A Comparison of the Environmental Performance of Olefin and Paraffin Synthetic Base Fluids (SBF)

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SUMMARY

This report reviews the environmental properties of olefin and paraffin synthetic base fluids (SBF). It includes a summary of existing toxicity, biodegradation and offshore seafloor drilling site test data assessing the environmental fate of these materials. In addition, a comparison of these materials is made to diesel oil based fluids, one type of oil base fluid (OBF).

The report evaluates toxicity test data for both water-dwelling and sediment-dwelling organisms. Toxicity test results show that olefin and paraffin SBF are non-toxic to the water-dwelling organisms studied. However, when sediment toxicity tests are considered, internal olefin and some alpha olefin products have significantly less toxicity (4 to 20 times) compared to most paraffin materials. The type of olefin or paraffin makes a difference in sediment toxicity results, as most paraffins have and some olefins may have toxicity similar to diesel oil.

Biodegradation test data for both aerobic and anaerobic conditions are evaluated. All olefin and paraffin SBFs and diesel oil base fluids biodegrade in the presence of oxygen (aerobic). In the absence of oxygen (anaerobic) SBFs prepared from linear alpha olefins (LAO) and internal olefins (IO) biodegrade much more extensively (> 50%) than OBFs prepared from paraffins and diesel oil (< 5%).

Seabed surveys for wells drilled with olefin and paraffin SBFs examined the impact of these fluids on seabed communities. Concentrations of synthetic base fluids in sediments may decrease with time after discharge by re-suspension, bed transport, mixing, and biodegradation. Sediment-dwelling organisms are able to use the SBFs as a source of nutrition. Biodegradation of SBFs in sediments results in a decrease in sediment oxygen concentration. If the initial base fluid concentration is sufficiently high, all oxygen in the sediment is consumed. Therefore, SBFs should be biodegradable under both aerobic and anaerobic conditions.

The seabed survey results are more conclusive for olefins than for paraffins. Olefins are shown to have minimal impact, while the impact of the paraffins is not clear. Reductions observed in these field studies were consistent with the anaerobic biodegradation results observed in laboratory tests. As a result, paraffin SBFs may persist in the environment for longer periods of time than olefin based SBFs.

INTRODUCTION

Synthetic drilling fluids are a new class of materials used to provide safe and cost-effective technology for drilling oil and gas wells. Their enhanced drilling performance decreases drilling time and provides advantaged safety, human health, and, in some cases, environmental performance above diesel oil fluids. Linear alpha olefins (LAO), internal olefins (IO), synthetic paraffins, and esters are some of the synthetic base fluids (SBF) used as part of a drilling mud formulation. These fluids provide lubricity, stability at high temperatures, and well-bore stability. In addition to delivering high drilling performance, these fluids may be an important component of an environmentally sound drilling operation. For some of them, cuttings generated while drilling can be discharged into the marine environment safely because of their environmental properties.

Due to an increased global view on environmental issues in oceans around the world, lower impact non-aqueous fluids are increasingly being used for drilling. Certain petroleum operating companies are facilitating this process as they move toward operating with consistent global environmental standards.

This report summarizes the environmental fate and effects of olefin and paraffin SBFs in oceans. The environmental impact of discharged olefin- and paraffin-generated cuttings will be a function of the amount and duration of exposure of the SBF in the environment. Existing laboratory toxicity test data, biodegradation test data, and field seafloor monitoring data at offshore drilling sites are assessed to summarize the environmental properties and impact of these SBFs.

IMPACT OF OLEFIN SYNTHETIC BASED MUD CUTTINGS DISCHARGES IN OCEANS

In general, the largest potential impact from discharges of synthetic based muds (SBM) will occur in the benthic community (sediment dwelling organisms) (USEPA, 2000; OGP, 2003; Neff et al., 2000). SBF adheres to discharged cuttings, which tend to clump together in particles that rapidly settle to the ocean floor. Because of this, SBF cuttings tend not to increase water column turbidity. Water column impacts are also minimized due to the low water solubility of the SBM and the short residence time of the solid cuttings as they settle to the sea floor (USEPA, 2000; OGP, 2003; Neff et al., 2000). These cuttings settle in a heterogeneous pattern on the bottom near the platform. The direction of the settling depends on the current direction and speed at different water depths. Impacts to the benthic community can result from smothering within the depositional field, chemical toxicity of the base fluid, depletion of oxygen due to base fluid biodegradation, and potential physical impacts due to changes in sediment grain size distributions. As a result, to understand the environmental impacts of SBF cuttings discharges, it is important to understand the toxicity and biodegradability of these materials.

OLEFIN AND PARAFFIN SYNTHETIC BASE FLUIDS

Paraffins consist of a broad class of compounds that have the general formula C_nH_{2n+2}, where "*n*" is the number of carbon atoms (carbon number) (Table 1). The carbon atoms in paraffins are joined by single bonds. Paraffins can be categorized as “normal”, meaning that they are linear, “iso”, meaning that they are branched, or “cyclo”, meaning they consist of ring structures. They can be isolated from refinery streams (followed by hydrogenation or dearomatization) or synthesized from specific starting materials via the Fischer-Tropsch or olefin hydroformylation processes (synthetic paraffins are co-produced).

