreated cuttings soiled sediments as compared to the unsoiled sediments.*

Rabke, S.P., J. Candler, and C. Trial. 1998. Development of acute benthic toxicity testing for monitoring synthetic-based muds discharged offshore. Presented at the IBC Conference on Monitoring the Environmental Effects of Offshore Drilling, Houston, TX. 26 pp.

Abstract: *Synthetic-based muds (SBM's) have performance advantages over traditional drilling fluids in offshore applications, especially deep water. These advantages can reduce the volume of waste generated. Because of the physical and chemical properties of cuttings coated with SBM, the investigation of potential impacts of SBM's on the environment has focused on the seafloor. Acute benthic toxicity tests are one method of evaluating potential seafloor environmental impacts from SBM's. This paper will look at benthic organisms, using EPA 600/R-24/025 and ASTM E1367-92, as possible test methods. It also presents information on reproducibility and variability of the tests and test organisms. The average acute toxicities of the base fluid to the benthic amphipod *Ampelisca abdita* were 0.9 mg/kg, 3.5 mg/kg, and 11.7 mg/kg for diesel fuel, C1618IO, and PAO, respectively. The relative toxicities of the three whole muds were 1.5 mg/kg, 2.5 mg/kg, and 3.7 mg/kg, respectively. Sediments in the test containers did not become anoxic during the tests, so anoxia did not contribute to the observed toxicity.*

Rabke, S.P. and J.E. Candler. 1998. Reducing potential seafloor impacts from synthetic-based muds with acute benthic toxicity testing. Presented at the 5th Annual International Petroleum Environmental Conference. Albuquerque, New Mexico, October 20-23, 1998. 16 Pages plus appendix and charts.

Abstract: *The use of synthetic-based mud (SBM) can improve drilling performance and reduce the volume of pollution for offshore operations. Because of the hydrophobic nature of cuttings coated with SBM, the cuttings will settle rapidly to the seafloor. Consequently the focus of investigations has been on the benthic community. Laboratory tests that measure acute benthic toxicity and biodegradation rates may be useful tools for predicting impacts of various SBM's on the seafloor. This paper reports the most updated information on development of benthic toxicity tests that can be used on SBM's. The mean acute toxicity to the benthic amphipod *Leptocheirus plumulosus* in solid phase tests was 407 mg/kg for diesel fuel and 1581 mg/kg for C1618IO.*

Rabke, S.P. and J.E. Candler. 1999. Maximizing the discriminatory power for non-aqueous fluids using modified *Leptocheirus plumulosus* sediment toxicity test method. Poster, SETAC Annual Meeting, Philadelphia, PA, Nov. 14-18, 1999. Manuscript from M-I L.L.C, Houston, TX.

Abstract: *Advanced drilling fluids used in offshore applications have been using non-aqueous base fluids to increase performance. In order to select non-aqueous products that minimized acute toxic effects when discharged into marine benthic environments, a toxicity test must be able to discriminate between different technologies. In this study, non-aqueous materials, used as base fluids for drilling offshore, were spiked into sediments to evaluate their toxic effect on the test organisms. The purpose of this paper is to evaluate the discriminatory power of a modified version of the sediment toxicity test using *Leptocheirus plumulosus*. The modifications evaluated included shortening the test duration from ten days to four days and using formulated sediments as the substrate. By modifying the test parameters, the test can increase its discriminatory power and repeatability can increase test performance. The average 96h LC50 for a diesel and an internal olefin, determined with the modified test, were 534±19 mg/kg and 3480±36 mg/kg, respectively.*

Robert Ayers & Associates, Inc., S. McKelvie, and R.C. Ayers, Jr. 1997. Environmental effects of cuttings from synthetic based drilling fluids. A literature review. Prepared by Robert Ayers & Associates, Inc., S. McKelvie of Rudall Blanchard Associates, and R.C. Ayers, Jr. Report for: American Petroleum Institute. Robert Ayers & Associates, Inc. Houston, TX. 33 pp.

Abstract: Synthetic based drilling muds (SBMs) have been developed for use in difficult drilling situations in response to restrictions on the discharge of cuttings associated with oil based muds (OBMs). SBMs exhibit drilling performance comparable to OBMs while the base fluid (synthetic) is less toxic and degrades faster than conventional mineral oils or diesels. A "synthetic material" or "synthetic" as defined by the U.S. EPA means a material produced by the reaction of specific purified chemical feedstocks. Synthetics differ in this way from traditional non-aqueous base fluids such as diesel and mineral oil. At this time (May 1997), SBMs have been used more in the North Sea than in the Gulf of Mexico; however, SBMs have great potential to lower drilling costs in deepwater areas of the Gulf, a region of increasing importance to the U.S. industry.

Recent studies, particularly in the UK, have suggested that the environmental effects resulting from the discharge of SBM cuttings may be similar to those associated with OBM. In order to determine if similar impacts occur in the Gulf of Mexico, a consortium of operators and mud suppliers is planning studies to evaluate the environmental impacts of SBM discharges in the Gulf. API commissioned this review to aid in the planning process.

SBMs may be classified into four general categories:

- synthetic hydrocarbons;
- ethers;
- esters; and
- acetals.

At this time, the most common SBMs used in the Gulf of Mexico are the synthetic hydrocarbons. Of these, linear alpha olefins (LAOs) and internal olefins (IOs) are most preferred. Esters and blends of an ester with a synthetic hydrocarbon are also being used.

