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Review

Impact of Synthetic Based Fluids and Base oil on Earthworm Toxicity

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Abstract

Purpose

Recently Synthetic Based Fluids (SBFs) have replaced traditional Oil Based Fluids (OBFs) which have similar characteristics to those of OBFs and are environmental friendly. During drilling activities, they could be spilled into the soil, affecting its quality. Earthworms are bio-indicators that also influence the quality of the soil. Thus any adverse effect on earthworms indirectly affects the dynamics of soil. Hence, earthworm toxicity was assessed for the given SBF.

Materials and Methods

Earthworm toxicity assay was carried out as per OECD Guideline

Results and Discussion

The LC50 concentration (14 days) for synthetic based drilling fluid was in the "practically non toxic" range while that of base oil was in the "very toxic" range. The effect of these chemicals on metabolic activity of earthworms is also discussed in this paper.

Conclusion

SBF was non-toxic as compared with base oil. This proves that when base oil is mixed with different ingredients and converted into SBF, it becomes less toxic than the base oil.

Keywords: Synthetic Based Fluids; Base Oil; Earthworms; Toxicity

Notations: SBFs: Synthetic Based Fluids; OBFs: Oil Based Fluids; WBFs: Water Based Fluids; OECD: Organization for Economic Co-operation and Development; LC50: Lethal concentration at which 50% mortality of test organism is observed

Introduction

Drilling fluids are of three types of *viz.* Oil Based Fluids (OBFs), Water Based Fluids (WBFs) and Synthetic Based Fluids (SBFs). These fluids are used for drilling of natural gas, oils and water wells. Traditionally, OBFs have been used which have the best performance in terms of drilling activities. But they have poor environmental performance in terms of eco-toxicity. WBFs do not provide optimal performance in challenging conditions. But they provide the best environmental performance in terms of their non-toxic nature and they also have an enhanced rate of biodegradation compared to OBFs. Recently, SBFs have been developed to provide a similar drilling performance as OBFs but with improved eco-toxicity and biodegradation characteristics which are similar to WBFs [1]. Some times these SBFs are also referred to as drilling mud. The base material (primary component)in SBF is base oil. which composes of hydrocarbons. Base oil usually represents about 30 to 90 percent of the total volume of the drilling fluid [2] and about 20 to 40 percent of the total mass of the drilling fluid [3]. SBFs consist of Internal Olefins (IOs), Poly Alpha Olefins (PAOs), Linear Alpha Olefins (LAOs), Acetals and Ester Based Fluids (EBFs). Other secondary components of SBFs include emulsifiers, wetting agents, thinners and gelling agents. Emulsifiers are added to aid in forming and maintaining the emulsion. Emulsifiers are modified to be compatible with the physical and chemical properties of the fluid [4]. Wetting agents like polyamines, fatty acids and oxidized oils are added to ensure the solids in the mud are wet phase. Lime is added to make calcium soaps that support the emulsification of water in the SBFs [5]. Rheology modifiers and organophilic clays like bentonite are added to keep drill cuttings in the drilling fluids in suspension [5]. Barite (barium sulfate) is added to increase the specific weight of the drilling mud [6].

Soil is a dynamic and complex system functioning as habitat for microorganisms, flora, fauna and humans. Addition of any contaminant to the soil may have an adverse effect on the soil

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macro- and micro fauna, where as earthworm belong to the soil macro-fauna [7]. When OBFs, WBFs and SBFs are used for drill cutting processes, they may get discharged accidentally into the soil and thus havean adverse impact on the biological system of the soil. The degree of their impact would depend on the type, dosage and duration of exposure of these chemicals on to the soil [8]. Earthworms are important members of the soil as they enhance the soil characteristics through litter breakdown. This process plays a major role inperpetuating soil fertility and also helps in maintaining the microstructure of the soil [9]. In many soils, earthworms play a major role in converting large pieces of organic matter (e.g dead leaves) into rich humus and thereby improving the fertility of soil. Earthworms keep the soil structure open due to their burrowing activities, creating multitude channels which support aeration and drainage.Therefore, earthworms are the standard test species to analyze the impact of any chemical substance on soil. They are also considered as 'barometers' or 'sentinels' and provide an early warning in deterioration of soil quality. Earthworms have been recommended as a critical (suitable) representative of soil organisms and as indicator for soil health (Table 1). Thus any adverse effect on earthworms would indirectly result in a deterioration of soil quality. This is important for protecting the health of soil and natural environment, and also in protecting human health [10,11].