Olefins are similar to paraffins but contain at least two fewer hydrogen atoms providing at least one double bond between adjacent carbon atoms (Table 1). Olefins with one double bond have the general formula C_nH_{2n}. Olefins can be produced from refinery streams or synthesized via ethylene oligomerization. Refinery olefins are highly branched while synthetic olefins are highly linear. LAOs are manufactured using ethylene as a feedstock, and for drilling fluid applications, the typical carbon chain length is C_{14}-C_{20}. The alpha olefin double bond is formed between the first and second carbon atoms of the alkyl chain. IOs are produced from LAO using an isomerization catalyst to move the olefin double bond from the alpha position to an internal position along the carbon chain length. For drilling fluid applications the typical carbon chain length for IO is C_{15}-C_{20}.

Carbon number range, branching and molecule type (e.g. olefins and paraffins) are generally known to impact biodegradation and aquatic toxicity. A summary of the characteristics of the olefin and paraffin SBFs that are addressed in this report is provided in Table 2.

Table 1: Olefin and paraffin structures.

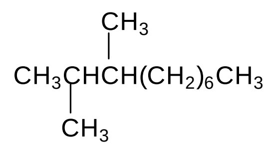
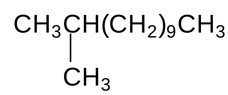
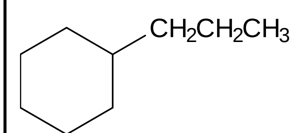
Class	Specific Compound Example	Formula	Molecular Weight	Structure
Linear alpha olefin (LAO)	1-tetradecene	$C_{14}H_{28}$	196	$CH_2{=}CH(CH_2)_{11}CH_3$
Internal olefin (IO)	3-hexadecene	$C_{16}H_{32}$	224	$CH_3CH_2CH{=}CH(CH_2)_{11}CH_3$
Linear or normal paraffin	n-tetradecane	$C_{14}H_{30}$	198	$CH_3(CH_2)_{12}CH_3$
Branched or iso-paraffin (examples with 1 or 2 branches)	2,3-dimethyl decane	$C_{12}H_{26}$	170	
	2-methyl dodecane	$C_{13}H_{28}$	184	
Cycloparaffin	propyl-cyclohexane	C_9H_{18}	126	

Table 2: Characterization of olefin and paraffin SBFs.

SBF	Manufacturing process	Carbon Number Range	Linearity	Comments
Olefins				
C14 Linear alpha olefin (LAO 14)	Ethylene oligomerization	14	Linear (>85%)	
C16 Linear alpha olefin (LAO 16)	Ethylene oligomerization	16	Linear (>85%)	
C1416 Linear alpha olefin (LAO 1416)	Ethylene oligomerization	14 – 16	Linear (>85%)	
C1618 Linear alpha olefin (LAO 1618)	Ethylene oligomerization	16 – 18	Linear (>85%)	50/50 16/18 LAO blend
C1518 Internal olefin (IO 1518)	Ethylene oligomerization	15 – 18 (>95%)	Linear (>85%)	
C1618 Internal olefin (IO 1618)	Ethylene oligomerization	16 – 18	Linear (60 - 95%) and branched (5 - 40%)	55-65% C16 35-45% C18 <10% C20
Paraffins				
C14-17 Linear paraffin	Fischer-Tropsch	14 – 17	Normal (> 90% linear)	
C10-13 Linear paraffin	Fischer-Tropsch	10 – 13	Normal (> 85% linear)	
C10-22 Mixed paraffin	Fischer-Tropsch	10 – 22	Mix of Normal and Iso Paraffins (Normal:Iso ~ 45:55)	
C11-14 Linear paraffin	Co-product from hydroformylation of olefin to produce alcohols	11 – 14	Normal (> 85% linear)	Contains approximately 15% C11-14 olefin
C15-16 Branched paraffin	Co-product from hydroformylation of olefin to produce alcohols	15 – 16	Iso (> 85% iso)	Contains approximately 10% C15-16 olefin
C11-17 Linear paraffin/olefin blend	Fischer Tropsch and co-product from hydroformylation of olefin to produce alcohols	11 – 17	Normal (> 95% linear)	Contains approximately 10% C11-14 olefin

Notes
1. All products meet EPA definition of synthetic (USEPA, 2000).
2. All products have < 10 mg/kg polynuclear aromatic hydrocarbon (PAH) content using EPA methods.

TOXICITY

Laboratory testing can be conducted to characterize the toxicity of materials to organisms in the water column or organisms in the benthic environment (sediment). Typically, toxicity-testing results are presented in terms of a lethal concentration, LC_{50}, or effective concentration, EC_{50}. These are concentrations at which 50% of the organisms are impacted in tests lasting between 96 and 240 hrs (4 – 10 days). Shorter-term tests are typically denoted as "acute" and longer tests performed to assess sensitive stages are termed "chronic". The laboratory tests usually include (1) a series of concentrations of the material, (2) a control for comparison, and (3) some amount of replication.