Perhaps the most important fluid properties that may affect environmental impacts are toxicity and rate of biodegradation. Laboratory studies have shown that, though toxicity levels vary considerably, most synthetics exhibit low toxicity and can generally meet toxicity requirements in all countries where toxicity data are required. Toxicity within a particular class of SBMs appears to be inversely related to molecular size, which affects water solubility. For example, the toxicity ranking for the olefins is LAO=IO>PAO. However, most standard toxicity tests, such as the U.S. EPA drilling fluid test, have limited application to the discharge of SBM cuttings because the cuttings settle quickly and exposure times in the water column are quite short. Solid phase bioassay tests have the potential of better estimating the toxicity of SBM cuttings. Biodegradation of SBMs has been studied in three types of experiments:

- standard laboratory tests;
- solid phase tests; and
- simulated seabed studies.

There has been some confusion regarding the biodegradability of SBMs from laboratory studies because of the wide variety of methods available, some of which may not be comparable or relevant to the conditions of discharge in the marine environment. Generally, test results suggest that biodegradation rate occurs in the following order: ester>LAO/IO>PAO>acetal.

Solid phase tests have been developed to better reflect seafloor conditions than standard biodegradation tests. These tests measure losses of SBM from all mechanisms, not just biodegradation. The results are in general agreement with the relative ranking obtained in the conventional biodegradation tests and also suggest that some SBMs degrade at rates similar to mineral oils. In addition these tests show that degradation rates are dependent on concentration and also sediment type.

Simulated seabed studies have found a similar ranking of degradation rates as those reported from solid phase tests. There are also indications of degradation being dependent on concentration in sediments. These studies also

found that the faster degrading SBMs have the greatest impact on the benthic fauna because of the resultant reduction in oxygen in the sediments.

Results from field surveys where SBMs have been used are limited and impacts are difficult to compare because of the wide range of factors involved (e.g. water depth, temperature, currents, mud type, geology, benthic fauna).

Based on available data, the LAOs, IOs and esters appear to be superior to other classes of synthetics in terms of the associated environmental effects. Each class has advantages and disadvantages. Esters biodegrade quicker than LAOs or IOs and may cause sediments to become anoxic resulting in a relatively more severe initial impact; however, the ester's faster biodegradation rate may also result in faster recovery.

While much is known about the environmental effects of synthetic use, a number of information gaps still exist. The most important need is a better understanding of SBM cuttings discharge in Gulf of Mexico environments. More information is needed on how environmental conditions at the seafloor affect impact and recovery. A key factor is to determine if SBM cuttings discharge will result in the formation of persistent cuttings piles similar to those found in certain areas of the North Sea. In addition to the seafloor field studies, laboratory studies designed to provide more information on toxicity of synthetics to benthic organisms and biodegradation rates under Gulf of Mexico seafloor conditions should be considered.

Rushing, J.H., M.A. Churan, and F.V. Jones. 1991. Bioaccumulation from mineral oil-wet and synthetic liquid-wet cuttings in an estuarine fish, *Fundulus grandis*. SPE 23350. Pages 311-320 In: The First International Conference on Health, Safety and Environment. The Hague, The Netherlands, 10-14 November 1991. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: The long-term effects of discharged oily drill cuttings on native fish populations are of major concern. This study investigates the uptake of oil and synthetic liquid by the mud minnow, *Fundulus grandis*, when exposed to three different concentrations of low-aromatic mineral oil-wet and synthetic liquid-wet cuttings in flow-through bioassay chambers.

Fish were introduced into the flow-through bioassay system and cultured for 30 days. Water, cuttings, and fish were sampled routinely for analysis. Fish samples were dissected; gut and tissue samples were analyzed separately. Flow-through water was analyzed by extracting the water sampling tube absorbent. The cuttings samples were analyzed by Soxhlet extraction. Fish tissue and gut samples were digested in sodium hydroxide and extracted with ether. The extracted organics in all the samples were analyzed by gas chromatograph/mass spectrometry.

Gas chromatograph/mass spectrometry identified uptake of the mineral oil in fish tissue and gut samples for all cuttings treated with mineral oil-based mud (MOBM). No uptake was measured in any of the tissue samples for all cuttings treated with synthetic liquid-based mud (SBM). An accumulation of synthetic liquid was only detected in one sample of fish gut from the lowest concentration of SBM. The contrast in uptake between the mineral oil and the synthetic liquid is perhaps due to the greater molecular size of the synthetic liquid over that of the mineral oil. It is hypothesized that the greater molecular size of the synthetic liquid restricts uptake by gill and digestive structures.

During the study, there was little migration of either base fluid from the cuttings. Hydrocarbon amounts in the water samples generally decreased during the 30-day test period. All collected organics were liberated as negligibly soluble microdroplets. Tests indicated no selective solubility of released microdroplets and little if any biodegradation for both SBM and MOBM.

Rye, H., T. Nordtug, A. Tobiesen, and A. Østeorøt. 1997. Drilling and well chemicals and their environmental impacts. A survey of amounts, ecotoxicological properties, dispersion and impacts in the marine environment. Paper in "Chemistry in the Oil Industry," 6th International Symposium. Ambleside, the Lake District, UK, 14-17 April, 1997. The Royal Society of Chemistry, UK. London. 21 pp.

Abstract: OLF (The Norwegian Oil Industry Association) has performed a survey on the potential for harmful environmental effects caused by releases from drilling and well operations in the Norwegian continental shelf. The project was divided into four different parts:

- *A survey of released chemicals from the Norwegian offshore industry during drilling and well operations through the years 1993 and 1994, on a component level.*
- *An ecotoxicological characterization of the most harmful compounds that amounted to more than 500 kg released per year in total to the Norwegian continental shelf.*
- *A calculation of the dispersion and expected deposition of the releases in the marine environments in order to determine the downstream distance to the estimate No Effect Concentration level for various compounds, both in the free water masses and on the sea bottom.*
- *An evaluation of possible (acute or chronic) impact on marine resources in the free water masses and on the bottom fauna (benthic community) from the most harmful compounds (including deposition of barite).*

The study comprises the releases of:

- *Water based drilling fluids (WBM)*
- *Water based cuttings (WBC)*
- *Synthetic based cuttings (SBC)*
- *Well chemicals.*

Oil based mud and cuttings (OBM and OBC) as well as synthetic based mud (SBM) are not allowed to be released on the Norwegian continental shelf. The (Oslo and) Paris Commission (PARCOM) and OSPARCOM has since 1980 recommended (in different “decisions”) that the use of oil based mud should be reduced or avoided, until the standard of 10 g/kg (1 percent) of oil content in cuttings is attained. This criterion has been in effect since 1 January 1997 (Decision 92/2, OSPARCOM 1993).