Table 1: Earthworm toxicity rating

Ratings	LC_{50} (mg/kg)
Super toxic	< 1.0
Extremely toxic	1.0 – 10.0
Very toxic	10.0 – 100.0
Slightly toxic	100.0 – 1000.0
Practically non toxic	> 1000.0

Note: LC_{50} is lethal concentration [15]

TOTAL Petroleum India Ltd has developed SBFs for drill cutting processes. Hence, the objective of this paper was to assess the LC50 (lethal concentration at which 50% mortality is observed) of earthworms to the test chemicals (synthetic based fluids and base oil) as per OECD 207 guidelines [12]. These earthworms could survive in presence of test chemicals but their metabolic activities could be affected. Hence, change in their body weight was taken as indicative of their metabolic activity.

Materials and Methods

Collection of Test organisms

Earthworm (*Eisenia fetida*) was used as test organisms in the experiment. These earthworms were brought from the nearby laboratory and they were cultured in a vemicompost unit. The earthworms were fed with dry vegetable waste. Earthworms of about 7 to 8 cm length were used in the experiment as test organisms. They were not fed during exposure in the experiment.

Test Chemicals

SBF and base oil were procured from TOTAL petroleum India Ltd. The technical specification of the SBF and its base oil (Table 2) and the composition of SBF (Table 3) were also obtained from TOTAL Petroleum India Ltd. The SBF consisted of 61% of base oil and the remaining 39% were secondary components.

Test Method

The earthworm toxicity assay was carried out according to the OECD 207 guidelines [12]. The tests were carried out in 1000mL long neck beakers (test units). These beakers were cleaned with distilled water and then used for the experiment. This toxicity assessment was carried out in soil which was brought from a nearby plant nursery. The soil was air dried and sieved and the sieved soil was used for the experiment. The physico-chemical characteristics of this soil were determined based on the standard methodology [13]. Different concentrations of SBF and base oil were prepared in 200g of sieved soil. Concentrations of 10,100,1000,30000 and 50000 mg/kg were prepared with SBF and used in the experiment while concentrations of 1,10,100,500 and 1000mg/kg were used in the experiment with base oil; and a control group (blank, no dosing of any contaminant).10 earthworms were added to each different test concentrations(no replication). Earth worms that were selected for the test were not fed for 24h prior to the experiment. Their cumulative weight was measured before adding them to their respective test concentrations. A blank containing 200g of soil without any chemicals were maintained. 10 earthworms were added to the blank and those earthworms were also pretreated as mentioned above. This toxicity assay was carried out 14 days and in this test period no food was given to earthworms.

Measurements

Lethality (number of dead organisms) was recorded daily by visual observation. An earthworm was considered to be dead if there was no visible movement, and/or touching them gently also showed no reaction. Dead earthworms were removed manually. After the end of experiment (14 days), the surviving earthworms were removed gently and they were washed in distilled water. Then the cumulative weight of the surviving earthworms was measured.