Water column toxicity

Water column toxicity testing has been conducted with a variety of organisms including marine organisms such as *Mysidopsis bahia* shrimp, and freshwater organisms such as fathead minnow, and *Daphnia magna* (water flea). The International Maritime Consultative Organization developed a system (Table 3) for classifying the toxicities of all chemicals that might be discharged into the sea according to ranges of LC_{50} values (GESAMP, 2002). Concentrations of SBF in solution in the water column are unlikely to exceed 1 mg/L at any time (acute or chronic) during cuttings discharges. This rating system provides a useful perspective to demonstrate the low water column toxicity of SBFs.

A summary of water column toxicity test results for some olefin and paraffin base fluids is shown in Table 4. The only material listed in Table 4 that shows any measurable water column toxicity is diesel oil. This is due to its aromatic content that can be up to 30 wt%. These aromatic compounds have higher water solubility than the olefin and paraffin materials, and as a result are more bioavailable and toxic to aquatic species. Because of the low toxicity of LAO, IO, and paraffins to water column organisms, there is little risk of direct toxicity of the settling SBF cuttings to water column organisms. SBF discharge behavior is different from that of water base fluid (WBF), because SBFs rapidly sink, being denser and less dispersible than WBF. The water column type exposure for toxicity tests is not environmentally relevant for SBF whereas testing using sediment dwelling organisms is most appropriate. If the fluid remained for a long time in the water column before reaching the bottom, water column testing would have relevance.

Sediment toxicity

Biological effects of the SBF cuttings will be restricted to the sediments near the platform where base fluid concentrations accumulate to more than approximately 1000 mg/kg. As a result, it is much more important to understand the toxicity of SBF to sediment-dwelling organisms. The discharge of SBF cuttings and their resulting accumulation on the seafloor can impact benthic organisms through smothering, reduction or elimination of oxygen diffusion into sediments, organic enrichment of the sediment, toxicity, and physical alteration of sediment texture. Smothering and sediment texture alteration may occur regardless of fluid type; however, the reduction of oxygen diffusion into bottom sediments, organic enrichment, and resultant anoxic sediment conditions are unique to SBF accumulations.

Sediment toxicity tests have been in development for more than 10 years. A summary of methods and ranking of preferred tests has been reviewed by the American Petroleum Institute (API, 1994). The five highest-ranking tests for the "marine lethal" category were *Ampelisca, Rhepoxynius, Eohaustorius, Amphioporeia* and *Leptocheirus.* A summary of sediment toxicity tests for olefin and paraffin SBF using *Leptocheirus* is shown in Table 5.

For comparison, the toxicity of a reference 1618 internal olefin (IO 1618) is shown for each specific test to allow for normalization to a reference component. This normalization adjusts for sediment toxicity test variability that results from differences in sediment types and in organism size and health. The sediment toxicity ratios of the olefins and paraffins ranged from 0.2 to 23. Values less than 1 indicate that a compound is less toxic than the IO 1618 reference and values greater than 1 indicate that a compound is more toxic than the IO 1618 reference. In general, internal olefins in the C15-C20 range had similar sediment toxicity to the IO 1618 reference. The LAO 14 and most of the paraffin products were significantly more toxic than the IO 1618 reference (4 to 23 times more toxic). Only the C14-17 Linear paraffin had similar sediment toxicity to the IO 1618 reference.

A comparison to diesel oil is also shown. All of the paraffin products (except the C14-17 Linear paraffin) and the LAO 14 had sediment toxicity similar to diesel.

Taken together, these toxicity test results show that both olefin and paraffin SBF are non-toxic to water column organisms. However, when sediment toxicity tests are considered, internal olefin and some alpha olefin products have significantly less toxicity compared to most paraffin SBF materials. The type of paraffin or olefin used makes a difference, as most paraffins and some olefins that can be used as SBFs have significant sediment toxicity (similar to diesel oil).

Table 3. Revised toxicity rating system* (GESAMP 2002).

Acute Toxicity		Chronic Toxicity	
Rating	**48- to 96-hr LC_{50} or EC_{50} (mg/L)**	**Rating**	**No Observed Effect Concentration (mg/L)**
(0) Non-toxic	>1,000	(0) Neglible	>1
(1) Practically non-toxic	>100 - ≤1,000	(1) Low chronic toxicity	>0.1 - ≤1
(2) Slightly toxic	>10 - ≤100	(2) Moderate chronic toxicity	>0.01 - ≤0.1
(3) Moderately toxic	>1 - ≤10	(3) High chronic toxicity	>0.001 - ≤0.01
(4) Highly toxic	>0.1 - ≤1.0	(4) Very high chronic toxicity	<0.001
(5) Very highly toxic	>0.01 - ≤0.1	--	--
(6) Extremely toxic	<0.01	--	--

* NOTE: Based on system originally developed by International Maritime Consultative Organization (IMO / FAO / UNESCO / WMO / WHO / IAEA / UN / UNEP 1969). The system was recently updated by GESAMP (2002).