Rymell, M.C., Z.A. Sabeur, M.O. Williams, and D.M. Borwell. 1997. Development and application of environmental models in the assessment of exploratory drilling in a sensitive coastal region, Isle of Man, UK. SPE 37872. Pages 257-265 In: 1997 SPE/UKOOA European Environmental Conference. Aberdeen, Scotland, 15-16 April 1997. Society of Petroleum Engineers, Inc., Richardson, TX.

Abstract: *Contamination of the seabed by drilling operation discharges and the potential for accidental oil spillage remains a significant environmental concern. A project commissioned by Elf Caledonia Ltd. has led to the development of a series of models that allow assessment of the environmental impact of contaminants associated with offshore drilling and prediction of possible oil spill scenarios.*

Three environmental modelling systems have been implemented. A current flow prediction system has been set up to provide a primary source of data on the hydrodynamics of the region. An oil spill model allows prediction of the trajectory and fate of oil in the event of an accidental spillage. The third model considers the drilling mud and cuttings discharges made during exploration. The three models use the same base set of hydrodynamics/bathymetry and run under the same base GIS user-interface.

This paper discusses the development of the various databases underlying the models, development of the models and the use of the models in planning the drilling programme. Development of models for future applications is discussed.

Sachez, G., N. Leon, M. Esclapes, I. Galindo, A. Martinez, J. Bruzual, and I. Siegert. 1999. Environmentally safe oil-based fluids for drilling activities. SPE 52739. Pages 469-478 In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: Diesel based drilling fluids had been widely used in the past due to its low price in the market. However, it has been well documented the adverse health and environmental effects of diesel mostly due to the high aromatic hydrocarbon content which makes it toxic. As an alternative to the use of diesel, PDVSA-Intevep has addressed efforts toward the development of environmentally safe drilling fluids. In that sense, new oil based mud formulated with mineral oil (< 0.1% aromatics) and palm tree oil (without aromatic), both produced in Venezuela, have been used for drilling operation purposes to overcome the environmental and health risks. The present work evaluated the toxic and biodegradability of mineral and palm tree oil-base drilling fluids compared to those formulated with diesel. Standard procedures were performed for both tests. U.S.-EPA protocols were followed for toxicity evaluation and A.S.T.M. for biodegradability tests. Biodegradation rate of drilling cuttings impregnated with the three fluids were estimated in soil pans at laboratory scale to determine bioremediation process of the waste. The results indicate that mineral and palm tree oil based fluids are not toxic ($LC_{50} > 30,000$ ppm) while diesel was more toxic (LC_{50} 19,000 ppm). Under anaerobic conditions, the palm tree oil based fluid was the only one biodegraded (>70%). From the soil pan studies, the three types of oil impregnated cuttings could be bioremediated; nevertheless, the palm tree oil cuttings biodegrade in soil compost even without aeration.

Schaanning, M.T. 1994. Test on Degradation of Aquamul BII Drill Mud on Cuttings under Simulated Seabed Conditions. NIVA rapport nr 3092.

Abstract: The biodegradation of an ether and ester SBM was compared with a mineral oil mud in the NIVA semi-enclosed experimental chambers. The biodegradation of the ester was similar to other studies. Biodegradation of the ether was slow with the half-life exceeding 100 days and oxygen consumption rates not significantly different from the mineral oil.

Schaanning, M.T. 1996. Environmental Fate of Synthetic Drilling Fluids from Offshore Drilling Operations. NIVA rapport nr. 3429-96.

Abstract: This study compared the biodegradation of three SBM mud systems, an ester, an ether and a PAO, in the NIVA semi-enclosed experimental chambers. Similar biodegradation rates were found for the PAO and ether fluids, except that the degradation of the ether was consistent with a 60-day lag phase before degradation was evident. A half-life of 210 days was calculated for the PAO even though 55-60% of the fluid was present at the end of the 5-month experimental period. The total loss of the ether was similar (half-life = 254 days) but the loss by biodegradation alone was slow (half-life = 387 days). Processes other than biodegradation were concluded to be more significant for the ether than the other two muds. The ester fluid degraded at the fastest rate (half-life = 92 days). However, this was associated with anoxic conditions as an accumulation of hydrogen sulfide was evident in the pore waters.

Schaanning, M, T. Bakke and J.A. Berge. 1996b. En totalvurdering av miljøkonsekvenser ved bruk av ulike syntetiske borevaesker ved leteboring og produksjonsboring. NIVA Rapport LNR 3534-96.

Abstract: This report summarized the results of many of the biodegradation studies on SBMs undertaken at NIVA. The comparison showed that, for all SBM types tested (e.g. ether, PAO, ester, internal olefin, linear olefin), rate of biodegradation was proportional to the initial concentration of mud in sediment.

The report provided further evidence for a 60-day lag phase in the degradation of ether SBM in sediment. Further analysis also demonstrated the higher sediment oxygen consumption and subsequent reduction in sediment redox potential associated with the rapid degradation of ester SBM in sediments compared to other SBM types.

The paper also reviewed data from field studies in the Norwegian sector of the North Sea by analyzing concentrations of mud in sediments normalized to barium concentration in order to separate biodegradation from other losses such as resuspension and sediment movement. These data showed that esters biodegraded within 1 year of discharge whereas there was little biodegradation of ether until 2 years after drilling.