Data Analysis

The susceptibility of earthworms to both SBF and base oil was determined using the probit method. The LC50 concentration(14

Table 2: Technical specification of synthetic based fluid(SBF) and base oil

Properties	Specification		Test Method
	Synthetic based drilling Mud	Base oil	
Density at 20°C (kg/m^3)	800	800	ASTM D 4052
Appearance at 25°C	Dark brown	Clear and liquid	Visual
Soybolt Colour	+30	>+30	ASTM D156
Boiling range (°C)	225-325	232.5-313.5	ISO 3405
Auto Ignition Temperature (°C)	>230	>230	ASTM E659
Sulphur content (ppm)	<1	0.1	ASTM D5453
Aromatics (%)	0.0020	0.0019	TOTAL IL 014
Flash point (°C)	99	100	ASTM D93
Pour point (°C)	-30	-39	ASTM D97
Viscosity (cSt)	3.8 (At 20°C) 2.5 (At 40°C)	2.5 (At 40°C)	ISO 3104
Aniline point (°C)	87		EN ISO 2977
Solubility in water (mg/l)	<1	<1 Soluble in many common solvents	OECD TG 105
Vapour Pressure (mbars)	0.013 (At 20°C) 0.076 (At 38°C) 1.274 (At 80°C)	<0.02(At 0°C)	Calculated

Table 3: Formulation or composition of synthetic based fluids (SBF)

Components	Concentrations (gm)	Volume (ml)
Base Oil	168.78	215.55
VG Supreme	5.0	3.18
VG Plus	5.0	3.18
Lime	10.0	5.0
Megamul	5.0	5.25
Versamul	5.0	5.25
Calcium Chloride	25.21	7.27
Mega Trol	2.5	1.41
Versa Trol M	2.5	2.36
Water	70.59	70.59
Barite	109.42	26.05
Versamod	0.5	0.5
Rev Dust	10.0	3.85

days) was obtained by using ToxCalc version 5.0 of the US-EPA. This program calculated LC50 values at 95% confidence limit by the probit method [14].

Statistical Analysis

LC50 values were obtained by using ToxCalc software (version 5.0) of USEPA [14]. Similarly, Chi square, one way ANOVA and probability values were obtained using statistical software SPSS Version 13.0 for windows.

Results and Discussion

The Chi square at 95% confidence level and probability analysis for base oil and SBF are given in Table 4. The one way ANOVA value was F =4.24 for base oil at P =0.02 and similarly F =107.34 for SBF at P =0.001.The physico-chemical characteristic of the soil which was used in the experiment is given in Table 5.

Table 4: Statistical analysis for Earthworms to Synthetic based fluids (SBF) and base oil

	P	Chi square
Synthetic based drilling fluids	0.27	5.22
Base oil	0.13	6.50

Where; P is probability, Chi-Square value is at 95% confidence level.

Table 5: Physico-chemical properties of soil used in the experiment

Properties	Results
pH	7.706
Electrical Conductivity (µs/cm)	206
Organic carbon (%)	44.01
Moisture (%)	22.18
Total Nitrogen (mg/kg)	451.4
Total Phosphorus (mg/kg)	170

The dose response relation (based on mortality) for SBF (Figure 1) and for base oil (Figure 2) shows, SBF is lesser toxic than base oil. The differences of the initial and final cumulative weight of earthworms with SBF as test chemical are given in Figure 3 while those of base oil as test chemical are given in Figure 4.100% mortality of earthworms was observed at the concentration of 50000mg/kg for SBF and at 1000mg/kg for base oil. No mortality was observed in the blank control, indicating that the soil used in the experiment was not contaminated with any harmful chemicals and that control earthworms performed well, which is a validity criterion of OECD 207. The number of earthworms surviving in experiment after end of 14 days is given in Table 6.

The LC50concentration (14 days) for SBF was 6999.64 mg/kg i.e.in the “practically non-toxic” range while that of base oil was 89.98 mg/kg, so in the “very toxic” range (Table 1) as per OECD