Table 4: Summary of water column aquatic toxicity data.

Compound	Species				Reference
	Mysid SPP [1] 96-h LC_{50} (ppm)	Mysid SPP [2] 96-h LC_{50} (ppm)	Fathead Minnow [3] 96-h LC_{50} (mg/L)	*Daphnia magna* [3] 48-h LC_{50} (mg/L)	
Internal olefins					
IO 1420	540,000 – 1,000,000				Chevron Phillips, unpublished
IO 1518	> 1000				Neff et al., 2000; Shell - unpublished
IO 1618	> 1000	103,000 – 124,000			Neff et al., 2000; INEOS Oligomers - unpublished
Internal olefins	> 1000				Neff et al., 2000
Alpha olefins					
LAO	> 1000				Neff et al., 2000
LAO 14		120,000		> 1000	Shell, INEOS Oligomers - unpublished
LAO 16		250,000		> 1000	Shell, INEOS Oligomers - unpublished
LAO 1416		17,000 - 45,000			INEOS Oligomers - unpublished
LAO 1618		124,000 - 177,000			INEOS Oligomers - unpublished
Paraffins					
C11-14 Linear paraffin			> 1000	> 1000	Shell - unpublished
C15-16 Branched paraffin	> 1000				Shrieve MSDS
C10-13 Linear paraffin	> 1000				Shell - unpublished
Other					
Diesel oil (C10-C22)			100 – 300		Clark et al., 2003
GTL Diesel oil (C10-C22) [4]			>1000		Clark et al., 2003

1 Seawater test.
2 Seawater test. Fluid tested as 10% v/v in Generic mud #7. INEOS Oligomers - unpublished
3 Freshwater test.
4 Gas-to-liquids (GTL) diesel is manufactured via a gas-to-liquids process and contains only a small amount of aromatics (< 0.05 wt%).

Table 5: Summary of sediment toxicity tests [1].

Compound	10-d LC_{50} (mg/kg)	Sediment Toxicity Ratio [2]	Reference
Internal olefins			
IO 14	850	4.3 – 5.0	Chevron Phillips - unpublished
IO 14/18	1062 - 1425	0.9 – 1.2	Chevron Phillips - unpublished
IO 1518	1878 - 4695	0.4 – 1.0	Shell - unpublished
IO 16	916 – 3896	0.6 – 1.5	Chevron Phillips - unpublished
IO 1618	922 - 6276	0.3 – 1.7	Shell, INEOS Oligomers, Chevron Phillips - unpublished
IO 18	3461 – 11977	0.2 – 1.2	Chevron Phillips - unpublished
Alpha olefins			
LAO 14	72 - 144	8.0 - 22.8	Shell - unpublished, Chevron Phillips - unpublished
LAO 1416	185	3.1	Chevron Phillips - unpublished
LAO 141620	496	1.2	Chevron Phillips - unpublished
LAO 16	1191 - 2588	0.5 - 0.8	Shell - unpublished, Chevron Phillips - unpublished
LAO 1618	1071 – 6015	0.7 – 1.2	Shell - unpublished, Chevron Phillips - unpublished
LAO 18	2760, 4069	NA[3]	INEOS Oligomers - unpublished
LAO 18	952	0.6	Chevron Phillips - unpublished
Paraffins			
C11-14 Linear paraffin	271	12.1	Shell - unpublished
C15-16 Branched paraffin	265	12.4	Shell - unpublished
C10-13 Linear paraffin	164	15.1	Shell - unpublished
C10-22 Mixed paraffin	497	5.0	Shell - unpublished
C16-18 Linear paraffin	2665 - 3818	1.9	Chevron Phillips - unpublished
C14-17 Linear paraffin	3192	0.8	Shell - unpublished
Fischer-Tropsch C11-17	517, 1189	NA[3]	INEOS Oligomers - unpublished
Other			
Diesel oil	255	12.3	API Project
Diesel oil	374	16.4	API Project
Diesel oil	138 – 635	NA[3]	INEOS Oligomers - unpublished

[1] All tests were conducted with formulated sediment.
[2] Sediment toxicity ratio = IO 1618 10-d LC_{50}/test compound 10-d LC_{50}.
[3] Test was conducted without IO 1618 reference standard.

BIODEGRADATION

Biodegradation is the breakdown of organic contaminants by microbial organisms into smaller compounds. The microbial organisms transform the contaminants through metabolic or enzymatic processes. Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane. Biodegradation is a key process in the natural attenuation of contaminants that may be released to the environment. Typically, biodegradation occurs more rapidly under aerobic conditions (oxygen containing) compared to anoxic or anaerobic conditions (oxygen depleted).

SBF chemicals are typically biodegraded completely under aerobic conditions, with the consumption of a large amount of oxygen, the electron acceptor for the biodegradation process. Aerobic biodegradation of SBFs may deplete the oxygen in sediments, making the sediments anoxic if the loading of the sediments with biodegradable organic matter from SBF cuttings is high and aeration of sediments is slow. Marine sediments tend to be anoxic except for the sediment surface layer and the zone of bioturbation (CSA, 2004b). Field studies of oil based fluid cuttings discharges have shown that sediments may become anaerobic if they contain > 1000 mg/kg of mineral oil (Vik et al., 1996).

