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Bioremediation Study of Olefins, Mineral Oils, Iso-Paraffin Fluids and Diesel Oils Used for Land-based Drilling

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Abstract

Increasing concerns over health and safety, as well as environmental impacts of diesel oil-based muds in land-based drilling applications, has prompted a search for safer drilling mud base fluids. There are two challenges. First, the drilling fluid must satisfy technical requirements. Second, it must reduce environmental health and safety risks. This paper summarizes research aimed at finding a synthetic base fluid that satisfies both requirements. Laboratory studies evaluated the degradability of diesel and synthetic base fluids, and the toxicities of the same fluids to a range of terrestrial flora and fauna. More specifically, biodegradation, seed germination and root elongation of two plant types, earthworm survival, and response of bioluminescent bacteria (Microtox™) were determined in a typical landfarm receiving soil containing the test fluids. Olefins demonstrated the fastest biodegradation and lowest toxicity after bioremediation, whilst iso-paraffin fluids and mineral oil degraded less readily and developed extreme toxicity during the three-month bioremediation period. Although 71% of the diesel oil disappeared through volatilization and biodegradation, it remained extremely toxic after bioremediation.

Introduction

The widespread use of diesel-based drilling muds has raised concerns regarding their impact on human and environmental health. Typically, diesel-based drilling muds and cuttings are characterized by extreme ecotoxicity, which can persist following bioremediation. This has stimulated a search for alternative base fluids that not only perform efficiently in the drilling operation but can be bioremediated with no adverse environmental consequences. The present research was conducted to (1) determine the degradability and ecotoxicity of 6 fluids being considered by BP Amoco for production of drilling muds for terrestrial drilling, and (2) to compare their toxicological attributes with those of diesel oil. Olefins were of particular interest since they are used extensively for offshore drilling and may possess the same low toxicity and biodegradability advantages in terrestrial systems as they do in marine systems.

Objectives. Specific objectives of the research were: (1) to determine the relative biodegradability of isomerized olefin, alpha olefin, isomerized tetradecene, isomerized paraffin, mineral oil and diesel oil when mixed into a receiving soil at 2 g/100 g dwt and, (2) to determine the ecotoxicity of the test fluids immediately following application to soil and after 93 days bioremediation in soil using lettuce, barley, earthworm and Microtox™ bioassays.

Methods

Receiving Soil. An uncontaminated, acidic subsoil (pH 5.1) from a coniferous forest site was used as the receiving soil. It was categorized as a loam with 41.2% sand, 39.6% silt and 19.2% clay and was low in organic matter (2.6%) and salts (electrical conductivity = 0.08 dS/m). Extractable N was < 1 ppm, phosphate P totalled 11 ppm and sulphate-S was 3 ppm.

Test Base Fluids. The test fluids were:

(1) C16-18 isomerized olefin. This fluid is prepared from a mixture of approximately 65% (wt) 1-hexadecene and 35% (wt) 1-octadecene. It is primarily linear isomerized olefin with 25% branched isomerized olefins and resembles isomerized tetradecene.

(2) C14-16 linear alpha olefin, a clear white oil which is a blend of 1-tetradecene and 1 hexadecene (60:40). It is comprised of 99.6% monoolefin and 0.4% paraffin. Branched isomers constitute 15% by weight. Carbon content is C12=1.3%, C14=64.7%, C16=33% and C18=1.5%.

(3) Isomerized tetradecene, a clear white oil that is 99.6% mono-olefin and 0.4% paraffin. Branched isomers are approximately 5% by weight. Carbon contents are C12=2%, C14=95.5% and C16=2.5%.
(4) Isomerized paraffin, a mixture of branched paraffins prepared by hydroisomerizing linear paraffins.
(5) Mineral oil, a clear, white oil consisting of a mixture of paraffins and <3% aromatics by weight.
(6) Winter grade diesel (#2 diesel fuel), a mixture of paraffins and aromatics.