Schaanning, M., K. Hylland, R. Lichtenthaler, and B. Rygg. 1996. Biodegradation of *Anco Green* and *Novaplus* drilling muds on cuttings deposited in benthic chambers. Report SNO 3475-96. Norwegian Institute for Water Research. Oslo, Norway. 77 Pages plus appendix.

Abstract: Discharge of drilling fluids attached to bore hole cuttings may affect the benthic environment of the deposition sites in the North Sea. The effects may vary according to dose and properties of the base fluid and other components of the mud recipe. In the present study, biodegradation and environmental effects of two new drilling muds, *Anco Green* (Based on an ester produced from fish oil fatty acids) and *Novaplus* (based on a linear olefin), was investigated in a six months simulated seabed experiment performed in benthic chambers at Marine Research Station Solbergstrand. Exponential regression analyses yielded the following rank of half-lives: *Anco Green* < *Petrofree* (reference ester) < *Ultidril* (reference olefin) < *Novaplus* < *Safemul* (reference mineral oil.). Effects of the ester based cuttings on redox-potentials and macrobenthic communities were more severe than the effects of olefin based cuttings. The most severe effects were observed in the *Petrofree* treatment. All chambers treated with olefin cuttings or low-organic control sediment, maintained diverse benthic communities classified by the end of the six months enclosure, as good or fair according to general criteria for fjord and coastal environments. Concentrations of drilling fluids, barium and two biomarker enzymes were measured in the polychaete *Hediste diversicolor* after six months exposure in the chambers. Several indications were found on bioaccumulation of olefins and mineral oil. Different levels of enzyme activities between control and treated chambers, showed that the polychaete had been affected by components present in some of the cuttings.

The ester mud showed rapid degradation with half lives of between 13.9 and 20.8 days, comparable with studies of other ester muds. Degradation of the internal olefin mud was slower than the linear olefin (half lives of 74 and 40-72 days, respectively) but faster than the mineral oil (half-life of 105 days). However, none of the tests showed complete disappearance of the olefin muds and the apparent low availability of olefins to sulfate reducing bacteria may slow down biodegradation of buried olefins.

Schaanning, M.T. and Laake, M. 1993. Test on Degradation of *Novadril* drill mud on cuttings under simulated seabed conditions. NIVA rapport nr. 2866.

Abstract: The biodegradation of a PAO mud was examined within the NIVA semi-enclosed experimental chambers. The biodegradation of the PAO was found to be slow. The half-life was 127 days at the lower initial concentration (2.2 mg/cm²). At a higher concentration (11.5 mg/cm²) there was little evidence of biodegradation. Oxygen consumption rates for the PAO did not differ significantly from those found for mineral oil.

Schaanning, M., R. Lichtenthaler, and B. Rygg. 1997. Biodegradation of esters and olefins in drilling mud deposited on Arctic soft-bottom communities in a low-temperature mesocosm. Report SNO 3760-97. Norwegian Institute for Water Research. Oslo, Norway. 57 Pages plus appendices.

Abstract: Discharge of chemicals from offshore drilling operations represents a matter of concern for the oil industry and pollution control authorities worldwide. As the industry expands towards higher latitudes and greater depths, mud chemicals attached to bore hole cuttings may become deposited on sediments with ambient temperatures below 0°C. In order to assess the fate of the most recently developed ester- and olefin-based chemicals under such conditions, a comparative study was performed in the soft-bottom laboratory at Marine Research Station Solbergstrand on sediment communities transferred from Arctic and temperate deep fjord locations. The sediments were initially treated with four levels of cuttings (zero, 5, 50, and 200 mg) and maintained at simulated seabed conditions at -0.5 and 7°C. Biodegradation and effects on the sediment environment were assessed from observations of concentration change of organic phase and barium in the sediment, oxygen consumption rates, redox potentials and the macrobenthic community structure. During the three months experimental period, increasing rates of oxygen consumption in the Arctic communities showed adaptation to degradation of the chemicals at rates no less than those observed in the Oslofjord communities. The Arctic communities appeared, however, more sensitive to sulphide toxicity produced in high dose ester treatments, and no evidence was found to support the hypothesis that better availability to anoxic degraders would yield shorter sea-bed remediation times of areas contaminated with esters as compared to areas contaminated with C₁₄-C₁₈ olefins.

Slater, M., M.H. Hille, and A. Molversmyr. 1995. Commonly used biodegradation techniques for drilling fluid chemicals, are they appropriate? SPE/IADC 29376. Pages 387-397 In: 1995 SPE/IADC Drilling Conference. Amsterdam, 28 February-2 March 1995. SPE/IADC Drilling Conference. Richardson, TX.

Abstract: *In order to assess the suitability of commonly used biodegradation techniques to simulate the environmental behaviour of pseudo oil-based fluids in the sea, a comprehensive study has been conducted. More than 40 biodegradation experiments, using different techniques, have been performed on one particular synthetic base fluid (an acetal). The results are compared to large-scale simulation tests and a seabed survey in an attempt to identify the biodegradation method that most closely resembles the natural biodegradation process. Acetal, poly alpha olefin, and ester have acute toxicities in water column tests with barnacles of 173,000, >69,000, and 100,000, respectively. Several biodegradability tests were performed on the acetal and produced degradation rates between 5 percent and 87 percent. A simulated seabed study by NIVA (Norway) showed loss of acetal varying from 31 to 67 percent after 5 months. Freshwater simulation studies seem to produce results similar to those for field studies.*

Stagg, R.M., B. Croce, A.D. McIntosh, C. Moffat, and S. Hird. 1996. Biodegradation of base-oils used in synthetic drilling muds in an experimental solid-phase sediment system. Fisheries Research Services Report No 3/96. Scottish Office Agriculture, Environment and Fisheries Department, Marine Laboratory. Aberdeen. 40 pp.