In the absence of oxygen, SBFs need an alternative electron acceptor to oxygen in order for biodegradation to occur. Viable alternatives include NO_3^{-1}, SO_4^{-2}, and CO_2. For marine environments, the most likely alternative is SO_4^{-2} as sulfate is abundant in seawater (~30 mM) and marine sediments (Neff et al., 2000). Thus, sulfate will be the dominant electron acceptor for the microbial oxidation of SBFs in anoxic marine sediments. Oil base fluid cuttings piles in the North Sea were shown to contain 30 to 879 mg/kg sulfide, suggesting that these oil based fluids were being degraded anaerobically by the sulfate-reducing bacteria (Cordah, 1998).

The biodegradability of olefin and paraffin SBF has been extensively studied using standard laboratory protocols for biological degradability and simulated seabed tests.

Standard laboratory tests include both aerobic and anaerobic biodegradation tests. Many of these test results are summarized and discussed in OGP (2003), USEPA (2000), and Neff et al. (2000). The standard laboratory tests include:

- OECD 301B, 301D, 301F, 306 – aerobic 28-d tests that either measure oxygen consumption or CO_2 evolution. The OECD 306 test uses seawater to simulate a marine environment.
- BODIS freshwater test – aerobic 28-d test
- BODIS marine test – aerobic seawater 28-d test
- ISO 11734 – anaerobic closed bottle 60-d test

Other types of biodegradation tests have been developed for SBF. These tests were designed to better simulate the environmental conditions for SBF discharged on cuttings. These other tests include:

- Modified ISO 11734 – static anaerobic 275-d test that contains sediment under marine conditions (Herman and Roberts, 2005; Roberts and Herman, 2004; Roberts, 2002)
- SOAEFD solid phase test – mixed aerobic and anaerobic 120-d test to simulate seafloor conditions. Oxygenated seawater flows over the sediment and diffusion is required for the oxygen to reach the lower layers of sediment, which are typically anoxic or anaerobic.
- NIVA test – simulated seabed 160-d test

Aerobic biodegradation

A summary of aerobic biodegradation test data for olefin and paraffin SBFs is shown in Table 6. These results indicate that, in general, olefin and paraffin SBFs are significantly biodegraded aerobically. In almost all cases, the test results exceed 60% biodegradation, the level considered to be an indicator of good aerobic biodegradability. Diesel oil also biodegrades significantly via the aerobic mechanism.

Anaerobic biodegradation

The most relevant biodegradation tests for SBFs are those conducted in comparable marine anoxic conditions. The best example of this test is the solid phase test, which uses seawater and marine sediment in a static anaerobic closed bottle test. A summary of anaerobic biodegradation data for olefin and paraffin SBFs is shown in Table 7.

In general, LAO and IO SBF biodegrade much more extensively than paraffins in anaerobic biodegradation studies. The 10 – 55% biodegradation observed in the paraffin/olefin blends (C11-14 Linear paraffin, C15-16 Branched paraffin, LAO 14/ C11-17 Fischer-Tropsch paraffin blend) is likely due to the presence of 15 – 60% olefins in these materials. The amount of diesel oil anaerobic biodegradation was very low (0 – 3%) and similar to that of the n-paraffin (5%). Scientific literature indicates that there is no known mechanism for the initiation of anaerobic alkane (paraffin) biodegradation (Candler et al., 1999).

Some broad generalizations can be made from the set of laboratory biodegradation testing data presented in Tables 6 and 7:

- Biodegradation of olefin and paraffin SBFs typically occurs more rapidly under aerobic conditions than under anaerobic conditions.
- LAO, IO, paraffins, and diesel oil have similar aerobic biodegradation rates.
- LAO and IO have similar anaerobic biodegradation rates. These materials are likely to be substantially degraded in the field on a time scale of one to a few years based on the laboratory testing results.
- Paraffins and diesel oil show limited anaerobic biodegradability and their rate is significantly slower than olefins. This may result in persistence of paraffin base fluids, as benthic conditions are often anaerobic.
- Degradation in situ is likely to be by both aerobic and anaerobic pathways and largely limited by the availability of suitable electron acceptors. Aerobic biodegradation is likely to occur at the periphery of areas where cuttings are observed, while anaerobic biodegradation is likely to occur in the internal portions of the cuttings area.

Table 6: Summary of aerobic biodegradation data.