Biodegradability. Aliquots of field moist receiving soil, each equivalent to 100 g dwt, were sprinkled with 2 g of each test fluid. There were 3 replicate aliquots per test fluid and 3 untreated controls. Each fluid and control sample was supplemented with 400 µg N/g dwt soil so fluid degradation would not be limited by poor nutrient conditions. After thorough mixing, each sample was placed in a glass jar, closed with a vented lid and incubated at room temperature (22°C). Respiration, measured as headspace CO_2, was determined at regular intervals for 93 days to determine the potential for degradability and to identify the biological treatment endpoint. The treatment endpoint is defined as the point at which respiration stabilizes and there is very little difference in CO_2-C release between successive sample times. This endpoint signals the exhaustion of easily available hydrocarbons and the initiation of the slow decay phase. A biological treatment endpoint had been achieved in all treatments after 93 days.

In addition, hydrocarbons in soil samples treated with each of the test fluids were analyzed at the initiation of the biodegradability study and after a biological treatment endpoint had been achieved as indicated by stable respiration measurements. Samples were extracted with methylene chloride/carbon disulfide/acetone, and the extract was analyzed by gas chromatograph with flame ionization detection (GC/FID) for C11 to C60 extractable hydrocarbons (US EPA Method 3550, 8000 and 3610A).

Ecotoxicity. Three ecotoxicity tests representing various trophic levels were conducted immediately following fluid application and after 93 days bioremediation when hydrocarbon degradation had stabilized. The assays included phytotoxicity tests with lettuce and barley; earthworm survival; and the Microtox™ bioassay. Because of the amount of soil required to conduct the assays, bulk samples of contaminated soil were incubated in conjunction with, but separate from, the respiration samples. Moisture, nutrient and temperature conditions of the bulk samples were identical to those of the respiration samples. Lime ($CaCO_3$) was added to each bulk sample at a rate of 1 g/100 g dwt soil to counteract acidification of the soil during the bioremediation process. Application of lime was necessary to maintain the soil pH at a level where it would not interfere with performance of the test organisms.

Phytotoxicity. Seeds (30 lettuce, 20 barley) were planted in undiluted soil containing each of the test fluids and in the untreated soil. There were 3 replicates/plant species/treatment and the plastic dishes containing the soil were incubated under controlled moisture, temperature and light conditions in a growth chamber with 18 h photoperiod. Total number of emergent seedlings and root length of 10 randomly selected seedlings per dish were measured after 4 (barley) or 5 (lettuce) days growth. Plant response in the fluid treatments was determined relative to that in untreated soil.

Earthworm Survival. Individual composting earthworms (*Eisenia fetida*) were placed in small containers holding either fluid-treated or untreated soil and survival was measured after 7 and 14 days exposure at room temperature. Three replicate batches of 15 earthworms were tested in each of the 7 treatments at both the initial and final sample times. Survival in the fluid treatments was expressed relative to that in the untreated control.

Microtox™ . A standardized method (Environment Canada 1992) was used. Aliquots (25 g dwt) of fluid-treated and untreated soil were slurried in a 1:4 soil:water solution for 24 hours and dilutions of the supernatant tested for reductions in light production by *Vibrio fischeri*. The concentration of supernatant which caused a 50% reduction in light output after 15 min exposure (IC50) was determined for 2 replicates/treatment initially and also after 93 days bioremediation.

Results and Discussion

Biodegradability. Respiration rates and cumulative CO_2-C loss from the each of the fluid treatments and the control are given in Figs. 1 and 2. Microbial activity was most stimulated by the application of isomerized olefin, linear alpha olefin and isomerized tetradecene demonstrating that these three fluids were the most degradable. The very rapid increase in respiration within 7 days of olefin application is strong evidence that these fluids are highly bioavailable and readily utilized by the microbial biomass for growth and reproduction. Isomerized paraffin, mineral oil, and diesel also stimulated microbial activity but not to the same extent as the olefins. Cumulative carbon loss as a result of microbial release of CO_2-C from the hydrocarbons was clearly greater for the olefins than the isomerized paraffin, mineral oil and diesel.

Assuming that each fluid type contains approximately 85% carbon, per cent loss of hydrocarbon attributable to microbial respiration was estimated for the different fluids over the term of the study. Based on respiratory carbon loss, fluid degradability could be ranked with isomerized olefin>linear olefin>isomerized tetradecene>isomerized paraffin>mineral oil>diesel (Table 1).