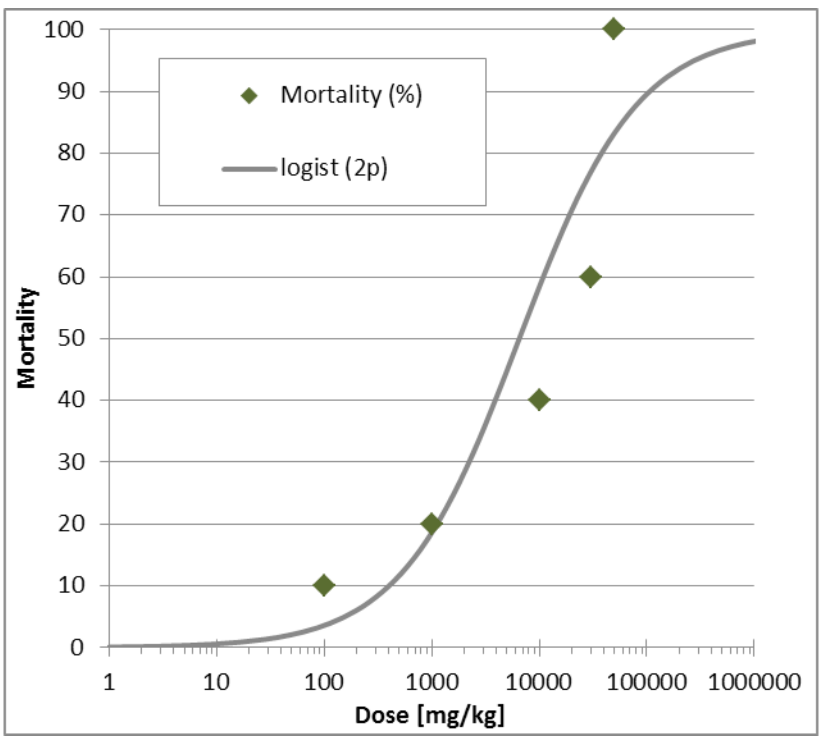

Figure 1: Dose response relation (based on mortality) for Synthetic Base Fluid (SBF) (Charts from an anonymous reviewer)

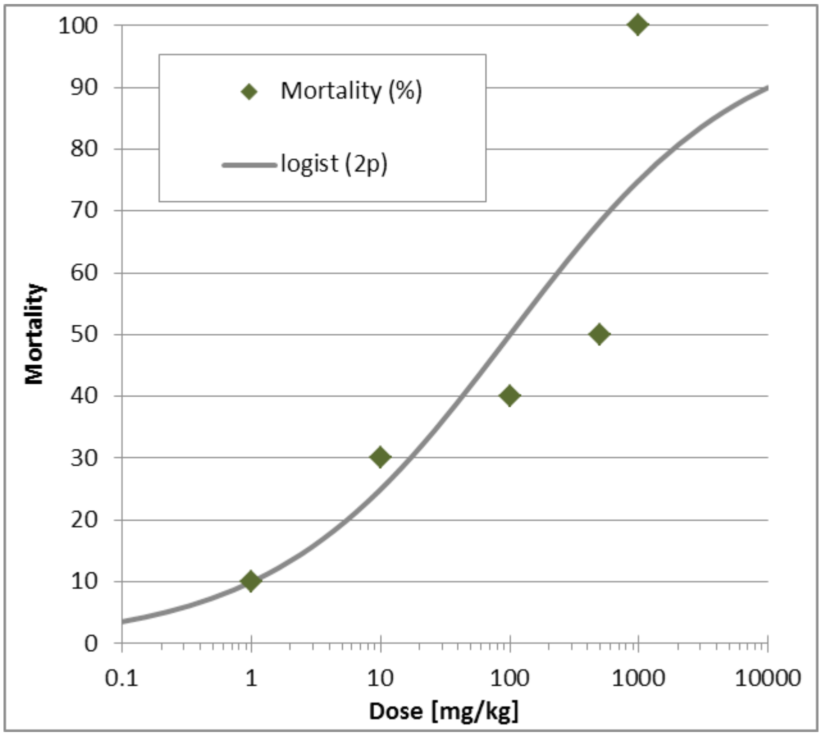

Figure 2: Dose response relation (based on mortality) for base oil (Charts from an anonymous reviewer)