Abstract: *The results are described of a trial designed to evaluate the performance of a solid-phase biodegradation test set up to assess the fate in marine sediments of base oils used in synthetic drilling muds (SMs) used for drilling offshore wells. The test was intended to provide conditions for degradation that more closely paralleled those that would be encountered in the marine environment, with particular respect to temperature, microbial flora and anaerobic characteristics.*

The method was evaluated by determining the effects on biodegradation of the following factors:

- *Synthetic oil type. Two different SM base oils were used in the study: an ester type and a blend of n-alkanes, poly-alpha olefin, and linear-alpha olefin.*
- *Oil concentration. The oils were mixed with the sediments to give concentrations of 100, 500, and 5,000 ppm. These were selected because such concentrations have been determined in and around mineral oil cuttings piles.*
- *Sediment type. A sand, a mud, and a 1:1 sand/mud mixture were chosen to provide a range of particle size variance.*

Suitable control treatments for the experiment were also investigated with the use of olive oil treated sediments as positive controls and mercuric chloride treated sediments to provide a measure of abiotic losses from the system. The parameters measured included: the amount of SM base oil remaining in the sediment at the stated sampling times (using gas chromatography with flame ionization detection); the oxidation-reduction potential of the sediments; the oxygen consumption of selected sediments; and population of microbes in the sediments.

The test was able to reproducibly distinguish between easily biodegradable and poor biodegradable oils. In this system, primary biodegradation rates for the ester were faster than for the n-alkane/alkene. However, the rapid metabolism of the ester resulted in a depletion of oxygen, a drop in the redox potential and the occurrence of sulphide events in the sediments.

In 1:1 sand/mud mixtures, the rates of primary biodegradation of the ester were not significantly different when the dosing concentrations were 100 and 500 ppm (mean rate 15 ppm d⁻¹, half-life 13 d) but the rate of degradation significantly increased in sediments dosed with 5,000 ppm ester (rate 40 ppm d⁻¹, half-life 83 d). Although not statistically significant, the same effect was seen for the blended oil which, at 100 and 500 ppm, had a mean primary biodegradation rate of 5 ppm d⁻¹ and a half-life of 77 d; this rate increased to 15 ppm d⁻¹ with a half-life of 236 d when the concentration was increased to 5,000 ppm. Biodegradation of the ester was

significantly slower in sand as compared to mud. No measurable biodegradation of the blended oil took place in the sand treatments.

Olive oil stimulated a high degree of microbial activity in the sediments that made it suitable as a reference compound for this test system. Sediments "poisoned" with mercuric chloride showed similar losses of test oils after a 60-d incubation to those determined in their unpoisoned counterparts. This was thought to be caused by sediment binding effects decreasing the effective toxicity of the mercuric chloride which did not provide the abiotic conditions intended.

Steber, J., C.-P. Herold, H. KGaA, and J.M. Limia. 1994. Solving fluid biodegradation in seabed drill cuttings pile. Offshore. 57-60.

Abstract: The European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) screening test was used to evaluate the biodegradability of several base oils for drilling muds. Alkylbenzenes were not biodegraded. Fatty acid esters, oleyl alcohol, and 2-ethyl hexanol muds were degraded by 79 to 89 percent under anaerobic conditions. Mineral oils, di-octyl ether, di-hexadecyl ether, and polyalpha olefin muds degraded slowly by 0.6 to 12 percent during the test.

Steber, J., C.-P. Herold, and J.M. Limia. 1995. Comparative evaluation of anaerobic biodegradability of hydrocarbons and fatty derivatives currently used as drilling fluids. Chemosphere. 31(4):3105-3118.

Abstract: The examination of a number of potential and currently used carrier fluids for invert emulsion drilling fluids in the ECETOC screening test revealed clear differences with respect to their easy anaerobic biodegradability. Fatty acid- and alcohol-based ester oils exhibited excellent anaerobic degradation to the gaseous final end products of the methanogenic degradation pathway, methane and carbon dioxide. Mineral oils, dialkyl ethers, α -olefins, polyalphaolefins, linear alkylbenzenes and an acetal-derivative were not or only slowly degraded. Although the poor degradation results obtained in the stringent ECETOC screening test may not be regarded as final proof of anaerobic recalcitrance, nevertheless, these results were found to be in line with the present understanding of the structural requirements for anaerobic biodegradability of chemicals. The validity of the conclusions drawn is corroborated by published results on the anaerobic biodegradation behaviour of ester oils, mineral oils and alkylbenzenes in marine sediments.

Still, I. and J. Candler. 1997. Benthic toxicity testing of oil-based and synthetic based drilling fluids. Eighth International Symposium on Toxicity Assessment. Perth, Australia, 25-30 May 1997. (Cited in EPA, 1999).

Abstract: A two-phase sediment toxicity study was performed to examine applicability of established sediment toxicity test methods for synthetic base fluids (SBFs). During Phase I, the marine amphipod *Ampelisca abdida* was tested with one drilling fluid formulation dosed individually with the following five base fluids: a diesel oil (DO), an enhanced mineral oil (EMO), a linear paraffin (LP), and internal olefin (IO), and a poly alpha olefin (PAO). Range finder tests were performed with test concentrations of 5,000 and 10,000 mg/kg. The ranking of relative toxicity was PAO>IO>LP at 5,000 mg/kg and LP>PAO>IO at 10,000 mg/kg. In Phase II, toxicity tests were performed with four species of marine amphipods. The response of each species was different:

- *Ampelisca abdida* – EMO (557 mg/kg)>DO (879 mg/kg)>IO (3,121 mg/kg)>PAO (10,680 mg/kg)
- *Corophium volutator* – DO (840 mg/kg)>EMO (7,146 mg/kg)>IO (>30,000 mg/kg)>PAO (>30,000 mg/kg)
- *Rheposynius abronius* – DO (24, mg/kg)>EMO (239 mg/kg)>IO (299 mg.kg)>PAO (975 mg/kg)
- *Leptocheirus plumulosus* – EMO (251 mg/kg)>DO (850 mg/kg)>IO (2,944 mg/kg)>PAO (9,636 mg/kg).