Changes in hydrocarbon mass during bioremediation as determined by analytical methods (total extractable hydrocarbons, carbon scans) are summarized in Table 1. All the test fluids had relatively short carbon chain lengths (<C20 except diesel which was <C25). However, the molecular structure of the fluid, rather than carbon chain length, determines degradability. In the case of the isomers, degradation appeared to be related to degree of branching with isomerized tetradecene (5% branched isomers by weight) and linear alpha olefin (15% branched isomers by weight)

degrading to a greater extent than isomerized olefin (25% branched isomers by weight). It is clear that the linear structure and relatively short carbon chain length of the isomerized tetradecene, linear alpha olefin and isomerized olefin made them readily available for microbial degradation. Paraffins with their greater degree of branching are less accessible to the microorganisms, hence the lower degradation potentials of the isomerized paraffin, mineral oil and diesel. Mass loss of the olefins (90-95%) was more than double that of the isomerized paraffin and mineral oil (39-45%) over the 93 day bioremediation period. When respiration and analytical data were combined, it was estimated that 50-60% of hydrocarbon mass loss in the olefin treatments was a result of respiratory carbon loss, while 35-45% was transformed into microbial biomass and soil organic matter. Rapid degradation of alpha olefins has been observed also by Melchor et al. (2001) in a field study conducted with drill cuttings applied to a tropical wetland in Venezuela.

In general, respiratory data supported analytical data with isomerized olefin, linear alpha olefin and isomerized tetradecene being the most degradable, followed by isomerized paraffin and mineral oil which exhibited moderate degradability (Table 1). The exception was diesel oil, which exhibited high degradability based on total extractable hydrocarbon (TEH) analysis, but low degradability based on its respiration profile. This discrepancy may be explained by the high volatile component in diesel oil, which disappears abiotically, and, thus, would not be considered in respiratory carbon loss. Also, the paraffins and aromatics in the non-volatile component of the diesel and slightly longer chain length relative to the other fluids, may make diesel less susceptible to microbial attack.

Ecotoxicity.

Phytotoxicity. Barley was very sensitive to the fresh fluids with little or no germination in any of the treatments immediately following application (data not shown). Bioremediation significantly improved barley response with almost 100% germination in the isomerized olefin, alpha olefin and isomerized tetradecene treatments and 60% in the mineral oil and diesel treatments. However, root elongation which is a more sensitive indicator of toxicity, clearly showed that barley root growth was significantly inhibited by isomerized paraffin, mineral oil and diesel (20-25% of control) following remediation. Barley growth in the isomerized olefin, alpha olefin and isomerized tetradecene treatments was greater than in the untreated soil.

Lettuce responded differently than barley to both the fresh and bioremediated fluids. Initially, all fluids inhibited lettuce germination with isomerized olefin being the least toxic and isomerized tetradecene the most toxic (Fig. 3). Also, root growth was inhibited by the fresh fluids with root lengths averaging about 50% of the untreated reference (Fig. 4). However, following bioremediation, there was no toxicity evident to either lettuce germination or root elongation in the isomerized olefin, alpha olefin and isomerized tetradecene treatments (Figs. 3, 4). In contrast, both isomerized paraffin and mineral oil developed extreme toxicity to lettuce (no germination) during bioremediation. Toxicity of diesel to lettuce germination and root growth also increased after bioremediation. These observations suggest that during the degradation of the paraffin constituents in the isomerized paraffin, mineral and diesel fluids, breakdown products are produced which are extremely toxic to plant growth. Further studies to identify the toxic components are warranted.

Based on the barley and lettuce germination and root elongation assays, only isomerized olefin, alpha olefin and isomerized tetradecene would exhibit little or no toxicity following bioremediation. These three fluids also demonstrated the greatest decomposition potential and had almost completely disappeared from the soil when the phytotoxicity assays were conducted.

Earthworm Toxicity. Prior to bioremediation, fresh isomerized olefin, alpha olefin, isomerized tetradecene and isomerized paraffin tested slightly to not toxic to earthworms while mineral oil was moderately toxic and diesel extremely toxic (complete mortality after 7 days exposure) (Fig. 5). After bioremediation, the pattern of earthworm response to the test fluids resembled that observed in the plant bioassays in that isomerized olefin, alpha olefin and isomerized tetradecene were non-toxic. Thus at fluid residuals of 1422 µg isomerized olefin, 577 µg alpha olefin and 584 µg isomerized tetradecene/g dwt soil no earthworm toxicity was detected. Of interest are the isomerized paraffin and mineral oil, which, as observed in the plant bioassay, developed extreme toxicity during the bioremediation process. Again, breakdown products of the paraffins in these fluids may explain the increase in toxicity. Although hydrocarbon loss from the diesel was extensive as a result of volatilization and microbial action, it was still extremely toxic to the earthworms after a treatability endpoint of 4176 µg TEH/g dwt soil had been achieved.