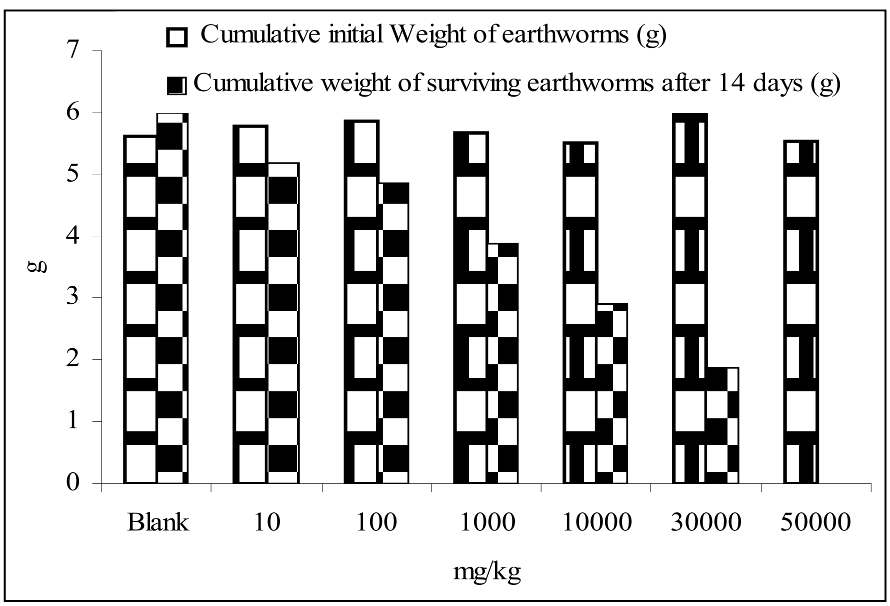

Figure 3: Initial and final weight of earthworms exposed to SBF

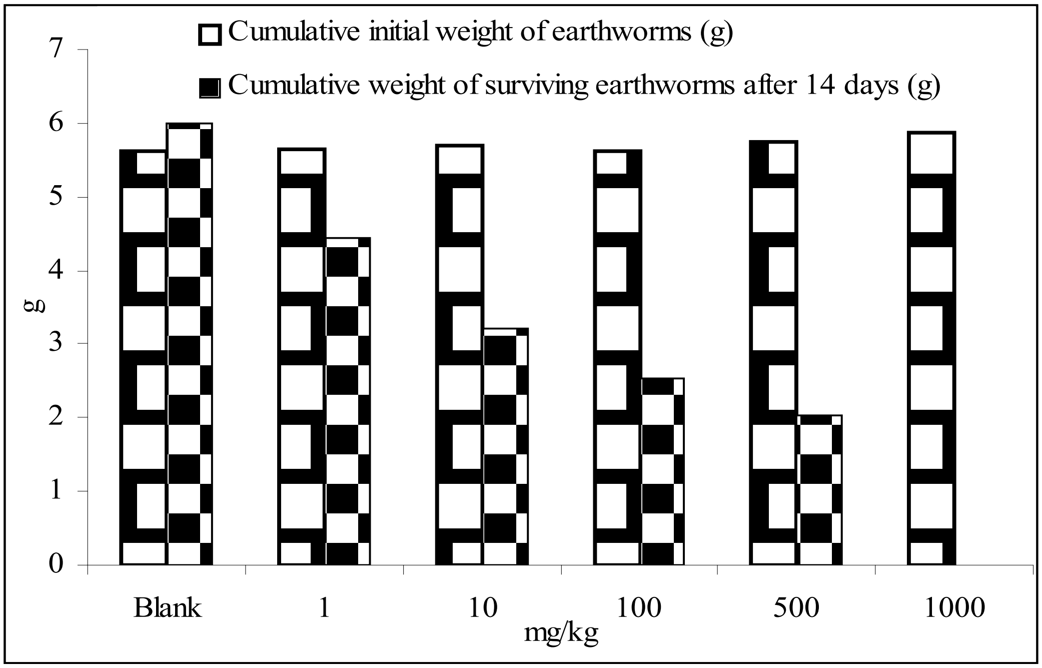

Figure 4: Initial and final weight of earthworms exposed to base oil

Table 6: Surviving earthworm after end of 14 days of experiment

Concentration	Number of earthworm surviving after 14 days of experiment	
	Synthetic Base Fluids (SBF)	**Base oil**
Blank (no chemical added)	10	10
1 mg/kg	Not used in experiment	9
10 mg/kg	10	7
100 mg/kg	9	6
500 mg/kg	Not used in experiment	5
1000 mg/kg	8	0
10,000 mg/kg	6	Not used in experiment
30,000 mg/kg	4	Not used in experiment
50,000 mg/kg	0	Not used in experiment