Story, J. and B. Lee. (Amoco Corporation). 1997. Solid phase extraction (SPE) method for determination of crude oil contamination in drilling fluids: a field method. Draft report. 2 pp.

Abstract: This is a draft protocol for detection of petroleum in SBM by solid phase extraction with quantification by fluorescence. The liquid phase of a SBM is applied to an active silica column and eluted with a MTBE solvent. The column is viewed under UV light and the fluorescing aromatic hydrocarbons are visualized and compared to standards.

Terrens, G.W., D. Gwyther, M.J. Keough, and R.D. Tait. 1998. Environmental assessment of synthetic based drilling mud discharges to Bass Strait, Australia. SPE 46622. Pages 1-14 In: 1998 SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production. Caracas, Venezuela, 7-10 June 1998. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: Esso Australia Ltd. (Esso) on behalf of the Esso/BHP joint venture undertakes exploration and development drilling activities to produce oil and gas from the Gippsland Basin in eastern Bass Strait. As part of the environmental management of the operation, a field monitoring program was undertaken to verify the predicted limited effect on the seabed of the discharge of residual synthetic based mud (SBM) adhered to drill cuttings.

Esso's standard drilling fluid in Bass Strait is an environmentally acceptable water based mud (WBM). However, due to the high frictional forces involved the greater lubricating properties of a non-water based drilling mud were required to drill the long reach, high angle sections of seven of the additional wells. The ester SBM was chosen on the basis of its lubricity and biodegradability, to reduce any potential environmental effects from the persistence of non-water based mud in seabed sediments.

A seabed monitoring program was undertaken around the Fortescue platform by taking seabed samples from August 1995 to August 1997 at sites along a transect following the predominant ocean current and at control sites, before, during and after the period in which SBM cuttings were discharged. The seabed sediments were measured for esters, barium, biological changes and grain size. Results show clearly the increase in esters concentration in sediments during drilling, then the rapid decrease after completion of cuttings discharge. After a recovery period of 11 months from completion of SBM drilling, SBM esters were not detected in sediments. Sediment barium concentration was also found to be elevated, but only after SBM had been used, indicating greater dispersion of WBM than the more cohesive SBM. The barium concentrations found generally do not have measurable effects on biota. The impact on the sediment biology was found to be limited to the sampling site 100 m from the platform with recovery evident within four months of completion of drilling. Mechanisms for recovery of the minimal zone of effect are thought to be a combination of the biodegradation of the ester SBM used and the physical seabed dispersion process evident in eastern Bass Strait generated by the continuous series of storms that pass through especially in winter.

Thaemlitz, C., A. Patel, G. Coffin, and L. Conn. 1997. A new environmentally safe high-temperature, water-base drilling fluid system. SPE/IADC 37606. Pages 263-268 In: 1997 SPE/IADC Drilling Conference. Amsterdam, The Netherlands, 4-6 March 1997. Society of Petroleum Engineers & International Association of Drilling Contractors Drilling Conference. Society of Petroleum Engineers, Richardson, TX.

Abstract: A new, environmentally safe water-based polymer system has been developed for drilling applications with temperatures up to 232°C (450°F) and high pressures. The system components are newly developed synthetic polymers that do not contain chromium or other environmentally harmful materials. These new synthetic polymers are designed to perform specific functions at high temperatures and the innovative designs of these thermally stable polymers allow for the use of a minimum number of products in the formulation of high-temperature fluids.

The new system consists of two basic polymeric components for rheology and filtration control at high temperatures. High-temperature fluid formulations are greatly simplified utilizing this new system, with only the two polymeric components being required, along with a pH control additive, weight material, and small amounts of clay for filter cake quality. This simplicity is a significant advantage over "traditional" high-temperature systems, which normally require use of a large number of additives to control or limit the effects of thermal degradation.

The new system may be formulated with fresh water or seawater, providing flexibility for a variety of drilling environments. Excellent resistance to common contaminants, such as calcium and magnesium hardness and solids accumulation, is another important characteristic of this new system.

This paper will review the previous state of the art with respect to high-temperature, water-based muds and will generically discuss the unique chemistry of the newly developed polymer system components. System formulation and application will be discussed.

Uhler, A.D., J.M. Neff, and T. Gulbransen. 1997. Survey of monitoring approaches for the detection of oil contamination in synthetic-based drilling muds (SBMs). Draft Report submitted to: American Petroleum Institute, Washington, DC. Battelle. Duxbury, MA. 47 pp.

Abstract: *The U.S. EPA recommends the bucket sheen test for determining if a drilling mud contains sufficient petroleum material that it should not be discharged to the sea. The sheen test is not suitable for evaluating synthetic-based drilling fluids. Several methods were evaluated for determining petroleum in synthetic-based drilling muds. The top-ranked methods for use on the platform are: direct photoionization detection of monoaromatic hydrocarbons; reverse solid-phase extraction for determination of crude oil contamination; solid-phase extraction for determination of crude oil contamination; and thin layer chromatography with UV fluorescence detection to detect aromatic hydrocarbons. Gas chromatographic methods are suitable for mud analysis in the laboratory.*

United Kingdom. 1997. Synthetic mud (SM) system control in the UK - an update. SEBA 97/5/1-E. Presented by the United Kingdom at the Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Sea-Based Activities (SEBA). Biarritz, France, February 17-21, 1997. 6 pp.