Microtox™ Toxicity. The Microtox™ assay was conducted on water extracts of the treated soils to determine toxicity of any leachates that potentially could be generated by the fluids both before and after bioremediation. Relative to the untreated soil, alpha olefin and isomerized tetradecene were non-toxic initially and remained so following bioremediation (Fig. 6). Isomerized olefin was moderately toxic immediately after application to the soil, but this toxicity disappeared during bioremediation. Isomerized paraffin and mineral oil confirmed the observations made in the plant and earthworm bioassays in that toxicity increased significantly during bioremediation. Clearly, these two fluids generate toxic breakdown products during their degradation which, based on the Microtox™ results, are water soluble and thus, mobile. Although still extremely toxic after treatment, diesel did demonstrate some loss in toxicity over the time span of the study.

Overall Toxicity. Using a rating scheme of 1 for no toxicity to 4 for extreme toxicity, the 6 test fluids were ranked based on plant, earthworm and Microtox™ bioassays conducted on bioremediated soil (Table 2). Using this approach, the fluids

were easily separated into two groups: isomerized olefin, linear alpha olefin and isomerized tetradecene which exhibited no toxicity and isomerized paraffin, mineral oil and diesel which tested moderately to extremely toxic after fluid bioremediation to a stable endpoint.

Conclusions

1) Bioremediation of isomerized olefin, alpha olefin and isomerized tetradecene resulted in almost complete degradation of these fluids. Not only were these fluids highly biodegradable but they were also non-toxic after remediation based on short-term plant, earthworm and Microtox™ bioassays.
2) Degradation of isomerized paraffin and mineral oil was less than 50% that measured for the olefins (only 39-45% mass loss compared with 91-96% for the olefins). Although relatively non-toxic immediately following application to soil, both fluids were extremely toxic after bioremediation. Paraffins and their breakdown products may have contributed to this increase in toxicity.
3) Disappearance of diesel (71%) is attributed primarily to the abiotic loss of the large volatile component in this fluid. Respiratory activity was low in the diesel treatment suggesting poor degradability of the residual paraffins and aromatics remaining after the volatiles had disappeared. Diesel was still extremely toxic following bioremediation even though 70% of the hydrocarbons had disappeared.
4) Based on TEH analyses, the fluids were ranked from most to least degradable as follows: linear alpha olefin = isomerized tetradecene > isomerized olefin > diesel > isomerized paraffin > mineral oil.
5) Based on short-term ecotoxicity assays, the test fluids were ranked from least to most toxic as follows: isomerized olefin = linear alpha olefin = isomerized tetradecene > isomerized paraffin > mineral oil > diesel.
6) Olefins are highly recommended for use in drilling muds because they biodegrade readily and are non-toxic following remediation. It appears that these fluids offer the same low toxicity and high biodegradability advantages under terrestrial conditions as they do in marine situations.

Acknowledgements

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References

1. “Biological Test Method: Toxicity Test Using Luminescent Bacteria (*Photobacterium phosphoreum*). Report EPS 1/RM/24. Environment Canada (Nov. 1992).

2. Melchor, A.E. *et al*.: “E&P Waste Management in the Orinoco Delta,” paper SPE 66577 presented at the 2001 SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, Texas, Feb. 26-28.

Table 1. Total extractable hydrocarbons (C11-C60) and % mass loss of test fluids applied to receiving soil at 2 g/100 g dwt and bioremediated for 93 days. Fluid degradability rank based on most to least TEH loss and respiration rank based on most to least CO_2-C loss after 3 months remediation. All data corrected for background TEH and respiration.

Treatment	Initial TEH (µg/g dwt)	Final TEH (µg/g dwt)	TEH Lost (µg/g dwt)	% Mass Loss	TEH Decay Rank	Respiration Rank*
Isomerized olefin	16384	1422	14962	91.3	2	1
Linear alpha olefin	14720	577	14143	96.1	1	2
Isomerized tetradecene	15488	584	14904	96.2	1	3
Isomerized paraffin	16768	9175	7593	45.3	4	4
Mineral oil	16640	10088	6552	39.4	5	5
Diesel	14336	4176	10160	71.0	3	6

* See Fig. 2 for cumulative carbon losses from test fluids.