Note: The experiments were performed with 10 earthworms per test concentration

guidelines [15]. Thus, this study indicates that the base oil was 78 times more toxic than SBF. The addition of secondary components while preparing the SBF appears to have made it considerably less toxic. Other researchers also reported the similar results [16].The earthworm was chosen as test organism, as they are highly sensitive to many chemical contaminations in the soil [17,18]. Earthworms influence organic matter breakdown, soil structural development and nutrient recycling in soil [19]. Research [20] showed that the addition of external chemicals to soil may lead to changes in soil pH, electrical conductivity and organic content. These changes in soil properties affected the distribution of earthworms in soil. Similarly, a study [21] demonstrated that changes in soil organic matter, organic carbon content, total nitrogen and depth of soil affected the distribution and survival of earthworms in soil. In this study, addition of SBF had no effect on the survival of earthworms at lower concentrations. In case of base oil, it affected the survival of earthworms at considerably lower concentrations. While [22] also demonstrated that OBFs were more toxic to earthworms than SBFs. When industrial detergents and corrosion inhibitors were used as test chemicals, earthworm toxicity results were observed to be within the "slightly toxic" range [23]. Various researchers reported that heavy metal concentrations in soil affected the survival of earthworms [7,24]. Nickel, chromium and mercury were absent in the test chemical provided by TOTAL Petroleum Ltd [25]. So the deaths of earthworms were not due to heavy metal contaminations but due the components of SBF and base oil.

The rate of metabolic activity of earthworms was determined indirectly as change in body weight. Studies [26] reported that changes in the metabolic activity of earthworms were directly proportional to their change in body weight. This study shows that body the weight of earthworm increased in the blank group at the end of 14 days as they fed on the organic matter present in the soil. This indicates that the metabolic activity of earthworms was unaffected in blank. In case of the test concentrations, though there was survival of earthworms at lower concentrations their body weight decreased. At 10mg/kg of SBF, all ten individuals survived during the 14 days of the experiment. But their body weight decreased, indicating that their metabolic activity was impaired in presence of the test chemicals. Thus, the test chemicals were not only responsible for the death of earthworms but also induced sub-lethal effect, i.e. changes in their metabolic activity.

Conclusions

The LC_{50} concentrations (14 days) was determined for both SBF and base oil with earthworm, *Eisenia fetida* according to the OECD 207 guideline. The result showed that the LC_{50} concentration (14 days) for SBF was in the "practically non toxic" range while that of base oil was in the "very toxic" range (Table 1). The SBF consisted of 61% base oil and the remaining 39% were secondary components like barite, emulsifier, $CaCl_2$ etc. The addition of these secondary components appears to have reduced its toxicity compared to base oil. Thus, these SBF should preferably be used for drill cutting activities as they have less environmental impact. At lower concentrations of SBF (10mg/kg), no earthworm mortality was recorded; however there were sub lethal effects i.e. lower body weights of the surviving earthworm were observed compared to the blank control. This indicates that although lower concentrations of SBF did not affect survival of the earthworm their metabolic activity may be affected. Hence, not only the LC_{50} concentration but also the change in metabolic activity must be considered when evaluating toxicity.

The SBF is the recent development in the field of drilling fluids which are considered to have similar performance characteristics as those of OBF, but they were found to be considerably less toxic. This study shows that the SBF which was procured from TOTAL Petroleum Ltd. Was in the "practically non toxic" range according to the OECD guidelines.

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