Compound	Test	% Biodegradation	Reference
Internal olefins			
IO 1518	OECD 306	80	Shell - unpublished
IO 1518	BODIS	73	Shell - unpublished
IO 1518	OECD 301D	55 - 61	Shell - unpublished
IO 1618	OECD 306	50 - 67	INEOS Oligomers - unpublished
IO 1618	BODIS	54	Chevron Phillips – unpublished
Alpha olefins			
LAO 1416	OECD 301D	73	Shell - unpublished
LAO 1416	OECD 306	73	INEOS Oligomers - unpublished
LAO 14	OECD 301D	62-65	Shell - unpublished
LAO 14	OECD 301B	48-65	Shell - unpublished
LAO 14	OECD 306	72	INEOS Oligomers - unpublished
LAO 16	OECD 301C	55-73	Shell - unpublished
LAO 16	OECD 301D	94	Chevron Phillips - unpublished
LAO 16	BODIS	48	Shell - unpublished
LAO 141618	OECD 306	71	INEOS Oligomers - unpublished
Paraffins			
C11-14 Linear paraffin	OECD 301D	55-60	Shell - unpublished
C11-17 Linear paraffin/olefin blend	OECD 306	>90	Shrieve MSDS
n-paraffin	SOAEFD	23-86	Neff et al., 2000
C14-17 Linear paraffin	OECD 306	63	Shell - unpublished
C11-14 Linear paraffin	OECD 306	58	Shell – unpublished
C15-16 Branched paraffin	OECD 306	64	Shell – unpublished
C10-22 Mixed paraffin	OECD 306	60	Shell - unpublished
Other			
Diesel oil	OECD 301F	60	Clark et al., 2003
GTL Diesel oil (C10-C22)	OECD 301F	74	Clark et al., 2003

Table 7: Summary of anaerobic biodegradation data (275-d; Modified ISO 11734).

Compound	% Biodegradation	Comments	Reference
Internal olefins			
IO 1518	56	Average of 2 tests	Roberts and Herman, 2004
IO 1518	60	Average of 8 tests	Shell - unpublished
IO 16	57	Average of 3 tests	Chevron Phillips - unpublished
IO 1618	53	Average of 2 tests	Roberts and Herman, 2004
IO 1618	49	Average of 4 tests	Candler et al., 2000
IO 1618	48	Average of 2 tests	Roberts and Herman, 2004
IO 1618	48	Average of 3 tests	INEOS Oligomers
IO 1618	51	Average of 10 tests	Chevron Phillips – unpublished
IO 18	33	Average of 3 tests	Chevron Phillips – unpublished
Alpha olefins			
LAO 14	80 – 83		Shell - unpublished, INEOS Oligomers - unpublished
LAO 1416	64	Average of 4 tests	Candler et al., 2000
LAO 16	59		Roberts and Herman, 2004
LAO 16	60	Average of 3 tests	Shell - unpublished
LAO 16	63	Average of 4 tests	Chevron Phillips – unpublished
LAO 1618 (50/50 blend)	52		Roberts and Herman, 2004
Paraffins			
n-paraffin	5	Average of 4 tests	Candler et al., 2000
C11-14 Linear paraffin	18		Shell - unpublished
C15-16 Branched paraffin	10		Shell - unpublished
C11-17 Fischer-Tropsch paraffin	20		INEOS Oligomers - unpublished
LAO 14/C11-17 Fischer-Tropsch paraffin blend (60:40)	55		INEOS Oligomers - unpublished
Other			
Diesel oil	3		Roberts and Herman, 2004
Diesel oil	0		INEOS Oligomers - unpublished

SEA FLOOR STUDIES

A variety of sea floor studies have been conducted to examine the fate, effects, and impacts of SBFs that have been discharged via cuttings to the environment. Many of these studies are summarized in USEPA (2000), OGP (2003), and Neff et al. (2000).

A total of seven field studies have been published to date with data on cuttings discharges based on either LAO or IO SBF. These studies covered Ireland, the North Sea, Eastern Canada, Norway, and the Gulf of Mexico. The combined set of six studies covers a total of more than 143 wells at water depths ranging from 20 to 565 m. Most of these studies are summarized in USEPA (2000), OGP (2003), and Neff et al. (2000). In addition, detailed data from the individual studies are provided in CSA (1998), Fechhelm et al. (1999), Gardline (1998), JWEL (2000), Neff et al. (2000), Akvaplan-niva (1997), Sintef Applied Chemistry (2000), Det Norske Veritas (2000) and CSA (2004a, 2004b, 2004c).

A large-scale joint industry, academia, and government study was recently completed in the Gulf of Mexico (CSA, 2004a, 2004b, 2004c). This study covered 4 separate cruise surveys of approximately 15 locations. All but one of these locations used IO as the SBF. Key findings were summarized as follows:

- No large, multi-meter thick cuttings piles, such as those seen in the North Sea, were detected at any of the 15 sites visited in this study;
- Discharges were deposited in a patchy distribution limited to the vicinity of the discharge location (<250 m);
- In general, sediment quality and biological communities were not severely affected, and impacts were limited to the vicinity of the discharge (<250 m); and
- Where impacts were observed, progress toward physical, chemical, and biological recovery appeared to occur during the 1-year period between the two sequential sampling cruises.