Table 2. Toxicity ratings for 6 test fluids applied to receiving soil at 2 g/100 g dwt and bioremediated for 93 days. Ranking from least toxic (1) to most toxic (4)*.

Treatment	Phytotoxicity				Earthworm Survival	Microtox	Rating Total	Toxicity Rank
	Lettuce		Barley					
	Emerg.	Root	Emerg.	Root				
Isomerized olefin	1	1	1	1	1	1	6	1
Linear alpha olefin	1	1	1	1	1	1	6	1
Isomerized tetradecene	1	1	1	1	1	1	6	1
Isomerized paraffin	4	4	1	4	4	2	19	2
Mineral oil	4	4	2	4	4	3	21	3
Diesel	4	4	2	3	4	4	21	3

* Rating Scheme (relative to control)
1 = not toxic (no inhibition)
2 = moderately toxic (25-50% inhibition)
3 = very toxic (50-75% inhibition)
4 = extremely toxic (> 75% inhibition)

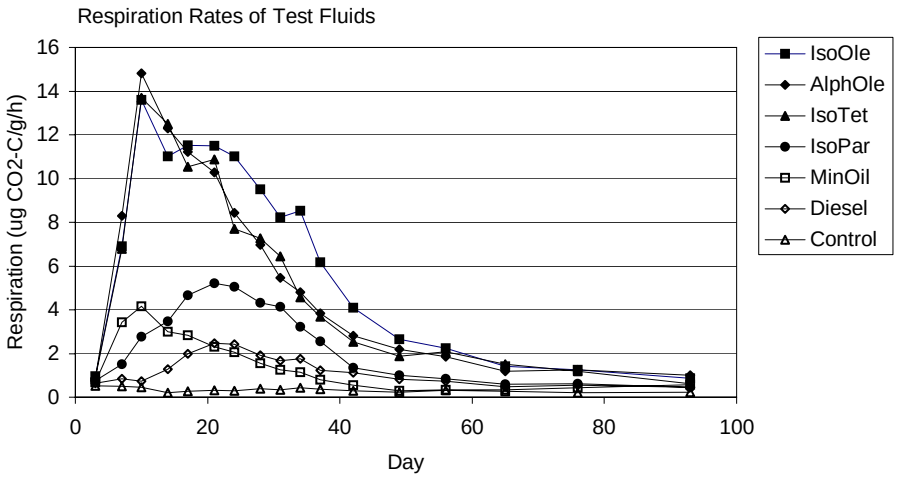

Figure 1. Respiration rates during bioremediation of untreated soil and soil treated with 6 test fluids at 2 g/100 g dwt. Data are means (n = 3).

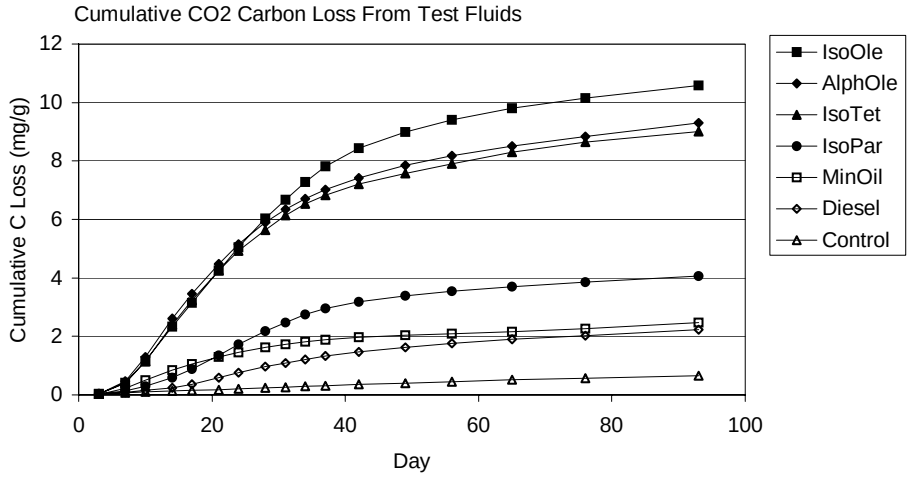

Figure 2. Cumulative CO_2 carbon loss from control soil and soil treated with 6 test fluids over a period of 93 days. Data are means (n = 3).