Abstract: *Degradability of SBMs was evaluated. Several SBM base chemicals were no more degradable than OBMs and will be phased out for offshore disposal by 2001. Other muds, including esters, may be discharged unless seabed surveys show unacceptable impact on the marine environment.*

Biodegradation of acetal, ester, internal olefin, linear alpha olefin, poly alpha olefin and n-paraffin were evaluated at 100, 500, and 5,000 mg organic carbon/g dry sediment. Four of the base materials, acetal, internal olefin, n-paraffin, and poly alpha olefin, did not perform better than mineral oil in terms of their relative degradation. Although linear alpha olefin performed significantly better than the mineral oil at all concentrations, 76 percent of the base fluid still remained after 120 days at the highest concentration. The rate of degradation of the base materials decreased as concentration in sediments increased. The rate of degradation of different chemicals decreased with increasing proportion of branching and complexity of the molecules. Some base materials had an apparent 28-day lag phase before degradation began.

United Kingdom Offshore Operators Association and United Kingdom Department of Trade and Industry. 1997. Synopsis of review of drill cuttings piles on the United Kingdom Continental Shelf. Agenda Item 5. SEBA 97/5/3-E. Presented by the United Kingdom at the Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Sea-Based Activities (SEBA). Biarritz, France, 17-21 February 1997. 3 pp.

Cuttings piles were observed around approximately 60 platforms in the northern and central North Sea. Shallow water depths in the southern North Sea allow dispersion of cuttings and cuttings piles do not accumulate. Cuttings piles range from less than 2 m to a maximum height of about 20 m. the piles are "soft" and contain 20% to 60% water. Hydrocarbons are biodegraded on the surface sediments in the pile but not below the surface. Severe impacts on benthic fauna are observed out to about 500 m; there is a transition zone of lesser impact out to about 2 km.

United Kingdom Offshore Operators Association and United Kingdom Department of Trade and Industry. 1997. Technical note on the use of synthetic drilling fluids. Agenda Item 5. SEBA 97/5/4-E. Presented by the United Kingdom at the Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Sea-Based Activities (SEBA). Biarritz, France, 17-21 February 1997. 1 pp.

Abstract: *With the phase-out of OBM, the UK oil industry has developed criteria for selection of replacement SBMs. Biodegradation studies, modelling, and seabed surveys are used to evaluate the environmental impacts of SBM cuttings.*

Veil, J.A., C.J. Burke, and D.O. Moses. 1996. Synthetic-based muds can improve drilling efficiency without polluting. *Oil & Gas Journal*. 94(10):49-54.

Abstract: *The authors describe the environmental benefits of synthetic-based drilling muds. These include: less waste is produced from a recyclable product (compared to WBMs); elimination of diesel as a mud base lessens the pollution hazard, improves worker safety through lower toxicity and diminished irritant properties, and reduces consequent risk (compared to OBMs); increased use of horizontal drilling reduces the areal extent and the environmental impacts of offshore oil and gas operations (compared to WBMs); shortened drilling time results in reduced air-emissions from drilling power sources (compared to WBMs); and improved drilling performance decreases waste-generating incidents, such as pipe stuck in the hole. Such incidents necessitate the use of diesel or other oil "pills" that add to the waste load from the mud (compared to WBMs).*

Veil, J.A. and J.M. Daly. 1999. Innovative regulatory approach for synthetic-based drilling fluids. SPE 52737. In: 1999 SPE/EPA Exploration and Production Environmental Conference. Austin, TX, 28 February-3 March 1999. Society of Petroleum Engineers, Inc. Richardson, TX. 5 pp.

Abstract: *The oil and gas industry has historically used water-based muds (WBMs) and oil-based muds (OBMs) in offshore drilling operations. WBMs are less expensive and are widely used. Both the WBMs and the associated drill cuttings may be discharged from the platform to the sea provided the U.S. Environmental Protection Agency (EPA) discharge limitations are met. In some wells, however, difficult drilling conditions may force a switch from a WBM to an OBM. Neither the OBM nor the associated drill cuttings may be discharged. The OBM is hauled to shore, where it is processed for reuse, while the associated cuttings are injected in a disposal well at the platform or hauled to shore to a disposal facility. Both of these options are expensive. Synthetic-based muds (SBMs) are drilling fluids that use synthetic organic chemicals as base fluids. SBMs were developed to replace OBMs in difficult drilling situations. SBMs are more expensive than OBMs; however, they have superior environmental properties that may permit the cuttings to be discharged on-site. Like OBMs, SBMs are hauled ashore for processing and reuse after the well is drilled.*

The existing national effluent limitations guidelines (ELGs) for the offshore industry do not include requirements for SBM-cuttings since SBMs were not commonly in use at the time the ELGs were adopted. In late 1997, EPA announced that it would modify the offshore ELGs to include requirements for discharges of cuttings drilled with SBMs. For the first time in the history of the ELG program, EPA is following an innovative expedited rulemaking process that will lead to development of draft regulations in one year rather than the 4- to 6-year period usually needed. With direction from the federal government to stakeholders concerning information needs for the regulatory development, the industry has established several working groups to collect new scientific information on SBMs. This paper describes the expedited rulemaking process and summarizes the findings of the workgroups to date.

Veil, J.A., J.M. Daly, and N. Johnson. 1999. EPA speeds regs for offshore synthetic-based mud. *Oil and Gas Journal*. 97(37):78-85.