A summary of these olefin field studies is provided in Table 8. These studies include both LAO and IO SBF. A review of the information provided in Table 8 provides for several general conclusions for these seafloor studies:

- High concentrations of olefin SBF were typically only observed near the drilling platform (<100 – 250 m)
- No significant cuttings piles were observed
- The amount of olefin SBF appears to be decreasing over time
- One study in Ireland showed that 90% of the LAO discharged on cuttings was degraded within 2 years

A total of six field studies have been published to date with data on cuttings discharges based on paraffin SBF. These studies covered Ireland, the North Sea, Eastern Canada, and Australia. The combined set of six studies covers a total of more than 22 wells at water depths ranging from 78 to 380 m. These studies are summarized in USEPA (2000), OGP (2003), and Neff et al. (2000). In addition, detailed data from the individual studies are provided in Oliver and Fisher (1999), Gardline (1998), JWEL (2000), and Neff et al. (2000).

A summary of these paraffin field studies is provided in Table 9. These studies include both linear and iso-paraffin SBF. A review of the information provided in Table 9 provides for several general conclusions for these seafloor studies:

- In some cases, the paraffin was observed to decrease significantly over time.
- Paraffin removal and rapid recovery was often attributed to sediment dispersal mechanisms.

- Paraffin distributions tended to be very uneven.

These paraffin field studies are somewhat inconclusive with respect to the fate of these materials, as the data do not elucidate the paraffin removal mechanism.

Concentrations of synthetic base fluids in sediments may decrease with time after discharge by resuspension, bed transport, mixing, and biodegradation. Sediment-dwelling organisms are able to use the SBFs as a source of nutrition, and biodegradation of SBFs in sediments results in a decrease in sediment oxygen concentration. If the initial base fluid concentration is sufficiently high, the sediments become anoxic. The anaerobic biodegradability of SBF represents an essential prerequisite for the prevention of long-term persistence of SBFs and harmful impacts on marine benthic environments (Steber, 1995). Therefore, SBFs should be biodegradable under both aerobic and anaerobic conditions.

CONCLUSIONS

This report evaluates the environmental fate and effects of olefin and paraffin SBF. Toxicity test results show that olefin and paraffin SBF are non-toxic to the water-dwelling organisms studied. However, when sediment toxicity tests are considered, internal olefin and some alpha olefin products have significantly less toxicity (4 to 20 times) compared to most paraffin materials. The type of olefin or paraffin makes a difference in sediment toxicity results, as most paraffins have and some olefins may have toxicity similar to diesel oil.

Biodegradation test data for both aerobic and anaerobic conditions are evaluated. All olefin and paraffin SBFs and diesel oil base fluids biodegrade in the presence of oxygen (aerobic). In the absence of oxygen (anaerobic) SBFs prepared from linear alpha olefins (LAO) and internal olefins (IO) biodegrade much more extensively (> 50%) than base fluids prepared from paraffins and diesel oil (< 5%).

Seabed surveys for wells drilled with olefin and paraffin SBFs examined the impact of these fluids on seabed communities. Concentrations of synthetic base fluids in sediments may decrease with time after discharge by re-suspension, bed transport, mixing, and biodegradation. Sediment-dwelling organisms are able to use the SBFs as a source of nutrition. Biodegradation of SBFs in sediments results in a decrease in sediment oxygen concentration. If the initial base fluid concentration is sufficiently high, all oxygen in the sediment is consumed. Therefore, SBFs should be biodegradable under both aerobic and anaerobic conditions.

The seabed survey results are more conclusive for olefins than for paraffins. Olefins are shown to have minimal impact, while the impact of the paraffins is not clear. Reductions observed in these field studies were consistent with the anaerobic biodegradation results observed in laboratory tests. As a result, paraffin SBFs may persist in the environment for longer periods of time than olefin based SBFs.

Table 8: Summary of seafloor surveys for olefin projects.

Source	Fluid type (specific/ generic)	Location (field)	Number of wells	Volume SBM discharged	Water Depth (m)	Comments/Conclusions
Gardline, 1998	Linear paraffin/LAO/ PAO	Ireland			380	• Substantial decline of synthetic fluid over 2 years • 90% of linear alpha olefin degraded within 2 years • Highest concentration of synthetic base fluid within 100 m of site
Neff et al., 2000	LAO	North Sea		115 tons LAO adhered to cuttings	185	• Average concentrations of LAOs declined between Year 1 and Year 2 surveys
JWEL, 2000	IO	Eastern Canada-Sable Island - 3 sites: Venture field (V), Thebaud field (T), North Triumph (NT)	V-5; T-5; NT-1	V 1821.4 m3 adhered to cuttings; T 1832.8 m3 adhered to cuttings; NT 194.1 m3 adhered to cuttings	V 20-22; T 20-22; NT 80	• Cuttings accumulation smaller in radius than model predictions • Elevated levels of TPH and barium detected at 250 m and 500 m from platform immediately after and during drilling discharge • Dispersion or burial appeared to occur within a six-month period • Biodegradation of the synthetic fluid possibly a contributing factor • Fluid characteristics resulted in low impacts and rapid recovery of the sea floor
Fechhelm et al, 1999	Petrofree LE (LE)-90% LAO, 10% ester	Gulf of Mexico	7 (Develop-ment)	7659 bbls adhered to cuttings	565	• 4 months following drilling, cuttings were dispersed over the bottom in a patchy fashion • Most of the cuttings were distributed in the direction of surface and mid-level currents rather than bottom currents • Maximum base fluid concentrations were measured at a distance of 75 m • No cuttings piles observed
CSA (Continental Shelf Associates, Inc.), 1998	GI-IO SMI-LAO/IO ST-IO	Gulf of Mexico - 3 sites: Grand Isle (GI), S. Marsh Island (SMI), S. Timbalier (ST)	GI-5; SMI-2; ST-1	GI-1315 bbls adhered to cuttings; SMI-94 bbls adhered to cuttings; ST-2390 bbls adhered to cuttings	GI-61; SM-39; ST-33	• Elevated concentrations were restricted to within 50-100 m of platform and were patchy in distribution • Highest fluid content at 50 m • No cuttings piles were detected