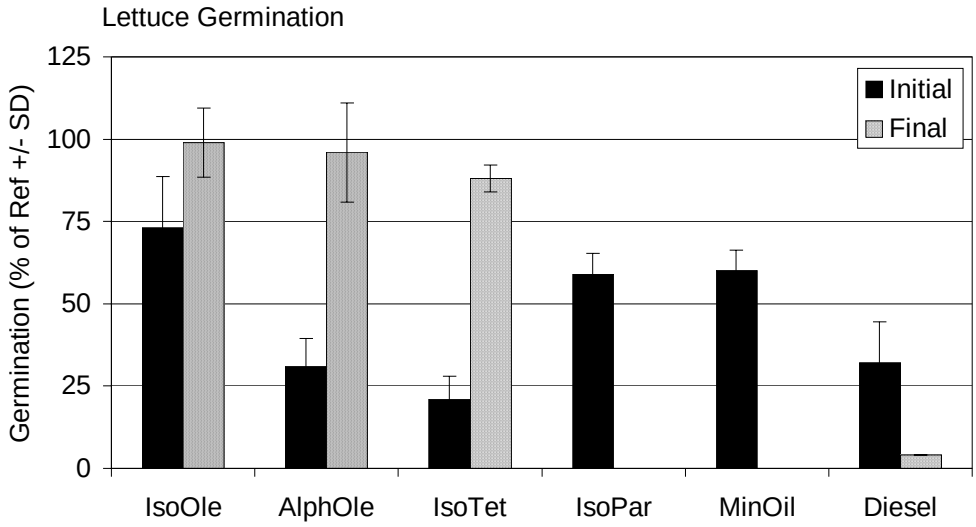

Figure 3. Lettuce germination immediately following application of test drilling fluids to receiving soil at 2 g/100 g dwt(intial) and following 93 days bioremediation (final). Data are means (n = 3) ± standard deviation.

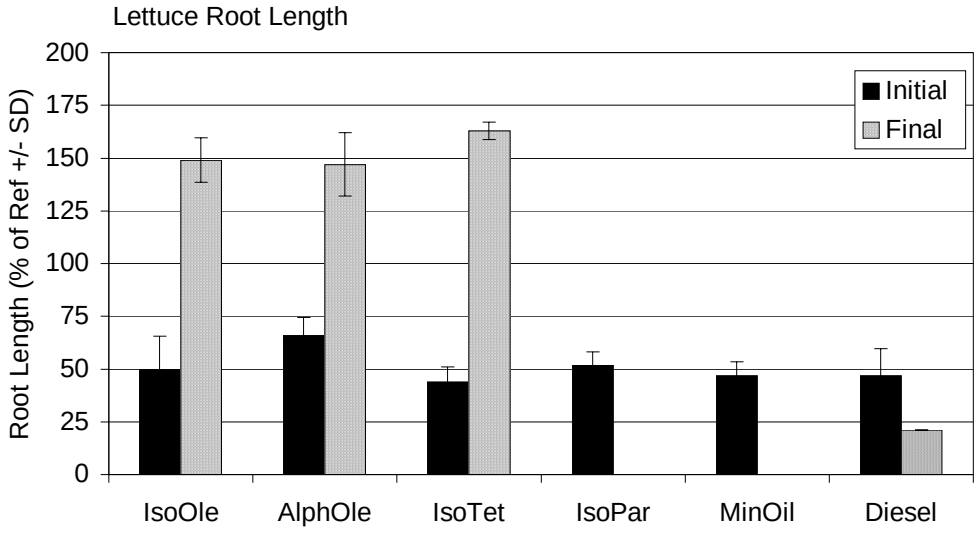

Figure 4. Lettuce root length immediately following application of test drilling fluids at 2 g/100 g dwt (initial) and after 93 days bioremediation (final). Data are means (n = 3) ± standard deviation.