Abstract: *The U.S. Environmental Protection Agency is collaborating with oil industry working groups to develop regulations for the discharge of SBM-cuttings to offshore waters of the Gulf of Mexico. The working groups include analytical, retention on cuttings, toxicity, seabed effects and biodegradation.*

The analytical work group has developed and evaluated methods for detecting petroleum in SBM. The recommended method for on-platform use is a reverse-phase extraction method, with confirmation for selected samples by GC/MS. The cuttings work group surveyed the percent of SBM on screened cuttings discharged to the ocean. They determined that there is between 4 and 25% SBM, average 12%, retained on washed cuttings. The toxicity work group is evaluating different bioassay protocols for determining the toxicity to marine organisms of SBM cuttings in marine sediments. The seabed work group is designing a multi-year survey to examine the effects of SBM cuttings discharges on benthic biological ecosystems. The biodegradation work group is evaluating different methods for measuring biodegradation of SBM in marine sediments. EPA has chosen a discharge option for regulating SBM, based on its assessment that water-quality impacts of appropriately controlled SBM discharges are less harmful to the environment than the non-water quality environmental impacts (fuel use, air emissions, etc.) that would occur if zero discharge had been selected. Proposed regulations include the following:

1. Zero discharge of neat SBM (fluids not attached to cuttings);
2. Limitations on SBM cuttings characteristics, including no more than 10 ppm PAH on cuttings, a minimum rate of biodegradation of SBM in sediments using the UK solid phase test, and a maximum 10-day sediment toxicity test using the amphipod *Leptocheirus plumulosus*;
3. Discharge limitations of cuttings containing SBMs, including no free oil by the static sheen test, a limit on contamination by crude oil, and a maximum of 10.2% retention of SBM on cuttings;
4. SBM cuttings discharges remain subject to current requirements for WBM, including a maximum of 1 mg/kg mercury in stock barite, a maximum of 3 mg/kg cadmium in stock barite, and no discharge of diesel fuel;
5. Other controls being considered include a maximum sediment toxicity of whole drilling fluid, a maximum aqueous phase toxicity of the whole SBM, and a maximum potential for bioaccumulation of base mud.

Vik, E.A., S. Dempsey, and B.S. Nesgard. 1996. Evaluation of available test results from environmental studies of synthetic based drilling muds. Version 4. Aquateam Report Number: 96-010. OLF Project. Acceptance Criteria for Drilling Fluids. Aquateam-Norwegian Water Technology Centre A/S. Oslo, Norway. 127 pp.

Abstract: This report includes a summary of all information brought forward to Aquateam for completion of an evaluation of test results from environmental impact studies of synthetic based mud systems. The project is carried out on behalf of OLF's Working Group on Acceptance Criteria for Discharges of Drilling Fluids.

The report includes an evaluation of laboratory test results, results from simulated seabed studies and from field surveys for the different synthetic mud systems. The report compares test results obtained under different test conditions and gives recommendations to a set of criteria and future work concerning implementation.

A marine anaerobic biodegradation test is needed to predict the persistence of synthetic based muds in the marine environment. The ultimate selection of the most environmentally friendly SBM should, however, not only compare environmental fate (percent biodegradation), but take into consideration the overall environmental impact. Field studies of SBM impacts are the best methods for evaluating the environmental behavior of SBMs, but are expensive. Mesocosm tests, such as the NIVA test, produce good results at lower costs. Acceptance criteria for ocean disposal of SBM cuttings should include:

- Requirements for documentation of absence of heavy metals, aromatic hydrocarbons, and other hazardous chemicals, evidence of biodegradability, and low potential to bioaccumulate.
- Risk assessment of environmental impact using CHARM.
- Validation of the CHARM model using specially designed mesocosm experiments (e.g., NIVA test).
- Standard test protocols for anaerobic degradation tests, determination of $\log K_{ow}$, and assessment of bioaccumulation.

Vik, E.A., B.S. Nesgard, J.D. Berg, S.M. Dempsey, D.R. Johnson, L. Gawel, and E. Dalland. 1996. Factors affecting methods for biodegradation testing of drilling fluids for marine discharge. SPE 35981. Pages 697-711 In: International Conference on Health, Safety & Environment. New Orleans, Louisiana, 9-12 June 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: This paper presents the results from a three-year research program performed on behalf of Conoco Norway Inc. (CNI) on the standardization of biodegradation test protocols for poorly or non-water-soluble SBMs and summarizes experiences from work conducted by chemical suppliers and oil operators, and evaluated on behalf of the Norwegian Oil Industry Association (OLF) in a project on acceptance criteria for drilling muds. Results from

the CNI project include information on parameters of importance for standardization of the biodegradation test and their influence on deviations in test results. Results from the OLF project are used to compare biodegradation test results of SBMs using different test protocols, as well as for looking at the biodegradation test in the context of evaluating overall environmental impact.

Zevallos, M.A.L., J. Candler, J.H. Wood, and L.M. Reuter. 1996. Synthetic-based fluids enhance environmental and drilling performance in deepwater locations. SPE 35329. Pages 235-242 In: SPE International Petroleum Conference & Exhibition of Mexico. Villahermosa, Tabasco, Mexico, 5-7 March 1996. Society of Petroleum Engineers, Inc. Richardson, TX.

Abstract: *Deepwater drilling in the Gulf of Mexico is a challenging opportunity for drilling fluid performance. Synthetic-based muds (SBMs) applied in the Gulf of Mexico have overcome performance shortfalls of currently available water-based and oil-based muds. This paper will compare environmental, health, and drilling performance factors of polyalphaolefins (PAO) and internal olefins (IO) SBMs with emphasis on rheological profiles, acute toxicity, benthic toxicity, bioaccumulation, and biodegradation rates. Field case histories of PAO and IO SBMs used in deepwater projects are compared to water-based muds (WBM) and oil-based muds (OBM).*

The toxicity of a C1618 IO mud and a C2030 PAO mud in the suspended particulate phase test with mysids is below EPA test requirements. Both drilling muds also pass the North Sea zooplankton toxicity test. They also pass the solid-phase sediment bioassay with the amphipod Corophium volutator. The median lethal concentrations were >10,000 mg/kg for PAO and 7,000 mg/kg for IO. The SBMs have a low potential to bioaccumulate. The muds experienced 50 to 80 percent degradation in 28 days in two aerobic biodegradation tests. Between 35 and 40 percent of the two SBMs degraded.



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.