Table 8: Summary of seafloor surveys for olefin projects (continued).

Source	Fluid type (specific/ generic)	Location (field)	Number of wells	Volume SBM discharged	Water Depth (m)	Comments/Conclusions
Akvaplan-niva, 1997; Sintef Applied Chemistry, 2000; Det Norske Veritas, 2000	IO LAO PAO ester	Norwegian Sea Region I	95	IO – 4831 MT LAO – 97 MT ester – 2031 MT PAO – 1939 MT	70 – 90	• Minimal seabed impact of large discharges of IO in a field after a few years of inactivity. This material quickly degraded in these regions and there were no major disturbances of the fauna either qualitatively or quantitatively. • PAO based discharge residues may be slightly more permanent in the fields but without impact on the biological fauna. PAO is a fully hydrogenated paraffin fluid, suggesting that offshore discharge of paraffin fluids should be minimized. • The use of esters has been quite extensive in some fields but they have seldom been used without some admixing of other fluids. Their degradation with time is apparent in some results. However, one cannot conclude that they behave much better than all olefins in the field.
CSA (Continental Shelf Associates, Inc.), 2004a, 2004b, 2004c	IO – 6 wells, LAO – 1 well, ester – 1 well	Gulf of Mexico – 8 sites: Green Canyon (GC112), Eugene Island (EI346), Mississippi Canyon (MC496), South Timbalier (ST160), Ewing Bank (EW963), Main Pass (MP299, MP288), Viosca Knoll (VK783)	GC112-4, EI346-3, MC496-1, ST160-1, EW963-3, MP299-3, MP288-4, VK783-1	GC112 – 5,470 bbl adhered to cuttings; EI346 – 10,300 bbl adhered to cuttings; MC496 – 1,700 bbl adhered to cuttings; ST160 – 930 bbl adhered to cuttings; EW963 – 600 bbl adhered to cuttings; MP299 – 970 bbl adhered to cuttings; MP288 – 1,300 bbl adhered to cuttings; VK783 – 440 bbl adhered to cuttings	GC112-534, EI346-92, MC496-556, ST160-37, EW963-540, MP299-60, MP288-119, VK783-338	• Average nearfield (within 250 m of platform) SBF concentrations at initial sampling ranged from 0 – 11,000 mg/kg; after 1 year, average nearfield SBF concentrations ranged from 0 – 4,000 mg/kg • No large, multi-meter thick cuttings piles observed • Discharges were deposited in a patch distribution limited to the vicinity of the discharge location (< 250 m) • Sediment quality and biological communities were not severely affected, and impacts were limited to the vicinity of the discharge (< 250 m) • Where impacts were observed, progress towards recovery appeared to occur during the one year period between sequential sampling cruises

Table 9: Summary of seafloor surveys for paraffin projects.

Source	Fluid type (specific/ generic)	Location (field)	Number of wells	Volume SBM discharged	Water Depth (m)	Comments/Conclusions
Neff et al., 2000	Linear paraffin	North Sea		13 ton	95	• Maximum concentration of 1600 mg/kg • Number of benthic individuals decreased with increase base fluid concentration • Distribution of linear paraffin was very uneven
Neff et al., 2000	Linear paraffin	North Sea		58 ton	78	• Maximum concentration 28,000 mg/kg • Distribution of linear paraffin was very uneven
Neff et al., 2000	n-paraffin, linear paraffin	North Sea	9			• Approximately 1 year after drilling, fluid concentration in the surface layer often decrease; however, concentrations at greater depths may increase or decrease
Gardline, 1998	Linear paraffin	Ireland			380	• Substantial decline of synthetic fluid over 2 years • 90% of linear paraffin degraded within 2 years • Highest concentration of synthetic base fluid within 100 m of site
Oliver and Fisher, 1999	Linear paraffin (XP-07)	Australia	1	160 ton	78	• Cuttings piles significantly reduced after 10 months • Rapid recovery of area attributed to sediment dispersal mechanisms
Jewel, 2000b	Isoparaffin (IPAR-3)	Eastern Canada	12		80	• Drilling wastes appear to have been transported further from wells than originally predicted by fate and effects models; models did not account for severe storms that are believe to contribute to sediment transport

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