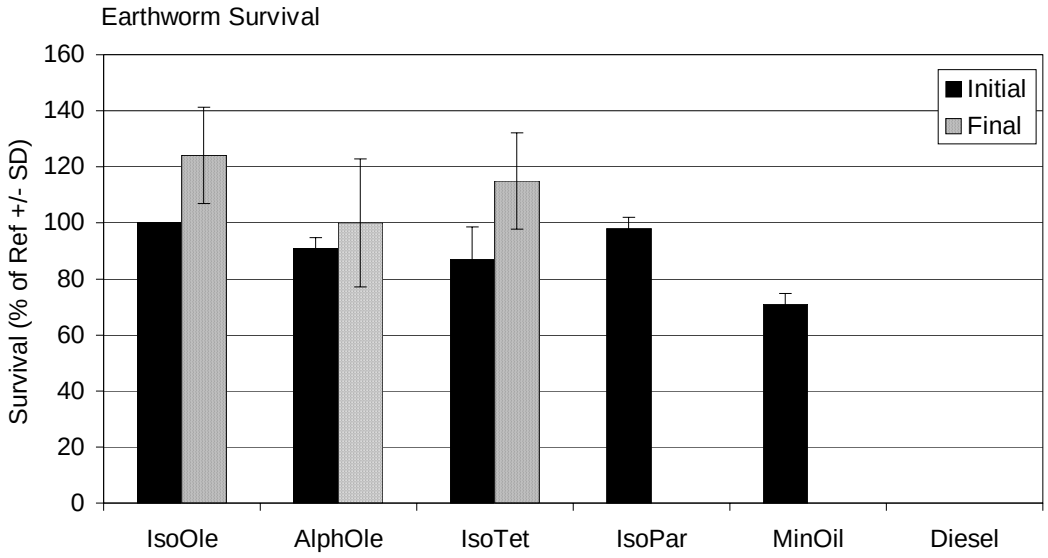

Figure 5. Earthworm survival after 14 days exposure to test drilling fluids immediately following application to receiving soil (initial) and after 93 days bioremediation (final). Data are means (n = 3) ± standard deviation.

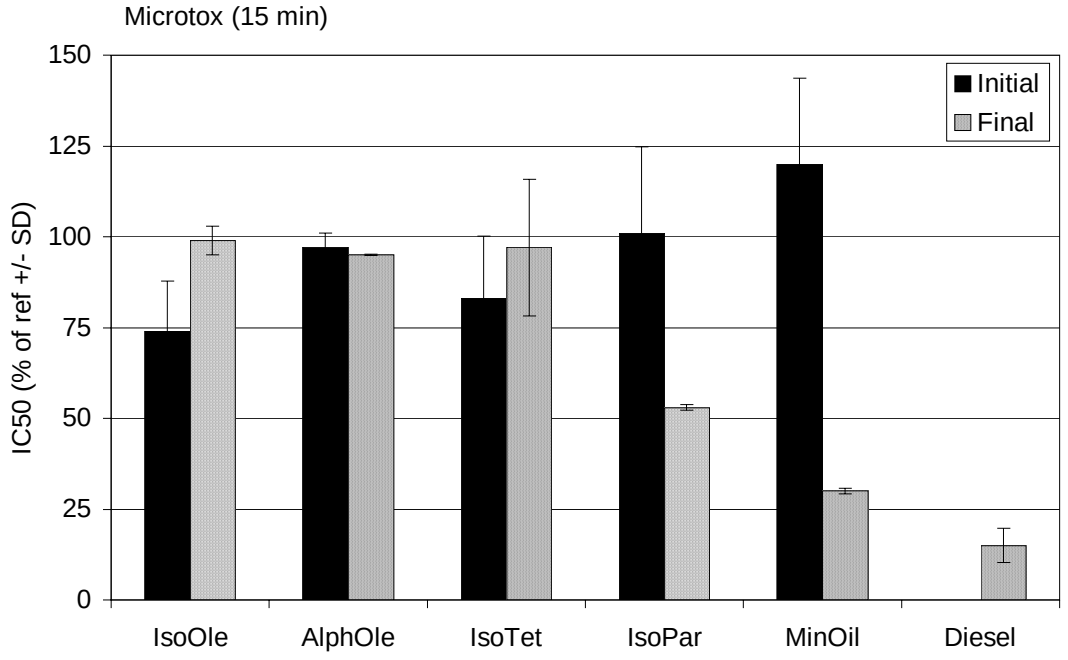

Figure 6. Microtox™ IC50s for test drilling fluids immediately following application to receiving soil (initial) and after 93 days bioremediation (final). Data are means ± standard deviation.